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Use of NIR for structural characterization of urea–formaldehyde resins

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Abstract

In this paper, the effect of pH and temperature on the structure of urea–formaldehyde resins was studied. GPC, NMR and Raman measurements were performed to elucidate the structural characteristics of the resin systems. Fourier Transform Near Infrared (FT-NIR) spectroscopy via optical fibers was used to monitor the reaction progress in situ. It was found that the reactions of urea and formaldehyde at different temperatures and pH values result in resins with different structures and properties: Resins produced at high temperatures and acidic pH values exhibit higher degrees of condensation, presumably because of the development of more cross-linked structures.

Keywords: A. Adhesives for wood; C. Infrared spectra; Reaction kinetics

1. Introduction

Urea–formaldehyde resins are widely used as adhesives in the wood panel industry. Their wide potential as wood adhesives was recognized after the Second World War and since then, they are considered one of the most important wood adhesives. Depending on manufacturing conditions, UF resins can have a variety of properties to match the different kinds of demands in wood bonding. However, their main disadvantage remains the reversibility of the aminomethylene link, which decreases their water resistance and results in formaldehyde emission. To overcome this problem, industry has responded by producing resins of low formaldehyde content during the last 20 years.

Urea–formaldehyde resins are water-based thermosetting resins built up by condensation polymerization [1]. Reaction parameters that mostly affect the properties of the final product are the molar ratio of formaldehyde to urea, pH, temperature, concentration and time.

The synthesis of UF resins from urea and formaldehyde often proceeds in two steps [1,2]:

(1) The first is the so-called methylolation reaction, which is catalyzed by both acids and bases and leads to the formation of hydroxymethyl compounds. Monomethylol-, dimethylol-, and trimethylolurea have been isolated by controlling the ratio of the reactants and identified by means of NMR spectroscopy, while tetramethylolurea has never been observed.

(2) Subsequently, condensation reactions between the various methylol species and urea are taking place. These reactions are mainly acid catalyzed and lead to a complex mixture of low molecular weight UF adducts (oligomers). The condensing moieties link together by methylene or by dimethylene ether links (N–CH_2–N and N–CH_2OCH_2–N, respectively). Dimethylene ether links can be formed under alkaline conditions inter- or intramolecularly. In the latter case cyclic compounds are formed.

The as produced UF resins cure irreversibly to form a cross-linked network at low pH (best pH value being around 2–4). The cure reaction can be induced by any

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method that lowers the pH (e.g. addition of catalysts or hardeners) and proceeds quickly upon heating resulting in the formation of three-dimensional networks and ultimately a thermosetting resin.

Commercial UF adhesives are low viscosity resins that contain methylol end groups through which the curing reaction proceeds. Resin molecular weight may vary from a few hundred to a few thousand, with a wide range of molecular sizes. In board manufacture, control of the average molecular size is essential since it affects the viscosity and rheological properties of the resin, the wetting behavior of a wood surface and penetration into the wood surface.

The complex chemistry of UF resins has been the subject of numerous structural investigations. The most detailed picture has emerged from NMR data. Chiavarini et al. [3] interpreted the ^{1}H-NMR spectra of UF condensates while Ebdon and Heaton [4] were the first to report ^{13}C-NMR analysis of UF resins. In both publications, known urea–formaldehyde adducts were used as reference compounds. A combination of experimental techniques was used by Dankelman et al. [5] to provide insights into the composition of selected UF resins. Information on low molecular weight compounds was obtained from gas chromatograms of silylated resin samples while the ratio of low to high molecular weight components was estimated from GPC analysis. To obtain a more detailed picture, ^{1}H-NMR spectra of resin samples were acquired. Tomita and Hatono [6] used ^{13}C-NMR to establish a method for quantitative analysis of reacted formaldehyde in UF resins. By combining the NMR method with chemical analysis, they were able to measure the concentration of characteristic functional groups. ^{13}C solid-state NMR with a judicious selection of rotors and pulse techniques has also been used by Jada [7] for the quantitative determination of the various functional groups present in uncured UF resins synthesized at different values of pH. Resins prepared under acidic conditions were found to exhibit more methylene units in the polymer branch and less methylol moieties in the polymer chain compared to resins prepared under alkaline conditions.

In their very thorough ^{13}C CP/MAS NMR investigation, Chuang and Maciel [8] focused on the effects of urea concentration, formaldehyde-to-urea (hereafter *F/U*) molar ratio and pH on the structure of UF resins prepared at room temperature. The resins prepared under acidic conditions ranged from simple structure to very complicated, depending on the other two parameters. Resins prepared under neutral or basic conditions mainly consisted of methylolureas and/or structures with dimethylene ether connections between two urea units. The effects of *F/U* molar ratio and of pH value were larger for the more concentrated reaction mixtures. The degree of cross-linking increased by increasing the *F/U* molar ratio from 1 to 2 and by decreasing the pH from 5 to 1. The same authors also reported the formation of substantial amounts of cyclic compounds (urons) under acidic conditions from concentrated reaction mixtures with *F/U* molar ratios of 2 and 3. The formation of cyclic compounds at pH higher than 6, or lower than 4 was also reported by Soulard et al. [9]

Braun and Bayersdorf [10,11] monitored the growth of urea–formaldehyde reaction products using gel permeation chromatography. They employed polyvinyl acetate gel and DMF/DMSO mixtures to investigate the influence of pH and *F/U* molar ratio on molecular weight distribution and reported that acidic reaction conditions were more effective than alkaline catalysis. The influence of pH, temperature and *F/U* molar ratio was also examined by Kumlin and Simonson [12] by means of liquid chromatography. They showed that the formation of oxymethylenediurea compounds was favored at alkaline pH and increased with increasing pH from 8.0 to 9.4 whereas the formation of diurea compounds containing a methylene bridge was strongly favored when the reaction mixture was made acidic and increased with decreasing pH from 5.1 to 3.5. At low *F/U* molar ratios (from 1.4 to 1.6) a minimum in the formation of condensed products was found at a pH value of about 8, while with increased molar ratio ($F/U=2.2$), the reaction minimum appeared at neutral pH. In all cases, a high reaction temperature greatly increased the condensation.

Overall, these studies demonstrate that a great variety and diversity of UF structures leading to resins with different performance can be produced by manipulating the synthetic conditions. In turn, the control of the synthetic conditions during industrial synthesis is critical in defining the quality and reproducibility of the product. Unfortunately, none of the established experimental techniques for the structural analysis of the UF resins has a true potential for in situ application. It is therefore essential to establish a method for the in situ monitoring of the reaction system to assess in real time the pathway(s) followed during UF resin synthesis.

The use of NIR spectroscopy in remote monitoring has been widely addressed in the chemical literature. Optical spectroscopic techniques lend themselves to process analysis because of their short response time and their ability to perform multicomponent chemometric determinations [13]. By coupling fiber optics to a FT-NIR spectrometer, reactions can be monitored in real time quickly and easily. Typical applications of NIR process monitoring include pharmaceuticals, oil, food and fermentation analysis, as well as certain polymer systems [14,15].

In the NIR frequency range (typically 4000–12,000 cm^{-1}) overtone and combination vibrational modes of the sample are active. Depending on the

symmetry and anharmonicity of the corresponding fundamental vibrational modes, the first overtone and combination bands in the near infrared region are 10–100 times weaker than their fundamentals. Longer pathways can therefore be used (1–20 mm) allowing data acquisition by transmission through thick samples and eliminating the need for sample dilution. Mainly overtone and combination bands of functional groups containing hydrogen atoms (C–H, N–H, O–H) are observed in the NIR region, but spectral assignments to specific vibrational modes are not always possible.

It is the purpose of this study to explore the capabilities of NIR spectroscopy for the on line monitoring of the aminoplastic resin synthesis. Model UF compounds and adhesives have been synthesized and measured at systematically varying temperature and pH conditions. The various reaction products have been studied also by gel permeation chromatography (GPC), ^{1}H- and ^{13}C- Nuclear Magnetic Resonance (NMR) spectroscopy and FT-Raman spectroscopy to provide reference structural information and assist the interpretation of the NIR spectra.

2. Experimental

2.1. Synthesis of model compounds

These compounds are low molecular weight adducts produced from urea (pro-analysis, 99.5%, J. T. Baker) and formaldehyde (37%, stabilized with 9–15% methanol, J. T. Baker) under alkaline or acidic conditions and are the so-called model compounds. Their synthesis and purification was according to Ludlam [16] with minor modifications and their characterization by NMR. More specifically:

2.1.1. Monomethylol urea

A 33% w/w aqueous urea solution was prepared containing 11% w/w of a 10% w/v disodium hydrogen orthophosphate solution. 37% w/w aqueous formaldehyde was added to a F/U molar ratio equal to 0.5 and the mixture was allowed to react for 30 min. Urea was added again to a molar ratio of 0.25, which was readjusted to 0.5, after the urea was completely dissolved, by the addition of 37% formaldehyde solution. During synthesis, the temperature of the reaction mixture was kept below 25°C and the pH was kept constant at a value of 7.3. The crude product was kept at 0°C for 24 h, after which time it precipitated. Using industrial methanol, a slurry was formed and the crude product was filtered off and recrystallized twice from ethanol containing 1% v/v of a 10% w/v disodium hydrogen orthophosphate solution.

2.1.2. Dimethylol urea

A 33% urea solution was prepared containing 11% of a 10% disodium hydrogen orthophosphate solution. Thirty-seven percent formaldehyde solution was added in four stages to F/U molar ratios of 0.5, 1, 2 and 2.5, respectively. The temperature was kept below 25°C and the pH at 7.3. The crude product was kept at 0°C for 24 h and then filtered and recrystallized twice from industrial methanol. According to NMR analysis the product was exclusively N, N' dimethylol urea.

2.1.3. Methylene diurea

A 50% urea solution was prepared containing 0.3% w/w of a 85% w/w phosphoric acid solution. Thirty-seven percent formaldehyde solution was added to a molar ratio F/U equal to 1/20. The temperature was kept at 30°C and the pH at 3.5. The crude product was kept at 0°C for 24 h and was then filtered off and recrystallized twice from water. Even after the recrystallizations the product was found to contain some unreacted urea due to the large excess (1/20).

2.1.4. Dimethylol methylenediurea

A 5% w/w aqueous solution of methylene diurea (MDU) was prepared containing 0.4% w/w disodium hydrogen orthophosphate. When methylene diurea was completely dissolved, 37% w/w aqueous formaldehyde was added to a F/MDU molar ratio equal to 1/1.3 and the mixture was allowed to react for 30 min at 24°C. Formaldehyde was added again to increase the molar ratio F/MDU to 2.1. The mixture was allowed to react overnight at room temperature (not exceeding 30°C) and was then evaporated to dryness in a rotary evaporator. The solid product was recrystallized from a 20% w/w aqueous ethanol solution.

2.2. "Model" resin synthesis

Seven urea–formaldehyde adhesive resins were prepared under constant temperature (75°C, 85°C and 90°C) and pH (5.5, 6.5, 7.5 and 8.5) conditions with a molar ratio of formaldehyde to urea, F/U, equal to 2. The general synthetic procedure employed was as follows:

A 2-l, 4-neck, round bottom flask, equipped with a mechanical stirrer, a thermometer, a pH meter (and a NIR probe for on line measurements) was charged with 37% formaldehyde solution and heated up to 10° below the desired temperature. The pH of the solution was adjusted to the desired value and urea was added to a F/U molar ratio of 2. Urea dissolution was an endothermic phenomenon and lowered the temperature of the solution by up to 20°. A few minutes later, the temperature rose again to the desired value because the exothermic reaction of urea and formaldehyde started taking place. Both the pH and temperature were

kept constant throughout the synthesis, which lasted typically 2.5 h. The pH was then adjusted to 8.5 and the product was quickly cooled to 30°C.

2.3. Vibrational spectroscopic measurements

Raman spectra were measured on a Fourier-transform instrument (Bruker RFS 100) employing ca. 400 mW of the 1064 nm Nd:YAG laser line. The spectra represent averages of 100–400 scans, and they were collected at a 4 cm^{-1} resolution with a back scattering geometry.

The near-infrared spectra were measured with a Fourier-transform spectrometer (Bruker Vector 22N) in the fiber-optic data acquisition mode. A 2 m long quartz single fiber optical cable coupled to a quartz transmission probe (Hellma QX, 1.00 mm optical path) was employed. Data acquisition was performed on-line by immersing the transmission probe directly in the reactor. These single beam spectra were referenced against air and reported in the Absorbance formalism. Spectra were collected at 8 cm^{-1} optical resolution at a zero filling factor of 2 and represent averages of ca. 100 scans. The acquisition time for each spectrum was ca. 1 min, and was repeated periodically every 2–5 min, depending on the reaction. Second derivative spectra were calculated by the Savitsky–Golay algorithm (9 point smoothing) available in the Bruker OPUS software [17].

2.4. Gel permeation chromatography

Gel permeation chromatography was performed using a Shimadzu chromatograph equipped with a pump, model LC-9A, a Rheodyne injection valve with a 20 μl loop and a refractive index detector, model RID 6-A. Dimethyl formamide (p. a. Merck)/0.1 M LiCl (p. a. Merck) was used as eluent solvent and the separation was carried out on two PL-Gel columns (500 and 100 Å) thermostatted at 70°C with an elution rate of 1 ml/min. It has been shown that the lithium salt disrupts intermolecular hydrogen bonds, which are responsible for the association effect [18]. 0.5% weight solutions of resin samples in dimethyl sulfoxide (Chromasolv, Riedel-de Haën) were prepared and filtered with 0.45 μm filter. For the calibration of the GPC system polyethylene glycol (PEG) standards were used.

2.5. NMR spectroscopy

^{1}H and ^{13}C-NMR spectra were recorded using a Gemini 2000, Varian-NMR (300 MHz-^{1}H) spectrometer. ^{1}H-NMR spectra were acquired with a pulse width of 14.7 μs, 20 scans and a probe temperature set to 25°C. For the ^{13}C-NMR spectra, a pulse width of 22.5 μs, 10,000 scans and a probe temperature of 25°C were used. Resin samples were dissolved in spectroscopic grade DMSO-d_6 (Acrōs Organics). 80–120 mg of the samples in 1 ml DMSO-d_6 were used for each measurement.

3. Results and discussion

3.1. Model compounds

The ^{1}H and ^{13}C-NMR spectra of UF model compounds were measured and found to be virtually identical to those reported in the literature [3–8]. The chemical shifts corresponding to the various species are compiled in Tables 1 and 2. Also, the Raman spectra of urea, *N*, *N'* DMU and MDU (Fig. 1) agree with those published [19].

NIR was used to measure online the stepwise synthesis of dimethylol urea (vide supra). Representative spectra acquired during the discrete steps of formaldehyde addition are shown in Fig. 2. The absorption spectra are dominated by the broad combination and overtone bands of water (at ca. 5200 and 7000 cm^{-1}, respectively) and barely allow for the detection of the sharper NH and CH vibrations, mainly in the combination regime (ca. 4200–4800 cm^{-1}). This overlapping of broad and narrow features precludes the use of spectral deconvolution as a means to monitor individual bands. Instead, the spectra were analyzed in the 2nd derivative formalism, which effectively filters out the broad bands and increases the resolution of the narrow components [20]. Details of the 2nd derivative spectra in the combination and overtone ranges are shown in Fig. 3 (a and b, respectively)

Table 1
^{1}H-NMR assignments of UF model compounds (where s and t denote singlet and triplet, respectively)

Model compound	NH_2	$NHCH_2OH$	$HNCH_2NH$	NCH_2N	CH_2OH	CH_2OH
Urea	5.479 s	—	—	—	—	
Monomethylol urea	5.612 s	6.552 t	—	—	4.407 t	5.226 t
N, *N'* dimethylol urea	—	6.629 t	—	—	4.459 t	5.272 t
Methylene diurea	5.677 s	—	6.539 t	4.183 t	—	—
N, *N'* dimethylol methylenediurea	—	6.619 t	—	4.274 t	4.442 t	5.268 t

Table 2
^{13}C-NMR assignments of UF model compounds

Model compound	NCON	CH_2OH	NCH_2N
Urea	160.1	—	—
Monomethylol urea	158.5	63.6	
N, *N'* dimethylol urea	157.2	63.5	
Methylene diurea	159.1		45.6
N, *N'* Dimethylol methylenediurea	157.7	63.5	45.3

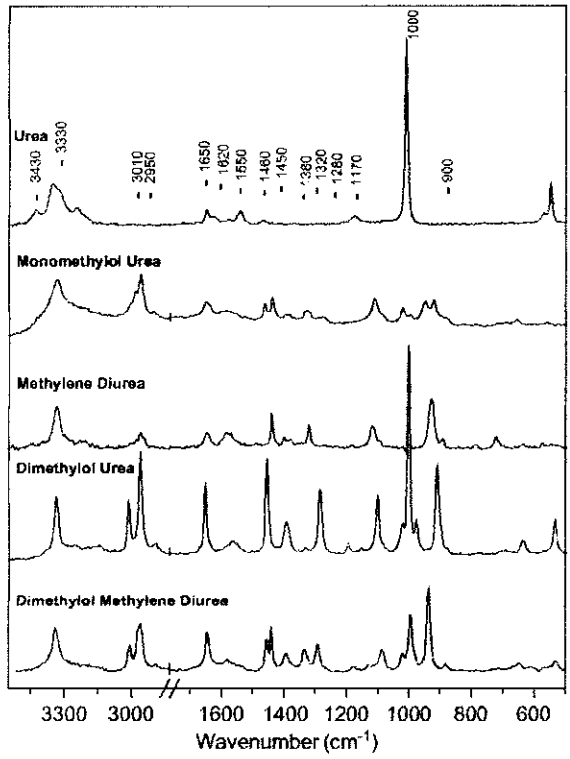

Fig. 1. Raman spectra of model compounds.

Starting from the low-frequency end of the urea solution spectrum (Fig. 3a, $F/U=0$), two doublets are identified at 4645, 4549 and 4950–5028 cm^{-1}. They are attributed to combination modes between the N–H stretches and the rocking and bending modes of the NH_2 group, respectively. At higher frequencies (Fig. 3b, $F/U=0$), the 2ν overtones as well as the ($\nu_{sym}+\nu_{asym}$) combination modes of the N–H stretches at 6570, 6667, 6737 and 6802 cm^{-1} are observed. The stepwise addition and reaction of formaldehyde results in significant spectral changes. A new feature, attributed to the CH_2 stretching-bending combination mode appears at 4449 cm^{-1}. Several weak and sharp features appear in the 5600–5800 cm^{-1} range where the overtones of the C–H stretching modes are expected. These features change in relative intensity as formaldehyde reacts to methylolate urea, but a more detailed assignment is not currently available. The well-defined combination

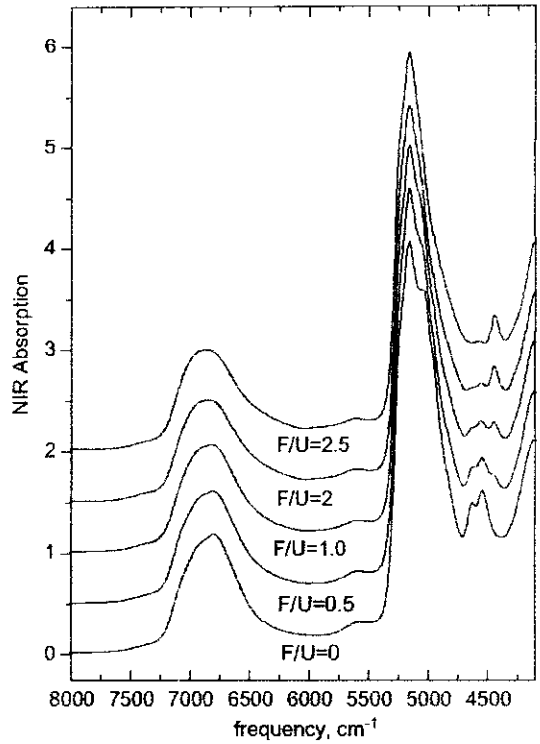

Fig. 2. NIR Absorption spectra acquired during the synthesis of dimethylol urea.

modes of the NH_2 group decrease in intensity and nearly vanish at $F/U=2.5$. The N–H overtone profile also decreases in intensity although a feature at ca. 6730 cm^{-1} persists even at $F/U=2.5$. This latter feature is reasonably assigned to the overtone of the secondary NH bond stretch, indicating the formation of *N*, *N'*-disubstituted amide species. Note that such a species would lack a stretching-rocking combination mode in the 4500–4650 cm^{-1} range.

A question that remains open concerns the vibrational signature of the $-NH_2$ group in a mono- or *N*, *N*-disubstituted ureas, which cannot be taken a priori as identical to that of $-NH_2$ in unsubstituted urea. This would be important in probing the formation of intermediate species during the formation of DMU.

In a recent publication [21] we had reported the spectra of aqueous urea solutions as a function of concentration. Over very broad concentration ranges, these solutions are characterized by the 4645 cm^{-1} combination band at a fixed frequency and with intensity scaling with concentration. Indeed, a quantitative Beer–Lambert calibration (with $R^2>99.9\%$) can be set to predict the concentration of urea on the basis of the intensity of the 2nd derivative spectrum at 4645 cm^{-1}.

Armed with this spectroscopic analytical tool, we present in Fig. 4 the evolution of the 4645 cm^{-1} intensity during the synthesis of DMU, and its expression into

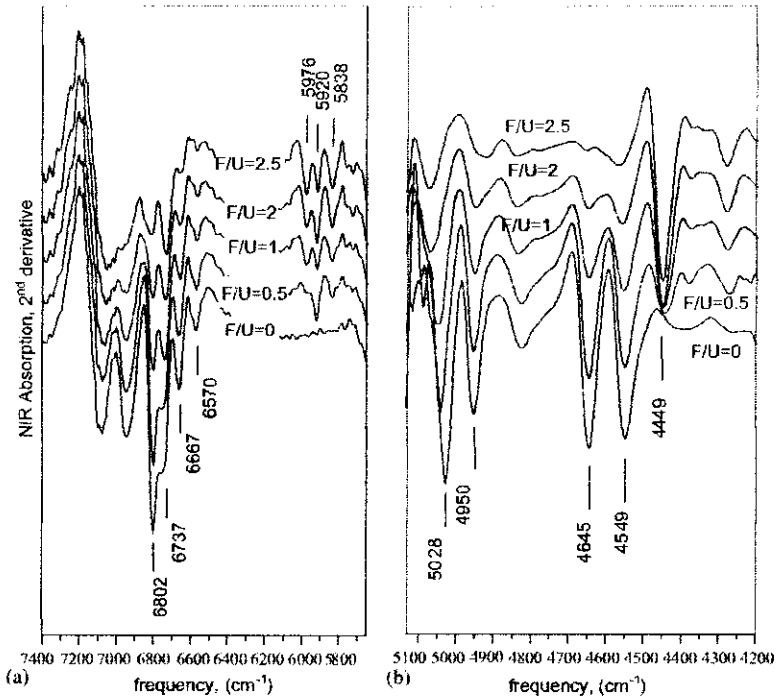

Fig. 3. Details of the 2nd derivative of the NIR absorption spectra shown in Fig. 1 in the combination (a) and overtone (b) ranges.

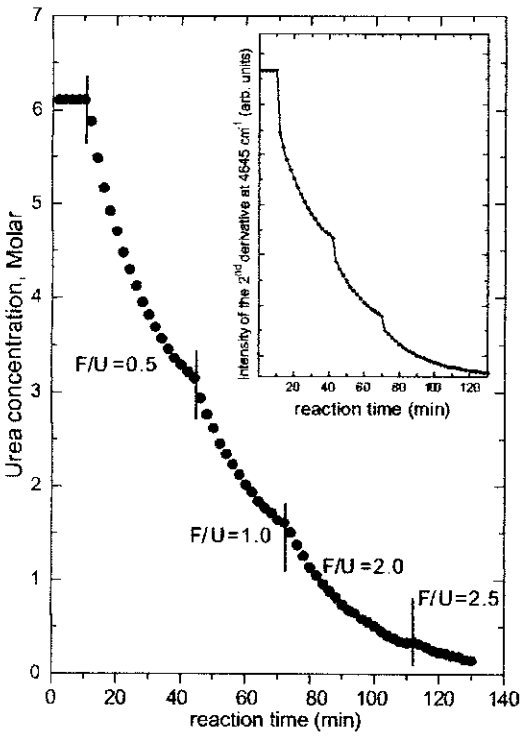

Fig. 4. Kinetics of the urea consumption during DMU synthesis. Vertical bars mark the adjustments of stoichiometry described in the Experimental. The inset shows the time evolution of the NIR intensity (2nd derivative) at 4645 cm^{-1}. For details see text.

urea molar concentration. Each data point corresponds to 1 min data acquisition, repeated every 2 min. Concentrations are plotted after correction for the volume changes induced by the additions of the formaldehyde solution. Fig. 4 shows that the concentration of urea decreases quasi-exponentially after every formaldehyde addition. Already at $F/U = 0.5$, the initial concentration appears reduced by ca. 50%. At this molar ratio, no more than 50% of the urea could have reacted towards MMU, while more than 75% of the overall $-NH_2$ species present must have remained intact. Therefore, the kinetic data suggest strongly that the 4645 cm^{-1} band is a selective probe of molecular urea and not a generic probe for unreacted $-NH_2$ groups.

3.2. UF "model" resins

UF model resins were prepared under constant temperature and pH conditions with a molar ratio F/U equal to 2 to examine which characteristic groups are favored at each set of pH and temperature.

3.2.1. Molecular weight distributions

The average molecular weights of the "model" UF resins were determined by gel permeation chromatography. Table 3 assembles the molecular weight data for each resin sample and typical resin chromatograms are shown in Fig. 5. The broad peak corresponding to high molecular weight polymers eluting early in the sample (retention time 11–13.5 min) is more intense in "model" resins prepared at acidic pH and becomes more extended by increasing reaction temperature. The two sharper peaks that follow correspond to medium and low molecular weight adducts, respectively, the latter

Table 3
Average molecular weights of the "model" UF resins

Temperature (°C)	pH	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	Polydispersity, z
75	8.5	1.7×10^2	2.0×10^2	2.4×10^2	1.17
75	7.5	1.8×10^2	2.0×10^2	2.4×10^2	1.11
75	6.5	1.9×10^2	2.3×10^2	2.9×10^2	1.21
75	5.5	2.2×10^2	3.0×10^2	4.1×10^2	1.36
85	5.5	3.2×10^2	5.2×10^2	8.9×10^2	1.63
85	8.5	1.8×10^2	2.1×10^2	2.6×10^2	1.17
90	8.5	1.7×10^2	2.0×10^2	2.5×10^2	1.17

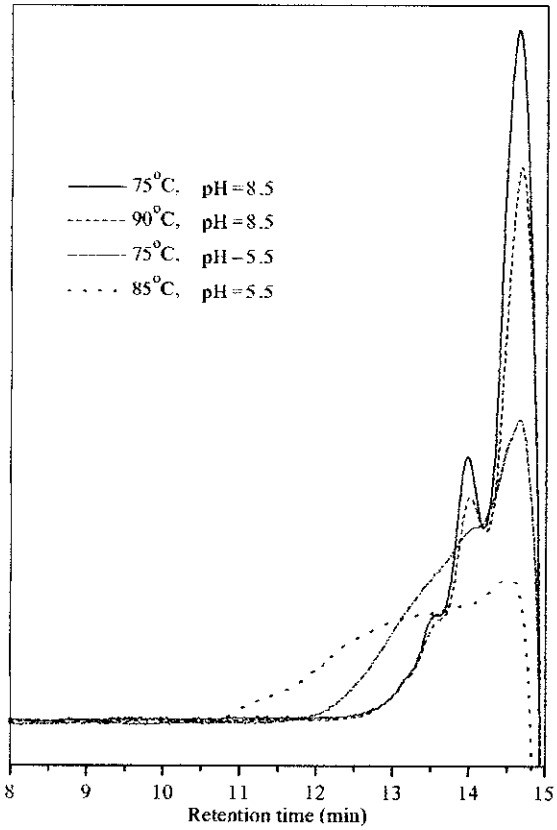

Fig. 5. Typical chromatograms of "model" UF resins.

being attributed to methylol ureas, based on the retention times of the model compounds. These species are more evident in resins prepared at alkaline or neutral pH and are not affected by increasing reaction temperature (from 75°C to 90°C). High molar mass molecules are only observed at acidic pH (5.5) and increase by increasing reaction temperature.

3.2.2. *Spectroscopic analysis of final "model" resins*

NMR analysis was used to study the structure of "model" UF resins produced at different temperature and pH conditions. Peak assignments of the resins are made with reference to the NMR spectra of model compounds and are compiled in Tables 4 and 5. It

Table 4
^{1}H-NMR assignments of "model" UF resins.

Structural unit	Value (ppm)
$=NCH_2OCH_2N\underline{H}-$	7.000–7.200
$=NCH_2N\underline{H}-$	7.000–7.300
$-N\underline{H}CH_2OCH_2N\underline{H}-$	6.800–7.000
$HOCH_2N\underline{H}CO-$	6.500–6.800
$CH_2(N\underline{H}CON\underline{H}-)_2$	6.600–6.800
$N\underline{H}_2CO-$	5.600–5.800
$\underline{H}OCH_2N$	5.200–5.500
$HOC\underline{H}_2N$, $NC\underline{H}_2OC\underline{H}_2N$, $NC\underline{H}_2N$	4.350–4.950

Table 5
^{13}C-NMR assignments of "model" UF resins

Structural unit	Value (ppm)
$-N\underline{C}ON-$	153.0–160.1
$HNCH_2O\underline{C}H_2N=$	74.1–74.6
$HO\underline{C}H_2N=$	69.3–70.2
$-HN\underline{C}H_2O\underline{C}H_2NH-$, $=NCH_2O\underline{C}H_2NH-$	66.5–67.6
$HO\underline{C}H_2N$	63.5–64.3
$=N\underline{C}H_2NH-$	51.8–55.0
$-NH\underline{C}H_2NH-$	45.5–48.8

should be noted that ^{13}C-NMR analysis is extremely useful in identifying the structural units present in UF resins. In contrast to the ^{1}H-NMR spectra of UF resins, where the peaks of $-CH_2-$ protons appear overlapping, the different kinds of carbons are well resolved in the ^{13}C-NMR spectra (Fig. 6).

^{1}H-NMR spectra consist of bands corresponding to $-CH_2-$, $-OH$, $-NH_2$ and $-NH-$ protons and can be used for quantitative characterization of the resins. By calculating the relative peak areas of the above-mentioned groups, the percentage abundances of the non-substituted, *N*-substituted and *N*, *N*-disubstituted amide groups as well as methylol groups can be obtained [22]. The relative peak areas *I* of the groups are given as

$$I_{(-CH_{2,total}-)} = a,$$
$$I_{(-CH_2OH)} = b,$$
$$I_{(-NH_2)} = c,$$
$$I_{(-NH-)} = d.$$

The total moles of formaldehyde can then be expressed as $a/2$. If the molar ratio of formaldehyde to urea is set as R, the total moles of urea can be written as $a/(2R)$ containing a/R total nitrogen atoms. Nitrogen atoms in $-NH_2$ and $-NH-$ groups are expressed as $c/2$ and d respectively and thus $-N=$ nitrogen atoms can be given by $(a/R)-(c/2)-d$. By dividing the above expressions with the total number of nitrogen atoms, the percentage abundances of the amide groups can be calculated:

$$\%-NH_2: 100\frac{R}{a}\cdot\frac{c}{2}, \quad (1)$$

$$\%-NH-: 100\frac{R}{a}\cdot d, \quad (2)$$

$$\%-N=: 100\left[1-\frac{R}{a}\left(\frac{c}{2}+d\right)\right]. \quad (3)$$

The ratio of methylol groups $-CH_2OH$ to total moles of formaldehyde-$CH_{2,total}-$ can be expressed as

$$\%-CH_2OH: \frac{-CH_2OH}{-CH_{2,total}-}=2\frac{b}{a}. \quad (4)$$

The percentage abundances of the characteristic groups in "model" UF resins are listed in Table 6. The resin prepared at 75°C and pH 7.5 shows the highest percentage abundance of $-CH_2OH$ groups, which, in combination with a high percentage of $-NH-$ and a low of $-N=$, indicates a low degree of condensation. According to the ^{1}H-NMR spectrum of the resin (Fig. 7) the reaction mixture consists mostly of low molecular weight products even though it was allowed to react for 2.5 h. Its structure can be assigned to a mixture of dimethylolurea and to a condensation product of two dimethylol-ureas via ether link formation. The ^{13}C-NMR spectrum (Fig. 8) also verifies the presence of mainly two carbonyl groups at 157.7 and 157.5 ppm, methylol groups, which appear at 63.6 ppm and an ether bridge at 67.6 ppm. $-HNCH_2O\underline{C}H_2N=$, $-NH\underline{C}H_2N=$ groups appear in very low abundance.

At 75°C and slightly acidic conditions (pH = 6.5) the condensation degree remains low (58%–CH_2OH) and the presence of more $-N=$ nitrogen atoms underlies the formation of *N*, *N* methylolated compounds, in addition to dimethylol urea. In accordance with this observation, the ^{13}C-NMR spectrum indicates that both methylene (54.3 ppm) and ether (67.5 ppm) bridges exist, the methylene bridge being attached to a tertiary N atom.

At 75°C and 8.5 pH the condensation degree remains low but ether bridges predominate (the ^{13}C-NMR spectrum shows no methylene links). In the ^{1}H-NMR

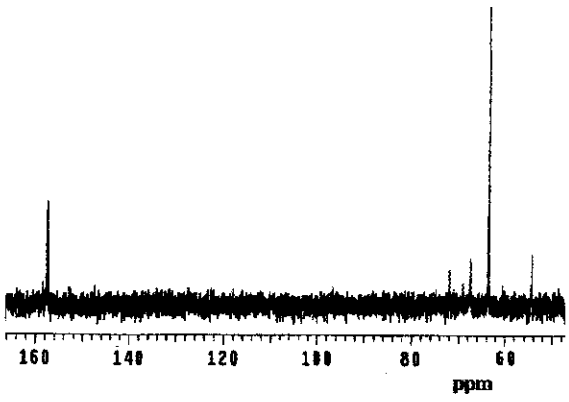

Fig. 6. Typical ^{13}C-NMR spectrum of a "model" UF resin prepared at 75°C and 6.5 pH.

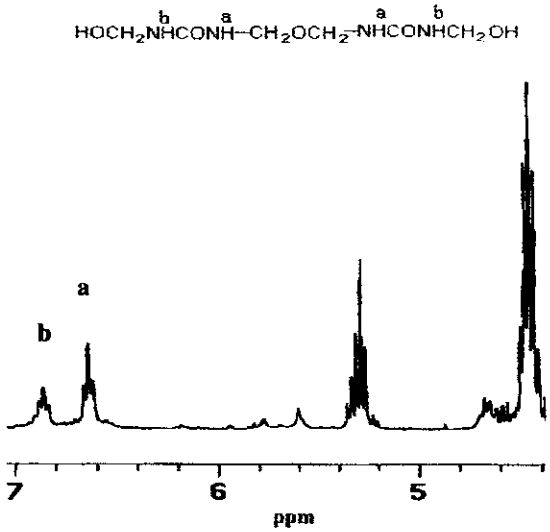

Fig. 7. ^{1}H-NMR spectrum of a "model" UF resin prepared at 75°C and 7.5 pH.

Table 6
Percentage abundances of the characteristic groups in "model" UF resins

Characteristic groups	75°C, pH = 8.5	75°C, pH = 7.5	75°C, pH = 6.5	75°C, pH = 5.5	85°C, pH = 5.5	85°C, pH = 8.5	90°C, pH = 8.5
%–NH_2	5	1	5	6	7	6	11
%–NH–	85	86	62	57	51	79	68
%–N=	10	13	33	37	42	15	21
%–CH_2OH	57	67	58	22	17	44	27

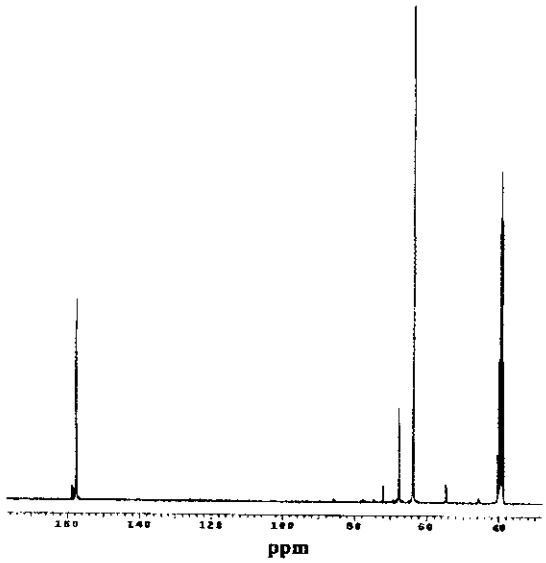

Fig. 8. ^{13}C-NMR spectrum of a "model" UF resin prepared at 75°C and 7.5 pH

spectrum new peaks become evident at 4.8–5.0 ppm. These structures become more pronounced at 90°C and pH = 8.5. Under these conditions, condensation takes place, since the abundance of $-CH_2OH$ groups decreases to 27%, mostly through ether bridges attached to secondary and tertiary N atoms (^{13}C-NMR data). The GPC chromatograms indicate a lack of high molecular weight molecules, it is therefore concluded that condensation is happening to a significant extent intramolecularly. As a result, the peaks at 4.8–5.0 ppm in the ^{1}H-NMR spectra are assigned to CH_2 protons in cyclic compounds.

Resins prepared at acidic pH (5.5) contain a multitude of methylolated species and methylene bridges attached to secondary and tertiary N atoms forming high molar mass molecules (as verified also by the GPC analysis). Increasing reaction temperature (from 75°C to 85°C) results in higher degree of condensation. In ^{1}H-NMR, this is manifested by increase in –N= and decrease of $-CH_2OH$ (Table 6).

According to the ^{13}C-NMR spectra of the resins, the presence of ether bridges (peak at 66.5–67.6 ppm) is relatively more pronounced in the ones prepared at 75°C and 90°C and pH = 8.5 than in the resins prepares at 75°C and pH = 7.5 and 6.5.

Contrary to NMR, the vibrational assignments of urea formaldehyde compounds remain difficult to interpret due to the fact that the moieties present are strongly interacting, but also because of the possibilities for hydrogen bonding. Some assignments can be advanced with reference to the spectra of the model compounds (Fig. 1). In the high frequency range, 3300–3450 cm^{-1}, the N–H stretching vibrations are Raman active [23]. While both primary and secondary amine groups exhibit a strong peak between 3320 and 3350 cm^{-1}, the former are usually distinguished by a distinct component at ca. 3430 cm^{-1} that can be attributed to the asymmetric $-NH_2$ stretching mode. It is noted than this component is absent from the spectrum of methylene diurea. The strong peaks in the 2950–3020 cm^{-1} range are attributed to the stretching modes of the CH_2 groups. The presence of methylol groups seems to be related to a strong peak at 3005–3010 cm^{-1}, presumably due to strong coupling with the OH stretch mode. In the 1650–1640 cm^{-1} region, a medium intensity band is associated with the carbonyl stretch (amide I). The weak feature at 1620–1600 cm^{-1}, observed in urea, monomethylol urea and methylene diurea, is attributed to NH bending of the NH_2 group and is characteristic of the presence of NH_2 end groups [24]. The band at 1520–1570 cm^{-1} is attributed to the amide II vibration, involving contributions from the N–H bending and C–N stretching modes. A weak feature at 1467 cm^{-1} in the spectrum of urea is attributed to the asymmetric N–C(=O)–N stretch [25]. In the spectra of the remaining compounds, and over the same frequency range, the CH_2 bending mode is also expected. Single bands are observed for DMU and MDU at 1454 and 1440 cm^{-1}, respectively; while both bands can be found in the spectrum of DMMDU. MMU exhibits two characteristic bands at 1461 and 1437 cm^{-1}. The peak at 1385–1375 cm^{-1} is due to the CH bending of the CH_2OH final groups and appears mostly in the spectra of dimethylol urea, monomethylol urea and dimethylol methylene diurea, whereas the peak at 1330–1320 cm^{-1} is assigned to the NCN linkage and as a result it is more distinct in methythele diurea and dimethylol methylene diurea. The bands at 1290–1270 cm^{-1}, mostly seen in dimethylol urea and dimethylol methylene diurea, are attributed to the bending mode of the OH group in CH_2OH. The combination of the rocking mode of the NH_2 group and the symmetric stretching mode of the CN group results in weak bands at 1180–1160 cm^{-1} (seen in urea and methylene diurea) and strong to medium bands at 1030–990 and 920–890 cm^{-1}. The peak at 1100–1090 cm^{-1} is assigned to CH_2OH groups and finally, the band at 560–530 cm^{-1} is due to the bending mode of CO and CN groups.

Based on the Raman spectra of the model compounds, some details on the structure of the model resins can be advanced. From the spectral comparison shown in Fig. 9a) it becomes evident that the resins synthesized at pH = 5.5 are clearly differentiated by their broad and overlapping features. It is therefore evident that these resins have a pronounced amorphous character. On the contrary, all five resins prepared at pH = 6.5 or higher exhibit sharp and relatively distinct features typical of crystalline compounds. Indeed, in all these latter resins, the vibrational signature of DMU is clearly identifiable

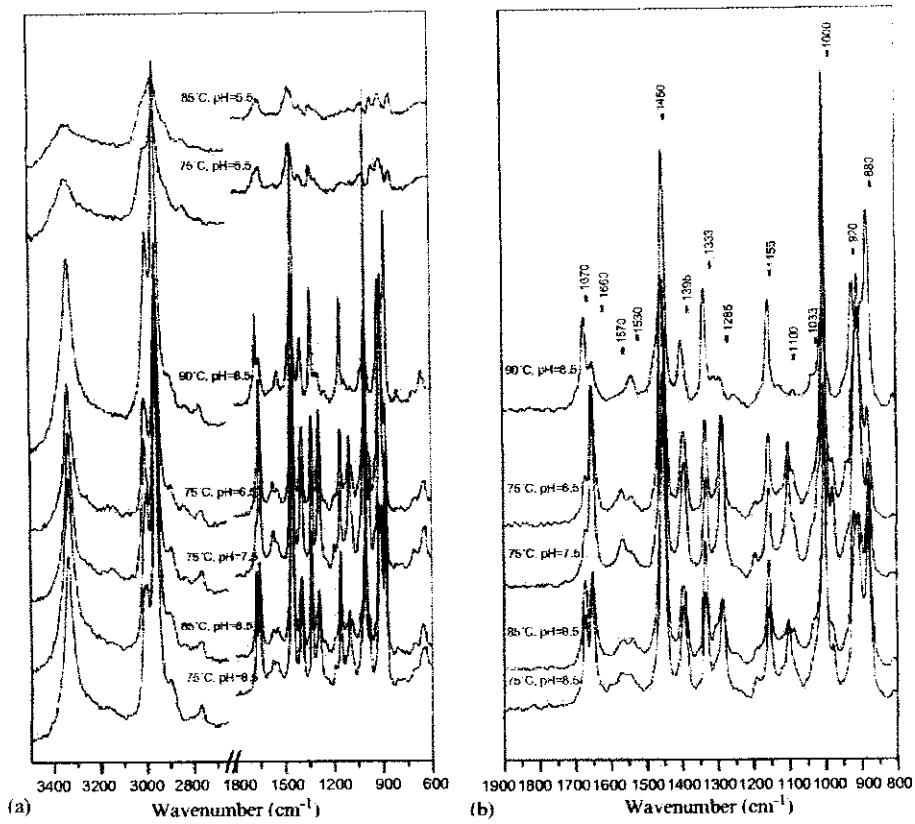

Fig. 9. (a) and (b). Raman spectra of solid model resins.

via the characteristic bands at 1653, 1565, 1455, 1393, 1283, 1101, 1000 and 908 cm^{-1} (cf. Fig. 1). However, in these resins, DMU is found to coexist with another crystalline compound with characteristic bands at 1670, 1530, 1450, 1397, 1335, 1157 and 879 cm^{-1}. The relative content of this compound can be qualitatively deduced from the relative intensity of the amide I peaks at 1670 vs. 1653 cm^{-1}. The new compound is favored at pH = 8.5, and appears maximized at 90°C. This compound cannot be identified on the basis of the reference spectra in Fig. 1. We tentatively assign this compound to cyclic structures, because their relative abundance shows the same pH and temperature dependence with that deduced from the ^{13}C-NMR spectra. In a recent infrared investigation of urea–formaldehyde resins [26], Su et al. claim that such cyclic structures can be identified by the frequency lowering of the amide II mode, which is in qualitative agreement with our assignment.

3.2.3. NIR monitoring of model resin synthesis

Fig. 10 depicts the 2nd derivative absorption spectra (C–H and N–H combination range) acquired during the synthesis of the model resin with $F/U = 2$ at 75°C and pH = 7.5. Similar were been acquired for all model reactions. The onset of the data series presented in Fig. 10 coincides with the addition of solid urea to the hot formaldehyde solution, and all the features observed between ca. 4500 and 5100 cm^{-1} are associated with N–H vibrational modes. C–H bonding is manifested below 4500 cm^{-1}, where the most prominent spectral changes observed are presumably due to the de-protection of formaldehyde from the methoxy capping groups. It is quite instructing to compare the N–H range of the $t = 0$ spectrum with that of the aqueous urea solution (Fig. 2 and dashed line in Fig. 11). Of the four characteristic bands of the urea solution, the lower frequency stretching rocking combination modes appear at identical frequencies (4645 and 4549 cm^{-1}) in the two systems. However, the stretching–bending combination mode of aqueous urea at 5028 cm^{-1} appears shifted to 5087 cm^{-1} in the reaction mixture, even at $t = 0$. This new frequency of the stretching bending combination mode is found to be independent of the temperature and the pH of the system and seems to characterize the interaction of urea with formaldehyde solutions. In an early NIR investigation of primary and secondary amines in various solvents, Lohman et al. [27] reported that the corresponding stretching bending vibration of primary amines exhibits a pronounced solvent dependence, which could not be attributed to shifts of the $-NH_2$ stretching modes but rather to 50–60 cm^{-1} shifts of the $-NH_2$ bending mode. They also proved that

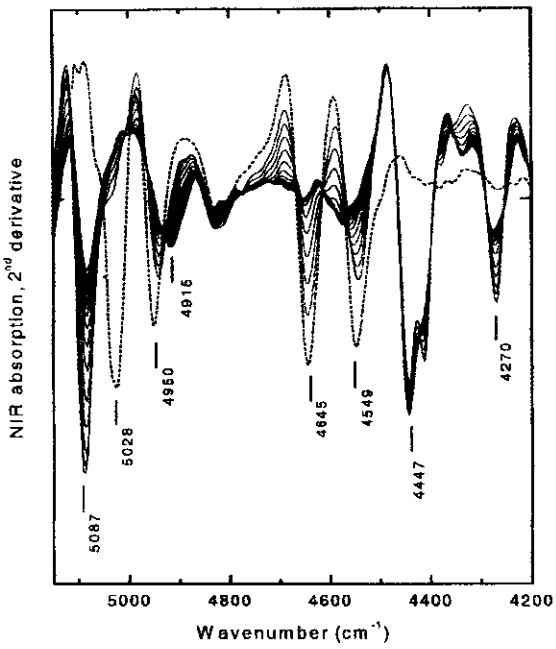

Fig. 10. Near Infrared absorption spectra (2nd derivative) during the synthesis of a model resin with $F/U = 2$ at 75°C and pH = 7.5. Each spectrum corresponds to 1 min spectral acquisition and the time interval between the spectra shown is 4 min. The onset of the monitoring coincides with the addition of the urea to the formaldehyde solution (for details see the Experimental). The total reaction time was 110 min. The dashed line depicts for comparison the corresponding spectrum of a 40 wt% aqueous urea solution.

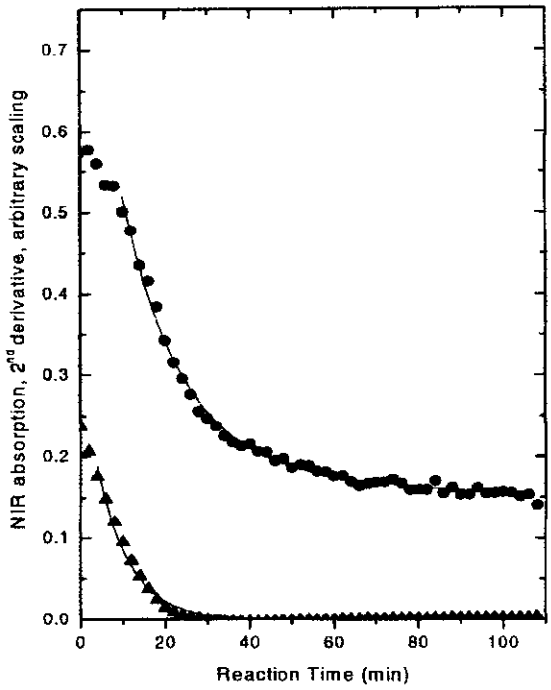

Fig. 11. Time evolution of the NIR absorption (2nd derivative) at 4645 and 5087 cm^{-1} (triangles and circles, respectively) corresponding to the reaction shown in Fig. 10. Lines are the results of exponential decay fitting. For details see text.

secondary amide species are transparent in the vicinity of 5000 cm^{-1}, because they are obviously lacking the $-NH_2$ bending mode.

Although both bands at 4645 and 5087 cm^{-1} are clearly related to the concentration of unreacted $-NH_2$ groups, the time dependence of their intensity is markedly different (Fig. 11). Intensity at 4645 cm^{-1} is shown to decrease quickly in a manner that can be described by a single exponential with $t = 7.5 \pm 0.5$ min and vanishes ca. 30 min after the onset of the reaction. Intensity at 5087 cm^{-1} exhibits a more complicated time dependence: Initially, a quasi-plateau is observed and associated with the time necessary for the dissolution of urea and the establishment of the chemical interactions that lead to the appearance of the 5087 cm^{-1} feature. A careful inspection of the data in Fig. 10 indicates that during this "induction" period traces of the 5028 cm^{-1} band, which is typical of the aqueous solution of urea, are still visible in the spectra. Beyond this period, intensity at 5087 cm^{-1} decreases in a manner that can be fitted with atl least two exponential functions, the first with $t_1 = 13.7 \pm 0.7$ min (ca. two times lower than the corresponding time constant of the 4645 cm^{-1} indicator) and the second with $t_2 = 600 \pm 200$ min. This kinetic analysis brings up the difference between the two NIR indicators for $-NH_2$. While the band intensity at 4645 cm^{-1} yields the concentration of intact urea molecules, that at 5087 cm^{-1} correlates simply with the presence of (unreacted) $-NH_2$ groups. At the end of the reaction, an appreciable fraction of the latter (ca. 20%) is still found in the reacting mixture.

The effect of pH and temperature on the kinetics of urea consumption can be deduced from Fig. 12. Both near-infrared indicators exhibit similar time dependence when the reaction temperature is 75°C, and the pH ranges between 5.5 and 7.5. The fastest decrease in $-NH_2$ concentration is observed at alkaline pH (8.5) and high temperature (90°C), conditions that favor the kinetic formation and precipitation of compounds with cyclic structures.

4. Conclusions

The effect of pH and temperature on the structure of UF resins was investigated by the systematic synthesis of resins at iso-pH and isothermal conditions. These "model" resins can serve as a reference for structural characterization. NMR spectroscopy was employed for the qualitative as well as quantitative characterization of

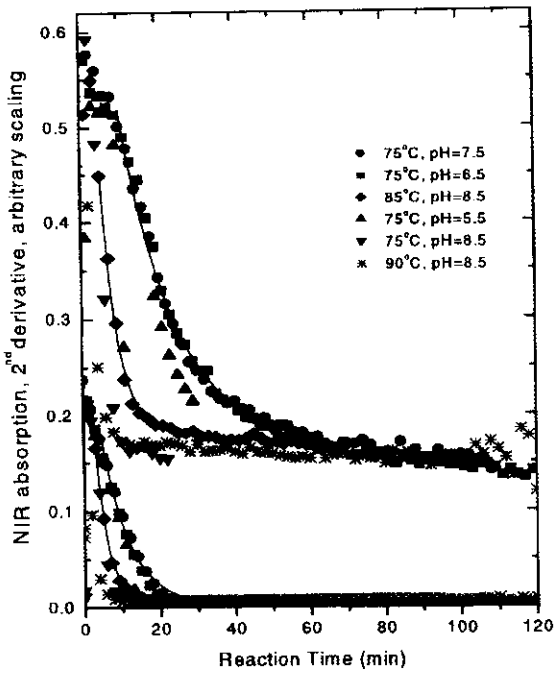

Fig. 12. Time evolution of the intensity of the bands at 4645 and 5087 cm^{-1} for all model resins.

the system. GPC was used to determine the molecular mass distribution of the resins. FT-Raman spectroscopy is useful in identifying the presence and nature of low molecular weight species in the final product. It is concluded that pH and temperature play a significant role in the reaction between urea and formaldehyde and have a strong effect on the type of linkages formed during synthesis, which determine the final resin properties. The results of the various analytical techniques employed are in good mutual agreement and indicate that:

- Resins prepared at higher reaction temperatures (90°C) and acidic pH values (5.5) show higher degrees of condensation, resulting in molecules with higher molar masses and yield more *N*, *N*-disubstituted amide groups that account for the formation of three-dimensional networks whereas
- Resins prepared at slightly acidic or alkaline pH (7.5 and 6.5) consist mostly of low molecular weight adducts, namely dimethylol urea and a condensation product of two dimethylol ureas via ether or methylene link formation, resulting in high abundance of CH_2OH groups.
- At strongly alkaline conditions, pH = 8.5, and especially at high temperatures (90°C), a new condensation product with presumably cyclic structure is kinetically detected.
- Finally, it has been demonstrated that FT-NIR spectroscopy can be used for the on-line monitoring of the consumption of $-NH_2$ groups during the early stages of the synthesis.

Acknowledgements

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