

# Testing by Fourier Transform Infrared Species Variation During Melamine–Urea–Formaldehyde Resin Preparation

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**ABSTRACT:** The preparation of an industrially used sequential formulation of a melamine–urea–formaldehyde resin was followed with Fourier transform infrared (FTIR). The analysis allowed us to identify the increases and decreases of the main groups in the resin and to compare this system of resin analysis with results previously obtained by <sup>13</sup>C-NMR analysis. The FTIR analysis, although considerably more limited than <sup>13</sup>C-NMR analysis, allowed us nonetheless to iden-

tify and follow the appearance, increase, decrease, and disappearance of several of the main chemical groups during the preparation of the initial urea–formaldehyde (UF) phase of the reaction and the subsequent reaction of melamine with the UF resin that was formed. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2192–2197, 2007

**Key words:** adhesives; FTIR; resins; structure

## INTRODUCTION

Melamine–urea–formaldehyde (MUF) thermosetting resins are extensively used as exterior-grade adhesives in the wood industry, particularly in the wood-panel industry.<sup>1</sup> The wood-panel industry relies heavily on the use of these synthetic resins as adhesives, bonded products constituting the majority of the wood products on the market today. Over many years, excellent formulations have been developed for these resins for wood applications. Although some trial-and-error industrial research has been and is still carried out in the field of resin formulations, nonetheless resin knowledge has progressed to such an extent that scientific principles are used today to develop resins of ever-improving performance.

Notwithstanding the considerable tonnage of MUF resins produced yearly, their economic importance, and the trade literature on the subject, the scientific literature on MUF resins is still rather limited.<sup>2–5</sup> This has improved in the last few years. However, much remains to be defined in the field of MUF resins. Only recently did a study appear that followed the development of the different mass fractions and, by inference, the development of the average molecular species as functions of the type of formulation used.<sup>6</sup> A later study<sup>7</sup> investigated in depth what chemical species are formed during the preparation of MUF resins and how they evolve throughout the complete prepa-

ration procedure of the resins by using <sup>13</sup>C-NMR and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry to examine a sequential MUF formulation. Although a great variety of MUF formulations exist and are used industrially, the greater majority of them are produced according to so-called sequential formulations, in which the sequence of addition of the chemicals follows well-defined species reactivity principles.<sup>2–5</sup> The greater majority of MUF resins fall in this category, as these resins produce real cocondensates of melamine and urea and their performance is good.<sup>3–5</sup>

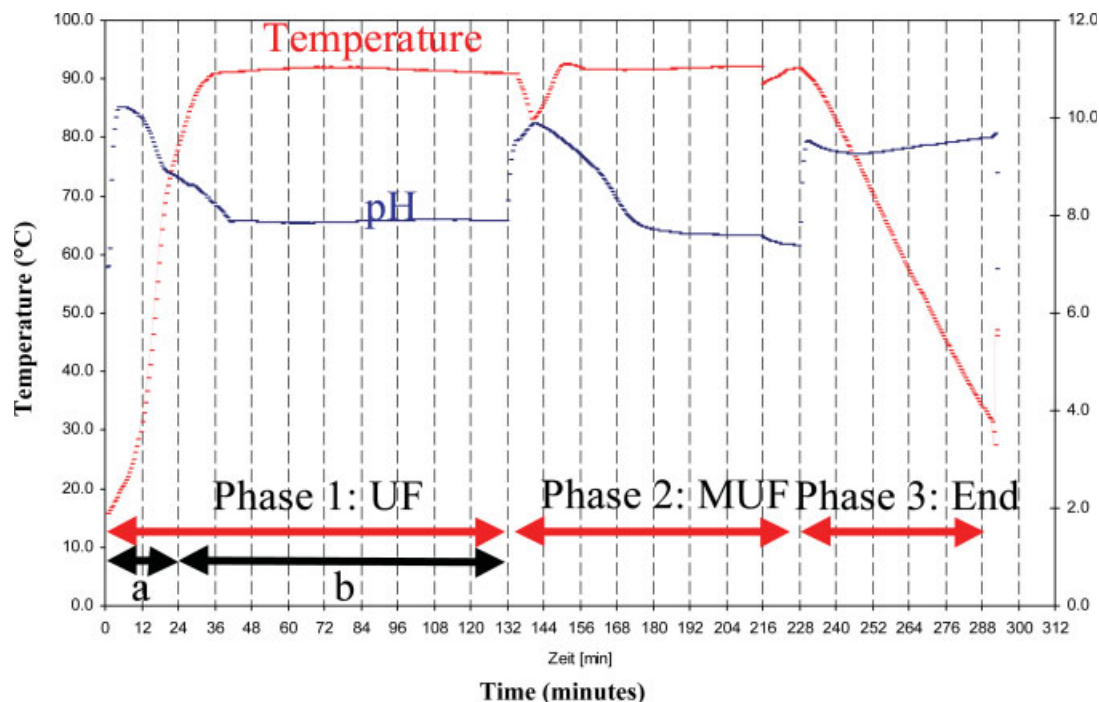
This article deals then with investigating to what extent one can follow the different chemical species that form during the preparation of an industrially used MUF resin sequential formulation by a simpler technique, Fourier transform infrared (FTIR) spectroscopy; it is simpler exclusively because the equipment is more readily available in many industrial laboratories. This is compared with already available data previously obtained by gel permeation chromatography, <sup>13</sup>C-NMR, and MALDI-TOF mass spectrometry.

## EXPERIMENTAL

### Resin preparation<sup>7,8</sup>

An MUF resin with a melamine–urea/formaldehyde molar ratio of 1 : 1.2 and a melamine/urea weight ratio of 47 : 53 was prepared according to a modification of a known sequential manufacturing procedure<sup>7</sup> as follows. To 71.11 parts of formurea (a precondensate of 23% urea, 54% formaldehyde, and 23% water) were added 8.18 parts of urea and 15 parts of water. The

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**Figure 1** Schematic preparation diagram for an MUF resin showing temperature and pH variations as functions of the reaction time. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

pH was set at 10–10.4, and the temperature was brought to 92–93°C under mechanical stirring. The pH was then lowered to 7.8, and the reaction was continued at the same temperature. To bring the pH to 9.5 or higher, a 22% NaOH solution was added, and then 40.0 parts of melamine were premixed with 21.0 parts of water. Two parts of dimethylformamide were then added to the reaction mixture, and a temperature of 93°C was maintained. The water tolerance percentage of the resin was checked every 10 min, whereas the pH was allowed to fall by itself back down to 7.4–7.6. When the water tolerance (the percentage of water that could be added to the liquid resin) reached a value of 180–200% (the pH was ca. 7.2), 21.4 parts of urea together with 5 parts of water were added, and the pH was again brought up to 9.5. The reaction was continued until the water tolerance was lower than 150% (the pH was 7.7 at this stage).

The pH was then corrected to 10.0–10.2 by the addition of a solution of NaOH, and the resin was cooled and stored.

The reaction system was equipped with a Schott Steamline online pH electrode and PT 1000 temperature sensors (Schott AG, Mainz, Germany).

The pH profiles were recorded and adjusted electronically during the reaction with a MultiT system from Jensen Systems (Hamburg, Germany).

The reaction times of each phase according to the outlined procedure are shown in Figure 1.

The times at which the samples were taken, reported on the scale in Figure 1, were as follows:

- Sample 1: From the start of the reaction to reaching 76°C to the end of phase 1a in Figure 1.
- Sample 2: From reaching 92°C and the minimum pH value to the end of phase 1b in Figure 1.
- Sample 3: Immediately after melamine addition to the end of phase 2 in Figure 1.

#### FTIR spectroscopy

FTIR spectroscopy measurements (Table I) were continuously performed *in situ* during resin synthesis with an attenuated total reflectance multireflection diamond-crystal immersion probe, which was connected by an optical light guide to an AutoChem system (Mettler-Toledo, Gießen, Germany). Spectra in the range of 650–4000  $\text{cm}^{-1}$  were recorded versus air as the background spectrum every 2 min at a scan rate of 128 scans per spectrum with the ReactIR 3.0 software package (Mettler-Toledo, Gießen, Germany). To analyze the changes in the composition of the reaction mixture, several subsequent IR spectra were plotted in a single graph.

#### DISCUSSION

The same multistage MUF resin used in a previous investigation was used.<sup>8</sup> It was manufactured according to an industrial formulation with just one variation, this being an important one.<sup>7</sup> In industrial urea-formaldehyde (UF) and MUF formulations, the UF condensation stage is performed at a pH between 5 and 6. In our case, the pH was kept relatively high

TABLE I  
Wave Numbers of the FTIR Bands

| Wave number<br>( $\text{cm}^{-1}$ ) | Band   |
|-------------------------------------|--|
| 3578                                | —OH stretch  |
| 3200–3440                           | Urea N—H stretch   |
| 3320–3360                           | Monosubstituted urea N—H stretch   |
| 3400–3440                           | Asymmetric monosubstituted urea —NH <sub>2</sub> stretch   |
| 1656–1660                           | C=O stretch, primary amide —NH <sub>2</sub> (urea)   |
| 1644                                | C=O stretch, secondary amide —NH— (methylol and methylene urea)                                    |
| 1629                                | Primary amide —NH <sub>2</sub> (urea; N—H bending)   |
| 1625                                | Secondary amine —NH— (methylol and methylene melamine)   |
| 1556                                | C—NH— of melamine  |
| 1544                                | Secondary amide —NH— (methylol and methylene urea; N—H bending)                                    |
| 1513                                | N—C—N of a proper methylene bridge (—CH <sub>2</sub> —)  |
| 1459–1463                           | Broad-band O—H of water  |
| 1459                                | —CH <sub>2</sub> — (deformation) of methylol groups on urea  |
| 1374                                | N—C of substituted melamine  |
| 1363                                | Asymmetric N—C—N stretching of substituted melamine  |
| 1359                                | Asymmetric N—C—N stretching  |
| 1336–1339                           | —CH <sub>2</sub> — (wagging) of methylol groups on urea  |
| 1293                                | Methylol groups on urea  |
| 1282–1285                           | —CH <sub>2</sub> — of —CH <sub>2</sub> —O—CH <sub>2</sub> —  |
| 1258–1262                           | —CH <sub>2</sub> — of —CH <sub>2</sub> —O—CH <sub>2</sub> —  |
| 1140–1190                           | N—C—N symmetric stretch, urea, and monosubstituted urea  |
| 1150                                | Asymmetric C—O—C of —CH <sub>2</sub> —O—CH <sub>2</sub> — and CH <sub>3</sub> —O—CH <sub>2</sub> — |
| 1135                                | Symmetric C—O—C of —CH <sub>2</sub> —O—CH <sub>2</sub> — between melamines                         |
| 1100–1104                           | C—O—C of —CH <sub>2</sub> —O—CH <sub>2</sub> — and CH <sub>3</sub> —O—CH <sub>2</sub> —            |

at 7.8. This was done first to slow down considerably the reaction and second to check that at this pH (1) UF oligomers could be formed just by the joining of the ureas by methylene ether bridges and (2) the rearrangement to methylene bridges could be induced by the addition of melamine at the same pH by a coreaction with the preformed UF condensate and alternatively to show that (3) methylene bridges could form also at a very alkaline pH as the condensation reaction properly starts only at pHs of less than 8 and (4) a relatively high proportion of methylene ether bridges could be carried over also to the end of the reaction after melamine addition.

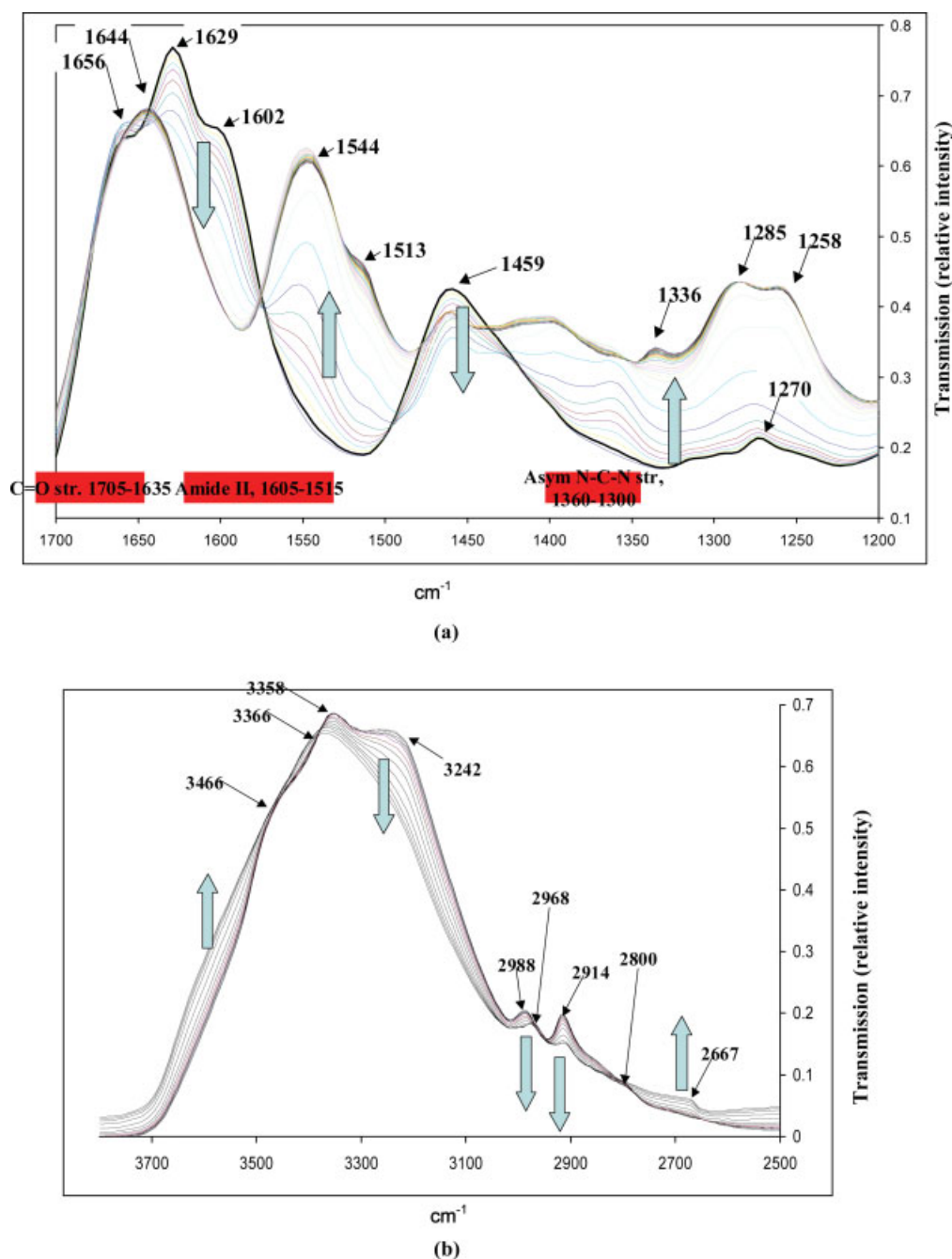
The MALDI-TOF and NMR investigation found that, in agreement with the classical theory of UF polycondensation, at an alkaline pH, only methylol groups (—CH<sub>2</sub>OH) and methylene ether bridges (—CH<sub>2</sub>OCH<sub>2</sub>—) between ureas formed, the latter leading only to very short oligomers.<sup>9,10</sup> Methylene bridges (—CH<sub>2</sub>—) between ureas, which were not supposed to form at a very alkaline pH, were nonetheless formed but to a very low degree.

In Figure 1, the course of the temperature and pH during the reaction is shown. The different phases of the resin manufacturing process are also shown: the first phase is the building of the UF resin skeleton, the second phase is the condensation of melamine on the methylol groups of the UF resin to form the MUF cocondensates, and the third phase is the addition of the final urea to mop up any excess free formaldehyde. The same figure shows the points in the prepa-

ration at which the samples were collected: (1) at the beginning of the UF reaction (phase 1a), (2) when 90°C and the lower pH of the polycondensation part of the UF reaction were reached (phase 1b), and (3) well into the condensation reaction of melamine with UF, which yielded the MUF cocondensates.

The FTIR spectrum in Figure 2(a) shows the initial phase of the reaction of urea and formaldehyde (phase 1a) from the beginning to 75°C. In Figure 2, the —CONH<sub>2</sub> unreacted amide group of urea (1629  $\text{cm}^{-1}$ ) decreases as it begins reacting with formaldehyde, whereas simultaneously, the 1544- $\text{cm}^{-1}$  band, representative of the —CONH—C— reacted amide group of urea, increases. This indicates that the UF reaction starts already in the very initial phase of the preparation, even at relatively low temperatures. The shoulders at 1602 and 1513  $\text{cm}^{-1}$  are indications of differently substituted ureas reacting further and thus decreasing. Equally, in Figure 2(a), the series of bands in the 1258–1359- $\text{cm}^{-1}$  range indicate the increase in the proportion of methylene (—CH<sub>2</sub>—) bridges. However, comparing this with the results obtained by MALDI-TOF and NMR<sup>7</sup>, we find that the majority of these bands belong to methylene groups participating in methylene ether bridges (—CH<sub>2</sub>OCH<sub>2</sub>—) between ureas rather than just to methylene bridges directly between ureas. It does not appear possible at this stage to distinguish which of these methylene bands belong to which groups.

In Figure 2(b), one can observe —OH of water increasing as water is eliminated in the condensation of



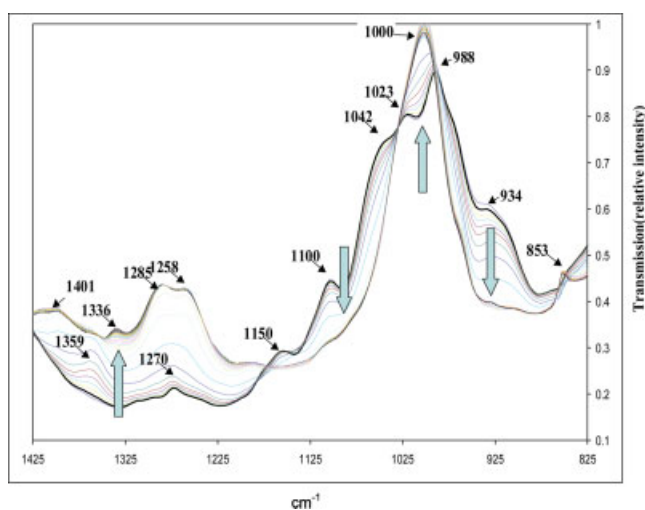
**Figure 2** FTIR spectra of the band variations of a resin sample in phase 1a of the UF resin preparation from the beginning of the reaction to 76°C: (a) 1200–1700 and (b) 2500–3700  $\text{cm}^{-1}$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

urea and formaldehyde, and this is followed by a decrease in the water content due to evaporation and the reaching of the reflux phase of the resin preparation.

In Figure 3, still representing the situation during UF phase 1a, a few other band variations are noticeable. Thus, the two bands at 1150 and 1100  $\text{cm}^{-1}$  decrease slightly, indicating the decrease in the C–O–C bonds and thus either (1) the progressive decrease of two types of the  $-\text{CH}_2\text{OCH}_2-$  urea to urea bridges as these reorganize into  $-\text{CH}_2-$

bridges and methylol groups or (2) the progressive decrease of the  $-\text{CH}_2\text{OCH}_2-$  urea to urea bridges for one peak and for the other peak of the hemiacetals formed by a reaction of the methanol obtained by Cannizzaro side reaction.<sup>8,9,11</sup> The second option appears to be the most likely one. It is remarkable that even at this early stage, the Cannizzaro reaction occurs to an extent sufficient to be detected.

In Figure 4(a) (phase 1b), which shows the situation of the reaction of urea and formaldehyde now at the

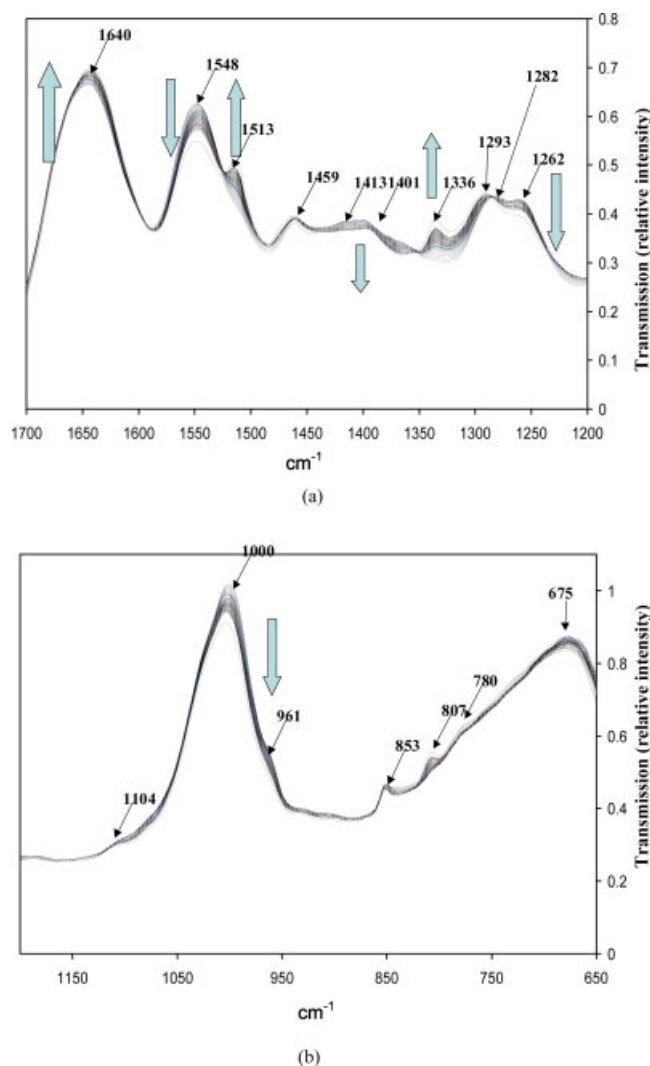


**Figure 3** FTIR spectrum of the band variations of a resin sample in phase 1a of the UF resin preparation from the beginning of the reaction to 76°C in the range of 825–1425  $\text{cm}^{-1}$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

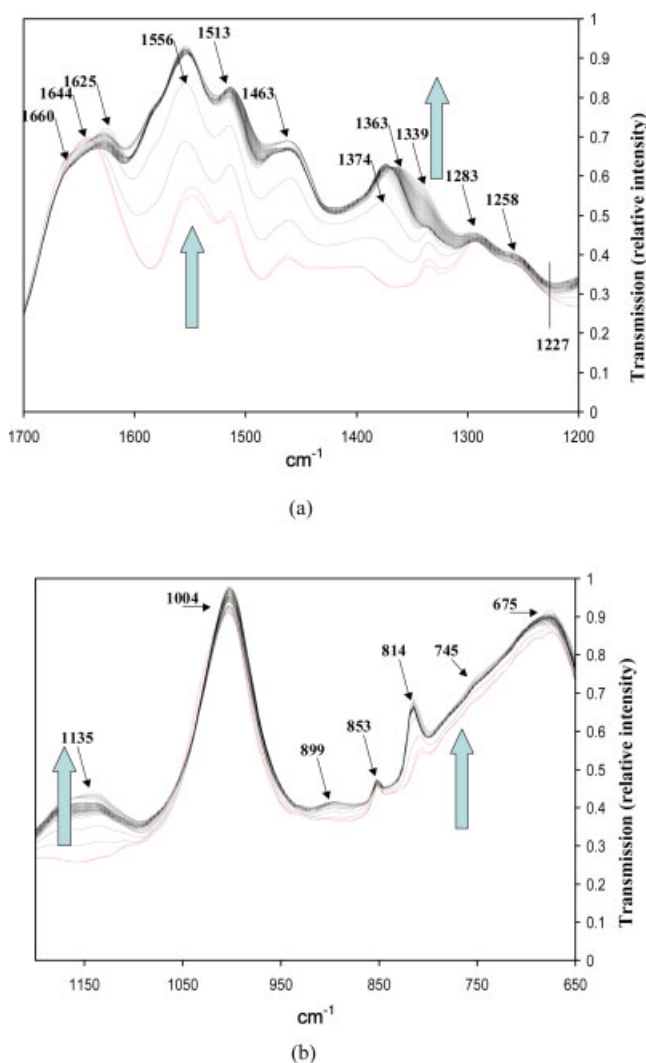
reflux and maximum temperatures (see Fig. 1), one can note the increase in the number of methylol groups ( $-\text{NH}-\text{CH}_2\text{OH}$ ) at 1640  $\text{cm}^{-1}$  and the decrease in  $-\text{CONH}-\text{CH}-$  groups at 1544  $\text{cm}^{-1}$ , which is representative of  $-\text{CH}_2\text{OCH}_2-$ , as can be noticed by the simultaneous small increase in the 1513- $\text{cm}^{-1}$  peak, which could hence be identified as representative of methylene ( $-\text{CH}_2-$ ) bridges. The 1459- $\text{cm}^{-1}$  peak appears to be stationary, and this indicates that with reflux, the proportion of water has reached a steady state. The series of peaks in the 1336–1262- $\text{cm}^{-1}$  range increase, and these are representative of methylol ( $-\text{CH}_2\text{OH}$ ) groups under different environments. They all increase nonetheless with the progress of the reaction. In Figure 4(b), the only notable feature is the decrease to low levels of the methylene ether bridge signal at 1104  $\text{cm}^{-1}$ . This might appear at first in sharp contrast to the predominance of these groups, as previously found by other techniques,<sup>7</sup> but it confirms what was found previously by other techniques: the reaction proceeds through the alternation of high and low concentrations of some groups, the group in question being one of them.

In Figure 5(a,b) (phase 2), the appearance of the spectra changes dramatically because of the addition of melamine. Noticeable are the increases in the bands at 1660, 1625, 1374, and 1363  $\text{cm}^{-1}$ , the former two representing different situations of methylol groups linked to melamine and the latter two representing different situations of methylene groups linked to melamine. Equally noticeable and in a sense unexpected is the sudden increase in the 1644- $\text{cm}^{-1}$  band of the methylol groups of urea. This is confirmed by MALDI-TOF and NMR<sup>7</sup> and is due to the

melamine-induced rearrangements of some methylene ether bridges to methylene bridges with the liberation of formaldehyde, which then forms a urea-linked methylol group. The 1566- $\text{cm}^{-1}$  band is the  $-\text{N}=\text{CNH}-\text{CH}-$  of substituted melamine, drowning the 1544- $\text{cm}^{-1}$  band of the  $-\text{CONH}-\text{CH}-$  of substituted urea. An increase in  $-\text{CH}_2-$  substituted ureas is shown by the increases in the 1339-, 1283-, and 1258- $\text{cm}^{-1}$  bands, which are also derived from the formaldehyde generated by the reorganization of methylene ether bridges induced in this phase by the addition of melamine to the reaction. In short, as expected and as supported by what was found by other techniques, the melamine-linked  $-\text{CH}_2\text{OH}$  and  $-\text{CH}_2-$  bridges increase markedly.<sup>7</sup> Also increasing markedly, however, are the  $-\text{CH}_2\text{OCH}_2-$  bridges



**Figure 4** FTIR spectra of the band variations of a resin sample in phase 1b of the UF resin preparation from 92°C to the end of the phase: (a) 1200–1700 and (b) 650–1200  $\text{cm}^{-1}$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 5** FTIR spectra of the band variations of a resin sample throughout phase 2 of the MUF resin preparation (Fig. 1): (a) 1200–1700 and (b) 650–1200  $\text{cm}^{-1}$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

(a fact again supported by other techniques), but this time, these are linking melamine to melamine.

The patterns of peaks found from following the MUF resin preparation confirm what was established previously by MALDI-TOF mass spectroscopy and  $^{13}\text{C}$ -NMR.<sup>7</sup>

## CONCLUSIONS

FTIR has been shown to clearly detect the same trends of molecular species at different stages in the preparation of an MUF resin as those detected by  $^{13}\text{C}$ -NMR and MALDI-TOF mass spectrometry. Although the analysis by group by FTIR does not give the distribution and structure of all the species obtained as the NMR and MALDI-TOF do to a much greater extent, it is nonetheless an excellent but simpler technique for deducing what the main trends are in the changes of the distribution of just the main groups of molecular species during MUF resin preparation. In this context, it can be considered mainly a good routine analysis tool to follow the progress of MUF resin preparation.

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