

Investigation of Urea-Formaldehyde Polymer Cure by Infrared

GEORGE E. MYERS, *Forest Products Laboratory, Forest Service, U.S. Department of Agriculture, Madison, Wisconsin, 53705*

Synopsis

An examination has been made of the capability of conventional infrared analysis to define the structure of urea-formaldehyde (UF) polymers in the cured, crosslinked state. Proton NMR and infrared measurements of model compounds and uncured UF polymers were combined with infrared observations during polymer cure. The existing interpretation of UF polymer infrared spectra was clarified and a partial confirmation of the UF polymer cure mechanism obtained. However, it was concluded that conventional infrared possesses distinct limitations for defining the UF cure process in great detail, and it is hoped that the new solid-sample NMR methods will prove capable of the desired structural determination in the cured state.

INTRODUCTION

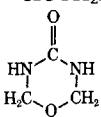
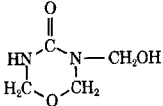
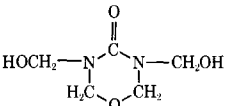
Over the past 30 years much effort has been expended in establishing the structure of the products of reactions between urea (U) and formaldehyde (F), using a variety of techniques as they became available. Most recently the application of ^1H and ^{13}C NMR has begun to provide definitive information about the structures present in *soluble* UF reaction products.¹⁻¹¹

At the Forest Products Laboratory we have been interested in the structural factors that control the hydrolytic degradation of UF wood adhesives in the cured, and thus *insoluble*, state, in the hope that optimized structures could be found which would lead to greater durability of UF-bonded wood products and to lowered formaldehyde emission. As part of that program we have examined the capability of infrared to define possible critical structural differences in the cured state where conventional ^1H and ^{13}C NMR are, of course, not informative. Since definite points of confusion exist in the literature regarding some infrared band assignments in these materials, infrared and proton NMR (60 MHz) spectra were also obtained for a number of model compounds and uncured UF polymers. These data were combined with the existing infrared literature on UF-related materials and employed to clarify the assignments of infrared bands in UF polymers before and after cure. We summarize here the spectra and band assignments as well as our conclusions regarding cured UF adhesive structure and the ability of infrared to identify such structures.

BACKGROUND

Table I lists some of the structural elements and compounds which have been identified in *soluble* UF reaction products by the use of ^1H and ^{13}C NMR. It can be anticipated that most of these structures will be found in uncured (soluble) UF polymers and will also be present in varying amounts after cure. Unfortu-

TABLE I
 Species Identified by NMR in Soluble UF Reaction Products

Formula		References
$\begin{array}{c} \\ \text{—NCONHCH}_2\text{OH} \end{array}$	methylol	1-6, 9-11
$\begin{array}{c} \\ \text{—NCONHCH}_2\text{OCH}_2\text{OH} \end{array}$	hemiformal	1, 8-10
$\begin{array}{c} \\ \text{—NCONHCH}_2\text{OCH}_2\text{OCH}_2\text{—} \end{array}$	polyformal	5
$\begin{array}{c} \\ \text{—NCONHCH}_2\text{OCH}_2\text{NH—} \end{array}$	dimethylene ether bridge	1-6, 9-11
$\begin{array}{c} \\ \text{—NCONHCH}_2\text{NHCON—} \end{array}$	methylene bridge	1-6, 8-11
$\begin{array}{c} \text{—N—CH}_2\text{—} \\ \\ \text{CH}_2\text{OH} \end{array}$	methylol on tertiary N	9-11
$\begin{array}{c} \text{—N—CH}_2\text{—} \\ \\ \text{CH}_2\text{—} \end{array}$	methylene branch points at tertiary N	9-11
$\begin{array}{c} \\ \text{—NCONHCH}_2\text{OCH}_3 \end{array}$	methoxyl	3-10
$\text{H}_2\text{NCONHCH}_2\text{OH}$	monomethylolurea	2, 3, 9-11
$\text{HOCH}_2\text{NHCONHCH}_2\text{OH}$	<i>N,N'</i> -dimethylolurea	2, 3, 7-11
$\text{H}_2\text{NCON}(\text{CH}_2\text{OH})_2$	<i>N,N</i> -dimethylolurea	2, 7
$\text{HOCH}_2\text{NHCON}(\text{CH}_2\text{OH})_2$	trimethylolurea	7, 11
	uron	10, 11
	monomethyloluron	10
	dimethyloluron	10, 11, 13

nately, the evidence reported, primarily infrared combined with thermal degradation,^{12,13} is not definitive enough to identify the presence of these compounds in the cured resin. It is quite reasonably presumed, but not proven, that cross-linking (cure) occurs via conversion of secondary amides to tertiary amides. There are additional uncertainties as to the fate of the various linear and cyclic ether linkages during the usual hot press cycle employed in bonding wood with acid-catalyzed UF adhesives. Small amounts of formaldehyde are evolved upon heating UF polymers at temperatures below 150°C,¹²⁻¹⁵ and this is believed, but again not proven, to be partially due to the breakdown of the ether linkages to form methylene links plus formaldehyde.

Thus, it is now generally believed that a cured UF adhesive contains crosslink points at the amide nitrogen and a backbone chain composed largely of

$\text{>NCONCH}_2\text{NCON<}$ groups. However, the network may well also contain cyclic methylene urea derivatives as well as linear and/or cyclic ether structures, the relative amounts of the various structures probably being dependent upon both the initial polymerization and the ultimate cure compositions and conditions. It should be noted that different UF polymers can exhibit markedly different hydrolytic degradation behavior in the cured state, a further indication of the existence of quite different structures.¹⁶

EXPERIMENTAL

Materials

Model compounds and polymers were either prepared in our laboratory or purchased. These are listed in Table II along with a brief description of their source or method of preparation. Polymers were cured for various times at different temperatures as thin films in covered stainless steel pans under a nitrogen purge, using 3% of a catalyst solution composed of 20% NH_4Cl , 2.5% concentrated NH_4OH , 1.0% triethylamine, and 76.5% H_2O .

Spectra

All model compounds and polymers were dried to constant weight in vacuo at room temperature prior to obtaining the spectra. Proton NMR spectra were obtained in deuterated DMSO (approximately 5% concentration) using a 60 MHz Varian A60 instrument. Tetramethylsilane was used as the reference, and spectra were obtained before and after addition of D_2O to the solution. Infrared spectra were obtained in the absorbance mode using KBr pellets (>0.5% concentration) and a Beckmann IR 12 instrument.

RESULTS

Proton NMR

Figure 1 shows a representative polymer NMR spectrum. The NMR results are summarized in Table III as the approximate molar amounts of various H-containing groups relative to total CH_2 content. The frequency assignments employed in making the calculations from the integrated spectra are listed in Table IV; those assignments are based upon the changes which were observed in this study to be produced by the different model compounds and by the effects of D_2O thereon, as well as upon the numerous literature reports in recent years on proton NMR spectra for similar compounds.¹⁻⁷

For groups such as NH_2 , NH , OH , CH_2 , CH_3 , and OCH_3 the assignments can be considered well established, although the absorption bands for polymers are quite broad. Resolution of the CH_2 band from 60-MHz spectra into its contributing structures (e.g., OCH_2O , OCH_2N , NCH_2N) and identification of those structures are not nearly so firm; the quantitative breakdown given in Table III

TABLE II
 Material Preparation^a

Material	Formula	Synthesis procedure ^b	Ref- erence
Model compounds			
Dimethylolurea dimethyl ether, FPL-35-1	$(\text{CH}_3\text{OCH}_2\text{NH})_2\text{CO}$	dimethylolurea + CH_3OH with H_3PO_4 , 23°C/24 hr, $T_M = 99-100^\circ\text{C}$	17
Methylenediurea, FPL-39-1	$(\text{H}_2\text{NCONH})_2\text{CH}_2$	F/U 0.12, pH 2.4, 20-25°C/48 hr	18
Trimethylenetetraurea, FPL-40-2	$\text{H}_2\text{NCONH}-(\text{CH}_2-\text{NHCONH})_2-\text{CH}_2\text{NHCONH}_2$		18
Pentamethylenehexaurea, FPL-40-1	$\text{H}_2\text{NCONH}-(\text{CH}_2-\text{NHCONH})_4-\text{CH}_2-\text{NHCONH}_2$		18
Monomethylolmethylenediurea, FPL-41-1	$\text{H}_2\text{NCONHCH}_2\text{NHCONHCH}_2\text{OH}$		18
Methylenebismonomethylolurea, FPL-41-2	$(\text{HOCH}_2\text{NHCONH})_2\text{CH}_2$		18
Polymers			
FPL-31-1		F/U = 1.64, pH 8.4, reflux/2 hr	19
FPL-36-2		0.50 mole dimethylolurea, 0.167 mole each of F and U, total F/U = 1.75, pH 5.0, reflux 1 hr and neutralize	
FPL-37-1		F/U = 1.70, pH 7.5, reflux 45 min, pH 5.0, 23°C/24 hr, neutralize	
FPL-37-2		F/U = 2.2, as in 37-1 except 23°C/96 hr	
FPL-38-1		F/U = 1.85, pH 7.3, reflux 1 hr, pH 7.6, 23°C/16 hr, pH 8.0	20

^a All prepared at the Forest Products Laboratory.

^b Quoted pH and F/U are initial values. Formalin contained approximately 10% methanol.

for some of the materials is therefore very approximate. Such differentiations among the CH_2 in UF polymers have been reported, however, by combining 60-MHz spectra with chemical analyses^{1,3,6} and by the use of 100-MHz proton NMR,⁸ and 220-MHz proton NMR⁴ and ¹³C NMR.⁹⁻¹¹ Thus, it seems very probable that some or all of these structural variants are present in the uncured UF polymers examined here. Some of the complexity of the polymer spectra in the CH_2 region might conceivably result from rotational restrictions, but no evidence of this has been reported for these low molecular weight polymers.

The NMR results in Table III for the model compounds demonstrate the difficulties in preparing pure materials of this type and perhaps thereby provide an explanation for some of the apparently contradictory interpretations in the literature of the infrared spectra of UF materials. For example, the preparations FPL-41-1 and 41-2 must certainly be regarded as mixtures.

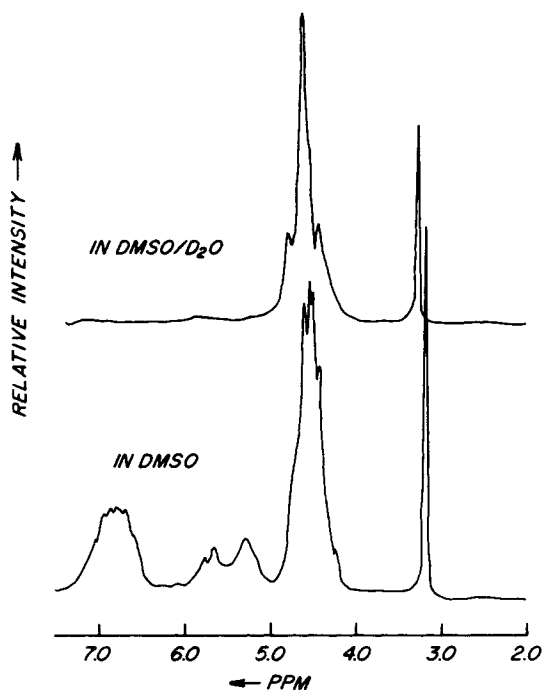


Fig. 1. NMR spectrum of UF polymer FPL-37-1.

Infrared

Figure 2 presents the infrared spectra for three of the model compounds studied, while Figure 3 illustrates the changes that may occur in the infrared during polymer cure. The infrared spectra will be considered here only over the region of $1000\text{--}1700\text{ cm}^{-1}$ since above or below this region the observed bands were either too weak or too broad to permit any quantification. All of the infrared spectra were quantified on the same relative basis by normalizing the measured absorbances to that of the carbonyl ($\sim 1650\text{ cm}^{-1}$) in each spectrum. Since the carbonyl intensity did not appear to change during polymer cure, the same normalization procedure was employed as a means of detecting changes in other bands during cure. The dashed lines on the bottom spectra in Figures 2 and 3 illustrate the baselines employed to determine the various absorbancies. Since the baseline selection is to some extent arbitrary and since no attempt was made to resolve overlapping peaks, the quantification cannot be considered to be on an absolute basis; however, it does possess the virtue of consistency. The results of the calculations are given in Table V for model compounds and for some of the polymers investigated.

It may be seen from Table V and Figure 3 that several changes occur in the spectra during cure. (Quantitatively similar changes have also been observed by us for several commercial UF polymers.) These changes are (1) a rapid and significant decrease in the intensity of the broad $1020\text{--}1040\text{ cm}^{-1}$ band and usually a simultaneous shift toward 1040 cm^{-1} ; (2) a significant decrease in the $1550\text{--}1560\text{ cm}^{-1}$ and possibly the $1250\text{--}1260\text{ cm}^{-1}$ bands; (3) the sudden appearance and rapid growth of a band at $1500\text{--}1510\text{ cm}^{-1}$ and, less obviously, at $1290\text{--}1300\text{ cm}^{-1}$; (4) a possible initial increase in bands at about 1180 and 1140

TABLE III
Approximate Molar Amounts of Various H-Containing Groups Relative to Total CH₂ Content from NMR Spectra

Material/source	Moles of specified group per mole total CH ₂ groups (observed/theory)										Comments	
	NH ₂	NH	OH	OCH ₂ O	OCH ₂ N	NCH ₂ N	OCH ₃	N(CH ₃) ₂				
Dimethylolurea/commercial, recrystallized + D ₂ O	0.04/0	0.94/1.0	0.84/1.0									low OH and NH, some NH ₂
Dimethylolureadimethyl ether/FPL-35-1 + D ₂ O	0/0	0/0	0/0		1.0/1.0							OK within experimental error
N,N-Dimethylurea/ commercial + D ₂ O	0/0	0/0	0/0		1.0/1.0			1.0/1.0				OK within experimental error
Methylenediurea/FPL-39-2 + D ₂ O	1.8/2.0	1.9/2.0	0.1/0							1.0/1.0		small amount OH, con- densation incomplete
Trimethylenetetraurea/FPL-40-2 + D ₂ O	0.67/0.67	1.7/2.0	0/0									OK within experimental error

Methylenebismonomethylolurea/ FPL-41-2 + D ₂ O	0.1/0	1.2/1.3	0.46/0.67							mixture
Monomethylolmethylenediurea/ FPL-41-1 + D ₂ O	0/0 0.22/0.50	0/0 1.3/1.5	0/0 0.44/0.50	~0.1/0	~0.47/0.67	~0.42/0.33				NH ₂ very low
UF polymer/FPL-31-1 + D ₂ O	0/0 0.16/—	0/0 1.1/—	0/0 0.28/—		0.47/0.50	0.53/0.50				OCH ₂ O < NCH ₂ N < OCH ₂ N
UF polymer/FPL-36-2 + D ₂ O	0/0 0.18/—	0/0 0.70/—	0/0 0.26/—							variety of CH ₂ 's, not quantifiably resolvable
UF polymer/FPL-37-1 + D ₂ O	0/0 0.13/—	0/0 0.88/—	0/0 0.32/—							
UF polymer/FPL-37-2 + D ₂ O	0/0 0.11/—	0/0 0.56/—	0/0 0.16/—	~0.22/—	~0.67/—	~0.20/—				variety of CH ₂ 's, not quantifiably resolvable
UF polymer/FPL-38-1 + D ₂ O	0/0 0.08/—	0/0 0.76/—	0/0 0.24/—							variety of CH ₂ 's, not quantifiably resolvable
	0/0	0/0	0/0							0.13/— 0.12/— 0.04/— 0.04/— 0.12/— 0.13/— 0.09/— 0.12/— 0.09/— 0.11/—

^a Values are relative to number of CH₃ groups.

TABLE IV
 Proton NMR Assignments^a

Structure	Frequency, ppm	References
—CONH ₂	5.50–5.70	1–5, 7
—CONH—	6.50–6.90	1–5, 7
—CH ₂ OH	5.20–5.30	2–5, 7
>NCH ₂ N<	4.20–4.35	1–5
—OCH ₂ N<	4.40–4.60	1, 3, 4
—OCH ₂ O—	4.65–4.80	1, 3, 4, 7
—OCH ₂ CH ₃	3.10	1
—OCH ₂ CH ₃	1.65	1
—OCH ₃	3.15–3.30	1–3
—NHCH ₂ CH ₂ NH—	3.00–3.05 ^b	
—N(CH ₃) ₂	2.55 ^b	

^a Frequency in ppm relative to TMS in deuterated DMSO. Each value represents the frequency at peak center or maximum. A range of frequencies reflects differences observed for different compounds or resins. Assignments based upon our data plus literature.

^b FPL data.

cm⁻¹, but these last changes are uncertain due to questions about baseline and resolution. The changes in some of these absorbances are plotted against cure time for one of the polymers in Figure 4.

INTERPRETATION OF POLYMER INFRARED

As indicated earlier, existing infrared band assignments were of only limited value in interpreting the polymer spectra and their changes during cure. Upon examining this question we have arrived at the assignments summarized in Table VI. The following discussion presents the justification for those band assignments where significant doubt might arise. In some instances the assignments must still be regarded as tentative, particularly in view of the recognized complexity of infrared motions in the fingerprint region.

Bands 1550–1560 and 1510–1520 cm⁻¹

The 1550–1560 cm⁻¹ amide II band is strong in our spectra of uncured UF polymers and of a variety of UF model compounds in the solid state which possess secondary amides. Similar results for related compounds are reported in the literature.^{12,13,23,24,29,31} During polymer cure our spectra show the appearance and growth of a band at 1510–1520 cm⁻¹; similar observations were made by Chabert during cure of dimethylolurea¹² and by Pshenitsyna and co-workers during acid cure of UF resins.³²

Bellamy reports the amide II band for noncyclic (trans) secondary amide at 1515–1570 cm⁻¹ in the solid state and at 1510–1550 cm⁻¹ in solution, with no absorption in these regions for cyclic secondary amides or for either linear or cyclic tertiary amide.³³ Recent data, however, demonstrate that cyclic urea derivatives having secondary or tertiary nitrogens, and also linear urea derivatives having tertiary nitrogens, can all have infrared absorptions in the 1490–1525 cm⁻¹ region, whether in solution or in the solid state. Jung et al. report amide II bands

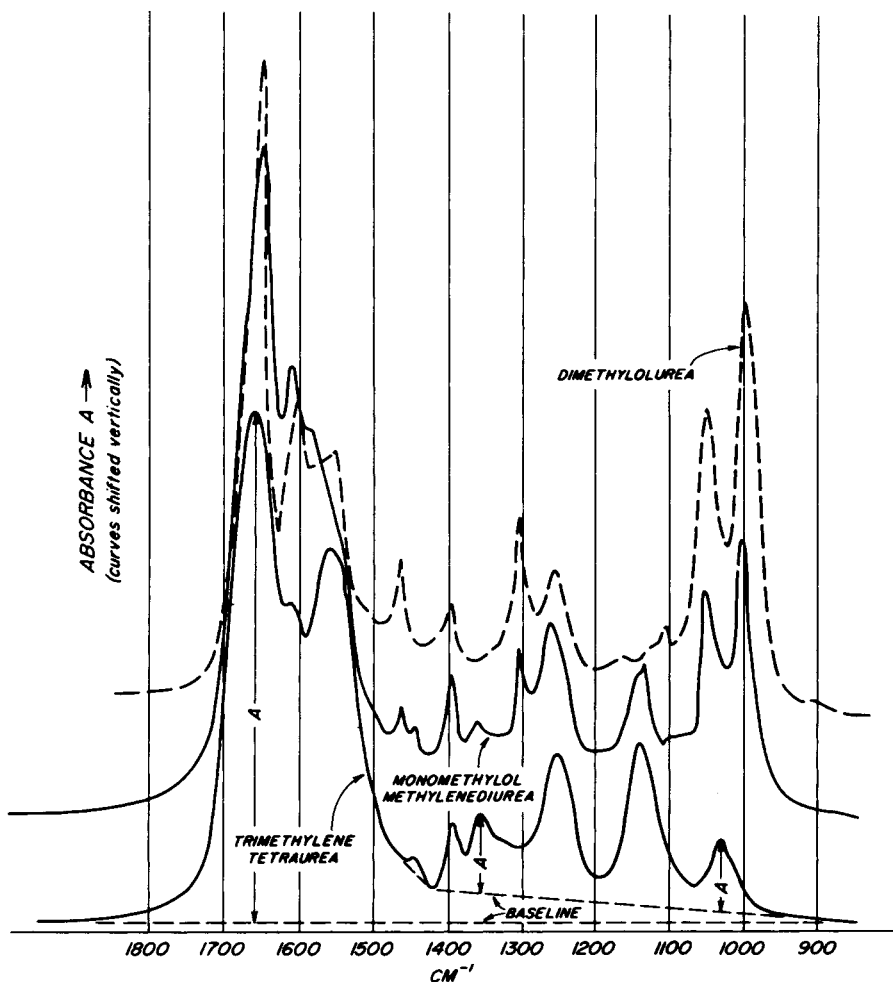


Fig. 2. Infrared spectra of model compounds.

between 1493 and 1524 cm^{-1} for the crystalline forms of cyclic ethyleneurea and propyleneurea and their N,N' -dimethylol derivatives.³⁰ Amide II bands are reported for crystalline tetramethylurea^{25,34} at 1510 and 1515 cm^{-1} and at 1510 cm^{-1} for DMSO solutions.³⁴ For several six-membered ring cyclic urea derivatives, Pshenitsyna et al. observed amide II bands at about 1550 cm^{-1} in the solid state and at 1520 cm^{-1} in solution when secondary amide nitrogens were present, but these absorptions shifted to about 1515 cm^{-1} in the solid state and to 1505 cm^{-1} in solution when those secondary amides were converted to tertiary amide.³⁴

Thus, we offer the following explanation for our observed changes in the 1510–1560 cm^{-1} region during polymer cure: In the uncured, solid form the predominantly secondary amide exists primarily as a linear chain in a highly hydrogen-bonded state. After cure this secondary amide will exist in an environment where such hydrogen bonding is repressed due to steric constraints or it will have been converted to tertiary amide, either linear or cyclic.

TABLE V
Normalized Infrared Absorbance

Material/source/ ^{b/}	Treatment	Wave number (cm ⁻¹)											
		1700	1600	1500	1400	1300	1200	1100	1000				
<u>Model compounds:</u>													
Dimethylolurea/commercial, recrystallized	Vacuum dried, 20°C	100	46	39	13	7	24	16	~4	~4	10	45	62
Dimethylolurea dimethyl ether/PPL-33-1	Vacuum dried, 20°C	100	84		16, 14, 11, 11	22	27	12	44	17	65	59	59
Methylene bis urea/PPL-39-2	Vacuum dried, 20°C	100	56	57	~4	9	24	~6	31			tr.	
Trimethylene tetraurea/PPL-40-2	Vacuum dried, 20°C	100	-21	71	~3	13	16	29	31			14	
Pentamethylene hexaurea/PPL-40-1	Vacuum dried, 20°C	100	-17	68	~3	13	~10	33	30			20	
Methylene bis monomethylol-urea/PPL-41-2	Vacuum dried, 20°C	100	-60	-40	~5	11	18	23	14			34	45
Monomethylol methylene bis urea/PPL-41-1	Vacuum dried, 20°C	100	-63	-45	5	11	~6	14	19	16		27	39

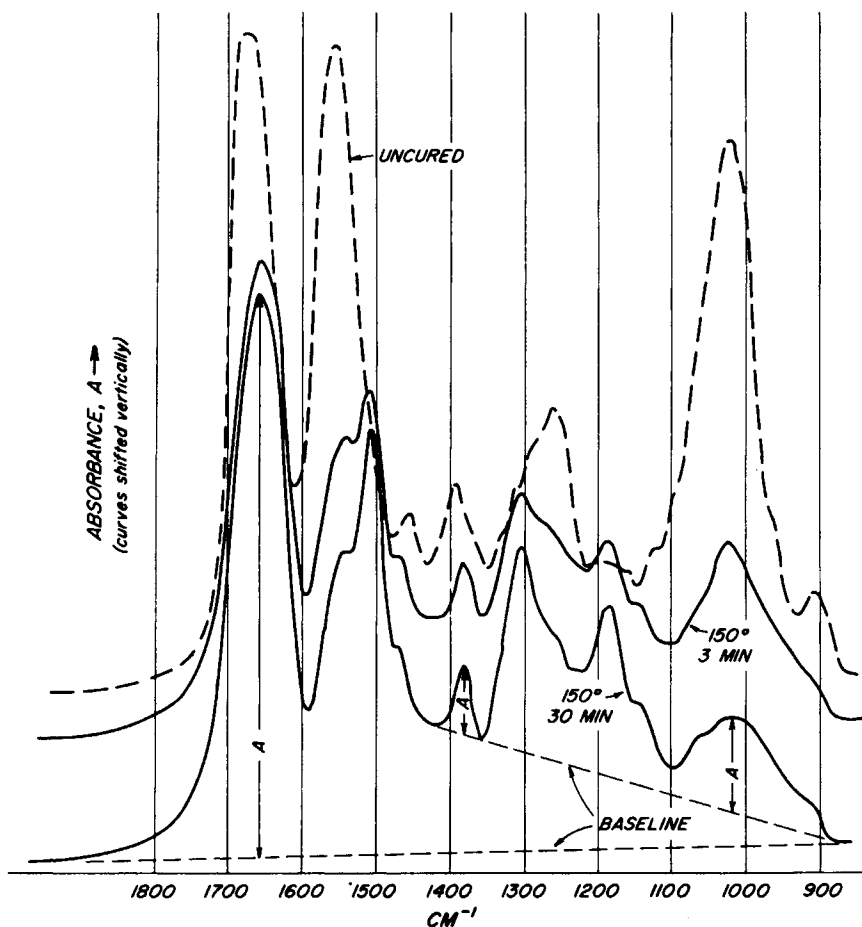


Fig. 3. Infrared spectra of polymer FPL-37-2 during cure.

Band 1290–1300 cm^{-1}

This band appears as a shoulder on the 1260 cm^{-1} peak in our spectra for uncured polymers. During polymer cure our spectra and those of Pshenitsyna et al.³² indicate that it becomes much more distinct. Chabert reports an initial band in polymers at 1310 cm^{-1} which shifts to 1290 cm^{-1} during cure.¹² Pshenitsyna and co-workers³² find that tertiary amides in uronic ring structures exhibit an amide III band at 1300 cm^{-1} . Our spectra for model compounds also show a band to be present (weak) in this region for compounds possessing CH_2OH , e.g., mono- and dimethylolurea, methylenebismonomethylolurea, and monomethylolmethylenediurea, but absent where NMR showed little or no CH_2OH , e.g., methylenediurea, trimethylenetetraurea, and dimethylolurea dimethyl ether.

Primary alcohols exhibit an OH deformation absorption³⁵ at about 1300 cm^{-1} . This very likely accounts for the absorptions noted for methylol-containing model compounds and for uncured polymers. However, the CH_2OH content in polymers must decrease during cure so that the observed increase in the $1290\text{--}1300\text{ cm}^{-1}$ region during cure must reflect the growth of structures other than CH_2OH .

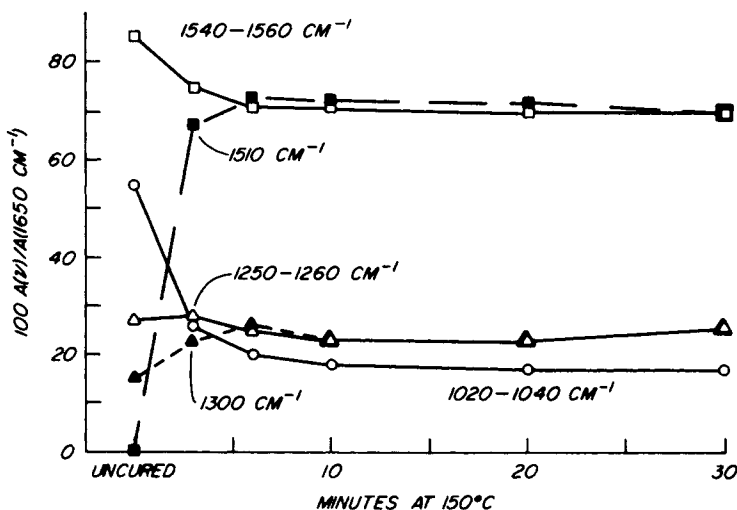


Fig. 4. Infrared changes during cure of polymer FPL-37-1.

Following Pshenitsyna et al.,³² we conclude that the new structures are very likely intrachain uronic rings formed by condensation between neighboring methylol groups. The resultant cyclic tertiary amides cause an upward frequency shift of the normal secondary amide III band of secondary amides at 1250–1260 cm^{-1} .

Band 1180–1200 cm^{-1}

This band is absent to medium strength in our polymer spectra and absent in our model compound spectra. *N*-Alkylureas and *N*-alkylamides exhibit absorptions in this general region, but this has been attributed to the methyl group.^{26,27,36} Becher assigns a band in this region of the spectra of *N,N'*-dimethyluron³⁷ and *N,N'*-dimethyloluron dimethyl ether³⁸ to the CH_3 , but we do not observe the band in several materials where NMR says OCH_3 is present. Its assignment remains unclear.

Band 1130–1150 cm^{-1}

This is an absent to medium strength band in our polymer spectra, possibly increasing during early cure, and weak to medium in our spectra of UF model compounds of varying types, both methylol- and nonmethylol-containing molecules. Chabert reports that a band at 1130–1140 cm^{-1} appears upon polymerizing dimethylolethyleneurea or dimethyloldimethylurea, either of which can polymerize only by formation of $\text{NCH}_2\text{OCH}_2\text{N}$ linkages.¹² He further reports that a similar band appears during the polymerization of dimethylolurea and that its intensity increases with additional cure but decreases upon prolonged heating at 140°C; these findings also are consistent with the expected behavior of CH_2OCH_2 linkages.¹² Bellamy states that the general range of 1060–1150 cm^{-1} is observed for alkyl ethers,³⁹ and Szymanski reports frequencies of about 1110–1120 cm^{-1} for aliphatic ethers.⁴⁰ These frequencies would also be qualitatively consistent with the 1130–1150 cm^{-1} band observed in the polymers

TABLE VI
Assignment of Infrared Bands in Urea-Formaldehyde Polymer Spectra between 1000 and 1700 cm^{-1}

Frequency, cm^{-1}	Characteristics ^a	Structural assignment
1650–1670	VS, ^a apparently constant during cure	amide I, primarily C=O stretch but with some C—N stretch and NH deformation ²¹
1600–1610	VW or absent from most polymer spectra, probably often masked by 1650 and 1550 cm^{-1} bands	amide II, NH ₂ deformation for primary amide ²²
1550–1560	S in uncured polymer spectra, intensity decreases during cure of some polymers	amide II, combined C—N stretch and NH deformation, primarily due to secondary, linear amide in hydrogen bonding environment (see Interpretation)
1510–1520	usually absent from uncured polymer spectra, appears during cure and can become strong on extended cure	amide II, due to linear or cyclic tertiary amide and possibly secondary amide in a constrained, nonhydrogen bonded environment (see Interpretation)
1460–1470	VW to W in our spectra of both polymers and models	most likely CH bending in NCH ₂ N, CH ₂ O, and OCH ₃ , ^{13,23–28} although some have assigned to NCN vibration ^{29,30}
1380–1400	W in our spectra of polymers and some models	CH mode in CH ₂ and CH ₃
1290–1300	W in our spectra of most UF polymers, difficult to resolve from 1250 to 1260 cm^{-1} initially, becomes more distinct upon cure	OH deformation in CH ₂ OH plus contribution from cyclic amide III (see Interpretation)
1250–1260	M in our polymer spectra, little obvious change during cure	amide III bond for secondary amide, combined CN and NH
1180–1200	varies from absent to M in our polymer spectra	unknown, see Interpretation
1130–1150	absent to M in our polymer spectra, quantification frequently questionable	aliphatic ether (C—O stretch) plus C—N stretch in secondary amide (see Interpretation)
1000–1050	W to S and rather broad in our polymer spectra, decreases during cure and may shift from maximum at ~1020 cm^{-1} to ~1040 cm^{-1}	see below
1030–1050	usually not resolved from 1000 to 1020 cm^{-1} absorption in polymers	probably an NC or NCN mode (see Interpretation)
1000–1020		C—O stretch in methylol (see Interpretation)

^a VW = very weak; W = weak; M = medium; S = strong; VS = very strong.

prepared by us, in which NMR shows significant OCH₃ and possible presence of methylene ethers. In contrast, however, Becher attributes bands at 1130 and 1150 cm^{-1} in methylenediurea to NH₂ rocking and NCN asymmetric stretching, respectively,²⁹ and bands at 1130–1150 cm^{-1} in monomethylolmethyleneurea and methylenebismonomethylolurea also to NCN asymmetric stretch.²³ This last assignment is consistent with our own observation of the 1130–1150 cm^{-1} band in methyleneurea derivatives, where NMR indicates no methylene ether.

Thus, we conclude that absorptions in this area can be due to both C—N stretch and to C—O—C stretch.

Band 1000–1100 cm^{-1}

In this region the polymers examined by us show absorptions only between 1000 and 1050 cm^{-1} , in the form of apparently single, rather broad absorptions or of varying proportions of absorptions at ~ 1020 and ~ 1040 cm^{-1} . During cure, an initially broad absorption at about 1020 cm^{-1} significantly decreases in intensity and shifts toward 1040 cm^{-1} . In our model compound spectra and in some UF polymers and model compounds reported upon in the literature, various peaks are observed over the entire range of 1000–1100 cm^{-1} . We conclude that the existing data are best rationalized on the basis of three types of absorption occurring in this region. These are: ether stretch at ~ 1040 –1100 cm^{-1} , amide (probably C—N or C—N₂ stretch) at ~ 1030 –1050 cm^{-1} , and methylol (C—O stretch) at 1000–1020 cm^{-1} . Arguments for and against these assignments are discussed in the following, with particular reference to the significance of the 1010–1040 cm^{-1} absorptions in polymers.

Ether

Becher^{23,37} and Yoshimi²⁴ have attributed bands at 1000–1060 cm^{-1} in a variety of UF model compounds to the grouping —OCH₂NHCONHCH₂— and a strong band at 1085–1100 cm^{-1} in methyl, ethyl, and butyl ethers of methylolureas to the aliphatic ether link. Lady et al.¹⁵ assign a weak band at 1075 cm^{-1} in butylated UF polymer also to aliphatic ether. In poly(ethylene glycol ether) a 1060 cm^{-1} band^{41,42} and in phenol-formaldehyde resins and model compounds a 1065 cm^{-1} band⁴³ are also attributed to CH₂OCH₂. Gavat et al.³¹ have also attributed a 1050 cm^{-1} band, which was observed in early cure stages of dimethylolurea, to the presence of methylene ether. Our own spectra for dimethylolurea dimethyl ether exhibit strong peaks at 1030, 1050, and 1070 cm^{-1} , with the NMR indicating little or no hydroxyl. As discussed in connection with the 1130–1150 cm^{-1} region, the work of Chabert,¹² plus other data, provide strong indication that aliphatic ether absorptions in UF polymers appear at 1130–1150 cm^{-1} . Finally, Bellamy³⁹ reports the general range of 1060–1150 for aliphatic ethers, and Szymanski⁴⁰ reports a frequency of about 1110 cm^{-1} for ethers of possible concern here. In general, therefore, aliphatic ether absorptions are not frequently observed below perhaps 1050 cm^{-1} , and it seems very probable that the 1020–1040 cm^{-1} band in UF polymers does not contain a contribution from ether bands but is more likely the result of alcohol (1000–1020 cm^{-1}) and a NCH₂N grouping (1040–1060 cm^{-1}), as noted below.

Amide and Hydroxyl

Our spectra for dimethylolurea and the two methylolmethylene compounds, monomethylolmethylenediurea and methylenebisonomethylolurea, possess two separate peaks, at 1000–1010 and 1040–1060 cm^{-1} . Moreover, our spectra for methyleneurea derivatives (e.g., trimethylenetetraurea and pentamethylenehexaurea), which by NMR contain little or no hydroxyl or ether, show in-

frared absorptions within this region only at $\sim 1040\text{ cm}^{-1}$. In a variety of non-methyl *N*-alkylureas and in methyleneureas, absorptions observed between 1010 and 1040 cm^{-1} have been attributed to C—N or C—H₂ stretch.^{25,27,29,36} Along with the behavior reported here during polymer cure, these data argue strongly for the assignment in polymers to hydroxyl at $\sim 1000\text{--}1020\text{ cm}^{-1}$ and to NCH₂N linkages at $\sim 1030\text{--}1050\text{ cm}^{-1}$. This assignment is supported by Chabert's¹² observations of a decreasing absorption intensity at $1000\text{--}1020\text{ cm}^{-1}$ during cure of mono- and dimethylolurea, which he also attributed to —CH₂OH, and observation of a weak band at 1050 cm^{-1} in these same systems, which he ascribed to NCH₂N. Akutin⁴⁴ and Pshenitsyna et al.³² also ascribe the band at 1020 cm^{-1} to CH₂OH in UF polymers, which they find decreases in intensity during cure. Partial contradiction of these conclusions is introduced by Becher and Yoshimi, however. Becher,²³ for example, reports that 1050 and 1000 cm^{-1} bands in dimethylolurea and a 1015 cm^{-1} band in monomethylolurea are due to "backbone" vibrations from the grouping OCH₂NHCONHCH₂, while Yoshimi offers the same explanation for 1020 and 1025 cm^{-1} bands observed by him for dimethylol- and monomethylolurea, respectively.¹³ Nevertheless, we conclude that on balance the available evidence supports the assignment in polymers to amide linkage at $\sim 1030\text{--}1050\text{ cm}^{-1}$ and to methylol at $\sim 1000\text{--}1020\text{ cm}^{-1}$.

SUMMARY AND CONCLUSION

This investigation has combined ¹H NMR and infrared measurements upon model compounds and uncured UF polymers with observations upon changes in infrared of UF polymers during cure. From this data combination we have achieved both a significant clarification of the interpretation of UF polymer infrared spectra and a partial confirmation of the UF polymer cure process. Nevertheless, it is also clear that there are still regions in the infrared spectrum of UF polymers where the interpretation remains tentative.

Several distinct changes occur in the infrared spectrum during UF polymer cure and these now appear to be generally consistent with the accepted chain extension and crosslinking processes in these systems. The major changes and their interpretation are summarized as follows:

(1) The methylol group decreases in concentration due to condensation with itself or with primary and secondary ureaamides. This decrease is manifested by a loss in absorbance of the peak at $1000\text{--}1040\text{ cm}^{-1}$ and a tendency of that peak to shift toward 1040 cm^{-1} . The peak does not go to zero even after extensive cure, however, probably because of an absorption due to the CN or NCN grouping at about 1040 cm^{-1} . (It seems unlikely that significant quantities of the reactive and labile methylol group still remain under the acidic cure conditions employed.) The behavior of a second, less intense, methylol absorption at 1300 cm^{-1} is also complicated by an additional absorption in that same region.

(2) The secondary amide II and amide III absorptions, at $1550\text{--}1560$ and $1250\text{--}1260\text{ cm}^{-1}$, respectively, do not change greatly in intensity during cure due to the gain in secondary amide concentration from methylol–primary amide condensation and partially compensating loss due to a methylol–secondary amide branching reaction. The latter reaction, of course, produces tertiary amides and these, either linear or cyclic, exhibit an amide II absorption at $1510\text{--}1520\text{ cm}^{-1}$. Simultaneously, the cyclic tertiary amide also exhibits an amide III absorption at $1290\text{--}1300\text{ cm}^{-1}$.

(3) No definitive conclusions can be drawn from the infrared regarding the presence of ether linkages (dimethylene ether, hemiformal, formal) or their formation and loss during polymer cure. An absorption at 1130–1150 cm^{-1} may be attributable to both C—O—C stretch and C—N stretch, and distinction between these modes in UF polymers is not now apparent.

Overall we conclude that conventional infrared spectroscopy is unfortunately of limited value in defining those possibly subtle differences in cured UF adhesives' structures which are important in controlling differences in hydrolytic stability. It is our hope that such insights may be derived from applying the new solid-sample ^{13}C and ^{15}N NMR techniques.

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References

1. S. M. Kambanis and R. C. Vasishth, *J. Appl. Polym. Sci.*, **15**, 1911 (1971).
2. B. Richard and A. Gourdenne, *C. R. Acad. Sci. Paris*, **281**, 761, 815 (1975).
3. M. Chiavarini, N. Del Fanti, and R. Bigatlo, *Angew. Makromol. Chem.*, **46**, 151 (1975).
4. W. Dankelman, J. M. H. Daemen, A. J. J. de Breet, J. L. Mulder, W. G. B. Huysmans, and J. de Wit, *Angew. Makromol. Chem.*, **54**, 187 (1976).
5. C. Duclairoir and J. Brial, *J. Appl. Polym. Sci.*, **20**, 1371 (1976).
6. M. Chiavarini, R. Bigatto, and N. Conti, *Angew. Makromol. Chem.*, **70**, 49 (1978).
7. K. Kumlin and R. Simonson, *Angew. Makromol. Chem.*, **72**, 67 (1978).
8. B. Tomita and Y. Hirose, *Mokuzai Gakkaishi*, **22**, 59 (1976).
9. A. J. J. de Breet, W. Dankelman, W. G. B. Huysmans, and J. de Wit, *Angew. Chem.*, **62**, 7 (1977).
10. B. Tomita and S. Hatano, *J. Polym. Sci. Polym. Chem., Ed.*, **16**, 2509 (1978).
11. J. R. Ebdon and P. E. Heaton, *Polymer*, **18**, 971 (1977).
12. B. Chabert, *Bull. Inst. Text. Fr.*, **20**, 205 (1966).
13. N. Yoshimi, T. Yamauchi, M. Yamao, and S. Tanaka, *Kogyo Kagaku Zasshi*, **65**, 1131 (1962).
14. I. Gavut, O. Pascu-Butufei, C. Stoicescu, and V. Kenyeres-Ursu, *Rev. Roum. Chim.*, **13**, 599 (1968).
15. J. H. Lady, R. E. Adams, and I. Kesse, *J. Appl. Polym. Sci.*, **3**, 65 (1960).
16. G. E. Myers, "Hydrolytic Stability of Cured Urea-Formaldehyde Resins," to be submitted.
17. B. E. Sorenson, U.S. Pat. 2,201,927 (1940).
18. H. Kadowaki, *Bull. Chem. Soc. Jpn.*, **11**, 248 (1936).
19. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience, New York, 1968, pp. 458–459.
20. N. G. Gaylord, Ed., *Macromolecular Synthesis*, Vol. 3, Wiley, New York, 1969, pp. 45–48.
21. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., Wiley, London, 1958, p. 209.
22. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., Wiley, London, 1958, p. 216.
23. H. J. Becher, *Chem. Ber.*, **89**, 1951 (1956).
24. N. Yoshimi, T. Yamauchi, and S. Tanaka, *Kogyo Kagaku Zasshi*, **65**, 1246 (1962).
25. K. Ramiah and M. R. K. Murthy, *Curr. Sci.*, **41** (18), 673 (1972).
26. M. Beer, H. B. Kessler, and G. B. B. M. Sutherland, *J. Chem. Phys.*, **29**(5), 1097 (1958).
27. Y. Saito, K. Machida, and T. Uno, *Spectrochim. Acta*, **31A**, 1237 (1975).
28. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., Wiley, London, 1958, pp. 13–25.
29. H. J. Becher, *Chem. Ber.*, **89**, 1593 (1956).
30. H. Z. Jung, R. R. Benerito, E. J. Gonzales, and R. J. Berni, *J. Appl. Polym. Sci.*, **13**, 1949 (1969).
31. I. Gavut, V. Kenyeres-Ursu, and C. Stoicescu, *Rev. Roum. Chim.* **13**, 809 (1968).

32. V. P. Pshenitsyna, N. N. Molotkova, M. D. Frenkel, E. E. Tikhomirova, I. M. Gurman, B. Ya. Akselrod, E. S. Potekhina, N. S. Maizel, E. S. Lagucheva, and I. M. Kochnov, *Vysokomol. Soedin. Ser. A*, **21**(9), 1945 (1979).
33. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., Wiley, London, 1958, p. 205.
34. V. P. Pshenitsyna, N. N. Molotkova, M. P. Noskova, and B. Ya. Akselrod, *J. Appl. Spectrosc.*, **29**(3), 486 (1978).
35. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., Wiley, London, 1958, p. 96.
36. Y. Mido and H. Morata, *Bull. Chem. Soc. Jpn.*, **42**, 3372 (1969).
37. H. J. Becher and F. Griffel, *Chem. Ber.*, **91**, 2032 (1958).
38. H. J. Becher and F. Griffel, *Chem. Ber.*, **91**, 2025 (1958).
39. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., Wiley, London, 1958, pp. 114-117.
40. H. A. Szymanski, *Prog. Infrared Spectros.*, **3**, 111 (1967).
41. A. Novak and E. Whalley, *Trans. Faraday Soc.*, **55**, 1484 (1959).
42. T. Tadokoro et al., *J. Chem. Phys.*, **35**, 369 (1961).
43. P. J. Secrest, *Official Digest*, Feb., p. 187 (1965).
44. M. S. Akutin, B. A. Murashov, and L. N. Shcheglova, *Trudy*, **57**, 129 (1968).

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