Raman Spectroscopy of Urea–Formaldehyde Resins and Model Compounds

CHARLES G. HILL, JR., ALICIA M. HEDREN, *Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706,* GEORGE E. MYERS, USDA, *Forest Products Laboratory, Madison, Wisconsin 53705,* and JAMES A KOUTSKY, *Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706*

Synopsis

Laser Raman spectroscopy was used to analyze the structures of urea–formaldehyde resins. Band assignments were made on the basis of Raman studies of model compounds. Methylol and certain methylene functionalities could be differentiated in both the model compounds and the resins. Spectra of the resins at various stages of cure were also examined. Trends noted agreed with earlier studies on the kinetics and the proposed mechanism of the cure process. Laser Raman spectroscopy offers promise for elucidating the structures of urea–formaldehyde resins and for providing insight into the molecular phenomena of the cure and degradation of these resins.

INTRODUCTION

Urea–formaldehyde (UF) resins are thermosetting materials used primarily as adhesives in plywood, fiberboard, and furniture manufacture. These applications account for 70% of all urea–formaldehyde consumption in the United States.[1] As a wood adhesive, urea–formaldehyde resins are advantageous because they are inexpensive, have good processing and cure properties, and are resistant to fungi, wood rot, and termites.[2] Greater utilization of urea–formaldehyde resins is impeded, however, by their hydrolytic instability. This affects the durability of the eventual bonded product[3–5] and the release of formaldehyde from the resin and bonded product.[6] In applications where lack of ventilation leads to an accumulation of formaldehyde vapors, humans and animals will experience discomfort.[6]

UF prepolymers contain a wide variety of structures[2,7–11] (see Table I). Many of these are undoubtedly present after cure, and it is believed that the instability of the cured resin is caused primarily by particularly labile moieties—e.g., —CH_2OH, —CH_2OCH_2OH, —NCH_2OCH_2N—. However, our ability to define and prepare optimum structures in the cured state has been hindered by the absence of techniques that will provide detailed knowledge of the exact structures present and of their resistance to hydrolysis. Conventional infrared spectroscopy has been shown[8] to have only limited capabilities in this regard, although the use of Fourier transform infrared spectroscopy (FTIR) may well extend these capabilities. Recent application of new solid sample ^{13}C-NMR techniques to cured UF resins has given evidence that this tool may supply valuable insights in the future.[12]

The present study was initiated to determine whether laser Raman spectroscopy could aid significantly in defining critical structural details in

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TABLE I
Probable Structures in Cured Urea–Formaldehyde Resins[9]

R = H or CH$_2$OH
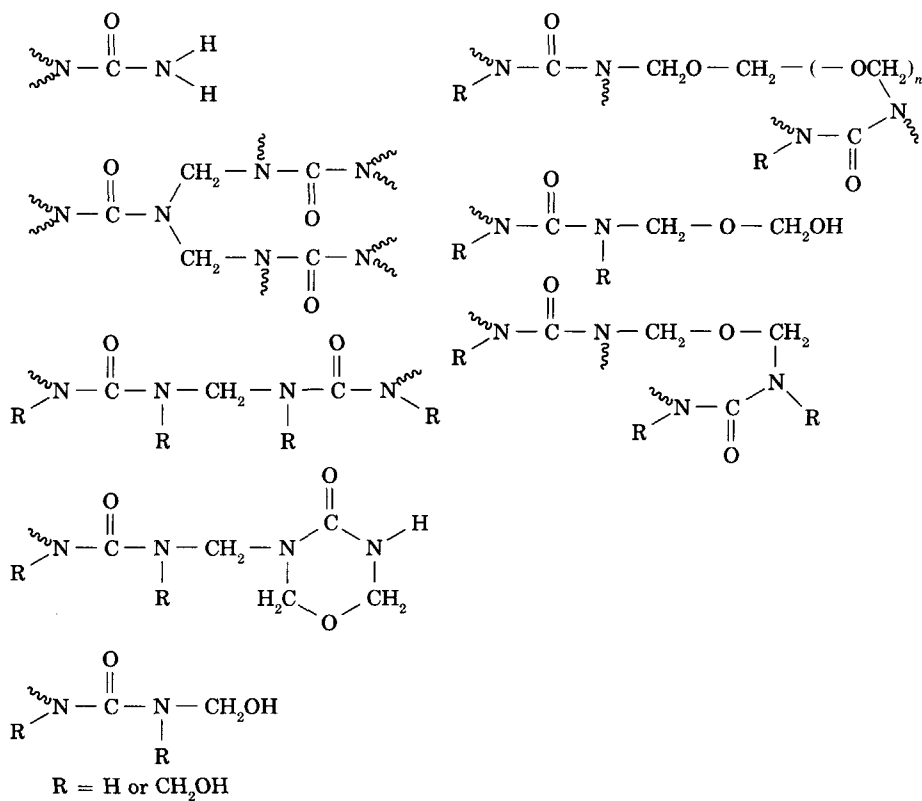
cured UF systems. Spectra were obtained for a series of UF model compounds, and these data were used in conjunction with the available literature to correlate absorption frequencies with structural moieties. A limited application of those findings to a cured UF resin indicated that this approach is indeed promising and served to indicate directions for further study.

EXPERIMENTAL

Materials. Table II lists the model compounds and indicates their source or method of preparation. The same compounds were used in the study by Myers.[9]

The UF prepolymer was prepared in two steps. First, a solution with a formaldehyde to urea molar ratio of 1.7, 30 mL NH$_4$OH, 0.5 mL of a 20% NaOH solution, and 38.5 g methanol was heated to 88°C and allowed to react for 30 min. The pH at the start was 7.41. After 30 min the pH dropped to 6.29. In the second step, formic acid was added to lower the pH to 4.8. With the temperature still at 88°C the mixture was allowed to react for another 20 min. The resulting solution was neutralized with NaOH to pH 7.8 and freeze-dried.

To prepare cured resin samples, the prepolymer was dissolved in water

TABLE II
Sources of Model Compounds

	Compound	Formula	Synthesis procedure[a]
1	Formalin	CH_2O	Obtained commercially, 99.8% purity
2	N,N'-dimethylolurea	$HOCH_2NHCONHCH_2OH$	Obtained commercially, 98.0% purity
3	Dimethylolurea dimethylether	$(CH_3OCH_2NH)_2CO$	Sorenson,[13] dimethylolurea + CH_3OH with H_3PO_4, 23°C/24 h
4	Methylene diurea	$(H_2NCONH)_2CH_2$	Kadowaki,[14]; U:F = 8.33; pH 2.4; 20–25°C/48 h
5	Trimethylene tetraurea	$H_2NCONH(CH_2NHCONH)_2CH_2NHCONH_2$	Kadowaki[14]
6	Pentamethylene hexaurea	$H_2NCONH(CH_2NHCONH)_4CH_2NHCONH_2$	Kadowaki[14]
7	Monomethylol methylenediurea	$H_2NCONHCH_2NHCONHCH_2OH$	Kadowaki[14]
8	Methylene-bismonomethylolurea	$(HOCH_2NHCONH)_2CH_2$	Kadowaki[14]

[a] Compounds were prepared by referenced procedures when not available from commercial sources.

to form a 27% solution by weight. The solution was acidified to pH 4.0 with H_3PO_4, and aliquots added to shallow, teflon-coated metal pans which were covered loosely to allow for escape of a slow N_2 purge. The pans were then placed on a temperature-controlled hot plate and heated for selected times. Other cured samples were similarly prepared using approximately 1% NH_4Cl as catalyst. After cure the samples were vacuum dried for several days at room temperature and then stored in tightly capped jars at ca. 5°C.

Raman Spectroscopy. The Raman spectrometer was a Spex Ramalog 5 (Model 14018) equipped with a third monochromator. The light source was a Spectra-Physics Model 164-06 Argon Ion Laser powered by a Spectra-Physics Model 265 Exciter. Rated power output of the laser was 2 W (all lines). The Raman spectrometer was interfaced to a PDP 11/03 Minicomputer System to facilitate data acquisition and manipulation.[15]

Scattered light was collected at 180° to the incident beam with a 180° backscattering cell. This sample cell reduced the fluorescence in the cured resin spectra and kept the signal-to-noise ratio at acceptable levels.

All spectra were recorded using the 488.0 nm line of an argon laser for excitation. Spectrometer variables (laser power, slit height, slit width, scan speed) were optimized for each scan, but a period of 2 s was used for all spectra reported here. The actual parameter values employed are listed with each spectrum reported herein. All spectra were smoothed and corrected for background fluorescence using procedures described elsewhere.[15,16]

RESULTS AND DISCUSSION

Model Compound Spectra

Spectra for eight model compounds (Table II) are shown in Figures 1–8. The first three compounds will be termed the "methylol series." They were selected to illustrate the influence of the—CH_2OH and —COC— moieties. Compounds 4–6 constitute the "methylene series" and possess only the —NCH_2N— linkage between urea residues. The "mixed series," compounds 7 and 8, contain both the —NCH_2N— and —CH_2OH groups and indicate their spectral interactions.

Most of the spectra have very low fluorescent backgrounds and low noise levels. The spectrum of dimethylolurea dimethylether (Fig. 3) is an exception. This compound easily degrades in the laser beam producing a highly fluorescent background and a low signal-to-noise ratio. Attempts to decrease degradation were not successful.

Table III summarizes the frequencies and intensities observed in the model compound spectra. It also includes brief indications of the band assignments that were derived on the basis of infrared and Raman spectra reported in the literature and comparisons among these spectra and those obtained in this work. The rationale for the assignments is discussed below and is best followed by reference to Figures 1–8 and Table III.

~3427 cm^{-1}. A weak band in this region is noticeable only in the methylenediurea spectrum (Fig. 4). Becher[17] has assigned the NH_2 stretch to this region.
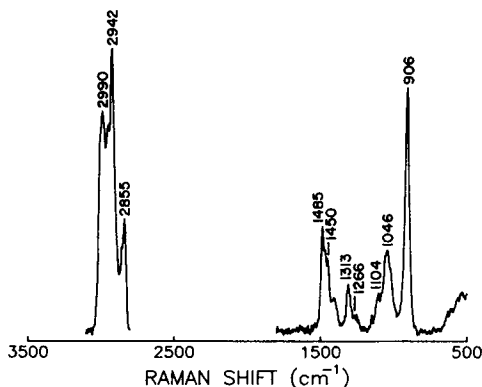
Fig. 1. Raman spectrum of aqueous formaldehyde (incident power = 0.20 W; spectral bandpass = 5.5; scan speed = 0.5 cm^{-1}/s; number of scans = 2).

3342–3334 cm^{-1}. This band is medium to strong in the spectrum of each model compound except that of dimethylolurea dimethylether (Fig. 3), where it may be obscured by the strong fluorescence observed in this case. The band is attributed to NH$_2$ and NH stretching.

3050–2800 cm^{-1}. In this region the bands are associated with methylene stretching.[17] The spectra of formalin (Fig. 1) and dimethylolurea dimethylether (Fig. 3) are more complex than those of the other model compounds, and the 2833 cm^{-1} band in the ether is clearly indicative of the methoxy group.[18] The other compounds possess only two bands in this region, at 3011–2996 cm^{-1} and at 2962–2957 cm^{-1}. The latter band is fairly constant in frequency and is relatively strong in all cases. The 3011–2996 cm^{-1} band tends to be weaker and at a lower wave number in the compounds where the methylenes are present only in NCH$_2$N moieties. It seems unlikely, however, that this region could prove highly useful for distinguishing clearly among various types of methylenes in resins.
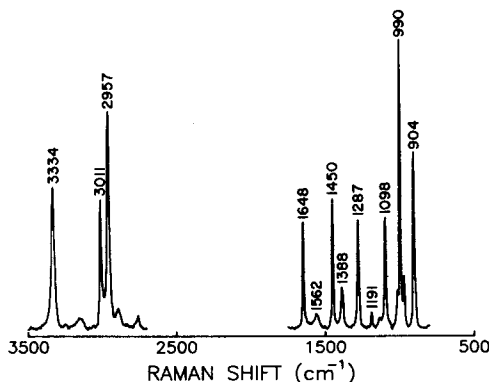

Fig. 2. Raman spectrum of N,N'-dimethylolurea (incident power = 0.30 W; spectral bandpass = 5.5; scan speed = 0.5 cm^{-1}/s; number of scans = 2).
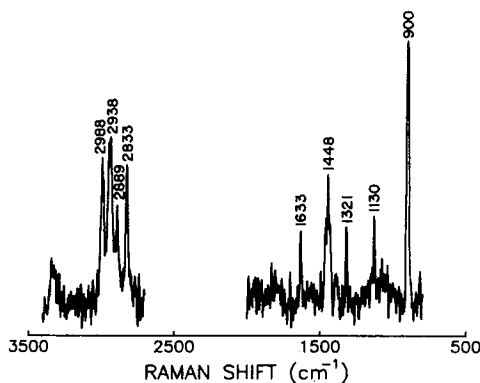
Fig. 3.   Raman spectrum of dimethylolurea dimethylether (incident power = 0.30 W; spectral bandpass = 6.84; scan speed = 0.5 cm^{-1}/s; number of scans = 2.

1650–1630 cm^{-1}. Bands in this region are associated with a carbonyl stretch.[19] In infrared spectra these bands are usually strong,[8] while in the Raman they are of weak to medium intensity. The location shifts between 1630 cm^{-1} and 1650 cm^{-1} but there are no apparent correlations with molecular structure.

1590–1580 cm^{-1}. Bands in this region are discernible only in two of the spectra of the methylene series (Figs. 4 and 5) the intensity decreasing as the chain length increases. The infrared spectra of the model compounds do not contain bands in this region.[8,17,19] Tobin[20] suggests that bands in this region could denote the presence of ring structures. However, no other evidence for ring structures has been seen in the spectra of these compounds, and we leave these bands unassigned.

1570–1520 cm^{-1}. Bands associated with an amide II or NH stretch are located in this region. Myers[8] and Chabert[21] used infrared bands in this region to follow the curing of urea–formaldehyde resins and dimethylolurea, respectively. Unfortunately, most of the model compounds have no clear Raman bands in this region.
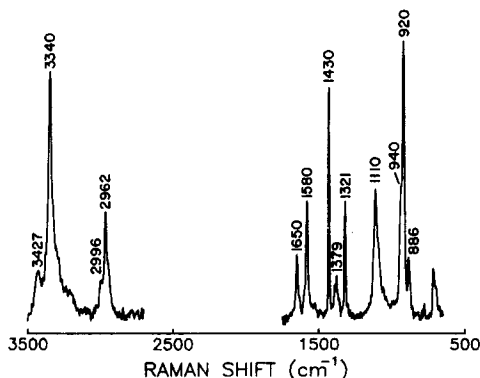

Fig. 4.   Raman spectrum of methylene diurea (incident power = 0.30 W; spectral bandpass = 6.84; scan speed = 0.5 cm^{-1}/s; number of scans = 1).
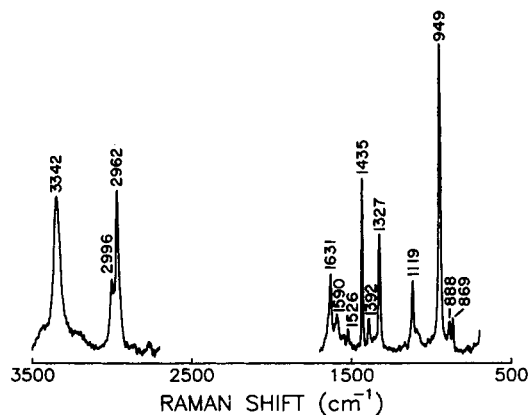
Fig. 5. Raman spectrum of trimethylene tetraurea (incident power = 0.20 W; spectral bandpass = 6.84; scan speed = 0.5 cm⁻¹/s; number of scans = 1).

1485–1448 cm⁻¹. This region has been assigned in infrared spectra to CH_2 bending. In the present spectra, absorptions appear *only* in those compounds possessing the —CH_2O— moiety (Figs. 1–3, 7 and 8), —NCH_2OH (Figs. 2, 7 and 8), —OCH_2OCH_2— (Fig. 1), or —NCH_2OCH_3 (Fig. 3).

1436–1430 cm⁻¹. In distinct contrast to the 1485–1448 cm⁻¹ region, this medium to strong absorption band occurs in both the methylene (Figs. 4–6) and the mixed (Figs. 7 and 8) series, i.e., in compounds containing the NCH_2N linkage. Becher and Griffel[19] have suggested that this band can be associated with N—CH_2—N bending, but the resolution of his infrared spectra was not sufficient to permit one to distinguish this band from the band in the 1485–1448 cm⁻¹ region. The Raman spectra of the mixed compounds (Figs. 7 and 8) show that the bands can be distinguished and suggest that spectral differentiation of the two linkages can be attempted. Further discussion of this region is presented later.

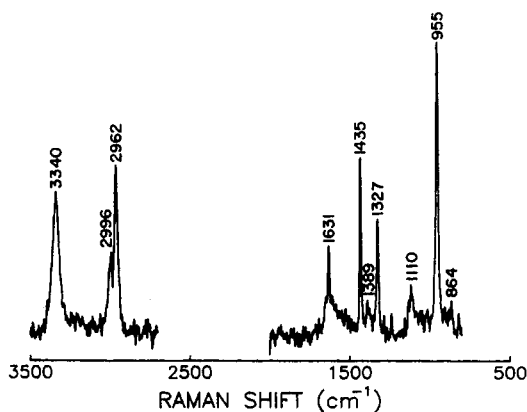**1400–1370 cm⁻¹.** All spectra show a weak band in this region. Myers[8]

Fig. 6. Raman spectrum of pentamethylene hexaurea (incident power = 0.30 W; spectral bandpass = 6.84; scan speed = 0.5 cm⁻¹/s; number of scans = 1).

TABLE III
Summary of Model Compound Spectra[a]

Compound	~3427	3342-3334	3050-2800	Wave number (cm⁻¹) 1650-1630	1590-1580	1570-1520	1485-1448	1436-1430
Formalin			2990 (S) 2942 (S) 2855 (M)				1485 (M) 1450	
N,N'-Dimethylurea		3334 (M)	3011 (M) 2957 (S)	1648 (M)		1562 (W)	1450 (MS)	
Dimethylolurea dimethylether			2988 (M) 2938 (M) 2889 (WM) 2833 (M)	1633 (WM)			1448 (MS)	
Methylenediurea	~3427 (W)	3340 (S)	2996 (W) 2962 (WM)	1650 (W)	1580 (M)			1430 (S)
Trimethylene tetraurea		3342 (MS)	2996 (W) 2962 (MS)	1631 (W)	1590 (W)	1526 (VW)		1435 (MS)
Pentamethylene hexaurea		3340 (M)	2996 (W) 2962 (MS)	1631 (W)				1435 (MS)
Monomethylol methylenedi-urea		3336 (MS)	3005 (M) 2962 (S)	1640 (M)			1452 (WM)	1436 (MS)
Methylene-bismonomethylol-urea		3338 (MS)	3005 (M) 2960 (S)	1648 (M)			1451 (M)	1430 (MS)
Band assignment	—NH₂ stretch	—NH₂, >NH stretch	—CH stretch, 2833 = CH₃O—	Carbonyl stretch	Unassigned	Unassigned	CH₂ bending in —CH₂O—	CH₂ bending in —NCH₂N—

TABLE III. (Continued from the previous page.)

| Compound	Wave number (cm^{-1})							
	1400–1370	1330–1320	~1280	1120–1110	1105–1080	~990	955–920	~900
Formalin	1400 (W)		(1313 W) 1266 (?)		1104 (W)	(1046 WM)		906 (S)
N,N'-Dimethylolurea	1388 (W)	1321 (WM)						904 (MS)
Dimethylolurea dimethylether	1389 (?)		1287 (M)		1098 (M)	990 (VS)		900 (S)
Methylenediurea	~1379 (W)	1321 (M)		1110 (M)			920 (S) (~940 M)	886 (W)
Trimethylene tetraurea	1392 (W)	1327 (M)		1119 (W)			949 (S)	~888 (W)
Pentamethylene hexaurea	1389 (VW)	1327 (M)		1110 (W)			955 (S)	~864 (VW)
Monomethylol methylenedi- urea	1389 (W)	1331 (WM)	1286 (WM)	~1123 (W) ~1106 (W)	1081 (M)	992 (MS)	932 (S)	~882 (W)
Methylene-bismonomethylol- urea	1389 (W)	1330 (WM)	1287 (WM)		1083 (M)	991 (MS)	932 (S)	881 (W)
Band assignment	—CH$_2$— deformation?	—NCH$_2$N—	—CH$_2$OH	—NH$_2$ rocking	—CH$_2$OH	990= —CH$_2$OH 1046= —COC— or —CH$_2$OH	—NCH$_2$N—	—COC—?

^{a} VS = very strong; S = strong; M = medium; W = weak.
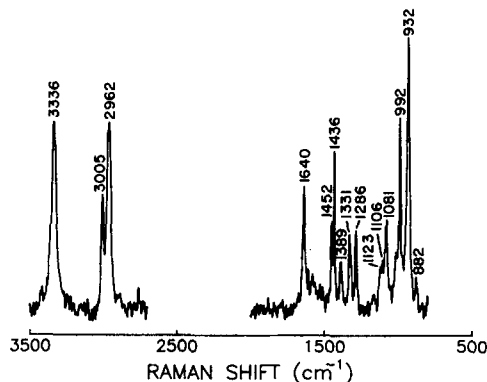
Fig. 7. Raman spectrum of monomethylol methylenediurea (incident power = 0.30 W; spectral bandpass = 5.5; scan speed = 0.5 cm⁻¹/s; number of scans = 1).

attributed this band to CH_2 deformation. The similarity of the bands in all spectra prevent a more specific structural assignment.

1330–1320 cm⁻¹. This band is of medium strength in the methylene series, somewhat weaker in the mixed series, but absent from the spectra of dimethylolurea and formalin. It seems reasonable to attribute it to the NCN linkage. A weak 1321 band also shows in Figure 3, but this sample is suspect due to its instability in the beam.

∼1280–1300 cm⁻¹. A band at this location is seen in the spectra of all UF compounds with a methylol substituent group (Figs. 2, 7 and 8). It is not seen in the methylene series spectra (Figs. 4–6) or the spectrum of dimethylolurea dimethylether (Fig. 3). These facts indicate that the band is due to —CH_2OH, and this interpretation is consistent with infrared assignments.[8]

1130 cm⁻¹. This was observed only in dimethylolurea dimethylether and is probably due to COC vibrations[18] of the methoxy ether.

1120–1110 cm⁻¹. In the spectra of the methylene series (Figs. 4–6) there is a band which decreases in intensity as the chain length increases. This
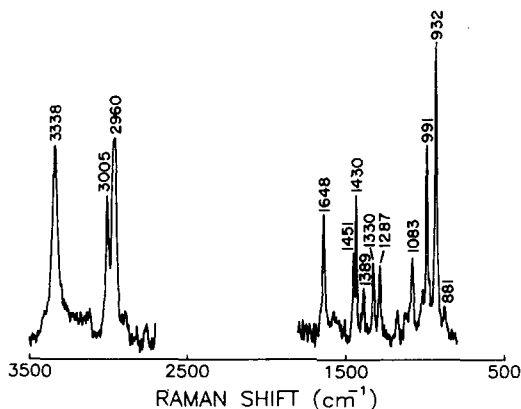

Fig. 8. Raman spectrum of methylene-bismonomethylolurea (incident power = 0.30 W; spectral bandpass = 6.84; scan speed = 0.5 cm⁻¹/s; number of scans = 1).

suggests that the band is due to an NH_2 component. Myers[8] attributed peaks in this region to NH_2 rocking. The spectrum of monomethylol methylene-diurea (Fig. 7) contains a weak, but discernable peak, which is consistent with this interpretation.

1105–1080 cm^{-1}. We attribute this weak to moderate band to a —CH_2OH since it appears only in the compounds containing that group (Figs. 1, 2, 7 and 8).

~990 cm^{-1}. This is a rather strong band appearing only in the UF compounds possessing —CH_2OH groups. It presumably corresponds to the ~1000 cm^{-1} infrared band that is assigned to the —CH_2OH group.[8] The weaker 1046 cm^{-1} absorption in formalin may be due either to this same moiety or to —COC— since it has been observed in the spectra of both ethylene glycol and trioxane.[22]

955–920 cm^{-1}. This strong absorption parallels that at 1440–1430 cm^{-1} and appears only in compounds with —NCH_2N—. Note that the frequency appears to be somewhat dependent on structural details—e.g., chain length in the methylene series.

~900 cm^{-1}. Assignment here remains ambiguous. The strong 906 cm^{-1} band in formalin (Fig. 1) is very likely due to the presence of ether groups in hemiformal and formal structures.[18] Similarly, the strong 900 cm^{-1} band in dimethylolurea dimethyl ether may be attributed to the COC linkage.[18] Whether there could be sufficient COC formation by cyclization or chain extension reactions in the commercial dimethylolurea to account for its rather strong 910 cm^{-1} band is not clear. Such impurities could possibly account for the weak absorptions in the 870–890 cm^{-1} for the other compounds.

Resin Spectra

The model compound spectra indicated that several spectral regions might provide some differentiation among such moieties as CH_2OH, NCH_2N, and CH_2OCH_2 in cured resins. In this exploratory study the 1400–1500 cm^{-1} methylene bending region was selected for emphasis. As illustrated in Figure 9, this region provides a clear separation between CH_2OH and NCH_2N groups when present in the same model compound (monomethylol methylenediurea). It should be kept in mind, however, that the 1450 cm^{-1} band appears also to reflect the presence of COC linkages since it was observed in the spectra of formalin and dimethylolurea dimethylether. The following discussion will, therefore, refer to generalized —CH_2O— groups at 1450 cm^{-1} and —NCH_2N— groups at 1435 cm^{-1}.

The effect of cure time on resin spectra is illustrated in Figure 10. Although resolution between the 1450 cm^{-1} and 1435 cm^{-1} bands is less than in the model compounds, there is a clear shift in their relative intensities as cure progresses. The concentration of —NCH_2N— groups increases with cure relative to the concentration of —CH_2O— groups, the ratio of peak heights (1450/1430) before cure and after 10 min at 120°C being approximately 0.79 and 0.95, respectively. Similar patterns were also observed during cure at temperatures from 80°C to 150°C. Figure 11 shows the distinct differences in this spectral region between samples cured under rather extreme conditions.
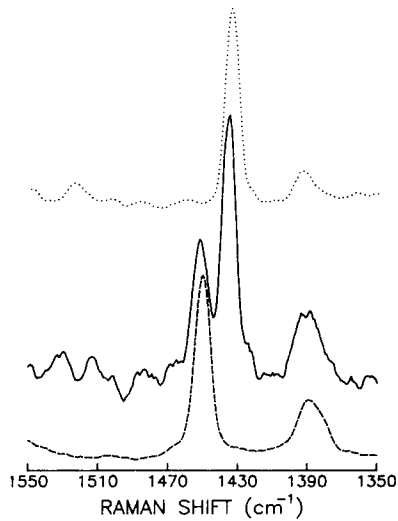
Fig. 9. Comparison of the 1350–1550 cm^{-1} region of three urea–formaldehyde model compound spectra: monomethylol methylenediurea (——), trimethylene tetraurea (. . .), and N,N'-dimethylolurea (—).
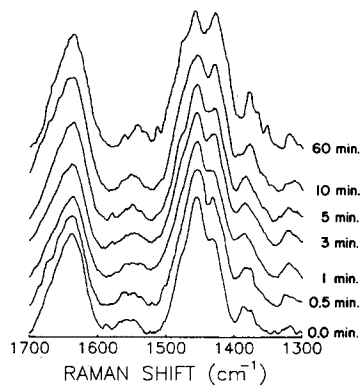

Fig. 10. Raman spectra from 1300–1700 cm^{-1} of a urea–formaldehyde resin cured with H$_3$PO$_4$ at 120°C for various times (incident beam = 0.2–0.3 W; spectral bandpass = 4.11–6.84; scan speed 0.5 cm^{-1}/s; number of scans = 2).
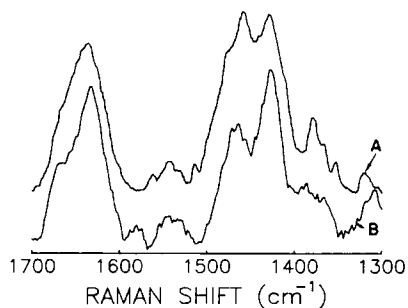

Fig. 11. Comparison of two urea–formaldehyde resins cured under different conditions: (A) H$_3$PO$_4$, 120°C, 60 min; (B) NH$_4$Cl, 150°C, 60 min.

These observed changes in —CH$_2$O— and —NCH$_2$N— concentrations are, of course, consistent with what is known about the acid catalyzed cure process in these systems.[2,8,12] Methylols are lost by reaction with —NH$_2$ to form —NCH$_2$OCH$_2$N— linkages; the latter type of —CH$_2$O— moiety is also removed by loss of formaldehyde to yield additional —NCH$_2$N—.

SUMMARY AND CONCLUSIONS

The laser Raman spectra of several UF model compounds indicate that there are several spectral regions that have promise for distinguishing critical structural differences in cured UF resins. Those regions include absorption bands around 3000 cm^{-1}, between 1400 and 1500 cm^{-1}, and between 900 and 1000 cm^{-1}. Examination of the 1400–1500 cm^{-1} region during resin cure, for example, demonstrated that relative changes can be observed in the concentrations of —NCH$_2$N— and —CH$_2$O— moieties.

Thus, it seems likely that laser Raman spectroscopy can become a useful complement to other techniques, such as infrared and solid sample NMR, for the determination of structure in cured UF systems. Before that goal can be realized, however, additional work will be required to answer the following questions:

(1) What information can be obtained about resin structural changes during cure from spectral regions other than 1400–1500 cm^{-1}?

(2) What is the effect of fluorescence on the relative intensities of the peaks?

(3) How can one cope with the loss of resolution as the resin becomes more complex?

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