A very simple empirical kinetic model of the acid-catalyzed cure of urea-formaldehyde resins
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ABSTRACT

The hot pressing operation is the final stage in MDF (medium density fiberboard) manufacture; the fiber mat is compressed and heated up in order to promote the cure of the resin. The aim of the investigations is to study the curing reactions of UF resins as commonly used in the production of MDF, and to develop a simplified kinetic model. This investigation has combined Raman spectroscopy to study the reaction cure and $^{13}$C NMR for the quantitative and qualitative characterization of the liquid and still uncured resin. Raman spectroscopy was found very interesting for the study of the resin cure and permitted to obtain kinetic data as the basis for a simple empirical model, considering a homogeneous irreversible reaction of a single kind of methylol group and ureas with rate constants depending on their degree of substitution. Although these results can provide a better understanding of the composition and the cure of an UF resin, several issues remain open, such as the influence of the reversibility of the reactions taking place during the curing process as well as the possible formation of cyclic groups in the resin.

**Key words:** urea-formaldehyde resins, curing of resins, kinetics, Raman spectroscopy, $^{13}$C NMR, fiber bonding
INTRODUCTION

Urea-formaldehyde resins are the most widely used adhesives in the manufacture of wood-based panels, such as MDF; this is mostly due to their high reactivity, low cost and excellent adhesion to wood. The development of the adhesive bond interferes with the rheological behavior during the hot-pressing of the wood and adhesive. This process is quite complex as it involves simultaneous and coupled heat and mass transfer, polycondensation of the adhesive and forming the densified structure of the board. To understand the effects of the resin cure on mat consolidation, it is necessary to investigate with more detail the cure reaction of the urea-formaldehyde resins. This will lead to a kinetic model for the curing process of UF resins as done here in this work, to be further integrated in a global model including all mechanisms involved in the panel formation: heat and mass transfer, chemical reaction and mechanical behavior 1,2. A better understanding and possible optimization and control of these effects could be achieved through simulation using this new model.

The condensation of UF resins has been the subject of several works, often covering both physical and chemical aspects. These results have provided much knowledge about these systems, but still many questions remain open concerning the structure of the uncured and cured resin, the kinetic behavior of the resin during curing and the mechanisms of forming the board and the bonding strength. The large variety of structural elements in UF resins, like methylene bridges, ether bridges, methylols, amide groups or even cyclic derivatives like uron rings and the variety of possible reactions make their study difficult. On the other hand, the content of these structural elements in the still uncured resins has an obvious influence on their curing rate and on the structure and the mechanical properties of the final network. Despite of the progress within the last two decades in the characterization of formaldehyde condensation resins, new, better, and more efficient analysis methods are still required. 3 It is now possible to analyze the polydisperse structure of the resins, as well as various individual structural elements in the resins; the achievement of reliable quantitative results, however, is
not always possible.\textsuperscript{4} To characterize a liquid UF resin, several analytical tools have been widely used, namely \textsuperscript{13}C NMR \textsuperscript{5-8} and FTIR \textsuperscript{9,10} for investigations of the resin structure, and GPC/SEC \textsuperscript{11-13} for the determination of average molecular weights (MW) and molecular weight distribution (MWD). More recently, the capabilities of FT-NIR spectroscopy have been exploited \textsuperscript{14} and this technique was shown to be useful for the on-line monitoring of the consumption of –NH\textsubscript{2} groups during the early stages of the synthesis.

Kinetics and mechanisms of the early stages of the condensation process have been thoroughly studied already in the 1950s by de Jong and de Jonge. \textsuperscript{15-17} Thus, formaldehyde addition reactions to urea were found to be base and acid catalyzed, with rate constants depending on the degree of substitution of urea, whereas condensation reactions between two methylol groups or between a methylol group and urea are acid-catalyzed. Reverse reactions were assumed to be unimolecular, but this may be a hasty conclusion, as only experiments in dilute water solutions were carried out in these studies.

Besides these older results, the only contributions, which might be used for establishing a kinetic model of the curing reaction were: a) a few higher temperature experiments by Price et al. \textsuperscript{18} who followed the formaldehyde concentration decrease in closed batch reactors; b) a more recent study by Mejdell et al. \textsuperscript{19} with three kinetic runs including GPC measurements.

A fundamental problem concerning this kind of models is: does indeed the reactivity of urea depend only on its degree of substitution (first shell substitution effect FSSE), or else does it depend also on the presence of groups not directly linked to the nitrogens, leading to a distinctive reactivity depending on whether methylol groups or methylene bridges are attached? In the latter case, a higher order substitution effect would be present. Experiments on model compounds can give some hints to this important matter. A crucial check of the FSSE hypothesis is the equality of the first order hydrolysis constants of methylol groups in mono- and dimethylolurea: rate constants per mole of the chemical substances should be the double for dimethylolurea, as it is explained by the equations (4)-(6) below. If a lumped
methylol group could be defined, $k_1'$ should be equal to the common hydrolysis constant ($k_h$) and so $k_2'$ should be equal to $2k_h$.

![Reaction Equations](image)

The value of this ratio is 1.68 with a standard deviation of 0.42 for 15 values reported by Landqvist measured at various buffered pH conditions (pH 6.7, 9.2, and 10) at the three temperatures 20, 30 and 40 °C. However, de Jong and de Jonge reported this ratio to be 6.9. Nevertheless, a common value for the activation energy of the hydrolysis reaction was reported to be 83.6 kJ mol$^{-1}$ for both reactions.

The equilibrium constants $k_1/k_1'$ and $k_2/k_2'$ of the first and second hydroxymethylolations of urea are, respectively 990 and 253 at 35 °C, and there is a decrease with a factor of about 3 in the forward rate constants of the successive substitutions (see equations 1, 2 and 3). Therefore, $k_1/k_2 \approx 3$ and $k_2/k_3 \approx 3$. Interestingly, the rate constants for the reaction of methylenediurea with formaldehyde or monomethylolurea are identical, respectively, to those...
observed for urea + formaldehyde and urea + monomethylolurea. \(^{16,17}\)

So, there seems to be enough data to take into account FSSE for urea, but it seems unfortunately there might be no moiety like a single “-CH\(_2\)OH” group, and a second (or even higher) shell order substitution effect should be needed for fully describing this chemistry.

Kumar and Sood \(^{20}\) have put forward a FSSE (First Shell Substitution Effect) model for the early stage of the urea-formaldehyde condensation process and have been able to fit the data of Price et al. \(^{18}\) assuming the hydrolysis reactions to be bimolecular. Both de Jong and de Jong \(^{16}\) and Price et al. \(^{18}\) have considered them to be unimolecular. However, available experimental data could not clarify this question, since water concentrations were always the same. This matter needs to be solved, because higher initial concentrations of formaldehyde are nowadays often used. Mejdell et al. \(^{19}\) have slightly extended the Kumar-Sood model \(^{20}\) now including condensation reactions and achieved a good agreement with their limited experimental data, but it should be noticed that their rate equations in terms of functional groups do not reflect the correct situation concerning the reverse reactions. A slightly more consistent model has been proposed by Costa and Bachmann \(^{22}\), but as it is discussed in that same reference, it only takes into account FSSE effects. The use of second and higher order substitution effects in models of reversible polymerizations requires the simulation of the whole isomer distribution \(^{22}\), and this makes such models difficult to use.

A further issue is the partial solubility of water and the higher oligomers of the resin, which means that the distribution of several components in the two phases has to be considered. An extensive study of phase equilibrium will have to be carried out if a detailed modeling is needed to be established.

During the curing stage of the resins their insolubility becomes ultimately an important limitation of most analytical techniques. The chemistry in this stage is even less well understood, because of the presence of a much higher temperature than in resin synthesis, which might lead to hypothetical ladder structures, such as fused uron rings.
In recent years, several techniques such as solid state $^{13}$C CP MAS NMR $^{23-26}$ and FTIR $^{27}$ have lead to a better understanding of the high temperature, acid catalyzed cure of UF resins. Chemical curing (building up of the three-dimensional network) can be monitored by DSC $^{28-30}$ allowing the estimation of the degree of chemical curing, as well as of the heat of polymerization. Mechanical curing in the sense of the increase in cohesive bond strength can be monitored by TMA $^{31,32}$, DMA $^{33}$ or ABES (Automatic Bonding Evaluation System) $^{34}$. Some investigations were also focused on the influence of synthesis parameters in the structure of the resins examined by $^{13}$C NMR and their effect on the performance of wood-based panels $^{35-40}$; this was also done in order to establish suitable correlations between various properties of these wood-based panels and the chemical structure of the uncured resins used $^{41,42}$. The achievement of reliable quantitative results is not always possible, because some of these techniques have limitations. NMR can only be used at the early stages of cure, due to resin insolubility. Solid state CP-MAS NMR is a powerful technique, but the molecular interactions and the consequent enlargement of bands reduce its capabilities for quantitative analysis. The drawback of FTIR is the need of a careful preparation of samples and the possible interference of water, as well as the lack of clear assignments of some bands.

Laser Raman spectroscopy, normally used as complement to FTIR, was introduced by Hill et al. $^{43}$ in order to analyze the structure of UF resins. An important advantage of this latter technique consists in a possible analysis of liquid resins, cured resins, or even cured resins in wood-based panels. Hill et al. $^{43}$ observed that methylol and certain methylene functionalities could be differentiated and they hence concluded that this technique offers promise for elucidating the structure of cured UF systems, as a complement to other techniques such as infrared and solid state NMR. Later, only Minopoulou et al. $^{14}$ used this technique to verify the synthesis of four model compounds of UF. A major problem has been the effect of fluorescence and consequent loss of resolution, but further technical improvements have
permitted to reduce this problem considerably.

Another tool, MALDI-TOF-MS, can be used for investigating the full molecular weight distribution. In this technique the polymer is dispersed in a matrix of a UV-absorbing compound; when it is hit by a laser shoot, the absorbed energy is capable to vaporize some of the polymer molecules between two electrodes at high voltage. The electric field between the electrodes will accelerate the polymer molecules, which will hit the detector with an acceleration inversely proportional to its molar mass. This technique had already been used for investigations on phenolic resins and novolacs. Unfortunately, the degree of ionization changes with the molar mass and the composition in a partly non-specific manner. This fact undermines its use as a quantitative tool, but valuable information about the chain length distribution can be obtained anyway. Finally, it should also permit the study of the influence of wood in the polycondensation reaction of UF resin.

The present study has attempted to assess the quantitative changes of some reactive functional groups in order to develop a preliminary kinetic model for a UF resin used in the manufacture of MDF. Also it should be determined whether laser Raman spectroscopy could be used to study the UF curing process. Spectra were obtained for a series of UF model compounds and several samples of resins cured for different time spans and at various temperatures in a sealed reactor. The possibility of using NMR for this purpose was also investigated, because this technique is more sensitive, and quantitative information is also available. However, it would be necessary to find a system with a plasticizing effect on the cured resin in order to reduce the interactions and the enlargements of spectral bands. Several swelling tests were therefore performed on the cured resin using different solvents and test conditions. The content of various structural elements in the still uncured UF resin was determined using $^{13}$C NMR. Unfortunately, even considering that the targeted application of this kinetic model is in the modeling of the hot-pressing of MDF, the effect of the wood substrate on resin curing was not taken into account. In fact, wood constituents could have an

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accelerating/catalytic effect on resin curing as reported in literature in the case of PF. Some of the reported methods, as DSC, TGA, or IR were used for that purpose, but the possibility of using Raman spectroscopy to study the reaction kinetics of mixtures of UF resin + wood should be investigated.

MATERIALS AND METHODS

**Urea-formaldehyde resin**

A commercial UF resin (supplied by Euroresinas, Sines, Portugal) for the production of MDF was used within this work and had the following characteristics: molar ratio F/U = 1.3; density=1260 kg/m³ (at 25 °C) (according to ISO 649/2); viscosity=350 mPas (at 25 °C) (according to ISO 2555); solid content = 64 % (drying at 120 °C for 2 h); pH=7.4 (according to ISO 6353-1); gel time = 60 s (boiling water, 0.25 ml of a glue mix: 100 g of liquid resin diluted to 50 % solid content plus 3 ml of 20 wt % of an aqueous solution of NH₄Cl).

**Model compounds**

Model compounds of UF were not commercially available, except dimethylolurea. They were synthesized in the laboratory by methods reported elsewhere and are listed in Table 1.

*(insert Table 1)*

**Swelling tests**

Several swelling tests on cured resins were carried out using different conditions and various solvent systems: pyridine, ethylene glycol, 2,2,2-trifluoroethanol, DMF with 5 % LiBr, DMF with 5 % LiClO₄, DMSO with 5 % LiBr, m-cresol, formamide, and 2-pyrrolidone. For the first test series, the resin was cured in covered metal pans immersed in a temperature controlled oil bath at 150 °C for 10 minutes, using 3 % solid hardener (based on solid resin) of a catalyst solution with 20 % wt NH₄Cl. The cured resin was grinded into very fine
particles which then were vacuum dried at ambient temperature and immersed into the solvent at 60°C for three days. For the second test series the resin was cured as a thin film on a glass plate placed on a heated oven, using the same conditions as for the first series. The films were then investigated using an optical reflection microscope. In case of formamide as solvent the particles out of the first test series were also analyzed using a scanning electron microscope.

**Curing reactions in a sealed reactor**

The UF resin was cured for various time spans of 3 to 40 min at different temperatures (110, 130, and 150 °C) in sealed stainless steel tubes using 1.5 wt % of a catalyst solution with 20 % wt NH₄Cl. In order to avoid the sticking of the resin to the tube walls, the liquid resin was poured into silicone tubes, which were then inserted into the stainless steel tubes. The stainless steel tubes were immersed into a temperature-controlled oil bath at the various temperatures as indicated above. After the preset time span the tubes were immediately immersed into ice water in order to stop the ongoing curing reactions. The samples were vacuum dried at ambient temperature and stored in sealed containers at –20°C.

**Raman spectroscopy**

The 2000 NIR FT Raman spectrometer used was supplied by Perkin-Elmer (Wellesley, MA, USA) and equipped with a Nd:YAG laser as an exciting source. All spectra were recorded with a resolution of 8 cm⁻¹ with a spectral domain of 3600 - 200 cm⁻¹. The laser power was 200 mW, except in the case of the liquid resin (100 mW), and the number of scans was 50. For liquid samples a quartz cell was used. The model compounds in powder form were tested in glass capillaries. The cured samples in powder form were compressed in open cavities for frontal lightening. While still keeping their cylindrical form, they were fixed on the cell, and the laser beam was focused in a conical cavity on the sample surface. The solid polymers often showed fluorescence, caused by traces of contaminants. So it is important to carefully
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clean the surface by acetone or to cut a fine layer off from the surface. All spectra were quantified on the same relative basis by normalizing by the carbonyl band and subtracting a baseline as below described. For the cured samples, the quantitative analysis was done on a relative basis, normalizing the peak area above the baseline to the peak area of carbonyl, since the carbonyl intensity did not appear to change during the polymer curing.

NMR spectroscopy

The $^{13}$C NMR spectra of model compounds were obtained on a AC 200 spectrometer Bruker (Madison, WI, USA) at ambient temperature. Chemical shifts were calculated relative to DMSO. The samples were prepared in DMSO-d$_6$, using concentrations of 100 g/l and placed in into the NMR tubes. The spectrum of the liquid UF resin was obtained with a Bruker AMX 300 apparatus at room temperature. About 1 ml of the liquid UF resin with 65 % solid contents was pipetted into the NMR sample tube and about 0.4 ml of deuterium oxide containing the sodium salt of 3-(trimethylsilyl)-1-propanosulfonic acid, (CH$_3$)$_3$Si(CH$_2$)$_3$SO$_3$Na, was added. The quantitative analysis was performed using a gated decoupling of proton without nuclear Overhauser effect (NOE). To obtain quantitative peak intensities out of the $^{13}$C NMR spectra, a sufficient delay time between the individual pulses must be given in order to allow the relaxation of all carbons. A five second pulse interval is sufficient to obtain reliable spectra as seen from the measurement of the spin-lattice relaxation time $T_1$.  

RESULTS AND DISCUSSION

Qualitative analysis of chemical groups

In order to permit the use of NMR for the quantitative determination of reactive species in the cured resin it would be necessary to find a system that acts like a plasticizer of the cured resin. Several swelling tests were therefore performed using different solvents and conditions,
but these tests were not sufficiently successful. So, Raman spectroscopy was used to investigate the cure of the UF resin on the basis of spectra of the various model compounds. The spectra of several model compounds (as described in Table 1) helped to clarify the assignment of some characteristic bands, although there are some regions where the interpretation remains ambiguous. The band assignments were also supported Hill et al. \(^{43}\); improved equipment performance extended further the capabilities of this technique and provided an increase of resolution and a decrease of fluorescence.

The Raman spectra of resin samples cured at temperatures of 110, 130, and 150 °C and for different times between 3 and 40 min show important changes indicating chain extension reactions and crosslinking occurring in these systems.

The most interesting bands for describing the structure of the resins are those around 3000 cm\(^{-1}\), between 1700 and 1300 cm\(^{-1}\) and between 1000 and 800 cm\(^{-1}\), as can be observed in the normalized spectra of oligomers presented in Figures 1 and 2. The complete assignment of all relevant bands was reported in a previous work \(^{52}\). Table 2 summarizes the frequencies and intensities observed for the uncured resin and those resin samples cured at 110 °C and for 10 minutes, as well as a brief indication of the band assignment.

\textit{(insert Table 2)}

\textit{(insert Figures 1, 2)}

All spectra have been normalized as below described:

- Subtraction of a baseline consisting in two linear domains:
  
  1) one below 2600 cm\(^{-1}\) found by fitting between wavenumbers 1800 and 2600 cm\(^{-1}\); 
  2) the other above 2600 cm\(^{-1}\) defined by the intensities at 2600 cm\(^{-1}\) and 3600 cm\(^{-1}\).

- Since the cells and the laser intensity changed, only relative intensities within the same spectra are meaningful. Hence, the reported intensities have been obtained after baseline subtraction through division by the integrated area of the carbonyl band with
wavenumbers between 1615 and 1690 cm\(^{-1}\).

Figure 3 shows a comparison of the 1350-1500 cm\(^{-1}\) region for three oligomers: dimethylolurea FUF, trimethylene tetraurea U(FU)\(_3\) and monomethylol methylenediurea FUFU. The region at 1400-1500 cm\(^{-1}\) enables to distinguish the group –CH\(_2\)O- (1485-1448 cm\(^{-1}\)) from the group -NCH\(_2\)- (1436-1430 cm\(^{-1}\)).

(Insert Figures 3 and 4)

The region 800-1000 cm\(^{-1}\) (see Figure 4) provides additional information. The strong 900 cm\(^{-1}\) band in the individual spectra of dimethylolurea, dimethylolurea dimethylether, and dimethyloluron dimethylether might be attributed to -COC- linkages, as already suggested by Hill et al.\(^{43}\). It is not evident whether there was a visible –COC- formation by chain extension or by cyclization\(^{43}\), but this was not confirmed because the spectra of a cyclic compound like uron has not been presented. However, the cyclization could be attributed to the band around 848 cm\(^{-1}\) which appears only in the spectrum of dimethyloluron dimethylether.

(Insert Figure 5)

In the region 2800-3600 cm\(^{-1}\) (Figure 2) the bands attributed to -NH\(_2\) and –NH- stretching (3342-3334 cm\(^{-1}\)) and also to –CH< stretching (3050-2800 cm\(^{-1}\)) can provide some quantitative information for the ratio between mole concentrations of methylene and urea groups. Indeed, a significant linear correlation can be found between the ratio of those band areas for –CH and -NH\(_2!/–\text{NH}-\) and the relative amounts of methylene groups and urea. However, its use for chemical analysis is not recommended because of the presence of numerous overlapping bands, some of them belonging to -OH groups. A better prospect consists in using the region 1250-1700 cm\(^{-1}\) as below reported.

It may be observed that a band around 1650 cm\(^{-1}\) resulting from carbonyl stretch is present in
all samples and yields a convenient internal standard as above described.

There are two close, yet separable bands, at about 1430 and 1460 cm\(^{-1}\), which can be assigned respectively to CH\(_2\)-N and CH\(_2\)-O, and yet another strong CH\(_2\)-N band at 1320 cm\(^{-1}\). The band at around 930 cm\(^{-1}\) might also be used in the absence of interference of other bands.

In Figures 6 and 7, a comparison between the spectra of the uncured resin and resin samples cured at 110\(^\circ\)C for the regions 1290 - 1360 cm\(^{-1}\) and 1410 - 1500 cm\(^{-1}\) is shown.

\textit{(insert Figures 6 and 7)}

As the curing process progresses, increasing intensities of the bands at wavenumbers 1410-1445, 1310–1342 (as well as the one at 930-990 cm\(^{-1}\), not shown) indicate an increase of the concentration of –NCH\(_2\)N – groups; conversely, the intensity of the bands assigned to –CH\(_2\)O – groups (1448-1485 cm\(^{-1}\)) falls at the same time.

At the beginning of the reaction, the formation of methylene groups increases smoothly towards a limiting value. For the temperature of 150 \(^\circ\)C, an inflexion in the curve is observed, possibly due to the vitrification observed on these samples. This fact may indicate that an intramolecular reaction starts to occur at this temperature.

\(^{13}\)C NMR was used for the qualitative and quantitative characterization of the starting liquid resin. The assignment of signals was done on the basis of model compounds spectra and results as reported in the literature \(^{5, 41, 53, 39, 36, 26}\). The data here reported were useful to identify and quantify the structure of the various oligomers and also to confirm whether the synthesis had been correctly done. A quantitative analysis of the liquid resin was then performed using the \(^{13}\)C NMR signal ratios to calculate the portion of some structural components. The assignment of relevant signals and the respective areas are shown in Table 3. It is important to notice that the peaks normally assigned to uron derivatives or to cyclic ureas \(^{35, 54}\) were not found.

\textit{(insert Table 3)}
The estimation of group concentrations using the Raman spectra

From the above discussion, a few bands show clearly the conversion of the –CH₂OH end groups (which will be called $F_1$) and the formation of new methylene-urea groups -CH₂N< (which will be called $F_2$). However, the overlapping of bands with different intrinsic intensities makes the task of establishing correlations intensity / concentration not straightforward. Note also that since no model compound with the tertiary urea group could be successfully synthesized and purified, some information about the interpretation of the spectra of resins is still missing. From the several possible bands pointed out in the previous sub-section only with one of them a fairly good correlation emerged: the isolated band with a peak around 1330 cm⁻¹ and half-width of about 30 cm⁻¹. Its normalized area $a_{1330}$ (relatively to the area of the carbonyl band, as above discussed) was observed to depend on the concentrations $F_1$ and $F_2$ according to eq (7) below

$$a_{1330} = 1.1 \frac{F_1}{c_{C=O}} + 0.26 \frac{F_2}{c_{C=O}}$$

(7)

where $c_{C=O}$ is the concentration of carbonyl groups, which is easily obtained for a UF resin given its initial mole ratio formaldehyde:urea. The sum of $F_1$ and $F_2$ is constant along the cure, so that eq (7) can be used for obtaining $F_1$ and $F_2$ if that information is available, as it was the case for our experimental runs.

Figure 8 shows a comparison between predicted and measured normalized band intensity at 1330 cm⁻¹ according to eq (7) for the available model compounds and for the uncured resin. There is some scatter, mostly when primary ureas and methyol groups are both present in the same molecule (especially large with the uncured resin, which shows some peculiarities in its spectra, possibly due to methylene ether linkages still being present), but the error is usually only around 20 %, which is low enough for the preliminary study of the kinetics here.
undertaken.

(insert Figure 8)

A simplified kinetic model of the curing reactions

With the aim of determining an empirical equation for the curing reaction of UF resin, an apparent first order kinetic law has been used to fit the data relative to the initial state of the cure at zero time. However, a model based on the known chemistry of this system and hopefully with some predictive value is likely a better alternative. It is based on the following assumptions:

1. Only the reactions between the methylol groups and the ureas in different polymer molecules (no cyclizations) are considered and formaldehyde condensations are completely neglected, whereas they played a major role in the initial reaction with urea.

2. The reverse hydrolysis reactions are neglected. This is hard to accept for these closed systems, and these reactions should be taken into account in further studies, but the available spectra show that the final conversion of methylol groups is quite high. Even if the polymer remains essentially saturated with water, the decrease of concentration of the terminal hydrophilic groups such as the ureas and the methylols should reduce very much the concentration of water in the polymer-rich phase and make this assumption not too inaccurate.

3. All methylol groups are considered equivalent. This is known not to be true for the lower oligomers as above discussed, and we would certainly like to be able to distinguish the terminal methylols of the pendent ones, but the data are too scarce and inaccurate for this to be possible. Therefore, “average” rate constants assigned to the ensemble of the various methylols will be estimated.

4. Primary ureas will be lumped together into a group with some “average” reactivity,
and the substituted ureas will also be lumped, except if the neighboring urea is doubly substituted, as it is known from the reactions between oligomers that the negative substitution effect of urea is so large that it behaves as if it were trifunctional, not tetrafunctional.

Using these assumptions, the kinetic scheme described by eq (8) below is obtained:

\[
\begin{align*}
U_0 + F_1 &\rightarrow U_1 + F_2 \quad k_0 = 2k_P \\
U_1 + F_1 &\rightarrow U_3 + F_2 \quad k_1 = k_P \\
U_2 + F_1 &\rightarrow U_4 + F_2 \quad k_2 = k_P \\
U_1 + F_1 &\rightarrow U_2 + F_2 \quad k_3 = k_S \\
U_3 + F_1 &\rightarrow U_4 + F_2 \quad k_4 = k_S
\end{align*}
\]

(8)

The nomenclature of groups is described by Table 4.

(insert Table 4)

The model has three parameters:

1. A common activation energy \( E \) for both rate constants \( k_P \) and \( k_S \);
2. The rate constant of the reaction between primary ureas and methylols \( k_P \);
3. The rate constant of the reaction between secondary ureas and methylols \( k_S \), which is however nil for the group >NCONH- as above discussed.

Neglecting the volume change of the phase containing the swollen resin where the condensation reactions occur (as the amounts of oligomers in the water-rich phase are also neglected), the population balance equations of the reactive groups can be established as eq (9) below:
\[
\begin{align*}
\frac{dU_0}{dt} &= -k_0 F_1 U_0 \\
\frac{dU_1}{dt} &= F_1 [k_0 U_0 - (k_1 + k_2) U_1] \\
\frac{dU_2}{dt} &= F_1 (k_3 U_1 - k_4 U_2) \\
\frac{dU_3}{dt} &= F_1 (k_1 U_1 - k_4 U_3) \\
\frac{dU_4}{dt} &= F_1 (k_3 U_2 + k_4 U_3) \\
\frac{dF_1}{dt} &= -\frac{dF_2}{dt} = -F_1 [k_0 U_0 + (k_1 + k_2) U_1 + k_3 U_2 + k_4 U_3] 
\end{align*}
\]

The initial concentrations of these several groups (per unit mass of dry resin) are known from quantitative $^{13}$C NMR analysis (as described in Table 3):

\[U_0 = 0.55 \text{ mol/kg} \; ; \; U_1 = 3.98 \text{ mol/kg} \; ; \; U_2 = 0.29 \text{ mol/kg} \; ; \; U_3 = 6.53 \text{ mol/kg} \; ; \; U_4 = 0.69 \text{ mol/kg} \; ; \; F_1 = 8.94 \text{ mol/kg} \; ; \; F_2 = 5.97 \text{ mol/kg} .\]

The Raman spectra only yields the concentration of methylenes $F_2$ with a conspicuous uncertainty (as above discussed) and there is unfortunately no independent confirmation of the concentrations of other groups given the complexity of the spectra and its numerous overlapping bands.

The experimental methylene concentrations $F_2$ were computed using the ratios $a_{1330}$ of the areas of the bands assigned to methylene groups (at around 1330 cm$^{-1}$) and the carbonyl group at 1615-1690 cm$^{-1}$, as discussed in the previous sub-section, taking into account that $F_1 + F_2 = 14.91 \text{ mol/kg}$, as determined by NMR, is constant. The experiments carried out for three different curing temperatures lead to the optimized values of the parameters $E$, $k_P$ and $k_S/k_P$ below:

\[E = 22.0 \text{ kJ/mol} \; ; \; k_P = 0.107 \text{ kg mol}^{-1} \text{ min}^{-1} \text{ (at 110 °C)} \; \; k_S/k_P = 0.148 \]

Note that only the first two concentration measurements at 150 °C (up to 5 minutes) were used. At that higher temperature some other reactions might occur$^{55}$.

A comparison of the measured and predicted values of methylene concentrations (Figure 9)
shows an acceptable agreement (the sum of quadratic errors is 0.66 mol$^2$ kg$^{-2}$ for the 13 data points). An example of the predicted change with time of the chemical groups as predicted by this model is illustrated in Figure 10. It is unfortunate that no confirmation by NMR of these predictions is (yet?) possible.

(Insert Figures 9 and 10)

This activation energy is slightly lower than the literature values measured by DSC $^{56}$. This discrepancy can be explained by the fact that nearly all DSC studies have been done with open samples (even if they are closed, they will not sustain the pressure caused by water vapor pressure), leading to an inherent lack of reproducibility due to the unknown degree of evaporation of water and due to possible losses of formaldehyde during the test. On the other hand, water might play an important role in the curing of UF resins. Water can directly influence the chemical reactions in curing, which are all reversible; it also acts as a plasticizer, increasing the mobility of chemical groups and the possibility of mutual reaction, therefore preventing the so-called “glass effect”.

Conclusions

In order to develop a simplified kinetic model for the cure of an urea-formaldehyde resin commonly used in the production of MDF, an experimental program has been undertaken. This investigation has combined FT-Raman spectroscopy to study the reaction cure and $^{13}$C NMR for the quantitative and qualitative characterization of the starting liquid resin.

The Raman spectra of several model compounds have permitted to clarify the presence and the proportion of certain structural components in the resin. A simplified kinetic model for the formation of methylene groups as a measure for the curing process enabled the study of the resin curing process and the evaluation of the relevant kinetic data of this process. The existing fluorescence on the spectra of cured resin may affect the relative band intensities and therefore the quantitative results. This drawback might be overcome using an internal
standard. On the other hand, the reversibility of reactions as well as the possible formation of cyclic molecular structures will also have to be considered for the eventual prediction of mechanical and rheological properties of the adhesive during and after cure.

Using $^{13}$C NMR, it was possible to identify and quantify the structure of oligomers and to determine quantitatively some structural elements in the uncured UF resin. Although these data seem to provide new insights into the curing process, a detailed kinetic description needs additional analytical results provided by improved analytical techniques. As an example, a detailed characterization of UF resins with different F/U molar ratios could be performed using a Raman spectrometer of state-of-art performance in combination with solid state NMR. Through the recent availability of suitable near infrared spectroscopy, additional information could be achieved by possible evaluation of suitable bands for the quantitative analysis of various chemical structures.
REFERENCES

5. Ebdon, J.; Heaton, P. E. Polymer 1977, 18, 971.
17. de Jong, J. I.; de Jonge, J. Rec Trav Chim 1953, 72, 139.


47. ISO 2555: 1989, Plastics: Resins in the liquid state or as emulsions or dispersions-Determination of apparent viscosity by the Brookfield Test method.


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<th>Compound</th>
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<td>Formaldehyde</td>
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<tr>
<td>Urea</td>
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<td>Ref. 50</td>
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<td>Raman shift (cm⁻¹)</td>
<td>~3427</td>
<td>3342-3334</td>
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<tr>
<td><strong>UF uncured</strong></td>
<td>3333(32)</td>
<td>2965(37)</td>
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<td><strong>UF cured</strong></td>
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<td>-NH₂</td>
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<th>~1280</th>
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<td>Free formaldehyde $\text{HOCH}_2\text{OH}$-{F}</td>
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<td>U₀</td>
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Captions of Tables and Figures

Table 1. Sources of used model compounds.

Table 2. Band assignment of Raman spectra of the uncured UF resin and the after curing at 100 °C for 10 minutes.

Table 3. Assignment of $^{13}$C NMR signals for urea-formaldehyde resins.

(aRef. 41 ; bRef. 35, cRef. 6)

Table 4. Nomenclature of groups in the simplified kinetic scheme of the polycondensation stage of urea-formaldehyde resins.

Figure 1. Raman spectra of urea, methylene diurea (UFU) and (FUF) between wavenumbers 800 and 1800 cm$^{-1}$.

Figure 2. Raman spectra of urea, methylene diurea (UFU) and (FUF) between wavenumbers 2700 and 3600 cm$^{-1}$.

Figure 3. Comparison of the 1350-1500 cm$^{-1}$ region in the normalized Raman spectra of three urea-formaldehyde model compounds dimethylolurea (FUF), trimethylene tetraurea U(FU)$_3$ and monomethylol methylenediurea (UFUF).

Figure 4. Comparison of the 800-1200 cm$^{-1}$ region in the Raman spectra of three urea-formaldehyde model compounds dimethylolurea (FUF), dimethylolurea dimethylether (MFUFM) and dimethyloluron dimethylether (MFUrFM)

Figure 5. Comparison of the 1250-1700 cm$^{-1}$ region in the Raman spectra of three urea-formaldehyde model compounds methylene diurea (UFU), monomethylol methylenediurea (FUFU) and dimethylolurea (FUF);

Figure 6. Comparison between the Raman spectra (region 1290 - 1360 cm$^{-1}$) of the UF resin before and after curing at 110 °C for various time spans.

Figure 7. Comparison between the Raman spectra (region 1410 - 1500 cm$^{-1}$) of the UF resin before and after curing at 110 °C for various time spans.

Figure 8. Comparison between predicted and observed intensity of the band at around
1330 cm\(^{-1}\) normalized by the area of carbonyl band for the available model compounds and uncured resin.

**Figure 9.** Fitting of the kinetic model to the experimental methylene concentrations.

**Figure 10.** Example of group concentrations predicted by the kinetic model (\(T = 130 \, ^\circ\text{C}\)).
Figure 1: Raman spectra of urea, methylene diurea (UFU) and (FUF) between wavenumbers 800 and 1800 cm$^{-1}$.
Figure 2: Raman spectra of urea, methylene diurea (UFU) and (FUF) between wavenumbers 2700 and 3600 cm$^{-1}$.

261x166mm (72 x 72 DPI)
Figure 3: Comparison of the 1350-1500 cm⁻¹ region in the normalized Raman spectra of three urea-formaldehyde model compounds dimethylolurea (FUF), trimethylene tetraurea U(FU)₃ and monomethylol methylenediurea (UFUF).

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Figure 4: Comparison of the 800-1200 cm$^{-1}$ region in the Raman spectra of three urea-formaldehyde model compounds dimethylolurea (FUF), dimethylolurea dimethylether (MFUFM) and dimethyloluron dimethylether (MFUrFM).
Figure 5: Comparison of the 1250-1700 cm$^{-1}$ region in the Raman spectra of three urea-formaldehyde model compounds methylene diurea (UFU), monomethylol methylenediurea (FUFU) and dimethylolurea (FUF).
Figure 6: Comparison between the Raman spectra (region 1290 - 1360 cm⁻¹) of the UF resin before and after curing at 110 °C for various time spans.

198x136mm (72 x 72 DPI)
Figure 7: Comparison between the Raman spectra (region 1410 - 1500 cm\(^{-1}\)) of the UF resin before and after curing at 110 °C for various time spans.

197x132mm (72 x 72 DPI)
Figure 8: Comparison between predicted and observed intensity of the band at around 1330 cm⁻¹ normalized by the area of carbonyl band for the available model compounds and uncured resin.

208x142mm (72 x 72 DPI)
Figure 9: Fitting of the kinetic model to the experimental methylene concentrations.

204x140mm (72 x 72 DPI)
Figure 10: Example of group concentrations predicted by the kinetic model ($T = 130$ °C).
\[
\text{NH}_2\text{CONH}_2 + \text{HOCH}_2\text{OH} \xrightleftharpoons[k_1']{k_1} \text{NH}_2\text{CONHCH}_2\text{OH} + \text{H}_2\text{O}
\]
\[
\text{NH}_2\text{CONHCH}_2\text{OH} + \text{HOCH}_2\text{OH} \xrightarrow{k_2} \text{HOCH}_2\text{NCONHCH}_2\text{OH} + \text{H}_2\text{O} \\
\text{FU} \quad \text{F} \quad \text{FUF}
\]
\[
\begin{align*}
\text{X-N-CO-N-CH}_2\text{OH} + \text{H}_2\text{O} & \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} \text{X-N-CO-N-CH}_2\text{OH} + \text{H}_2\text{O} \\
\text{CH}_3\text{OH} & \quad \text{CH}_3\text{OH}
\end{align*}
\]