



COST Action E13

Wood Adhesion and Glued Products

Working Group 1: Wood Adhesives

State of the Art – Report

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Manfred Dunky
Chairman of COST E13 WG 1 – Wood Adhesives
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Preface

By definition COST aims at developing cooperation in science and technology in Europe. The technical Committee for Forests and Forestry Products recognized the great value that adhesives and bonding technology can and have brought to wood and to forest products. It is for this reason that COST E13 on wood adhesives and wood gluing has been created. The aims of this group are multifold, being:

1. to create a platform for building scientific cooperation and partnership across Europe and to facilitate the development of consortia for EU funded research projects (R&D framework programmes).
2. To assess the strength and weaknesses on given areas or disciplines concerning the field of wood adhesives and wood bonding for the various countries, and even more important for the European Community as a whole in relation to the global context.
3. To address such strengths and weaknesses with apt transnational projects and even facilitate national approach of such problems.
4. To make the scientific and industrial community in the wood adhesives and wood gluing cluster more visible and with greater lobbying influence in Europe and abroad.

We have now completed the State of the Art report. I would like to emphasize the necessary and innovative aspects of this work. It is “Europe” with a single voice speaking for the first time through the pages of this report, through you which have contributed to write the different chapters, or that you have just contributed by voice or by organizing.

This is an important exercise as it is only through the dedication of all of you that from such a document, the real, perceived, and urgent areas of need determinant for the future survival of this speciality and of its related industries have started already to emerge. We have a couple of years to go to define and refine these areas even better, in short to distil the numerous points we have already defined in a series of important focuses in the adhesives, bonding and bonded products areas. Take this seriously as you have taken extremely seriously the compilation of this State of the Art report, as your own survival in this field might depend from it, even if you might not be able to perceive this today. “Sitting on the fence”, and just playing at the statesman is a losing proposition in these exercises aimed at a world already in fast forward gear: not to participate actively means not to have your ideas taken into consideration, whatever these ideas and wishes might be: financing from the EU, a bigger market share on the global scene, an innovative product or process, impact on the world scientific stage, or even just survival by defending your own patch from unfriendly, competitive raids. The message is clear: participate actively as the future is only in your own hands. It is through this State of the Art report that each of you will also identify similarity of interests and purpose, will then identify future partners, lobbying friends and common interests without losing but rather gaining in competitive advantage at the cutting edge of the speciality. Do not waste or belittle this opportunity: none of us know, but it might be the only one is ever offered to us.

A.Pizzi
Chairman
COST E13

Table of Contents

Executive Summary	vii
1 Introduction.....	1
2 Chemistry of Adhesives.....	3
2.1 Formaldehyde Resins	3
2.2 Polyurethane Adhesives	38
2.3 Adhesives Based on Natural Resources	46
2.4 Casein Adhesives	66
2.5 Other Woodworking adhesives	68
3 Analysis of Resins and Adhesives.....	75
3.1 Introduction	75
3.2 Main Adhesives Systems for Wood Based Products.....	75
3.3 Characteristic Values of Adhesives and their Analysis	76
3.4 Advanced Properties of Adhesives and their Analysis.....	79
4 Bonding Process.....	89
4.1 Theory of Bonding	89
4.2 Process of Adhesion	98
4.3 Properties of the Glue Line - Microstructure of the Glue Line.....	111
4.4 Binderless Gluing.....	113
5 Influence of the Wood Component on the Bonding Process and the Properties of Wood Products	121
5.1 Introduction	121
5.2 Wood Structure	121
5.3 Properties of Wood Surface	122
5.4 Moisture Content of Wood.....	127
5.5 Grain Orientation of Wood in the Glue Line.....	131
5.6 Temperature	133
5.7 Bonding Properties of Different Wood Materials	134
5.8 Summary	141
6 Influence of the Adhesive on the Bonding Process and the Properties of Wooden Products	145
6.1 Introduction	145
6.2 Basic Parameters	145
6.3 Aminoplastic Resins.....	148
6.4 Phenolic Glue Resins.....	151
7 Test Methods and Prediction of Performance	155
7.1 Introduction	155
7.2 Current Test Methods and Acceptance of Glues	155
7.3 Accelerated Ageing Tests.....	157
7.4 Prediction of Performance.....	158
8. Summary and Outlook.....	161

Executive Summary

This State of the Art - Report not only summarizes the knowledge available today but also especially addresses the main actual requirements in the development, production, application and performance of adhesives; these requirements on the other side are based on the various driving forces in the development, production, application and performance of the wood-based panels themselves.

The report is divided into 8 chapters:

Chapter 1 gives an introduction and an overview on the driving forces for new and better adhesives.

Chapter 2 describes all the various adhesives used in the wood based panels industry, dealing with chemical principles as well as with the application of the adhesives and glue resins.

Chapter 3 summarizes the analysis methods used to characterize the composition of the adhesives as well as their hardening and gelling behaviour.

Chapter 4 deals with the bonding principles, including the various theories of bonding, also describing the process of adhesion (working parameters and process conditions as influence parameters) and the properties and microstructure of the glue line.

Chapter 5 evaluates the wood component as one of the three main influence parameters in the production of wood based panels; it especially deals with the influence of the wood surface on the bonding process and bonding result.

Chapter 6 investigates the influence of the adhesive as the second important influence parameter.

Chapter 7 finally brings some details on test methods and prediction of performance.

Chapter 8 points out, that additional and especially sufficient resources and support is needed, to fulfil all the ideas and requirements listed in the chapters above.

Following for the various chapters 2 – 7 an overview, especially necessary R&D shall be given. This shall not replace a deeper contemplation of the details addressed in the questions and open R&D topics after each chapter, which also show the great variety in wood bonding.

Chapter 2: Chemistry of adhesives

The adhesives on the one side form the bond line itself; on the other side the interactions with the wood component and especially the wood surface are the decisive precondition for a good bonding quality. Therefore all properties of the adhesives influence both, the possible cohesive as well as the adhesive behaviour.

Main targets of the development of adhesives are:

- The speeding up of the formation of the glue line, disregarding the fact if it is a chemical or a physical process
- Various application properties: e.g. easy, safe and harmless application, long storage stability
- Optimisation of the interactions with the wood surface
- Cost efficiency.

This includes special formulations and raw materials as well as new types of cooking procedures. The price of the used adhesive always has to be seen in terms of efficiency and costs for a special bonding task. Sometimes the use of a more expensive type of adhesive finally is the more cost efficient way. This especially is an actual topic with the melamine fortification of UF-resins for the production of low swelling core boards for laminate flooring or for boards with a certain resistance against influence of humidity and water.

Using various co-monomers gives the chance to achieve the necessary requirements and to optimise the performance of the resin. In some cases however it is still not yet known if and how the various monomers react with each other, e.g. in PMF- or PUF-resins.

Especially for hardening adhesives two parameters are important for the performance of the resin:

- The gelling and hardening reactivity
- The achievable degree of cross-linking.

Looking at formaldehyde based resins with their low content of formaldehyde (in order to decrease the subsequent formaldehyde emission) both parameters became more and more critical due to the decrease of the various molar ratios of formaldehyde to amide groups in the resins.

The molar mass distribution of the adhesive („optimal“ degree of condensation or „optimal“ molar mass distribution) on the other side determines its behaviour during application, e.g. wetting vs. penetration. Tailor made adhesives also try to optimise these two parameters.

Development of new adhesives also needs better and more efficient analysis methods, as it is described in chapter 3.

A special task for further work is the prediction of properties of the bond line and the bonded products based on the results of chemical and physical analysis of the adhesive. This includes the investigation of the various influence parameters like the degree of condensation (viscosity) or the chemical composition.

Safety and environmental issues become more and more important. This includes questions like waste materials, effluents and emissions during the production and the application of the adhesives as well as questions concerning worker's safety in production and application, e.g. exothermic behaviour of a PF-cook. Other questions concern content of monomers in the adhesive and residual monomers after application.

Polyurethane adhesives, especially PMDI, are an alternative for formaldehyde-based resins for the production of wood based panels. Main interest in development is the reduction of the ability to stick to the press plates, the reduction of the amount of MDI and the enhancement of the reactivity (low press temperatures, cold-setting applications).

The use and application of adhesives based on natural and renewable resources by industry and the general public is often thought of as new approach that requires novel technologies and methods to implement. Despite the increasing trend toward the use of synthetic adhesives, processes based on the chemical modification of natural products offer opportunities for producing a new generation of high performance, high quality products. However, more efficient and lower cost methods of production will be precondition for wider use. Manufacturers need to have confidence that a continual uninterrupted supply of raw material can be sustained throughout the life cycle of a product. It is of equal importance that the feedstock should not be restricted by geographical and climatic conditions or that yield does not dramatically vary when harvested in different locations and at a particular time of the year.

Chapter 3: Analysis of resins and adhesives

Today a good knowledge of the chemical and structural composition of condensation resins is available. The methods used include (i) chemical tests like purity of raw materials, content of free formaldehyde during cooking and in the finished resins, content of formaldehyde in different form in the resins (total formaldehyde, methylol groups), content of urea, melamine and free and total alkaline as well as the calculation of various molar ratios, (ii) physical analysis like spectroscopic

methods (IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, $^{15}\text{N-NMR}$), thermal analysis methods for the monitoring of the gelling and the hardening process (DTA, DSC, DMA, ABES) and (iii) physical-chemical analysis like determination of the molar mass distribution and of the average molar masses of the resins (GPC/SEC, GPC-LALLS, VPO, light scattering, intrinsic viscosity) or chromatographic methods (HPLC, TLC) for the determination of low molar mass species and residual monomers in the resins.

Main interest in the analysis of adhesives is the use of the results achieved in the optimisation of the adhesives, especially in terms of performance in bonding. This also includes the evaluation of each method concerning its correlation to the technological behaviour of the adhesives and to the properties of the panels made by means of these adhesives.

Chapter 4: Bonding Process

The bonding process is the decisive step in the production of wood based panels and is influenced by all materials included in the process. Bonding only can be effectuated if adhesion as well as cohesion contributes to the final bond strength. We need a much better knowledge on the behaviour of the interface between the wood component and the adhesive to optimise the adhesion part of bonding.

Based on the various theories of bonding explanations had been tried to be given why certain results can be achieved or not. This includes the description of the surface in terms of its thermodynamic character and its wetting behaviour as well as the effect of weak boundary layers. Between various adhesives special thermodynamic differences might exist. Correlations between e.g. the contact angle of the adhesive on the surface to be glued and the resulting bond strength should enable a better prediction of ability for certain adhesives to solve a special bonding task. Chemical bondings always have been seen as the optimal form, but it is still unclear, if they really exist and what the portion of those chemical bonds in relation to the overall bonds is. Various adhesives show different bonding results, even the explanation is not always clear.

The process of adhesion includes the application of the adhesive in the various production types of wood based panels and especially deals with the distribution of the adhesive on the surfaces to be glued together and the water balance during gluing. Especially the later effect also influences the speed of the formation of the bonding strength and within the cost structure of the process. Optimal distribution of the resin e.g. in the particleboard production can save substantial part of the needed amount of adhesive and with this costs. Additionally some technological advantages can be reached. Much more basic knowledge in this field is necessary to achieve an optimisation of this parts of the bonding process.

A main interest in the bonding process concerns modelling of the press process. Research on internal mat conditions and simulation of hot pressing describes the formation of the bond strength and shall enable the prediction of the bonding result based on the various process parameters. Several such models exist but still much more improvement is necessary for optimisation.

The properties of the glue line also can be described by analysis of the microstructure of the glue line; this includes the adhesive penetration into wood, the effect of ageing of a glue bond as well as the description of the cohesive strength of the glue line in terms of an optimisation of the brittle and elastic ratio of the glue line. One important issue in this context is the analysis of the adhesive distribution on the furnish to be bonded and in the bond line after the pressing process. Main differences in the performance of various adhesives should be able to be explained with these informations, however still a lot of experience lacks for clear results. The glue lines changed.

Binderless gluing means, that no extra adhesive is added, but that the self-bonding ability of the wood surface (e.g. middle lamella of fibres) is used for this purpose. That is the old dream of the wood scientists to copy what nature makes since wood exist: to bond lignocellulosic material only

using the wood inherent bonding forces. Much work has been done on this field within the last decades, but much more effort is necessary to achieve a break through in this technology.

Chapter 5: Influence of the wood component on the bonding process and the properties of wood products

As already mentioned before, the bonding between two pieces of wood is influenced and determined also by the wood structure and the nature of the wood surface. We yet do not know, if there exist generally accepted experiences and rules concerning the influence of the properties of the wood surface on the quality of a bond line. Questions arise like which portion of the quality can be influenced by the properties of the wood surface and how adhesion and the forming of the interface between adhesive and the wood surface really works. We have to accept that many of these questions, as also defined below in chapter 5 still need an answer in order to proof which of the most important features and mechanisms usually described in literature really determine wood bonding and to attain the highest possible quality of the bond line.

Several individual parameters are known to have influence on the bonding result, even the exact correlations are not known in often cases. These parameters include the roughness of the wood surface, its surface chemistry and especially its age, which can alter the whole properties of a wood surface to a great extent, even causing severe bonding problems, e.g. due to a bad wetting behaviour. One special question still not answered in this context is if there exist correlations between the surface wettability, the possible adhesion and the hence achievable bond strength. In this context the question arises, how in principal to measure the real glue line strength and not only strength of the adjacent wood layers when wood failure occurs.

The moisture content of the wood to be bonded and during the bonding process is another very important parameter. A lot of work has been done when trying solve the problems concerning gluing of wood with different moisture content. The gluing of either high or low moisture content wood causes problems. It has to be investigated, which parameters or which properties of an adhesive should be adjusted when gluing of wood of different moisture content and e.g. which reasons for bad wettability of very dry wood exist. Another task is the minimization of the problem of moisture difference induced stresses.

Other topics to be taken into consideration are (i) the influence of the grain orientation of wood on the penetration of the adhesive in glue line and on strength of the bonded joint, (ii) the applied temperature during the bonding process, (iii) bonding of different wood species and (iv) bonding of preservative-treated wood (fire-retardant treated) and of modified wood.

As already indicated in chapter 4, the preparation and especially activation of the wood surfaces for gluing and bonding might help in reducing the necessary adhesive consumption or even enable a "binderless" bonding.

Chapter 6: Influence of the adhesive on the bonding process and the properties of wooden products

Even the basic parameters of an adhesive, like e.g. the viscosity, can have an important influence on the bonding process itself and on the achievable bond strength. The viscosity determines (based on the degree of condensation of the resin) the penetration behaviour into the wood surface; after the application onto the wood surface and during the press cycle the viscosity of an adhesive changes; therefore it is important to determine and to adjust the proper viscosity for a special gluing process.

Also the flow behaviour, the surface tension and wetting behaviour as well as the reactivity of the adhesive (resin) influences its behaviour and performance. For phenolic resins additionally the content of alkaline plays an important role.

On molecular basis two main parameters are given especially for the formaldehyde condensation resins:

- The molar ratios, e.g. F/U, F/(NH₂)₂, F/P/NaOH and other ratios
- The molar mass distribution (degree of condensation).

For the formaldehyde condensation resins formaldehyde is the essential reactive component. The reduction of the formaldehyde content in the aminoplastic resins in order to reduce the subsequent formaldehyde emission from the wood based panels hence has influenced the resins and especially their reactivity deeply. After all the good results the chemical industry has achieved in reducing the formaldehyde content, still much space for improvement is given.

The influence of the degree of condensation on the bond strength of wood based panels is not known exactly. As mentioned already, this degree of condensation influences the wetting and penetration of the resins on the wood surface. Up to now only few results really may clarify partly these effects.

Target of all these investigations is the yield of correlations between the composition of the resin and the properties of the wood based panels. It is not known, if there are commonly valid correlation equations valid for the individual types of formaldehyde resins and for all types of boards.

Chapter 7: Test methods and prediction of performance

This chapter gives an overview on test methods and testing philosophy, including questions concerning accelerated ageing tests and delamination tests, natural ageing phenomena as well as influence of high temperatures and even fire.

Testing of adhesives is currently done on the basis of best estimates of what happens to the adhesive and the bond line during the service life. The prediction of performance of glues for wood products is often difficult and often carried out only as a trial and error process. For many special requirements specific tests have been developed on the basis of experience and good practice, but often questions are raised about the applicability for the prediction of performance. Such a prediction of performance requires insight in the mechanical, physical, chemical and biological loads during the lifetime of the glued product.

Outlook:

Provided that sufficient support is given, the high capability for and commitment to innovation in the chemical and adhesives industry, in the wood based panels industry as well as at universities and research institutes guarantee, that also in future the development of adhesives and glue resins will continue to proceed quickly and in an efficient way. We all in the Working Group 1 of the COST action E 13 hence can look with great expectations into future.

1 Introduction

M. Dunky

Progress in research and development within the wood-based panel industry and within the adhesive industry has shown many successes during the last decades. On the other side many actual requirements again introduce considerable and important impulses. The main driving forces today are “cheaper”, “quicker” and “more complex”. The first two are caused by the high competition within these industries and try to minimize costs at a certain level of product quality and performance. The key word “more complex” stands for new and specialized products and processes. The applied adhesive resins play a central role within the wood based panels production. The quality of a bonding and hence the properties of the wood based panels are determined among others mainly by the type and quality of the resins. Development in wood-based panels therefore always is linked to development in adhesives and resins.

Despite of various prejudgements both, the wood-based panels industry and the adhesive industry show a high commitment and capability to innovation. The best evidence for this is the boundless diversity of different types of adhesives used for the production of wood-based panels. Well known basic chemicals are used since long time for the production of the adhesives and glue resins, whereby the most important are formaldehyde, urea, melamine, phenol and resorcinol. With these few raw materials the biggest part of the currently used glue resins for wood-based panels is produced. The “how to cook the resins” therefore becomes more and more complicated and sophisticated and is one of the key factors to meet today’s requirements of the wood-based panels industry.

Research and development in adhesives and glue resins mainly are driven by requirements of the bonding and production process and the properties of the wood-based panels themselves, the actual topics are summarized in the following table.

Actual topics and requirements in the production and in the development of wood adhesives
<ul style="list-style-type: none"> • Shorter press times • Better hygroscopic behaviour of boards (e.g. lower thickness swelling, higher resistance against the influence of humidity and water, better outdoor performance) • Cheaper raw materials and alternative products • Modification of the wood surface • Life cycle assessment, energy and raw material balances, recycling and reuse • Reduction of emissions during the production and the use of wood-based panels

The necessity to achieve shorter press times is omnipresent within the wood working industry, based on a permanent and immanent pressure on costs and prices. An increased production rate is still one of the best ways to reduce production costs, as long as the market takes up this surplus on products. Otherwise it will become a real inevitable devil’s circuit.

Shorter press times within a given production line and for a certain type of wood-based panel can be achieved among others by:

- High reactive adhesive resins with quick gelling and hardening behaviour and steep increase in bonding strength even at a low degree of chemical curing
- High reactive glue resin mixes, including the addition of accelerators or special hardeners, which both shall increase the gelling rate of a resin
- Optimization of the pressing process, e.g. by increasing the effect of the steam shock by (i) increased press temperatures, (ii) additional steam injection or (iii) an increased gap in the moisture content between surface and core layer
- Temporary constancy of as many parameters of the production process as possible.

Laminate floorings e.g. require a very low long-term thickness swelling of the core boards. After 24 hours the thickness swelling of these core boards, mostly MDF, must not exceed 8% or 10%, sometimes only 6% and even less, all figures based on the original thickness of the board.

The deterioration of a bond line can be (i) the failure of the resin due to hydrolysis, (ii) the failure of the interface between resin and wood surface or (iii) the breaking of bonds due to mechanical forces and stresses. There is a quite good industrial experience how to increase the ability of a bond line to resist against the influence of humidity and water, especially at higher temperatures. However it also is known, that e.g. in outdoors applications all adhesive systems are working at the upper limit of their performance. Hence wood based panels with optimised properties and performance, especially for new applications in construction purposes like facades, ask for exceptional new bonding ideas to step over existing road blocks.

Cheaper raw materials are another way to reduce production costs. This also includes e.g. the minimization of the melamine content in a MUF-resin (e.g. for boards with reduced thickness swelling or increased resistance to the influence of water and high humidity of the surrounding air). Impeding factor can be the (often temporary) shortage of raw materials for the adhesives, as it was the case with methanol or melamine within the last decade.

The wood component in a bonding, especially the wood surface including the interface to the bond line, also plays a crucial role for the quality of bonding and hence for the quality of the wood-based panels. Low or even no bonding strength can be caused by unfavourable properties of the wood surface, e.g. due to low wettability.

Adhesives and glue resins are one of the important and major raw materials of wood-based panels. So each question concerning life cycle assessment and recycling of boards also is a question of the glue resins used. This includes e.g. the impact of the resins to various environmental topics like waste water and effluents, emissions during the production and from the finished boards or the energetic reuse of panels. Also for several material recycling processes the type of the resin has a crucial influence on feasibility and efficiency.

The emissions from wood-based panels during the production can be caused by wood inherent chemicals, like terpens or free acids, as well as by volatile compounds and residual monomers of the adhesive. Especially the emission of formaldehyde is a matter of concern, but also possible emissions of free phenols or other monomers. The former problem of the subsequent formaldehyde emission fortunately can be regarded as more or less solved, due to

- Stringent regulations in many European countries, with Germany and Austria as outriders
- Successful long-term R&D expenses of the chemical industry, together with the wood working industry.

We hope, that this report will give for all readers and interested persons additional and profound information. Especially the many questions following each subchapter shall be evidence for the urgent need of further R&D-work and with this for additional resources.

Last but not least:

Let me say thank you very much to all authors and colleagues within Working Group 1 in COST E13, who have contributed to this State of the Art-Report. You all have done a really great job. You all can especially be proud of the fact that you have done this work beside of your daily business in industry, at the university, at research institutes or wherever you fulfil your daily job. It was a pleasure for me to work with you and I am looking forward with great pleasure and interest to the continuation of our work in Working Group 1 and in COST E13.

2 Chemistry of Adhesives

2.1 Formaldehyde Resins

M. Dunky

Condensation resins based on formaldehyde are formed by the reaction of formaldehyde with various chemicals like urea, melamine, phenol or resorcinol or of combinations of these substances. In form of delivery glue resins are liquid and consist of linear or branched oligomeric and polymeric molecules in an aqueous solution and partly as a dispersion of molecules in these aqueous solutions. During the duroplastic hardening and gelling they convert to insoluble and non-meltable three dimensionally cross-linked networks. The hardening conditions can be acidic (aminoplastic resins), highly alkaline (phenolic resins) or neutral to light alkaline (resorcinol resins).

Aging behaviour of resins:

Formaldehyde based resins are not stable compounds, but they react also at room temperature under further condensation. This leads to an increase of viscosity and hence to a limited duration of possible use. Depending on the molar ratio and the starting viscosity, the shelf life of a resin can vary between 1 and 3 months. The higher the temperature, the lower the storage stability.

Question

- a) *How to get longer storage stability without loss of reactivity of the resin?*
- b) *How to modelling the behaviour of a resin in a storage tank which has to be assumed more or less adiabatic, including exothermic behaviour of the aging/further condensation reaction?*
- c) *Which methods can be used to save a resin, which is going to gel in a storage tank?*

2.1.1 Urea Resins

Urea-formaldehyde resins (Dunky 1988, 1996, Lederer 1984, Meyer 1979, Petersen 1987, Pizzi 1983, 1994 a+b) are based on the manifold reaction of the two monomers urea and formaldehyde. Using different conditions of reaction and preparation a more or less innumerable variety of condensed structures is possible. UF-resins are the most important type of the so-called aminoplastic resins, approximately 6 billion tons are produced per year nowadays worldwide, based on a usual solid content of 66% of mass.

UF-resins are thermosetting duromers and consist of linear or branched oligomeric and polymeric molecules, always also containing some amount of monomers. Non-reacted urea often is welcome to achieve special effects, e.g. better storage stability. Free formaldehyde however is ambivalent. On the one side it is necessary to induce the hardening reaction, on the other side it causes the formaldehyde emission during the press cycle as well as the displeasing subsequent formaldehyde emission from the pressed boards, a fact which had led to a total change of UF-resins during the last 20 years. Now, at these days, the problem of the subsequent formaldehyde emission can be attested to be solved, at least here in parts of Europe, where in Germany and Austria the most stringent formaldehyde emission regulations worldwide exist. Other countries have already followed or will follow or at least should follow this step.

After the hardening process the UF-resins are an insoluble, more or less three-dimensional network and cannot be melted or thermoformed again. In the stage of application the UF-resins are still soluble or dispersed in water or spray dried powders, which however in most cases are redissolved in water for application.

Despite of the fact, that UF-resins consist of only the two main components urea and formaldehyde, there exists a broad variety of possible reactions and structures in the resins. The basic characteristics of UF-resins can be found on molecular basis:

- The high reactivity
- The waterborne behaviour, which renders the resins ideal for the use in the woodworking industry
- The reversibility of the aminomethylene link, which also explains the low resistance of the UF-resins against the influence of water and moisture, especially at higher temperatures; also it is one of the reasons for the subsequent formaldehyde emission.

2.1.1.1 Methylation and Condensation Reaction

The reaction of urea and formaldehyde basically is a two-step process usually with an alkaline methylation and an acidic condensation. Methylation means the addition of up to three (four in theory) molecules of the bivalent formaldehyde to one molecule of urea to give the so-called methylolureas. Each methylation step has its own rate constant k_i , with different k_i 's for the forward and the backward reaction. The reversibility of this reaction is one of the most determining features of the UF-resins and is responsible for both, the low resistance against hydrolysis caused by the attack of humidity or water, and the subsequent formaldehyde emission, because emittable formaldehyde is delivered subsequently by slight hydrolysis of weakly bonded formaldehyde. The formation of these methylols mostly depends on the molar ratio F/U and tends with higher molar ratio to the higher methylolated species (Jong und Jonge 1952, 1953). Side products are acetals, hemiacetals and etherified products with residual methanol always present in small amounts from the production of formaldehyde. The methylols are more or less stable in slight alkaline conditions, however also some small alkaline condensation might occur (Braun und Günther 1982), which however is of no industrial importance. Starting the reaction of urea and formaldehyde in the usual molar ratio but under acidic conditions gives methylene linked ureas which tend to be insoluble in water already with approx. 5 - 6 urea units (Kadowaki 1936, Zigeuner et al. 1955, Glauert 1957, Renner 1971). Methyleneureas are used as long term fertilizers, as neutral fillers and as white pigment, some other ideas of industrial and commercial use are still in the state of development (Stuligross, 1988, Salyer and Usmani 1978, 1979).

The building up of the UF-resin itself is performed in the acidic condensation step: the methylols, urea and free formaldehyde still present in the system react to give linear and partly branched molecules with medium and even higher molar masses. The type of bonding between the ureas depends on the given conditions: low temperatures and only slight acidic pHs preferably enable methyleneether bridges (-CH₂-O-CH₂-) to be formed, higher temperatures and lower pHs lead to the more stable methylene (-CH₂-) bridges. Ether bridges can be rearranged to methylene bridges under splitting off formaldehyde. One ether bridge needs two formaldehyde molecules and additionally it is not as stable as a methylene bridge, hence it is highly recommended and senseful to avoid such ether groups in the UF-resins under the common conditions of a low content on formaldehyde due to the low final molar ratio of the resins.

The acidic condensation step itself is performed still at the same high molar ratio as it was given in the alkaline methylation (F/U = 1,8 to 2,5). Molar ratios lower than approx. 1,8 lead to precipitations during the acidic condensation step, which causes problems in the determination of the proper endpoint of the reaction by water dilutability or by cloud point as well as inhomogenities in the solutions. The low molar ratio of the final UF-resin is adjusted by the addition of the so-called second urea, which also might be added in several steps (Pizzi 1994). Special knowledge in this step is important for the production of resins with good performance, especially at the low molar ratios usually in use now in the production of particleboards and MDFs.

2.1.1.2 Other Cooking Procedures

In the literature also various other types of resin cooking procedures are described, e.g. yielding an urone structure (DE 2 207 921, DE 25 50 739) or triazinone rings in the resins (USP 2, 605, 253,

USP 2,683,134). The last ones are formed by the reaction of urea and an surplus of formaldehyde under basic conditions in the presence of ammonia, a primary or a secondary amine, resp., these resins are used e.g. to enhance the wet strength of paper.

In the resin itself different chemical species are present:

- Free formaldehyde, which is in steady state with remaining methylol groups and the post added urea,
- Monomeric methylols, which have been formed mainly by the reaction of the post added urea with the high content of free formaldehyde at the still high molar ratio of the acidic condensation step,
- Oligomeric methylols, which have not reacted further in the acidic condensation reaction or which have been built by the above mentioned reaction of the post added urea, and
- Molecules with higher molar masses, which are the resin molecules in the closer sense of the word.

The condensation reaction and the increase of the molar masses also can be monitored by GPC (Dunky et al.1981). With longer duration of the acidic condensation step molecules with higher molar masses are built and the GPC-peaks are moved to lower elution volumes.

Questions and topics of R&D:

Which new types of cooking procedures are possible?

2.1.1.3 Hydrolysis of UF-Resins

Hardened UF-resins can be hydrolysed under the influence of humidity or water, due to the weak bonding between the nitrogen of the urea and the carbon of the methylene bridge, especially at higher temperatures. During this reaction formaldehyde can be liberated (Myers 1982 a, Myers and Koutsky 1987). The amount of this liberated formaldehyde can be taken under certain circumstances as measure of the resistance of a resin against hydrolysis. Main parameters for the hydrolysis are temperature, pH and degree of hardening of the resin (Myers 1985 a). Especially the acid, which had induced the hardening of the resin, can also induce the hydrolysis (see section 2.1.1.5b). The hydrolysis also leads to a loss of bonding strength.

Questions and topics of R&D (see also section 0):

- a) How to improve hydrolysis resistance of hardened UF-resins?*
- b) At which level of hydrolysis can bonding strength get lost?*

2.1.1.4 Reactivity and Hardening of UF-Resins

During the curing process a more or less three-dimensional network is built up. This causes an insoluble resin, which is not longer thermo formable. The hardening reaction is the continuation of the acidic condensation process. Whereas gelling in the reactor is to be avoided, the same process takes place in the glue line. The acidic conditions can be adjusted by the addition of a so-called latent hardener or by the direct addition of acids (maleic acid, formic acid, phosphoric acid and others) or of acidic substances, which dissociate in water (e.g. aluminium sulphate). Common latent hardeners are ammonium sulphate and ammonium chloride. The latter one however is not longer in use in the German and Austrian particleboard and MDF industry since several years because of the generation of hydrochloric acid during combustion of wood based panels causing corrosion problems and the suspected formation of dioxins. Ammonium sulphate reacts with the free formaldehyde in the resin to generate sulphuric acid, which decreases the pH; this low pH and hence the acidic conditions enable the restart of the condensation reaction and finally the gelling and hardening of the resin. The decrease of the pH takes places with a rate depending on the amounts of available free formaldehyde and of hardener and is accelerated highly by heat (Higuchi et al. 1979, Higuchi and Sakata 1979).

The UF-resins can be distinguished from other formaldehyde resins, e.g. MUF and PF, resp., by their high reactivity and the hence achievable short press times. With the modern and long

continuous press lines (up to 48 m, soon even 54 m) specific press times as low as 5 sec/mm and even 4 sec/mm are possible in the production of medium thickness of particleboards. This requires highly reactive UF-resins, an adequate amount of hardener, as high press temperatures as possible and a distinct gap between the moisture contents of glued particles in the surface and the core, resp. This moisture gradient induces the so-called steam effect even without an additional steam injection often used in North American plants. The optimal moisture content of the glued particles is 6 - 7% in the core and 11 - 13% in the surface. The lower the moisture content in the core, the higher the surface moisture content can be adjusted in order not to exceed a certain total moisture content in the mat causing problems with steam ventilation and even blisters. For this low moisture content of the glued core particles it is necessary to be thrifty with any too high addition of water in the core. The lower the gluing factor, the lower is this amount of water applied to the wood furnish and the lower is the moisture content of the glued core particles. For the surface layers on the other side additional water is necessary in the glue mix to increase the moisture content of the glued particles. This additional water, however, cannot be replaced by a higher moisture content of the dried particles before the blender, because this water must be available in short time for a strong steam effect. That would not be the case for water being still present as internal cell moisture content of the wood furnish.

The necessity to achieve shorter press times is omnipresent within the wood working industry, based on a permanent and immanent pressure on costs and prices. An increased production rate is still one of the best ways to reduce production costs, as long as the market takes up this surplus of products. Otherwise it will become an inevitable devil's circuit.

Shorter press times within a given production line and for a certain type of wood-based panel can be performed among others by:

- Higher reactive adhesive resins with quick gelling and hardening behaviour and steep increase in bonding strength even at a low degree of chemical curing;
- High reactive glue resin mixes, including the addition of accelerators or special hardeners, which both shall increase the gelling rate of a resin;
- Optimisation of the pressing process, e.g. increasing the effect of the steam shock by increased press temperatures or an increased gap between surface and core layer moisture content;
- Temporary constancy of as many parameters of the production process as possible.

In order to increase the capacity of a production line, which especially means the reduction of the necessary press times, glue resins with a reactivity as high as possible should be used. This includes two parameters:

- A short gelation time
- A quick and instantaneous forming of the bond strength, even at a low degree of chemical curing.

The reactivity of a resin at a certain molar ratio F/U or F/(NH₂)₂ mainly is determined by the cooking procedure and the quality of the raw materials. Figure 2.1 shows the comparison of two straight E1-UF-resins with the same molar ratio, but cooked according to different procedures. The differences between the two resins clearly are visible in the so-called ABES-test (Automatic Bonding Evaluation System, Humphrey 1996) as well as in the industrial experience. Resin A shows a distinct quicker increase in bonding strength during the press time than resin B.

**Temperature: 90 deg C
no cooling before shear test**

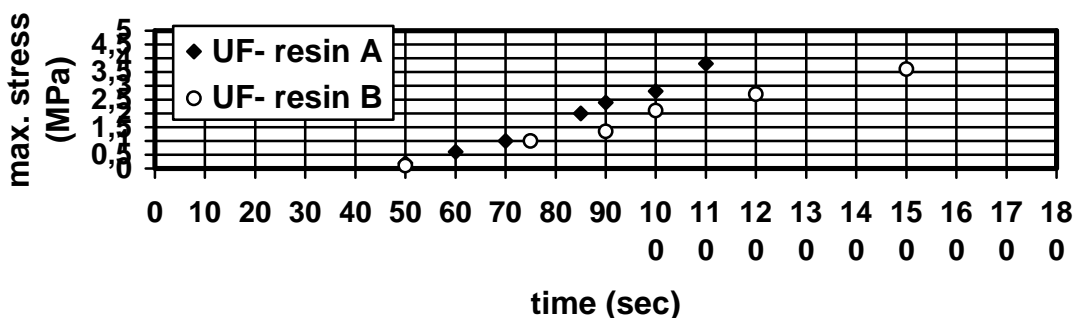


Fig. 2.1: Comparison of two UF-resins with the same molar ratio F/U, but with different reactivities, due to different cooking procedures, tested by means of the Automatic Bonding Evaluation System (ABES) according to Phil E.Humphrey (US-patent 5 176 028). UF-resin A: UF-resins with F/U = 1,08, special cooking procedure for high reactivity; UF-resin B: traditional UF-resin

The testing principle of the ABES-system, which consists of a small press and a tiny testing machine, is shown in figure 2.2. The bonds to be measured were pressed with heated blocks for a certain time, cooled within few seconds and then pulled in shear mode. These tests are repeated for different times and at various temperatures (Humphrey 1996).

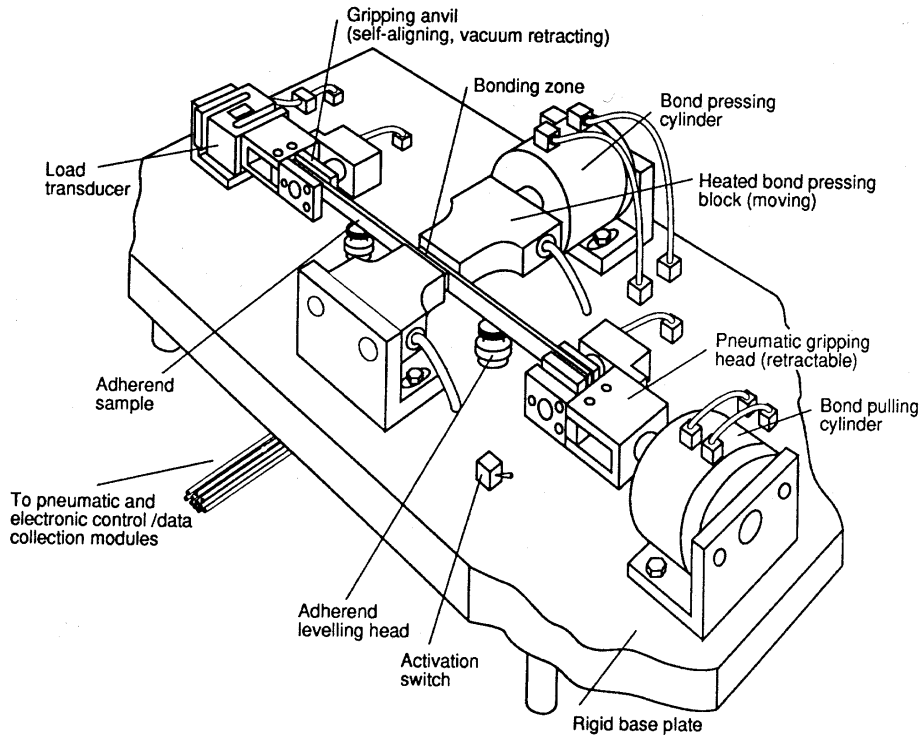


Fig. 2.2: Automatic Bonding Evaluation System (ABES) according to Phil E.Humphrey (US-patent 5 176 028).

During the hot press process it can be distinguished between the chemical curing of the thermosetting resin (building up of the three-dimensional network) and the mechanical forming of the bonding strength between the two adherents. The chemical degree of curing can be monitored using the so-called Differential Scanning Calorimetry (DSC); the forming of the bond strength (degree of mechanical curing) can be seen from DMA-experiments or by the above mentioned ABES-method. Plotting these both degrees of curing in a x-y-diagram shows the different hardening behaviours of various resins. When the press opens, a certain mechanical hardening and with this a certain bonding strength is necessary. The full chemical curing however can be completed outside of the press during hot stacking. Advanced formation of the bond strength already at the same degree of chemical curing will enable shorter press times and will therefore increase the production capacity and reduce production costs.

Table 2.1 describes an example for the use of an accelerator, which distinctly increases the gelling rate of a core layer glue mix, hence enabling a significant reduction of the necessary press time. Such accelerators enable a quick reaction of the hardener salt to generate the acid for the acidic induced hardening reaction of the resin. The accelerator is mixed with the resin just prior use. Since it does not content any hardener or acid, there is no limiting pot life of this premix. To compensate the additional formaldehyde small amounts of formaldehyde catchers are recommended to be added to the glue mix.

Table 2.1: Acceleration of aminoplastic resins by addition of an accelerator (EP 436 485)

Composition of the glue mix	standard glue mix	glue mix with accelerator
liquid UF-resin (F/U = 1,05)	100	100
accelerator	---	2,5
hardener solution (ammonium sulphate 20%)	10	10
formaldehyde catcher (urea)	---	2
Calculated molar ratio F/U of the glue mix	1,05	1,05
Gelation time at 100°C (sec)	44	36

2.1.1.5 Modification of UF-Resins

a) Amelioration of the Hygroscopic Behaviour of Boards for Application in Humid Conditions (see also section 2.1.2.)

The new laminate floorings require a very low long-term thickness swelling of the core boards. After 24 hours the thickness swelling of these core boards, mostly MDF, must not exceed 8% or 10%, sometimes only 6% and even less, all figures based on the original thickness of the board.

Such a low thickness swelling usually cannot be performed with straight UF-resins, the incorporation of melamine is a suitable way to achieve the desired results. Which degree of melamine fortification depends on various parameters, e.g. the type of wood furnish, the pressing parameters (pressure profile, density distribution, quality of particles and fibres) and the applied gluing factor, and can vary between a few percent up to approx. 25%, based on liquid MUF-glue resin. Due to the considerable costs this content of melamine always must be as high as necessary but as low as possible. To a high extent also the cooking procedure of the resin considerably influences the thickness swelling of the boards, even at the same gluing factor and the same content of melamine.

Questions and topics of R&D:

- a) Which amount of melamine in the board is necessary for a certain swelling behaviour?
- b) Based on an equal cost basis: is it better to use a higher gluing factor with a resin with less melamine content or is it better to use resins with higher melamine content but at a lower gluing consumption?
- c) What are the reasons for the better swelling behaviour with melamine fortified resins, especially seen on molecular level?

b) Fortified and Modified Resins for Boards for Use in Humid Conditions ("water resistant boards")

The aminomethylene link is susceptible to hydrolysis and therefore not stable at higher relative humidity, especially at elevated temperatures (Yamaguchi et al.1980). Also the influence of water causes a degradation of the UF-resin with greater devastating effect the higher the temperature of the water in which the boards or the samples during the test run are immersed. This different behaviour of the boards at various temperatures is the basis for standard tests and hence for the classification of bond lines, resins and wooden products, resp., into the different bonding classes. These include the lowest requirements (interior use) for usually produced UF-bonded boards up to more or less water and weather resistant boards (V 100 boiling test, V 313 cycle test, WBP and others) according to the different national and international standards.

The resin used has a crucial influence on the properties of the produced wood-based panels. Depending on the various requirements different resin types are selected for use. Whereas UF-resins mainly are used for interior boards (for use in dry conditions, e.g. in the furniture manufacturing), a higher hydrolysis resistance can be achieved by incorporating melamine and phenol into the resin (melamine fortified UF-resins, MUF, MUPF, PMF). The degree of the melamine fortification and especially the way, how melamine is incorporated into the resin, can be very different. This knowledge usually is proprietary and described in literature only in few cases (Mercer and Pizzi 1994, Maylor 1995).

The incorporation of melamine (MUF, MF+UF) and sometimes phenol (MUPF, PMUF) improves the low resistance of UF-bonds against the influence of humidity, water and weather. The characteristics of the resin however are more or less changed, especially concerning their reactivity. Additionally the costs for these modified and fortified products are incomparable because of the manifold higher price of melamine compared to urea. Therefore the content of melamine in these resins always is as high as necessary but as low as possible, pure melamine-formaldehyde resins are in use only in mixtures with UF-resins. The possible higher hydrolysis resistance as the advantage of the pure MF-resins is counteracted by their low storage stability in liquid form and their unfairly high price.

The different behaviour and resistance against hydrolysis depends on the type of the resin and is based on molecular level.

The addition of melamine to an UF-resin slows down the pH-drop after the addition of the hardener (Higuchi et al. 1979). The gelation time increases with the addition of melamine due to the buffer capacity of the melamine ring (Dunky 1988). This behaviour basically is independent if the melamine is added to the UF-resin just before the gelation test or if it is incorporated chemically in any way to the resin already during the resin cook.

Melamine also can be added in form of melamine acetates (Prestifilippo et al. 1996, Cremonini and Pizzi 1997), which decompose in the aqueous resin mix only at higher temperatures and give some savings of melamine for the same degree of water resistance compared to original MUF-resins.

The durability of a glue line under the conditions of weathering, which essentially means cyclic stresses due to swelling and shrinking (stress rupture) as well as hydrolytic attack on the chemical bonding can be repressed by the incorporation of flexible components like hydrophobic chains into the hardened network introducing some flexibility and hence decreasing internal stresses. This was done by Ebewele (1995) and Ebewele et al. (1991 a+b, 1993, 1994) by incorporating urea-capped di- and trifunctional amines containing aliphatic chains into the resin structure or by using the hydrochloride derivates of some of these amines as a curing agent. Wang and Pizzi (1997) replaced formaldehyde by succinaldehyde $\text{OHC-CH}_2\text{-CH}_2\text{-CHO}$, a dialdehyde with a short hydrocarbon chain. Both approaches introduce some flexibility into the hardened network which should decrease internal stresses as well as some enhanced water repellence of the cured network due to these hydrophobic hydrocarbon chains.

Another approach to increase the resistance of UF-resins against hydrolysis is based on the fact that the acidic hardening of the resin itself causes the residue of acids or acidic substances in the glue line. Myers (1983) pointed out that in case of an acidic hardening system the decrease in the durability of glue bonds can be initiated by the hydrolysis of the wood cell wall polymers adjacent to the glue line as well as by an acid-catalysed resin degradation in the case of UF-bonded products. A neutral glue line therefore should show a distinct better hydrolysis resistance. The amount of hardener (acids, acidic substances, latent hardeners) always should be adjusted to the desired hardening conditions (press temperature, press time and other parameters) and never be like "the more the better". It is just the opposite: a too high addition of hardener can cause brittleness of the cured resin and a very high residue of acidic potential in the glue line. However, neutralization must not take place as long as the hardening reaction has not yet finished, otherwise it would delay or even prevent curing. This aspect is quite an ambitious challenge, which has not yet really been solved in practice. Higuchi and Sakata (1979) found that the complete removal of acidic substances by soaking plywood test specimens in an aqueous sodium bicarbonate solution enables a striking increase in water resistance of UF glue lines. Yamaguchi et al. (1989) soaked plywood specimens in buffer solutions of different pHs and found the slowest decrease in bond strength at neutral pHs. Another attempt was made by this working group (Higuchi et al. 1980, Ezaki et al. 1982) by the use of a glass powder as an acid scavenger, which reacts only slowly with the remaining acid of the glue line and therefore does not interfere the acidic hardening of the resin. Dutkiewicz (1984) got some good results in the neutralization of the inherent acidity of a hardened UF-bonded glue line by the addition of polymers containing amino or amido groups. Also for PF-bonded joints the self-neutralization of the glue line increases the durability of the joint, especially preventing acid deterioration on solid wood (Pizzi et al. 1986).

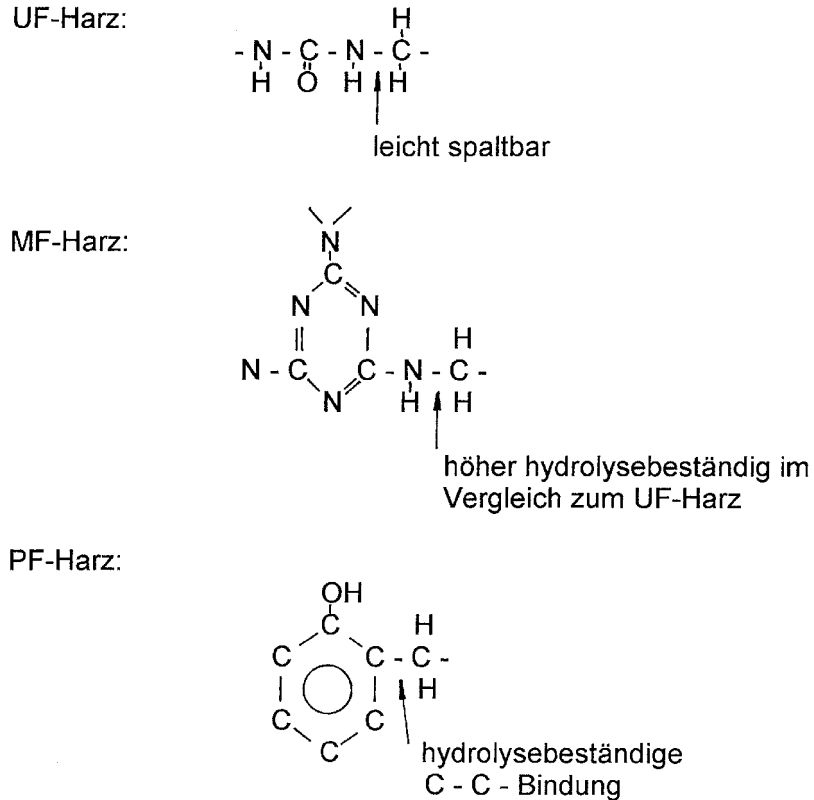


Fig. 2.3: Hydrolytic stability based on molecular level.

Note: "leicht spaltbar": bonding can be hydrolysed easily "höher hydrolysebeständig im Vergleich zum UF-Harz": better resistance against hydrolysis compared to an UF-resin "hydrolysebeständige Verleimung": bonding is resistance to hydrolysis.

The deterioration of a bond line can occur due to:

- The failure of the resin (low hydrolysis resistance, degradation of the hardened resin leading to the loss of bonding strength)
- The failure of the interface between resin and wood surface (replacement of physical bondings between resin and reactive wood surface sites by water or other non resin chemicals). Adhesion for UF-resins to cellulose is sensitive to water not only for the already mentioned lability to hydrolysis of the methylene bridge and of its partial reversibility, but also because theoretical calculations have shown, that adhesion of water to cellulose is stronger than of UF-oligomers; thus water can help to displace hardened UF-resins from the surface of a wood joint. The inverse effect is valid for PF-resins (Pizzi 1994 a).
- The breaking of bonds due to mechanical forces and stresses (influence of water will cause swelling and therefore movement of the structural component of wood based panels, like particles).

There is a quite good industrial experience how to increase the ability of a bonding line to resist especially against the influence of humidity, water and higher temperatures. However it also is known, that especially in e.g. outdoor applications all adhesive systems are working at the upper limit of their performance.

Special advantages of two or more resins and adhesives at the same time can be gained by mixing these different resins prior to their application. The addition of a MF- or MUF-resin to an UF-resin increases the moisture and water resistance of the UF-resins, whereby the degree of resistance

depends on the content of melamine in this mix. However, as long as the requirements can be fulfilled a lower content of melamine in the glue resin system will be a cost advantage.

PMDI can be used as an accelerator and as a special cross linker for UF-resins, with additions of less than 1% in the first case and up to 2% for the latter one, both numbers based on dry particles.

Questions and topics of R&D:

- a) *How does the amelioration of the hydrolysis resistance in melamine fortified resins work?*
- b) *In melamine fortified resins there are still many linkages between two urea molecules? Do these linkages have the same hydrolysis behaviour as in a pure UF-resin?*
- c) *Which bonding types are necessary for new construction applications like facades?*

c) Isocyanate (PMDI) as Accelerator and Fortifier for UF-Resins

UF-resin and PMDI can be sprayed separately without prior mixing onto the particles (Hse et al. 1995, Kehr et al. 1994).

In the usually done so-called mixing procedure the PMDI is pumped under high pressure into the UF-resin (Deppe 1977, Deppe and Ernst 1971). PMDI thereby acts as accelerator and fortifier (better cross linking). Usually 0,5 to 1,0% PMDI based on dry particles are in use beside of the in case slightly reduced UF gluing factor. The specific press time is said to be reduced up to 1 sec/mm.

Addition of PMDI also was recommended using UF-resins with very low molar ratio in order to achieve a low subsequent formaldehyde emission. The poor mechanical and hygroscopic properties can then be regained by the addition of PMDI (Dunky 1986, Roffael et al. 1993, Tinkelenberg et al. 1982, EP 25 245).

2.1.1.6 Content of Formaldehyde, Molar Ratio

The molar ratio F/U had been decreased significantly during the last two decades; this especially had been the case with resins for particleboards and MDF. Main purpose was the limitations of the subsequent formaldehyde emission. Table 2.2 summarizes the usual molar ratios of UF-resins as in use in Germany and Austria.

Table 2.2: Actual molar ratios F/U of UF-glue resins

F/U	description
1,55 to 1,85	classical plywood resin, especially for the combination with melamine for water-resistant boards, cold setting UF-resins
1,2 to 1,55	plywood resins with low content of formaldehyde, which are used together with special formaldehyde catchers
1,35 to 1,6	former particleboard resin with high subsequent formaldehyde emission
1,15 to 1,3	former particleboard resin with high subsequent formaldehyde emission
1,03 to 1,10	E1-glue resins for particleboard and MDF
< 1,00	glue resins with extreme low content of formaldehyde, in most cases modified or melamine fortified

2.1.1.7 Molecular Characterisation

The molar mass distribution can be investigated using the gel permeation chromatography GPC (Dunky 1980, Dunky and Lederer 1982, Hlaing et al. 1986, Hse et al. 1994, Katuscak et al.1981, Ludlam and King 1984). Main problem is the choice of the proper solvent and mobile phase to guarantee full solubility of the resin. Usually DMF is used, even sometimes small amounts of the resins stay unsolved. DMSO gives better solution of the resins, but some additional problems in the GPC analysis (Dunky 1980). Also the calibration of the chromatographic columns is a problem, due to missing UF calibration standards.

The averages of the molar mass can be (i) calculated from the gel chromatograms, taking into consideration the various problems with the calibration of the columns, and (ii) measured by

vapour pressure osmometry for the number average (Dunky 1980, Dunky et al.1981, Dunky and Lederer 1982, Katuscak et al.1981) or light scattering for the weight average (Dunky 1980, Dunky et al.1981, Dunky and Lederer 1982). Using GPC-LALLS the weight averages at each elution volume can be monitored during the GPC-run (Billiani et al.1990).

Also the condensation step of the resin can be followed using GPC (Armonas 1970, Braun und Bayersdorf 1980 a, Billiani et al.1990, Dunky u.a. 1981 b, Hope u.a. 1973, Tsuge u.a. 1974 b).

Questions and topics of R&D:

How to overcome the actual problems with the analysis of the molar mass distribution?

2.1.1.8 Influencing Technological Properties of UF-Resins

a) Influence of the molar ratio F/U on the properties of the UF glue resins

UF-resins consist of the two monomers urea and formaldehyde. Forced by the necessity to decrease the subsequent formaldehyde emission the molar ratio F/U of the two monomers was changed thoroughly during the last two decades. However it cannot be expected that under these circumstances no changes in the properties and the performance of the resins will occur. That really did occur; but on the other side it was the exceptional success of the UF-chemistry and the UF-chemists that still and even increasingly UF-resins are in use; they have more or less the same performance characteristics as many years ago, but with distinct lower content of formaldehyde and hence a distinct lower subsequent formaldehyde emission, as low that the former problem of formaldehyde emission is now solved.

The main differences between UF-resins with high and with low content of formaldehyde, resp., are the reactivity of the resin due to the different content of free formaldehyde on the one side and the degree of cross linking in the cured network on the other side. The degree of cross linking is directly correlated to the molar ratio of the two components during the condensation. Taking into consideration that an ideal linear UF-chain has a molar ratio of 1,0, assuming that there are no ether bridges, no unreacted branch methylol groups, no other wasting of formaldehyde, than the small surplus of molar ratio above equality stands for the cross linking. In practice, this calculation is not really exact, because there are always ether bridges and some unreacted methylol groups in the resin, even after hardening. This is not only a question of the proper cooking procedure but also a simple question of the mobility of the individual molecules with already higher molar masses during the hardening reaction and therefore often a question of steric hindrance, which renders some reactions impossible.

The higher the molar ratio F/U, the higher is the content of free formaldehyde in the resin. Assuming steady state conditions in the resins, that means that e.g. post added urea had enough time to react with the resin, the content of free formaldehyde is very similar even with different cooking procedures. In a coarse scale the content of formaldehyde in a straight UF-resin is approx. 0,1% at F/U = 1,1 and 1% at F/U = 1,8 (Dunky 1985). It also decreases with time due to aging reactions in the resin consuming parts of this free formaldehyde. Additionally the determination of the free formaldehyde requires exact conditions to avoid any cleavage of weakly bonded formaldehyde (Käsbauer et al.1976) therefore the content of free formaldehyde is only a coarse number.

It has to be considered, that it is neither the content of free formaldehyde itself nor the molar ratio, which eventually should be taken as the decisive and the only one criterion for the classification of a resin concerning the subsequent formaldehyde emission from the produced boards, because the composition of the glue mix as well as the various process parameters during the board production determine the formaldehyde emission. Depending on the type of board and process, sometimes it is recommended to use an UF-resin with already low molar ratio F/U (e.g. F/U = 1,03), hence low content of free formaldehyde; sometimes the use of a resin with a higher molar ratio (e.g. F/U = 1,10) and the addition of a formaldehyde catcher will give better results. Which of these possible ways will be the better one in practice only can be decided separately in each case by trial and error.

Questions and topics of R&D:

- a) *How to cook resins with a good reactivity and sufficient cross linking, but still a low formaldehyde emission during hardening and during use?*
- b) *Is there still a cross linked state after hardening with the molar ratios as used nowadays?*

b) Influence of the degree of condensation and of the molar mass distribution on the properties of the UF-resin

The molar mass distribution is determined on the one side by the degree of condensation, on the other side by the addition of urea (and sometimes also other components) after the condensation step; with this again low molar masses are present in the resin. This is the big difference for the formaldehyde condensation resins (UF-resins, MF/MUF-resins, also to some smaller extent PF/PUF-resins) in comparison with polyaddition resins and polymerised plastics. For this reason the molar mass distribution is much broader than for other polymers: it starts at the low molar mass monomers (the molecular weight of formaldehyde is 30, for urea it is 60) and goes up to more or less polymeric structures. However it is not clearly known, what the highest molar masses in an UF-resin really are. Billiani et al. (1990) and Dunky and Lederer (1982) have found molar masses up to 500.000 by light scattering. Especially using the low angle laser light scattering (LALLS) coupled to GPC the shear conditions in the chromatographic columns (Huber and Lederer 1980) should guarantee that all physically bonded associates are split off and that these high numbers between 100.000 and 500.000 really describe the macromolecular structure of an UF-resin in the right manner. A second important argument for this statement is the fact, that up to such a high number of the molar mass the on-line calibration curve gained in the GPC-LALLS run is persistent and more or less linear. It does not contain any sudden transition as this would be the case if by agglomeration after the column the molar mass would be increased sharply but inconsistently.

The higher the molar mass (the higher the degree of condensation), the lower is the water dilutability of the resin and the lower are the portions of the resin that remain soluble in water. Diluting the resin with an surplus of water causes precipitation of parts of the resin. This part contains preferably the higher molar mass molecules of the resin and increases with higher degree of condensation (Dunky and Lederer, 1982). At a given solid content, the viscosity increases with higher condensed structures.

Questions and topics of R&D:

- a) *Which is the „optimal“ degree of condensation or the „optimal“ molar mass distribution?*
- b) *Which are the highest molar masses within an UF-resin?*

2.1.1.9 Cold Tack Properties of UF-Resins

Cold tack means that the particle mat gets some strength already after the prepress, without any hardening reaction. This strength is necessary for instance, if the particle mat is handed over from one caul to another. This especially can be the case in multiopening particleboard presses, in special form presses or in plywood mills, where the glued veneer layers are prepressed to fit into the openings of the presses. Also some small cold tack is necessary to avoid the blowing out of the fine surface in the entrance mouth of continues presses with high belt speeds. On the other side cold tack can lead to agglomeration of fine particles and fibres in the forming station.

Cold tack is generated during the dry out of a glue line, up to a certain maximum. Than it decreases again, when the glue line is more or less dried out. Both, the intensity of cold tack as well as the optimum time span after the glue is spread, can be adjusted by the degree of condensation as well as by special cooking procedures (Dunky 1993, DE 26 55 327, EP 1596). Additionally also various additives can increase the cold tack of the glue resins, e.g. some thermoplastic polymers like polyvinyl alcohols.

Questions and topics of R&D:

- a) *How to enhance cold tack of resins?*
- b) *How to avoid undesirable cold tack?*
- c) *Which test method can describe the cold tack best, especially in the laboratory?*

d) *How to influence the time dependence of cold tack?*

2.1.1.10 Glue Resin Mixes (UF, MUF)

Table 2.3 summarizes some few glue resin mixes for different applications in the production of particleboard and MDF.

Table 2.3: UF- glue resin mixes for the production of particleboard (PB) and MDF

Components/resin mixes	PB-CL	PB-FL	PB-CL	PB-FL	MDF
PB-UF-resin (1)	100	100	-	-	-
MDF-UF-resin (2)	-	-	-	-	100
MUF-resin (3)	-	-	100	100	-
Water	-	10-20	-	10-20	30-80
Hardener solution (4)	8	2	15	6	2
urea solution (5)	up to 5	up to 5	up to 5	up to 5	15
(1) UF-resin with F/U = 1,03 to 1,08					
(2) UF-resin with F/U = approx. 0,98 to 1,02					
(3) MUF-resin with F/U = approx. 1,03 to 1,08					
(4) ammonium sulphate solution (20%)					
(5) urea-solution (40%)					
CL: core layer; FL: face layer					

Table 2.4 summarizes various glue resin mixes for different applications in the production of plywood, parquet and furniture.

Table 2.4: UF- glue resin mixes for the production of plywood, parquet and furniture

Components/resin mixes	A	B	C	D	E
UF-resin (1)	100	100	100	-	-
UF-resin (2)	-	-	-	100	-
UF-resin (3)	-	-	-	-	100
Extender (4)	20	40	10	-	-
Water	-	10-20	-	-	-
Hardener solution (5)	10	-	-	-	-
Hardener solution (6)	-	20	-	-	-
Powder hardener (7)	-	-	3	-	-
Powder hardener (8)	-	-	-	25	-
Liquid hardener (9)	-	-	-	-	10-20
(1) UF-resin with F/U = approx. 1,3					
(2) UF-resin with F/U = approx. 1,5 to 1,6					
(3) high viscous UF-resin with F/U = approx. 1,3 to 1,4					
(4) Extender:: rye- or wheat flour, in case containing some inorganic portions					
(5) e.g. ammonium sulphate solution (20%)					
(6) e.g. ammonium sulphate-urea solution (20%/20%)					
(7) e.g. ammonium sulphate in powder form					
(8) RTU powder hardener, containing powdered hardeners, formaldehyde catcher, extenders and other additives					
(9) high viscous filled hardener, containing inorganic fillers or organic thickeners, a hardener substance, in case a formaldehyde catcher and other additives					
Glue mix A: standard glue mix					
Glue mix B: higher degree of extension					
Glue mix C: high solid content, gives an enhanced water resistance of the glue line					
Glue mix D: two component glue mix:: liquid resin + RTU hardener in powder form, no addition of other components necessary					
Glue mix E: two component glue mix:: liquid high viscous resin + liquid high viscous hardener; the mixing of these two components usually is performed directly above the roll coater.					

2.1.2 Melamine Resins

2.1.2.1 Chemistry of Melamine- and Melamine-Urea-Resins

The low resistance of urea-formaldehyde-resins against hydrolysis can be increased by incorporating melamine in various forms to the resin. Due to the high costs pure MF-resins however are more or less not in use for wood gluing. Most important aspect in using MUF-resins is always to use as much melamine as necessary but as low as possible. In practice, the melamine content of a MUF-resin can vary between few percent (melamine fortified UF glue resins) up to 25% and sometimes even more.

The application of MUF-resins is very similar to the UF-resins, the hardener addition usually is distinctly higher. The basic reaction of the MF-production is the methylation and the following condensation. The production of melamine-fortified UF-resins and of MUF-resins can follow various paths:

- (i) Co-condensation of melamine, urea and formaldehyde in a multistep reaction (e.g. DE 2 455 420, DE 3 442 454, EP 62 389, USP 4 123 579, USP 5 681 917). A comprehensive study of various reaction types had been done by Mercer and Pizzi (1994). They especially compare the sequence of the additions of melamine and urea, resp.
- (ii) Mixing of a MF-resin with an UF-resin according to the desired composition of the resin (Maylor 1995, DE 3 116 547, EP 52 212)
- (iii) Addition of melamine in various forms (pure melamine, MF/MUF-powder resin, melamine acetates) to an UF-resin during the application of the glue mix. In the case of the addition of pure melamine the UF-resin must have a rather high molar ratio, otherwise there is not enough formaldehyde to react with the melamine in order to incorporate it into the resin.

The addition of melamine salts (acetates, formiates, oxalates) to UF-resins has two functions: they act as a hardener as well as the melamine is incorporated into the UF-resin, forming a MUF-resin. Furthermore it is reported that the amount of melamine needed in this form of the melamine salts is much lower than in a MUF-resin, on equal base of properties of the wood based panels (Cremonini and Pizzi 1997, 1999, Kamoun and Pizzi 1998, Prestifilippo et al. 1996).

The course of the concentration of various structural elements during the condensation of a MF-resin can be followed by ¹³C-NMR (Aarts et al. 1995) The lower the pH during the condensation, the higher is the portion of methylene bridges compared to ether linkages.

MUPF-resins (PMUF-resins) are mainly used for the production of so-called V100-boards according to DIN 68763 and EN 312-5 and -7, option 2. They usually contain small amounts of phenol. Production procedures are described in patents and in the literature (DE 2 020 481, DE 3 125 874, DE 3 145 328, Prestifilippo and Pizzi 1996, Cremonini et al. 1996 b).

PMF-resins usually contain only little or no urea at all. The analysis of the molecular structure of these resins has shown, that there is no co condensation between the phenol and the melamine, but that there are two distinct networks (Braun and Krauße 1982, 1983, Braun and Ritzert 1984 b+c). The reason for this is the different reactivity of the phenol- and the melaminemethylols, depending on the existing pH.

Questions and topics of R&D:

- a) *Is there a real co condensation between the urea and the melamine via methylene- or ether bridges? Braun and Ritzert (1988) and Nusselder et al. (1998) have stated this. However it has not been proved for a mixing of an UF- and a MF-resin. In this case both resins might harden as pure resins, only interpenetrating each other.*
- b) *PMF-resins: might there be any co condensation, despite of not proved yet? How to achieve a co condensation?*

2.1.2.2 Aging Behaviour

As the UF-resins also MF/MUF/MUPF-resins react during their storage under increasing the degree of condensation and the viscosity. The higher the temperature, the steeper this increase of the viscosity. Melamine containing resins usually show a shorter storage stability than pure UF-resins. At lower temperatures thixotropy can occur.

Questions and topics of R&D:

- a) *How to avoid thixotropy of MUF/MUPF-resins? What are the chemical reasons for such an effect?*
- b) *How to increase storage stability of melamine containing resins?*

2.1.2.3 Hydrolysis of Melamine- and Melamine-Urea-Resins

It has already been stated, that the addition of melamine to an UF-resin or the increase of the melamine content in an MUF-resin increases the stability of the resin against hydrolysis.

The fortification of the UF-resin by melamine is based on

- the quasiaromatic ring structure of the melamine, which leads to a stabilisation of the C-N-bonding between the amide group of the melamine and the methylolgroup
- the better hydrolysis resistance of the C-N-bonding between the melamine ring and the methylolgroup and
- the slower decrease of the pH in the bond line due to the buffer capacity of melamine (S.Chow 1973, Dunky 1984, Higuchi et al. 1979). This lower drop of the pH, however, also causes an decrease of the hardening reactivity and therefore an increase of the gel time and the necessary press time. This also is seen in the shift of the exothermic DSC-peak (Troughton and Chow 1975).

Questions and topics of R&D:

- a) *How to determine in easy way the lowest amount of melamine in the resin, which is necessary for a certain stability against hydrolysis?*
- b) *Can the hydrolysis resistance be measured on a molecular level?*
- c) *How works the protection of UF-bonds within a MUF-resin?*

2.1.2.4 Hardening of Melamine- and Melamine-Urea-Resins

The hardening reaction of a MUPF/PMUF-resin is not really clear. MUF-resins harden in the acidic range, whereas phenolic resins have a minimum of reactivity under these conditions. There is the danger, that the phenolic portion of the resin might not really be incorporated into the aminoplastic portion of the resin during hardening.

During the hardening of PMF-resins no co condensation occurs, in the hardened state two independent interpenetrating networks exist (Higuchi et al.1994). Only in model reactions between phenolmethylols and melamine indications for a co condensation via methylene bridges between the phenolic nucleus and the amid group of the melamine had been found by ¹H-NMR.

Questions and topics of R&D:

- a) *Is there a real co condensation during hardening of MUF/MUPF-resins? How to prove if yes or no? How to achieve such co condensation reactions? Will there be better properties of the hardened resin in case of such co condensations, e.g. concerning resistance against hydrolysis?*
- b) *How to find possible co condensation bonds in PMF-resins? Will there be better properties of the resin and of the glue line possible with co condensation bonding?*

2.1.2.5 Modification of Melamine- and Melamine-Urea-Resins

- a) Addition of tannins (Cremonini et al.1996 a)
- b) Fortification by isocyanate: additional cross-linking via the isocyanate, especially PMDI.

2.1.2.6 Content of Formaldehyde, Molar Ratio

Resins containing melamine can be characterised by the molar ratio $F/(NH_2)_2$ or by the triple molar ratio F:U:M. The mass portion of melamine in the resin can be described based on the liquid resin or based on the total mass of urea and melamine in the resin.

2.1.2.7 Molecular Characterisation

MUF-resins can be characterised by gel permeation chromatography GPC measuring the molar mass distribution (Braun et al.1985, Braun and Ritzert 1985, Maylor 1995, Tomita and Ono 1979) as well as via the measurement of molar mass averages (Braun and Pandjojo 1979 a).

One of the most interesting tasks is to clarify if there is a real co condensation within MUF-resins or if two independent networks are formed, which only penetrate each other.

Questions and topics of R&D:

- a) *How is the melamine distributed in terms of the molar mass distribution? Is the distribution equally over all molar masses?*
- b) *GPC-analysis with various detectors: RI-detector for the concentration, LALLS-detector for molar masses, UV- or IR-detector for the distribution in a MUF-resin.*
- c) *MUF-resins as co condensation resins: random co condensation or bulk co condensation?*

2.1.2.8 Influencing the Technological Properties of Melamine- and Melamine-Urea-Resins

a) Influence of the content of melamine

The higher the content of melamine, the higher is the stability of the hardened resin against the influence of humidity and water (hydrolysis resistance) (S.Chow and Pickles 1976, Neusser and Schall 1972 b).

Questions and topics of R&D:

How to protect UF-bonds in MUF-resins against hydrolysis?

b) Influence of the molar ratio

As in all aminoplastic resins, also in melamine containing resins the molar ratio $F/(NH_2)_2$ distinctly determines reactivity, the possible degree of cross linking and hence the bonding strength. If the molar ratio is decreased in order to lower the formaldehyde emission, the reactivity as well as the degree of hardening (degree of cross linking) might decrease.

Questions and topics of R&D:

How to decrease the formaldehyde emission from melamine containing resins but avoiding various disadvantages like less reactivity or lower degree of condensation?

c) Influence of the degree of condensation

The higher the degree of condensation, the higher is the viscosity at the same solid content. For mixtures MF + UF the degrees of condensation of the two components determine the viscosity of the mix according to the composition. The penetration behaviour of melamine containing resins has not yet been determined, but obviously should be similar to UF-resins.

Questions and topics of R&D:

- a) *Influence of the degree of condensation (viscosity) on the properties of the hardened glue line and the properties of the glued products?*
- b) *Penetration behaviour of melamine containing resins on wood surfaces, depending on their degree of condensation?*

2.1.2.9 Cold Tack Behaviour of Melamine- and Melamine-Urea-Resins

The cold tack behaviour is similar to all other aminoplastic resins. A higher degree of condensation as well as special cooking procedures can enhance the cold tack of these resins.

Questions and topics of R&D:

- a) Which chemical reactions are possible and important to optimise the cold tack?
- b) How to avoid cold tack, which might lead e.g. to blender build up?

2.1.2.10 Glue Resin Mixes (UF, MUF)

See section 2.1.1.10.

2.1.3 Phenolic Resins

Phenolic resins show a very high resistance of the C-C-bonding between the aromatic nucleus and the methylolgroup or methylene bridge and therefore are used for water and weather resistant glue lines and boards like particleboards, OSB, MDF or plywood. Another advantage of the phenolic resins is the very low subsequent formaldehyde emission also due to the strong C-C-bonding.

Disadvantages of the phenolic resins are the distinct longer press times necessary compared to UF-resins, the dark colour of the glue line and the darker colour of the board surface as well as a higher moisture content of the boards stored at higher relative humidity of the air due to the hygroscopicity of the alkaline used.

2.1.3.1 Chemistry of Phenolic Resins

a) Cooking Procedures

The cooking procedure of a phenolic resin is a multistage process, which is characterized by the time, sequence and the amount of the various additions of the raw materials, which are phenol, formaldehyde and alkaline as the most important ones. The raw materials also can be added in several steps.

As with all other formaldehyde condensation resins, there are two main reactions:

- **Methylation:** there is no special preference of an ortho- or para-substitution, which however could be achieved using special catalysts (Peer 1959, 1960). The methylation is strongly exothermic and includes the risk of an uncontrolled reaction (Kumpinsky 1994).
- **Condensation:** forming of methylene- and ether linkages, whereby the latter ones will more or less not exist at high alkaline conditions. In this stage chains of molecules are formed, which still carry free methylol groups; the stopping of the reaction by cooling down the kettle prevents from gelling the resin.

Phenolic resins contain oligomeric and polymeric chains as well as monomeric methylolphenols, free formaldehyde and not reacted phenol. The content of both monomers has to be minimized by the proper cooking procedure. Various cooking procedures are described in the chemical literature and in patents (Chen and Rice 1976, Gollob 1982, Mueller 1988, Sellers 1985, Walsh and Campbell 1986, USP 3 342 776, USP 4 433 120).

Special resins consist of a two-phase system with a highly condensated PF-resins, which is no longer soluble, and an usual PF-resin (Steiner et al. 1991). Another two-phase resin is composed by a highly condensated PF-resin still in an aqueous solution and a PF-dispersion (Higuchi et al. 1992, USP 4 824 896). Purpose of such special resins is the gluing of wet wood, where there exists the danger of over penetration of the resin into the wood surface exists hence causing a starved glue line.

The properties of the resins are determined mainly by the molar ratio F/P, the concentration of the two raw materials phenol and formaldehyde in the resin, the type and amount of the catalyst (in most cases alkaline) and the reaction conditions. The reaction itself is performed in an aqueous system without addition of organic solvents.

Questions and topics of R&D:

How to model the production reactions of a phenolic resin in order to avoid uncontrolled exothermic reactions?

b) Alkaline

Usually alkaline NaOH is used as catalyst, in an amount up to one mole per mole phenol (molar ratio NaOH/P), which corresponds to an portion of alkaline in the liquid resin of approx. 10 mass%. The pH of a phenolic resin is in the range 10 – 13. The biggest part of the alkaline is free NaOH, a smaller part is present as sodium phenolate. The alkaline is necessary to keep the resin water soluble via the phenolate formation, in order to achieve a degree of condensation as high as possible at a viscosity, which still can be used in practice. The addition of alkaline significantly drops the viscosity of the reaction mix. The higher the degree of condensation, the higher is the viscosity but also the shorter is the necessary press time.

Questions and topics of R&D:

a) *How to increase the degree of condensation to the outmost range without loosing storage stability?*

b) *How to minimize the content of alkaline but still maintaining a high degree of condensation?*

c) Other basic catalysts

Beside of NaOH also other basic catalysts principally can be used, like Ba(OH)₂, LiOH, Na₂CO₃, ammonia or hexamine, however in practice this is more or less not be done. The type of catalyst significantly determines the properties of the resins (Duval et al.1972, So and Rudin 1990, Wagner and Greff 1971). Replacing alkaline in PF-bonded boards could give some advantages. Ammonia as gas evaporates during the hot press process and does therefore not contribute to the alkaline behaviour and the hygroscopicity of the boards. Important is to hold the pH as long as possible fairly high during the hot pressing in order to guarantee a high reactivity and hence a short press time (Oldoerp 1997, Oldoerp and Miertzsch 1997).

Questions and topics of R&D:

a) *How to improve the properties of PF-resins cooked without alkaline?*

b) *Which other basic substances could be used as catalyst for PF-resins?*

d) Monitoring the condensation process

The condensation process of PF-resins can be monitored by means of the increase of the viscosity (correction to same temperature and solid content) and by GPC/SEC to measure the molar mass distribution. Chromatograms have been shown by Duval et al. (1972), Ellis and Steiner (1990), Gobec et al. (1997), Kim et al. (1983) and Nieh and Sellers (1991).

Questions and topics of R&D:

How to optimise the GPC working conditions? How to optimise the calibration of the GPC-columns investigating PF-resins?

e) Spray dried PF-resins

PF-powder resins are produced by spray drying of aqueous phenolic resins. During this process the resin is condensed further due to the thermal impact, the molar mass distribution is shifted to higher molar masses (Ellis and Steiner 1991); the higher the spraying temperature, the higher is this increase of the molar masses.

Due to the absence of water such spray dried resins are storable for several months. Important in the application of the powder resins is the fact that the powder must melt in order to wet the wood surface and to penetrate into it. The higher the molar masses, the higher is the risk that this flow behaviour is not more given in a sufficient degree.

Main area of application of spray dried PF-powder resins is the production of OSB. There are several advantages using powder resins:

- a lower needed gluing factor due to the fact, that there is no over penetration of the melted powder into the wood surface (Lambuth 1987)
- a better distribution of the resin on the strand surface
- a distinct lower moisture content of the glued strands and therefore a shorter press time (no hindrance of the gelling process by an excess of water)
- less contamination of the gluing drums
- a better storage stability of the resin.

f) Properties of phenolic resins

Table 2.5 summarizes the properties of various PF-resins.

Table 2.5: Properties of PF-glue resins

	particleboard CL	particleboard FL	AW100-plywood
solid content (%)	46 - 48	ca. 45	46 - 48
total alkaline (%)	7 - 9	3 - 4	7 - 10
free alkaline (%)	6 - 8	2 - 3	6 - 9
Viscosity (mPa*s)	300 - 700	300 - 500	500 - 800
density (g/ml)	approx.1,23	approx.1,18	approx.1,23
CL: core layer; FL: face layer AW100-plywood according to DIN 68705			

The content of free monomers (formaldehyde, phenol) depends on the type of the resin and the cooking procedure. Usual values are:

Free formaldehyde < 0,3 to 0,5 mass%

Free phenol < 0,1 to 0,3 mass%.

Questions and topics of R&D:

How to minimize the content of free monomers?

2.1.3.2 Aging Behaviour

The storage stability of liquid PF-resins is limited to few weeks up to several months, depending on the degree of condensation, the content of alkaline and the viscosity. Decisive parameter for the end of the possible storage stability is the viscosity of the resin in terms of a proper application onto the wood surface during blending and of course in term of the danger that the resin might gel in a storage tank. The lower the content of alkaline, the lower the storage stability. The aging behaviour can e.g. also monitored by means of GPC (Werner and Barber 1982).

Questions and topics of R&D:

How to elongate the storage stability of PF-resins, especially of resins with low content of alkaline?

2.1.3.3 Gelling and Hardening of Phenolic Resins

PF-core layer resins usually have the highest molar masses and hence show an high reactivity and quick gelation. They contain higher amounts of alkaline than face layer resins in order to keep the resin soluble even at higher degrees of condensation. The higher the degree of condensation during the production process (the higher the viscosity), the shorter is the necessary gelling time (Haupt and Sellers 1994 b). The limits of the increase of the degree of condensation in the production process of the resin is given by (i) the viscosity of the resin (the resin must be able to be pumped, a certain storage stability as well as a proper distribution of the resin on the particles during blending is required) and (ii) in the flow behaviour of the resin under heat, guaranteeing the wetting of the unglued second wood surface and a sufficient penetration into the wood surface. Decreasing the solid content of the resin is limited by a possible too high moisture content of the glued particles.

The hardening of a phenolic resin can be seen as the transformation of molecules of different size via elongation of the chains, branching and cross linking to a three-dimensional network with a theoretical endless high molar mass. The hardening rate depends on various parameters, like molar mass of the resin, molecular structure of the resin, portion of various structural elements as well as possible catalysts and additives.

Alkaline PF-resins contain free reactive methylol groups in sufficient number and can harden even without any further addition of formaldehyde, of a formaldehyde source or of catalysts. The hardening reaction is only initiated by heat. The methylol groups thereby react to methylene and methyleneether bridges. Under high temperatures ether bridges can be retransformed to methylene bridges. The lowest possible temperature for a technically sufficient gelation rate is approx. 100°C. In some cases potash in form of a 50 mass% solution is added in the core layer resin mix in an amount of approx. 3 – 5% potash solid based on resin solid content.

Pizzi and Stephanou (1993) investigated the dependence of the gel time from the pH of an alkaline PF-resin. Surprisingly they found an increase in the gel time in the region of very high pH-values (above 10); exactly such pHs, however, are given with the usual PF-resins with a content of NaOH of 5 to 10 mass%. A decrease of the pH in order to accelerate the hardening process is not possible, because a spontaneous precipitation would occur. A change of the pH of the resin however might occur, when the resin comes into contact with a wood surface. Especially with rather acidic wood species, the pH of the resin thereby could significantly drop (Pizzi and Stephanou 1994 a).

The gelling process can be monitored via DSC, ABES or DMA; the chemical hardening can be followed by means of solid state NMR, looking at the increase of methylene bridges based on the amount of aromatic rings (So and Rudin 1985, 1990, Young 1985), at the portion of 2, 4, 6-threesubstituted phenols (Young 1985) or at the ratio between methylol groups and methylene bridges (Schmidt and Frazier 1998 a+b). This chemical degree of hardening however is not equal with the chemical degree of hardening as monitored by DSC. Plotting one of these degrees of chemical hardening versus the degree of mechanical hardening, as measured e.g. via ABES or via DMA, exhibits the comprehensive hardening pattern of a resin (Geimer et al. 1990, Young 1985).

Lu and Pizzi (1998 a) showed, that lignocellulosic substrates have a distinct influence on the hardening behaviour of PF-resins, whereby the activation energy of the hardening process is much lower than for the resin alone (Pizzi et al. 1994 b). The reason is a catalytic activation of the PF-condensation by carbohydrates like crystalline and amorphous cellulose and hemicelluloses. Covalent bonds between the PF-resin and the wood, especially lignin, however play only a minor role.

The acidic induced gelling reaction can cause severe deterioration of the wood substance and therefore has lost more or less completely its importance. Pizzi et al. (1986) describe a procedure for the neutralization of acidic hardened PF-glue lines by adding a complex of morpholine and a weak acid in order to prevent the acidic deterioration of the wood substance. Several other attempts, which however failed, had been done by Christiansen (1985), incorporating the acid on chemical way into the resin or fixing the hardeners (high molecular polystyrenesulfonacids) physically in the glue line.

Acceleration of the hardening process of phenolic resins:

An acceleration of the hardening reaction is possible by using a degree of condensation as high as possible. Another way is the addition of propylene carbonate (Pizzi et al. 1997, Pizzi and Stephanou 1993, 1994 b, Riedl and Park 1998, Steiner et al. 1993, Tohmura 1998, Tohmura and Higuchi 1995). The way of working for this acceleration, however, is not yet clear: it might be due to the formed hydrogen carbonate ion after hydrolysis of the propylene carbonate (Tohmura and Higuchi 1995) or due to the formation of hydroxybenzyl alcohol and aromatic carbonyl groups in the reaction of the propylene carbonate with the aromatic ring of the phenol (Pizzi and Stephanou 1994 b). The higher the addition of propylene carbonate, the lower the gel time of the PF-resin (Pizzi and Stephanou 1993).

Other accelerators for PF-resins are potash (potassium carbonate), sodium carbonate (Higuchi et al. 1994, Tohmura 1998) or sodium- and potassium hydrogenecarbonate.

Also wood inherent chemicals might have an accelerating influence on the hardening reactivity of PF-resins (Tohmura 1998).

Post curing and maturing:

Since phenolic resins harden only thermically, the post curing during stapling is very important. In opposite to UF-bonded boards, PF-bonded boards should be stapled as hot as possible to guarantee a maximum post curing effect. On the other side, very high stapling temperatures might cause partial deterioration (seen as discoloration) of the wood.

Questions and topics of R&D:

- a) Which chemicals give the best accelerating effect for PF-resins?
- b) How does the acceleration with propylene carbonate work?
- c) How can the post curing effect for PF-bonded boards be optimised?

2.1.3.4 Modification of Phenolic Resins

a) Postaddition of urea:

The addition of urea to a phenolic resin gives several effects:

- Decrease of the content of free formaldehyde
- Decrease of the viscosity of the glue resin
- Acceleration of the hardening reaction via the higher possible degree of condensation of the resin at the same viscosity
- Reduction of the costs of the resin.

The urea usually is added to the finished PF-resin and causes a distinct decrease of the viscosity due to the breaking up of hydrogen bonds (Gramstad and Sandstroem 1969) and due to the dilution effect. There is obviously no co condensation of the urea with the phenolic resin. Urea only reacts with the free formaldehyde of the resin forming methylols, which however do not react further due to the high pH (Kim et al. 1990). Only for higher temperatures during the hot pressing Scopelitis and Pizzi (1993) suppose a phenol-urea-co condensation.

The higher the amount of post added urea, the worse are the properties of the boards. A reason for this might be the diluting effect of urea on the PF-resin. Amelioration of the co condensation process also could help in the optimisation of the urea addition. Oldoerp and Marutzky (1998) have found better board properties with an increased urea addition. Since, however, more or less the full added urea can be extracted from the boards, no significant co condensation between the urea and the phenolic resin seems to have occurred.

Using such PUF-resins, the gluing factor should be calculated only based on the PF-resin solid in the PUF-resin.

b) Cocondensation between phenol and urea:

A real co condensation between phenol and urea can be performed by two ways:

- Reaction of methylolphenols with urea (Tomita and Hse 1992, 1993, Tomita et al. 1994 a+b)
- Acidic reaction of UFC (urea-formaldehyde-concentrate) with phenol followed by an alkaline reaction (Tomita und Hse 1991, Ohyama et al. 1995).

The kinetic of the co condensation of monomethylolphenols and urea is reported by Pizzi et al. (1993) and Yoshida et al. (1995); model reactions for proving an urea-phenol-formaldehyde-co condensation (reaction of urea with methylolphenols) are described by Tomita and Hse (1991, 1992, 1998). Fast advancement and hardening acceleration of low condensation alkaline PF-resins by esters and copolymerised urea is reported by Zhao et al. (1999).

Questions and topics of R&D:

Will a co- condensation PUF-resin give better results than a post added urea PUF-resin?

c) Addition of tannins:

Purposes are:

- The acceleration of the hardening reaction (Kulvik 1977)
- The replacement of phenol or PF-resin (Chen 1982, Dix and Marutzky 1982, Drilje 1975, Long 1991, Suomi-Lindberg 1985).

Questions and topics of R&D:

Which special effects can be achieved adding tannins to PF-resins?

d) Addition of lignins:

The addition of lignin to phenolic resins can be (i) as an extender, e.g. in order to increase the cold tack or to reduce costs, or (ii) in order of a chemical modification of the resin, whereby the lignin is chemically incorporated into the phenolic resin. The basic idea behind is based on the chemical similarity between the phenolic resin and lignin or between phenol and the phenyl propane unit of the lignin. The lignin can be added at the beginning, during the cooking procedure or at the end of the condensation reaction (with a following reaction step between the lignin and the phenolic resin). It is not fully clear, if the lignin really is incorporated into the phenolic resin or not.

In practise lignin at the moment is used, if at all, only as a more or less neutral filler in glue resins, without adding any special advantage (sometimes even not in terms of costs).

Questions and topics of R&D:

Chemical modification with lignin: is the lignin really incorporated chemically into the phenolic resin? How to guarantee such an incorporation? Can the properties of a lignin modified phenolic resin improved by this chemically incorporation?

e) Isocyanate:

The use of isocyanate as a fortifier for phenolic resins is performed only in very seldom cases; Deppe and Ernst (1971) had reported a precurring reaction between the isocyanate and the phenolic resin, even if both components have been applied separately to the particles. On the other side, Hse et al. (1995) have described a similar system, which worked with good results. PMDI/PF and PMDI/UF have been investigated and final products clearly identified by Pizzi and Walton (1992), Pizzi et al. (1993) and in USP 5 407 908.

Questions and topics of R&D:

Is the fortification of a phenolic resin by isocyanate possible? Results in literature are not clear.

2.1.3.5 Content of Formaldehyde, Molar Ratios

Due to the resistant C-C-bonding between the aromatic ring and the methylolgroup it is not possible, to determine the molar ratio in the usual chemical way. This only is possible by ¹H or ¹³C-NMR. The molar ratio usually is between 1,8 and 2,5, depending on the type of resin. The higher the molar ratio, the higher is the reactivity but also the storage stability of the resin; additionally the hardened resin is more brittle due to the higher cross-linking.

Questions and topics of R&D:

Is there any other method to determine the molar ratio of phenolic resins?

2.1.3.6 Molecular Characterization

The molecular characterization can be performed without bigger problems by GPC/SEC. In the literature many chromatograms of very different resins are shown (Ellis 1993, Gobec et al. 1997, Holopainen et al. 1997, Riedl and Calvé 1991, Stephens and Kutscha 1987). Due to newer GPC-methods no modification of the resin before the analysis is any longer necessary.

Averages of molar masses can be determined via vapour pressure osmometry (VPO) for the number average (Gnauck et al. 1980, Kamide and Miyakawa 1978, S.Chow et al. 1975) and light scattering for the weight average (Kim et al. 1992). The calculation of averages from the gel chromatograms, however, includes possible errors due to uncertain calibration of the columns. Using GPC-LALLS-combination weight averages can be determined at least for parts of the chromatogram with sufficient accuracy (Gollob 1982, Gollob et al. 1985, Christiansen and Gollob 1985, Wellons and Gollob 1980a).

Questions and topics of R&D:

How to improve the GPC-characterisation of resins?

2.1.3.7 Influencing Technological Properties of Phenolic Resins

a) Influence of molar ratio F/P

The higher the molar ratio F/P, the higher is the hardening reactivity of the resin (Tohmura et al. 1992).

Questions and topics of R&D:

Which are the optimal molar ratios for various types of PF-resin?

b) Influence of the degree of condensation

As for all condensation resins the viscosity increases with a higher degree of condensation. Contact angles of phenolic resins on wood increase strongly with a higher viscosity of the resins, according to higher molar masses (Haupt and Sellers 1994 a). The higher the molar masses of a resin, the lower also are the penetration ability of the resin into the wood surface (Johnson and Kamke 1992, 1994). According to the porosity of the wood surface, a certain portion with higher molar masses must be present to avoid an over penetration into the wood, causing a starved glue line.

Questions and topics of R&D:

How to find the proper relation between wettability and over penetration for a certain wood species?

c) Influence of content of alkaline

The higher the content of alkaline, the higher is the possible degree of condensation of the resin at a constant and technically usable viscosity; hence the higher is the hardening reactivity of the resin.

Questions and topics of R&D:

How to maximize/maximize the degree of condensation in order to achieve a necessary press time as short as possible without increasing the content of alkaline in the resin?

2.1.3.8 Cold Tack Behaviour of Phenolic Resins

Pure phenolic resins usually have no cold tack, only urea modified PF-resins.

2.1.3.9 Glue Resin Mixes

Table 2.6 summarizes various glue mixes for different applications.

Table 2.6: Examples of PF-glue mixes for particleboard, OSB and plywood

Components	particleboard core layer	particleboard face layer	OSB	OSB	AW 100- plywood
PF-resin A	100	-	100	-	-
PF-resin B	-	100	-	-	-
PF-resin C	-	-	-	-	100
PF-powder resin	-	-	-	100	-
Water	-	-	-	-	-
Potash 50%	6	-	6	-	6
Extender	-	-	-	-	10 - 15

PF-resin A: medium content of alkaline (8 - 10%)
 PF-resin B: low content of alkaline (3- 5%)
 PF-resin C: high content of alkaline (10 - 12%)
 PF-powder resin: no addition of water, no dissolution of the powder before the use in blending the strands
 Extender: e.g. coconut shell flour

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2.1.4 Resorcinol Adhesives

E.B. Ormstad, M. Scheikl, A. Pizzi

2.1.4.1 Introduction

Resorcinol-formaldehyde (RF), and phenol-resorcinol-formaldehyde (PRF) cold-setting adhesives are used primarily in the manufacture of structural, exterior-grade glulam, finger joints, and other exterior timber structures. They produce bonds not only of high strength, but also of outstanding water and weather resistance when exposed to many climatic conditions [1,2]. PRF resins are prepared mainly by grafting resorcinol onto the active methylol groups of the low-condensation resoles obtained by the reaction of phenol with formaldehyde. Resorcinol is the chemical species that gives to these adhesives their characteristic cold-setting behaviour. At ambient temperature and on addition of a hardener, it provides accelerated and improved cross-linking not only to resorcinol-formaldehyde resins but also to the phenol-formaldehyde resins onto which resorcinol has been grafted by chemical reaction during resin manufacture. Resorcinol is an expensive chemical, produced in very few locations around the world (to date only three commercial plants are known to be operative: in the United States, Germany, and Japan), and its high price is the determining factor in the cost of RF and PRF adhesives. It is for this reason that the history of RF and PRF resins is closely interwoven, by necessity, with the search for a decrease in their resorcinol content, without loss of adhesive performance.

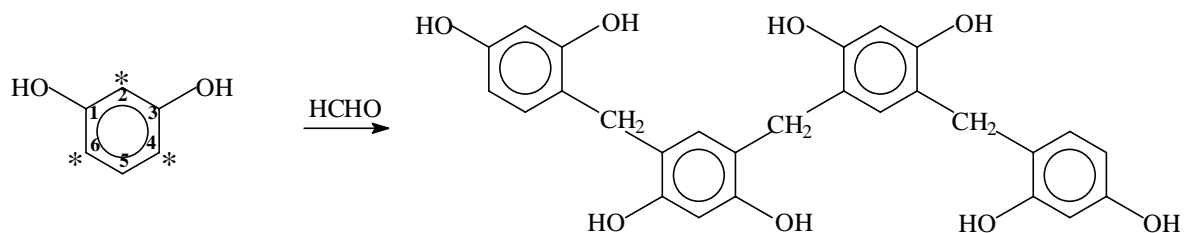
In the past decades, significant reductions in resorcinol content have been achieved: from pure resorcinol-formaldehyde resins, to PRF resins in which phenol and resorcinol were used in equal or comparable amounts, to the modern-day commercial resins for glulam and finger jointing in which the percentage, by mass, of resorcinol on liquid resins is on the order of 16 to 18%. A step forward has also been the development and commercialisation of the "honeymoon" fast-set system [3], coupled with the use of tannin extracts, which in certain countries are used to obtain PRFs of 8 to 9% resorcinol content without loss of performance and with some other advantages (such as gluing of high moisture content timber). This was a system improvement, not an advance on the basic formulation of PRF resins.

2.1.4.2 Chemistry of RF Resins

The same chemical mechanisms and driving forces presented for phenol-formaldehyde resins apply to resorcinol resins. Resorcinol reacts readily with formaldehyde to produce resins, which harden at ambient temperatures if formaldehyde is added. The initial condensation reaction, in which A-stage liquid resins are formed, leads to the formation of linear condensates only when the resorcinol/formaldehyde molar ratio is approximately 1:1 [4]. This reflects the reactivity of the two main reactive sites (positions 4 and 6) of resorcinol [5]. However, reaction with the remaining reactive but sterically hindered site (2-position) between the hydroxyl functions also occurs [4]. In relation to the weights of resorcinol-formaldehyde condensates, which are isolated, and on a molar basis, the proportion of 4- plus 6-linkages relative to 2-linkages is 10,5:1. However, cognisance must be taken of the fact that the first mentioned pair represents two condensation sites relative to one. The difference in reactivity of the two types of sites (i.e., 4- or 6-position relative to the 2-position) is then 5:1 [4]. Linear components always appear to form in preference to branched components in A-stage resins [4]; that is, terminal attack leads to the preferential formation of linear rather than branched condensates. This fact can be attributed to:

1. The presence of two reactive nucleophilic centres on the terminal units, as opposed to single centres of doubly bound units already in the chain.
2. The greater steric hindrance of the available nucleophilic centre (nearly always at the 2-position) of the doubly bound units- as opposed to the lower steric hindrance of at least one of the nucleophilic centres of the terminal units (a 4- or 6-position always available). The former is less reactive as a result of the increased steric hindrance. The latter are more reactive.

3. The lower mobility of doubly bound units, which further limits their availability for reaction.



The absence of methylol ($-\text{CH}_2\text{OH}$) groups in all six lower-molecular-weight resorcinol formaldehyde condensates which have been isolated [4] reflects the high reactivity of resorcinol under acid or alkaline conditions. It also shows the instability of its para-hydroxybenzyl alcohol groups and their rapid conversion to para-hydroxybenzyl carbonium ions or quinone methides. This explains how identical condensation products are obtained under acid or alkaline reaction conditions [4]. In acid reaction conditions methylene ether-linked condensates are also formed, but they are highly unstable and decompose to form stable methylene links in 0,25 to 1 hour at ambient temperature [6, 7].

From a kinetic point of view, the initial reaction of condensation to form dimers is much faster than the subsequent condensation of these dimers and higher polymers. The condensation reaction of resorcinol with formaldehyde, on an equal molar basis and under identical conditions, also proceeds at a rate which is approximately 10 to 15 times faster than that of the equivalent phenol-formaldehyde system [13]. The high reactivity of the resorcinol-formaldehyde system renders it impossible to have these adhesives in resol form. Therefore, only resorcinol-formaldehyde novolaks, thus resins not containing methylol groups can be produced. Thus all the resorcinol nuclei are linked together through methylene bridges with no methylol groups being present and generally without any presence of methylene-ether bridges either.

The reaction rate of resorcinol with formaldehyde is dependent on the molar ratio of the two constituents, the concentration of the solution, pH, temperature, presence of various catalysts and amount of certain types of alcohols present [8-11]. The effect of pH and temperature on the reactivity and gel time of the resorcinol-formaldehyde system presents the same trend as for all phenolic-formaldehyde reactions, with a minimum of reactivity at around pH 4 and the rate of reaction becoming rapidly faster at progressively more alkaline and more acid pH values [11, 12]. Methanol and ethanol slow down the rate of reaction. Other alcohols behave similarly, the extent of their effect being dependent on their structure. Methanol lengthens gel time more than that of other alcohols; higher alcohols being less effective. The retarding effect on the reaction is due to temporary formation of hemiacetals between the methanol (or other alcohols) and the formaldehyde. This reduces the reaction rate because of the lower concentration of available formaldehyde [9, 10]. Other solvents also affect the rate of reaction by forming complexes or by hydrogen bonding with the resorcinol [9,12].

In the manufacture of pure resorcinol resins the reaction would be violently exothermic unless controlled by the addition of alcohols. Because the alcohols perform other useful functions in the glue mix, they are left in the liquid glue. PRF adhesives are generally prepared firstly by reaction of phenol with formaldehyde to form a PF resol polymer, that has been proved to be in the greatest percentage and often completely linear [4]. This can be represented as follows:

In the reaction that follows the resorcinol chemical is added in excess, in a suitable manner, to polymer I to react with the $-\text{CH}_2\text{OH}$ groups to form PRF polymers in which the terminal resorcinol groups can be resorcinol chemical or any type of resorcinol-formaldehyde polymer.

Where resorcinol adhesives are not suitable, resins can be prepared from modified resorcinol [12]. Characteristic of these types of resins are those used for tyre cord adhesives, in which a pure resorcinol-formaldehyde resin is used, or alternatively, alkyl-resorcinol or oil-soluble resins

suitable for rubber compounding are obtained by pre-reaction of resorcinol with fatty acids in the presence of sulphuric acid at high temperature followed by reaction with formaldehyde. Worldwide more than 90% of resorcinol adhesives are used as cold-setting wood adhesives. The other most notable application is as tyre cord adhesives, which constitutes less than 5% of the total use.

2.1.4.3 Phenol-Resorcinol-Formaldehyde Adhesives

The PRF adhesives are always delivered as a liquid (50-60% solid content) and must be blended with a hardener before use. PRF mixed with in a powder hardener (mass/mass ratio of adhesive and hardener is 5:1) have been the most commonly used industrially system. Pure resorcinol-formaldehyde (RF) adhesives were used extensively earlier (some 20-30 years ago). They fell into disfavour because of the high price of the resorcinol chemical needed to make them and also due to the shortage of resorcinol supply in 1960th and 1970th (oil crises). They are still used in some industrial application, particularly at low temperate curing and when difficult wood-gluing problems arise. PRF adhesives together with liquid hardeners are used quite extensively in Europe, as they have several handling advantages for this market. These adhesives are mixed before use in a mass/mass ratio of adhesive to liquid hardener in a ratio from 5:1 to 2,5:1 or even 1:1 (depending from the type). The powder hardener is generally a mixture of equal parts paraformaldehyde fine powder and fillers, these latter being comprised of 200-mesh wood flour or a mixture of wood flour and nutshell flour, 200-300 mesh. Adhesives types presenting a liquid hardener use as hardener formaldehyde, paraformaldehyde, formurea and when needed, to avoid undue formaldehyde smell use also oxazolidine as hardener. In addition these hardeners also contain fillers and thickening agents.

All properly formulated resorcinol-based adhesives must have a viscosity low enough in aqueous-alcoholic-solutions to flow with ease into all the interstices of the wood surface. The alcohol promotes wetting ability. The paraformaldehyde used as hardener in powder hardener types is an addition polymer composed of a few to over 100 formaldehyde monomers. It dissolves slowly in water, by depolymerisation to formaldehyde monomers. The rate of depolymerisation depends on the degree of polymerisation of the paraformaldehyde, the size of the particles and the pH. Therefore, the working life or pot life of a glue mix can be adjusted by selecting the type of paraformaldehyde and the pH correctly, but the ratio of resorcinol to phenol will have an influence of the pH value to be chosen. Fillers are added to give consistency to the glue mix, to control viscosity and thixotropic characteristics, to form a fibrous reinforcement of the adhesive film and to lessen the cost. Wood flour is used as a filler to obtain better gap filling properties where rough or uneven surfaces must be bonded, or where low bonding pressures must be used. Nutshell flours, such as coconut shell flour, walnut shell flour, peach pip shell flour, macadamia nut shell flour or even olive stone flour are used as fillers as well and to provide smooth-flowing powder mixtures. Inorganic fillers are also used especially in Europe, although this is a practice to avoid as it is very heavy on saws afterwards. Clays and fumed silica can also be used in very small amounts to control the thixotropic consistency of the glue mix.

As the formaldehyde reacts with the resorcinol-based resin, condensation occurs, with the formation of high-molecular-weight polymers. There is considerable secondary orifices interaction between the growing resorcinol polymers and the non-crystalline hemicellulosic and lignocellulosic molecules of the substrate. The highly polar methylol groups and the phenolic hydroxyl groups link to cellulose and lignin groups by van der Waals, hydrogen, and electrostatic bonds. The growing adhesive polymers continue to interact to form colloidal particles and then a gelatinous film. This mechanism depends strongly on the moisture content of the wood, which determines the rate of water and solvent absorption.

The advantage of ambient-temperature curing is that the moisture escapes gradually from the hard film formed on curing, inducing a minimum of residual stresses on the joint and allowing the glue-line to assume the aspect of a molecularly-porous solid. As a consequence, the hard film is able to transpire in the same way as wood, which minimizes checking or crazing and allows the glued joint to survive exposure to the extremes of humidity cycles.

To shorten the curing time are often heating chambers (40-60°C) used in the manufacturing of glulam, and an even faster curing can be achieved with the use RF-presses. But due to the flexibility of the PRF glue line and the thin adhesive layer between the lamellae's, no differences can be discovered regarding bond performance under extreme conditions.

In Europe is the performance of the PRF adhesives for the load carrying construction controlled by approved laboratories in each country, and the quality is determined after the EN-Standards EN301 and EN302.

2.1.4.4 Special Adhesives of Reduced Resorcinol Content

a) Fast-Setting Adhesive for Fingerjointing and Glulam

Together with the more traditional finger jointing adhesives that have just been discussed, a series of ambient-temperature fast-setting separate application systems have also been developed. These eliminate the long delays caused by the use of more conventional phenol-resorcinol-formaldehyde adhesives, which require lengthy periods to set. These types of resorcinol adhesives are applied separately. They were first developed in the United States [15-18] to bond large components where presses were impractical. Kreibich [18] describes these separate application or "honeymoon" systems as follows: "Component A is a slow-reacting phenol-resorcinol-formaldehyde resin with a reactive hardener. Component B is a fast-reacting resin with a slow-reacting hardener. When A and B are mated, the reactive parts of the component react within minutes to form a joint which can be handled and processed further. Full curing of the slow-reacting part of the system takes place with time. The m-aminophenol used for component B is a frightfully expensive chemical and for this reasons these systems were discarded and not used industrially [14]. In their original concept component A is a traditional phenol-resorcinol-formaldehyde cold-setting adhesive at its standard pH of between 8 to 8,5 to which formaldehyde hardener has been added. Flour fillers may be added or omitted from the glue mix. Component B is a phenol/meta-aminophenol/formaldehyde resin with a very high pH (and therefore a high reactivity), which contains no hardener or only a very slow hardener.

More recently, a modification of the system described by Kreibich has been used extensively, in industry with good success. Part A of the adhesive is again a standard phenol-resorcinol-formaldehyde (PRF) cold-setting adhesive with powder hardener added at its standard pH. Part B can be either the same PRF adhesive with no hardener and the pH adjusted to 12 or a 50 to 55% tannin extract solution at a pH of 12-13, provided that the tannin is of the condensed or flavonoid type, such as mimosa, quebracho or pine bark extract with no hardener [3,19]. The results obtained with these two systems are good and the resin not only has all the advantages desired but also as a result of the use of vegetable tannins and of the halving of the resorcinol content of the entire adhesive system is considerably cheaper [3,19,20].

The adhesive works in the following manner. Once the component A glue mix is spread on one finger joint profile and component B on the other finger joint profile and the two profiles are joined under pressure, the reaction of component B with the hardener of part A is very fast. In 30 min at 25°C finger joints prepared with these adhesives generally reach the levels of strength that finger joints glued with more conventional phenolic adhesives are able to reach only after 6 h at 40 to 50°C or in 16 to 24 h at 25°C [3,20]. Clamping of laminated beams (glulam) bonded with these fast-set honeymoon adhesives is in average of only 3 hours at ambient temperature compared with the 16 to 24 hours necessary with traditional PRF resins [19,20]. These adhesives present also two other advantages, namely (i) are capable to bond without any decrease of performance at temperatures down to 5°C only and (ii) they are able to bond "green" timber at high moisture content, a feat that is used in industrial glulam bonding since their commercial introduction in 1981.

b) Branched PRF Adhesives

Recently another step forward has been taken in the formulation of PRF adhesives of lower resorcinol content. Liquid resorcinol or PRF resins appear to be mostly linear [4]. The original concept in "branching" erroneously maintained that if a chemical molecule capable of extensively branching (three or more effective reaction sites with an aldehyde) the PF and PRF resins is used after, before or during, but particularly during or after, the preparation of the PF resin, the polymer in the branched PRF adhesive has (1) higher molecular weight than in normal PRF adhesives where branching is not present and (2) higher viscosity in water or water/solvent solutions of the same composition and of the same resin solids content (concentration). It also needs a much lower resorcinol amount on total phenol to present the same performance of normal linear PRF adhesives.

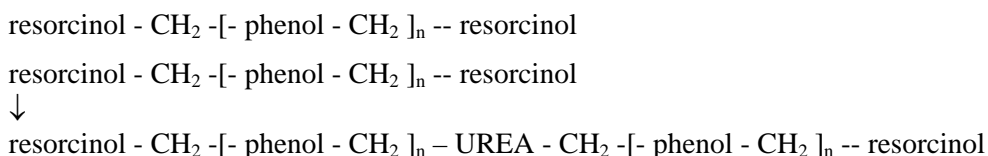
When comparing linear and branched resins for every n molecules of phenol used a minimum of 2 molecules of resorcinol are used in the case of a normal, traditional linear PRF adhesive, whereas only 1 molecule of resorcinol for n molecules of phenol is used in the case of a "branched" PRF adhesive. The amount of resorcinol has then been halved or approximately halved in the case of the branched PRF resin. A second effect caused by the branching is a noticeable increase in the degree of polymerisation of the resin. This causes a considerable increase in the viscosity of the liquid adhesive solution. Because PRF adhesives must be used within fairly narrow viscosity limits, to return the viscosity of the liquid PRF adhesive within these limits, the resin solids content in the adhesive must be lowered, considerably, with a consequent further decrease in total liquid resin of the amount of resorcinol and of the other materials, except solvents and water. This decreases the cost of the resin further without decreasing its performance.

Thus, to conclude, the decrease of resorcinol by branching of the resin is based on two effects:

1. A decrease of resorcinol percentage in the polymer itself, hence in the resin solids, due to the decrease in the number of the phenol-formaldehyde terminal sites onto which resorcinol is grafted during PRF manufacture.
2. An increase in molecular weight of the resin, which by the need to decrease the percentage resin solids content to a workable viscosity, decreases the percentage of resorcinol on liquid resin (not on resin solids).

It is clear that in a certain sense a branched PRF will behave as a more advanced, almost precured phenolic resin. While the first effect described is a definite advance on the road to better-engineered PRF resins, the second effect can also be obtained with more advanced (reaction wise) linear resins. The contribution of the second effect to the decrease in resorcinol is not less marked than that of the first effect. It is however, the second effect that accounts for the difference in behaviour between branched and linear PRF adhesives.

Branching molecules, which can be used, could be resorcinol, melamine, urea and others [21]. Urea is the favourite one, because it is much cheaper than the others and needs to be added in only 1,5 to 2% of total resin. When urea is used as a brancher, the adhesive assumes an intense and unusual (for resorcinol resins) blue colour, after a few days, hence its nickname, "blue glue." However, later work [22,23] has shown that three-dimensional branching has very little to do with the improved performance of these low-resorcinol content adhesives, with tridimensionally branched molecules contributing, at best, no more than 8 to 9% of the total strength [22,23]. In reality, addition of urea causes the reaction as foreseen, but not in three points branching but rather only in two sites of the branching molecule. This is equivalent to saying that most of the resin doubles linearly in molecular weight and degree of polymerisation, while the final effect, good performance at half the resin resorcinol content, is maintained [22,23]. This effect is based on the relative reactivity for phenolic methylols of urea and of unreacted phenol sites and thus while the macro effect is as wanted, at the molecular level it is only a kinetic effect due to the different relative reactivities of urea and phenol under the reaction conditions used. Thus



Half of the resorcinol content is still obtained, but between 90 and 100% of the polymers in the resin are still linear.

It is noticeable that the same degree of polymerisation and “doubling” effect cannot be obtained by lengthening the reaction time of a PF resin without urea addition [22,23]. These liquid resins then work at a resorcinol content of only 9 to 11%, hence considerably lower than that of

traditional PRF resins. These resins can also be used with good results for honeymoon fast-setting adhesives in PRF-tannin systems, thus further decreasing the total content of resorcinol in the total resin system to a level as low as 5 to 6%

Questions and topics of R&D:

The use of PRF adhesives has been significantly reduced in Europe the last ten years for the production of glulam.

The reason for this development is caused by the demand from the market to produce glulam with other properties and to reduce the production costs of glulam.

The main issues are light coloured glue line, adhesive of lower price and environmentally aspects such as TLV and waste water treatment (disposal).

The light coloured adhesive has been the driving force in this development, this means that if PRF adhesives should compete with the new type of adhesive in this field (MUF and PUR), a light coloured PRF adhesive has to be developed.

The main disadvantage in the use of PRF adhesives is the formaldehyde emission from the hardeners. For powder hardeners it is caused by a dust problem during the handling of the hardener and for the liquid hardeners the high concentration of free formaldehyde in the hardener itself. The second disadvantage when liquid hardener is used is the formaldehyde release from the glue mix during handling and curing. The use of liquid hardeners that are very popular due to easy handling can lead to high workplace concentration of formaldehyde and can come in conflict with the TLV regulation.

A liquid hardener, free of formaldehyde or very low in formaldehyde release, that will give the same glue line properties as powder hardener could be a development project.

The free phenol content in the PRF adhesives is also an environmentally aspect especially when we talk of waste water from the cleaning of equipment. As phenol is a poisonous chemical the level of free phenol must be low to avoid toxic labelling of the adhesives.

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2.2 Polyurethane Adhesives

D. Grunwald

The two primary products of polyurethane adhesives are polyols and isocyanates. Due to their chemical structure the polyurethane adhesives can be classified in four different sections (Zeppenfeld, 1991):

a) polyisocyanates (e.g. PMDI)

Polyisocyanates do not really belong to the class of polyurethane adhesives. They react with water and in a minor amount with wood and lignocellulosic materials. Polyisocyanates are used for the production of water resistant wood based panels.

b) Reactive hardening polyurethanes:

- One component system: synthesized from polyetherpolyole with an excess of di- or polyisocyanates

The system requires a high moisture content of the glued materials or higher humidity to optimise the hardening process. Because of the high viscosity the adhesive is often diluted with organic solvents or used at higher temperatures.

- Two component system: component I: polyol or polyamine
component II: polyisocyanate

The hardening process of this system is performed by polyaddition. The adhesive is usually solvent-free.

c) physically hardening hydroxy-polyurethanes:

- one component: synthesized from diisocyanates with an excess of polyesterdiols
- two component: as a) but with an isocyanate hardener

The main isocyanates used for this class of adhesives are 4,4'-diphenylmethane-diisocyanate (MDI) and toluene-diisocyanate (TDI). The adhesive is often dissolved in butanone.

d) polyurethane-dispersions in water

Polyurethanes with free isocyanate groups are polymerised with diaminocarbonic or diaminosulfonic-acids and suspended in water. The system can be modified with PVAc glues.

2.2.1 Adhesives for Wood Based Panels (Polyisocyanates)

2.2.1.1 Introduction

Adhesives based on PMDI are used for more than 25 years (Deppe 1977, Deppe and Ernst 1972) but still have a low market value in the woodworking industry compared to systems based on UF-, MUF- or PF-resins. Since a few years isocyanates as adhesives for wood based products get more attraction in the manufacture of particle board, oriented strandboard (OSB), laminated strand lumber (LSL), medium density fibreboard (MDF) or other special engineered composites (Sachs 1983).

PMDI adhesives have several process engineering and qualitative advantages, which compensates even a higher price. The vast majority of wood composites produced using PMDI are used in construction applications where the requirement for a hydrolytically stable bond is a necessity for moisture resistant properties with high durability. Furthermore, good dimensional stability in changing climatic conditions is a desired property in many applications. These advantages are coupled together with a productivity increase that can even be accelerated by special additives (Larimer, 1999). Today PMDI is quite extensively used to produce exterior-grade OSB and particleboard. Even products difficult to glue like straw, rice shells or sugar cane bagasse (annual

plants) can be bonded by PMDI. During hot pressing the viscosity of PMDI is lowered, allowing it to flow across and penetrate below the surface, locking in the adhesive as has been shown by Roll (1993). The low wetting angle of PMDI in comparison to water based condensation resins allows a rapid penetration into the surface.

The disadvantages of PMDI are:

- The unwanted ability to stick to the press plates. This requires that the board surface is glued with a different type of adhesive or external release agents have to be used.
- The toxicity and the low vapour pressure of MDI, which afford special working conditions.
- Their higher cost which can be lowered by higher press speeds (Pizzi 1994).

The impossibility of diluting PMDI with water was solved by the introduction of emulsified PMDI, often called EMDI, which allows a regular distribution of the adhesive during the gluing process. EMDI is a product of the reaction of PMDI with polyglycols. The system is manufactured under high pressure and dispersed in water. If the other problems can be solved in the future, PMDI can become one of the main adhesives beside of UF- and PF-resins.

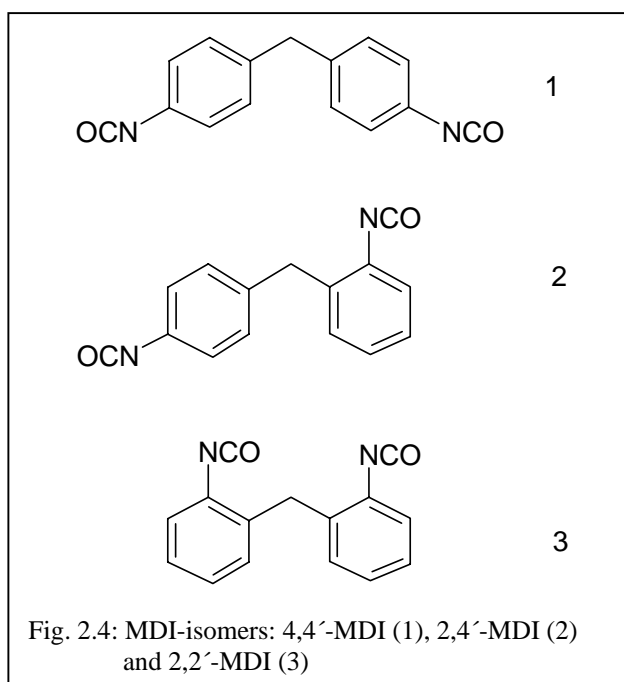
Questions and topics of R&D:

- Modifying PMDI with internal release agents or other adhesives to reduce the ability to stick to the press plates*
- Modifying PMDI to reduce the amount of MDI*
- New catalytic substances for low press temperatures and cold-setting applications*

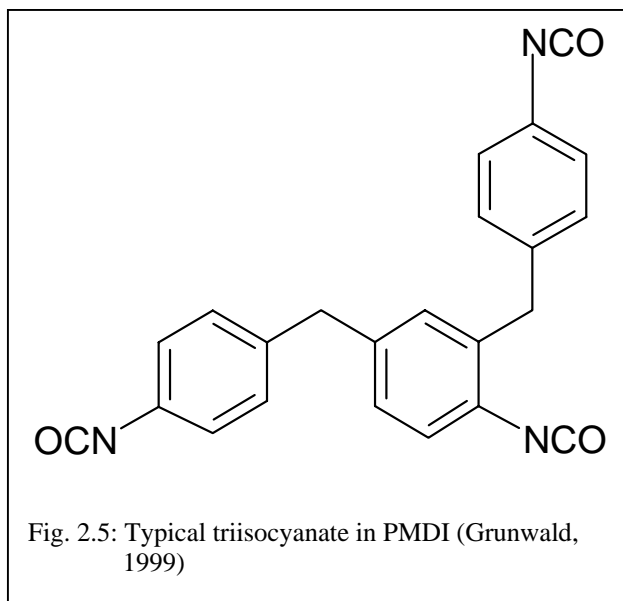
2.2.1.2 Raw Materials

a) Diphenylmethane-diisocyanate (MDI)

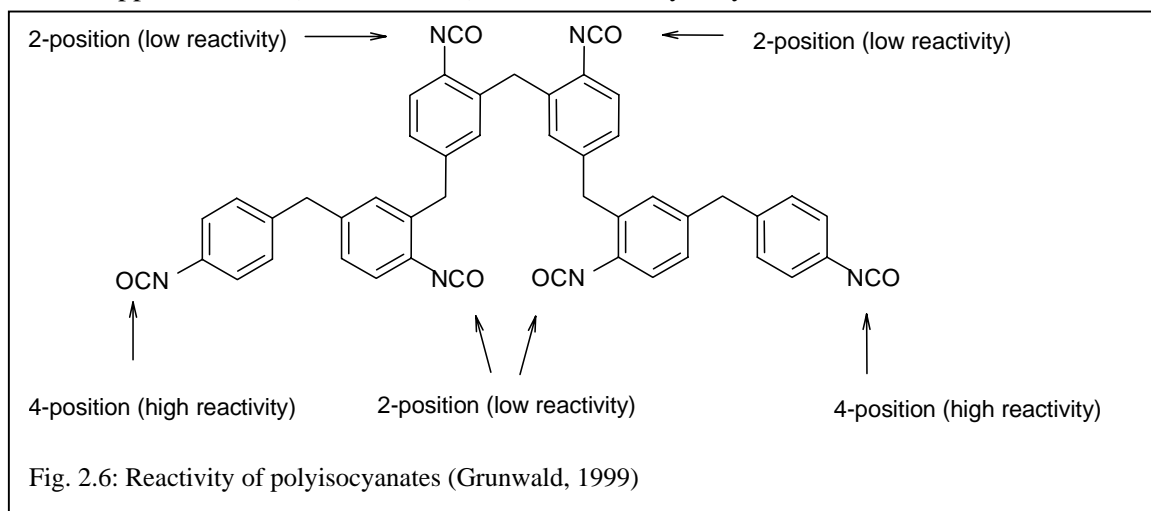
MDI is used as adhesive when high tensile strength, toughness and heat resistance are required (Lay and Cranley, 1994). The structure of the three isomers of MDI are shown in figure 2.4. In high quality products the typical supply grade is 98% of 4,4'-MDI. At room temperature 4,4'-MDI is a white solid (melting point 38°C). Several MDI products have been introduced that address the inconvenience of handling a solid. Some products contain elevated levels of the 2,4'- isomer. At a content of approximately 35% of the 2,4'-isomer the product becomes liquid at room temperature. A number of advantages are seen: slower reactivity, longer pot life and improved shelf stability.



b) Polymeric MDI (PMDI)

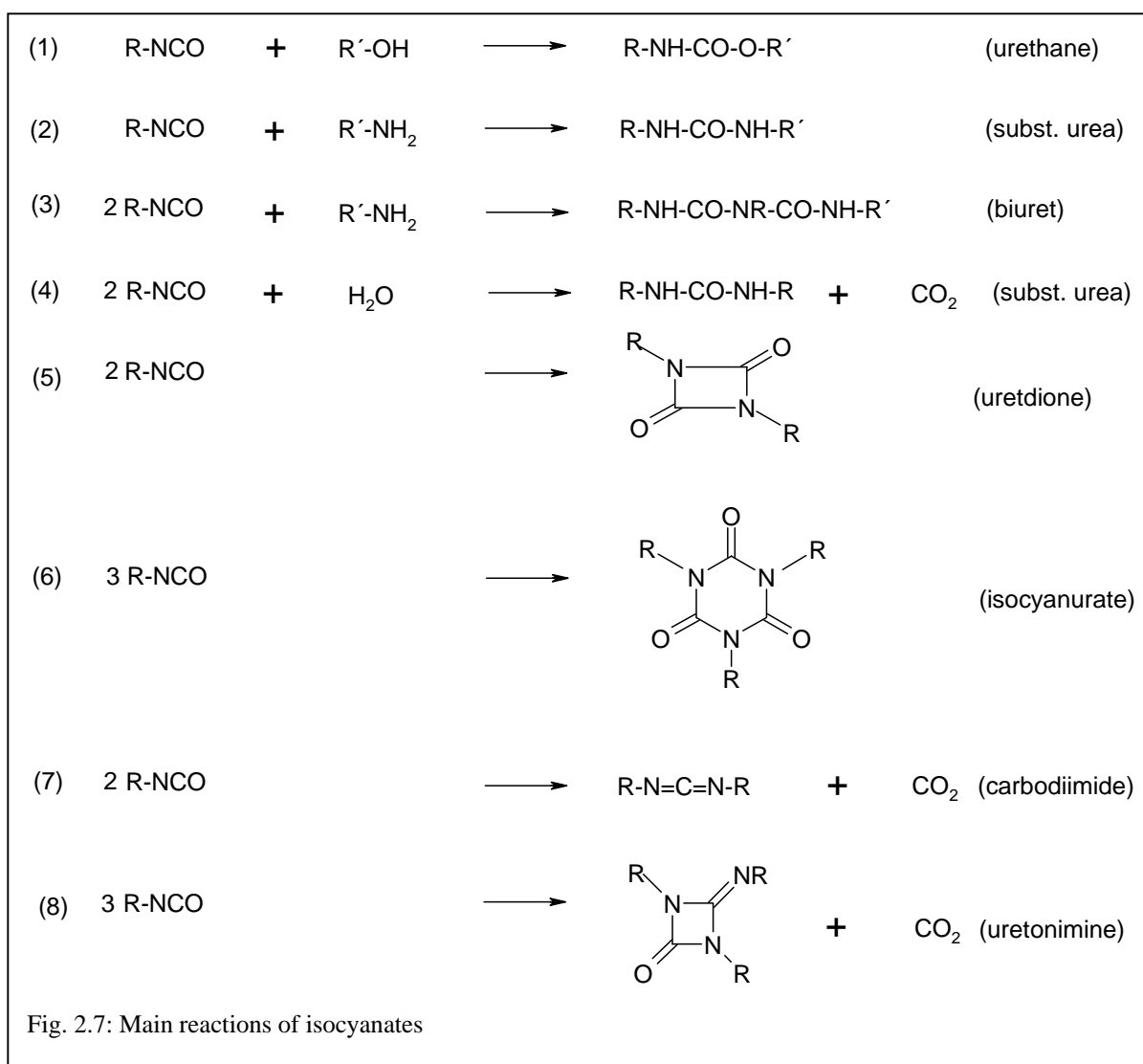


Polymeric MDI is produced during the manufacturing of monomeric MDI. The PMDI produced industrially by phosgenation of di-, tri- and higher amines contains a mixture of the three different MDI-isomers, triisocyanates (figure 2.5) and different polyisocyanates. The structure and the molecular weight depend on the number of aromatic rings (Grunwald, 1999). Like other adhesives PMDI is a specific mixture of different molecules. The bigger part of the functional groups of polyisocyanates are of low reactivity because of the different positions (figure 2.6). The molecular weight distribution influences the reactivity, but also the typical properties of adhesives like viscosity, wetting and fluidity (Dunky 1997). In the monomer form (MDI) the functionality is 2 and the NCO content is 33,5%, while PMDI has an average functionality of 2,7 and the NCO content is approx. 30,5% (Skinner, 1999). Much of the hydrolyzable chlorides and colour bodies



produced in the manufacturing process of MDI remains in these products. The acidity levels (in ppm HCl) can be 10 to 50 times the level found in pure MDI, and the products are dark brown in colour. The higher acidity level decreases the reactivity, however this decrease is offset somewhat by the higher functionality.

Polymeric MDI is usually cheaper than pure MDI and has a lower melting point (liquid at room temperature) because of the increased asymmetry. It is less prone to dimerization and as a consequence it is more storage stable than pure MDI. PMDI is used whenever the colour of the finished adhesive is not of concern (Lay and Cranley, 1994).



Questions and topics of R&D:

Get more knowledge about structure and reactivity of oligomers in PMDI

2.2.1.3 Chemistry

An overview about the main reactions is given in figure 2.7. The most important reaction of the isocyanate group is the one with water, which forms a cross-linked polyurea network and carbon dioxide (4). After hydrolysis of the isocyanate group the resulting amine is reacting immediately with one or two isocyanate molecules (2 or 3). In industrial scale the hardening process takes place under increased temperature in the presence of humidity and sometimes catalytic substances. In addition to that PMDI can react with all substances with reactive hydrogen atoms, like lignocellulosic materials (1). Uncommon but possible are reactions between the isocyanate groups itself (5 to 8). It is often assumed that the strong bonds achieved with PMDI are results of a higher amount of covalent bonds between the adhesive and the lignocellulosic substrate. This assumption is very controversy discussed in the literature. A few recent works have shown that the amount of covalent bonds is very small or not existent under industrial production conditions (Pizzi, 1994).

A description about the chemistry of PMDI is given by Pizzi (1994) and Frisch et al. (1983). More detailed information can be found by Dollhausen (1983), Schauerte et al. (1983) and Lay and Cranley (1994).

Not much information is available about the production of wood based panels with two-component systems (PMDI-Polyol), some informations have been given by Lay and Cranley (1994).

Questions and topics of R&D:

- a) *Improvement of PMDI by polyols for wood based panels*
- b) *Get more knowledge about the chemical reactions in the system PMDI-wood-water*

2.2.1.4 Catalysis

PMDI can be modified or contaminated with polyureas, carbodiimides, uretoneimines, uretdiones or chlorinated substances (Twitchett 1974, Arthur and Kerrigan 1975). A few catalytic substances or accelerators like tertiary amines (e.g. triethanolamine, triethylene-diamine, tetramethylbutane-diamine (TMBDA), 1,4-diaza(2,2,2)-bicyclo-octane (DABCO)) or organometallic compounds (e.g. dibutyltin-dilaurat (DBTDL), cobalt octoate, stannous octoate (SnOct)) can be admixed (Abbate and Ulrich 1969, Gudehn 1984). Both classes have features in common in which the catalytic activity can be described as a combination of electronic and steric effects. Electronic effects arise as the result of the molecules ability to donate or accept electrons. Steric effects arise from structural interactions between substituents on the catalyst and the reactants that will influence their interaction. Additionally the catalyst can improve the curing procedure of the glue line. Better cure leads to improved weather resistance and strength properties of the board. More information can be found by Lay and Cranley (1994).

Under normal conditions it is not necessary to use catalytic substances for the production of wood based panels due to the high temperatures used in the pressing process. But if faster press times and lower press temperatures are needed in the future, catalysts might get some importance.

Questions and topics of R&D:

New catalytic substances for low press temperatures and cold-setting applications

2.2.1.5 Adhesive Mixtures

In the past all formaldehyde-based resins (UF-, PF-, MF- and tannin-based resins) have been mixed with PMDI to improve the gluing properties. Depending on the adhesive system, the blending process, the gluing process, the mixture ratio, the pressing conditions etc. different results were achieved (Pizzi 1994). Newer results (Larimer 1999) show productivity increases due to the use of PMDI/aminoplastic resin blends in the core layer of particleboard produced in a continuous press.

Questions and topics of R&D:

Development of mixed adhesives in industrial scale

2.2.2 Adhesives for Surface Gluing and Load Bearing Structures**2.2.2.1 Introduction**

All four classes of polyurethane adhesives (see section 2.2) can be used to glue wood or wood based panels together or with other materials (e.g. metal, glass, plastics, rubber). Especially the two-component systems must be homogenized before application. The pot-life of an polyurethane adhesive influences the gluing process due to an irreversible increase of the viscosity. This process depends on the temperature and the humidity, too. The isocyanate-to-polyole ratio affects the mechanical behaviour of the adhesive film. Every non-stoichiometric ratio leads to an irregular network. An isocyanat excess causes a harder and an polyole excess a more elastic glue joint (Zeppenfeld 1991, Dollhausen 1983).

2.2.2.2 One-Component Systems

The most advanced adhesive is PMDI. Information about the raw materials and chemistry can be found in section 2.2.1. Some more information can be found in section 2.2.

2.2.2.3 Two-Component Systems

Basic information about two-component systems can be found in the chapters 2.2 and 2.2.2.1. The professional adhesive formulators have developed a great amount of different types. Only the main components and their chemistry are described below. Special information about recipes and formulations are normally not available.

Questions and topics of R&D:

Get more knowledge about the interactions in two-component systems

2.2.2.4 Raw Materials

a) Diphenylmethane-diisocyanate (MDI)

See section 2.2.1.2

b) Polymeric MDI (PMDI)

See section 2.2.1.2

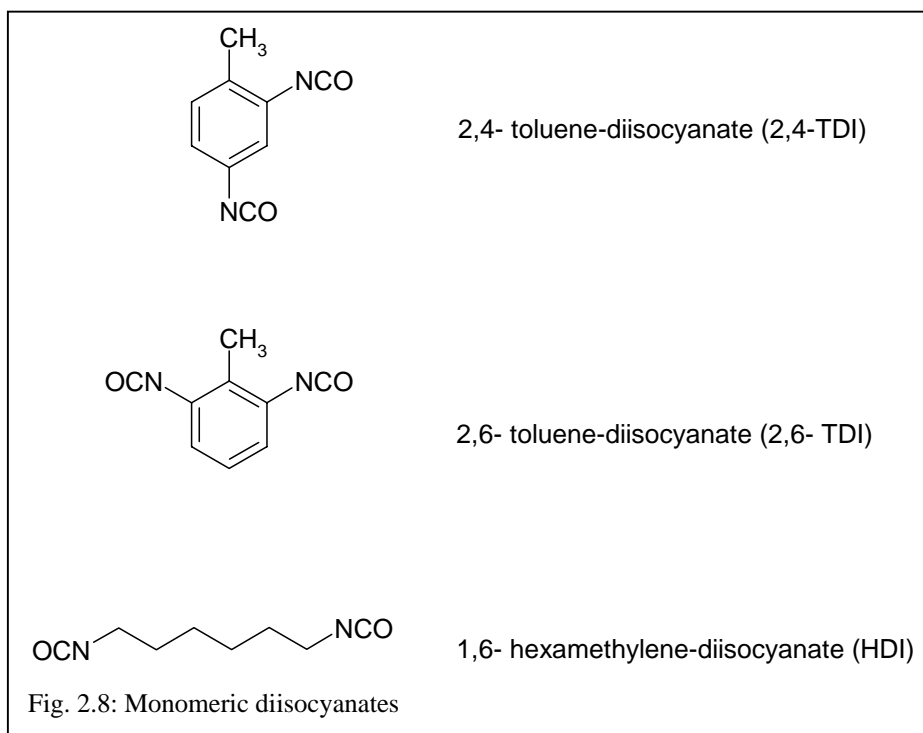
c) Toluene-diisocyanate (2,4 and 2,6-TDI)

The structure of the two isomers of TDI are shown in figure 2.8. The main reactions are equal to MDI (see section 2.2.1.3). 2,4- TDI is more reactive than 2,6-TDI because of the para-position of one NCO-group (Ferstandig and Scherrer 1959).

Since TDI is a monomeric diisocyanate, the higher volatility compared to PMDI has to be of concern during the application. To avoid this TDI is often converted into a polymer by reaction with polyols.

d) Hexamethylene-diisocyanate (HDI)

The structure of HDI is shown in figure 2.8. The main reactions are equal to MDI (see section 2.2.1.3).



Since HDI is a monomeric diisocyanate, the higher volatility compared to PMDI has to be of concern during the application. To avoid this HDI is often converted into a polymer by reaction with polyols.

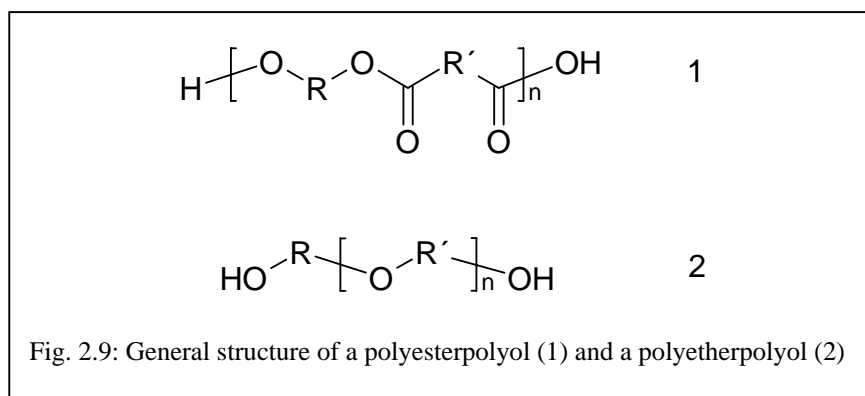
e) Polyols

- Polyesterpolyols

The general structure of a polyesterpolyol is shown in figure 2.9 (1). The main reaction with isocyanates can be found in figure 2.7 (1). Due to the polarity of the ester-group the adhesion is specific to many materials.

- Polyetherpolyols

The general structure of a polyetherpolyol is shown in figure 2.9 (2). The main reaction with isocyanates can be found in figure 2.7 (1). The main advantage of polyetherpolyols is their lower viscosity in contrast to polyesterpolyols. Even castor oil and fatty acid alcohols are used for adhesive formulations. The reaction rate of castor oil with isocyanates is very low if no catalytic substances are used. The resulting glue-line is flexible and resistant to hydrolysis, but due to the unsaturated castor oil sensitive to oxidation (Dollhausen 1983).



f) Catalytic substances

Especially in the cold-setting application for laminating wood catalytic substances are of some importance. More information can be found in section 2.2.1.4.

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2.3 Adhesives Based on Natural Resources

J. Tomkinson

2.3.1 Introduction

The use and application of adhesives based on natural and renewable resources by industry and the general public is often thought of as new approach that requires novel technologies and methods to implement. Natural adhesives based on polysaccharides, blood, collagen, milk, fish and plant extracts are just some of the materials used successfully by many industries until only relatively recently. Synthetic resins like the phenol/resorcinol/melamine/urea formaldehydes, unsaturated polyesters, acrylics and epoxies have only been used to any extent by industry over the last 60-80 years. A report by F.E. Keim¹ mentioned a book entitled Adhesives² published in 1943 where only six of the 150 pages are devoted to synthetic adhesives and many of these are combined with animal glue and other natural adhesives.

Despite the increasing trend toward the use of synthetic adhesives, processes based on the chemical modification of natural products offer opportunities for producing a new generation of high performance, high quality products. The distinct advantages in the utilisation of natural materials e.g., lower toxicity, biodegradability and availability, need to be paralleled by more efficient and lower cost methods of production. Using factors such as regional and species variation as an aid in selecting the optimum feedstock for a particular process, and through this to develop cost effective manufacturing techniques that will enable these materials to capture a wider percentage of the world market.

Manufacturers need to have confidence that a continual uninterrupted supply of raw material can be sustained throughout the life cycle of a product. It is of equal importance that the feedstock should not be restricted by geographical and climatic conditions or that yield does not dramatically vary when harvested in different locations and at a particular time of the year. The key to increased usage of natural products by industry is in the control of the above variables so that the end performance of the industry remains consistent.³

2.3.2 Classification of 'Natural Adhesives'

The term 'natural adhesive' covers any polymeric or pre-polymeric monomer/ oligomer derived from nature that will cure (normally irreversibly) to form a durable bond. Whilst this term includes the animal by-product adhesives; blood, collagen and fish glues, only plant derived adhesives will be discussed in this section.

Plant derived adhesives fall roughly into one of the four categories outlined below. At present only tannin and lignin are utilised by the wood based industry and then only to a small extent. Tannins are virtually all employed within the southern hemisphere with main areas of use being the panel products industry within South Africa, Australia and South America. Currently, lignin (both organosolv and spent sulphite liquor SSL from paper mills) is used as a co-reactant with commercial Phenol-Formaldehyde (PF) to add a specific property to the commercial resin, normally flexibility. Very few examples of true commercial lignin resins can be found. Both Tannin and Lignin are used as natural phenolic replacements in synthetic phenol/resorcinol based resins.

Very few examples exist of practical wood glues from polysaccharides and triglycerides.

Main Categories

- Tannins
 - Hydrolysable
 - Condensed

- Lignin
 - Spent Sulphite Liquor (SSL)
 - Organosolv
- Carbohydrates
 - Starch
 - Cellulose
 - Hemicellulose
- Unsaturated oils
 - Oil seed triglycerides
 - Cashew Nut Shell Liquid (CNSL)

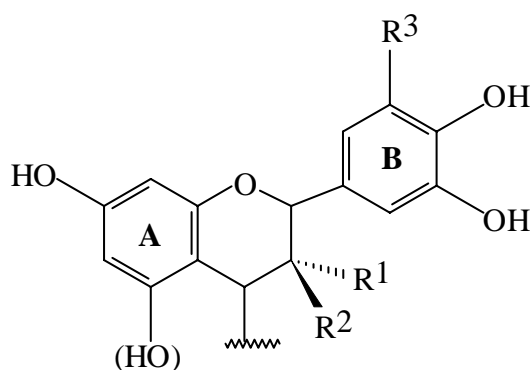
2.3.3 Tannins

2.3.3.1 Introduction

Tannins can be generally classed into two broad categories; hydrolysable and condensed. The hydrolysable tannins consist of many individual components and oligomers, but are all based on combinations of gallic acid and sugars (mainly glucose) and mixtures of simple phenols such as pyrogallol and ellagic acid. Hydrolysis with dilute sulfuric acid affords a mixture of gallic acids and the sugar component hence the name hydrolysable. However their low reactivity (nucleophilicity) and lack of macromolecular structure has limited their use to partial phenol replacements in commercial PF formulations.

Condensed tannins however constitute more than 90% of the total world production of tannins, *ca* 200,000 tonnes per annum. They are extracted from various species of *Acacia* (wattle or mimosa), *Schinopsis* (quebracho) and *Tsuga* (hemlock) bark and are predominately responsible for the brown colouration in wood after its exposed to air. In their pure form tannins are colourless, but they colour very rapidly after extraction due to the ease of oxidation of the phenolic sub-units to quinones.

It has been shown over many years that the aqueous extracts contain a series of compounds based on the substituted flavanoid structure shown in figure 2.10. Although many different variations exist, it is important to keep in mind that the substitution pattern appears to be characteristic for a given species, e.g., Mimosa, Quebracho and Hemlock, see figure 2.10.



Mimosa:	$R^2, R^3 = OH, R^1 = H$
Quebracho:	$R^1 = OH; R^2, R^3 = H$
Hemlock:	$R^1 = OH; R^2, R^3 = H$
	$R^2 = OH; R^1, R^3 = H$

Fig. 2.10: The structure of the repeating unit present in condensed tannins

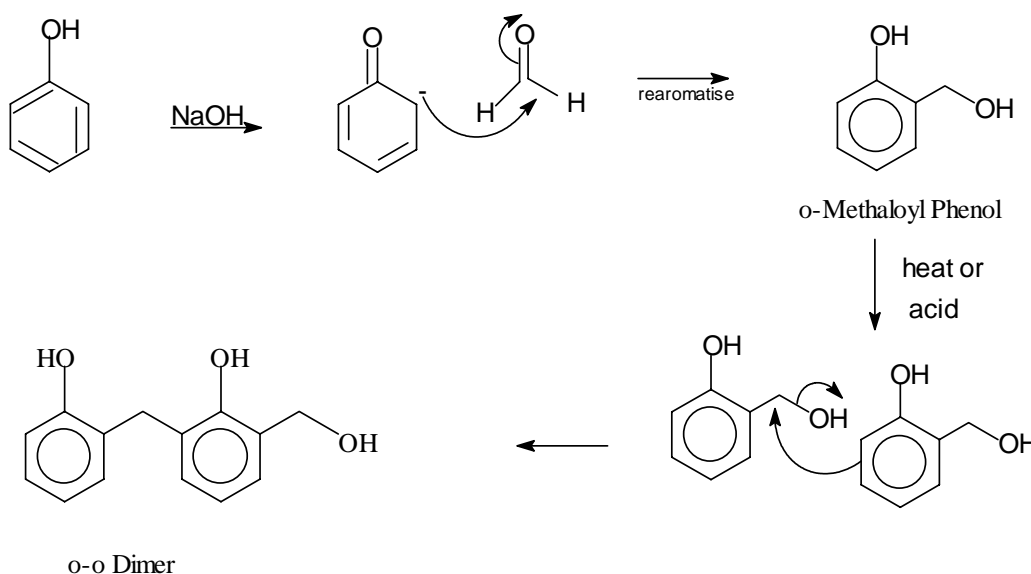
Generally, the hot water extract of bark tannin will compromise about 65 – 70% tannin polymers; the remainder will be a mixture of sugars, pectin, hemicellulose, lower molecular weight polyphenols (<300) and some amino acid residues. Cold water extraction affords a higher purity tannin extract, but overall yields based on the weight of the starting material are lower. Quebracho wood and Mimosa bark are unusual in that their water extract has a measured purity up to 75-80%, with the tannin in each case consisting of oligomers containing up to 12 repeating units with a DP of 2-9.

2.3.3.2 Current Work

Predominately all the tannin adhesives reported to date are synthesised through a polycondensation mechanism with formaldehyde or a suitable formaldehyde donor, e.g., paraformaldehyde, hexamine and in some cases urea formaldehyde pre-condensates.

As tannins contain many 'phenolic' type sub units one may be tempted to think that they will exhibit a similar reactive potential to that of phenol and therefore procedures used in standard PF production can be transferred to those containing tannin. This however is not the case, the real situation is that tannin is far more reactive than unsubstituted phenol due to the resorcinol and catechol rings present in the tannin, these rings are commonly termed the A and B ring respectively (see figure 2.10). This increase in hydroxyl substitution on the two aromatic rings affords an increase in reactivity to formaldehyde by 10 to 50 times when compared to simple phenol. This whilst initially sounding promising creates additional problems with respect to producing an industrially applicable resin.

High proportions of phenolic adhesives employed by the wood based industry today are synthesised using phenol, formaldehyde and a base, (normally a metal hydroxide, e.g., NaOH). These adhesives termed 'resoles' contain essentially monomers or oligomers of methaloyl phenol that crosslink together in service through the action of heat or acidic catalysis.



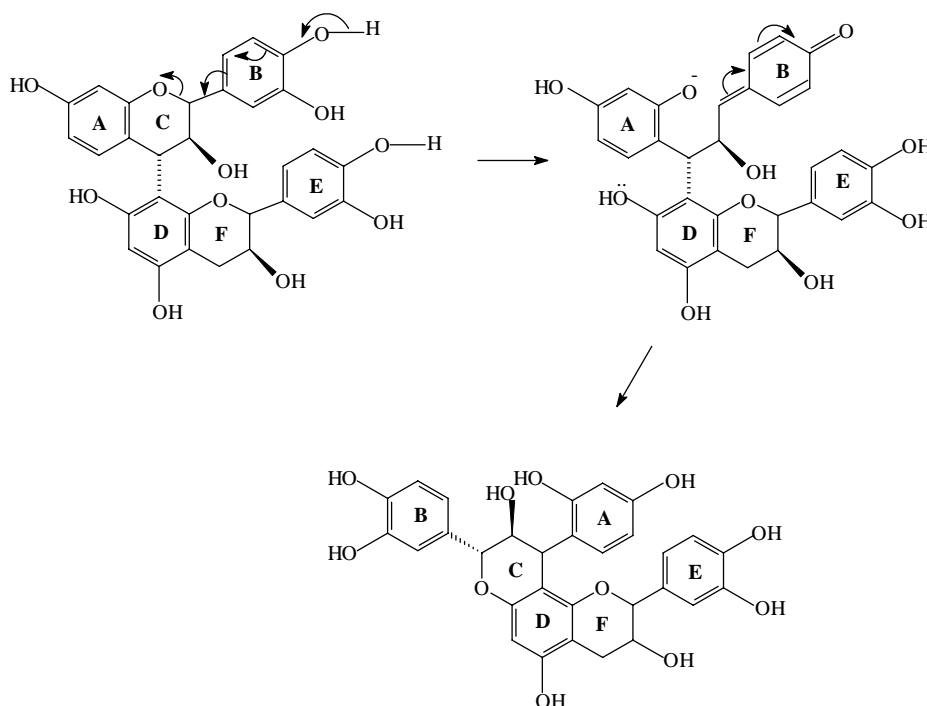
Scheme 1 – Condensation of Methaloyl Phenol

The o-o (ortho-ortho) dimer shown in scheme 1 is one of many species that can be formed using these conditions, e.g., mono, di and tri methoylation. The resin manufacturer then normally allows this condensation to continue until a product of known viscosity and reactivity is formed. This mixture of dimers and oligomers formed during the reaction are the actual species employed by industry as the adhesive.

However this methodology when applied to tannin fails to produce a resol resin as the tannin-methaloyl groups react in a very short time with the A and B rings of adjacent molecules to form larger polymers that have little adhesive potential on their own. This does not mean tannins cannot be used in current commercial resin systems; addition of small amounts of tannin with adhesives and other 'hardeners' prior to wood application offer significant improvements in product properties due to the reactivity and large hydrophobic potential conferred by the tannin.

Although extensively studied, the area of increasing resin (product) properties through the addition of chemicals that give increased hydrophobicity and/or strength is highly topical. Currently the panel product industry uses a high proportion of urea formaldehyde (UF) and mixtures of UF with melamine, resorcinol and phenol to achieve the range of properties required by the construction and furniture markets. Plant derived resin additives could be therefore an area of considerable growth if cost effective formulations can be optimised that provide additional properties to current industrial resins.

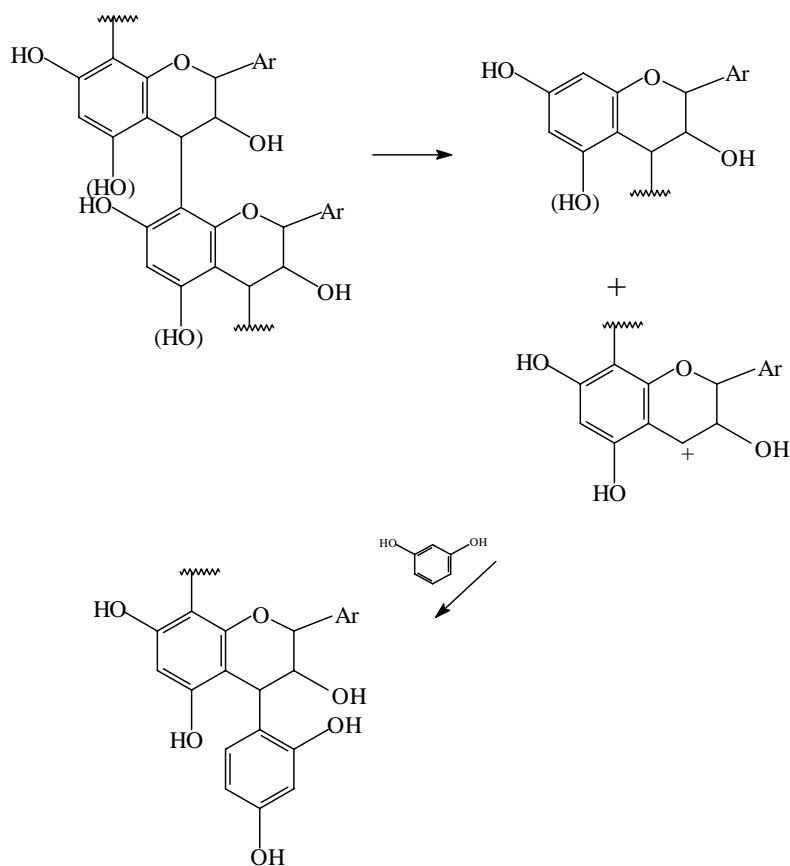
Alternative tannin (non-resol) resins that use formaldehyde have been widely reported in the literature⁷⁻¹⁰. Scheme 2 shows the mechanism of base induced isomerisation of procyanidin dimers (model compounds of tannin sub-units) leading to phlobatannins. Whilst it can be observed that the reactive A ring is released during the reaction the potential for resins with additional cross-linking and strength was found only to be limited in natural tannins. Some advantages were shown at short press times but it has been reported that this increase in property can be obtained by simply increasing the pH of the tannin solution at ambient temperature¹¹



Scheme 2

Hemmingway et al⁶ demonstrated the flavanoid bond cleavage reaction shown in scheme 3 to be useful in the preparation of cold set glulam adhesives where the added resorcinol adduct is connected to the C-4 site in the tannin. Whilst good results have been reported using this methodology¹⁰ it can be questioned that the need for a separate chemical modification is not always necessary as the family of 'honeymoon' type resins offer equally good results at extreme ranges of moisture content without the need for additional synthetic steps¹². Honeymoon end jointing adhesive formulations are comprised of a synthetic phenol-resorcinol component, a formaldehyde donor e.g., paraformaldehyde and a third component made up from a tannin sulfonate solution with an alkali catalyst. Reports using this methodology have shown good adhesive properties at wood moisture content ranges from 8 – 150%, with results indicating good bond strengths and durability

on both soft and hardwood samples without the need for external heat and can - in certain wood species - meet the requirements for structural exterior use products.



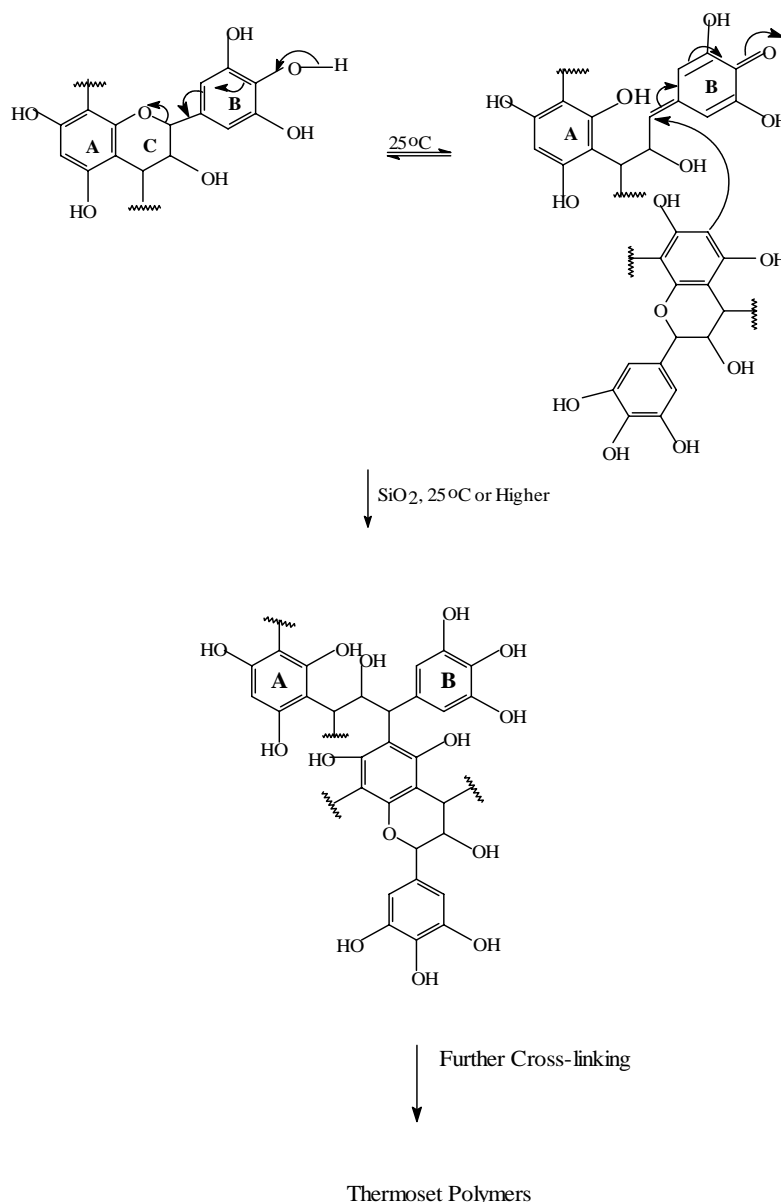
Scheme 3

2.3.3.3 Formaldehyde Free Tannin Adhesives

Resins comprised from pure tannin have been synthesised in laboratories all over the world but currently none of these routes are commercially exploited. Several good reviews of tannin adhesives exist which explain the characteristics and formulation of flavanoid tannins into adhesives⁴⁻⁶.

The ultimate goal of natural adhesives research is to create an adhesive that contains little or no synthetic reagent and that polymerisation does not depend on formaldehyde to act as a cross-linker. This latter requirement is not due to a lack of performance; on the contrary formaldehyde is an excellent choice for generating reactive cross-linking moieties on either aromatic or urea based monomers. The problem is one of toxicity as recent studies have demonstrated formaldehyde to be a potential carcinogen. Due solely to this factor it is envisaged that the allowable limit for exposure to formaldehyde will drop to levels below 0,5 ppm (currently 2,0 ppm in UK), which in many examples will make many procedures unusable.

Until recently, non-synthetic tannin adhesives that exhibited the bonding and durability properties of commercial systems were not available. Autocondensation reactions whilst well known from extraction technologies were never employed in the preparation of adhesives due to the long or non-gelling/hardening behaviour of the solution. However, a highly encouraging report by Pizzi et al demonstrated that a concentrated water solution of a tannin extract gelled and hardened in a very short time at alkali pH by the addition of small or even trace amounts of silica gel at ambient temperature¹¹.



Scheme 4 Tannin Autocondensation

It was shown that when natural polymeric tannin is placed in an alkali solution, *ca* pH 12, with small quantities of silica or other Lewis acids, the tannin undergoes a sterically hindered re-arrangement to form a semiquinone intermediate that favours inter molecular nucleophilic addition from an adjacent chain rather than the simple intramolecular re-arrangement seen earlier in scheme 2¹³. The mechanism of autocondensation was further studied and is shown in Scheme 4.

The application of autocondensation reactions of tannins in particleboard resin formulations was further enhanced following a study that reported the catalytic ability of cellulose (crystalline cellulose) to accelerate the cure profile of autocondensed tannin to form durable resins¹⁵. In particular widely available pine tannin showed excellent interior properties and fully cured without the addition of any Lewis acid.

The overall methodology of forming resins using autocondensation reactions has several advantages:

- Flexibility – synthesis can employ a wide range of tannin types especially EU grown *Pinus radiata*
- Tannin or substrate does not require any pre or post chemical modification

- When Pine bark tannin is used little or no catalysis (other than high pH) is required to form excellent interior grade particleboard – the lignocellulosic matrix catalyses the reaction itself
- Slower reacting tannins such as mimosa only require the addition of trace quantities of dissolved silica gel (sand) or other Lewis acids

An interesting finding in this work is that silica in the solid form does not afford the same resin properties than it does when dissolved in a strong alkali solution. The use of silica as a catalyst or even reagent support has been known in the chemical literature for many years. Normally the postulate is, that pore size and the acidic nature of the silica allows preferential reactions to be carried out within the pores at very high, often quantitative yields, *cf* zeolites. However in this system it is reported that dissolution of the silica in alkali promotes the catalytic effect, not the donation of protons. Whilst this statement cannot fully answer the question it does lend itself to the argument that the silica is acting as a Lewis acid, i.e., accepting electron density from normally an oxygen lone pair. The only real study in this area indicates Lewis behaviour through the formation of organosilicon intermediates observed using ^{29}Si NMR¹⁴.

Both aluminium chloride and boric acid (Lewis acids) are effective catalysts in the formation of autocondensed tannin resins. Both molecules have vacant pi orbitals in which oxygen lone pairs can donate their electrons and thereby cause a polarisation to be set up throughout the molecule, normally leading to nucleophilic attack, in this case by an adjacent tannin resorcinol sub-unit¹⁵.

Open questions and topics for R&D

Currently, autocondensation is the only methodology that has provided formaldehyde free tannin resins with acceptable commercial properties. However if these resins are to be made on a truly commercial basis, clear benefits have to be seen by the industry on both a cost and property basis. Further work should therefore investigate the role of tannin autocondensation at increased scale with particular reference to tannin type and availability, reactivity to wood substrates using a range of 'Lewis acid' catalysts, pH dependency of the reaction, processability, etc. The finding that pine tannin requires no other catalysts but the lignocellulosic matrix further enhances the desirability of this route.

2.3.4 Lignin

2.3.4.1 Introduction

Lignins are large 3 dimensional polymers produced by all vascular terrestrial plants, it is second only to cellulose in natural abundance and is essentially the 'natural glue' that holds plant fibres together. It is primarily obtained as a by-product in wood pulping processes with estimates exceeding 75 million tonnes per annum. Research into lignin based adhesives dates back over 100 years with many separate examples of resins involving lignin being cited. The chemical structure of lignin is very complex with the added difficulty that unlike tannin the individual molecules are not fixed to any particular structure, therefore no true generic molecule exists for lignin from softwood, hardwood or cereals. Usually the chemical composition is quoted from the products obtained through oxidation, e.g., nitrobenzene, of the *in-situ* lignin giving chemists the information on ratios of the generic sub-units, e.g., guaicyl-syringyl.

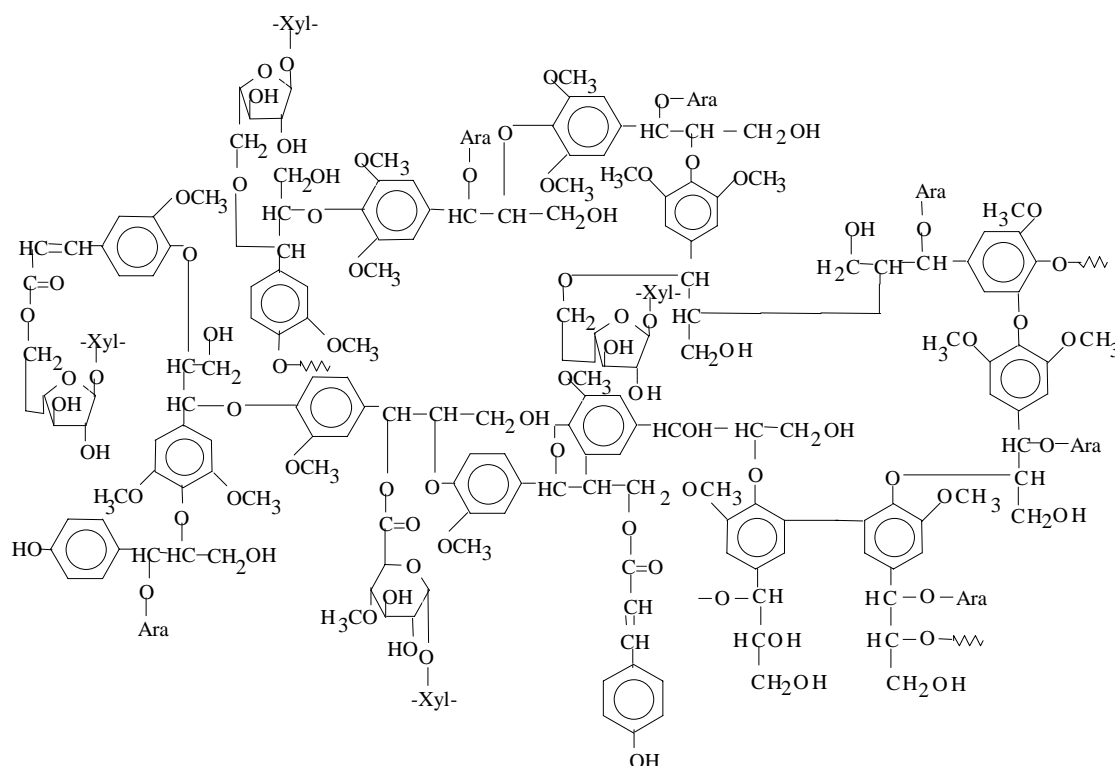
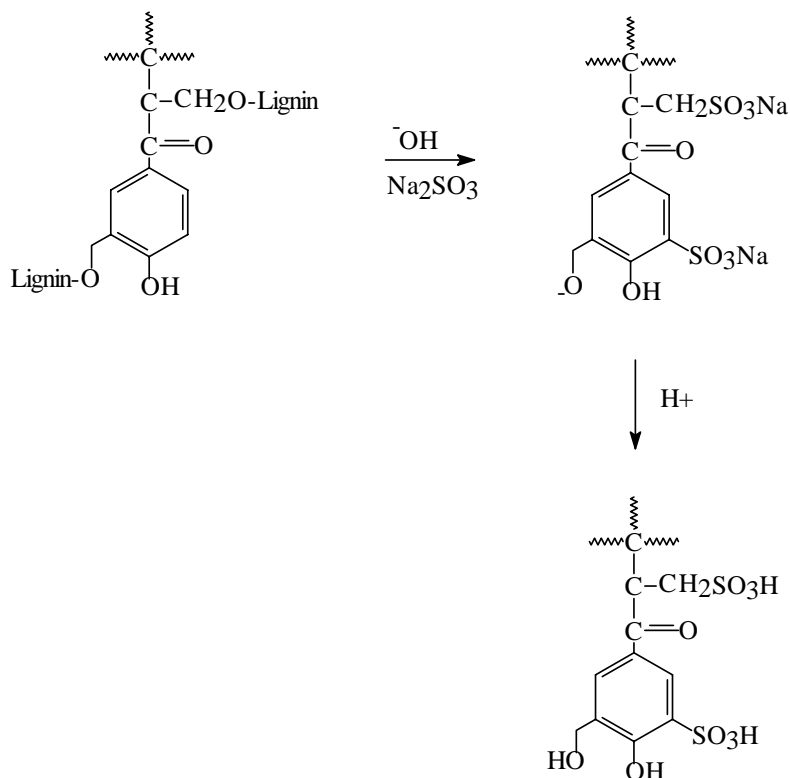


Fig. 2.11: Tentative Assignment of wheat straw Lignin

Due to this highly complex nature the chemical applications of lignin are limited and currently no wood adhesives are manufactured using solely lignin. The reasons given by industry for not using a pure lignin resins are mainly increased press times and the concern of chemical variation in the feedstock. However many wood based adhesives and resins use lignin as a co-reactant with phenol and formaldehyde to afford a product with increased or extended properties. Typically lignin imparts hydrophobicity and flexibility to the product in question be it a film for coating fibres or as a composite adhesive²¹.

The types of lignin that are available for industrial usage come predominately from the effluents of paper pulping processes – termed black liquors - that contain between 5-50% lignin depending on source. Lignins derived from pulping effluents are commonly obtained in sulfonated forms e.g., Kraft and Sulfite pulping, the only commercial non-sulfonated lignin is organosolv which is produced from an alcoholic pulping regimen that affords an unmodified and highly reactive type of lignin. However, organosolv lignin is highly expensive when compared to phenol and the increase in properties required for the additional cost (e.g., press times and physical board properties when compared to phenolic resins) have not been commercially realised. Black liquors from the sulfur-based processes are termed Spent Sulphite Liquors (SSL) and Kraft liquors and can be obtained at a negative or zero cost so they are highly cost effective.

However the lignins obtained from these sulfur mediated pulping processes are quite different from one another; lignin obtained from a Kraft process is highly polydisperse²⁷ and increases in molecular weight as delignification proceeds, the polysaccharides present in the raw material are normally degraded to saccharidic acids. Kraft liquors generally consist of lignin (*ca* 45%), hydroxy acids (*ca* 28%), inorganics and small quantities of other organics. SSL's are obtained from pulping carried out at a range of pH's and conditions which produces initially a highly solubilised lignin containing essentially monomeric sulfonated aromatics and monosaccharides. However as delignification increases then as with the Kraft process the molecular weight and polydispersity of the lignin increases²⁸.



Scheme 5 Sulfite mediated aromatic substitution

The reason for introducing sulfonic acid groups to lignin during pulping is to impart a greater solubility making it easier to remove the lignin by simple washing. As the delignification is done in an alkali media it means that up to three metal sulfonates -which are highly water soluble – can be introduced to each aromatic sub-unit. Taking the pH of the resultant solution to below 3 changes the sulfonate salt to a sulfonic acid, which in turn causes the majority of the lignin to precipitate from solution as the free acid, is only sparingly water-soluble.

2.3.4.2 Current Work

Considerable research activity has been directed toward producing wood adhesives from lignin with very little practical success in terms of commercial implementation. By themselves lignins offer no advantages in terms of chemical reactivity, product quality or colour when compared to conventional wood composite adhesives. Chemical modification on the other hand has demonstrated some positive results through the introduction of reactive cross-linking sites by means of methylation, epoxidation, isocyanation and phenolysis reactions. Methylation has been reported as long ago as 1965 with formaldehyde activated kraft lignin and PF resins²⁹ In these studies it was demonstrated that base catalysed condensation with formaldehyde and softwood kraft lignin introduced CH_2OH groups mainly at the C-5 position of the aromatic ring and to a lesser extent the β position. However even with the introduction of these additional cross linking sites the rate of condensation of methylolated kraft lignin is still far less than for the PF resin alone³⁰.

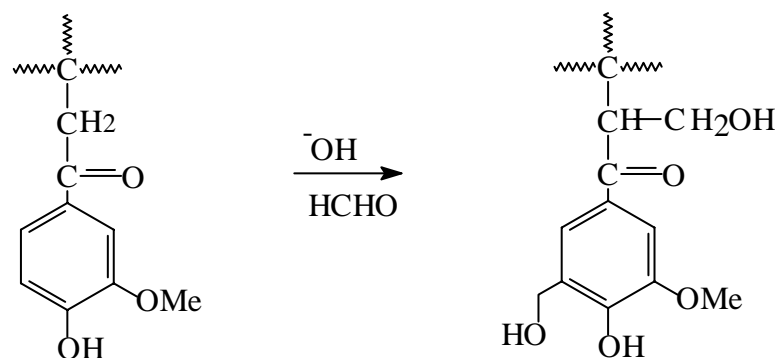
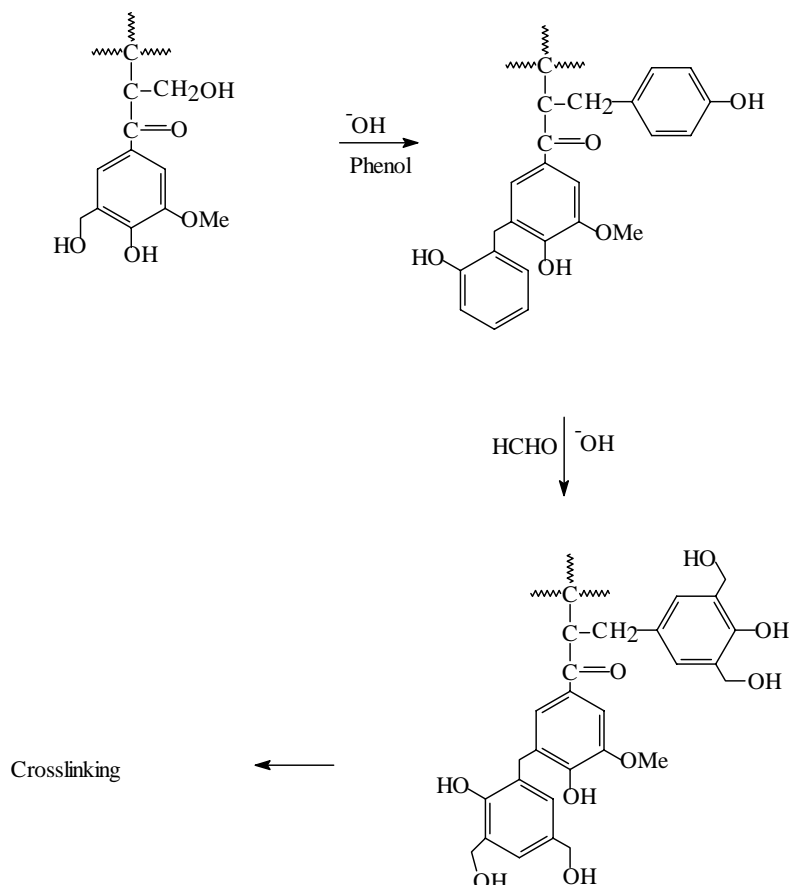


Fig. 2.12: Hydroxymethylation reactions of Lignin

One of the major problems encountered when working with lignin is an actual assignment of what reactive functionalities are present within a particular sample. Techniques such as ^1H / ^{13}C NMR, CPMAS NMR and FTIR have been employed in an effort to elucidate structure but these have met with limited success due to poor resolution and signal overlap. Essentially what is not known is the actual number (or ratios) of the number of available cross linking sites present within a particular lignin sample, e.g., excess of phenolic sites or excess of natural methoxyl sites ready for cross linking. For example, when a sample of organosolv lignin is placed in a suitable solvent such as *n*-butanol the viscosity rises markedly without the addition of any other reagent. After the initial large viscosity rise the lignin precipitates from solution and the recovered solid is essentially unreactive towards further resin synthesis. This has been attributed to molecular rearrangements in the solvent that have led to the sample cross-linking with itself. However introduction of phenol and base to the solution prior to lignin addition leads to a complex with much higher molecular weight that can be isolated and reacted further with formaldehyde to afford adhesive properties coming within experimental error of the pure PF²²⁻²⁶. It is believed that the addition of phenol inhibits the intra cross linking mechanism observed with pure lignin by reacting the natural cross linking sites (probably methoxyl) with phenol moieties. This naturally increases the number of reactive sites available and subsequent addition of formaldehyde to the complex affords a resin with good physical properties³¹.

Recent work by Ren et al³⁷ using a modified kraft lignin and Vazquez et al³⁸ who employed an acetosolv lignin showed that good resins can be made using this methodology. Ren demonstrated that modification of white birch lignin with sulfur and sodium hydroxide resulted in a lowering of the methoxyl content from 18,81% to 11,84%. The ratio of lignin substitution with respect to bond quality was studied and compared to a standard PF this showed that the bond quality was higher for modified lignin-phenol-formaldehydes (LPF) than the corresponding unmodified LPF. This was attributed to the lowering of the methoxyl content. However, Vazquez who studied lignins obtained from a pine acetosolv process showed through a structural analysis that methylolated lignins are suitable for the formation of adhesives. Whilst this may not be as contradictory as it sounds it does indicate that a more suitable method of structural elucidation is required. Standard methods used by chemists to understand structure e.g., NMR, Mass spec etc cannot be successfully employed with lignin due to the sheer number of different nuclei present in the sample. Although these techniques have been reported in the literature it appears that they are not always reproducible on lignin samples from other sources. Understanding the actual structure of any chemical starting material is paramount if further modifications are to be fully understood. But in short the literature demonstrates that either modified or unmodified phenolated lignin is a suitable raw material for PF resin synthesis. The parameters employed for optimum lignin addition were varied and not surprisingly did not (in the vast majority of cases) exceed 30-40% phenol replacement. However this still means that a large amount of the phenol used in the synthesis of PF's can be replaced with lignin from hardwood, softwood and non-woods.



Scheme 6 Modification of lignin with phenol and formaldehyde

Open questions and topics for R&D

Lignin is probably one of the best examples that show how an industrial waste can be employed in a commercial product. The literature clearly demonstrates that good adhesives can be made using a wide variety of lignin types. Virtually all the available types of reactions concerning lignin and PF's have been attempted over the years, e.g., methylation, epoxidation, isocyanation, phenolysis, oxidation, etc with varying amounts of success. Reactions employing hazardous reagents like ethylene oxide or peracids (epoxidations) whilst providing useful information will not be employed in industry unless the properties far exceed those currently observed. Isocyanates are excellent adhesives on their own and further modification with lignin is not required to form very durable composites. Phenolysis appears to be an ideal method to impart additional functionality to many types of lignin with the added benefit that all the chemicals employed are currently used by the resins industry, e.g., base, phenol and formaldehyde. However one of the major obstacles to market usage is the "unknown quantity" factor. Virtually all resin companies cite the same reason for not using lignin as a primary feedstock and that is that they do not know exactly what compounds are present in the mixture. Companies are prepared to use lignin in small percentages with PF's but only as extenders not as primary feedstocks. Further work should therefore investigate not only the scope of lignin reactions but to provide an elucidation methodology that can be used in a wide variety of lignin types that is acceptable to the resins industry.

2.3.5 Carbohydrates

2.3.5.1 Introduction

Carbohydrates in the form of polysaccharides, gums, oligomers and monomeric sugars have been employed in adhesive formulations for many years. They are all readily available from renewable

biomass resources and many such as starch are highly cost effective, however as is the case of lignin no commercial wood adhesive is manufactured using only carbohydrates. Gums such as arabic, guar, xanthan, tragacanth, etc upon dispersing in hot or cold water produce viscous lattices that cure through water loss, although these materials have ideal applications in many industrial sectors they are not employed as wood adhesives. Polysaccharides such as starch, hemicellulose and cellulose have a potential as wood adhesives but only as a co-reactant with another crosslinking species or through a chemical modification that will impart further crosslinking ability.

Carbohydrate polymers typically have one primary and two secondary hydroxyl groups per cyclic unit (in the case of pentosans only the two secondaries). These groups offer positions where reactive crosslinking moieties can be attached, however when using cellulose an additional step is required to solubilise the material prior to any chemical modification. Cellulose has for many years been used as a substrate for further modification, cellulose esters and ethers have found many adhesive applications in a wide industrial sphere from ceramics to paper but their applications with wood are limited³². Cellulosic adhesives derived from graft co-polymers with hydrophobic plastics like polystyrene show good potential in wood based composites.

Narayan et al describe a procedure to bond wood in the presence of hydrophobic materials using cellulose – polystyrene graft methodology that affords wood composites with good physical properties³³.

Conner et al showed that a significant proportion of a commercial PF could be replaced with carbohydrates (xylose based hemicellulose) when bonding plywood veneers³⁴. They determined that reducing sugars couldn't be used directly as they are degraded to saccharinic acids in the alkali conditions required to formulate the resin. Reducing sugars can be used to successfully modify PF resins if they are reduced to the corresponding alditols or converted to glycosides. They postulated that some carbohydrate is incorporated into the resin network predominately through ether bridges - although some methylene bridges are formed - however this percentage of incorporation can vary according to the amount of carbohydrate initially added.

2.3.5.2 Current Work

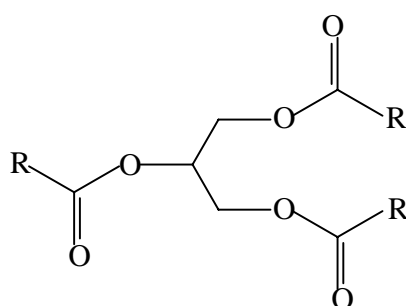
Ono and Yamada recently described the utilization of a liquefied product from cellulosic materials that when incorporated with reactive solvents showed good adhesive properties. They demonstrated that cellulosic materials were liquefied in the presence of sulfuric acid under normal pressure by using either phenol or ethylene glycol. Both solvents provided complete liquefaction products that dissolved in polar organic solvents. Fractionation was applied to the dissolving parts and the product residues. The cellulosic component in wood was found to lose its pyranose ring structure when converted to a liquefied product. The product is confirmed to have phenolic moieties when phenol is used for liquefaction. In the case of ethylene glycol liquefaction, glucosides were observed at the initial stage of liquefaction and levulinates after complete liquefaction. These findings indicate that the proper selection of liquefaction would make possible to prepare polymers of special use. The potential of the liquefied products for plastics including adhesives is discussed on the basis of chemical characteristics of the products. The performance of adhesion from liquefied products is also discussed³⁵.

Conner describes in recent proceedings a range of chemical intermediates derived from carbohydrates and carbohydrate polymers by either chemical or biological means for use as wood adhesives. The use of vegetable protein and carbohydrates, (cellulose, hemicellulose and starch) and the problems associated with that use are reviewed and compared to petroleum derived wood adhesives³⁶.

2.3.6 Unsaturated Oils

2.3.6.1 Introduction

Saturated and unsaturated oils obtained from the seeds and fruits of certain plants are now widely available in both the intermediate and bulk commodity scales. Their general uses range from cooking, food manufacture and the classical soap making process to ingredients in cosmetics, paints and more recently 'bio-derived' resins. Primary sources of vegetable oils are: coconut, corn, cotton seed, oil palm, olive, peanut (groundnut or arachis oil), linseed, safflower, soybean, sunflower seed, and rape seed. However all resin based research to date has centered on oils that contain at least one double bond. Some oil seed plants are grown solely for their oil, while others are primarily grown as food crops or for textile fibres, in which oil production is a secondary by-product. The oil is obtained by pressing the seeds and then extracting the oil with steam, water and/or solvents such as hexane; the high protein residue that remains after oil extraction (oil cake or oil seed cake) is a valuable nutritional component for livestock and in the case of Soya – humans



Basic Triglyceride Sub-unit

Where R=

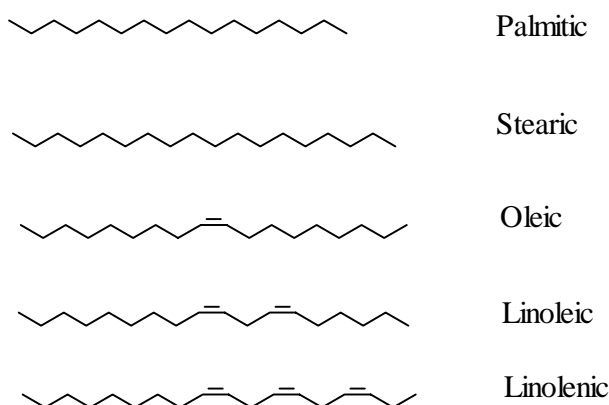


Fig. 2.13: Structure of Triglyceride sub-unit and some common fatty acids

The oil is predominately a mixture of triglycerides with a small quantity of free fatty acid, the amount of free fatty acid is dictated both by the plant and on extraction conditions. The triglyceride moiety is a tri ester comprised of one molecule of glycerol substituted with three molecules of fatty acid. Fatty acids are (commonly) even unit carbon chains bearing from 0 to 3 unsaturated units (double bonds) per chain and a carboxylic acid. The double bonds are predominately in the cis (Z) configuration and in the case of polyunsaturated acids, not conjugated. Some common examples of triglycerides and fatty acids are shown in figure 2.13.

The glycerol molecule is always substituted with a range of fatty acids, never a single type, although genetic manipulation can dramatically alter the ratio in favour of a particular desired fatty acid, e.g., oleic or linolenic. The acid of choice for an adhesive pre-cursor will depend on the chemical methodology in question, but it should be noted that as the number of double bonds increase so does the molecules overall reactivity and its potential for side reactions, in addition to its cost.

Fatty acids can be obtained from a variety of sources with some amounts of palmitic, oleic and linoleic acid being found in all fats and oils. The polyunsaturated linolenic acid is less common but can be found in relatively high concentration in Linseed oil, however this fact also makes it rather expensive for use as an adhesive pre-cursor.

2.3.6.2 Current Work

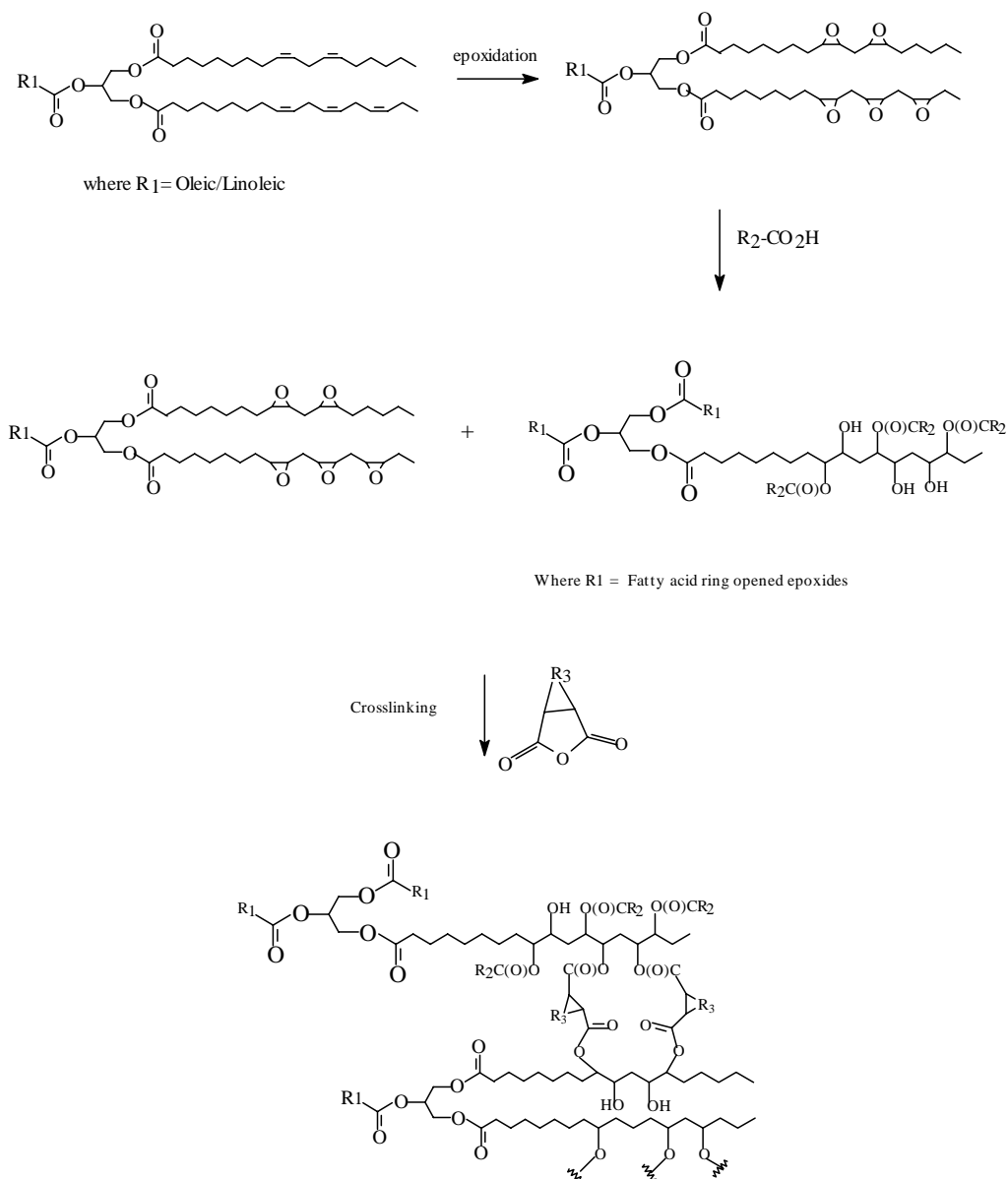
Until recently only two examples could be found where seed oil derivatives were being employed as wood adhesives. Preform Polymerwerkstoff GmbH used Linseed oil to create a resin that can be employed as an adhesive or surface coating material¹⁷. The chemistry centers on an epoxidation of the double bonds and then crosslinking with a cyclic polycarboxylic anhydride to build molecular weight. The reaction is started with a small quantity of polycarboxylic acid. Scheme 7 shows a schematic illustration of the crosslinking process.

The development of Preforms Polymer material from Triglycerides and Polycarboxylic anhydrides (PTP) was originally designed to generate plastic materials from renewable resources. However the researchers found that mechanical properties of the pure resin and when assessed as the adhesive in composite panels can be extensively controlled through the appropriate selection of triglycerides and polycarboxylic anhydrides. This enables a wide range of materials with quite different features to be manufactured. Preform believes possible candidates are materials that are plastically deformable from the outset or they acquire this property only after a suitable heat treatment. The plastic is well suited for use as a formaldehyde free binder for wood fibres and particles including fibres and chips from cereal residues, e.g., straw and fibre mats.

The literature claimed that cross linking time can be varied through the addition of specialised catalysts and several samples were prepared at a range of temperatures (e.g., 120-180°C) that exhibited high water tolerance even at elevated temperatures (pure resin samples); however no actual test data was included.

The following areas were cited as suitable applications for the material;

- Formaldehyde free binder for wood fibre and other cellulose containing products, e.g., elements of furniture making
- Infiltrated fibre materials, e.g., automotive trims
- Continuous mouldings – extrusion
- Manufacture or coating of flexible elements



Scheme 7 – Preform GmbH Resin protocol using Linseed oil

A bio-resin based on soy bean oil has been extensively studied by Prof Richard Wool University of Delaware / Cara plastics as a replacement for polyester type resins in Resin Transfer Moulding applications, e.g., agricultural eqpt, automotive, civil, marine, rail and construction materials based on a zero formaldehyde adhesive. The Cara liquid resins are usually prepared by first synthesising a low molecular weight polymer having the functional groups required for the crosslinking reaction, however to achieve the low viscosity's required the polymer may need to be dissolved in a reactive diluent prior to use, e.g., styrene.

The liquid resins were derived from plant and animal triglycerides by suitably functionalising the triglyceride with chemical groups, (e.g., epoxy, carboxyl, hydroxyl, vinyl, amine, etc) that render it polymerisable. The technology can utilise a wide range of fatty acids from C₁₂ - C₂₂ and 1-3 double bonds, but prefers 14 – 22 carbon atoms with only 1-2 double bonds. The report also mentions the benefits of genetically modified oils that can be obtained with a very narrow distribution of molecular species and relatively few saturated fatty acids residues.

The report¹⁸ claims that excellent inexpensive composites were made using natural fibres, such as hemp, straw, flax and wood in fibre, particle and flake form. That soy-based resins have a strong affinity for natural fibres and form an excellent fibre-matrix interface as determined by SEM analysis of fractured composites. That these resins can be viewed as candidate replacements for phenol formaldehyde, urethane and other petroleum based binders in particleboard, MDF, OSB and other board applications. However, no actual test data was supplied in the report.

Aiming at the industry needs and growing marked demands, The BioComposites Centre and DuPont UK started to investigate natural materials in an effort to develop wood based resins and identified Cashew Nut Shell liquid (CNSL) as an interesting candidate. The dual phenolic/fatty acid nature of CNSL makes it a potential natural raw material for the synthesis of water-resistant resins and polymers, see figure 2.14.

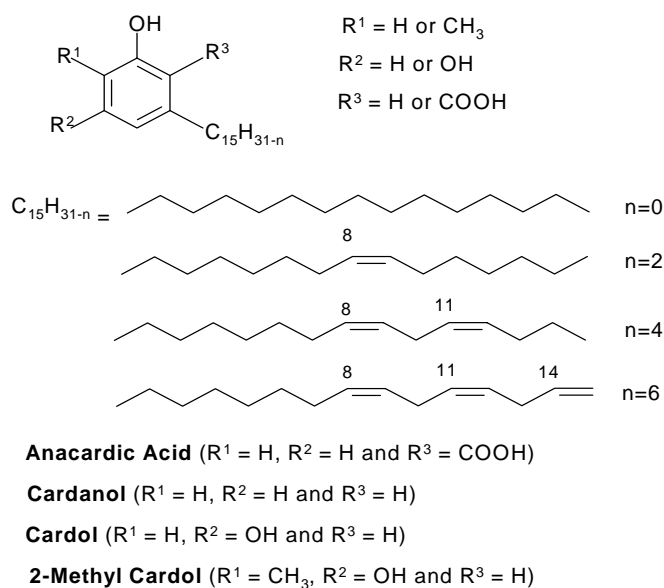


Fig. 2.14: Structure of CNSL

Important structural features of the CNSL molecules are its phenol moiety and 15- carbon alkenyl chain. The phenolic moiety and/or double bonds in the chain can be directly employed to polymerise into resins or solids. Currently, acid catalysed polymers of CNSL are being used as a component in the manufacture of friction dusts. Alternatively, alkenyl chains can be tailored in such a way so that more suitable functional groups are generated, such as aldehyde, hydroxyl, carboxyl, epoxy, etc. This can be achieved by traditional oxidation methods that need several synthetic steps and thus might not be economically viable. The BioComposites Centre (BC) investigated alternative ways of chemical modification of the alkenyl tail to desired functional groups. Ozone was thought to be an ideal reagent, to achieve this modification, as it would create a range of very similar reactive monomers through cleavage of the double bonds into aldehydes. In

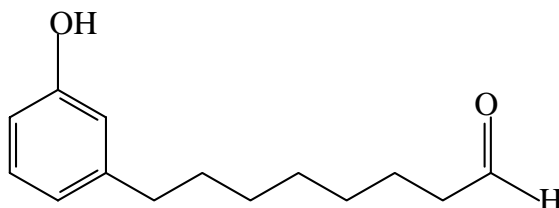


Fig. 2.15: CNSL aldehyde

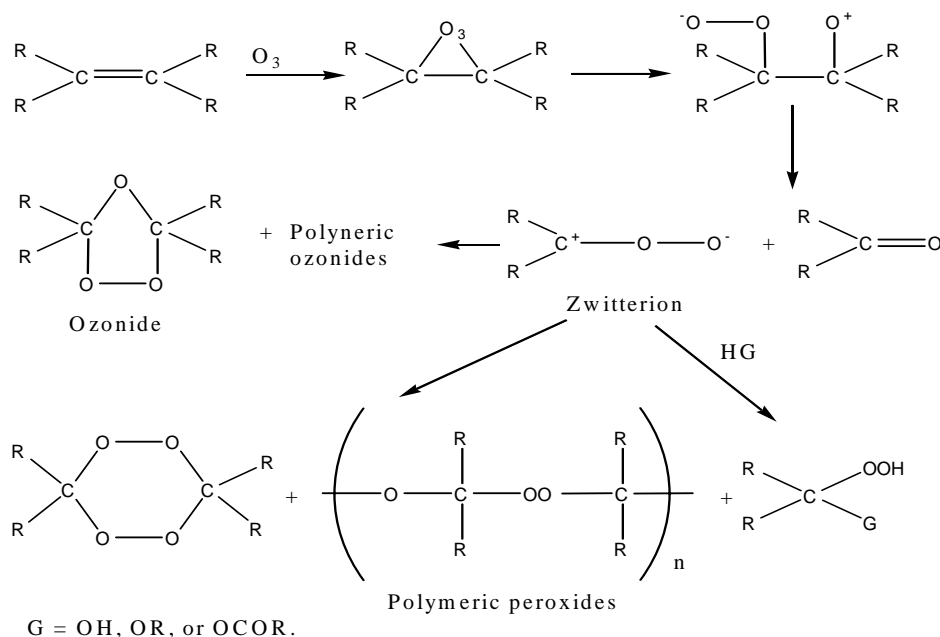
turn the phenolic moiety -in both alkali and acid conditions- is highly reactive towards electrophiles like aldehydes. As both a phenol and aldehyde functionality would be inherent in every new molecule (see figure 2.15), no further cross-linking agent would need to be added.

The remaining alkyl aldehyde groups would increase the reactivity of the system towards cross-linking and impart a high degree of hydrophobicity. Advantage of using ozone as oxidant over other traditional oxidants is, after ozonolysis the ozonolysis products can be converted selectively to aldehydes, alcohols, carboxyl acids and more over phenol moiety is inert to ozone attack.

2.3.6.3 Background of Ozonolysis

When a compound containing a degree of unsaturation is treated with ozone, a variety of peroxidic compounds are formed depending on the medium of the reaction. The basic mechanism of ozonolysis, as formulated by Criegee³⁹, is as follows (see Scheme 8). When non-participating solvents, e.g. dichloromethane, hexane, etc. are used the major product of ozonolysis is an ozonide along with some polymeric ozonides. Participating solvents, e.g. methanol, water, acetic acid, etc. generate hydroperoxides with corresponding alkoxy, hydroxy or acyloxy groups. All these compounds can be suitably converted to aldehydes (or ketones), alcohols or acids depending on the reductive or oxidative conditions

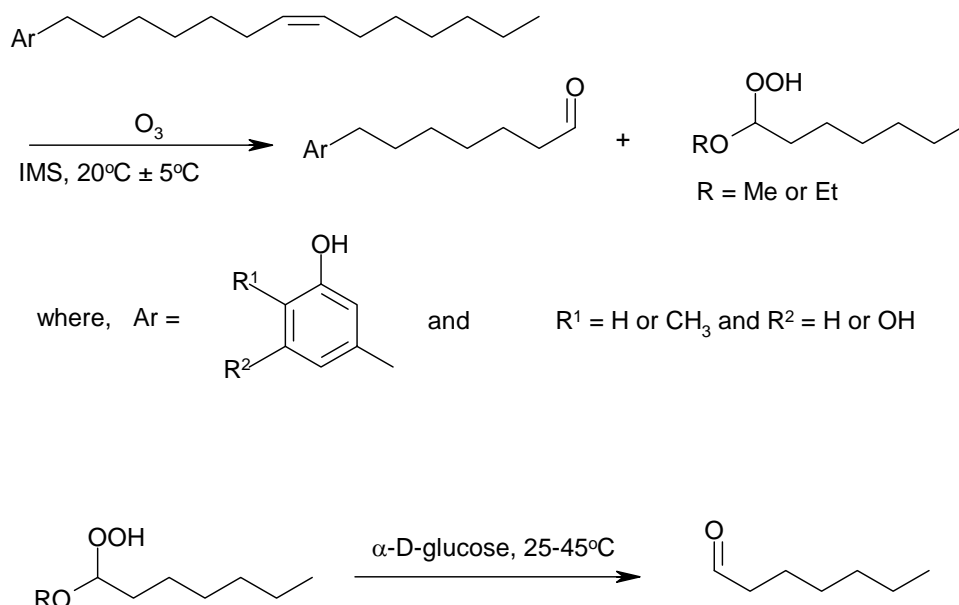
The nature of solvent can have striking effects on the ozonolysis of CNSL, i.e., the type of solvent determines the ozonolysis products. Broadly there are two different types of solvents: non-participating and participating. Dichloromethane, alkanes (pentane, hexane, petroleum ether), carbon tetrachloride, acetone and ether are examples of non-participating solvents. Examples of participating solvents are methanol, ethanol, acetic acid, water, water-acetone mixture. Solvents may



Scheme 8

also be divided into two groups from the viewpoint of reactivity or unreactivity toward ozone. Water, acetic acid, carbon tetrachloride are unreactive toward ozone whereas methanol, ethanol are reactive.

When ozonolysis is carried out in a non-participating solvent, the major products are ozonides and polymeric ozonides¹⁹. The principal ozonolysis products are hydroperoxides when participating solvents are used. Ozonolysis in non-participating solvents are normally carried out at lower temperature (-78°C to -10°C) whereas ozonolysis can be safely conducted at higher temperature (e.g. 25°C) when participating solvents are employed.



Scheme 9 Mechanism of CNSL Ozonolysis

It was observed that there was a risk of over-oxidation when excess ozone was passed through a solution of CNSL or oils in non-participating and unreactive solvents (e.g. dichloromethane). Carboxyl acids (unsuitable resin precursor) were identified when ozonolysis of CNSL was continued longer than necessary. Over-oxidation did not occur in participating and reactive solvents, most possibly, as the solvents absorbed the excess ozone.

Substituting the solvent in the reaction from dichloromethane to ethanol, methanol or IMS was successfully completed without any undesirable oxidised by-products being formed or loss in yield of the intermediate or aldehydic products. Industrial methylated spirit (IMS) was found to be the solvent of choice for the ozonolysis of CNSL. The resultant alkoxy hydroperoxides formed through this route²⁰ are thought to be safer to handle than the highly strained ozonides formed when aprotic solvents such as dichloromethane are used and easily converted to aldehydes by chemical reduction (zinc/acetic acid, glucose) or hydrolysis (steam distillation).

The alcohol can be either recovered at reduced pressure or reused in a continuous reaction, as the aldehydes are inert to further reaction by ozone. Alcoholic solutions of the aldehydes showed excellent resin strengths when catalysed with acids such as para toluenesulfonic acid at 180°C.

Table 2.7: Comparison of lap shear bonding strength cured at 180°C for 3 minutes.

Resin	Bond failure stress (mPa)
Phenol Formaldehyde (commercial)	5,55
CNSL (Zinc/Acetic acid reduced)	6,77
CNSL (α -D-glucose reduced)	6,02

From exploratory chipboard data it was found that the Internal Bond (IB) strength results corresponds roughly to the bond failure stress results presented above. For example a CNSL aldehyde resin at 10% application gave an IB of 1,05 N/mm² and an ABES value of 6,77 mPa compared to that of commercial PF resin that gave 0,69 N/mm² and an ABES value of 5,55 mPa. The resin also exhibited a good retained IB after soaking in water for 12 hrs and after immersion in boiling water for two hours, e.g., initial IB 1,05 N/mm² after 2 hrs boil 0,58 N/mm².

This methodology of using ozone is seen as a useful tool for producing reactive monomers from renewable oils. The monomers can be pre-reacted with various materials, e.g., tannin, to increase their viscosity, molecular weight and gel time so that properties can be tailored to suit a particular process. In addition, the oil can be used in the form of an emulsion or through changing pH as a water-soluble solution.

Open questions and topics for R&D

Natural oils represent a massive area for further work, they contain a range of functionalities that can be manipulated to provide ideal situations for cross linking to occur. They are naturally hydrophobic and can be obtained at reasonable costs, one benefit at present is that costs will be lowered if non-food grade oils are required at present virtually all vegetable oils are of food grade and therefore food grade cost.

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2.4 Casein Adhesives

Egil B. Ormstad

2.4.1 Introduction

Casein is a protein derived from milk and was early used as an adhesive (old China and the old empires around Mediterranean).

Casein adhesive is a powder to be dissolved in water prior to use. No heat is needed to dissolve the adhesive powder neither to cure the adhesive. It was therefore named “cold adhesive” in contrast to the other main adhesive until 1930, the animal adhesive which had to be applied warm and was thus named “warm adhesive”.

2.4.1.1 Manufacturing

Practically all the casein used for gluing purposes is, obtained from skimmed milk by precipitation with sulphuric, hydrochloric or lactic acid. After washing and drying it is milled to a yellowish powder. Due to the method of manufacture, casein is contaminated with other milk solids. The composition of the commercial product may vary between the following approximate limits: protein 80-90%, ash 1-4%, butter 0,1-3%, moisture 7-10%, lactose 0-4% and acids (expressed as lactic acid) 0-3%. The impurities affect the properties of the adhesive.

Casein is practically insoluble at its iso-electric point pH 4,6. The solubility increases with increasing acidity or alkalinity.

The casein adhesives are always produced as a powder. The adhesive powder consists of Casein, Calcium hydroxide, Sodium salts of calcium, phosphate, carbonate or fluoride and in addition different fillers to adjust the viscosity and to improve the properties of the adhesive. Casein adhesives are often added preservatives to prevent bacterial and fungal growth.

2.4.1.2 Adhesive Formulation

Adhesives are prepared by dissolving casein in aqueous alkaline solvent. The bonding power, the rheological behavior, the rate of hydrolyses, the working life, the water resistance and other properties of the adhesive may be varied by using different alkaline solvents and by changes in the amount used. The alkalinity of casein adhesives varies from pH 9 to pH 13.

When water is lost either by evaporation or diffusion from the adhesive solution the viscosity increases and gelation occurs. In its dry condition the casein gel is hard but is capable of reabsorbing moisture. Casein adhesives may be classified according to their degree of water resistance.

When the adhesive powder is mixed with water different reactions take place.

1. Water swells the casein powder, the sodium salt dissolves and some of the calcium hydroxide is dissolved (max. concentration at 20°C is 1,3g/l).
2. The sodium salt reacts with the dissolved calcium hydroxide under the formation of sodium hydroxide and unsolvable calcium salt.
3. Sodium hydroxide reacts with the casein to solvable sodium caseinate (the adhesive is ready for use).
4. As it is less sodium salt than calcium hydroxide, all will be used after some time and the rest of the calcium hydroxide will (as it is dissolved) react with sodium caseinate to unsolvable calcium caseinate.

This last part is a chemical curing reaction, giving the dissolved adhesive a limited pot life.

2.4.1.3 Adhesive Preparation and Use

Ready mixed adhesives are prepared according to the manufacturer's instructions (normally one part by weight of powder to two parts by weight of water). The normal procedure is to add the well-mixed powder slowly to gently stirred cold or tepid water. A working life of four to eight hours at 15° to 20°C is obtained.

After min. 15 minutes of ripening after the mixing, the adhesive is ready for use. Casein adhesives are normally used for wood gluing by cold pressing technique, but hot pressing at moderate temperatures is sometimes used. The pressing time at 20°C will be 1-2 hours for nonstructural gluing and 4-8 hours in the manufacturing of glulam. The adhesive is normally used in temperature range between 10-30°C, but even at temperatures down to 5°C it is possible to obtain high quality glue bond (NB long pressing times).

As the solids content is low, the use of casein adhesives will lead to a higher moisturizing of the wood than other adhesives. It is therefore recommended to dry the glued products before further processing.

2.4.1.4 The Strength and Durability of Casein Joints

Casein adhesives are not thermoplastics and possess satisfactory heat resistance for gluing of wood. The adhesive shows no cold creep properties and can therefore be used as an adhesive for load bearing constructions. The cured adhesive is not brittle and possesses gap-filling properties.

The limiting factor for the casein adhesive is the low water resistance. The most used types made with calcium hydroxide have a limited cold water resistance (after 24 hours cold water soak is the shear strength ca. 15% of dry test values), but will not withstand warm water. However the moisture resistance is sufficient for wood moisture content up to 18%, and glued products (glulam) have shown very good resistance for temperature and moisture variation in indoor climate and in protected external application (service classes 1 and 2). The adhesive will fail under exterior conditions where rainwater has access to the glue line. The failure may be due to alkaline hydrolyses or attack by microorganisms.

Due to the alkaline content, the casein adhesive has a tendency to discolour wood species with high content of tannins (oak, mahogany and walnut). But due to the alkaline nature of the adhesive, it can be used for gluing coniferous wood with high content of resins.

Another drawback of the casein adhesive is the high tool wear due to the content of calcium hydroxide.

2.4.1.5 Uses

Casein adhesives have been used in the production of furniture, plywood and laminated beams. The most important use has been in the production of glulam for indoor and covered exterior exposure. The long time experience in these climate classes with casein adhesive of the so-called water resistance grade has shown very high remaining strength after 50 years of service.

2.4.1.6 Standardization and Development

The casein adhesive will not fulfill the requirements given in EN 301/302 for adhesives for load bearing timber structures. However a new EN standard (prEN 12436) for casein adhesives to be used for load bearing timber structures is out for formal vote.

If the standard is accepted as an EN-standard, then the casein adhesive can be of some interest as a type II adhesive. The benefit of such an adhesive is that the raw materials are coming from natural resources and it is formaldehyde free. The drawback will be dust from the adhesive powder and the preservative to be used in adhesive formulation.

The casein adhesive has not been used to a large extent in the industry for the last two decades.

2.5 Other Woodworking adhesives

H. Heinrich

2.5.1 Hotmelt Adhesive

2.5.1.1 Introduction

Hotmelts are 100% solid thermoplastic compounds, whereby they are compounded and applied in the molten state at elevated temperature and whose resultant properties are obtained by cooling.

2.5.1.2 Advantages

- 100% solid, no water or solvent to evaporate
- Short set time allows high speed operation
- High seal strength
- Combine flexibility and toughness
- Adhesion on a wide variety of substrates even without primer
- Effective bonding of difficult surfaces: PE,PP, varnishes...
- Long storage life

2.5.1.3 Limitations

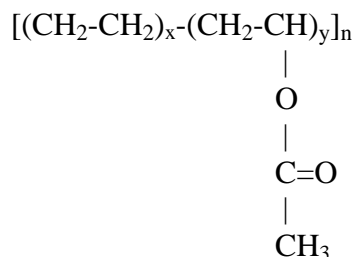
- Low heat resistance at elevated temperatures (loss of strength/tack)
- Degradation at elevated temperature (colour, viscosity)
- Sensibility of certain substrates to the required application temperature

2.5.1.4 Role of Ingredients in Adhesive Performance

a) Polymer / Elastomer

This is the main component and backbone of hot melt adhesive blend; it gives strength, cohesion and mechanical properties (filmability, flexibility). The most common polymers in the woodworking area are EVA and APAO.

Ethylene Vinyl Acetate (EVA)



VA% ↗

Adhesion ↗ Wetting ↗ Setting Time ↗

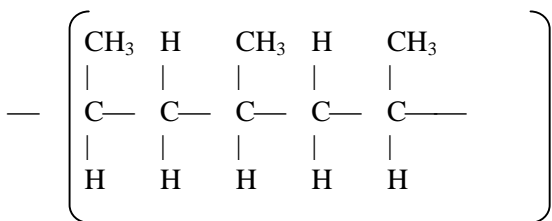
Heat resistance ↘ Cohesion ↘

MI (melt index, measures degree of polymerisation) ↗

Adhesion ↗ Wetting ↗

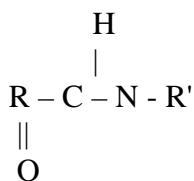
Mw ↘ Cohesion ↘ Viscosity ↘ Heat Resistance ↘

Amorphous Poly Alpha Olefin (APAO)



Properties: good adhesion to polyolefins, good flexibility, low cohesion, long open time, high heat and humidity resistance.

Polyamide



Properties: high setting speed, good cohesion, oil and solvent resistant, very high heat resistance

b) Tackifiers

- Improve Hot Tack
- Improve wetting characteristics
- Modify compatibility
- Improve open time
- Enhance adhesion

The most common are:

- Hydrocarbon resins (aliphatic C5, aromatic C9, or aliphatic-aromatic modified)
- Natural (Polyterpene, Terpene modified-terpene phenolic, rosin and rosin derivatives, tall oil rosin ester)

c) Other components:

Fillers (CaCO₃ and/or BaSO₄)

- Reinforce the cohesion (small particle size)
- Decrease sagging
- Decrease adhesion
- Decrease the price of the product

Pigments (TiO₂, etc...)

Plasticizers

- Decrease the viscosity and the heat resistance

Stabilizers

- Improve heat and ageing stability

2.5.1.5 Hotmelt Properties

a) Nature

- **EVA**: Filled or unfilled; most common technology; limited mainly for heat resistance.
- **Polyamide**: for high heat resistance or fast setting; limited by a high price.
- **APAO**: for better heat resistance than EVA, price between EVA and polyamide.
- **HMPU**: gives the best adhesive performances; high price and specific application methods.

b) Viscosity

Edge banding hotmelts have a viscosity between 30 and 180.000 mPa.s. at application temperature.

Profile wrapping hotmelts have a viscosity between 5.000 and 40.000 mPa.s at application temperature.

Viscosity is not a direct indication of performance. High viscosity products generally have a high green tack, but it may be possible to get high green tack with low viscosity materials that are fast setting. Low viscosity allows a lower coating weight and better wetting properties.

High viscosity is important for low quality panels (with a bad surface) because only high viscosity will give a sufficient glue joint (a low viscosity product will flow into the panels holes).

With very thin edges high viscosity gives sufficient adhesive to mask the panel's defaults and provide a smooth surface.

c) Density / Filler content

Depending on the filler content, the density is between 0,95 g/ml (unfilled) and 1,6 g/ml (high filled).

As the quantity of hotmelt required is a coating volume rather than a coating weight, the coating weight is lower with an unfilled product.

As adhesive properties of an unfilled product are better, it's also possible to reduce the quantity.

To be able to reduce the coating weight, the machine must have a fine roll (fine streak: approx. 1 mm).

d) Softening point (R&B)

Rough indication of heat resistance, tests must be carried out to measure heat resistance.

EVA: 90 - 145°C.

APAO : up to 165°C.

PA: 130°C

e) Tensile strength

Value indicating internal strength of the adhesive. Measured at high temperature, could provide information on heat resistance.

f) Green strength

Important parameter for thick or soft edges, which can spring back if initial tack is not good enough.

g) Setting time

Products with a very fast setting will be suitable for difficult edges. Very fast setting doesn't allow good adhesion because of a too short "open time". A long setting time could give problems during trimming.

h) Residual stickiness

A product having a residual stickiness or products with a slow setting speed could make the panel surface dirty during the trimming process. This mainly happens with unfilled products or APAO. To limit residual stickiness, reduce the coating weight. This however is a critical parameter for APAO because of its soft nature.

i) Wetting properties

Indication of possible edging. Some edges are critical because of a difficult wetting.

- Solid wood: with high resin or oil content.
- Laminates: sometimes primers must be preapplied.
- Plastics: a primer is always needed to improve the wetting.

Some products specially developed for paper edges could fail on other types because of low wetting properties. A product with high wetting properties can be used with critical working conditions such as "cold" panels.

j) Adhesion properties

Different from wetting but same comments. Adhesion will be very important for the final quality of the glue joint. During peel test, results are a mean of cohesion and adhesion failures.

k) Melting capacity

Products must have a quick melting to feed quick machines ("quick" depending on machine and consumption). New machines always have a quickmelter to feed the melting pot.

Overheating in a melting pot to increase melting speed will generally damage the product.

l) Flowing properties

Edge banding hotmelts have very high viscosities (up to 180.000 mPa.s) and they must be able to flow between the melting pot and the roll at application temperature.

This parameter is measured to ensure that the products are able to flow.

m) Thermal stability

This property is important for slow machines or when machines stop to avoid degradation of the product. Most products may be heated up to 240°C for a short time (1 hour) without degradation.

At application temperature they have a stability of more than one day.

n) Smell

Important as for any other hotmelt; depends on working temperatures. Some customers do not have good ventilation or extraction systems near the melting pot, then smell slowly increases during the day.

o) Stringing

Of course products should not string. Filled products usually never string. Some unfilled products may string. Using a roll with fine streak or increasing temperature will decrease stringing if it is a problem.

p) Granulate size

Important for melting systems:

- Quick melters have a heating plate with holes of 2 mm diameter.
- Particle size must be at least 3 mm to be sure they melt and do not pass directly through the holes.
- Some systems have a granulate minimum level detector with a light ray, if particle size is too small, a granule may block the hole, low level of granulate is then not detected.

q) Blocking

Depends on product residual stickiness, granulates must be separated with an anti-blocking agent.

Blocking can occur:

- In the packaging during summer time (this could block vacuum feeding systems)
- In the quickmelters, granulates being preheated before the heating plate by heat radiation.

Questions and topics for R&D:

- a) less odour
- b) less volatils (fumes)
- c) the line speeds increase more and more, the products have to be suitable

2.5.2 Polyvinylacetate

2.5.2.1 Introduction: What Is a Water-Based Adhesive ?

Thermoplastic materials. This is an aqueous dispersion of a polymer.

2.5.2.2 Advantages

- Ready to use
- Short setting time
- Flexible joint few abrasive
- Invisible joint
- Easy to clean
- Long storage life

2.5.2.3 Limitations

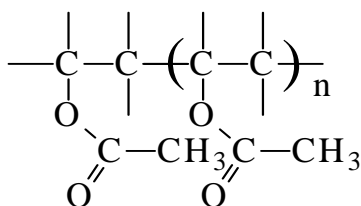
- Thermoplasticity
- Creep

2.5.2.4 Role of Ingredients in Adhesive Performance

a) Water based Polymer dispersion

It gives cohesion and adhesion, comes from the polymerisation in emulsion of one or several monomers (1 monomer: homopolymer; 2 monomers: copolymer; more monomers: ter, tetra polymer)

Example: Polyvinylacetate (PVAc)



The most common are:

- Vineleacetate homopolymers (PVAc): wood to wood assembly
- Vineleacetate Ethylene copolymers (VAE): lamination of paper and PVC to wood
- Miscellaneous (Polyurethane, acrylics)

b) Plasticizers

Soften the film, increase the adhesion, increase the setting speed

The most common are:

- Phtalates
- Adipates
- Benzoates

c) Other components

Filler (CaCO₃ and/or CaSO₄)

Increase the dry content of the glue

Antifoam

Surfactant which avoid the foam formation while using and manufacturing the product

Stabilizer

Bactericidal and fungicidal action used to avoid the hydrosoluble polymer's' degradation.

Filler dispersant

To keep the filler in homogeneous dispersion.

Thickener

To adapt the rheology of the adhesive to the application.

Polyvinyl alcohol

Water holder, helps to adjust the assembly open time and the green tack of the adhesive.

Other agents

For the particular characteristics: wetting, fireproofers, colouring, tackifier, etc...

2.5.2.5 Glue Properties

- a) Viscosity (mPa.s): resistance of the adhesive to flow when subjected to a shearing force (stress). It is measured in Pa.s or mPa.s (1 Pa.s = 1000 mPa.s = 1000cps). Viscosity depends strongly on temperature and shear rate (speed)
- b) Rheology: describes the behaviour of the adhesive as temperature and shear rate change
- c) Dry content (in%): percentage of solid obtain after drying, for instance 1 hour at 105°C
- d) Ash rate (in%): difference (in%) between residual weight of the product after calcination and dry content.
- e) Density
- f) pH
- g) Minimum Temperature of the Film Formation (MTFF): minimum temperature under which the glue film can not be obtained.
- h) Open time:
 - Adhesive Open Time
 - Starting from application, time while the adhesive is still tacky.
 - Machine Open Time
 - Time elapsed between adhesive application, and contact (compression) with the second substrate

-
- i) Closed assembly time: time elapsed between the second substrate application, and pressure
 - j) Tack: immediately after assembly, the initial strength of the bond is called Green Strength (initial tack)
 - k) Setting time: depending on nature of adhesive, Cohesion builds up gradually after assembly. As cohesion builds up, setting time is reached when the assembly can be manipulated safely.
 - l) Colour, smell
 - m) Frost stability: resistance of the product to freezing and heating cycles.
 - n) Wetting: capacity of the adhesive to «wet», i.e. spread over the substrate. Requires surface tension of adhesive lower than surface tension of substrate
 - o) Water resistance classification: according to the Standard EN 204 adhesives are classified in relation with the solicitations they have to support.

Classe	Conditions
D1	Dry Inside, HR% < 15%
D2	Inside, rare contact with water, HR% < 18%
D3	Protected Outside
D4	Outside, exposed to the weather

- p) Waiting time ("Gumming"): After adhesive application, waiting is required for some water or solvent removal before second substrate can be pressed on.

Waiting time strongly depends on temperature, porosity and relative humidity.

Question and topics for R&D:

- a) less VOC (AVM, acetic acid)
- b) the line speeds increase more and more, the products have to be suitable

3 Analysis of Resins and Adhesives

D. Grunwald

3.1 Introduction

Analysis or characterisation is essential when working with adhesives. Some efforts are focussed on specific problems like the curing process, material design at a molecular level, structural determination, process control or failure analysis (Hon 1994).

The majority of wood-to-wood bonds are formed using formaldehyde-based thermosetting resins or isocyanates. A short description of these main types of adhesives currently used is given in section 3.2. Although some of them are applied for more than 60 years, the adhesive characterisation in the wood working industry is almost completely based on simple laboratory tests. The adhesive properties are controlled during production by the supplier and on receiving by the consumer. Despite this the chemical industry and research institutes are using a large variety of powerful tools to characterise their adhesives and competitive products for more than 20 years. Together with laboratory tests and the characteristic values, the analytical tools give much more information on adhesive properties. The characterisation of adhesives is often a complex procedure due to the permanent ageing, which leads to chemical and physical variations, and the high polarity of these systems. Although the analytical tools have given more knowledge about adhesives, in many areas the correlation between adhesive performance and bond quality is not yet clearly recognised (Zeppenfeld 1991, Dunky 1997, Grunwald 1999). In this field more intensive research and development is necessary to achieve better and more reliable results.

Questions and topics of R&D:

- a) Research on correlations between bond quality and adhesive properties.
- b) Research on useful combinations of different analytical methods.
- c) Research on applied analytical methods.

3.2 Main Adhesives Systems for Wood Based Products

The adhesives used for wood based products are based on formaldehyde (with one exception: PMDI), condensed with other components. Their combined market value is noticeably higher than 90 percent. The market leaders are UF-resins. More information about these adhesives can be found in chapter 2.

- Aminoplastic glues:
 - Urea-formaldehyde-resins (UF)
 - Melamine-urea-formaldehyde-resins (MUF)Melamine-formaldehyde-resins (MF) are not used due to economic reasons.
- Phenoplastic glues:
 - Phenol-formaldehyde-resins (PF) in resol- or novolak-form
 - Resorcinol-resins (RF)
 - Phenol-Resorcinol-formaldehyde-resins (PRF)
- Mixed /Co-condensated glues
 - Melamine-Urea-Phenol-Formaldehyde-resins (MUPF)
 - Phenol-Urea-Formaldehyde-resins (PUF)
- Others
 - polymeric Diphenylmethane-diisocyanate (PMDI)

Adhesives fully or partly based on natural resources (tannin, lignin, cashew nut, etc.) have only a very small market share. Very special analytical procedures are necessary due to the different components and the broad range of adhesives used.

Questions and topics of R&D:*Research on mixed and combined adhesives.*

3.3 Characteristic Values of Adhesives and their Analysis

The characteristic values of adhesives are checked within the scope of a delivery by the producer and partly by the customer to guarantee the manufacture of the wood based product. The characteristic values give only a rough impression on the quality and performance of an adhesive. To compare different adhesives it is required to know more about properties like molar ratio, free formaldehyde or NCO-content (section 3.4).

3.3.1 Solid Content

The solid content of formaldehyde-based resins is determined by different drying methods (120°C, 2h; 103°C, 15h; 80°C, 1h then 103°C, 3h) During the process not only the existing water, but also formaldehyde and water from the ongoing condensation or pyrolysis is released by the adhesive. Due to different temperatures, drying times and drying kilns the results do not correlate exactly. The “real solid content” can be determined by freeze-drying or vacuum-drying the sample, which is much more time consuming . A correlation between solid content according to the most used method (120°C, 2h) and “real solid content” of UF-, MUF-, MUPF- and PF-resins determined by vacuum-drying can be found in figure 3.1 (Schmidt and Grunwald, 2000).

Since PMDI is not a hydrous dispersion the solid content is not determined and equal to 100%.

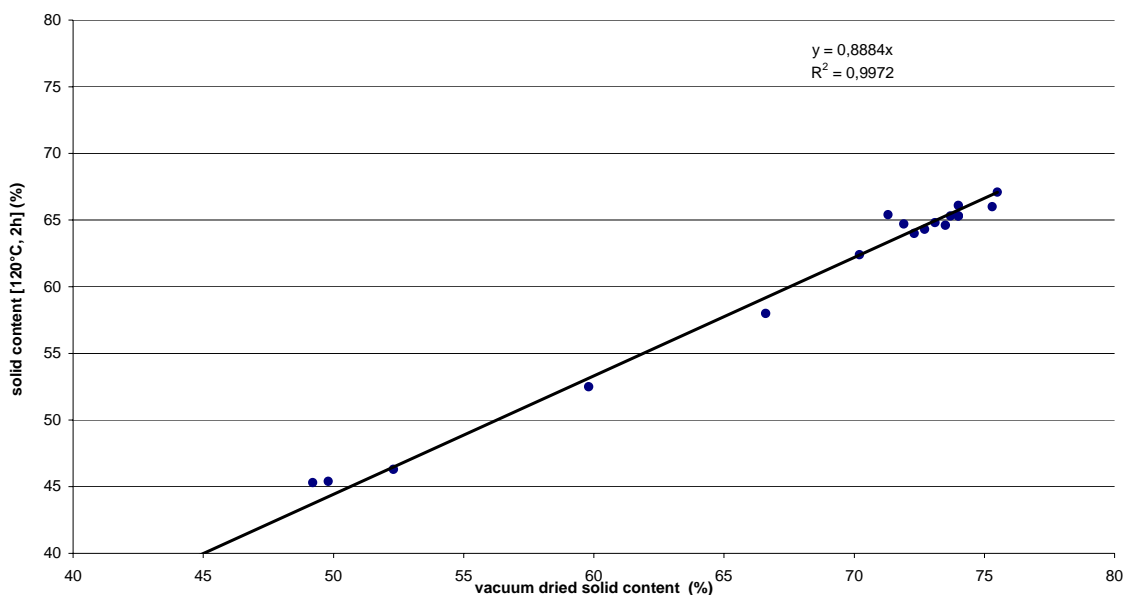


Fig. 3.1: Correlation of different drying methods

3.3.2 Density

The density (in g/m^3) of an adhesive is only determined if volumetric dosage is used during the gluing process. It can be measured according to DIN 51 757, ISO 2811 (pycnometer method) or ISO 3675 (hydrometer method). Due to the poor sensitivity the correlation between density, solid content and molar ratio is not clear. The dependency is influenced by other values and therefore has no practical value for the application of UF-resins (Marutzky and Ranta 1979).

3.3.3 Viscosity

The viscosity of an adhesive can be determined by a few methods (Zeppenfeld 1991). Very often a viscometer according to DIN 53018 (UF) or DIN ISO 9371 (PF) is used. The viscosity of an adhesive is influenced by other properties. Marutzky and Ranta (1979) found out that the average molecular weight, the molar ratio, the formaldehyde content, the methylol-group content and the grade of condensation have an influence on the viscosity of UF-resins. Newer results have shown that the viscosity is influenced by the colloidal behaviour of the resin, too (Pratt et al. 1985, Grunwald 1999). More information can be found in section 3.4.11.

The temporal increase of the viscosity is often checked to determine the stability and ageing of the adhesive. Voit et al. (1995) have examined the changes in the viscosity of urea-formaldehyde oligomers during gel formation under different conditions (oligomer content, resin content, curing agent and its content). They determined the activation energy and gel formation time of the process. More fundamental work of this study group (Malkin and Kulichikhin) can be found in section 3.4.10.

On the viscosity increase of PMDI during hardening is not much information available. Only the viscosity rise for two-component thermosetting polyurethane systems (MDI-polyol) has been studied in detail by Lipshitz and Macosko (1976), and Richter and Macosko (1980). They have shown that the viscosity rise is a function of molecular weight, which is in turn a function of extent of reaction given by branching theory.

3.3.4 pH-Value and Acidity (PMDI)

The pH-value of a liquid resin is determined according to DIN 53018 and has generally some significance for further processing. Due to the pH-dependence of the condensation process, especially reactive resins are influenced by pH-shifts (Marutzky and Ranta 1979). The influence of the pH and the type of catalyst on the chemistry of phenolic resins has been studied for many years. An actual review about the literature can be found by Gardziella et al. (1999). The pH-value of acid hardening UF-, MUF- and MUPF-resins is a characteristic value for the storage stability and the ageing behaviour of these systems (Dunky 1988).

The acidity of PMDI is checked in ppm HCl units. The storage stability of isocyanates can be raised due to acid additives. The low amount of hydrolysable chlorine from the phosgenation process, bonded to the isocyanate group, is used for stabilising. Higher amounts are hindering the polyurethane reaction and are therefore avoided. More information can be found at Schauerte et al (1983).

3.3.5 Curing Time and Gelation Time (formaldehyde based adhesives)

The gelation time describes the period between the dosage of the hardener (mostly NH_4Cl or $(\text{NH}_4)_2\text{SO}_4$) and the gel state. At low temperatures (20°C , 30°C) it is a characteristic value for the period of use. At higher temperatures (100°C , 130°C) the gelation time correlates roughly with the reactivity, the hardening behaviour and the press time. The operator needs experience to measure the gelation time. Not only the gelation time, but also the beginning and the end of the gelation process, the length of the gelation period and appearance and strength of the hardened resins provides information about the system. Despite this advantages the results received by different operators often differ slightly (Dunky 1997). An operator independent measurement of the gel time at a specific temperature is described in ISO 9396.

The curing time and behaviour of a formaldehyde-based resin represents an important processing parameter and provides information on whether a resin system cures rapidly or reacts according to a slower curing mechanism. The procedures described in ISO 8987 and ISO 9396 determine the reaction time that a phenolic resin requires for conversion to the "B stage" at a specific temperature

(Gardziella et al. 1999). More information about aminoplastic resins can be found at Dunky (1988) and about phenolic resins at Gardziella et al. (1999).

3.3.6 Alkali Content (PF-resins)

The alkali in phenolic resins is mainly composed of alkali hydroxide and alkali phenolate. Both are analysed together by titration with acids. Because of the high alkali content and as a result of the high pH-value (normally between 9 and 12) the phenolic resins are water-soluble. During the neutralisation with acids to analyse the alkali content especially bigger molecules are precipitated. The influence of the alkali content on the quality of wood based panels was studied very often. A review about this and several attempts to lower the alkali content in the resins can be found by Roffael et al. (1988). Pizzi and Stephanou (1994) studied curing behaviour and accelerators on PF-resins under very alkaline conditions.

3.3.7 Water Solubility and Water Miscibility (formaldehyde based resins)

To determine the water solubility of formaldehyde based resins 10 g of the glue is mixed with different amounts of distilled water. The water solubility is equal to the glue to water ratio where no sedimentation can be determined after 24 h. The water solubility is decreased by an increase of the grade of condensation of the resin, e.g. high condensated resins with cold gluing behaviour have always a lower water solubility. The amount of methylol groups has an influence on the water solubility, too. Polymethylene-ureas produced by condensation of urea and formaldehyde with a molar ratio of 1:1 are not soluble in water, but can be dispersed and analysed in a 4:6 water-glycerol mixture (Fomicheva et al. 1991). The reduced water solubility of UF-, MUF- and MUPF-resins has to be considered when the resin is diluted before the gluing process especially after a longer storage period which leads to a higher grade of condensation.

Questions and topics of R&D:

Research on correlations between colloidal behaviour and water solubility.

3.3.8 Ash Content (PF-resins)

The ash content of PF-resins is determined by carbonising between 2 and 3 grams of the glue in a glowing crucible and afterwards glowed at 800°C in a muffle oven. It can also be analysed according to ISO 3451-1,A or DIN 16945.

3.4 Advanced Properties of Adhesives and their Analysis

Most of the advanced properties of adhesives (3.4.1 to 3.4.4) are only checked in some laboratories of the woodworking industry with a few well-known methods. These properties and the characteristic values provide some insight on the performance and the quality of an adhesive. Typical performance questions are dealing with subjects like: Hydrolytic stability, fortification, emission potential and reactivity.

With the knowledge of the advanced properties it is much easier to compare different adhesives, but it is not possible to characterise the adhesive performance. The adhesives for wood based products are normally reactive mixtures of molecules with different size and structure. During the production process a highly cross-linked polymer is formed, that gives the wood based product its specific properties.

To get more information about important questions like bond strength, reactivity, curing speed, wetting, fluidity and colloidal behaviour it is necessary to use powerful analytical tools (section 3.4.5 to 3.4.11). More information about adhesive performance is expected to be given by these new techniques in the future.

3.4.1 Molar Ratio (formaldehyde based resins)

Different expressions are used to describe the molar ratio of an adhesive. Mostly terms like U:F, M:U:F and P:F can be found in literature. For aminoplastic resins sometimes ratios of F:NH₂ or F:(NH₂)₂ are preferred.

Dunky (1985) investigated UF-resins with different molar ratio for plywood. Reducing formaldehyde content yields a decrease of free and methylol formaldehyde, which is responsible for longer gelation times. Viscosity and density of adhesives with the same solid content decreases, too. Plywood bond strength is independent on molar ratio above 1:1,2, whereas below 1:1,2 a strong decrease occurs.

Low formaldehyde emission UF adhesives (E1) in the molar ratio range of 1:0,9 to 1:1,0 were synthesised by Pizzi et al. (1994). They presented a few main recipes, analysed the resins by ¹³C-NMR (see also 3.4.7) and produced laboratory (one layer) and industrial (three layer) boards.

Questions and topics of R&D:

Determination of molar ratios of unknown PF-, MUPF- and PUF-resins.

3.4.2 Free Monomer Content

The amount of free formaldehyde in UF-resins can be checked by a titrimetric method with sodium bisulfite. Above a molar ratio (U:F) of 1:1,6 the correlation between molar ratio and free formaldehyde content is very good. Below this molar ratio or below a free formaldehyde content of approx. 1% the correlation is not clearly visible (Marutzky and Ranta 1979, Dunky 1988).

The determination of residual phenol is done according to DIN ISO 8974 by gas chromatography. This procedure is only valid for novolak systems. Resols can not be investigated because some of the phenol is existing as phenolate and will not be eluted. The free formaldehyde in phenolic resins is analysed according to DIN ISO 9397. The amount of formaldehyde can be checked by a potentiometric titration after the reaction with hydroxylamine-HCl (DIN ISO 9397).

3.4.3 Melamine Content (MUF- resins)

The use of MUF-copolymers, MF/UF-blends or melamine in UF-resins makes desirable a rapid method for the detection and estimation of the melamine content of resin samples. A UV-

spectroscopic method is used which makes utility of the strong absorption of the melamine ion at 235 nm. The resin is hydrolysed to melamine by refluxing the sample in 0,1N hydrochloric acid.

Questions and topics of R&D:

Determination of melamine in MUPF-resins.

3.4.4 NCO-Content (PMDI)

The high reaction ability of isocyanates causes the necessity to control the isocyanate group content during manufacturing of MDI and storage. The NCO-content can be determined by IR-spectroscopy (Zharkov et al. 1987) or a spectrometric procedure (Latawlec 1991), but they are not widely distributed. The commonly used chemical methods of determination of isocyanate groups are based, as a rule, on the reaction of the isocyanate groups with excess of amines (e.g. DIN AGK 13). The adhesive is dissolved in a alcoholic solution of e.g. diethylamine. The excess of diethylamin is titrated by hydrochloric acid. Common indicators determine the endpoint. The NCO content can be calculated on the amount of diethylamine that has not reacted with hydrochloric acid.

According to Evtushenko et al. (2000) the nature of solvents and amines used is the main factor that influences the accuracy and precision of the results. Thus isocyanates are rather sensitive to impurity of water, tertiary amines catalyse cyclisation of isocyanates. It makes necessary to promote further investigations to develop analytical methods for determination of NCO-content in PMDI that are not complicated by concurrent reactions. Recently Evtushenko et al. (2000) published a method based on potentiometric titration of isocyanate groups in MDI.

The determination of the NCO-content in PMDI is necessary to check the adhesive quality, too. The average NCO-content in PMDI is between 30 and 35% per weight.

3.4.5 Molecular Weight and Molecular Weight Distribution

To understand the physical, mechanical and rheological properties of an adhesive, it is necessary to get a complete description of its molecular weight and molecular weight distribution. Both characteristic values are important during the preparation and application. The mechanical and bonding properties of an adhesive are strongly dependent on its molecular weight distribution (Dunky 1997). Molecular weight and molecular weight distribution of the adhesives can be established by GPC. The system calibration can be done with homemade oligomers, commercial grade polymers or low angle laser light scattering (LALLS).

Billiani et al. (1990) synthesised UF-resins with different degrees of condensation by different duration of the acidic condensation step. The adhesives were characterised in DMF by GPC with on-line LALLS. They found that the average molecular weight increases with longer condensation from several thousands up to more than 10^5 g/mol. Additionally UF-resins can contain fractions with molar masses up to $5 \cdot 10^5$ g/mol which are not only aggregates caused by physical intermolecular forces. Wellons and Gollob (1980) used an equal method to analyse PF-resins, but got some problems by using THF. Especially high molecular weight phenolics cannot fully dissolved in this solvent. Yazaki et al. (1994) got equal results by analysing PF-resins treated by an ion-exchange resin. Most researcher (e.g. Gobec et al. 1997) therefore modify THF by trichloroacetic-acid (TCAA) according to Riedl et al. (1988) and Bain and Wagner (1984). Alternatively DMF and /or DMSO and salts like LiCl or LiBr can be used to get rid of this problem. The influence of different production parameters (start molar ratio, time of methylation, time of condensation etc.) during UF-resins synthesis was investigated by this method (Grunwald 1996). Additionally it was found out that this solvent combination is able to dissolve all formaldehyde based adhesives (UF, MUF, MUPF, PF) and even PMDI after derivatisation and freeze-drying (Grunwald et al. 2000).

Different researchers (flakeboard: Stephens and Kutscha 1987; MDF: Park et al. (1998) presented results indicating that both low and high molecular weight components of PF-resins are needed to achieve optimum board properties.

Questions and topics of R&D:

- a) *Combination of GPC and NMR-techniques (online).*
- b) *Analysis of mixed and co-condensated adhesives (e.g. MUPF-, PUF-resins).*
- c) *Combination of different detection methods.*
- d) *Correlation of the molecular weight distribution with the adhesive performance.*

3.4.6 Analysis of Mono- and Oligomers

HPLC is widely used to analyse the monomer content or to characterise special oligomers and additives in adhesives. This method is very effective in establishing and identifying low molecular weight components in resins. Grenier-Loustalot et al (1994, 1996) used HPLC for the characterisation of PF-resins, although not especially focused on adhesives. They prepared different polymethylolated phenolic model compounds (monomeric and dimeric) and identified a great amount of components during the resol formation. For further identification they used ^1H -, ^{13}C -NMR and solid state ^{13}C -NMR (see also section 3.4.7) and described the results in a number of publications. Astarloa-Aierbe et al. (1998a, b, 1999) used the same techniques and studied the influence of several catalysts on the resol formation. The combination of HPLC separation, followed by ^1H - and ^{13}C -NMR was used by Mechin et al. (1984, 1986), too. The method allows the identification of compounds with up to five phenolic nuclei. For the examination of MUF-resins Nusselder et al. (1998) used HPLC. They identified both methylene and methylene-ether co-condensate linkages between melamine and urea. They were also able to differentiate between MUF-co-condensation and MF/UF-blends.

The isomeric ratios of MDI in isocyanates (PMDI) can be determined by HPLC (Schreyer et al. 1989) or ^1H -NMR (Grunwald 1999). Unfortunately the spectroscopic method is not valid if there is an overlap with the methylene signals from modified structures, as in case with diol- and polyol-modified isocyanates.

Questions and topics of R&D:

Combination of HPLC with GPC-techniques (Two-dimensional chromatography).

3.4.7 Structure and Structure Elements

The well-known infrared spectroscopy (FT-IR) is a very fast tool to distinguish between different kinds of adhesives without sophisticated sample preparation. The development in attenuated total reflection (ATR) and diffuse reflectance techniques have made the analysis of solid adhesives possible.

Urea-formaldehyde particles formed by acid-catalysed condensation were investigated by Schmolke et al. (1987) using infrared spectroscopy. Depending on the composition three different structures were found. At molar ratio (U:F) below 1:1,25 linear methylene ureas were obtained, at above 1:1,25 dimethylene ether linkages, and only when the reaction is carried out under strong acid conditions cyclic structures (urons) are formed. ^1H -NMR and IR measurements of model compounds and uncured UF polymers were combined by Myers (1981) with IR observations during polymer cure. The existing interpretation of UF polymer infrared spectra was clarified and a partial confirmation of the UF polymer cure mechanism obtained. However, it was concluded that conventional infrared possesses distinct limitations for defining the UF cure process in great detail.

The spectroscopic examinations are mostly done by ^1H -, ^{13}C - or solid state CP-MAS-NMR. The whole variety of structure elements like methylene bridges, methylol groups or amide groups can be determined, some of them even if the adhesive is already cured (solid state NMR). These methods for instance allow distinguishing between different MDI-isomers in PMDI as well

as between copolymers and blends in adhesives. The structures are responsible for the performance, suitability and efficiency of an adhesive.

A comparative evaluation of both ^1H - and ^{13}C -NMR techniques in the quantitative characterisation of UF-resins has been made by Taylor et al. (1982). Combination of NMR results with those obtained by classical methods gave reliable results. A quantitative ^{13}C -NMR study on UF-resins, at various stages in the synthesis and at various molar ratios revealed an improved descriptive chemistry of methylation and methylene bond-forming reactions (Kim and Amos 1990). The results also revealed the polymer molecular structure in more detail. Kim (1999) presented more results and studied different three step syntheses. For typical resin syntheses at start molar ratio (U:F) of 1:2,1, the resulting polymer was found to be a number-averaged pentamer having 3,25 polymer chain branches with about 80% of chain ends bonded to hydroxymethyl groups and the rest being free amide groups.

The effects of pH control (see section 3.3.4) of the condensation step on the properties of UF-resins have been studied by ^{13}C -NMR (Szesztay et al 1993). They supervised the conditions of the preparation with the aim to reduce formaldehyde emissions by influencing the ratio of methylene/dimethylene-ether bridge linkages in the product. A method based on the use of ^{13}C -NMR relative peak intensity ratios for different characteristic chemical groups supposed to contribute to UF-resins strength, formaldehyde emission and percent crystallinity in the resin-hardened state was presented by Ferg et al. (1993) A rough correlation of different peak ratios with experimental results allows the proposal of equations relating the sum of different peak ratios with the three mentioned physical properties, but only for resins which are synthesised in exactly the same manner (only difference: molar ratio). A comparison between different resin formulations is not possible.

First results about investigations on uron formation with ^{13}C -NMR in UF-resins have been published by Gu et al. (1995, 1996) and Hse et al. (1994), who additionally suggested a weak acid catalysts system (pH 4) to formulate UF-resins with improved bond strength and formaldehyde emission data. Soulard et al. (1998, 1999) compared uron- and uron-urea-formaldehyde resin with conventional UF-resins at molar ratios (U:F) between 1:2 and 1:1,2. They combined TMA (see 3.4.9), ^{13}C - and CP-MAS- ^{13}C -NMR techniques.

The first fundamental work about ^1H -NMR studies on the structure of PF-resins was presented by Woodbrey et al. (1965). They investigated different resols and novolacs. By mathematical transformation they calculated relative numbers of methylene-bridges, relative numbers of methylol-bridges, grade of condensation and the number-average molecular weight. The influence of different types of catalysts and molar ratios on the chemical structure and the cure characteristics were determined by King et al. (1974) with combination of ^1H -NMR, GPC and DSC techniques.

PF-resins that had experienced a variety of reaction conditions and/or ageing conditions were quantitatively characterized by ^{13}C -NMR (Werstler 1985). Ageing PF-resins for 60 days at 33°C resulted in extensive condensation and a drastic reduction in para-substituted methylol and hemiformal groups. The formation and curing reactions of PF-resols were analysed by So and Rudin (1990). The chemical compositions and molecular size distribution of a series of soluble resole phenolics was studied by ^{13}C -NMR, IR, GPC and viscosity techniques. The curing reactions were then followed by IR and solid-state ^{13}C -NMR techniques. The degree of cure achieved under given conditions is directly proportional to the molecular weight of the precursor resole. The condensation catalyst ($\text{Ba}(\text{OH})_2$, NaOH or Na_2CO_3) has a great influence on resole composition and molecular size. The curing pH affects the degree of cure as well as the type of linkages formed.

A method based on the use of ^{13}C -NMR relative peak intensity ratios for different characteristic chemical groups supposed to contribute to PF-resins strength and formaldehyde emission was presented by Panamgama and Pizzi (1995). A rough correlation of different peak ratios with experimental results allows the proposal of equations relating the sum of different peak ratios with the two mentioned physical properties, but only for resins that are synthesised in exactly the same manner (only difference: molar ratio). A comparison between different resin formulations is not possible.

Pizzi and Tekely (1996) have investigated the hardening mechanism of fast-reacting phenolic wood adhesives (resorcinol or resorcinol-formaldehyde resin (RF-resin)) by the use of hexamethylene-tetramine. These resins react with hexamethylene-tetramine under formation of benzylamine and methylene bridges to form hardened resins.

MUPF-resins for plywood were synthesised and analysed by Cremonini et al. (1996). They detected copolymerised networks by ^{13}C -NMR and correlated the results of the tensile strength of plywood prepared with the resins.

Pizzi et al. (1993) investigated the linear extension of PF-resins by small amounts of urea. They used IR, GPC (see 3.4.5) and ^{13}C -NMR. The resulting resins showed faster gel times and increased viscosity. In a further work Zhao et al. (1999) produced PUF-resins by copolymerisation of low-condensation resols with urea. The relevant peaks were checked by ^{13}C -NMR. Additionally they used an ester accelerator (glycerol triacetate) and investigated the performance by TMA (see section 3.4.9) and by preparation of wood particleboard.

The stability of UF-resins after hydrolytic treatment was investigated by ^{13}C -CP-MAS-NMR (Chuang and Maciel 1994). UF-resins prepared from starting mixtures with a molar ratio (U:F) of 1:1,0 show a high degree of stability toward hydrolysis. Cross-linking methylene linkages in the UF-resins show a higher susceptibility to hydrolytic treatments (pH 4, 86°C) than do linear methylene linkages. Additionally they found out that dimethylene ether linkages, methylols attached to tertiary amides and polyoxymethylene moieties are probably the main formaldehyde emitters.

As a very powerful method „Matrix assisted laser desorption/ionisation time of flight mass spectroscopy“ (MALDI-TOF-MS) is used to analyse adhesives with respect to the degree of polymerisation and the type and number of functional groups.

Pasch et al. (1996) published first results of MALDI-TOF-MS of phenolic resols and novolacs.

They investigated the degree of polymerisation and the type and number of functional groups up to molar masses of 1200 g/mol.

Questions and topics of R&D:

- a) Examination of industrial produced adhesives.
- b) Performance of different produced adhesives.
- c) Examination of mixed and co-condensated adhesives.

3.4.8 Thermal Behaviour

The thermal transformation of an adhesive during the curing reaction can be monitored by differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Both techniques determine either the heat evolution or absorption for any reactions that are occurring in a sample. The appearance time of an exothermic or endothermic reaction, the peak shape, the location of the peak maxima, the peak width and the slope of the diagram are characteristic parameters of this test method.

An early work of Chow and Steiner (1975) dealt with the exothermic reaction of UF-resins at temperatures less than 90°C in the presence of NH_4Cl catalyst studied by DTA. Supported by IR, thermogravimetric data and softening temperature, the exothermic peak was concluded to be associated with resin cure. This was further substantiated by bond quality of plywood made with this UF-resins pressed above and below the exothermic peak. The reactions of urea with formaldehyde were studied by means of ^{13}C -NMR (see section 3.4.7) and DSC (Sebenik et al. 1982). The activation energy, heat of polymerisation, reaction order and temperature maximum for the addition of formaldehyde to urea and for the subsequent condensation have been determined.

Holopainen et al. (1997) investigated a number of PF-resins by combination of GPC, ^{13}C -NMR and DSC. As the F:P molar ratio increases, the shapes of the DSC signals change from overlapping signals to separate ones. Additionally the temperature of the first one, which is caused by the condensation of methylol groups with phenol to form methylene bridges, and by the condensation of two methylol groups to form dibenzyl ether bridges, decreases slightly. The second exothermic

signal, representing the further reaction of the resin, e.g. the condensation of the dibenzyl ether bridges to methylene bridges eliminating formaldehyde, shifts to the higher temperature range.

Park et al. (1999) studied PF resol resins modified with three different carbonates (i.e. propylene carbonate, sodium carbonate and potassium carbonate) by DSC using a multi-heating method. By this method they obtained the activation energy and pre-exponential factor of the resins. These two parameters were used to calculate the rate constant for modified PF-resins. The results obtained in the experiments indicate that all carbonates used can accelerate the cure of PF-resins and could reduce the pressing time for panel manufacture. Among the three carbonates, sodium carbonate produced a consistent and controllable cure acceleration effect.

Questions and topics of R&D:

Correlation of the thermal behaviour with the hardening process under real conditions.

3.4.9 Mechanical Analysis and Bond Strength Development

The dynamic mechanic analysis (DMA), the thermo-mechanical analysis (TMA) and especially the automated bonding evaluation system (A.B.E.S., Humphrey 1999) enables the characterisation of the strength development characteristics of an adhesive. The DMA-type instruments are particularly useful in defining many mechanical factors related to cure, flow and flexibility of adhesives over a range of temperature. The instrument's descriptive data is relevant to many types of adhesives (Sellers and Haupt 1994). The ABES characterises the effect of temperature on the strength development rate of thermosets to be analysed at temperatures ranging from ambient to 200°C. It can be used to evaluate and compare the bonding characteristics of adhesives and to explore the effects of a wide-range of parameters such as compression pressure, spread rate, surface modification and precuring.

Umemura et al. studied (1996) the mechanical curing process of UF-resins treated under several conditions using DMA. They found that the curing process of liquid UF-resins with catalyst proceeds through a two-stage curing process with increasing oven temperature. Under hot-platen heating the curing of a preheated resin proceeds with increasing heating time. Additionally they found that UF-resins immediately cured to some degree, and then dilution and/or decomposition took place under steam-injection heating.

Phenolic resins heated by hot-platen and steam injection were analysed by Umemura et al. (1995) using techniques such as FT-IR, solid state-¹³C -NMR, solvent extraction and DMA. In the resin heated by steam injection, free water hindered the curing reaction, and by-products were contained. The curing reaction of the resin was somewhat delayed compared to that heated under conventional hot-platen heating.

The durability of PMDI adhesives for wood and the thermal properties when cured with water (1998) or several polyols (1999) were investigated by Umemura et al. The DMA results showed that EMDI (aqueous emulsion-type PMDI) cured only with water exhibited lower thermal properties than those of the cured PF-resins. Heat treatment at high temperatures was not very effective for improving the heat resistance. By adding small amounts of polyether polyols to EMDI the results are dependent on the type of polyol and its molecular weight.

Adcock et al. (1999) investigated UF-PMDI mixed adhesives and their possible use for straw based particleboard by DMA. They found two distinct cure regions in the tan δ spectra of samples bonded with UF-PMDI blends suggesting that separate cure occurs for the two adhesive-types. Copolymerisation of a UF-PMDI mixture, although theoretically possible, does not appear in practice to be the preferred reaction.

Non-isothermal and isothermal TMA of the cross-linking and hardening of wood joints bonded with UF-, MUF- and MUPF-resins were carried out by Yin et al. (1995). The method allows the determination of the variation of physical properties of these thermosetting adhesives in situ in the wood joint. Gelling, hardening and vitrification temperature and temperature at which relative elastic moduli reach their maximum were also determined for wood joints obtained by the

investigated resins. The increase in the mechanic durability of the wood joint during hardening was correlated with the cross-linking ratio.

The influence of lignocellulosic substrates on TTT and CHT curing diagrams of UF- and PF-resins was investigated by Pizzi et al (1999b). The chemical and physical mechanisms of the interactions of the resin and substrate causing such CHT diagram modifications are presented and discussed. The Di Benedetto equation (Nielsen 1969, Pascault and Williams 1990) has been slightly modified to take into account the modified CHT diagram. The modified CHT diagram can be used to describe the behaviour of polycondensation resins when used as wood adhesives during their curing directly into the wood joint. In a recent work Pizzi (1999a) combined older liquid and solid ^{13}C -NMR results of UF and PF-resins and internal bond strength of particle board produced with those adhesives with TMA results. The established mathematical relationships allow the calculation of various parameters of the techniques, if the systems are used under well-defined conditions.

First results on UF-resins with equal solid content and molar ratio but different reactivities checked on the A.B.E.S. were presented by Dunky (1999).

Questions and topics of R&D:

- a) *Research on correlations between applied bond test (e.g. A.B.E.S) with NMR-results especially of industrial produced resins.*
- b) *Correlation of bond strength development with the hardening behaviour under real conditions.*

3.4.10 Rheology

By a rheological examination not only the viscosity of an adhesive is measured: In special experiments the viscoelastic properties (storage modulus G' , loss modulus G''), which are very sensitive to molecular parameters, can be analysed. Kulichikhin et al. (1996) studied the rheokinetics of gelation of aqueous UF-oligomer suspensions. They showed that a maximum on a viscosity versus time curve is observed and it reflects sedimentation of rather large gelled particles. After that the gelation of the whole systems takes place. Experiments at different temperatures gave the apparent activation energy, which depends on the oligomer content. Malkin et al. (1989) presented equal results on MF-resins.

Questions and topics of R&D:

Combination of rheological examinations with analytical tools of structure elements of adhesives.

3.4.11 Colloidal Behaviour

Unique characteristics of UF-resin behaviour observed during preparation, storage and cure are difficult to explain by conventional mechanism of polycondensation. Pratt et al. (1985) interpreted these abnormalities more logically by analogy with established colloidal behaviour. Additional support for their coalesced dispersion theory is provided by:

- The known discontinuity in the viscosity of UF-resins during cure
- The observed requirement of a minimum threshold concentration of UF-resin necessary for gelation to occur
- The scanning electron micrographs (SEM) of fracture of cured UF-resins which exhibit distinct features that are characteristic of a coalesced sol structure.

The ultracentrifuge generates an increased gravitational field to fractionate especially colloids (e.g. UF-, MUF-resins). The fractions can be examined by other polymer-analytical methods to get more information about the colloidal behaviour of the system. Grunwald (1999) combined fractionation by ultracentrifuge with GPC and ^1H -NMR to explain differences between physical and chemical properties.

Questions and topics of R&D:

Research on new fractionation methods for colloids (e.g. FFF-flow field fractionation).

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4 Bonding Process

M. Scheickl, M. Wålinder, F. Pichelin, M. Dunky

4.1 Theory of Bonding

4.1.1 Introduction

M. Scheickl and M. Wålinder

To achieve optimised performance demands on adhesives, like easy universal application possibilities and environmental compatibility, requires ongoing modification of existing glues and the development of new adhesives.

In all bonding processes many controllable and uncontrollable factors exist, which may affect the quality of the adhesive bond directly or indirectly. Looking to the bonding process, two specific areas are of interest: bond formation and bonding performance. Bond formation involves the properties of the liquid adhesives and their conversion into solids. Bond performance deals with the properties of the adhesives in the hardened glue line and their behaviour when stresses and chemical degradation might occur.

Both, bond formation and bonding performance do not act independently, but interact since quality of bond formation determines bonding performance.

It is sometimes desirable to visualise a third parameter, product performance, in recognition of the possibility that performance of the final glued product may differ from that characterised by the quality of the bond itself. In other words, it is possible that even the bond may perform satisfactorily; the product might not fulfil the requirements (e.g. warping of panels or dimensional changes like thickness swelling). Therefore gluing wood is a joining process, which should aim for best product performance.

In his equation of performance Marra (1992) gives a survey which parameter affect the glued product performance. Here the bonding process is visualised as a sequence of events, where factors can be identified grouping themselves into different operations. Each group can be regarded as representing a distinct area of activity, all contributing accumulatively to the ultimate bond performance.

According to Marra (1992) the glued product performance results from the sum of the following seven groups:

- 1) Potential adhesion forces
- 2) Adhesive composition factors (see also chapter 1 and 6)
- 3) Wood property factors (see also chapter 1)
- 4) Wood preparation factors (see also chapter 1)
- 5) Adhesive application factors
- 6) Wood geometry factors
- 7) Product service factors

Topics 2-5 in the equation affect bond formation; topic 7 affects bond performance. Topic 6 affects both ends of the process i.e. bond formation and bonding performance.

According to Habenicht (1986) the final strength of a glue-bond results from the strength of the parts to be joined, the strength of the glue line itself and the strength of the boundary layer between glue line and joined parts.

Marra (1992) compares the anatomy of an adhesive bond with a chain, whereby the weakest link determines the quality of the bonding process. The chain consists of the following links: the

adhered itself, the adherend subsurface, the adhesive –adherend interface, the intra adhesive boundary layer and the adhesive film.

Different adhesion theories do exist. They all have in common to find an explanation for the mechanism of adhesion. The term adhesion may be defined as the attraction between one material and another (Marra 1992). Similarly, Kinloch (1987) defines adhesion simply as the attraction between substances. Schultz and Nardin (1999) pointed out, however, that the term adhesion is ambiguous and covers a variety of concepts and ideas. In fact, adhesion could represent both the formation of interfacial bonds and the mechanical load required to break an assembly. Further, the term cohesion is defined as the attraction that exists within a material. It is important to note that ideal adhesives should have a high capacity to achieve both adhesion and cohesion.

Knowledge about fundamental adhesion mechanisms involved in various wood composites or in the gluing and coating of wood is important. Such information is essential in the development of efficient processing methods, and for the prediction of the durability and in-service performance of especially wood based composites and glued or coated wood products.

Six main mechanisms of adhesion may be recognized (Kinloch 1987; Schultz and Nardin 1999): 1) wetting (also referred to as adsorption); 2) mechanical interlocking; 3) diffusion; 4) electrostatic forces; 5) weak boundary layers and interphases; and 6) chemical bonding.

It has been generally accepted that each of these approaches may be appropriate and valid to some extent in certain circumstances and to a particular class of adhesives (Schultz and Nardin 1999; Kinloch 1987; Pizzi 1992). Therefore, they may all contribute to the intrinsic adhesion forces, which act across the interface between the adhesive and adherend, and their respective importance depends strongly on the system chosen. The wetting theory is, however, certainly the most widely used approach in adhesion science at present (Pizzi 1992; Schultz and Nardin 1999).

The following sections will briefly review the adhesion approaches based on wetting, mechanical interlocking, weak boundary layers, and chemical bonding. Reviews about the diffusion and electrostatic adhesion theories can be found in e.g. Schultz and Nardin (1999) and Kinloch (1987).

4.1.2 Wetting

M. Wålinder and M. Scheikl

Introduction (M.Wålinder)

The term “wetting” may be defined as “macroscopic manifestations of molecular interaction between liquids and solids in direct contact at the interface between them” (Berg 1993a). Such manifestations involve 1) the formation of a contact angle θ at the solid/liquid/gaseous interline, 2) the spreading of a liquid over a solid surface, and 3) the wicking of a liquid into a porous solid. However, in this definition, wetting does not include dissolution or swelling of the solid by the liquid or any kind of chemical reaction between the materials that changes the system composition.

Wetting phenomena may be characterized by using thermodynamic wetting parameters, for example contact angles, surface free energy, and work of adhesion. It is important to remember that such parameters are by definition bulk measurements, and they do not directly describe the interaction at a molecular level (Berg 1993a).

A deeper understanding of the wetting phenomena must be traced to the origin and nature of intermolecular forces. Overviews of fundamental theories and basic knowledge about intermolecular forces and wetting phenomena can be found in e.g. Jensen (1991), Lee (1991), Mittal and Anderson (1991), Mittal (1993), van Oss (1994), Good (1993) and Berg (1993a).

Perhaps the most convenient way of interpreting the wettability of a low-energy surface, such as that of various polymer or ligno-cellulosic materials, is by the formulation of the work of adhesion, W_a , defined as the work required to separate unit area of the solid-liquid interface.

a) Lewis acid-base concept (M.Wälinder)

Intermolecular forces may be divided into physical and chemical related forces. Recently, it has been proposed that the former can collectively be referred to as "van der Waals" (LW) forces, and, in case of wetting-related phenomena, the latter can mainly be considered as acid-base (AB) interactions (Fowkes 1983; van Oss et al. 1987; Berg 1993a). This approach is here referred to as the Lewis acid-base concept in wetting-related phenomena (see also Jensen 1991; Good 1993; Berg 1993a; van Oss 1994; Chehimi 1999). In such acid-base interactions, an electron pair is donated by the base (electron-donor) and is shared with the acid (electron-acceptor), together forming an "adduct". According to Fowkes (1983) and van Oss et al. (1987), the total work of adhesion in interfacial interaction between solids and liquids can be expressed as the sum of the LW and the AB interactions.

To obtain a durable wood-adhesive bond, especially when exposed to moisture variations, an acid-base interaction between wood and adhesive, equal to the interaction between wood and water should be achieved. A large amount of literature has recently been devoted both to fundamentals and to the practical aspects of the Lewis acid-base concept at solid-liquid interfaces (see e.g. Mittal and Andersen 1991; Berg 1993a; Good 1993; Lee 1993; van Oss 1994; Della Volpe and Siboni 1997; Dwight 1999; Chehimi 1999).

Recently, the Lewis acid-base concept and the determination of so-called acid and base surface free energy components, as described by Good (1993) and van Oss (1994), has been debated and evaluated in many studies (e.g. Berg 1993b; Della Volpe and Siboni 1997; Douillard 1997; Janczuk et al. 1996; Kwok et al. 1994 and 1998; Lee 1993 and 1996; Qin and Chang 1995; Wu et al. 1995). For example, Kwok et al. (1994) and (1998) advocated the use of the 'equation of state' for the determination of the solid surface free energy, and rejected the acid-base approach on the basis of experimental findings. On the other hand, Wu et al. (1995) advocated acid-base approach and rejected the 'equation of state' on the basis of experiments, which included polar surfaces, in contrast to the experiments by Kwok, and co-workers, which included only non polar surfaces.

Della Volpe and Siboni (1997) proposed a modified calculation procedure in order to enable more reliable Lewis acid-base analyses of liquids and solids. However, they also suggested that better data on advancing and receding contact angles at fixed temperatures on well-defined surfaces and with controlled purity are necessary. Lee (1996) also suggested some modified data of liquid parameters used in the acid-base analyses.

b) Contact angle measurements (M.Wälinder)

It is of great importance to find and develop methods for measuring and evaluating the strength and role of intermolecular forces in wetting phenomena. In this situation, contact angle measurements of well-defined probe liquids on the surface of interest are in most cases the basis for estimations of wetting properties of the material. Neumann and Good (1979) reviewed the classical techniques for measuring contact angles (see also Adamson and Gast 1997). The most widely used technique, also regarding wood, involves direct measurement of the angle from the profile of a drop deposited on a horizontal or inclined surface, referred to here as the drop method. Similar techniques involve digital image analysis of the dimensions of a drop profile on a surface from which the contact angle can be calculated. Other techniques are e.g. the Wilhelmy method (see e.g. Johnson and Dettre 1969 and 1993; Andrade et al. 1985), capillary rise on a vertical plate (see e.g. Neumann and Good 1979), and column or thin layer wicking (see e.g. van Oss 1992).

Some important causes of contact angle hysteresis are 1) surface roughness; 2) surface heterogeneity; 3) reorientation of molecules and functional groups; 4) penetration, adsorption and swelling (Andrade et al. 1985; Good 1993).

Apart from contact angle measurements, e.g. inverse gas chromatography (IGC) (see e.g. Lloyd et al. 1989), Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS, also referred to as ESCA), and microcalorimetry are available techniques for assessing, for instance, a material's wetting properties, surface energetics, surface

composition, and acid-base properties (Chehimi 1999). In addition, interfacial force microscopy (IFM), atomic force or scanning tunnelling microscopy (AFM and STM) may enable adhesion forces on the molecular scale to be measured (Chehimi 1999).

c) Wetting studies on wood (M.Wålinder)

It is important to bear in mind that wetting parameters, e.g. contact angles, measured on any wood surface are indeed phenomenological parameters, influenced by e.g. surface roughness and heterogeneity, and do not exclusively represent surface thermodynamics. In this case, it is preferable to use the expression apparent wetting parameters, e.g. apparent contact angle instead of the contact angle, which is strictly defined for perfectly smooth and homogeneous surfaces.

Historically, wood wettability has been determined by direct optical measurement of static and equilibrium contact angles or time-dependent contact angles caused by liquid absorption. The drop method has been widely used on wood (Gray 1962; Herczeg 1965; Jordan and Wellons 1977; Nguyen and Johns 1979; Liptáková and Kúdela 1994). However, precise direct optical measurement of contact angles to determine the surface thermodynamic characteristics is inherently difficult with wood because of its chemical heterogeneity, surface roughness, porosity, and hygroscopic nature (see e.g. discussion by Marian and Stumbo 1962).

According to the classical Washburn equation, see e.g. van Oss (1992), if a liquid contacts a porous media such as wood, and the contact angle formed on the material is less than 90° , then spontaneous wicking (penetration) of the liquid into the porous medium will occur. Similarly, a surface structure, e.g. like tracks in a gramophone record, may also result in capillary forces, causing wicking of the liquid along the surface (see e.g. Gerdes 1998). All wood surfaces have a pronounced surface roughness. This surface structure mainly originates from the intrinsic wood cell structure. In addition, the processing of wood by different machining operations generally results in an irregular surface structure of damaged and raised wood cells. Accordingly, when a liquid contacts a 'technical' wood surface, the intrinsic wood surface structure combined with the irregular surface structure resulting from different machining processes may cause liquid transport along the surface by capillary forces. Wålinder (2000) has studied spontaneous wicking that occurs during wetting measurements on wood. Due to such wicking effects and to the hygroscopic nature of wood, it is often not possible to achieve a wetting equilibrium or static contact angle until the wood is saturated with the liquid.

Extractives play a central role in wetting analyses of wood (Gardner et al. 1995). As mentioned above, extractives are stored in the resin channels under pressure and after e.g. machining operations on sawn and dried timber, some extractives presumably migrate to the exterior surfaces. Extractives probably also diffuse to 'newly' created wood surfaces which may be considered as a natural surface inactivation process to lower their energetic state (see also Back 1991; Nussbaum 1996 and 1999). In wetting studies on wood, it was demonstrated (Wålinder 2000) that there is a risk for severe contamination of used probe liquids by the wood extractives. Such contamination will in some cases distinctly decrease the surface tension of the probe liquids, which certainly complicates the wetting analysis.

Zavarin (1984) pointed out that the chemical composition of a machined wood surface is significantly different from that of the bulk of the wood (see also Jaic et al. 1996; Liptakova et al. 1995), and that wood surfaces in general are covered with polar and non-polar extractives. He also stated that the conditions and methods of wood surface formation could strongly influence its chemical composition. For instance, if the easily movable extractives are excluded, cross sections have a chemical composition similar to that of the bulk wood, whereas tangential and radial sections deviate significantly, presumably due to more exposed middle lamella with their high content of lignin (Zavarin 1984).

A large amount of literature (see e.g. Gray 1962; Chen 1970; Nguyen and Johns 1979; Hse and Kuo 1988; Christiansen 1994; Gardner et al. 1995; Nussbaum 1999; Wålinder 2000) has dealt with the influence of e.g. aging, drying and extractives on wood wettability and gluability. From these studies, it is clear that significant changes in the wood surface wettability and gluability occur due

to aging, and due to the presence and migration of extractives. Gardner et al. (1995) suggested that preferential molecular reorientation of the extractives will occur depending on the surrounding environmental conditions. Chen (1970) showed that solvent-extraction of wood surfaces improved their wettability.

Christiansen (1994) summarized the mechanisms for changes of wood surfaces that may influence the physical and bonding properties of wood: 1) migration of hydrophobic extractives during drying 2); oxidation 3); molecular reorientation of functional groups in the surface; 4) acidity or reactivity of extractives affecting the curing time of adhesives; 5) closure of micro-voids in the wood substance which reduces adhesive penetration. Hse and Kuo (1988) also concluded that oxidation of extractives tends to increase the acidity of wood.

Recently, Nylund et al. (1998) investigated the surface free energy and wettability of various wood resins in spruce. They found that wood resins were rather hydrophobic, although extensive acid-base interactions with surrounding media were observed. It was suggested that an orientation of the carboxyl groups of the resin acids and fatty acids occurred towards an aqueous phase which enables hydrogen bonds to be formed at the surface.

One way to address some of the difficulties in wood wetting measurements may be to apply the Wilhelmy method (Wilhelmy 1863). In contrast to direct measurement of contact angles, as in the drop method, the Wilhelmy method involves determining the force acting on a specimen when it is immersed in and withdrawn from a liquid. An apparent contact angle can then be estimated from an analysis of the recorded force (Johnsson and Dettre 1993; Vogler 1993; Kistler 1993). The Wilhelmy technique has been applied for determining the wettability properties of wood pulp fibres (Young 1976; Klungness 1981; Hodgson and Berg 1988; Berg 1993b; Deng and Abazeri 1998), and it has also been applied in wetting analyses of solid wood by e.g. Cassilla et al. (1981), Gardner et al. (1991), Mantanis and Young (1997), Shen et al. (1998a), and Wålinder (2000).

Other promising techniques for measurements of apparent contact angles on wood may be the Axisymmetric Drop Shape Analysis-contact diameter (ADSA-CD) technique (Kazayawoko et al. 1997) and a similar technique suggested by Scheikl and Dunky (1998); contact angle measurements determined as constant wetting rate angle values (cwra) presented by Nussbaum (1999); and also a capillary rise technique (column wicking) applied to wood particles by Gardner et al. (1999) and Wålinder and Gardner (1999a).

Inverse gas chromatography (IGC) is a useful technique for determining surface energetics of particle surfaces (Lloyd et al. 1989). By using appropriate gas probes, IGC can provide information on the surface thermodynamic characteristics of particles including surface free energy, acid-base interactions, enthalpy, and entropy. IGC has been applied to many materials such as polymers (see e.g. Lloyd et al. 1989), wood pulp fibres (see e.g. Kamdem and Riedle 1992; Jacob and Berg 1994; Shi et al. 1997), and wood particles (see e.g. Kamdem et al. 1993; Tshabalala 1997; Gardner et al. 1999; Wålinder and Gardner 1999b).

Based on contact angle analysis and IGC, the Lewis acid-base approach has been applied on wood fibres and cellulose (e.g. Berg 1993b; Jacob and Berg 1994; Dourado et al. 1998; Shen et al. 1999), and on solid wood and wood particles (e.g. Kamdem et al. 1993; Gardner 1996; Mantanis and Young 1997; Tshabalala 1997; Shen et al. 1998a; Gardner et al. 1999). Generally, the results from the contact angle analysis in these studies of both wood and wood fibres show that the surface character of these materials is predominantly Lewis basic. On the other hand, results from IGC show that the corresponding surfaces are pronouncedly bifunctional or predominantly Lewis acidic. Shen et al. (1998b) suggested that the acid-base characterization of wood surfaces by wetting methods corresponds to the outermost surface, whereas the characterization by some spectroscopic methods (XPS and FT-Raman) relates to the sub-surface region. They also showed that the sub-surface region of pinewood might exhibit lower basicity than the outermost surface.

When techniques and methods successfully applied to other materials are applied on wood, it is important to pay attention to its complex nature and how this may influence the wetting

measurements. This knowledge may make it possible to detect and control such influences, and to develop new and more suitable measurement techniques for 'reliable' wetting studies of wood.

d) Surface energetics of glue resins, solid wood and wood based panels (M. Scheikl)

The composition of the liquid glue resin itself has an influence on its surface tension and its penetration behaviour into wood. Therefore also the choice of the glue resin system influences the appearing contact angle and the whole wetting and bonding process.

Several authors have carried out some work for thermodynamic characterization of glues with concentration on UF- and PF-resin systems (Scheikl and Dunky 1996; Scheikl et al. 1995; Elbez 1985; Elbez 1978; White 1977; Hse 1972; Freeman and Wangaard 1960).

Herczeg (1965) measured some bond strengths with UF-glues of differing surface tension. Good bond strength was achieved with those resins, where the surface tension of the resin was close to the critical surface tension of the wood.

Surface tension or free surface energy of solid wood was determined by Scheikl and Dunky (1998), Liptakova and Kudela (1994) and Gray (1962). Physical and chemical properties of the wood surface have an influence on the contact angles of liquids and the resulting bond strength (see also chapter 5). The surface roughness (Hameed and Roffael 1999; Bogner 1991; Hse 1972; Gray 1962), the wood moisture content (Rozumek and Elbez 1985; Elbez 1985; Wellons 1980), the grain angle (Suchsland 1957), the age of the wood surface (Kalnins and Katzenberger 1987; Nguyen and Johns 1979; Herczeg 1965), the pH value of the wood surface (Popper 1978; Kehr and Schilling 1965; Plath 1953) and the amount and type of extractives (Roffael and Rauch 1974; Chen 1970; Narayanamurti 1957) are the most important factors of influence.

It is possible to improve or deteriorate the wettability by chemical modification of the wood surface. Changing it to a hydrophilic surface will result in lower contact angles with better wettability, changing the wood surface into a hydrophobic one will result in increasing contact angles with lower wettability (Pecina and Paprzycki 1990).

First attempts to characterize also the surface energy of wood based panels were made by Wulf et al. (1997) and (Scheikl and Dunky 1996). Due to the great variety of panel more data concerning surface energies are required for final evaluation.

For the nowadays most common used glue resins in the European woodworking industry (UF-, PF-, MUF-, MUPF- and isocyanate adhesives) still a lack of information concerning the surface thermodynamic data exists.

Questions and topics for R&D:

- a) *Comparative thermodynamic characterization of UF-, PF-, MUF-, MUPF-, and isocyanate adhesives*
 - *measurement of resin surface tension and its polar and disperse fraction*
 - *contact angle measurements on wood and wood-based panels*
- b) *Are there special thermodynamical differences between formaldehyde based and isocyanate based adhesives?*
- c) *Is it possible to change the thermodynamic behaviour of adhesives in order to optimise the wetting process for practical needs?*
- d) *Thermodynamic characterization of wood-based panels (especially particleboard , MDF and OSB) produced with different glue-systems.*
- e) *Optimisation of the wetting process; development of new techniques to improve wettability of wood based panels (important for new coating technologies like powder coating of MDF-panels)*
- f) *Is it possible to predict bond strength by determination the surface energetic parameter of the glue-system and/or the parts to be joined ?*
Is there a correlation between e.g. the contact angle of the adhesive on the surface to be glued and the resulting bond strength?

4.1.3 Mechanical Interlocking

M. Wålinder

This mechanism involves mechanical interlocking of the adhesive into the irregularities of the adherend (Kinloch 1987; Schultz and Nardin 1999) and was proposed by McBain and Hopkins (1925). Among others, this approach has been reviewed recently by Davis (1991), Critchlow and Brewis (1995) and Packham (1998). McBain and Hopkins stated that mechanical interlocking was only possible with porous materials, for example adhesion to wood, in contrast to materials with surfaces which are merely rough (Packham 1998). In addition, the pore shape is of great importance for the magnitude of the mechanical keying (Schultz and Nardin 1999).

Since good adhesion is attained even for perfectly smooth surfaces, mechanical interlocking cannot be considered as universal and probably do not operate on its own. It may therefore be difficult to conclude if an increase in the surface roughness that increases the measured strength of an adhesive joint arise from a contribution from mechanical interlocking or from other causes, e.g. wetting factors (Kinloch 1987). In addition, some roughened surfaces, like grit-blasted metallic substrates, reveal little indication of cavities like ‘inc-bottle’ pits, which could cause mechanical interlocking.

Packham (1998) further states that the mechanical interlocking now is generally an accepted mechanism of adhesion. Because of the porous nature wood and its pronounced surface roughness, it is obvious that mechanical interlocking plays a significant role in adhesion. Bogner (1991) recently demonstrated a good correlation between bond strength and increased penetration. McBain and Lee (1927) also stated that mechanical keying occur for joints with wood due to penetration of the adhesive into the wood substance on the ultra-microscopic scale.

4.1.4 Weak Boundary Layers

M. Wålinder

A surface may be classified according to the state of aggregation of the phases, which they separate such as liquid-gas, liquid-liquid, solid-gas, solid-liquid, and solid-solid surfaces. Surfaces between “condensed” phases, i.e., between two liquids, two solids, or a liquid and a solid, are also referred to as interfaces. An interface (or a surface) is strictly a mathematical two-dimensional plane, i.e. with no thickness.

An interphase, on the other hand, has a certain thickness and is situated between two other phases. A, so-called, weak boundary layer, a term which was introduced by Bikerman (1961), is equivalent to a weak interphase. A survey of the weak boundary layer theory was presented by Stehr (1999a). Good (1972) defined a weak boundary layer as “layers of thickness greater than typical atomic dimensions, with mechanical strength considerably less than that of either phase”. According to Bikerman (1967) when a failure seems to occur along the adherend-adhesive interface, usually a cohesive failure of a weak boundary layer is the real event. On the contrary, several authors (Crocker 1968; Good 1972; Wu 1982) have questioned the universality of Bikerman’s ideas about weak boundary layers and argued that true interfacial (or adhesional) failure does exist.

In the area of wood adhesion, Stehr (1999a) also introduces a subdivision of weak boundary layers into chemical weak boundary layers and mechanical weak boundary layers, where the former is a layer on the molecular level and the latter on a particle level. The former may consist of wood extractives and the latter may for example; consist of crushed and damaged wood fibres at the surface caused by a certain machining operation. In order to improve the adhesional properties of wood, Seltman (1995) introduced a new technique based on laser ablation for removal of such mechanical weak boundary layers. This irradiation treatment of wood surfaces and its effect on end-grain gluing of pine has been further investigated by Stehr et al. (1999) and Stehr (1999b). The results show that the laser ablation technique enables a removal or reduction of the weak boundary layers.

It was also indicated that the adhesive itself is the weak point in an end-grain joint and that if a glue with higher cohesive strength is used an efficient end-grain gluing might be possible.

4.1.5 Chemical Bonding

M. Scheikl

Chemical bonding is always correlated with isocyanate resins (pMDI). Until now there is no clear answer, if chemical reactions exist between the wood components (cellulose, hemicellulose and lignin) and pMDI (Roffael, 1999). Some papers mention that the superior bonding behaviour of pMDI in comparison to urea- formaldehyde based can be explained by the chemical bonding of the NCO - group to the hydroxyl groups of wood by urethane-bonds (Kramer 1998).

Diisocyanates are used quite widely and extensively to produce exterior-grade particleboard and OSB-panels. The initial problems of PMDI to be widely accepted as thermosetting wood adhesives has been due to several factors: (1) the problem of sticking of the board to the press, requiring the board surfaces to be glued with a different type of adhesive; (2) the toxicity and low vapour pressure; (3) the impossibility of using them in plywood production, (4) the impossibility of diluting them with water (partially solved by the introduction of emulsified diisocyanates); (5) the higher cost; and (6) the resistance to the introduction of a new different bonding system. Some of these problems have been solved, others persist (Pizzi 1994).

Questions and topics for R&D:

- a) *Do chemical bonds really exist between glue resins and the wood substrate? What is the portion of those chemical bonds in relation to the overall bonds?*
- b) *Why is it possible to achieve the same panel properties with lower resin loadings of pMDI in comparison to formaldehyde-based resins?*
- c) *What is the effect when pMDI is blended with UF-resins in terms of their surface energetic parameter and the penetration behaviour into the wood surface?*
- d) *Comparative thermodynamic characterization of UF-, PF-, MUF-, MUPF-, and isocyanate adhesives*
 - *Measurement of resin surface tension and its polar and disperse fraction*
 - *Contact angle measurements on wood and wood-based panels*
- e) *Are there special thermodynamical differences between formaldehyde based and isocyanate based adhesives? Is it possible to change the thermodynamic behaviour of adhesives in order to optimise the wetting process for practical needs?*
- f) *Thermodynamic characterization of wood-based panels (especially particleboard , MDF and OSB) produced with different glue-systems.*
- g) *Optimisation of the wetting process; development of new techniques to improve wettability of wood based panels (important for new coating technologies like powder coating of MDF-panels)*
- h) *Is it possible to predict bond strength by determination the surface energetic parameter of the glue-system and/or the parts to be joined ? Is there a correlation between e.g. the contact angle of the adhesive on the surface to be glued and the resulting bond strength?*
- i) *What really happens when a liquid contacts wood? Is it possible to separate surface thermodynamic characteristics from other influences caused by e.g. surface roughness, porosity, heterogeneity, wood extractives etc?*
- j) *Does any relevant contact angle or surface energetic data on wood exist? A Round Robin between different laboratories should be performed regarding the measurement of contact angles and surface energy on various wood surfaces.*
- k) *Is the Lewis acid-base concept applicable to wood? Is it possible to achieve an acid-base interaction between wood and the adhesive or coating similar to that between wood and water, and could so-called preferential wetting therefore be avoided?*
- l) *Is mechanical interlocking maybe the most important adhesion mechanism in wood bonding?*

- m) Does an increase in the roughness of a wood surface mainly change its interlocking or wetting properties?*
- n) Is end-grain gluing possible?*
- o) Do chemical bonds really exist between glue resins and the wood substrate? What is the portion of those chemical bonds in relation to the overall bonds*
- p) Why is it possible to achieve the same panel properties with lower resin loadings of pMDI in comparison to formaldehyde-based resins?*
- q) What is the effect when pMDI is blended with UF-resins in terms of their surface energetic parameter and the penetration behaviour into the wood surface?*

4.2 Process of Adhesion

F. Pichelin and M. Dunky

4.2.1 Chemical Curing and Forming of the Bond Strength

During the hot press process it can be distinguished between the chemical curing of the thermosetting resin and the mechanical forming of the bonding strength. When the press opens or at the end of the continuous press, a certain mechanical hardening and with this a certain bonding strength is necessary. The full chemical curing however can be completed outside of the press during hot stacking. Accelerated forming of bond strength at the same degree of chemical curing will increase the production capacity and will therefore reduce costs.

Especially at the University of Wisconsin, Madison, WI, and at the USDA Forest Products Laboratory, Madison, WI, investigations have been done on the chemical and mechanical degree of curing of various resins, especially PF-resins (Geimer et al.1990, Geimer and Christiansen 1991).

Questions and topics of R&D:

How to accelerate the formation of the bonding strength even at a low degree of chemical hardening?

4.2.2 Application of the Resin

4.2.2.1 Technique of Application of the Resin on Particles and Strands

The amount of glue resin applied to the particles has to be analysed and judged under several sights:

- Quantitative amount of resin on individual particles
- Quantitative amount of resin on particle fractions
- Quantitative overall amount of resin on the whole particle mix in the blender
- Distribution of the resin on the surface of the particles, portion of surface, which is covered by the resin.

The mass-gluing factor describing the resin consumption is one of the central parameters in the production of particleboards. From the technological standpoint a certain minimum amount of resin is necessary to guarantee the required properties of the particleboard by sufficient bonding of the individual particles. This minimum amount of resin can vary in broad ranges, according to the many influence parameters. However an excessive gluing factor imparts some technological disadvantages, like high moisture content and hence possible problems with high vapour pressure during hot pressing. Since the resin contributes significantly to the cost of the boards, a resin consumption as low as possible always is important from economical reasons.

The usually described gluing factor (% resin solid based on dry particles), however, only is an average over the total particle mix in the face layer or in the core layer; differences concerning size and shape of the various particles are not considered thereby. Additionally, this average mass based gluing factor does not give any indication on the surface area specific amount of resin (resin solid content based on square unit of particle surface). The surface area of particles with different sizes can vary between less than 1 m² up to more than 10 m², both values based on 100 gr. of dry chips. Based on this great gluing relevant surface area of fine particles, the mass based gluing consumption of fine particles is much higher than for coarse particles.

Particles as raw material for particleboards show a great variety in wood species, origin, method of preparation and age and especially a great variety of size and shape. They can be described in simplifying way as squared flat pieces with:

- Length l (mm)

- Width b (mm)
- Thickness d (mm)
- Slenderness ratio $s = l / d$.

The volume of a particle size is given as: $V = l \times b \times d$ (mm³).

Considering particles with $l \gg d$, the gluing efficient surface area is: $F = 2 \times l \times b$ (mm²).

The area form factor (Duncan, 1974) can be considered as measure for the gluing efficient surface area based on the volume and is inverse proportional to the thickness of the particles:

$$F/V = 2 / d = 2 \times s / l.$$

The influence of the particle size and shape on mechanical and hygroscopic properties of boards is described in several papers in the literature (Post, 1958, 1961, Neusser and Krames, 1969, May and Keserü, 1982, Rackwitz, 1963, Lehmann, 1974). The central statement of these papers is an increase of bending strength, compression and tension strength in board plane, but a decrease of internal bond with greater particle length. Indication of an optimal slenderness ratio must be combined with the indication of the thickness itself.

For homogenous particle fractions i with uniform size (l_i , b_i , d_i) and squared flat shape some basic correlations can be described. The number of particles N_i in a fraction can be expressed as:

$$N_i = (10^3 m_{Hi}) / (\rho \times l_i \times b_i \times d_i)$$

With: m_{Hi} amount of particles (gr) in the fraction

ρ density of the wood species or of the wood mixture (gr/cm³).

Therewith the total gluing efficient surface area (m²) of all particles (following called surface area) in this fraction is:

$$F_i = 2 \cdot 10^{-6} \times N_i \times l_i \times b_i = (2 \cdot 10^{-3} m_{Hi}) / (\rho \times d_i).$$

The gluing factor can be described in two ways:

- (i) Mass gluing factor $m_{0,spec,i}$ of a fraction (% or g resin solid content / 100 gr dry particles):

$$m_{0,spec,i} = m_{0,i} / m_{Hi} \times 100$$

with $m_{0,i}$ amount of resin solids in the fraction

- (ii) Surface specific gluing factor $m_{0,Fi}$ (gr resin solid content / m² surface area):

$$m_{0,Fi} = m_{0,i} / F_i = (m_{0,i} \times \rho / d_i) / (2 \cdot 10^{-3} m_{Hi})$$

If one of the two terms is known, the other one can be calculated assuming an uniform distribution of the resin on the particle surfaces.

In the production of particleboards always mixtures of particles are used as raw material, whereby the particles differ in size and shape. A classification of the particles can be performed according to their size by screening, whereby two of the three dimensions of the particle must be smaller than the standard measure of the actual screen to be passed. An exact screening of the particles to their size therefore is only possible for rather similar shapes. Particles however can widely differ in shape; for a simplifying description the shape is assumed squared flat with length l , width b and thickness d for medium and coarse particles and rather cubic for the fines. Since the gradation of the screens usually has a logarithmic scale, for the theoretical calculations as following the particle size distribution also was assumed to be logarithmic and similar to a Gaussian distribution. Distributions in industrial scale might differ from this model, but this is without influence on the basic results and conclusions as given below.

Each particle fraction has a certain relation to its gluing factor according to the size of the particles. The question arises, which the consequences are for the gluing of particle mixtures. Assuming gluing to be exact specific to the total surface area of a fraction, the following correlations can be described:

$$m_{0,i} = m_0 \times (F_i / \sum F_i)$$

with $\sum F_i$ total surface area of all fractions: $\sum F_i = (2 \cdot 10^{-3} m_{Hi}) / (\rho \times d_i)$

The average area specific gluing factor $m_{0,F}$ of all fractions can be expressed as:

$$m_{0,F} = m_0 / \sum F_i$$

Because of the great surface area of the fine particles their gluing factors increase strongly (linearly with the term $1/d_i$). Although if there is only a small mass fraction of very fine particles in the mixture, the high consumption of resin solid content of these fractions might have a negative impact on the gluing factor of the coarse particles, causing a low mass gluing factor of the other coarser particle fractions. The expression "resin voracity" of the fines is well known and describes the exceedingly high consumption of adhesive based on mass of particles owing to the great surface of the fine particles.

Figure 4.1 shows an example of a particle size distribution with the calculated mass gluing factors and the distribution of the resin solid content on the different fractions of the particle size distribution. Particle length was assumed to differ from 25 mm for the coarsest particles to 0,6 mm for wood dust, accordingly to practical particle mixtures (Dunky 1998).

Because of the reasons shows above usually core layer and face layer are glued separately, whereby - simply expressed - in the core layer rather coarse particles, in the face layer rather fine particles predominate. However the two distributions might overlap to some extent. This separate gluing enables using different compositions of the glue resin mixes (e.g. different addition of water and hardener) and different gluing factors for the individual layers.

Also samples of industrial unglued and glued core layer and face layer particles, resp., can be fractionated by sieving and analysed for their gluing consumption. In the case of aminoplastic resins this easily is done via a nitrogen analysis, with correction for the nitrogen content of the unglued particles. Knowing (i) the content of nitrogen as well as the resin solid content in the glue mix and (ii) the moisture content of the glued as well as of the unglued particles in the various fractions, the mass gluing factor of each glued particle size fraction can be determined. Figure 4.2 shows an example of such an analysis result for glued core layer and face layer particles, resp. Even the absolute values can be different to the above-described calculated ones, there is exact the same shape of the correlation between the mass gluing factor and the particle size (Dunky 1998).

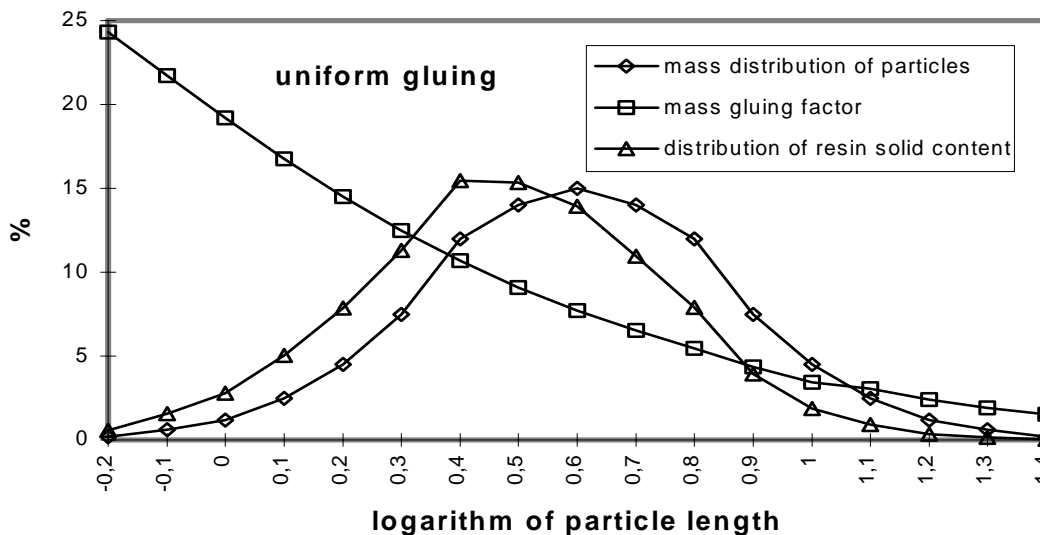


Fig. 4.1: Example of a particle size distribution, the calculated mass gluing factor and the distribution of the resin solid content (Dunky 1998). The overall glue resin consumption was assumed 8% resin solid content / dry wood.

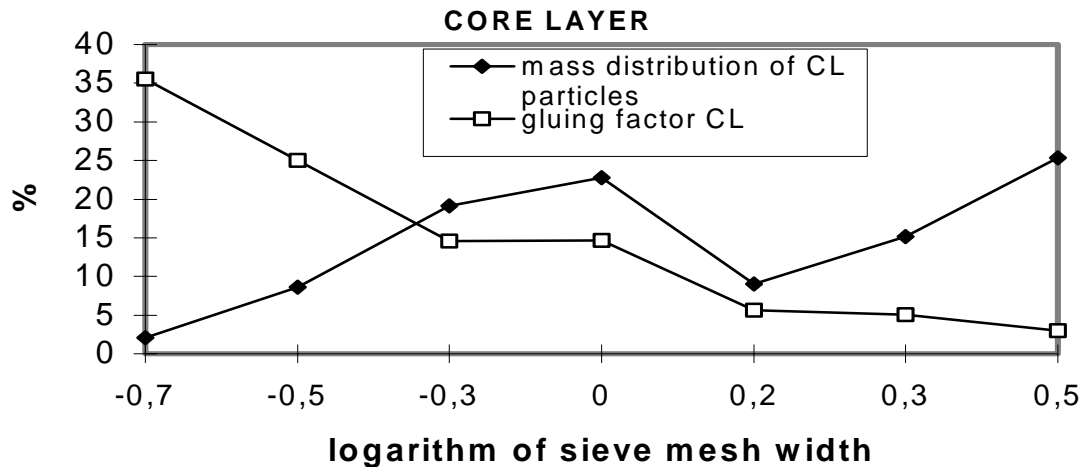


Fig. 4.2: Fractionated mass gluing factors of industrially glued core layer particles (Dunky 1998). The set mass gluing factor during blending was 9,5% resin solid / dry particles.

Assuming that the gluing of particles of different sizes is performed randomly with their surface area as decisive parameter, for various homogenous particle size fractions and for different particle size mixtures the theoretical mass gluing factors and the distribution of the resin solid content can be calculated as well as be proved by analysis. These results show a good conformity with particle size distributions in practical scale and their distribution of resin solid content. Though the calculated and analysed figures may differ, the ratios in the mass gluing factors between coarse and fine particles are consistent.

There are some indications (Meinecke and Klauditz 1962, Wilson and Hill, 1978, Eusebio and Generalla, 1983), however, that gluing is not performed exactly based on surface of the particles, but with a certain preference to coarser particles. The reasons for this fact may be the performance of the gluing itself, separation and distribution of glue droplets or post mixture of the glue on the particles (wiping effect), but these factors are not definable within this paper. The area specific gluing principle obviously loses its validity, if glue droplets and the surface to be glued have similar size. Meinecke and Klauditz (1962) mentioned diameters of glue droplets of 8 to 110 μm , depending on type of spraying, Lehmann (1965) of up to 200 μm . At least these latter numbers are in the same order of magnitude as the size of the finest particles used for the calculations above.

Beside of the surface area of the particles several other parameters also have some influence on the necessary resin consumption, as e.g. the type of the boards, thickness of the sanding zone, type and capacity of the blenders, separation and spraying of the glue resin (only wiping effect or spraying of the resin by air or liquid pressure), shape of the particles for the same particle sizes, dependence of the slenderness ratio on particle length, concentration and viscosity of the glue resin or the deterioration of the coarser particles in the blender. Other parameters more also might have some influence.

The theoretical results of the mass gluing factors highly depend on the various parameters used as input in the calculations, especially the particle size distribution and the shape of the particles in the different fractions. Changing these parameters also changes the results. Notwithstanding the correlations between the particle size and the mass gluing factor remain similar. Due to the higher surface area of the finer particles, the consumption of resin is much higher, even the surface specific gluing factor might not be constant but higher for coarser particles.

New strategies in blending pay tribute to the fact of the higher resin consumption of the finer particles and intend to remove the dust and the finest particles from the particle mix before blending. Also an exact screening and classifying of the particles before blending can improve the distribution of the resin on the particle surfaces and can help to spare resin.

A lower consumption of resin not only means lower costs for the raw materials, but also helps to avoid various technological disadvantages. With the resin also water is applied to the particles. As long as this amount of water is low enough, especially in the core layer, no problems should occur with a too high vapour pressure during hot pressing. Often however the moisture content of the glued core particles is too high, due to an excessive gluing factor. The high vapour pressure in the board at the end of the press cycle tends to expand the fresh board; if venting is not done very carefully, blistering of the boards after the continuous press or after the opening of the press might occur. Additionally the heat transfer can be delayed if the vapour pressure difference between the face layer and the core layer is smaller. If the moisture content of the glued core layer particles is high, the moisture of the glued face layer particles must be reduced. Also spraying water onto the belt before the forming station and to the surface of the formed mat cannot be performed due to the problems with too high moisture content in the mat and hence with too high vapour pressure.

Questions and topics of R&D:

- a) Which new developments on blenders are necessary and/or available in order:
- to reduce the deterioration of the particles,
 - to guarantee an uniform blending,
 - to avoid an over gluing of the fines?
- b) How to avoid excess particle destruction?
- c) How to avoid excess gluing of fines?
- d) Spraying of the glue resin into the blender versus pure wiping effect (distribution of the resin due to friction between two particles). Optimal diameter of resin droplets during spraying?
- e) Which is the optimal glue spread: uniform thin glue resin layer or individual droplets with small diameters (spot welding theory)
- f) Which are the special features of strand blending?

4.2.2.2 Gluing of Fibres in the MDF-Production

Blending system in the MDF industry (Blowline) is a very simple device, composed of a stainless steel tube connecting the refiner to the dryer. Steam and fibres flow down this tube from the refiner to the dryer.

The main advantage of blowline blending over mechanical mixing of dry fibres and resin are :

- Lack of resin spots
- Easy use and maintenance
- Lower drying energy
- Lower fire hazard in dryer

The main disadvantage is :

- Higher resin consumption

At present the process of blowline blending is not yet understood. Waters (1990) described blowline blending as a « Black Box ».

At an industrial scale, Frashour (1990) observed practice in blowline blending so as to gain more information about this process. He concluded that each plant develops its own technology, and if one technology works in one MDF plant it may not work in another one.

Robson (1991) published a largely theoretical paper in 1991 which attempted to model the steam flow in a blowline, to describe resin drop size using empirical equations developed for use in twin fluid atomisers and to estimate fibre collisions as a mean of distributing resin drops across the surface of fibres.

The main problem with this publication was that there was no proven connection between blowline flow conditions and MDF board properties.

Robson et al. (1991) developed models of industrial and pilot scale blowlines, and predictions of the models have been compared with measurements on both industrial and pilot scale blowlines.

The models show good agreement with the measures values.

Boards properties are strongly influenced by blowline design, which in turn affects blending efficiency.

More work is required in order to confirm these results. However it can already been concluded that the model developed enables to assess and compare the performances of blowline.

Questions and topics of R&D:

- a) *How to reduce resin consumption*
- b) *How to reduce resin precuring during the drying*
- c) *Optimal diameter of the blowline*
- d) *Blowline blending with PMDI-*

4.2.2.3 Technique of Application of the Resin on Solid Wood and Veneers in the Production of Plywood and for Veneering

The application of the resin on solid wood and veneers in the production of plywood and for veneering usually is done using roll coaters. The common glue spreads for various products are as follows:

- Plywood: 150 – 180 g glue mix/m²
- Solid wood gluing (e.g. glulam): 250 – 300 g glue mix/m²
- Veneering: 80 – 120 g glue mix/m².

One of the actual topics in using high reactive aminoplastic glue resin mixes is the necessary pot life.

In traditional glue resin systems the hardener is mixed with the glue resin in greater amounts. The limit in the reactivity of such mixes is a too short pot life causing gelling of the glue mix in the storage vessel or in the roll coater. In this connection the differences in pot life between a small amount in the laboratory, e.g. 100 grams, and a glue mix in practice of approx. 100 kg must be taken into consideration. The curing reaction is exothermic. If the amount of this glue mix is small, the curing heat can escape into the surrounding air. In a greater amount of glue mix however the thermal diffusion is not high enough to get rid of the heat. That has the consequence that the temperature of the glue mix increases. This higher temperature however speeds up the curing reaction again. Therefore the pot life of a glue mix also depends closely on its amount and can be as low as the half or even one third of the pot life of small amounts in the laboratory.

The increase of the reactivity of a glue mix therefore is limited by the pot life after the addition of the hardener. Decreasing the amount of ready use glue mix therefore gives a good chance to increase the reactivity. With this presupposition reactive hardeners can be used. They decrease the gelation time of the glue mix and hence the necessary press times. It has been shown in experiments, that such reactive hardeners can be performed in favourable way in liquid form. This enables the use of various acids or acidic substances within the formulations of such hardeners. Such glue resin systems usually consist of two liquid components, which are the glue resin or a premix of the glue resin with an extender on the one side and the liquid hardener on the other side. The hardener also can contain some filler. The mixing of these two components is performed just prior the roll coater. This guarantees that there is ready use glue mix only in the roll coater, but that there is no additional amount on stock. The turnover of this small amount in the roll coater is very quick, and in the case of a longer stop of the production the lost amount of ready use glue mix is small.

The extender, which usually is used in a glue mix to increase the viscosity, can be present in the systems in different form:

- 1) The extender, e.g. rye or wheat flour, is mixed with the glue resin. This premix is the one liquid component, the hardener is the second component. This system has the advantage, that low viscosity glue resins can be used, which have a good storage stability and which usually are lower in price; another advantage is, that the degree of filling of the glue mix can be adjusted

according to special requirements. It also is possible to use organic flours as extenders to avoid high tool abrasion, which can occur with inorganic fillers. The disadvantage is the additional preparation step necessary for the premix of the glue resin and the extender. Additionally this premix should not be greater than the consumption for approximately one day due to the limited stability of organic flours in a water suspension and because of a possible increase of the viscosity.

To avoid such a premix of the glue resin and the extender it is also possible to use a mixer for two liquid components (liquid glue resin, liquid hardener) and one powder component (extender). Such mixing stations are in use in the woodworking industry since long time with good success; the three components are mixed together at the same time, depending on the request of the roll coater. What however must be taken into consideration here is that the tubes from the mixing station to the roll coater are as short as possible.

- 2) Instead of a separate addition of an extender, a high viscosity glue resin and a filled liquid hardener can be used. The advantage of this system is, that both components can be pumped directly from the storage tanks or the containers to the glue resin mixer, without any additional mixing and without any powder in use. One disadvantage of these two component systems is the fixed ratio between extender and hardener. If the amount of extender should be changed, also the amount of the hardener substance is changed and hence the reactivity and the pot life. Additionally these high viscous resins usually have a lower storage stability, and they are more expensive.

The gelation time and hence the reactivity of such a glue resin system can be adjusted by the proper choice of:

- a) the type of resin
- b) the type of hardener
- c) the amount of hardener, usually between 10 and 20 mass% of the liquid hardener in form of

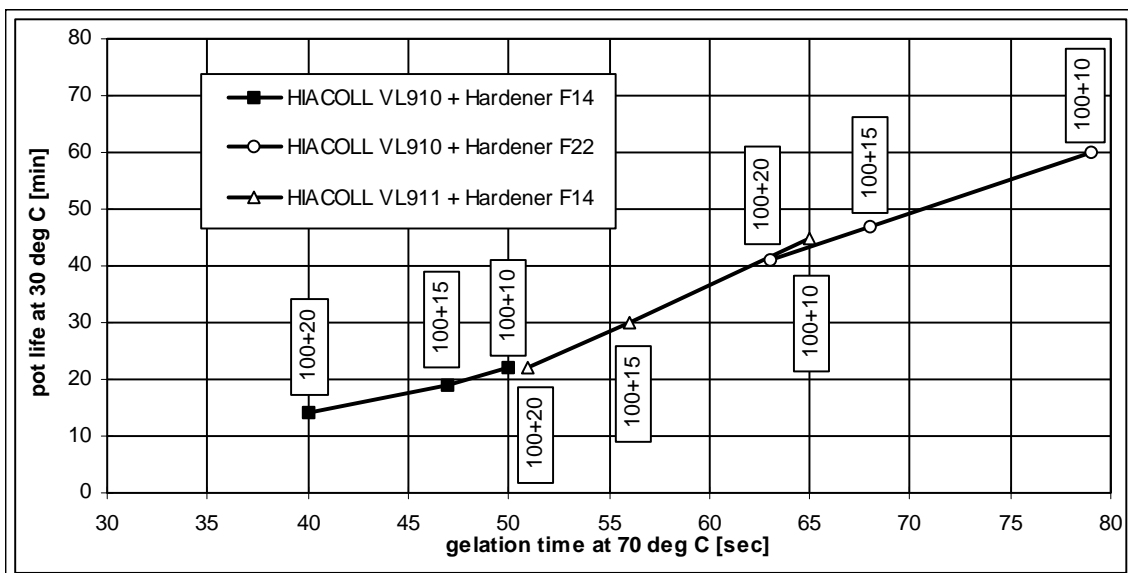


Fig. 4.3: Correlation between the gelation time at 70°C and the pot life at 30°C for two components - UF glue resin systems with different additions of hardener (Petrovic and Dunky 1997). Amounts of added hardener: resp. 10 / 15 / 20 mass% based on liquid glue resin. No extender or filler added.

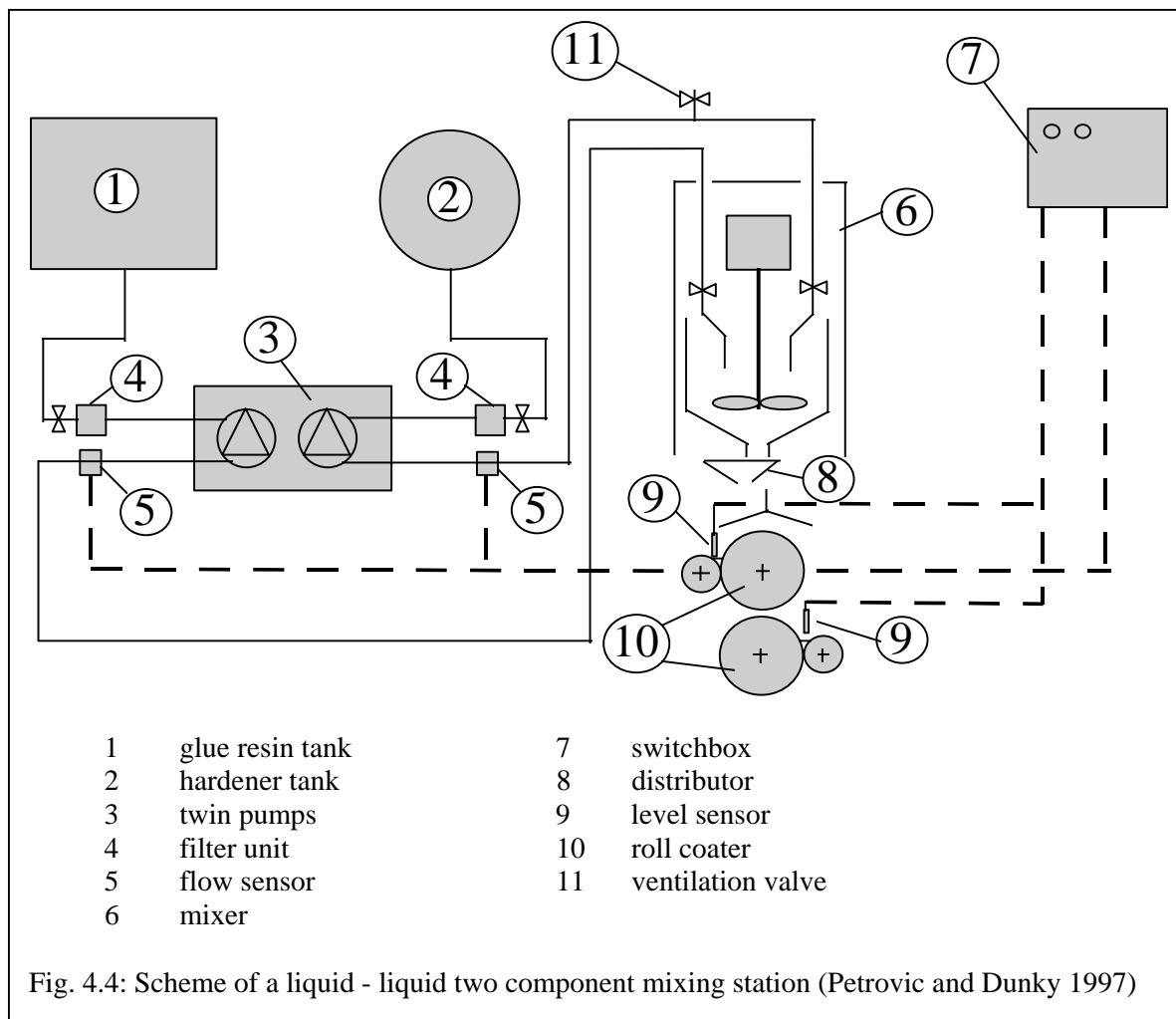
delivery based on liquid glue resin.

Figure 4.3 shows some correlations between the gelation time and the pot life for some examples of two components glue resins systems (Petrovic and Dunky 1997). The higher the addition of the

hardener the higher is the reactivity and hence the shorter is the gelation time and the necessary press time. However also the pot life of the resin mix decreases. The correlation between the gelation time and the pot life is shown to be more or less linear, with different lines for the various systems.

The higher the temperature during application, the shorter is the pot life of the resin mix. An increase of 10°C usually means a reduction of the pot life to the half or even one third of the value at the lower temperature, according to the equation of Arrhenius.

Because of the high reactivity and hence the short pot life of such glue resin systems a liquid-liquid-two component mixer is recommended for use. This mixer preferably is installed directly above the roll coater, in order to reduce the amount of the prepared glue mix to the smallest possible amount, which is the amount of glue mix in the roll coater. There is no additional glue mix on stock ready for use. With the installation of the mixer above the roll coater also the tubes with the resin mix are as short as possible. Because of the strong influence of the temperature on the pot life it is necessary to cool the whole system using a chilled water section. The raw glue resin should have a temperature not higher than 15 deg C, which especially is important for the summer time with the higher room temperatures. Cooling of the glue resin can be performed in a 50 litres vessel with cooling coils, which is installed between the storage tank and the mixer. Because of the lower amounts it rather is not necessary to cool also the hardener or the extender. In case of a premix of



the glue resin with the extender however this premix should be stored in a cooled vessel.

The roll coater itself also needs cooled cylinders in order to stabilize the temperature well below 20°C, a temperature of approx. 15°C would be ideal.

Figure 4.4 shows the scheme of a liquid-liquid-two component mixing station (Petrovic and Dunky 1997).

Questions and topics of R&D:

How to elongate the pot life of high reactive glue resin mixes?

4.2.2.4 Foam Gluing

Purpose of the foam gluing is an optimal use and therewith a minimization of the used glue resin. The resin is foamed to five- to six fold of its original volume by air and mechanical agitation (Deppe and Hasch 1990, Deppe and Rühl 1993, Myers 1988, Sellers 1988, Walker 1996). Via an extrusion head many stripes of the foamed resin are applied separately onto the wood surface.

Questions and topics of R&D:

Is foam gluing also applicable to particleboard?

4.2.3 Influence of the Gluing Factor on the Properties of Wood Based Panels

Questions and topics of R&D:

Which gluing factor is necessary for a special application, depending on the type of the adhesive?

4.2.4 Water Balance

The water balance and its controlling is one of the most important problems in the production of wood based panels. This was recognized already in the very first beginnings of the particleboard production (Kollmann 1955). Especially using aminoplastic resins with a low content of formaldehyde the water balance during the production process is extreme critical. The distribution of the resin on the wood surface depends on its dilution and therefore on its viscosity. The amount of water, which is applied together with the resin, however, must be evaporated again. If the vapour pressure exceeds at the end of the press time the bonding strength of the just pressed board, blistering of this fresh board occurs. Very important in this context is the evaporation behaviour of the mat and of the board. Also the moisture content of the glued particles influences the plasticity of the particles. This plasticity is important for the deformation of the particles in order to perform enough contact areas between the particles for a proper bonding.

4.2.4.1 Wood Moisture Content Before and After Blending

- a) Influence of the moisture content on the behaviour of the applied resin on the wood surface and on the hardening behaviour of resins

Higher moisture contents of the glued particles cause a better flowing of PF-resins and hence an enhanced penetration into the wood surface. As long as there remains enough glue resin in the glue line, good bonding strengths can be achieved. Too high moisture contents, however, may cause over penetration and hence starved glue lines (Steiner et al.1993). Additionally the chemical hardening of the resin can be retarded due to the high content of water, which drives the equilibrium again back to the left side (raw materials). The ability of a resin to flow can also be influenced by special cooking procedures, e.g. using dispergated PF-resins. The flowing ability decreases with enhanced degree of condensation and hence with increased molar masses. The use of such resins in gluing high moisture content wood however is limited by the technically possible viscosity of the resin.

Depending on the press temperature various optimal regions of the moisture content of the wood exists. It also had been suggested already early, that beside of the temperature also the

moisture content in close proximity of the glue line can influence the hardening mechanisms and hence the forming of the bond strength (Graf 1937, Kuch 1943, Strickler 1959).

Humphrey and Ren (1989) varied nearly isothermal temperature and moisture conditions in gluing Douglas fir veneers with phenolic powder resin. Inserting steam during the press cycle enabled to keep the moisture content of the veneers on the original level after the preconditioning. The bond strength was tested immediately after the end of the press time and increased after various press times. The temperature in the glue line had been measured, the moisture content had been calculated according to models. At the beginning of the curve there is a delay in the increase, obviously due to melting of the powder, penetrating into the wood surface and yielding a first degree of hardening. After a certain press time there is also a characteristic time span, where the bond strength does not increase, the reason for this effect is not really clarified. Such experiments can be performed at various temperatures, the slope of the increase of the bonding strength can be plotted against the absolute temperature, yielding a type of activation energy ("reactivity index").

b) Drying of particles:

The drying process can influence the physical and chemical properties of the particles.

c) Calculation of the moisture content of the glued particles:

The calculation of the moisture content of the glued particles (calculation is also possible for fibres and strands) is based on the moisture content of the dried particles and the composition of the glue mix. Table 4.1 shows such a calculation for a particleboard core layer.

Table 4.1: Example for the calculation of the moisture content of glued core layer particles

Assumptions:			Moisture content of the dried particles (before gluing): 2%
			Solid contents of the glue resin: 66%
			Concentration of the hardener solution: 20%
			Concentration of the paraffin emulsion: 60%
			Gluing factor: 8% resin solid content based on absolutely dried particles
			Hardener addition: 2,5% Hardener solid based on resin solid contents
			Addition of paraffin: 0,6% solid paraffin based on absolutely dried particles
			No additional water added to the glue mix.
102,0 kg	dried particles	100,0 kg	absolutely dried particles
12,1 kg	glue resin	8,0 kg	resin solid content
1,0 kg	hardener solution	0,2 kg	solid hardener
1,0 kg	emulsion	0,6 kg	solid paraffin
		108,8 kg	sum solid contents
			2,0 kg water (particles)
			2,0 kg water (glue resin)
			0,8 kg water (hardener)
			0,4 kg water (emulsion)
			7,3 kg sum water
Calculated moisture content of the glued particles (sum water/sum solid contents): 6,7%			

There exist three different types of moisture in a glued particle: (i) water within the wood cell wall, (ii) water within the cell lumen (from glue spread), (iii) water still at the wood surface (also partly from glue spread and from water sprayed onto the mat just before the press). Water (iii) can be evaporated very rapidly and easily and is therefore important for the steam shock effect in order to increase the temperature in the core layer. Especially an additional steam effect occurs by spraying water on the top of a mat just before the press entrance. Also water (ii) will evaporate, however with lower speed. Water (i) does not seem to play a part in the warming up of the core layer.

Usual moisture contents are:

- For UF: 7 – 9% in the core layer; 10 – 13% in the face layer;
- For PF: 11 – 14% in the core layer; 14 – 18% in the face layer.

4.2.4.2 Open and Closed Assembly Time

Open assembly time starts with the application of the adhesive to the wood surface and ends with the addition of the second surface. During the open time water can evaporate to the surrounding air,

which reduces the water content of the glue line and hence also reduces the increase of moisture content of the wood to be bonded. On the other side a too long open time might cause a too high increase of the viscosity of the applied adhesive due to the loss of water; additionally the forming of a dry film on top of the adhesive layer might occur. Both effect will lead to a decreased wetting behaviour, which might cause low bonding strengths.

During the closed assembly time, which ends with the application of the press pressure, water also can penetrate into the second wood surface, causing e.g. even strong swelling of veneers, which might be the reason for cracks in the veneered board during use in dry conditions.

4.2.4.3 Steam Shock During Press Cycle and Warming of the Mat

The warming up of the core layers is based on the evaporation of water in the face layer and the transportation of the heat via the steam shock; in the cold core layer of the mat the vapour condenses and warms up the core layer. The higher the amount of vapour and the steeper the vapour pressure gradient, the quicker is the warming up of the core layer, enabling shorter press times. However, this vapour contributes to the overall moisture content of the core layer. The moisture content of the face layer therefore always should be as high as possible, the moisture content of the core layer as low as possible.

A too high moisture content within the mat and the board also (i) causes long venting times during the press cycle (in order to prevent blistering), (ii) hinders the chemical hardening reaction and (iii) leads to high densities in the face layer and a steep density profile between face and core layer.

During the hot pressing of a particle or fiber mat, resp., quick changes in temperature, moisture content and vapour pressure occur. The resulting gradients of temperature and moisture content significantly influence the forming of the bond strength and the hardening of the resin. All these processes together with the applied mechanical pressure determine the formation of the density profile and in this way the mechanical and other properties of the boards.

Questions and topics of R&D:

How to calculate the heating up of a particle or a fiber mat within the press?

4.2.4.4 Steam Pressure within the Mat and the Produced Board

Due to the moisture content of the glued core layer particles as well as due to the vapour flowing from the face layer to the core the vapour pressure in the core increases with elongated press time. If the vapour pressure is too high, it will exceed the bonding strength of the still hot board at the end of the press time (at the end of the continuous press), in such a case blistering occurs. Influence factors are the moisture content of the glued surface and core particles (especially determined by the composition of the glue mix and the gluing factor), resp., the portion of core and face layer in the board, press temperature and press time and the density and venting behaviour of the mat and the board.

Very recently presses have been built with a special cooling zone in the approx. last third of the length of the press. At the moment only little (though promising) results are known. A final judgement on this technology is not yet possible.

Questions and topics of R&D:

- a) *Which effects of the new cooling zone at the end of the continuous press are possible? Can the steam pressure be decreased significantly?*
- b) *Which strategies are necessary to obtain a strong steam effect and a quick heating up of the core layer but nevertheless to avoid a too high vapour pressure in the core, causing in case blistering?*

4.2.5 Press Process

4.2.5.1 Different Pressing Methods

a) Multi-daylight pressing

This method, which is equally the oldest one, relies on the use of a multi-daylight press. Heat is transferred into the mat via the mat surface. The main advantages of this system are the considerably lower initial investments costs and the long experience of the OSB industry with this kind of pressing system. For this reason almost all OSB plants in America are equipped with multi-daylight presses.

b) Continuous pressing

Contipresses are double-steel belt pressing systems, capable of producing all board types. The steel belts are directed by drums and supported on a roller rod carpet. Siempelkamp has successfully managed to adapt the ContiRoll® for the production of OSB. At the moment three plants are running and two other have already been sold.

Compared to multi-daylight presses, the continuous pressing method enables shorter curing times and yields products with homogenous properties (Sitzler 1998).

Besides, the ContiRoll® system ensures a higher flexibility when changing board size and thickness.

c) Steam injection

The steam injection method is the most effective one if the aim is to produce homogenous products. Such a rapid heat supply system allows extremely short pressing times and good wood plasticization. Production capacities up to 1.100 m³ / day can be achieved in a single daylight press (Sitzler 1998).

d) Preheating

Basically, preheating a mat requires two major considerations:

- The closer the preheater is to the hot press, the lesser the risk of the adhesive precuring and the more effective the preheating is.
- Energy costs are higher with a High Frequency (HF) or microwave preheating than by injection of hot air or of a air/steam mixture.
- The combination of a preheater ContiTherm® with a ContiRoll press allows the production of board thickness greater than 40 mm (Sitzler 1998).

4.2.5.2 Modelling of the Press Process

a) Research on internal mat conditions

Numerous investigations have been conducted in order to improve board properties. Most of this research aims at understanding the physical processes involved during the hot-pressing of flakeboards (Suchsland 1967; Strickler 1959).

Kamke and Casey (1988 a,b) measured the temperature, gas pressure, and compaction pressure in the face and core regions of flakeboard panels during manufacture. The effect of press temperature and closing time on heat and moisture transfer was investigated for moistures up to 15%.

The interaction of temperature, moisture content, and compaction is responsible for the formation of a vertical density gradient in the board (Strickler 1959 ; Wolcott et al. 1990).

Mathematical models have been developed to predict internal mat temperature and moisture content in particleboard during hot-pressing. Data measured in the board were compared with

values predicted by the model (Bolton et al. 1989 a,b,c; Humphrey and Bolton 1989 a,b ; Kamke and Wolcott 1991).

Questions and topics of R&D:

Internal conditions when pressing at very high moisture content

b) Simulation of hot-pressing for the batch process

Humphrey (1982) developed a computer-based simulation model of the thermodynamic mechanisms occurring during hot-pressing of wood based composites. Densification and stress relaxation of the mat were subsequently incorporated.

Questions and topics of R&D:

- a) Influence of adhesive curing on stress relaxation*
- b) Wood plasticization when pressing at high moisture content*
- c) Simulation of the pressing at high moisture content*

c) Simulation of the hot-pressing for the continuous pressing

4.2.6 Hot Stacking and Maturing

Hot stacking and maturing is a very important part of the panel manufacture. There is rather little fundamental literature research on this item.

Questions and topics of R&D:

- a) Simulation of hot-stacking conditions at laboratory scale*
- b) Modelling of board cooling during hot-stacking*
- c) Post-curing of PF adhesives during hot-stacking*
- d) Influence of hot-stacking on board mechanical and dimensional properties*

4.3 Properties of the Glue Line - Microstructure of the Glue Line

M. Scheikl

4.3.1 Adhesive Penetration into Wood

The amount of adhesive penetrating into wood substrate during the manufacture of plywood or other wood composite materials like OSB is known to affect bond quality. Speculations concerning the flow characteristics of the thermosetting adhesives have been based primarily on qualitative observations. Excessive adhesive penetration into veneers or strands will create starved glue lines. Low penetration into the wood surface allows only little internal surface contact for chemical bonding or mechanical interlocking. An optimum adhesive penetration is needed to repair processing damage of the wood surface and to allow better stress transfer between laminates (plies). Other wood composites also benefit from optimum adhesive penetration, which promotes strong bonds and more efficient use of the adhesive (Johnson and Kamke 1992).

Adhesive movement through wood is usually classified as penetration into wood tissue and cell wall penetration. Penetration into wood tissue refers to movement of the adhesive through the large voids in the porous structure whereas cell wall penetration involves movement of adhesive through the micro voids within the wood cell walls (Johnson and Kamke 1992).

4.3.2 Penetration into Wood Tissue

Usually some adhesive penetration occurs during wetting of the wood surface. Wood anatomy, surface energies, adhesive viscosity and wood moisture content are primary variables involved in the wetting and penetration of wood surfaces. In the production of wood composites with thermosetting adhesives, variables like applied pressure, press temperature, press closing rate and particle geometry, are introduced. These variables interact to create a dynamic environment involving temperature and vapour pressure gradients in the mat during hot pressing (Johnson and Kamke 1992).

Brady and Kamke (1988) have studied the effect of the hot pressing parameters on phenol-formaldehyde resin penetration into thin wood flakes. Penetration was evaluated by using fluorescence microscopy and a manual digitalisation technique.

Two conclusions regarding the effect of pressing parameters on resin penetration can be drawn:

- (i) The uniformity of resin penetration is influenced more by the natural variability of the wood than by temperature, moisture content, time or pressure resp.
- (ii) The parameters (temperature, moisture content and time) influence the resin penetration by controlling the viscosity of the resin. Pressure influences penetration because it is the driving force for hydrodynamic flow. Moisture content and the interaction of temperature with time influence resin penetration by affecting the viscosity of the resin.

4.3.3 Effect of Ageing of a Glue Bond

The effect of weathering on adhesive joints is an important consideration for structures in exposed areas.

The primary problem of investigating such effects is the time required for investigation. It may require a number of years for naturally exposed structures to deteriorate significantly. To enable a short-term investigation of such effects, various accelerated aging tests have been developed. The basic principle utilised has been severe shrinking and swelling in cycles, producing stresses that cause checking of wood and failure of a glued bond. The various tests developed utilise vacuum and pressure cycles along with soaking and drying cycles (Lehtinen and Koponen 1998).

Aging of PF-bonded plywood had no effect on the structure of adhesive, but it caused cracking mostly on the wood material. Aging deteriorated the mechanical adhesion between the wood tissue and adhesive. The clearest effect of aging was enlarging of cracks (Lehtinen et al. 1999).

4.3.4 Cohesive Strength of the Glue Line

Cohesive strength of a glue line is determined by the

- Molar weight and the average polymerisation degree
- Shape of the molecules, e.g. the chemical structure of macromolecular substance
- Orientation of the molecules
- Chemical nature of the molecules
- Composition and amount of other substances (fillers, extenders, solvents, plasticizers)

During formation of cohesion forces of a glue line the flexibility and rigidity have a big influence on the strength of the glue line. Long chains with only a few branches result in high strength, due to the low viscosity. In a hardened glue line they are solidified and still show sufficient elasticity. If molecules for glues are branched excessive, inelastic rigid and brittle glue lines will result. Therefore such molecules are unsuitable for binding agents. For a proper glue-quality therefore a certain ratio between rigid and elastic components in the molecules of binding agents is necessary.

Questions and topics for R&D:

- a) Resin distribution on wood and coverage of wood-furnish (solid wood, strands, particles, fibres) for different resin systems (is there a possibility for staining UF-, MUF- resins and pMDI)*
- b) GLUE-SCAN (Alberta Research Council) works for PF-resins in OSB industry. Is such a system also possible for pMDI resp. for particleboard furnish and fibres for MDF-industry?*
- c) What is the effect of wood deterioration during aging a glue line?*
- d) Micro structural investigations of the interface wood - adhesive during aging of glue-bonds for all commonly used resin systems.*
- e) How can the cohesive strength be improved or the properties of the glue lines changed (optimisation of brittle and elastic ratio of the glue line) ?*

4.4 Binderless Gluing

M. Scheikl

For recycling purposes it would be an advantage if it would be possible to produce wood based panels without any glue under consideration of economical aspects.

The progress in this field of research is still too small to be optimistic. Nevertheless it can be assumed that this goal will be reached more likely for fibreboard (MDF) than for particleboard (Roffael 1999).

Already at the beginning of the development of wood based panels researchers tried to produce binderless wood based panels by activation of lignocellulosic material of the wood itself. This technology was used the first time for fibreboard produced according to the wet process. Due to environmental problems with the wastewater this process is nowadays of less importance.

Suchsland (1986) did some investigations with dry-formed MDF with binderless hardboard faces.

Pecina (1993) describes 4 mechanisms, which are responsible for the binding of fibres without glue during the wet process of fibreboard production.

- a) presence of coordinative forces (hydrogen bond) including friction forces
- b) covalent bond between chemical components of the wood
- c) mechanical interlocking according to the macro- and microscopic structures
- d) bonds from fiber to fiber supported by sticking wood inherent or non-wood substances

The adhesive power of fibres depends on the number of reactive groups, which are available during the bonding process. The properties of the glued boards depend on the number of reactive groups, which were activated during the production process.

In the thermohydrolytic activation process of wood inherent adhesion forces, the hemicelluloses are of great importance. Hemicelluloses are decomposed under wood inherent acidic conditions to sugars, which are transformed to furan derivatives.

The furan derivatives then may result in the formation of furan resins (Ellis and Paszner 1994).

Another approach to achieve fibre-to-fibre bonds is the microbiological way. The surfaces of the fibres are activated with enzymes of white rot fungi (Roffael 1999).

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5 Influence of the Wood Component on the Bonding Process and the Properties of Wood Products

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5.1 Introduction

The adhesive bond joint in wood product has been likened to a chain with five or even more links. Gillespie (1980) says that the strength of a glued joint in timber depends on the weakest of those links: wood interior (adherend), wood subsurface, interface, boundary layer and adhesive. Wood interior depends on the strength of wood. Subsurface of wood can be damaged and therefore weakened e.g. by coarse or blunt tools. The strength of the adhesive is dependent on the adhesive type and formulation, on its correct application and on curing temperature.

The most critical bonding area between the glue and wood in a glueline is called the interphase. It is composed of both wood and glue so that the critical bonding zone is affected by the chemical composition of both the wood and adhesive. The strength of the bond at the interface depends e.g. on the planeness of the wood surface, on the amount of dust, extractives and other contaminants on wood surface and on the moisture content of the wood.

The migration of the smaller adhesive particles to and through the interface in the boundary layer affects the composition and hence the strength of this area of the adhesive. The performance of adhesive bonded joint depends upon how well we understand and control the factors determining the strength of each link.

The stresses in each layer depend on the external loading, on dimensional changes in the adherends and adhesive due to changes in temperature and moisture content, and on the stress / strain curves of the adherends and adhesive.

Given its environment and the type and duration of loading to which a glued joint is subject, its strength will depend on:

- The strength of the adhesive itself and its response to stress and its environment
- The effects of moisture and e.g. preservatives in timber
- Timber properties which affect the strength of the adhesive bond
- Timber properties which cause internal stresses in the joint
- The mechanical properties of the timber

Adhesives are used to bond wood in solid form (lumber), and as veneer, flakes or particles, and fibers. They are also used in secondary manufacture to fasten bonded panel products to lumber and to other materials.

5.2 Wood Structure

Wood is a cellular material that is produced by a systematic growth mechanism in woody plants. There are thousands of species of trees throughout the world, each with unique properties. However, they all have common characteristics because of how trees grow. Some of these common characteristics include a cellular structure, arranged in a concentric ring formation that produces orthotropic physical and mechanical properties (e.g. strength, stiffness, shrinkage/swelling) that directly relate to their orientation to the principal orthotropic axis. Another common characteristics of all species of wood is the occurrence of growth characteristics e.g. growth rings (caused by annual growth of wood cells), knots, splits, checks and cracks (a separation of the wood cells caused by growth, drying, or mechanical stresses at weak locations), grain orientation (orientation of the longitudinal direction of the wood cells relative to the geometric axis of member). In solid wood products, mechanical properties are affected by these growth characteristics.

5.3 Properties of Wood Surface

The wood surface is a complex heterogeneous polymer composed of cellulose, hemicellulose and lignin. The surface is influenced by polymer morphology, extractives chemicals, and processing conditions. A good enough understanding of the wood surface and adhesive bonding is necessary because the mechanism of wood adhesion is not fully understood and may change significantly with different adhesive systems (Cote 1983).

Because adhesives bond by surface attachment, the physical and chemical conditions of the adherend's surface is extremely important to satisfactory joint performance. A general rule is, that wood surfaces should be smooth, flat, and free of machine marks and other surface irregularities, including planer skips and crushed, torn, and chipped grain. The surface should be free of burnishes, exudates, oils, dirt, and other debris (Forest Products Laboratory, 1999).

The forces that cause an adhesive to wet, spread and attach to the surface of a solid have been ascribed to chemical bonds, to mechanical entanglement, to physical and chemical absorption due to polar groups, to electrostatic forces of attraction inherent in all matter and to a combination thereof (Marra 1983).

Two important surface characteristics affecting gluing quality of wood are surface roughness and surface chemistry.

Questions and topics of R&D:

- a) *Are there generally accepted experiences and rules concerning the influence of the properties of the wood surface on the quality of a bond line?*
- b) *Which portion of the quality can be influenced by the properties of the wood surface?*
- c) *How does adhesion really work? How to proof which of the most important features and mechanisms usually described in literature really determine wood bonding?*
- d) *Is there a certain minimum quality of the wood surface necessary or is it just a question of e.g. using a special adhesive or a special technology?*
- e) *Which parameter is more critical when trying to get the best possible quality for the bond line: the quality or properties of wood surface or the choosing the right kind of adhesive and gluing-technology.*
- f) *How to proof which of the features and mechanisms usually described in the literature really have an effect on bonding strength in wood bonding? Do we have enough knowledge about the adhesion between adhesives and wood surfaces in order to attain the highest possible quality of the glue line?*

5.3.1 Roughness

The inherent anatomy of wood and methods of surface preparation cause the roughness of wood surfaces. Vessel elements, ray cells and resin canals, when cut during surface preparation, create openings or porosity at the wood surface. In a positive way, this adds the surface area and improves regions for penetration and interlocking of the adhesive, but negatively, air can be entrapped and good contact between opposite wood faces is difficult to achieve because of the surface roughness (Young 1985).

Parallel and flat surfaces allow the adhesive to flow freely and form a uniformly thin layer of adhesive that is essential to the best performance of water-based wood adhesives. Experience and testing have proven that a smooth, knife-cut surface is best for bonding. Surfaces made by saws usually are rougher than those made by planers and jointers. However, surfaces sawn with special blades on properly set straight-line rip saws are satisfactory for both structural and nonstructural joints (Forest Products Laboratory, 1999)

Dull cutting edges of planer or jointer knives crush and burnish the wood surface. The crushed and burnished surface inhibits adhesive wetting and penetration. If the adhesive does not completely penetrate crushed cells to restore their original strength, a weak joint results (Forest Products Laboratory, 1999)

Caster et al. (1985) have researched the gluability of sanded lumber. Sanded lumber here means the same as abrasively planed lumber. Results are compared with the results when gluing of knife planed lumber. Abrasive planning with grit sizes from 24 to 80 causes surface and subsurface crushing of wood cells. Such damaged surfaces are inherently weak and result in poor bond strength. Dull planer knives or saws can cause similar damage. There is some evidence that sanding with grits finer than 100 may improve an abrasive-planed surface. However, abrasive planning is not recommended for structural joints that will be subjected to high swelling and shrinkage stresses from water soaking and drying. The crushed cells at the surface may prevent adhesive penetration down to the undamaged cells. The adhesive bonds to the crushed cells, but these cells pull loose very easily, giving low shear strength with the appearance of high percent wood failure. The glueline wet shear strength values with sanded lumber after accelerated aging soak test are lower than for knife-planed values. If abrasive planning is to be used before bonding, then belts must be kept clean and sharp, and sanding dust must be removed completely from the sanded surface.

The surface properties of veneer are essentially no different from those of lumber; however, manufacturing processes, including cutting, drying, and laminating into plywood, can drastically change physical and chemical surface properties of veneer. Special knowledge and attention to these characteristics are required to ensure good wetting, flow, and penetration of adhesive. As the knife peels veneer from the log, the knife forces the veneer away from the log at a sharp angle, thereby breaking or checking the veneer on the knife side. Adhesive over penetration into lathe checks usually is not a problem if the adhesive spread rate is adjusted correctly (Forest Products Laboratory, 1999).

Johansson and Stehr (1997) introduced the concept of a "mechanical weak boundary layer" (MWBL). The MWBL consists of damaged cells on the wood surface, caused by different kinds of machining of the surface (Johansson, 1994).

Stehr (1999) and Stehr et al. (1999) have investigated the effect of removing the mechanical weak boundary layer (MWBL) on the strength of glued end-grain joints. In their investigations, a laser ablation technique (Seltman 1995) has been used to remove this layer of damaged cells. Investigations within this field have shown no major effect of removing the MWBL (Stehr et al. 1999), although there is a considerable difference in structure between an ablated and unablated surface. Maybe the best means to avoid the effects of MWBL on the strength of bond quality is to prepare wood surfaces as good as possible.

Questions and topics of R&D:

- a) *Is there any optimal surface roughness for gluing? If so does it depend on wood species or do different adhesives have different requirements for surface qualities in order to give good gluing results?*
- b) *But how to avoid the building up of mechanical weak boundary layers during preparing a new wood surface?*

5.3.2 Surface Chemistry

Over drying and overheating deteriorates the physical condition of the wood surfaces by forcing extractives to diffuse to the surface, by reorienting surface molecules, and by irreversibly closing the larger micropores of cell walls. Wood surfaces can be chemically inactivated with respect to adhesion by airborne chemical contaminants, hydrophobic and chemically active extractives from the wood, oxidation and pyrolysis of wood bonding sites from over drying (at higher than regular drying temperatures), and impregnation with preservatives, fire retardants, and other chemicals. Unfortunately, some of these surface conditions are difficult to detect. Physical deterioration and chemical contamination interfere with essential wetting, flow, and penetration of adhesive but can also interfere with the cure and resulting cohesive strength of the adhesive (Forest Products Laboratory 1999).

There is evidence for a direct reduction in adhesive bond strength in comparisons between aged, inactivated wood surfaces with fresh or solvent-extracted wood surfaces (Stumbo 1964; Chen 1970; Roffael and Rauch 1974; Moredo et al. 1996).

5.3.2.1 Age

Hydrophobic wood inherent chemicals (extractives) might migrate with time to the surface of the wood and can there undergo chemical reactions. In most cases this means a decrease of the wettability and therefore of the gluability of wood surface; e.g. for the glulam industry it is the rule to use only fresh surfaces (within 24 hours after cutting). The speed and the degree of this deactivation depend on the wood species and the storage temperature, as already shown by Gray (1962). Back (1991) describes various mechanisms of changes, which will lead to an inactivation of the surface, especially the migration of various chemicals to the wood surface. Herczeg (1965) found similar results on surfaces of Douglas fir. Gardner et al. (1995) could show, that distinct lower wetting angles (identical with better wettability) could be found, if the surfaces had undergone an extraction

Control of the time dependent formation of resinous layers is therefore of importance in the achievement of optimum adhesion conditions. A substantial reduction in wettability during the first 24 hours after cutting of wood has been demonstrated by contact angle measurements on smooth surfaces of Douglas fir and redwood (Herczeg 1965; Nguyen and Johns 1979). On rough surfaces of finely sawn spruce, no decrease in wettability was seen until 2,5 to 3 days after cutting (Nussbaum 1996, 1999)

Questions and topics of R&D:

- a) *How to overcome the problems with aged surfaces?*
- b) *Which types of wood inherent chemicals tend to migrate to the surface?*
- c) *Which types of chemical reactions can take place with the wood inherent chemicals after they had migrated to the surface?*
- d) *Could it be possible to develop adhesives so that they are less dependent upon the quality or age of wood surface?*

5.3.2.2 Extractives

It was recognized already long ago that the migration of very small amounts of both saturated and unsaturated fatty acid extractives to the wood surface could significantly alter the wood surface properties. The extractives on wood surfaces are the principal physical and chemical contributors to surface inactivation, hence to poor wettability by adhesives.

Most wood adhesives contain water as a carrier; therefore, they do not properly wet, flow, and penetrate extractive-covered surfaces. The acidity of extractives can also interfere with the chemical cure of adhesives. The acid may accelerate the cure of an alkaline phenolic adhesive, causing the adhesive to gel prematurely and reducing its ability to wet, flow, and penetrate (Back 1991, Hse and Kuo 1988, Christiansen 1991, Nussbaum 1999). Various surface treatments, such as heat, solvent extraction, and plasma treatment have been studied in an effort to control surface properties (Liu et al. 1998).

Although the importance of wood surface chemical structure and the impact of small molecules on surface properties have long been appreciated, investigations have just begun to focus on establishing the surface structure-property relationships. Dynamic contact angle measurements have been used to define changes in wood veneer wettability with extractive content of the surface. Extra cellular compounds including terpenes and fatty acids, which can comprise as much as 12% (by weight) of certain wood species may dramatically influence the surface properties of these materials, such as wetting (Liu et al 1998).

The rate and the extent of the inactivation process may vary, depending on wood species and temperature. Fairly small differences in mean values, less than 5 degrees, are statistically

significant. Studies of surface wettability evaluated as the constant wetting rate angle (cwra), are useful for evaluating the surface inactivation of wood (Nussbaum, 1999).

Questions and topics of R&D:

Is there correlations between surface wettability, glue adhesion and bond strength?

5.3.2.3 Contaminants

A clean, solid surface is one of the basic requirements for optimum adhesion between a substrate and an adhesive. Wood is no exception, but in addition to regular airborne contamination, such as dust particles, a wood surface is subjected to what can be described as self-contamination (Nussbaum, 1999). This is as a result of a natural surface inactivation process where low-molecular wood extractives migrate to the surface (Back 1991).

Questions and topics of R&D:

How to avoid the contamination of wood surfaces, e.g. from the air is one basic problems in wood gluing.

5.3.3 Density and Porosity

Wood substance without void volume has a density approximating 1,5 g/cm³ regardless of the wood species. But density varies greatly between wood species, and even within a species, because species vary in void volume and thickness of cell walls. High-density woods have thick walls and small lumen volumes, whereas low-density woods have thin walls with large lumen volumes. The strength of wood is directly related to its density because thick-walled cells are capable of withstanding much greater stress than are thin-walled cells. Wood cells are an integral part of the wood–adhesive interphasing region; therefore, the adhesive bond must be at least as strong as the wood if the strength capability of the wood adherend is to be fully utilized (Rowell 1984).

The strength of adhesive bonds to wood increases with wood density up to a range of 0,7 to 0,8 g/cm³ (moisture content 12%). Above this level, joint strength decreases. Although strength increases with wood density, wood failure decreases gradually up to a density range of 0,7 to 0,8 g/cm³, and then decreases more rapidly above 0,8 g/cm³. As wood density increases, high strength joints with high wood failure are more difficult to achieve consistently (Forest Products Laboratory, 1999)

High-density woods are difficult to bond for several reasons. Because of thicker cell walls and less lumen volume, adhesives do not penetrate easily into wood, so important mechanical interlocking of adhesives is limited to one or two cells deep. Much greater pressure is required to compress stronger, stiffer, high-density wood to bring contact between wood surface and adhesive. Higher concentrations of extractives that may interfere with the cure of adhesives are common in high-density species, particularly oaks and tropical hardwoods. The severe stresses produced by high-density species as they change dimensions with changes in moisture content also contribute heavily to bonding difficulties (Forest Products Laboratory, 1999)

Density is perhaps a crude indicator, but as previously noted, it is useful for estimating the bondability of a great variety of wood species. However, a species that bonds poorly with one adhesive may develop much better bonds with another adhesive (Forest Products Laboratory, 1999)

The void volume of wood, which can range from 46% to 80% of total volume, strongly affects the depth and direction that an adhesive flows. To attain the highest joint strength, the adhesive must penetrate and mechanically interlock several cells deep into sound, undamaged cell structure. In wood, porosity varies according to the grain direction. It is most porous on end-grain surfaces, being many times greater than on radial or tangential surfaces. Adhesives penetrate deeply into open fibers and vessels along the grain, so deeply that over penetration occurs when pressure is applied to end-grain surfaces. This is a primary reason why it is so difficult to form strong, load-bearing bond lines in butt joints. Across the grain, porosity is limited because of fewer pathways in which adhesive can flow (Forest Products Laboratory, 1999)

The porosity of hardwoods and softwoods, both as species groups and as species within a group, varies greatly, which dramatically affects the amount and direction of adhesive flow. Highly porous softwoods have fibre lumens that are interconnected by open pits. Pits are the small openings between fibres that permit lateral transfer of fluids in living trees. They form a complex capillary system that also allows adhesives to penetrate deeply, even in tangential and radial directions. The relatively large vessels in hardwoods have no end walls, so adhesive can penetrate indefinitely along the end grain. The remaining fibres have relatively few pits for lateral transfer of adhesive, except that hardwoods, have radially oriented rays that can allow excessive flow and over penetration (Forest Products Laboratory, 1999).

Questions and topics of R&D:

- a) *Is there an optimum between better strength of the wood substance and the penetration behaviour into the wood?*
- b) *How to measure real glue line strength and not only strength of the adjacent wood layers when wood failure occurs?*
- c) *Are different adhesives systems necessary/useful gluing wood species with different densities?*
- d) *The highest joint strength will be achieved when the adhesive has penetrated deeply enough into wood. Is the adequate depth of penetration the same for each type of adhesives and which penetration depth is enough?*

5.4 Moisture Content of Wood

Water occurs naturally in living trees - as free water in cell lumens and as absorbed water within the cell walls. Total water content of wood can range well above 200%, but when the free water is removed from cell lumens by drying, approximately 30% remains bound within the cells. Water has strong molecular attraction to wood, primarily through hydrogen bonding with hydroxyl groups of wood celluloses. Therefore, cell walls remain saturated with moisture (called the fiber saturation point) until the moisture content of the surrounding air falls below that of saturated cell walls. Actual moisture content at fiber saturation (roughly 30%) varies, depending on species, tree, temperature and pressure. This is the critical point at which wood begins to shrink. If wood dries below the fiber saturation point, then regains moisture, the wood will swell (Rowell 1984).

These dimensional changes differ with three principal directions, or grain directions in wood, that is, longitudinal, radial, and tangential, with intermediate changes varying with the angle between the principal directions. Longitudinal dimensional change along the grain is least and amounts to less than 1% in drying from fiber saturation point to oven dry. Dimensional change is greatest across the grain, but the amounts differ with the direction; dimensional change varies with and within species. As a rule of thumb, tangential dimensional change is about twice that of the radial direction; but again, there are variations by species (Rowell 1984).

For these reasons there are standards, which specify a maximum permitted difference between the moisture content of timber components at assembly and in service, and between the components to be joined at the time of assembly. Differences in the moisture content of pieces bonded together should be no greater than about 5% for lower density species or about 2% for higher density species.

As regards the humidity of the wood the best results are obtained by using wood which at the time of gluing is as far as possible the same as it will reach when exposed to the conditions in which it will be used, naturally taking into account the appropriate characteristics in relation to the application of the glue. The less the variations to which the wood is subjected by ambient changes the less is the possibility of developing defects in the structure of the wood itself and the product into which it is made (Bandel 1995).

For wood used in enclosed warm locations the best starting humidity would generally be between 8 and 12%. In enclosed, unheated conditions the humidity will depend on the external climate and can reach a higher value, depending on the latitude about 14-15%.

Products intended for use in external covered locations will reach a moisture content of 18%. Higher values may easily be reached if the wood is exposed to intemperate conditions.

5.4.1 Moisture Content of Wood in Bonding Process

The amount of moisture in wood combined with water in adhesive will greatly influence wetting, flow, penetration, and cure of aqueous wood adhesives. In general, these adhesives bond satisfactorily across moisture content levels ranging from 6% to 14% and even below and above this range when adhesives are formulated for specialized processing. The optimum moisture content range for bonding a specific adhesive is determined from practical experience and product performance. Aqueous adhesives tend to dry out when applied to wood below 6% moisture content. Wood absorbs water from the adhesive so quickly that adhesive flow and penetration into the wood is drastically inhibited, even under high pressure. Wood may become so dry below 3% that it temporarily resists wetting by the adhesive because insufficient water remains bound to the wood to establish intermolecular attraction forces with water in the adhesive (Forest Products Laboratory 1999).

When wood contains excess amounts of moisture, then the wood can absorb less water and adhesive. This leads to excessive adhesive mobility, followed by squeeze-out when pressure is applied. Control of moisture content is particularly critical to bonding in hot presses because excess

moisture increases adhesive mobility, followed by over penetration of the adhesive. Furthermore, high vapor pressure builds internally as water boils, and on release of platen pressure, sudden release of internal pressure actually separates laminates along the bond lines, called blows. Even if blows do not occur, excess moisture within thermosetting adhesives can prevent complete cross-linking with accompanying weakened adhesive film and bond. Although appropriate moisture content levels of wood for bonding by hot-press methods are well known, control of moisture content in bonding of wood materials is not easily achieved. After adhesive selection, the next important factor contributing to trouble-free service of adhesive bonds is control of wood moisture content before and during the bonding process. Moisture content strongly affects the final strength and durability of joint, development of surface checks in the wood and dimensional stability of the bonded assembly (Palardy 1989, Sellers 1990).

Determining the proper moisture content for bonding depends primarily on the amount of moisture that is contained in the wood and adhesive and whether or not the adhesive curing process involves heating. For example in bonding thicker boards at room temperature, proper drying of the wood mainly controls the desired final moisture content. When using a waterborne adhesive moisture content of wood will increase only 1% to 2%. However, in bonding veneer or other thin pieces pressed at room temperature, the moisture added by the adhesive itself may increase the moisture content of the dry wood as much as 45%, or well above the desired in-service level. Thus thickness of the lamellae, number of lamellae, density of the wood, water content of adhesive, quantity of adhesive spread and bonding process (hot pressing or cold pressing) all affect the cumulative moisture content of the wood. In hot pressing, a moderate amount of water is evaporating reducing the moisture content of the product when removed from the press. However, to minimize plastic flow of the hot and moist wood and prevent steam blisters or blows, the total moisture content of the assembly should not exceed 10% during hot pressing. Lumber with moisture content of 6% to 7%, assuming 1% to 2% will be added by aqueous adhesives, is satisfactory for cold pressing of furniture and interior millwork. Lumber being laminated for exterior use should contain 10% to 12% moisture before bonding. Moisture content of 3% to 5% is satisfactory in veneers at the time of hot pressing (Forest Products Laboratory 1999).

Moisture content of wood at the time of bonding has much to do with the final strength and durability of joints, development of checks in the wood, and dimensional stability of the bonded assembly. Large changes in the moisture content of the wood after bonding cause shrinking or swelling stresses that may seriously weaken both the wood and the joints, while causing warping, twisting, and other undesirable effects. It is generally unwise to bond green wood or wood at high moisture content, particularly high density hardwoods that have high coefficients of shrinkage, unless the end product is also at high moisture content (Rowell 1996).

Expanding this thought to a general rule, the wood should be dry enough so that, even if moisture is added in bonding, the moisture content is about the level desired for service.

The tendency today especially in board gluing, e.g. plywood or waferboard, is for bonding higher than normally moisture content veneers or particles. Advantages over conventional gluing methods are e.g. lower energy consumption or reduced dryer emissions. Problems to overcome are associated with excessive adhesive migration from the glue line and retardation of resin cure.

Steiner et al. (1993) have studied the bonding of high moisture content veneers with aqueous phenolic dispersions. The primary objective of the study was to improve curing speed and to reduce over penetration of adhesive into wood.

To succeed in bonding high moisture content wood with PF adhesive, the adhesive is required to have specific polymer properties that enhance cure and limit resin solubility in the glue line. Conventional liquid PF resins are limited by solubility requirements and viscosity restrictions to satisfy these requirements. Adhesives with improved moisture tolerance and bonding properties can be formulated from a two-phase, high molecular weight PF system and an advanced, dispersed phase resin, which is insoluble but swellable in a highly alkaline, aqueous solution. The dispersed system can be produced in a variety of ways, including combinations of acid precipitation, spray-drying and thermal treatment. After these resin systems were developed, one particular concern

was preventing over penetration of low molecular weight PF components from the soluble phase into the wood. Improved bonding performance of these PF-dispersion-resin-formulations with high MC wood could though be achieved.

Sellers et al. (1990) have researched the bonding of intermediate moisture content southern pine veneers (~ 9%) into plywood with phenol-formaldehyde adhesives containing one of three different fillers.

When attempting to bond high-moisture content veneers, the first problem to overcome is excess flow and penetration of the resin binder. Another bonding problem involves the slower cure of traditional plywood PF resins in high moisture environments. Yet another operational problem is the potential of having a wider range of veneer MC from very low to very high (within and among pieces of veneer), which requires the adhesive to be able to tolerate a wide MC range.

The following problems have been reported by plywood plants gluing at high MC: 1) panel compression losses 2) increased panel blows (ruptures) at the hot press and 3) buckling of panels that contain veneer sheets with very high MC (15% to 20%) and veneer sheets with very low MC (2% to 4%) in the same construction.

The extender / filler components of plywood adhesive mix have an important role in high MC bonding. In this research the fillers were pecan shell flour and two furfural-process residues. For the three fillers examined, pecan shell flour provided the most stable mix over a 24-hour period. The corncob-based furfural-process residue required a substantial increase in the predispersion resin amount to reach the desired initial mix viscosity. All the filler types made exterior-grade plywood (>85% wood failure) as defined by U.S. Product Standard PS 1-83. Panel MC out of the hot press (ex-press) averaged 5,6% (average of specimens from two panels). These panel MCs are typical of published results of bonded panels with intermediate MC veneers. Plywood bonded with the pecan shell flour mix yielded the least knife wear on plywood edges when compared to plywood bonded with the furfural-process residues. Since only the fillers were altered in the adhesive mixes, the wear at the glue lines is probably due to differing characteristics of the fillers.

Jablonski et al. (1998) studied gluing and properties of water resistant plywood produced from veneers (beech and pine) with moisture content of 15%. The glue was phenol formaldehyde adhesive. The quality of plywood fulfilled the requirements of EN 314-2 standard for class 3.

Palardy et al. (1989, 1990) have researched the bonding of waferboard and flakeboard in high moisture content and moderate temperature (HMMT) using diphenylmethane diisocyanate (MDI) adhesive. With the myriad of polyurethane and polyurea chemistries currently available, many pathways to material and process improvement are possible.

Aspen flakeboards were pressed at 99°C (210°F) and 25% MC using diphenylmethane diisocyanate (MDI) adhesive catalysed with a tertiary amine. Three adhesive levels (3,0, 5,5 and 8,0 percent) and three pressures were used. Press time was 9,5 to 10,5 minutes. At the 3,0 percent resin level, the high moisture, moderate temperature panels compared favourably to the control panels in flexural apparent modulus of elasticity (MOE) and thickness stability, but the modulus of rupture (MOR) and internal bond strength (IB) were less than the control group. The IB, MOR, and thickness stability of the high moisture, moderate temperature panels improved with increasing adhesive level. The high moisture, moderate temperature panels exhibited a more uniform vertical density profile than did the control panels. The results also suggests that HMMT pressing can potentially produce panels of superior thickness stability, but more research will be necessary to realize this goal.

Questions and topics of R&D:

- a) *A lot of work has been done when trying solve the problems concerning gluing of wood with different moisture content. The gluing of either high or low moisture content wood causes problems. Which parameters or which properties of a resin should be adjusted when gluing of wood of different moisture content.*

- b) *Which reasons exist for bad wettability of very dry wood: Too less water (see paragraph 1 in section 5.4.1.) or case hardening due to a stringent drying process?*

5.4.2 Effect of Moisture Content on Bonded Joint

Dimensional changes of wood that accompany changes in moisture content in air have broad ranging and significant consequences on performance of bonded joints. As wood in bonded assemblies swells and shrinks, stresses develop that can be great enough to rupture adhesive bond and wood. Ruptures may develop when adjacent pieces of wood in a bonded joint differ in grain direction and shrinkage coefficients, for example, radial grain bonded to tangential grain, or in the worst case, longitudinal grain bonded to either tangential or radial grain. Even if moisture content levels in adjacent pieces are equal, but changing, stresses could be severe. Moreover, if moisture content in one piece is at equilibrium with surrounding air, that is, stable, but the other piece with differing grain direction is shrinking as it approaches equilibrium moisture content (EMC), then resultant stresses would be compounded and almost sure to rupture either the adhesive bond or the wood, whichever is weaker. Some wood adhesives are elastic enough to yield to stresses so that fracture does not occur. Severe stresses on bond lines can be minimized by bonding pieces of wood with compatible grain directions of low shrinkage coefficients at a uniform moisture content equivalent to that which the bonded assembly will encounter in service (Rowell 1996).

The less the variations to which the wood is subjected by ambient changes the less is the possibility of developing defects in the structure of the wood itself and the product into which it is made (Rowell 1996). One of the main goal of the modification research of wood has been to minimize the shrinking and swelling properties of wood and in that way overcome the problem of moisture difference induced stresses. The price of modified wood material is higher than that of unmodified wood and so the use of it has been so far limited and can of course bring along new gluing problems. One method to solve the problems of induced stresses caused by moisture difference of wood is to develop adhesives and glue mixes so, that they can withstand those stresses, are elastic enough and at the same time give enough strength and durability for the glue line.

Questions and topics of R&D:

How can the problem of moisture difference induced stresses be diminished? How can the glue mix (type of adhesive, composition of the glue mix) help thereby?

5.5 Grain Orientation of Wood in the Glue Line

5.5.1 Swelling and Shrinking of Wood in Different Directions

Wood swells and shrinks in different ways along its three principal directions. The movement of wood and its behaviour are completely different depending on whether the moisture content is greater or less than the saturation point of the fibres (about 28 - 32%). For wood with a moisture content below saturation point of the fibres the variations of wood are greatest in a tangential direction, medium in a radial direction and negligible in the longitudinal direction (Bandel 1995).

For example beech, for every one per cent change in its moisture content shows a negligible change in the longitudinal direction, about 0,2% in the radial direction and 0,4% tangentially. The absorption and release of moisture takes place by hydrogen bonding between the hydroxyls of the polymers which constitute the wood and the atmospheric moisture.

Questions and topics of R&D:

How can the problem of moisture difference induced stresses be diminished? How can the glue mix (type of adhesive, composition of the glue mix) help thereby?

5.5.2 Influence of Grain Orientation of Wood on Penetration of Adhesive in Glue Line

In addition that swelling and shrinking of wood is different in different directions, penetration of adhesive into wood is varying along the three principal directions of wood (radial, tangential and longitudinal). Penetration of adhesive along grain (longitudinal direction) is many times greater than the rate of penetration of adhesive into other directions. A most extreme example of the penetration along grain occurs in a scarf joint (Furuno 1983).

In softwoods, flat grain surfaces in some species may be more effective than the edge-grained surfaces in the removal of liquids from the glue line because the structure of the wood rays and their weakness which results in open capillaries (checks) facilitates liquid movement in a radial direction. Edge-grain surfaces, on the other hand, though more free from fine surface checks, may be sealed against moisture migration because of the closure of the bordered pits (in heartwood) that are more abundant on the radial surface of the cell walls (Furuno 1983).

Hameed (1999) has researched the wettability of three wood species (Pine, Douglas fir and Larch) on the cross, radial and tangential section with water and various glues (UF-, PF-, MUPF- and PMDI-resins). Results have established that the wettability of sapwood is better than that of heartwood. In most cases, the tangential section in sapwood and heartwood was less wettable than radial and cross sections. Using alkaline phenolic resins, which cause wood to swell, wettability in the tangential direction was improved. Sernek (1999) has researched the penetration of liquid urea-formaldehyde adhesive into beech wood and did not get quite identical results. Penetration in the tangential direction was greater than in the radial direction. Beech contains thin latewood bands with fewer and smaller vessels, thus inhibiting radial penetration. Beech vessels have more pits in the radial surface than in the tangential surface, which could contribute to greater penetration in the tangential direction.

5.5.3 Influence of Grain Orientation of Wood on Strength of Bonded Joint

Sandberg (1997, 1998) has researched the influence of annual ring orientation on strength and dimensional changes during moisture variation in glued products. He has also researched the effect of star sawing on dimensional stability. As an anisotropic material wood swells and shrinks, and this takes place mainly across the fibre direction. For pine and spruce, it is usually assumed that the tangential movement is approximately twice as large as the radial movement. This means that

changes in shape appear as distortions and angular changes in the cross-section if the side surfaces of the wood are not parallel with the main direction of the wood. The importance of the annual ring orientation for moisture movement e.g. of furniture boards is a widely researched area. It has been stated that in order to obtain a dimensionally stable furniture board, it shall be constructed of wood with vertical annual rings, i.e. the annual rings shall be largely perpendicular to the surface of the board.

In Sandberg's research were prepared finger jointed boards either by using the same annual ring orientation in both pieces or by joining pieces with vertical and horizontal annual rings. Since the tangential shrinkage and swelling due to moisture movement was about twice as large as the radial shrinkage, non-uniform swelling occurs in the finger joint with crossed annual rings, i.e. in the finger jointed boards with both vertical and horizontal annual rings. In finger joints with a uniform annual ring orientation the swelling was uniform. As a result of non-uniform swelling and shrinkage in the joint when boards with different annual ring orientations are joined, stresses will develop in the joint. These stress variations may, ultimately, lead to a weakened joint. As for appearance, a uniform annual ring orientation is preferable.

The result of the dry-strength tests did not show any significant differences in failure strength between the two groups, i.e. finger jointed boards with the same annual ring orientation contra finger jointed boards with both vertical and horizontal annual rings.

The triangular profiles obtained in star sawing constitute a high-quality raw material for the manufacture of wood products. Triangular profiles have vertical annual rings and are without pith. Finger jointing and further gluing of triangular profiles into blocks results into profiles that are stable in shape.

Questions and topics of R&D:

- a) *Which influence by the grain angle exists on the bonding strength of a glue line?*
- b) *Might there be a distinct difference in wood failure due to different grain angles of the wood near the glue line?*

5.6 Temperature

Temperature has an effect alike in the bonding process and on the short- and long-term performance of bonded products.

To increase the process rates in the gluing of wooden lamellae it is essential to minimize the pressing time. The faster the curing speed of the glue, the shorter the pressing time needed for the gluing process. The curing speed of the glue can be increased by the use of accelerators or heat. With conventional heating methods it has been impossible to get heat into the glue line during pressing. Suomi-Lindberg et al (1999) have researched the use of preheating technology to heat the wood surface just before the gluing process so that the temperature in glue line is high already at the beginning of the pressing phase. In this study the preheating of wood surface was carried out by means of an IR-heater. By means of the preheating system of wood surface it is possible to reduce the several hours' pressing time very often used in wood gluing even down to 5 minutes. The pressing time needed depends also on the adhesive type. In order to apply the preheating technology in practise, the whole gluing process should be developed to a continuous working process (Forest Products Laboratory 1999).

In the short term, mechanical properties of wood, adhesives and bonded products vary in specific environments. In most cases, all properties decrease as the temperature and moisture levels increase. Strength and stiffness may return to their original levels if the yield points of the materials have not been exceeded while under load. The properties of rigid thermosetting adhesives like resorcinol formaldehyde (RF), phenol formaldehyde (PF), melamine formaldehyde (MF) and urea formaldehyde (UF) change less than do wood properties under equivalent temperature and moisture changes. Therefore, evaluating short-term performance of products made with these adhesives is simply a matter of testing bonds at room temperature in dry and wet conditions. Thermoplastic adhesives like casein, polyvinyl acetate (PVAc) and elastomers, whose properties change more rapidly than those of wood with changes in moisture and heat, are tested dry, dry after water soaking and after prolonged exposure to high humidity environments (Forest Products Laboratory 1999).

In the long term, wood adhesives and bonded products deteriorate at a rate determined by the levels of temperature, moisture and stress. Many adhesives in bonded products have decades of documented performance in many environments. Thus it is possible to predict with a high degree of certainty the long-term performance of similar products. Well-designed and well-made joints with any of the commonly used woodworking adhesives will retain their strength indefinitely if the moisture content of the wood does not exceed approximately 15% and if the temperature remains within the range of human comfort. However some adhesives deteriorate when exposed either intermittently or continuously to temperatures greater than 38 °C for long periods. Low temperature seems to have no significant effect on strength of bonded joints (Forest Products Journal 1999).

Products made with PF-, RF- and PRF-adhesives have proven to be more durable than wood when exposed to warm and humid environments, water, alternate wetting and drying and even temperatures sufficiently high to char wood. MUF-, MF- and UF-adhesives are less durable than wood when exposed to warm and humid environments.

5.7 Bonding Properties of Different Wood Materials

5.7.1 Bonding of Different Wood Species

Adhesion and hence strength of the glue bonds, is affected by the surface properties of the substrate. The surface characteristics of woods, that may affect glue bond formation are, as already mentioned earlier, quite complex. One of the factors that affect adhesion is the amount and type of extraneous components present in the wood. In many species there is a measurable difference between the gluing characteristics of sapwood and heartwood. When this occurs, it may be due to the nature and the amounts of extractives found in the latter. Extractives may interfere with the spread and penetrability of fluid adhesives and hence with the formation of the molecular bonds in the glue line (Deppe 1995).

Tropical woods have come for use in large quantity. Gluing difficulties have often been experienced when some tropical woods such as Kapur etc. have been used in adhesive joint composites. And although glue bond quality and durability can be affected in many ways, such as density, porosity and smooth surface of the adherend, the presence of the wood extractives including the inorganic components is one of the reason for the bonding problems. In pine the high resin content may sometimes create problems in the gluing process, which is due in particular to the fatty oil contents (Deppe, 1995).

Removal of extractives is the simplest way of minimizing their negative effects on bonding. A number of studies have been made regarding countermeasures to remove them at least from the wood's surface before bonding to improve the bonding strength. Solvent extraction is an effective method but a commercially expensive process. Also methods to improve the bonding strength without directly removing these substances has developed (Moredo 1998 and Sakata 1998).

Boehme et al (1996) explains, that a material characteristic dictated by wood structure, wood moisture content, wood density and wood extractives is the water absorption ability. Assuming equivalent moisture contents of the wood species, the water absorption velocity varies among wood species and is affected by grain direction. A slow water sorption velocity on a particular wood type allows more open-air storage time prior to pressing and affects pressing time. In addition, the adhesion quality depends upon the mechanical bonding of the glue with the wood particles. He points out, that little has been reported so far about the water sorption differences of native European and tropical wood species. Since the water absorption characteristics is of utmost importance for the adhesion quality, e.g. it determines the open and press times in the gluing process, one of the objectives of his study was to obtain values for water sorption for representative variety of native European and tropical wood species.

The water absorption ability on a variety of 40 representative tropical and native European wood species was researched. A tendency that wood species with higher water absorption coefficient have a low wood density can be presumed, but no statistical proof for this conclusion can be given. Differences in water absorption ability may depend strongly upon the wood extractives of the individual wood species, since interfacial forces between wood and water are regulated by individual wood type. The relatively oily species of Niangon possess a significantly lower water absorption coefficient compared to samples of the same wood species with a lesser amount in oily compounds.

The t_{50} -value explains the time required for individual wood species to absorb 50g of water. In the gluing process about this amount of water has to migrate from the PVAC-glues into wood in order to guarantee good adhesion or gluability. Comparing the t_{50} -values, it is worthwhile to note the differences between wood species. Native European wood species, e.g. beech proved to possess t_{50} -value less than 10 minutes. In contrast, western red cedar, a common North American wood type, had a t_{50} value of 10 hours. Other native European wood species showed t_{50} -values of 20 minutes and under, whereas this value for North American wood species lies above 30 minutes.

The tropical wood samples exhibited significant differences among species: t_{50} -values of 20 minutes and under were obtained for niangon. Whereas in contrast, water sorption times around 1 hour were obtained for oily niangon.

Quite remarkable observations in the studies were the variations among individual wood species in their t_{50} -values. These variations indicate the risk in the gluing process with these wood species.

A lot of work has been made to research the effect of extractive removal on adhesion and wettability of tropical woods. In Chen's (1970) research machined wood surfaces of eight tropical species were treated with a 10% solution of sodium hydroxide, acetone, and alcohol-benzene respectively. After reconditioning wood blocks were glued with UF- and RF-resins. Untreated wood blocks were glued for comparison. Extractive content and pH determinations were made and wettability was obtained for each sample. Adhesive joint strength was improved by all treatments in all but one species. In the case of the 10% solutions of sodium hydroxide, some species were affected more by one treatment than the other without regard for the adhesive used. Extractive removal treatment improved wettability and increased pH of the wood in all species tested. A positive linear correlation existed between wettability and joint strength of blocks glued with urea, however no such correlation existed for blocks glued with resorcinol. Roffael (1974) got identical results when gluing of oak of different ages. Particles of old oak particles were found to be more difficult to bond with alkaline phenolic-formaldehyde (PF)-resins than those of young oak particles. After extraction with water, only small differences between young and old oak particles were detectable as regards the bonding behaviour towards alkaline PF-resins. Extraction with 1N sodium carbonate instead of water causes a further improvement in the gluability of oak, when using PF-resins. After extraction with this reagent no significant differences in the bonding behaviour between young and old oak could be found.

Despite of the gluing difficulties, the many good properties or the need of use of the less used wood species and fast-growing plantation timbers has increased the interest for these wood materials. This has further contributed to the need to develop new adhesives and gluing techniques for these non-common wood materials.

Questions and topics of R&D:

- a) *In which cases could it be senseful not only to choose the proper adhesive system, but also the proper wood species?*
- b) *Which properties of the hardened glue line or of the assembly itself are determined mainly by the wood species?*

5.7.2 Bonding of Preservative-Treated Wood (fire-retardant treated)

The advent of durable adhesives that will outlast wood itself under severe conditions has made it possible to bond wood treated with wood preservatives and fire retardants. Experiments have shown that many types of preservative-treated lumber can be bonded with phenol-resorcinol formaldehyde (PRF), resorcinol formaldehyde (RF) and melamine formaldehyde (MF) under properly controlled bonding conditions. But a lot of differing results about the gluability of treated wood material also exist. It is usually necessary to control bonding conditions more carefully when bonding treated wood in comparison with untreated wood of the same species; it may also be desirable to use a somewhat higher curing temperature or a longer curing period with treated wood.

The acidic nature of some waterborne salt preservatives can hinder the cure of neutral- or alkaline-curing adhesives like RF or PRF. Research has shown improved success in bonding wood and plywood treated with these salts by washing the surfaces to be bonded with a 10 percent caustic solution and redrying before bonding.

Vick. et al. (1990, 1990) have researched the gluing of preservative treated wood with PF-adhesive. Four waterborne emulsion preservatives and waterborne salt preservative, ammoniacal copper arsenate (ACA), were tested for their compatibility with phenol-formaldehyde (PF) adhesive. Aspen veneers were treated with preservatives and then bonded with PF-adhesive. Effectiveness of

adhesion was determined by measuring shear strength and wood failure of bonds while saturated with water. Preservative type, retention level, and length of assembly time significantly affected the durability of bonds. Generally, wood failure decreased as retention time increased. Vick, et al (1992,1995) have made a lot of research to improve the adhesion between preservative treated wood and adhesives. A new hydroxymethylated resorcinol coupling agent (HMR), when used as a dilute aqueous primer on lumber surfaces before bonding, physicochemically couples phenol resorcinol-formaldehyde (PRF) adhesives to lumber surfaces of CCA-treated southern pine. When lumber surfaces were primed before bonding with a 5% aqueous solution of the HMR coupling agent, PRF adhesives met the 5% maximum delamination requirement of ASTM 2559. Vick et al. (1997) have stated that MUF and MF-adhesives have the same adhesion problems with preservative treated wood as above PRF-adhesive. By the use of HMR-coupling agent it appears that properly formulated MUF and MF adhesives could meet requirements of the qualifying standard ASTM D2559 on HMR-primed CCA-treated wood.

According to the Vick's results (1998) HMR-coupling agent can be also used to increase the durability of epoxy bonds to wood. Epoxy adhesives develop strong bonds to wood, but they lack the structural durability to withstand the severe stresses from repeated water soaking and drying. HMR physicochemically couples to both epoxy adhesive and lignocelluloses of wood to produce bonds that are extraordinary resistant to delamination.

Sellers et al. (1997) have researched the bonding of three adhesive mix types for chromated copper arsenate (CCA)-treated lumber for possible glulam industry application. The adhesives included commercial resorcinol-formaldehyde (RF) and emulsion-isocyanate (EPI) adhesives and a laboratory-modified resorcinol (RF) adhesive mixture. The two RF-adhesive systems provided excellent block shear and delamination test results according to the standards from the American Institute of Timber Construction for routine production inspection of approved adhesives. The delamination allowed in glulam production using southern pine lumber is 5% of the glue line after one cycle or 10% after two cycles. The emulsion-isocyanate adhesive failed the first cycle with 5,9% delamination percent, had 7,9 percent delamination after two cycles, and 11,7 percent delamination after three cycles. So the glulams of CCA-treated lumber bonded with emulsion-isocyanate adhesive passed the dry block shear test requirement, but failed the standard delamination tests.

Dimri et al. (1993) have researched effect of preservative treatment of veneers on the glue bond quality. Rotary cut, dry veneers of *Chukrasia tabularis* and *Grevillea robusta* were dipped in 5% solution of preservatives: ACC, CCA, CCB, boric acid and borax. Treated veneers were allowed to dry to a moisture content of about 8-10 percent and glued with PF resin. Treated plywood was tested in dry and wet state. Statistical analysis of data reveal that for both of the species no adverse effect on glue bond strength of plywood was observed due to CCB and ACC treatment. The effect of boric acid and borax was observed significantly adverse in both species whereas the effect of CCA differs from one species to another on glue bond strength of plywood.

Wood materials are most often glued after treatments with preservatives. Another possibility could be to carry out the gluing process first and then treat glued wood samples. Demands for adhesives in that case are not known.

Questions and topics of R&D:

Which is the better way: impregnation of woods first and then gluing or treating the assembly after gluing and pressing?

5.7.3 Bonding of Modified Wood

There are several national and international research projects where wood properties are modified by means of various physical, mechanical and chemical treatments. Chemical modification processes of wood are primarily developed in order to obtain dimensional stabilisation. Improvements in physical and mechanical properties, increased durability against physical, chemical, and biological degradation have also been objectives in wood modification. The

treatments can range from application of heat to impregnation with monomers for in situ polymerisation or alteration of chemical composition of wood by chemical reactions. Modification of wood has offered possibilities to tailor wood properties and to develop new wood products with improved performance.

Rowell (1995, 1996) has researched the adhesion properties of chemically modified wood materials. The mechanism of adhesion is an important factor in failure analysis in composites. Some adhesives work due to a physical entanglement of the resin into the wood whereas others require a free hydroxyl group on one of the cell wall polymers of wood to participate in a chemical reaction with resin. Substitution of hydroxyl groups has shown to decrease adhesion between chemically modified veneers due to the loss of hydroxyl functionality. Resins that are water-soluble and depend on a hydrophilic substrate for penetration will be less efficient in chemically modified wood due to the decreased hydrophilic nature of the cell wall resulting from modification.

Many different types of adhesives have been studied in the gluing of chemically modified wood, especially acetylated wood. The level of acetylation reduced the adhesion of 18 thermoplastic and thermosetting adhesives, some to a minor degree and others to a severe degree. Many adhesives were capable of strong and durable bonds at a low level of acetylation (8WPG) but not at higher levels (14-20 WPG). Most adhesives contained polar polymers, and all but four were aqueous systems, so that their adhesion was diminished in proportion to the presence of the non-polar and hydrophobic acetate groups in acetylated wood. Thermosetting adhesives were capable of high shear strength in the dry condition. With the exception of an acid-catalysed phenol formaldehyde adhesive, thermosetting adhesives that were hot-pressed became mobile and tended to over penetrate to wood because of the limited capacity of the acetylated wood to absorb water from the curing bond line. The abundance of hydroxyl groups in a highly reactive resorcinol adhesive permitted excellent adhesion at room temperature despite the limited availability of hydroxyl groups in acetylated wood.

An emulsion polymer-isocyanate adhesive, a cross linked polyvinyl acetate adhesive, a resorcinol-formaldehyde adhesive (RF), a phenol-resorcinol-formaldehyde adhesive (PRF) developed bonds of high shear strength and wood failure at all levels of acetylation in the dry condition. Only cold-setting RF- and a PRF-adhesives developed bonds of high strength and maximum wood failure at all levels of acetylation when tested in a water-saturated condition.

Vick et al. (1993) have researched the bonding properties of a resorcinol-formaldehyde (RF), a phenol-resorcinol-formaldehyde (PRF), a cross linking polyvinyl acetate (PVAc) and an emulsion polymer-isocyanate (EPI) adhesive in laminates of acetylated and unmodified Scandinavian pine (*Pinus silvestris* L.) and spruce (*Picea abies* Karst). The effects of different degrees of acetylation in adjacent lamellae were also examined. The effectiveness of adhesion was determined by measuring delamination after three cycles of vacuum-pressure soaking in water and drying, and by measuring shear strength and wood failure in dry and water-saturated conditions. Acetylation stabilized laminates so that essentially no stress fracturing developed in the wood during severe cyclic delamination tests. Bonds to acetylated and unmodified wood with RF and PRF adhesives resisted delamination well, whether adjacent lamellae were of equal or unequal degrees of acetylation. Acetylation affected adhesion of both adhesives as indicated by lower percentages of wood failure after water saturation. The PVAc adhesive also resisted delamination well in acetylated wood so long as individual lamellae had equal acetyl content. Acetylated laminates with PVAc effectively resisted stress fracturing near bond lines and within the wood, but the unmodified laminates fractured severely. The EPI adhesive bonded the unmodified laminates so well that no delamination and remarkably stress fracturing developed during cyclic delamination tests. Acetylation affected adhesion of the EPI adhesive as indicated by low wood failure in wet shear tests; however, shear strength and wood failure were high in acetylated wood in the dry condition.

Chowdhury et al. (1999) has researched the effect of acetylation of wood on the shear strength development kinetics of phenolic resin-to-treated wood bonds. At the early stages of cure, bonds formed between acetylated pieces were always weaker than those formed between untreated control pieces. Even the modest levels of acetylation affect the earliest stages of bonding, but these

effects decrease when bonds attain higher strength. This finding is consistent with the hypothesis that adhesion depends only on surface modification and because surface modification may not vary with higher bulk treatment levels, the bonding level does not change.

Although acetylation does have some effects on the curing rates of adhesives and their final strengths, it may well prove useful to acetylate materials used in wood-based composites in order to reduce the hygroscopicity and improve dimensional stability and bioresistance of finished panels.

Lin et al. (1993) has researched effects of dimensional stabilization treatment (DST) and various chemical surface extraction methods on the wettability, gluability and bond durability of three wood species (red oak, Ramin and rubber wood). Treatment agents were linseed oil, oil-based sealer, nitrocellulose lacquer sealer and PEG 1000. From the investigation of the effect of DST on gluability, results show that epoxy adhesive is the best choice for all treated wood surfaces both in gluability and wettability. Although bonded members that have been treated with oil-based agents have less wood failure, their gluing properties can be further improved by extracting them with 10 percent sodium hydroxide, and either, 5 percent sodium hydroxide or methanol, respectively.

Many different types of adhesives have been studied with different types of modified wood materials, but still the knowledge of gluing of modified wood materials is deficient, especially of heat-treated wood. For the wider use of these new modified wood materials it is essential that the gluing of these materials will be successful.

Questions and topics of R&D:

- a) *Is the bonding strength usually lower or higher using modified wood?*
- b) *Which modifications could increase bonding strength?*
- c) *Which bonding technology must be applied gluing modified wood surfaces?*

5.7.4 Activation / Preparation of Wood Surfaces for Gluing

Back's (1991) activation of wood surface refers to the process of increasing bonding efficiency between the wood polymer chains and adhesive. This increase may be achieved by the addition of small amounts of reactive chemicals or by the application of radiation energy before spreading the adhesive. Part of the process of activation relates to the creation of reactive groups, primarily in the lignin of wood and to a lesser extent in the cellulose polymers. Another part relates to the reactivation of aged wood surfaces by oxidizing the layers of oleophilic extractives, more or less removing it. Bondability is then promoted by improved penetration of the adhesive and by increasing the adhesive contact area.

Balfas (1994) has studied the effect of surface activation on wettability and glue bond strength of regrowth karri and jarrah by using of lithium (LiOH) and sodium (NaOH) hydroxides. Surface activation with NaOH modifies the wood surface by reducing surface tension of wood surface removing extractives and increasing the ability of the adhesive to dissolve extractive materials on the wood surface. However, this activation may swell the wood surface extensively, or even disintegrate it to some extent and cleave some of the hydrogen bonds of cellulose, which results in high dry shear strength with no water resistance. This indicates the beneficial effect of NaOH treatment to improve the performance of glued timber joint in interior uses, but not for outdoor uses. Surface treatment using LiOH gives identical modified surface as NaOH-treatment.

In gluing tests the wood blocks were treated with three different concentrations of each hydroxide prior to gluing with resorcinol formaldehyde (RF) resin. Both lithium and sodium hydroxides significantly increased wettability and dry shear strength of the two regrowth eucalypts. Lithium hydroxide gave higher improvement in both dry and wet bond strengths than sodium hydroxide (NaOH). Treatment using 0,5 M lithium hydroxide was the most effective method to protect strength loss on wetting.

Belfas (1993) researched the effect of sanding on wettability and shear strength when bonding Karri and Jarrah with RF-adhesive. The improvements in wettability and bonding strength obtained with the coarsest abrasive treatment could be due to two effects. Firstly, removal of the most

contaminated (outer) layer of wood surface by sanding would reduce the effect of extractives and other inactivating agents and hence increase wettability. Secondly, abrasion caused by sanding could provide more area for contact at the liquid wood interface, hence giving higher rates of spreading and penetration of adhesive.

Nussbaum (1993) has researched the effects of oxidative activation of some different wood surfaces by flame treatment. Flame treatment markedly increased the wettability. No improvement in glue adhesion was discerned for a water-borne PVAc-glue.

Stehr (1999) has tested the effect of removing the layer of damaged cells - the mechanical weak boundary layer (MWBL)- from wood surface. The goal has been to determine whether the glue joint strength is influenced by the mechanical weak boundary layer and to show how the laser wavelength affects the glue joint strength. The wood surfaces have been ablated using different types of lasers of different wavelengths. The statistical evaluation of the results shows however no great differences between glue joints made of ablated and glue joints made of unablated wood surfaces. Nor are there any real differences between the different lasers and different wavelengths. This may be because there are indeed no differences between ablated and unablated surfaces, in terms of a mechanical weak boundary layer, but it may also be due to cracks, which occurred, in the wood specimens. But in the gluing tests it was also possible that the glue itself was too weak. An ESEM (Environmental Scanning Electron Microscope)-analysis showed that fracture occurred primarily in the glue line and not in the boundary layer.

Bonding of wood samples without the use of adhesive has for long been one of the goals of the research work concerning activation processes of wood surfaces. In principle the idea is good because wood itself contains a lot of compounds, which can act as glue. But really a lot of research is still needed to achieve that goal.

5.7.5 Bonding of Wet Wood

Parker et al. (1991) have patented a method for joining pieces of unseasoned or dried wood, by finger jointing or by other gluing techniques. The wood may have a moisture content above the fibre saturation point of the wood, and as high as 50% or 100% or higher moisture content. An adhesive having sufficiently high molecular weight or viscosity to avoid adhesive degradation or migration from moisture in the wood during forming and curing of the joint is employed. Optionally a cure promoter or chemical, which increases the rate of cure of the adhesive, may be used. Preferred adhesives are formaldehyde-based adhesives. Preferred cure promoter or chemicals are ammonia or amine compounds, organic acids including low molecular weight carboxylic acid.

Liu (1986) has researched the gluing of high moisture content wood with RF-adhesives. RF-adhesive with 56% solid content could bond well with wood containing moisture below 25%, but above 40% its bonding strength and wood failure were significantly decreased, especially for high specific gravity wood. By adding hardeners and extending the spreading time, the bonding strength for China fir improved, but it has no significant effect when gluing of Hemlock. To increase the solid content of resin or extent synthesis time of the resin did not significantly affect on their bonding properties. By treating of wood surfaces with heat just before gluing process could improve the bonding properties of high moisture content wood when gluing with RF-adhesives. A general rule is that the higher the moisture content of wood the slower the bonding strength developed in gluing process.

The Greenweld technology enables structural grade products to be made from wood with any level of moisture content, at almost any temperature. It provides a very robust system enabling further processing of the timber "immediately" after finger jointing (in real terms in 10 minutes) and achieves fast curing without the need for heat or RF treatment. It should be noted that this quick setting characteristic could offer substantial improvement for the speed of processing dry timber as well.

The Greenweld process technology for finger-jointing and laminating has been running commercially for up five years in various countries around the world. It has been proven on most of the leading brands of finger-jointing equipment and on some thirteen different species.

Conventional gluing processes require that the wood material when used in gluing processes has been dried to a moisture content below fibre saturation point before joining and preferably at around 12% moisture content to achieve the required strength and reliability. Despite that gluing of unseasoned wood has many advantages, there still exist a lot of open questions in gluing of wet or unseasoned wood.

Questions and topics of R&D:

- a) *Which type of adhesives are most suitable for gluing of wet wood or how to modify gluing processes in order to facilitate gluing of wet wood.*
- b) *How to overcome the problem with higher formaldehyde emissions when gluing of veneers of high moisture content.*
- c) *Are there differences in bonding strength when gluing either seasoned or unseasoned wood.*

5.8 Summary

The function and properties of wood products are greatly influenced by the natural properties of the wood and how these are used in the produce concerned. There are four main properties, which are characteristic to wood. It is an anisotropic and heterogeneous material, a material with great variability and a material with pronounced hygroscopicity. All this is related to the fact that the wood material is built up in an optimum way to meet the specific requirements of the living tree. When the log is divided into planks and boards to be used in different products, complications can arise if one does not use the available knowledge. By starting from an understanding of the properties of the wood material, it is in many cases possible to manufacture a product, which meets the specific demands of different uses. For wood, such requirements are often related to accuracy in measurements and geometry, crack-freeness and controlled movement during moisture changes.

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6 Influence of the Adhesive on the Bonding Process and the Properties of Wooden Products

M. Dunky

6.1 Introduction

For the production of wood based panels various adhesives are in use like aminoplastic resins (UF, MUF), phenolic resins (PF) or isocyanate (PMDI). The proper choice of the adhesive depends on the required properties of the wood based panels, on the working conditions during the production as well as often on the costs for the adhesive system; this not only means the net price of the adhesive but also the costs of the gluing system including glue spread factor, capacity of the line and other parameters. Also environmental aspects and national requirements can have a significant influence on the choice of the adhesive system.

6.2 Basic Parameters

Table 6.1 evaluates the three adhesives UF, PF and PMDI concerning to various parameters.

Table 6.1: Judgement of the three adhesive types UF, PF and PMDI concerning various parameters (according to Hsu 1993)

Property	UF	PF	PMDI
Price	low	medium	high
Necessary hardening temperature	low	high	low
Susceptibility against wood species	high	low	low
Efficiency	low	medium to high	high
Manipulation	easy	easy	difficult
Resistance against boiling water	no	high	high

6.2.1 Viscosity

The viscosity of a glue mix is determined by the viscosity of the resin (mainly depending on the degree of condensation and the solid content) and the composition of the glue mix. If the viscosity or the degree of condensation, resp., of the resin is too low, a big portion of the resin might penetrate into the wood, causing a starved glue line. In such a case no glue line and hence no bonding strength can be formed. At a too high viscosity on the other side there might lack a proper wetting of the non-glued wood surface with no or a very low penetration into the wood surface and hence no mechanical locking. Also in these cases a low bonding strength will be caused.

Beside of the viscosity of the glue resin itself also the viscosity of the glue mix plays an important role. A higher dilution of the resin gives a higher volume to be spread and with this a better distribution of the resin on the particles or fibres with hence better bonding strength (Kollmann et al. 1955). This also gives the chance to save costs.

Questions and topics of R&D:

- a) How to determine the proper viscosity for a special gluing process?
- b) How to easily measure the penetration behaviour into the wood surface?
- c) How can the viscosity be measured during the hot press cycle?
- d) How does the viscosity of an adhesive change after the application onto the wood surface?

6.2.2 Flow Behaviour

The flow ability of a resin depends on its viscosity, the solid content as well as the changes in the viscosity at elevated temperatures in the hardening glue line. A low flow ability causes a poor penetration of the resin into the wood surface and low bonding strengths. A too high flow ability on the other side leads to an over penetration of the resin into the wood and to a starved glue line. Flow ability and hardening run in opposite directions during the hot press process. Main parameters for the flow behaviour are the molar mass distribution and the concentration on reactive sites on the molecules.

Questions and topics of R&D:

- a) How to determine the proper flowing ability of a resin?
- b) How to influence the flowing ability on a molecular level?

6.2.3 Surface Tension and Wetting Behaviour

Aqueous glue resins behave similar to water concerning surface tension and wetting behaviour. The higher the molar ratio F/U the lower is the surface tension. The surface tension can be decreased adding a detergent or few percent of a PVAc-adhesive (Scheikl and Dunky 1996 b). The wetting behaviour also depends strongly on the molecular composition of an UF-resin (Scheikl and Dunky 1996 b). The proper wetting of the wood surface is the precondition, that high adhesion strengths can be formed in the interface layer between resin and wood surface.

6.2.4 Reactivity

Target of the development of glue resins is to achieve reactivities as high as possible, however under consideration of e.g. the storage stability of the resin or the pot life of the glue mix. The reactivity of a glue resin and of a glue mix is determined by various parameters:

- Type of glue resin
- Composition and cooking procedure of the resin
- Type and amount of hardeners
- Additives: might accelerate or retard
- Hardening temperature
- Properties of the wood surfaces.

6.2.5 Liquid and Powder Resins

In the production of particleboards and MDF only liquid resins are used; in the OSB-production in Europe rather liquid resins are used, in North America rather powder resins. Table 6.2 summarizes the advantages and disadvantages of liquid and powder resins.

Table 6.2: Advantages and disadvantages of liquid and powder resins

Type of resin	advantages	Disadvantages
Liquid resin	low costs; no molestation by dust	short storage stability; higher necessary gluing factor because of the poorer distribution;
Powder resins	lower gluing factor; better resin distribution on OSB-strands; less contamination of OSB-gluing drums; longer storage stability; quicker gelation: no evaporation of water necessary; lower costs for overseas transport	higher price due to costs for the spray drying and packaging; danger of molestation by dust

6.2.6 Combination of Various Adhesives

For the purpose of special effects combinations of adhesives or glue resins might be used, e.g.:

- Addition of PVAc to UF-resins in order to get a better wetting of the wood surface (Scheikl and Dunky 1996 b) and a more elastic glue line (Dunky and Schörgmaier 1995)
- UF/MUF + PMDI (see section 0.c, 0.b, 0.e and 2.2.1.5)
- Combination of adhesives in the particleboard or OSB-production:
- Core layer: PMDI
- Face layer: UF/MUF-resin or PF-resin
- Production of a MUF-resin by mixing an UF- and a MF-resin or an UF-resin with a MF-powder resin.

6.3 Aminoplastic Resins

6.3.1 Influence of the Molar Ratios F/U and F/(NH₂)₂

Table 6.3 summarizes the various influences of the molar ratio on various properties of wood based panels.

Table 6.3: Influences of the molar ratio on various properties of UF-bonded wood based panels

Decreasing the molar ratio leads to:	
A decrease of	the formaldehyde emission during the production of the wood based panels; the subsequent formaldehyde emission; the mechanical properties; the degree of hardening
An increase of	the thickness swelling and water absorption; the susceptibility for hydrolysis.

In table 6.4 and 6.5 an overview on the actual molar ratios of UF- and of MUF-resins are given.

Table 6.4: Molar ratios F/U and F/(NH₂)₂, resp., of the pure and melamine fortified UF-resins currently in use in the wood based panels industry (see also section 2.1.1.6)

1,55 to 1,85	classical plywood-UF-resin, also cold setting; use is only possible with special hardeners and additives, e.g. melamine containing glue mixes for an enhanced water resistance.
1,30 to 1,60	UF-plywood resin; use for interior boards without special requirements concerning a water resistance; in order to produce panels with low subsequent formaldehyde emission, the addition of formaldehyde catchers is necessary.
1,20 to 1,30	plywood or furniture resin with low content of formaldehyde; also without the addition of catchers products with a low subsequent formaldehyde emission can be produced.
1,00 to 1,10	E1-particleboard and E1-MDF-resins; especially in the MDF-production further addition of catchers is necessary. In case modification or fortification with melamine.
Below 1,0	special glue resins for boards with a very low formaldehyde emission; in most cases modified or fortified with melamine.

Table 6.5: Molar ratios F/(NH₂)₂ of MUF/MUPF-resins currently in use in the wood based panels industry

1,20 to 1,35	resins for water resistant plywood, in case addition of a formaldehyde catcher.
1,08 to 1,15	E1-particleboard- and E1-MDF-resin for water resistant boards (EN 312-5 and 312-7). For boards according to option 1 (V313-cycle test) MUF-resins can be used; for boards according to option 2 (V100-boiling test) MUPF with approval are necessary. In case, especially for the MDF-production, formaldehyde catchers are added.
1,00 to 1,08	similar to E1-resins above
Below 1,00	special resins for boards with a very low subsequent formaldehyde emission (Lehmann 1997, Wolf 1997)

The following topics will be covered by the State of the art-report of WG2:

- Formaldehyde emission during the production of wood based panels
- Subsequent formaldehyde emission
- Methods for production of wood based panels with low subsequent formaldehyde emission
- Regulations concerning the subsequent formaldehyde emission.

Questions and topics of R&D:

- a) *How to improve the properties of resins with a very low content of formaldehyde, concerning:*
- reactivity

- *storage stability*
- b) *How to optimise (minimize) the content of melamine in a resin for given application requirements?*

6.3.2 Influence of the Molar Mass Distribution (degree of condensation)

Surprisingly there are only few and partly rather old papers describing the influences of the degree of condensation of aminoplastic resins. The overall picture of this topic is not really clear, the results presented in the literature are not unanimous at all.

The influence of the degree of condensation preferably is given during the application and the hardening reaction. The reactivity of an aminoplastic resin seems to be independent of its viscosity (degree of condensation), if the same molar ratio is given. The wetting behaviour and the penetration into the wood surface in dependence of the degree of condensation have been already mentioned in section 6.2.3 above.

Ferg (1992) mentioned, that the bonding strength increases with the degree of condensation of the applied UF-resin. The higher molar masses (higher viscous portions) give a more stable glue line and determine the cohesion properties (Pizzi 1983). Also Rice (1965) and Nakarai and Watanabe (1962) reported, that the resistance of a bond line against watering and redrying increased with the viscosity of the resin. The reason again might be, that resins with advanced degree of condensation remain to a bigger part in the glue line, avoiding starving of the bonding. Rice (1965) found an increase of the thickness of the glue line with an increased viscosity of the resin: the higher the viscosity of the resin, the less is the penetration into the wood substance (Scheikl and Dunky 1996 a, 1998). Also it must be taken into consideration, that (i) the wetting ability of a resin decreases with the degree of condensation (Scheikl und Dunky 1996 b) and that (ii) the strength and stability of a glue line decreases with increased thickness (Neusser and Schall 1972 a). Another point of consideration is the press temperature: at higher temperatures the viscosity of the resin drops, before the hardening reaction again leads to an increase of the viscosity up to the hardened network. With this temporarily lower viscosity the wetting behaviour improves significantly.

According to Sodhi (1957 a) the bonding strength decreases with longer waiting time for the glue mix (including the hardener) prior to application. Again the already started hardening reaction and therefore the increase in molar masses seem to worsen the wetting behaviour and the penetration into the wood surface.

Questions and topics of R&D:

- a) *How to clarify better the influence of the degree of condensation on the properties of the bond strength?*
- b) *How to measure the influence of the temperature on the behaviour of the resin in the glue line?*

6.3.3 Correlations Between the Composition of the Resin and the Properties of the Wood Based Panels

The basic aim of such experiments is the prediction of the properties of the wood based panels based on the composition and the properties of the resins used. For this purpose various structural components are determined by means of NMR and the ratios of the amounts of the various structural components, e.g.

- (i) For UF-resins:
 - free urea related to total urea
 - methylene bridges with cross linking related to total sum of methylene bridges
 - sum of methylene bridges in relation to sum of methylol groups
- (ii) For MF-resins:
 - not reacted melamine to monosubstituted melamine
 - not reacted melamine to total melamine

- methylene bridges related to methylol groups
- degree of branching: number of branching sites at methylene bridges related to total number of bondings at methylene bridges

(iii) For MUF-resins:

- sum of not reacted melamine and urea to sum of substituted melamine and urea
- methylene bridges related to methylol groups or to the sum of methylene bridges and methylol groups are calculated and correlated to various properties of the wood based panels, e.g.
 - internal bond
 - subsequent formaldehyde emission.

Various papers in the chemical literature describe examples of such correlations:

UF-resins: Ferg (1992), Ferg et al. (1993 a+b)

MF-resins: Mercer and Pizzi (1996 b)

MUF-resins: Mercer and Pizzi (1996 a), Panamgama and Pizzi (1996).

For certain boards, some good correlations exist. However, it must be assumed, that a general correlation for various resins and various panels will not exist and that may be other correlation equations must be used. Nevertheless, these results are very important, because they show that at least for a special combination of resin type and board type correlations exist at all. Furthermore it can be assumed, that the various parameters as mentioned above also will be the decisive parameter for other combinations, even the numbers within the individual equations might differ. However, it also must be considered, that the range of molar ratio under investigation in the papers mentioned above is rather broad. At the moment it is not possible to use these equations for predictions within narrow ranges of the molar ratio, e.g. the usual range of an E1-UF-resin with F/U = approx. 1,03 to 1,10. It also will have to be shown, how different cooking procedures at the same molar ratio can be included in these correlation equations.

Questions and topics of R&D:

- a) Are there commonly valid correlation equations valid for all types of UF-resins and for all types of boards?*
- b) How to improve the accuracy of this correlation, in order to get accurate correlations also within narrow ranges of the molar ratio?*
- c) How can be different cooking procedures at the same molar ratio (same overall composition) of the resin being described?*

6.4 Phenolic Glue Resins

Phenolic glue resins usually are produced under alkaline conditions with a surplus of formaldehyde. The characterisation of phenolic glue resins is done in similar way to all other condensation resins:

- Molar ratio of the main components: F/P/NaOH or F/P or NaOH/P
- Composition of the resins, based on the liquid form of delivery
- Degree of condensation, molar mass distribution and molar mass averages
- Content of reactive sites and functional groups and their distribution in the resin, type of bridges between the aromatic rings of the phenol molecule, branching sites and others.

6.4.1 Resin Content and Solid Contents, Moisture Content of the Glued Particles

The solid content of PF-glue resins usually is in the range of 45 - 48%, urea modified phenolic resins (PUF) are higher concentrated (55- 60%), all values based on the liquid form of delivery and measured as usually done at 120 deg C for 2 hours. Depending on the content of alkaline the pure resin content (phenolic resin solid content) in a phenolic glue resin is only 40%. At a same gluing factor as with UF-resins, the moisture content of PF-glued particles therefore is distinct higher, this is one of the most important parameters in the application of phenolic glue resins.

6.4.2 Content of Alkaline

The content of alkaline in phenolic resins is one of the factors, which influence the reactivity of the resin. The higher the alkaline content, the higher is the possible degree of condensation at the same temperature and the higher therefore is the hardening reactivity.

On the other side the alkaline content has some disadvantages. The equilibrium moisture content in humid climates increases with the alkaline content as well as some hygroscopic (longitudinal stability, thickness swelling, water absorption) and mechanical properties (creep behaviour) become worse.

The alkaline content also causes a cleavage of the acetyl groups of the cellulose; this leads to an enhanced emission of acetic acid compared to UF-bonded boards. The higher the content of alkaline, the higher is the emission of acetic acid. In EN 312-5 and 312-7 the content of alkaline is limited to 2,0% for the whole board and 1,7% for the face layer.

Questions and topics of R&D:

- a) How to reduce the possible emission of acetic acid using phenolic resins? What are the decisive parameters for this emission (content of alkaline, press temperature, moisture content of glued particles or others)?*
- b) How to reduce the alkaline content of a phenolic resin without elongating the press time and therefore reducing the productivity of the production line?*

6.4.3 Molar Masses and Mass Distribution

The penetration behaviour highly depends on the molar masses present in the resin: the higher the molar masses (more or less equivalent to the viscosity of the resin at the same solid content), the worse is the wettability and the lower is the penetration into the wood surface. The lower molar masses are responsible for the good wettability, however too low molar masses can cause over penetration and hence starved glue lines. The higher molar masses remain at the wood surface and form the glue line, but they will not anchor as well in the wood surface. For a proper gluing and to achieve a good bonding strength therefore a certain ratio between low and high molar masses is

necessary (Ellis 1993 a, Ellis and Steiner 1990, 1992, Nieh and Sellers 1991, Park et al. 1998, Perlac 1964, Petersen 1985, Stephens and Kutscha 1987, Wilson et al. 1979, Wilson and Krahmer 1978). Gollob (1982) and Gollob et al. (1985) found a decrease of the wood failure with increased molar mass averages of PF-resins.

The penetration behaviour of resins into the wood surface is influenced by various parameters, like wood species, type of the glue resin, amount of glue spread, press temperature and pressure, hardening time and viscosity of the resin. The temperature of the wood surface and of the glue line and hence the viscosity of the resin (which itself also depends on the already reached degree of hardening) influences the penetration behaviour of the resin (Young et al.1983).

Questions and topics of R&D:

- a) *How to determine the optimal ratio between low and high molar masses in a PF-glue resin? How to find the optimal molar mass distribution?*
- b) *Experimental determination of the molar masses that have penetrated to various depths of a wood surface.*

6.4.4 Molar Ratios

The higher the molar ratio F/P, the higher is the degree of branching and hence the three-dimensional cross-linking. At lower molar ratios F/P preferably linear molecules are present. S.Chow et al. (1975) found an increase of the bonding strength of plywood with increasing molar ratio F/P, however the bonding strength remains constant for molar ratios higher than already 1,4; this still is lower than the usual molar ratios for PF-glue resins.

Questions and topics of R&D:

Which is the optimal molar ratio in a PF-resin?

6.4.5 Correlation Between the Composition of the Resin and the Properties of the Wood Based Panels

Similar to the investigations described in section 6.3.3 NMR-results of the liquid resins can be correlated with certain board properties (Panamgama and Pizzi 1995). For this purpose various structural components are determined by means of ¹³C -NMR and the ratios of the amounts of the various structural components, e.g.:

- Methylol groups to methylene bridges
- Ratio of free ortho- and para-sites related to all possible reaction sites
- Methylol groups related to all possible reaction sites
- Methylene bridges related to all possible reaction sites
- Ether bridges related to all reaction sites are calculated and correlated to various properties of the wood based panels, e.g.:
 - Internal bond after cooking or after cooking + drying
 - Subsequent formaldehyde emission.

As for the correlations of aminoplastic glue resins with the board properties also for phenolic resins it is not clear, if commonly valid correlation equations will exist or if they will differ for various types of resins and boards. Nevertheless it can be assumed, that at least the various parameters will be the same in all cases, even the numbers within the individual equations might be different.

Questions and topics of R&D:

- a) *Are there commonly valid correlation equations valid for all types of PF-resins and for all types of boards?*
- b) *How to improve the accuracy of these correlations, in order to get accurate correlations also within narrow ranges of the molar ratio?*

- c) *How can be different cooking procedures at the same overall composition of the resin being described?*

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7 Test Methods and Prediction of Performance

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7.1 Introduction

The prediction of performance of glues for wood products is often difficult and often carried out as a trial and error process. A search is performed in order to find out the best combination of glue (incl. hardener types) and timber for a certain application. In order to do so, a type of test is developed which often depends on the application but also on the type of glues used. For timber and timber products the requirements that are set to glues can be focussed on two main items:

Requirements to glues during the production of the timber products

Requirements to glues during the lifetime of the products in its application

The first requirement has been dealt with in the previous chapters and is not discussed here. This chapter focuses on the second item: the requirements during the lifetime and the prediction of the performance of glues. The prediction of the performance includes the testing of the glues and the design of glued joints and connections. The testing of the glues is currently done on the basis of best estimates of what happens to the glue and the glue line during the service life. The following items can be distinguished:

- Handling of products during installation
- Mechanical performance
- Resistance against biological attack
- Resistance against moisture
- Resistance against temperature
- Resistance against UV
- Combinations of the previous.

For many of these items specific tests have been developed on the basis of experience and good practice, but often questions are raised about the applicability for the prediction of performance. Prediction of performance requires insight in the mechanical, physical, chemical and biological loads during the lifetime of the glued product.

7.2 Current Test Methods and Acceptance of Glues

In Europe, based on history, many different approaches and test methods have been developed in the different countries for testing and approval of wood adhesives and glued wooden products. Therefore many different test methods exist today in the field of testing of wood adhesives and glued wooden products, some of them only used by individual test institutes, some of them used on a national level and some of them generally accepted and internationally used as European Standards. This chapter only deals with the test methods that are generally accepted as European Standards.

The existing European Standards in the field of testing of wood adhesives and glued wooden products can be divided into two groups. The first group covers all European Standards, which are used to evaluate the performance of wood adhesives. For this purpose, a classification standard gives classification and performance requirements. The adhesive shall meet the requirements to be approved and classified for a certain field of application within the production of glued wooden products or of application of the end product. When using the respective test methods, an adhesive can be classified according to its performance. The standards of this group are summarised in table 7.1.

Table 7.1: Standards for acceptance of glues

Standard	Title
EN 204	Evaluation of non-structural adhesives for joining of wood and derived timber products
EN 205	Test methods for wood adhesives for non-structural applications, determination of tensile shear strength of lap joints
EN 301	Adhesive, phenolic and aminoplastic, for load bearing timber structures, classification and performance requirements
EN 302-1	Adhesives for load-bearing timber structures, test methods. Part 1: Determination of bond strength in longitudinal tensile shear
EN 302-2	Adhesives for load-bearing timber structures, test methods. Part 2: Determination of resistance to delamination (laboratory method)
EN 302-3	Adhesives for load-bearing timber structures, test methods. Part 3: Determination of the effect of acid damage to wood fibres by temperature and humidity cycling on the transverse tensile strength.
EN 302-4	Adhesives for load-bearing timber structures, test methods. Part 4: Determination of the effects of wood shrinkage on the shear strength

The second group covers all European Standards, with which glued wooden products are tested, mainly for quality control purposes. These standards are used to evaluate if a glued wooden product meets certain requirements or shows a certain performance. The standards of the second group are summarised in table 7.2.

Table 7.2: Standard for quality control of glued products

Standard	Title
EN 300	Oriented Strand Boards (OSB). Definitions, classification and specifications
EN 310	Wood-based panels. Determination of modulus of elasticity in bending and of bending strength
EN 311	Particleboards. Surface soundness of particleboards, test method
EN 314-1	Plywood. Bonding quality. Part 1: test methods
EN 314-2	Plywood. Bonding quality. Part 2: requirements
EN 317	Particleboards and fibreboards. Determination of swelling in thickness after immersion in water
EN 319	Particleboards and fibreboards. Determination of tensile strength perpendicular to the plane of the board.
EN 321	Fibreboards. Cyclic tests in humid conditions.
EN 385	Finger jointed structural lumber. Performance requirements and minimum production requirements.
EN 386	Glued laminated timber. Performance requirements and minimum production requirements.
EN 391	Glued laminated timber. Delamination test of glue lines.
EN 392	Glued laminated timber. Shear test of glue lines.
EN 1087-1	Particleboards. Determination of moisture resistance. Boil test

The acceptance of adhesives and glued wooden products is currently based mainly on three major characteristics, namely resistance against water/moisture, delamination of glue lines and strength properties, which may be for example shear strength, bending strength or tensile strength perpendicular to the glue line.

Regarding delamination of the glue line, it is often required that failure of bond is only allowed to a certain extent and that a certain amount of wood failure is necessary before a product can be accepted. However, interpretation of wood failure or bond failure is often difficult and depends on the person making the observation. No unambiguous rules are specified and thus the interpretation of test results varies among different laboratories. In addition, there is sometimes no reason to require a certain minimum amount of wood failure. Also bond failure can be perfectly acceptable if this is taken into consideration in the design and the required reliability index is achieved.

For the time being, no general consensus exists within Europe concerning testing, requirements, acceptance and approval procedures for the so-called „new adhesives“, like e.g. one-component-PU-adhesives, EPI-systems and others, to be used for the production of glued load bearing timber structures. Such „new adhesives“ may show different properties compared to the well known phenolic and aminoplastic wood adhesives, which have commonly been used in Europe for many years for the production of glued load bearing timber structures. Therefore it might happen, that other and/or additional tests are necessary during the approval process, compared to the testing of a phenolic or aminoplastic adhesive.

Generally, all „new adhesives“ have to be tested concerning their performance under permanent load, as there is no sufficient experience with industrial applications available so far with these adhesives. Unfortunately, generally accepted test methods in testing wood do not exist so far in Europe for the evaluation of properties like time to failure, creep-rupture or creep.

7.3 Accelerated Ageing Tests

In many cases the standards mentioned in paragraph 7.2 contain accelerated ageing tests as for instance boiling of glued products. In addition to these standards procedures have been developed in laboratories to simulate the influence of climates on the performance of glues. The type of test depends mainly on the glue type and the application of the glue in a certain structure but often include climatic cycles, varying from consecutive heat, water and freezing cycles.

7.4 Prediction of Performance

7.4.1 State-of-the-Art

The prediction of the performance of glues is generally based on a number of tests chosen from the previous paragraphs. The choice of tests depends on the end use of the product and is mostly taken from the viewpoint of the end-user. This viewpoint is strongly influenced on the experiences of the end-user with glues. The viewpoint is generally not based on a scientific basis regarding the resistance of bonding against biological or physical attack. A short overview of the decision sequence that is followed when glues are chosen, tested and accepted or rejected is given in figure 7.1.

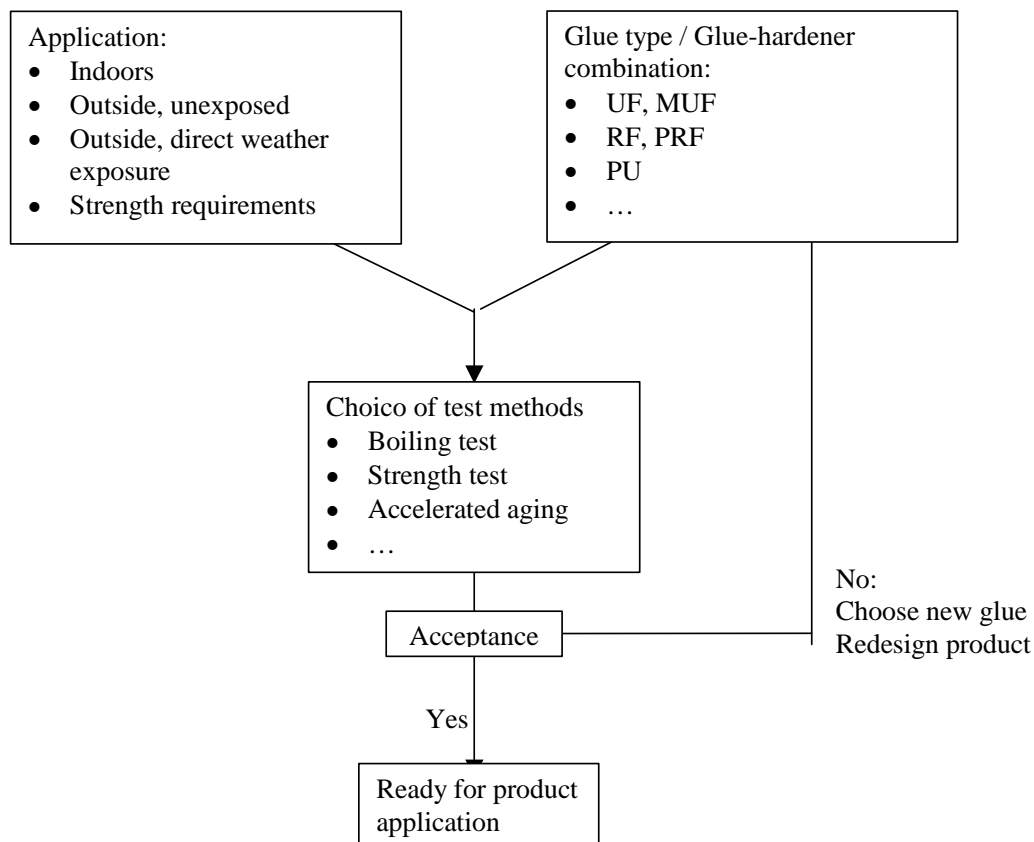


Fig. 7.1: Flow chart for the acceptance of glues

7.4.2 New Developments

New types of approaches to predict the performance of glues are under development. These approaches are based on probabilistic design philosophies. Normally, the probability function for failure reads:

$$Z = R - S \quad (7.1)$$

In which:

Z is the limit state function;

R is the resistance of the component;

S is the load on the component.

In the case of glue there are time dependent phenomena that influence both R and S , making them a function of t and equation (1) should be written as:

$$Z(t) = R(t) - S(t) \quad (7.2)$$

A graphical representation is given in figure 7.2.

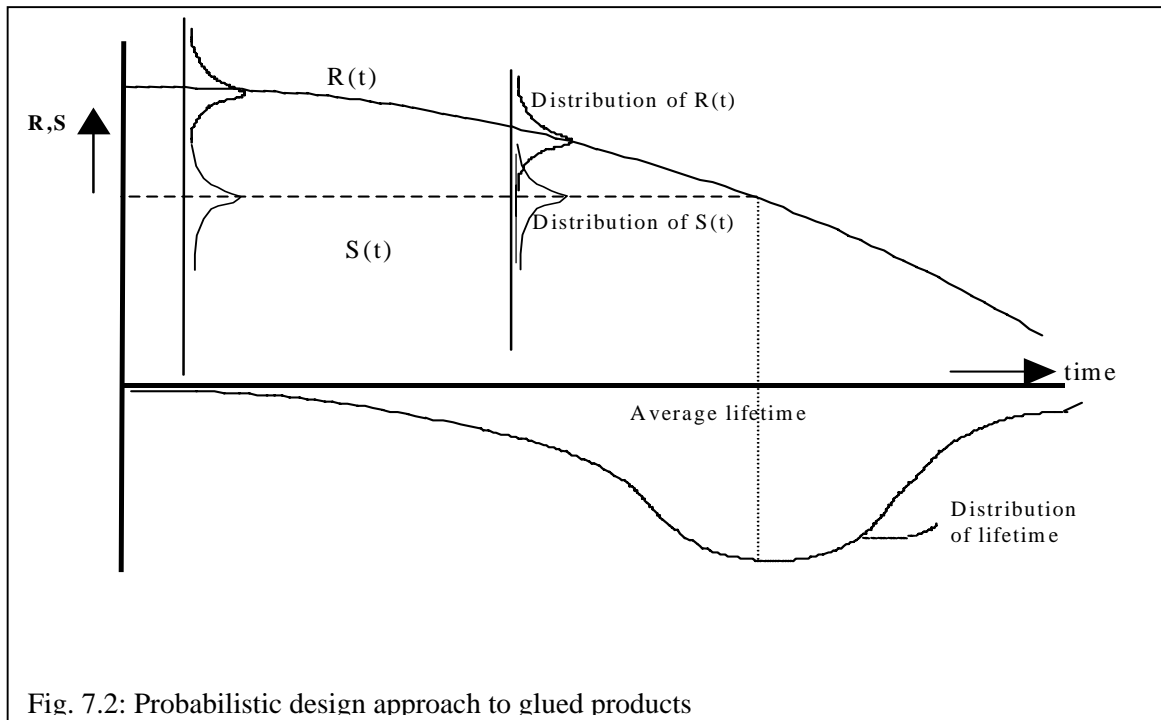


Fig. 7.2: Probabilistic design approach to glued products

Failure occurs when $Z(t) < 0$. To predict the performance of glues insight must be gained in degradation mechanisms, occurring from mechanical loads, moisture, temperature etc. When mechanical loads influence the resistance (long term strength), $R(t)$ becomes a function of S and shall be written as $R(S, t)$. Damage accumulation models used in timber engineering may be used for this approach.

CIB/RILEM has published a general approach to predict the performance of glues and glue bonds. The method consists of:

1. a combination of standard design calculation according to the current building regulations;
2. analysis and modelling of possible degradation mechanisms in the final application;
3. series of tests in extreme conditions for accelerated ageing;
4. series of tests in conditions coinciding with the intended application;
5. a comparison between modelling and test results
6. interpretation and discussion.

Questions and topics for R&D:

a) *Accelerated ageing tests and delamination tests:*

Each test method (function of the end use) consists of a certain combination of humidity conditions, temperature, test specimen dimensions, number of cycles and test duration.

The way each one of these parameters is likely to affect the glue line strongly depends on the chemical nature of the particular glue. Thus, the relative score of a number of glues intended for the same end use may vary considerably with the particular test method.

Should test method and evaluation criteria be specified as a function of the nature of glue?

- b) *It is expected that natural ageing phenomena (under given environmental conditions: temperature, humidity cycles and light exposure) is a function of the type of glue, possibly timber species, size of "particles", thickness and surface of the specific wooden product, degree of exposure of the glue lines, interaction between several glue lines, applied stresses... Different accelerated ageing test methods will affect different glued products differently. It seems necessary to validate test results with the effects of natural ageing /weathering.*
- c) *It is frequently claimed that under a fire event, glue lines enclosed in the wood are protected from quick heating and will hardly attain dangerous temperatures. This is not always true. Besides, high service temperatures (around 50° or 60°C) are frequently maintained for many hours in roof structures, enabling internal glue lines temperature to rise up to (maybe) dangerous levels. Should resistance against temperature be evaluated on glue lines or on glued products?*
- d) *Some less common timber species are frequently used in Southern European countries, and must be glued, for instance when repairing old structures. Some standards specify that the evaluation of glued timber (glue line strength) should be done by reference to (meaning a percentage of) the shear strength of clear wood of the same species. Under these criteria, some very strong timbers may never produce good enough glue lines, even if their glue line strength is much higher than Redwood glue line shear strength. These criteria should be changed.*
- e) *Should there be specific test methods / evaluation criteria for assessing the gluing ability of preservative treated timber?*

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8. Summary and Outlook

M. Dunky

This State of the Art – Report of Working Group 1 (Adhesives) of the COST action E 13 has summarized in a concentrated form the existing experiences and knowledge using wood adhesives, including the various influence parameters. Together with the State of the Art – Report of Working Group 2 (Glued Products) it gives a comprehensive view on the whole wood based panels and wood working industry.

The main purpose of the report was especially to show where questions are not yet answered and where need for further research and development is given. All the questions and open topics for research and development also shall be a guide for the responsible officials within the European Commission to provide additional and sufficient financial support for future research projects within the member countries of the European Community and the COST action E 13.

Provided that sufficient support is given, the high capability for and commitment to innovation in the chemical and adhesives industry, in the wood based panels industry as well as at universities and research institutes guarantee, that also in future the development of adhesives and glue resins will continue to proceed quickly and in an efficient way. We all in the Working Group 1 of the COST Action E 13 hence can look with great expectations into future.