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Urea–formaldehyde (UF) adhesive resins for wood

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Abstract

Urea–formaldehyde (UF) resins are the most important type of adhesive resins for the production of wood based panels. They convince by their high reactivity and good performance in the production and by their low price, however they lack in water resistance of the hardened resin owing to the reversibility of the aminomethylene link and hence the susceptibility to hydrolysis. This need can be overcome by introducing other components like melamine to the UF resin molecules. The former problem of subsequent formaldehyde emission can be considered as solved owing to the decrease of the content of formaldehyde in the resins during the last two decades. Modern laboratory test methods enable a deep insight into the chemical structure and the gelling and hardening behaviour of the resins. © 1998 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Urea–formaldehyde resins; molar ratio; degree of condensation; gelling and hardening behavior; water resistance and hydrolysis; melanine

1. Introduction

Urea–formaldehyde (UF) resins are based on the manifold reaction of two monomers, urea and formaldehyde. By 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. Currently, approximately 6 billion tons are produced per annum worldwide, based on a usual solids content of 66% by mass.

UF resins are thermosetting duromers and consist of linear or branched oligomeric and polymeric molecules, which also always contain some amount of monomer. Non-reacted urea is often beneficial to achieve special effects, e.g. better stability during storage. However, the presence of free formaldehyde is ambivalent. On the one hand, it is necessary to induce the hardening reaction. On the other, it causes formaldehyde emission during the press cycle as well as subsequent, displeasing, formaldehyde emission from the pressed boards, a fact that has led to a total change in the formulation of UF resins during the last 20 years. These days the problem of subsequent formaldehyde emission has been solved, at least in Europe, where the most stringent formaldehyde emission regulations in the world exist. Other countries have already followed, will follow or should follow this trend.

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

There are several papers and monographs concerning UF resins in the literature [1–8], which contain considerable additional information for the more interested reader. This review deals rather with some special aspects of UF resins, the industrial experience of the author having biased the selection of the different topics.

2. Chemistry of urea–formaldehyde adhesive resins

Despite the fact that UF resins consist of only two main components, namely urea and formaldehyde, they present a broad variety of possible reactions and structures. The basic characteristics of UF resins can be explained at the molecular level by:

- their high reactivity;
- their water solubility, which renders them ideal for use in the woodworking industry; and

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- the reversibility of the aminomethylene link, which also explains the low resistance of UF resins against the influence of water and moisture, especially at higher temperatures. This is also one of the reasons for their subsequent formaldehyde emission, when hardened and in service.

2.1. Methylolation and condensation reaction

The reaction of urea and formaldehyde is basically a two-step process: usually an alkaline methylolation followed by an acid condensation. Methylolation refers to the addition of up to three (four in theory) molecules of the bifunctional formaldehyde to one molecule of urea to give the so-called methylolureas. Each methylolation step has its own rate constant, k_i, with different k_i values for the forward and backward reactions. The reversibility of this reaction is one of the most important features of UF resins, and is responsible for both the low resistance against hydrolysis caused by the attack of moisture or water and the subsequent formaldehyde emission. This is so because emittable formaldehyde results from the slight hydrolysis of weakly bonded formaldehyde. The formation of methylol groups mostly depends on the F/U molar ratio, with higher molar ratios increasing the tendency to form highly methylolated species [9,10]. Products of side reactions are acetals, hemiacetals and etherified products, with residual methanol always present in small amounts from the production of formaldehyde. The methylol groups are more or less stable in slightly alkaline conditions. Alkaline condensation might also occur to a limited extent [11], but this 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 with *ca.* five or six urea units [12–15]. Methyleneureas are used as long-term fertilizers, as neutral fillers and as a white pigment, with some other ideas for industrial and commercial use still being at the development stage [16–18].

The UF polymer builds up in the acid 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 bond between the urea molecules depends on the conditions used: low temperatures and only slightly acidic pH favour the formation of methylene ether bridges ($-CH_2-O-CH_2-$), while higher temperatures and lower pHs lead to the more stable methylene ($-CH_2-$) bridges. Ether bridges can rearrange to methylene bridges by splitting off formaldehyde. One ether bridge needs two formaldehyde molecules and it is not as stable as a methylene bridge. Hence it is recommended to avoid such ether groups in UF resins under today's common conditions of low formaldehyde content by virtue of the low final molar ratio of the resins.

The acid condensation step itself is still performed at the same high molar ratio as given in the alkaline methylolation step (F/U = 1.8 to 2.5). Molar ratios lower than *ca.* 1.8 lead to some precipitation during the acid condensation step, causing inhomogenities in the solutions as well as problems in the determination of the proper endpoint of the reaction by water dilutability or by cloud point. 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 [7]. Special knowledge of this step is important for the production of resins with good performance, especially at the low molar ratios usually in use today in the production of particleboards and medium-density fibreboards (MDFs).

In the literature various other resin preparation procedures are also described, e.g. yielding of uron structures [19,20] or triazinone rings in the resins [21,22]. The latter are formed by the reaction of urea and an excess of formaldehyde under basic conditions in the presence of ammonia, a primary or a secondary amine, respectively. These resins are used, among other applications, 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 methylol ureas, which have been formed mainly by reaction of the post-added urea with the high content of free formaldehyde at the still high molar ratio of the acid condensation step;
- oligomeric methylol ureas, which have not reacted further in the acid condensation reaction or which have been built up by the above-mentioned reaction by 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 in molar mass can be monitored by gel permeation chromatography (GPC) (Fig. 1) [23]. A longer condensation step yields molecules with higher molar masses and the GPC peaks move to lower elution volumes.

2.2. Influence of F/U molar ratio on the properties of UF adhesive resins and UF-bonded wood-based panels

UF resins consist of the two monomers urea and formaldehyde. Forced by the need to decrease the subsequent formaldehyde emission, the F/U molar ratio of the two monomers that is commonly used has changed during the last two decades. However, it cannot be expected that under these circumstances no changes in the properties and performance of the resins occur. Today's resins now have more or less the same performance characteristics as many years ago, but with a distinctly lower content of formaldehyde and hence a distinctly lower subsequent formaldehyde emission—so low, in

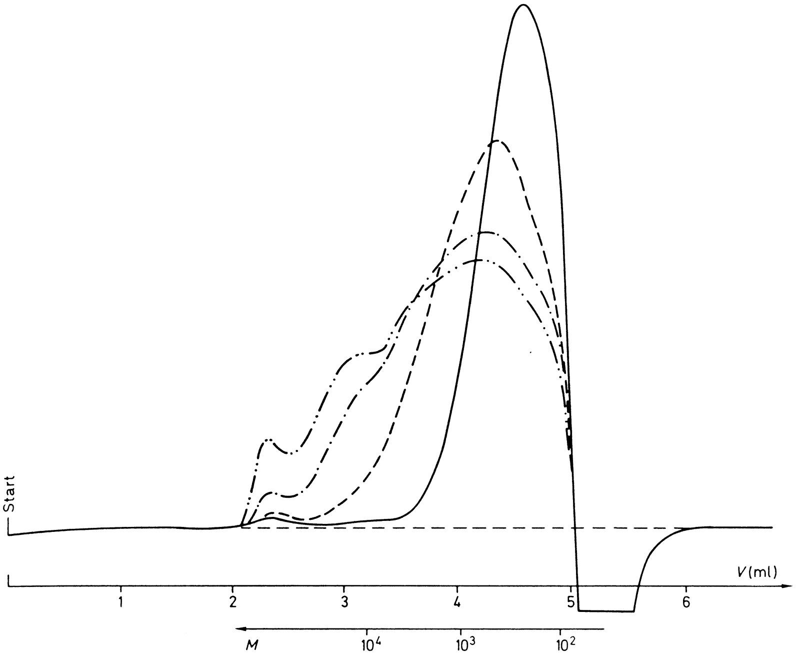

Fig. 1. Monitoring of the acidic condensation process by GPC [23]. Steps of the condensation process: alkaline condensate (———), acidic step 2 min (----), acidic step 4 min (– · –), acidic step 5 min (– · · –). Conditions of GPC: coiled PTFE column 0.2 cm × 200 cm, filled with Fractogel PVA 20 000; mobile phase: dimethyl sulfoxide (DMSO); flow rate: 2 ml h^{-1}.

fact, that the former problem of formaldehyde emission can now be considered as solved.

The main differences between UF resins with high and with low contents of formaldehyde are their reactivity as a consequence of the different free formaldehyde content and their degree of crosslinking in the cured network. The degree of crosslinking is directly correlated to the molar ratio of the two components. 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-site methylol groups and no other free formaldehyde, then the small molar excess of formaldehyde above molar equality is what yields the final crosslinking. 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 preparation 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 F/U molar ratio, the higher the content of free formaldehyde in the resin. Assuming steady-state conditions in the resins—which means, for instance, that post-added urea has had enough time to react with the resin—the content of free formaldehyde is very similar even with different resin preparation procedures. On a rough scale the content of formaldehyde in an unmodified UF resin is *ca.* 0.1% at F/U = 1.1 and 1% at F/U = 1.8 [24]. This also decreases with time because aging reactions in the resin consume parts of this free formaldehyde. Additionally, determination of the free formaldehyde requires exact conditions to avoid any cleavage of weakly bonded formaldehyde [25]. Therefore the content of free formaldehyde is only a coarse approximation of reality.

It has to be considered that it is neither the content of free formaldehyde itself nor the molar ratio, that eventually should be taken as the decisive and only criterion for the classification of a resin regarding the subsequent formaldehyde emission from the boards produced. This is because the composition of the adhesive mix as well as the various process parameters during board production determine the extent of formaldehyde emission. Depending on the type of board and process, sometimes it is recommended to use a UF resin with an already low F/U molar ratio (e.g. F/U = 1.03) and, hence, a low content of free formaldehyde. On the other hand, 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 best in practice can only be decided separately in each case by trial and error.

2.3. Influence of molar mass distribution on the properties of UF resin

The molar mass distribution is determined by (1) the degree of condensation and (2) the addition of urea (and sometimes also other components) after the condensation step; with this latter addition, again low molar masses are present in the resin. This is the big difference between the formaldehyde condensation resins [UF resins, melamine–formaldehyde/melamine–urea–formaldehdye (MF/MUF) resins and also, to a smaller extent, phenol–formaldehdye/phenol–urea–formaldehyde (PF/PUF) resins] in comparison with polyaddition resins and polymerized 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 a UF resin really are. Billiani et al. [26] and Dunky and Lederer [27] have found molar masses of up to 500 000 by light scattering. In particular, by the use of low-angle laser light scattering (LALLS) coupled to GPC, the shear conditions in the chromatographic columns [28] 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 a 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 would be the case for agglomeration; in the latter case the molar mass would increase sharply but inconsistently.

The higher the molar mass (the higher the degree of condensation), the lower the water dilutability of the resin and the fewer the portions of the resin that remain soluble in water. Diluting the resin with an excess of water causes precipitation of parts of the resin. This resin portion contains the higher-molar-mass molecules of the resin and its proportion increases as the degree of condensation increases [27]. At a given solids content, the viscosity increases with a higher proportion of condensed structures.

2.4. Production of UF resins

The production of UF resins is performed in a discontinuous as well as in a continuous way; the latter is useful only for the production of large batches to avoid too often the preparation of off-grade products. The reaction is influenced by several parameters and requires precise control of purity, amount and sequence of addition of the raw materials and of alkaline and acid catalysts. The preparation conditions are adjusted and monitored with respect to temperature, pH and concentration of the reactants. Usually, a three-stage process is used [8,29].

The first stage is always the methylolation step which is usually performed under alkaline conditions and at high molar ratio (F/U = 1.8 to 2.5). This step is necessary to build up the different methylolureas, the types and proportions of the methylols formed being dependent on the F/U molar ratio.

The polycondensation reaction takes place in the subsequent acid condensation step to form polydisperse patterns of oligomers and polymers of different molar masses. The determination of this molar mass distribution can be done by means of GPC. The molar mass distribution (according to the degree of condensation) is one of the most important characteristics of the resin and determines several of its properties, e.g. viscosity and flow behaviour, wetting behaviour of a wood surface [30] and penetration into the wood surface [31,32].

The last production step includes distillation of the resin solution usually to 65–66% solids content, which is performed by vacuum distillation in the reactor itself or in a thin layer evaporator. Before or after this step an addition of urea in one or more steps at different temperatures, including also maturing times, can take place in order to decrease the final molar ratio. Different examples for the production of UF resins are described in detail in the literature [6,33].

2.5. Curing reaction

During the curing process a more or less three-dimensional network is built up. This yields an insoluble resin that is no longer thermoformable. The hardening reaction is the continuation of the acid condensation step. Whereas gelling in the reactor is to be avoided, the same process needs to take place in the glueline. The acid 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 acid compounds which dissociate in water (e.g. aluminium sulfate). Common latent hardeners are ammonium sulfate and ammonium chloride. The latter, however, has not been used in the German and Austrian particleboard and MDF industry for several years now, because of the generation of hydrochloric acid the during combustion of wood-based panels causing corrosion problems and the suspected formation of dioxins. Ammonium sulfate reacts with the free formaldehyde in the resin to generate sulfuric acid, which decreases the pH. This low pH and the ensuing acid conditions enable resumption of the condensation reaction and finally the gelling and hardening of the resin. The rate of decrease of pH depends on the amounts of available free formaldehyde and hardener, and is greatly accelerated by heat [34,35].

3. Advantages and disadvantages of UF resins

3.1. UF resins have no water and weather resistance

The aminomethylene linkage is susceptible to hydrolysis and therefore is not stable at higher relative humidities, especially at elevated temperatures [36]. Water also causes degradation of the UF resin, the effect being more devastating the higher the water temperature. This different behaviour of UF-bonded wood boards at various temperatures is the basis for standard tests and hence for the classification of bondlines, resins and wooden products, respectively, into different bonding classes. These include the lowest requirements (interior use) for 'run-of-the-mill' 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 different national and international standards [37].

The incorporation of melamine (MUF, MF + UF) and sometimes phenol (MUPF, PMUF) improves the low resistance of UF bonds to the influence of humidity, water and weather. However, this changes the characteristics of the resins, especially concerning their reactivity. Additionally, the costs for these modified and fortified products are not comparable because of the much higher price of melamine compared with urea. Therefore, the content of melamine in these resins is always as high as necessary but as low as possible, pure melamine–formaldehyde resins being in use only in mixtures with UF resins. The advantage of higher hydrolysis resistance for pure MF resins is counteracted by their low storage stability in liquid form and their very high price.

The addition of melamine to a UF resin slows down the pH drop after addition of the hardener [34]. The gel time increases with the addition of melamine because of the buffering capacity of melamine's triazine ring [1]. This behaviour is basically the same if the melamine is added to the UF resin just before gelation or if it is incorporated chemically in any way during resin manufacture.

Melamine can also be added in the form of melamine acetates [38,39], which decompose in the aqueous resin mix only at higher temperatures and thus give some savings of melamine for the same degree of water resistance compared with totally reactor-made MUF resins. Also, partially hydrolysed Nylon (polyamide) might be a possible fortifier, having enough tertiary amide groups to react with the UF methylols [40].

The weather durability of a glueline, which essentially means its resistance to cyclic stresses arising from swelling and shrinkage of the joint, as well as hydrolytic attack on the chemical bonds, can be reduced by the incorporation of hydrophobic chains into the hardened network. This has been done by Ebewele et al. [41–45], who incorporated urea-capped di- and trifunctional amines containing aliphatic chains into the resin structure and used the hydrochloride derivates of some of these amines as a curing agent. Wang and Pizzi [46] replaced formaldehyde by succinaldehyde, $OHC–CH_2–CH_2–CHO$, a dialdehyde with a short hydrocarbon chain. Both approaches introduce some flexibility into the hardened network, which should decrease internal stresses, as well as impart some enhanced water repellancy of the cured network owing to the presence of these hydrophobic hydrocarbon chains.

Another approach to increase the resistance of UF resins against hydrolysis is based on the fact that acid hardening of the resin itself causes residues of acids or acid compounds in the glueline. Myers [47] pointed out that, the in case of an acid-hardening system, the decrease in bond durability can be initiated by hydrolysis of the wood cell-wall polymers adjacent to the glueline as well as by an acid-catalysed resin degradation in the case of UF-bonded products. A neutral glueline, therefore, should show a distinctly improved hydrolysis resistance. The amount of hardener (acids, latent hardeners) should always be adjusted to the desired hardening conditions (press temperature, press time and other parameters) and never be like 'the more the better'. In fact, just the opposite occurs: an addition of too much hardener can cause brittleness of the cured resin and a very high acid content in the hardened glueline. However, neutralization must not take place until the hardening reaction has finished, otherwise it would delay or even prevent curing. These divergent requirements are a problem which has not yet been solved fully in practice.

Higuchi and Sakata [35] found that complete removal of acidic substances by soaking plywood test specimens in an aqueous sodium bicarbonate solution results in a marked increase in the water resistance of UF gluelines. Another attempt was made by this same research group [48,49] through the use of glass powder as an acid scavenger, which reacts only slowly with the remaining acid of the glueline and therefore does not interfere with the acidic hardening of the resin. Dutkiewicz [50] also obtained some good results in neutralization of the inherent acidity of a hardened UF-bonded glueline by the addition of polymers containing amino or amido groups. Moreover, for PF-bonded joints, self-neutralization of the glueline increases the durability of the joint, especially preventing acid deterioration on solid wood [51].

3.2. Subsequent formaldehyde emission from UF-bonded boards

The formaldehyde emission from panels in service is caused, on the one hand, by residual formaldehyde present in the UF-bonded boards trapped as gas in the structure of the substrate as well as dissolved in the water content of the boards (moisture). On the other hand, hydrolysis of weakly bound formaldehyde from *N*-methylol groups, acetals and hemiacetals, and, in more severe cases, hydrolysis of methylene ether bridges (e.g. at high relative humidity), also increase the content of emittable formaldehyde. Contrary to phenolic and polyphenolic resins, a permanent pool of emittable formaldehyde is generated from these structures. This explains the slow release of formaldehyde from UF-bonded

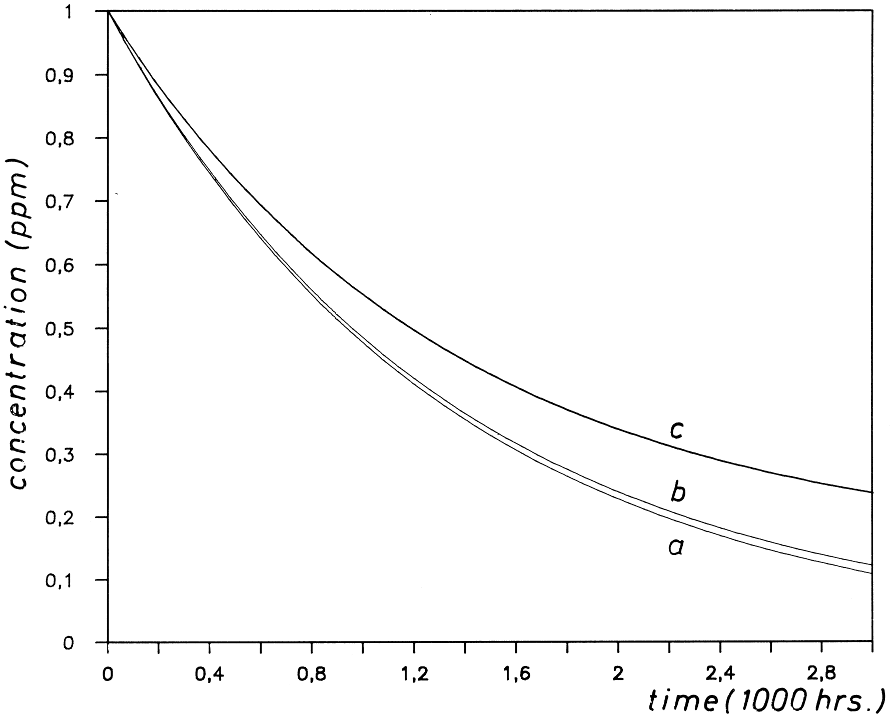

Fig. 2. Calculation of the decrease of equilibrium concentration, C_{eq}, with time for $C_{eq,0} = 1$ (ppm), $K = 1$ (m h^{-1}) [52]: (a) without hydrolysis; (b) hydrolysis constant $k_H = 4.0 \times 10^{-8}$ (h^{-1}); (c) hydrolysis constant $k_H = 4.0 \times 10^{-7}$ (h^{-1}).

wood-based panels even over longer periods. However, it depends also on the conditions—which might be described overall as a hydrolysis constant—whether or not this weakly bound formaldehyde pool leads to unpleasantly high emissions [52]. Fig. 2 shows the calculated decrease of formaldehyde emission from a wood-based panel on the basis of assumed values of the degree of hydrolysis [52]. The higher the hydrolysis rate, the higher is the inherent reserve of formaldehyde which contributes to the subsequent formaldehyde emission.

The problem of the formaldehyde emission by UF-bonded wood products was prevalent in former times. Now it can be considered as solved, owing to the stringent regulations introduced in many countries. The so-called E1 emission class describes a formaldehyde emission that is sufficiently low to avoid irritation or inflammation of the mucous membranes in the eyes, nose and mouth. However, it is important that not only the boards themselves, but also veneering and carpenter's glue resins, laquers and varnishes and other sources of formaldehyde are under control [53–55].

It has been the main challenge for UF chemists over the last 20 years to reduce the content of formaldehyde in UF resins, and this without any major changes in the performance of the resins. In theory this is not possible, because formaldehyde is one of the two main reactive partners in the reaction with urea during the condensation reaction and during curing. Decreasing the F/U molar ratio means lowering the degree of branching and crosslinking in the hardened network, which unavoidably leads to a lower cohesive bonding strength. UF chemists did not manage to fully square the circle, but they did revolutionize the chemistry of UF resins. For example, for an unmodified particleboard UF resin, the above-mentioned F/U molar ratio had been approximately 1.6 at the end of the 1970s. It is now in the range 1.02 to 1.08, but the board performance requirements as given in the relevant quality standards [37] are still the same.

Beside the degree of crosslinking of the cured resins, which shows the difference between the types of resin mentioned above, the rate of hardening also depends on the availability of formaldehyde in the system. New types of reaction and revolutionary ideas concerning both basic UF chemistry and resin application [56] have achieved an acceleration of the hardening reaction and hence a steep increase in productivity on board production lines. In the last decade and a half, the board production lines have also changed. Most new lines now consist of a continuous press with specific press times far below the values that were common 20 years ago. Fortunately, all of this progress clearly contradicts the concept held 10 years ago, that nothing was and is left to be developed in the field of UF resins. The author is sure that even now, after all this progress, we have not yet reached the end of the line in new developments and that the chemistry of UF resins is still a good area for research and development.

3.3. High reactivity and low press times, including full hardening

UF resins can be distinguished from other formaldehyde resins, e.g. MF, MUF and PF, by their high reactivity and hence by the shorter press times achievable. With the modern and long continuous press lines (up to 48 m, soon even 54 m) in use today, specific press times as low as 5 s per mm and even 4 s per mm are possible in the production of medium-thickness 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 core of the board. This moisture gradient induces the so-called steam-shock effect, even without the additional steam injection often used in North American plants. The optimum 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 moisture content level in the total particleboard mat (which would cause problems with steam elimination and even steam blisters in the final panel). To achieve such a low moisture content of the glued core particles it is necessary to limit the addition of water in the core. The lower the percentage of adhesive used on the wood, the lower this amount of water applied to the wood furnish and the lower the moisture content of the glued core particles. For the surface layers, on the other hand, additional water is necessary and is added through the glue mix, to increase the moisture content of the glued particles. However, this additional water cannot be replaced by a higher moisture content of the dried particles before the glueing blender, because this water must be available at short notice to induce a strong steam-shock effect. This is not the case for the water present as the moisture content of internal wood cell walls.

3.4. Clear glueline

All aminoplastic glue resins usually give clear and unvisible gluelines after hardening, contrary to phenolic or polyphenolic gluelines. However, it might happen that the acid hardener causes some discoloration of the glueline, which might vary from light yellow to even dark red or violet. This might occur especially when separate application methods are used for the acids. In this case the hardener is either spread before the adhesive or it is applied onto the second, matching wood surface. Depending on the type of wood, it can be rather tedious to find at least one acid or acid salt not causing such discoloration. An excess of hardener salts, especially of ammonium chloride, may also cause a slight change in colour.

3.5. Cold tack

Cold tack means that the particle mat attains some strength 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 is particularly 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 level of cold tack is necessary to avoid blow out of the fine surface particles once the board mat reaches the inlet of a continuous press with a high belt speed. On the other hand, cold tack can lead to agglomeration of fine particles and fibres in the forming station.

Cold tack is generated by drying out of a glueline, up to a certain maximum. Then it decreases again, when the glueline is more or less dried out. Both the intensity of cold tack and the optimum time span after the glue is spread can be adjusted by the degree of condensation, as well as by special reaction procedures [57–59]. Additionally, various additives can increase the cold tack of the adhesive, e.g. some thermoplastic polymers like poly(vinyl alcohol).

3.6. Aqueous system (absence of organic solvents)

UF adhesive resins are partly aqueous solutions and partly dispersions in this aqueous solutions [27]. Usually no organic solvent is used for UF resins in the wood-based panels industry, neither for the adhesive nor for impregnating resins. This avoids any necessity of safety devices for the storage and use of inflammable materials. The emission of organic carbon is, therefore, much lower than for any solvent-borne system.

3.7. Synergic effects with other adhesives

Special advantages in the simultaneous use of two or more resins and adhesives can be obtained by mixing these different resins prior to their application. The addition of an MUF resin to a 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 performance requirements can be fulfilled, a lower content of melamine in the adhesive system will also be a cost advantage.

PMDI can be used as an accelerator and as a special crosslinker for UF resins, with additions of less than 1% in the first case and up to 2% in the latter, both numbers being based on dry particles [60].

3.8. Non-flammability

Because of their high content of nitrogen, UF resins are non-flammable and burn only with the support of a flame.

3.9. Low price

Urea is rather inexpensive compared with melamine and phenol. Formaldehyde also is relatively inexpensive, and thus, together, they give a resin of low cost but nevertheless high performance. However, such resins are not as inexpensive as desired by the wood-based panels industry. In some part, their low price is a question of the current industrial overcapacity for such resins. However, a multiple increase in the price of methanol, as has already occurred once in this decade, leads to much higher costs for formaldehyde and hence for UF resins.

Addition of melamine, use of phenol, modification or fortification of the UF resin—all of these factors increase costs and thus the price compared with unmodified UF resin. It needs the daily consideration of each mill manager to use unmodified UF resins for most boards produced while using other, more expensive resins only for special boards, e.g. for particleboards and MDFs with very low thickness swelling such as those required for flooring applications. On the other hand, a special, higher cost resin might introduce savings to such an extent, e.g. on the density of the board, that it would be worth spending money on its use.

4. Characterization of urea–formaldehyde glue resins

The characterization of UF resins has undergone great progress within the last two decades. It is now possible to analyse the polydisperse structure of the resins and the individual structural elements in the resins, even in a partly quantitative way. The curing reaction can also be monitored by means of adequate methods. Nevertheless, there is great need for quick test methods for characterizing the resins, especially laboratory methods to predict the bond strength achievable in practice.

4.1. Basic technological tests

Solids content, refractive index, density, viscosity, pH and reactivity are all usually measured as part of the laboratory quality systems of the resin producers and the mills using these resins. These tests are generally easy to perform, but nevertheless they yield important information about the quality and performance of the resins. Most of these test methods are standardized or at least commonly acknowledged, but they can give wrong results if not performed conscientiously. The solids content for instance, which is found by drying the sample for 2 h at 120°C, can be influenced by the type of oven used (fresh air or circulating air ventilation), the number of dishes in the oven, possible openings of the oven and other parameters which may appear unimportant to unskilled personnel. During the drying procedure not only the water of the aqueous solution but also the dispersion itself evaporates. There is also an advance in the condensation process which leads to a nearly cured resin during the test. This generates a considerable amount of condensation water which, of course, also evaporates. Adding up all components of the resins in their original form yields a number *ca.* 10–15% (in absolute figures) higher than the solids content measured under the conditions described above. Also, freeze drying of the resin increases the solid content by approximately the same extent. Other test methods for the solids content can give different results: whether these are lower or higher depends on how thorough the drying has been—the more severe the test conditions, the lower the value of residual solids content found.

The gel time is one of the most important resin parameters not only for their application, but also to understand their curing reaction. The test method is performed in boiling water (usually at 100°C) after the addition of a certain amount of hardener (usually the resin mix is 100 g of the liquid resin plus 10 g of a 15% aqueous solution of ammonium chloride). The result of this test does not just include the time during which the resin gels. Important further information may be obtained, e.g. whether the resin gels sharply within 1 or 2 s, or whether its gel point spans 10 s or more; the latter case forecasts a slow generation of cohesion bonding strength. The behaviour of the resin in the test tube (e.g. foaming) and also the consistency and strength of the gelled plug can be evaluated. However, it is necessary to understand that the gel test depends also on the individual doing it; from time to time parallel tests with one and the same resin but performed by different people should be done to avoid false conclusions. In the author's laboratory some mechanical gel timers have been tested. On the whole, however, the manual gel time test is still to be preferred.

4.2. Curing reaction and build-up of bonding strength

Condensation resins are systems that gel and harden, and this reaction can be monitored by means of various methods. The gel test, as described above, is a coarse method to describe the gelling behaviour of a resin. More sophisticated methods follow the thermal behaviour of the resin during curing. The method of differential thermal analysis (DTA) [61,62] measures the difference in temperature between two cells, both heated up according to a certain temperature program, whereby the one of the two cells contains the sample under investigation. Differential scanning calorimetry (DSC) uses the same type of instrument, but measures directly the heat flow necessary to compensate for the temperature difference [63–66]. Usually one but sometimes two exothermic peaks can be found in such a temperature scan. The temperatures at the onset and top of an exothermic or endothermic peak, the slope of the up curve and the width of the peak can all

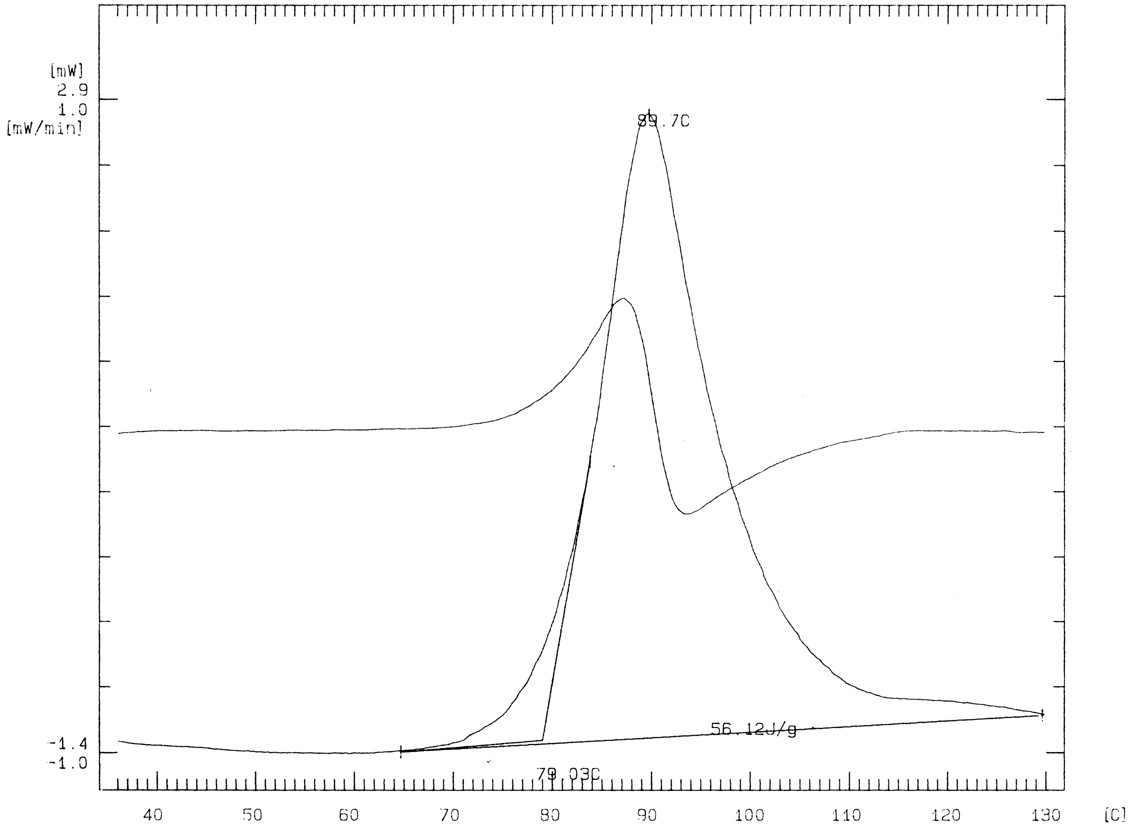

Fig. 3. DSC plot of a modified UF resin, heating rate 10°C min^{-1}. Resin mix: 100 g of the liquid UF resin + 10 g of an aqueous solution of ammonium chloride (15%) [59].

be evaluated to characterize the curing behaviour of the UF sample (Fig. 3). The DSC run is generally performed in sealed capsules or under a certain external pressure to prevent the large endothermic peak due to evaporating water, which would fully cover the curing peak of interest.

Other methods directly monitor the generation of bonding strength: e.g. dynamic mechanical analysis (DMA), where the liquid resin is applied to a substrate like a glass-fibre mat, or Automatic Bonding Evaluation System (ABES), where real gluing of veneers takes place. In the DMA method [59] the samples are heated up following a special temperature program and a cyclic deformation is applied. The response of the second bar, which includes the behaviour of the resin during gelling and hardening, is the basis for calculation of the storage modulus, E', the dissipative modulus, E'', and of the loss factor, $\tan \delta = E''/E'$ (Fig. 4). More modern *in situ* thermomechanical analysis (TMA) tests have also been proposed recently [67]; they give directly the average length of polymer segments between crosslinking nodes of the hardened adhesive network.

In the ABES test [68,69], joints containing the bonds to be measured are prepared by pressing with heated

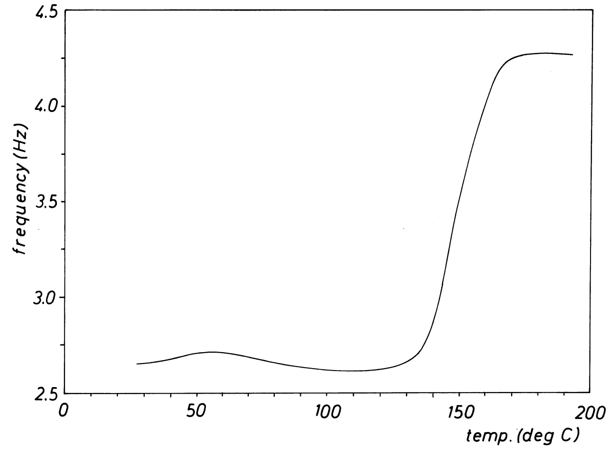

Fig. 4. DMA plot of an unmodified UF resin, heating rate 10°C min^{-1}. Resonance frequency is plotted as a function of time (= increasing temperature). Resin mix: 100 g of the liquid UF resin + 10 g of an aqueous solution of ammonium chloride (15%) [59].

blocks for a certain time, cooled within few seconds and then pulled in shear mode. This test is repeated for different times and various temperatures of the heated blocks. Fig. 5 shows a typical result of the ABES test with

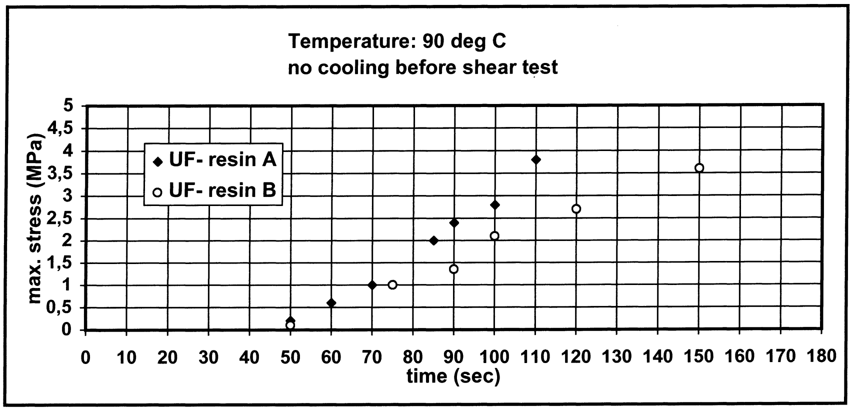

Fig. 5. Comparison of two unmodified UF resins with the same solids content and the same F/U molar ratio, but with different reactivities, measured by the ABES method [70]. UF resin A—newly developed unmodified UF resin (F/U = 1.08) with high reactivity; UF resin B—standard unmodified UF resin with the same molar ratio; the two resins differ in their mode of preparation.

the bond strength given as function of time [70]. The two resins compared are two unmodified UF resins, in which the first (resin A) was prepared according to a special procedure to give a distinctly better reactivity than the second (resin B), which was a standard UF resin.

4.3. Degree of condensation and molar mass distribution

As already mentioned, UF resins contain molecules with different molar masses, from monomers to oligomers and polymers. The determination of this molar mass distribution [molecular weight distribution (*MWD*)] can be performed by gel permeation chromatography [size exclusion chromatography (SEC)]. This method divides the molecules according to their hydrodynamic volume which, to a high extent, is proportional to the molar mass. The greatest problem with UF resins and GPC is the poor solubility of the resins in most of the solvents usually used for GPC. It is necessary to use dimethyl formamide (DMF) or even DMSO [27] to get solubility of higher molar masses. These solvents also have to be used as eluents, shortening the lifetime of the chromatographic columns. They additionally cause some other problems, such as high pressures as a consequence of the higher viscosity compared with other organic solvents, and low refractive index increments. Moreover, calibration of the columns can only be done with compounds that often have poor similarity to UF resins, especially in the oligomeric and polymeric region, because no UF compounds with a definite monodisperse molar mass and molecular structure are available. This fact induces great uncertainty in the calculation of molar mass averages on the basis of chromatograms.

It is also possible to use the GPC together with light scattering (GPC–LALLS) [71]. The eluent with the dissolved UF molecules passes a light scattering cell, the weight-averaged molar mass is measured directly for each chromatographic run, and no external calibration is necessary [26]. However, only the high molar masses can be determined by this method. Fig. 6 shows a chromatogram of several UF resins with different degrees of condensation and hence different molar mass distributions. In the low-molecular-weight region (this is the part of high elution volume) peaks of urea, monomethylol urea and the dimethylolureas can be discerned. Fig. 7 uses GPC coupled with LALLS to determine, directly on-line, the weight-average molar mass in the elution volume. Hence this method avoids the need for external calibration with all problems the latter would generally entail.

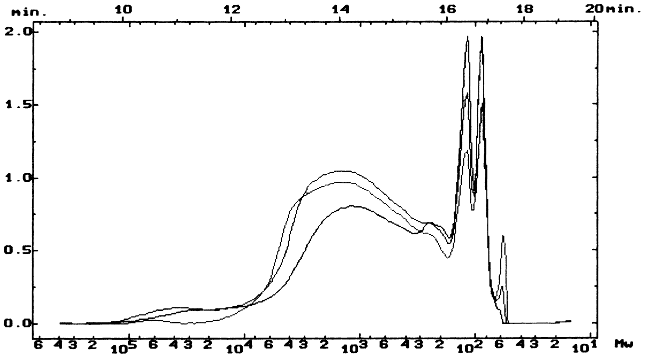

Fig. 6. GPC plots of three different UF resins. Column: Hibar LiChrogel PS-20 (Merck) and Aquagel 100K (Chrompack); solvent and mobile phase: DMF; detection: refractive index; temperature: 60°C [59].

4.4. Chemical composition of the resins and analysis of the structural components

Determination of the chemical composition of UF resins can be done by using several basic chemical methods. The total amount of formaldehyde can be determined after hydrolysis of the UF resin with concentrated sulfuric or phosphoric acid; thereby methylols, methoxymethylols and ether and methylene bridges are

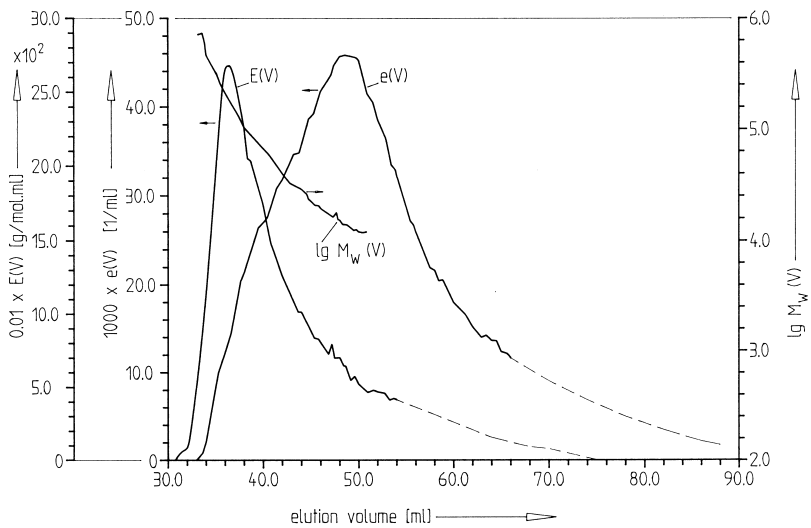

Fig. 7. GPC coupled with light scattering (LALLS) of an UF resin: $e(V)$ = signal concentration; $E(V)$ = normalized response of the LALLS detector; $\log M_w(V) = E(V)/e(V)$ = measured weight-average molar mass as a function of elution volume, V [26].

cracked under the formation of formaldehyde which can be determined afterwards. The content of nitrogen is accessible with the Kjeldahl method or by means of elemental analysis. The latter method also can be used for determining the amount of carbon in the resin; however, calculation of the amount of formaldehyde from this carbon content involves consideration of a possible small residue of methanol in the resin coming from the residual content of methanol in formaldehyde. The content of urea can be calculated for unmodified UF resins from the content of nitrogen, if other possible nitrogen sources are known. In one of the basic papers on UF chemistry, Staudinger and Wagner [72] used elemental analysis for the analysis of various stuctures in UF condensates.

Analysis of the structural components can be performed by various spectroscopic methods such as infrared (IR) [64,73–78], nuclear magnetic resonance (NMR)—i.e. ^{1}H-NMR [79–82], ^{13}C-NMR [33,64, 73,83–88] and ^{15}N-NMR [89–91]—and Raman spectroscopy [92]. All of these methods allow some insight into the structure and the nature of linkages in the resins to be gained. In particular, they help UF chemists to obtain correlations between (1) different preparation strategies and the resulting structures, and (2) these structures and the properties of wood-based panels produced with these resins.

5. Trends and prospects in UF chemistry and in the application of UF resins

The best way to characterize the trends and prospects in UF chemistry is to relate a story that happened to the writer some years ago. At that time, there was another step down in the limit of the perforator value as a criterion for formaldehyde emission, from 10 mg iodometric value to 6.5 mg photometric value. Although, because of the change in the analysis method, the real decrease necessary was only *ca.* 2–2.5 mg and not 3.5 mg, nevertheless this represented a reduction of 20–25% in the former limit. We had a plant trial with a new resin having a formaldehyde content lower than that of all other previous resins, we added different types of scavenger, we used accelerators to maintain a good reactivity of the resin; in short, we used a really state-of-the-art resin to fulfil these stringent requirements. We had not yet done the work, when suddenly the managing director asked: ‘Can we run with this new system also faster than with the actual one in use?’ Just this question is one of the most important features concerning trends in the production of bonded wood-based panels. Higher reactivity of the resins and of the resin glue-mix (hence shorter press times) and at the same time a decrease of the subsequent formaldehyde emission (which itself increases with one and the same resin with shorter press time), these are the challenges in this industry we have to face.

Even if UF resins are the cheapest type of condensation resins, nevertheless they are an important cost factor in the production of particleboards. Although the main approach to a lower consumption of resin in production must be better preparation of the particles (avoiding too many fines [93]), the resin characteristics also can help towards better effectiveness of the resin. This includes the adjustment to an optimum viscosity based on the proper molar mass distribution: a low degree of condensation can lead to a too high penetration of the resin into the wood surface, causing starved gluelines, whereas high-molar-mass resins can cause insufficient wetting of the substrate surface [30–32].

A further trend is the need for improved analysis methods. Determination of the molar mass distribution is possible, but still rather troublesome. The sample preparation, the duration of one chromatographic run, the lifetime of the columns, the need to use rather difficult and displeasing solvents and eluents like DMF and DMSO, the long time necessary to get the system into steady-state conditions and, last but not least, the old story with the calibration of columns not only for comparing chromatograms but also for evaluating molar masses; this is a long list of problems to overcome.

An analysis system or a test to forecast reliable bonding strengths would also be highly welcome. At the moment there is still a gap between all the analysis results, which have been performed with the liquid resins, and the bonding strengths of the wood-based panels after gluing and hardening. There are some attempts that promise success. Ferg et al. [73,94,95] have obtained correlation equations evaluating the chemical structures of various liquid UF resins with different F/U molar ratios and different preparation methods, on the one hand, and the achievable internal bond of the panel (hence of the hardened resin) and the subsequent formaldehyde emission, on the other hand. Even if these equations cannot stand for all resins and all cases, they describe how such a universal equation might work. It will be the task of chemists and technologists to evaluate in detail all possible parameters and to judge their influence on the performance of the resins and the wood-based panels.

As stated above, formaldehyde emission is no longer a problem nowadays as long as the stringent regulations in force are fulfilled [96,97]. Nevertheless, new and even more stringent regulations are under discussion and already partly in force [98]. The main task for the development of new UF resins was and still is to decrease the formaldehyde content in the resins and hence obtain an even more marked decrease in the subsequent formaldehyde emission from wood panels.

6. Summary

In the future, UF adhesive resins will be the most important adhesive systems for wood-based panels as a consequence of the advantages of these resins, even keeping in mind their limitations. The great progress achieved during the last 20 years and in the very recent past allows us to predict that, even in the future, the various requirements on UF-bonded boards will be met. Certainly co-condensation with other monomers and with other resins will become more important, in order to combine their individual properties and advantages with the low price of the UF resins. This is possibly the most important field of future developments and of new applications.

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