

# Polyamine-Modified Urea-Formaldehyde Resins.

## I. Synthesis, Structure, and Properties

ROBERT O. EBWELE,<sup>1</sup> GEORGE E. MYERS,<sup>1,\*</sup> BRYAN H. RIVER,<sup>1</sup> and JAMES A. KOUTSKY<sup>2</sup>

<sup>1</sup>USDA Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, Wisconsin 53705-2398, and

<sup>2</sup>University of Wisconsin, Madison, Wisconsin 53706

### SYNOPSIS

The objective of this study was to improve the durability and stability of urea-formaldehyde-bonded wood products by decreasing the internal stress developed during resin cure and by improving the ability of the cured resin to withstand cyclic stresses. This paper presents initial results from modifying a urea-formaldehyde resin by incorporating di- and trifunctional amines. The amines were incorporated by adding them as amines during resin synthesis, by adding urea-capped amines during resin synthesis, and by using amine hydrochlorides as acidic curing agents. Addition of amines during resin synthesis produced uncureable resins. However, modification with urea-capped amines or curing with amine hydrochlorides provided cure rates comparable to that of unmodified resin cured with ammonium chloride. These modifications also reduced the tendency of the resin to crack and fracture and substantially improved the resistance of bonded joints to cyclic stress imposed by cyclic wet-dry exposures. Resins cured with amine hydrochlorides had lower formaldehyde liberation than those cured with ammonium chloride. Thus, incorporation of flexible di- and triamines offers promise for improving the durability and stability of urea-formaldehyde-bonded wood products.

### INTRODUCTION

For some time, most wood adhesive bonding has been done with urea-formaldehyde (UF) and phenol-formaldehyde (PF) adhesives. In 1986, for example, total UF-resin usage for wood bonding in the United States was approximately 750 metric tons (t); the comparable figure for PF-resin usage was approximately 800 t.<sup>1</sup> This preponderance is expected to continue for the foreseeable future, particularly for UF resins because their precursors, methanol and urea, are less dependent on petrochemical supplies.

Bonding with UF resins is cheaper than bonding with PF resins, and it permits the formation of strong bonds under a wider variety of conditions. However, the poor durability and stability of UF-bonded products limits their use to interior, non-structural applications. These limitations are evidenced, for example, in strength losses of UF-bonded joints, irreversible swelling of UF-bonded composite panels, and formaldehyde release.<sup>2-9</sup> A significant improvement in the durability-stability of UF-bonded wood products would broaden the applications and markets for such products and thereby allow substitution of the UF-resin system for the more expensive, less versatile, and more supply-dependent PF system.

We have initiated a study whose ultimate objective is to improve the durability-stability of UF-bonded wood products by modifying the UF resin structure. This report provides the background and rationale, describes our approach, and presents the results of screening experiments using amine modifiers.

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## BACKGROUND

Two general bond-degradation processes appear to be responsible for the poor durability–stability of UF-bonded products: hydrolytic degradation<sup>10–18</sup> and stress rupture.<sup>19–22</sup> Most empirical studies have examined the effects of resin mole ratio [formaldehyde/urea (F/U) ratio—from about 2.0 to 1.2], added modifiers, or acidity on durability of UF-bonded products. Decreasing mole ratio usually, though not always, decreases the durability–stability of wood joints<sup>23</sup> and particleboard,<sup>24,25</sup> and increases particleboard swelling.<sup>24,25</sup> One report claimed that reduced mole ratio decreases cured resin tensile strength and stiffness.<sup>19</sup> In contrast, others have reported that reduced mole ratio increases cured resin strength and stiffness,<sup>26</sup> and that cured resin glass transition temperature increases at lower mole ratios.<sup>26,27</sup> In agreement with these last findings, it is likely that lower mole ratio decreases resin methylol content and branching, leading to lower water sorption, greater interchain bonding, and decreased flexibility.

A variety of modifiers have been examined, and some have been found to be beneficial for durability; a few, such as melamine, furfuryl alcohol, and certain fillers, are used in commercial applications. The mechanisms by which these materials act are not clear; they are postulated to involve an increase in hydrolytic stability as a result of alteration of the polymer network,<sup>28–30</sup> increases in flexibility and crack arrest properties,<sup>17,31</sup> or both of these mechanisms.

Hydrolysis of UF resins is catalyzed by acids,<sup>16,18,32</sup> and increases in durability have been reported as a result of employing materials capable of neutralizing the acid catalysts required for good UF-resin cure. Examples include addition of glass powder<sup>33</sup> to the adhesive, posttreatment of boards with sodium bicarbonate,<sup>17</sup> and addition of melamine, which may act as a buffer.<sup>34</sup>

The available data are far from conclusive about the effects of UF-resin structure and composition on the failure mechanisms of UF-bonded wood joints, and about the constitution of an optimum system. However, the results of previous studies suggest that the failure of UF-bonded wood products from hydrolytic or stress scission can be attributed to several underlying molecular structure–property factors that are somewhat interdependent:

1. Bonds that may be particularly susceptible to hydrolysis; e.g.,  $-\text{NHCH}_2-\text{O}-\text{CH}_2\text{NH}-$  linkages in the resin or  $-\text{NHCH}_2-$  cellulose

and  $-\text{NHCH}_2-\text{O}-$  cellulose bonds between polymer and wood.

2. Very strong interchain hydrogen bonding, which can cause insolubility, even crystallinity, in the uncured resin and lead to a nodular structure with severely nonuniform crosslink density in the cured state. Such a structure is likely to have weak bonding between nodules and thus poor fracture properties.
3. Low crosslink density, as a result of low reactivity of secondary amides, which prevents the effective functionality of urea from rising much above 2. This may also lead to inefficient load-bearing ability and to sensitivity to losses in crosslink density from hydrolysis or stress scission.
4. Brittleness of the cured resin, as a result of the inherent rotational stiffness of the urea structure and/or interchain hydrogen bonding. This brittleness, or lack of flexibility, makes the system unable to respond reversibly to stresses arising from cure shrinkage and from wood swell and shrinkage caused by moisture uptake and loss.

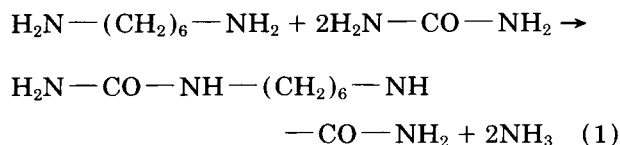
In recent years, evidence has mounted that resin hydrolysis per se (factor 1) is not the major cause of poor durability. For example, Pratt et al.<sup>35</sup> and Koutsky<sup>36</sup> provided good evidence that strong hydrogen bonding between UF molecules can produce insolubility, crystallinity, and a nodular structure, particularly in low mole ratio systems. Therefore, their work suggests that the conventional concept of a 3-dimensional, infinite network in a crosslinked thermoset may not always apply with UF resins. Moreover, existing structures may be far from optimum (factors 2 and 3). In addition, Irle and Bolton<sup>22</sup> argue that irreversible swelling in particleboard is lower with PF resins than with UF resins as a result of the greater ability of PF resins to relax under the swelling stresses (factor 4). This greater flexibility of PF resins apparently arises, in part, from plasticization by water sorbed by sodium hydroxide.

## APPROACH

Given the literature, we concluded that the durability and stability of UF-bonded wood products could be enhanced if the structure of UF resins were modified by incorporating flexible comonomers into the polymer chains. We anticipate that the consequences would include (a) reduction in interchain bonding as a result of greater chain irregularity and thereby greater resin solubility, lower crystallinity,

and a more effectively cured network, and (b) more random crosslink density and more flexible chains, thereby a lower sensitivity to small amounts of hydrolytic degradation and greater ability to respond reversibly to stress.

To modify the structure of UF resins, we chose several commercially available aliphatic and alkylene oxide di- and trifunctional amines with flexible backbones. Table I lists the initially selected modifiers by their commercial names and includes their chemical structures and our alphabetic code. We attempted to incorporate these amines into the UF polymer chains via three routes: (a) direct reaction of the amines with urea and formaldehyde during resin synthesis, (b) conversion of the primary amine groups to their urea derivatives [as illustrated in eq. (1)], which were subsequently reacted with formaldehyde during resin synthesis, and (c) conversion of two amines to their hydrochloride salts, which were then used as acidic curing agents in place of the conventional ammonium chloride. For the first two approaches, the modifiers were added early in resin synthesis rather than at the end to ensure their random distribution within the UF chains.



## EXPERIMENTAL

### Materials and Synthesis

The chemicals employed are described in Table II. Throughout this paper, we use either the commercial

names of the amines or our code names. For urea-capped amines, the final A in the code name is replaced by U; e.g., HMDA and TEATA become HMDU and TEATU. The hydrochloride salts of the amines are designated, for example, as HMDA · 2HCl and TEATA · 3HCl.

### Formaldehyde

The formaldehyde solution was prepared as follows: 1600 g paraformaldehyde and 1600 g distilled water were charged into a 2-L round-bottom flask fitted with a mechanical stirrer. The pH of the slurry was adjusted to 7.8 with 0.1 N NaOH. The mixture was heated with continuous stirring for 3 days while the temperature was maintained at 96°C. A blanket of nitrogen was maintained over the mixture during heating. The resulting solution was stored in an oven at 70–75°C, and its formaldehyde concentration was determined by a sodium sulfite method.<sup>37</sup>

### Amine Derivatives

Except for bis-hexamethylenetriamine (BHMTA), the amines were urea-capped in the presence of an approximately stoichiometric amount of urea. In these cases, 1 mol amine and the relevant stoichiometric [eq. (1)] amount of urea (plus 0.5 mol excess urea) were charged into a reaction kettle equipped with a mechanical stirrer. Water (80 g) was added and the mixture refluxed (ca. 115–125°C) for 4–5 h. For hexamethylenediurea (HMDU), the hot solution from refluxing was poured into 1 L of stirred ethanol. The resulting precipitate was filtered, washed several times with ethanol, and then dried in a vacuum oven at 80°C (about 0.1 MPa) to con-

**Table I** Resin Modifiers

Modifier	Structure	Code	Comments
<b>Difunctional amines</b>			
Hexamethylenediamine	$\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$	HMDA	Aliphatic, flexible
Triethyleneoxidediamine (Jeffamine EDR 148)	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-\text{NH}_2$	TEODA	Flexible ether
<b>Trifunctional amines</b>			
Bis-hexamethylenetriamine	$\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}-(\text{CH}_2)_6-\text{NH}_2$	BHMTA	Aliphatic, flexible
Triethylaminetriamine (Tren)	$(\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2)_3\text{N}$	TEATA	Aliphatic
Poly(propyleneoxide)triamine (Jeffamine T403)	$\begin{array}{c} \text{CH}_2 - [\text{OCH}_2\text{CH}(\text{CH}_3)]_x \text{NH}_2 \\   \\ \text{CH}_3\text{CH}_2 - \text{C} - \text{CH}_2 - [\text{OCH}_2\text{CH}(\text{CH}_3)]_y \text{NH}_2 \\   \\ \text{CH}_2 - [\text{OCH}_2\text{CH}(\text{CH}_3)]_z \text{NH}_2 \\ (x + y + z = 5.3) \end{array}$	PPOTA	Flexible ether

**Table II** Experimental Materials

Material	Source	Remarks
Hexamethylenediamine (HMDA)	Du Pont Petrochemicals, Wilmington, DE	85% aqueous solution
Bis-hexamethylenetriamine (BHMTA)	DuPont Petrochemicals	Brown viscous liquid with bp 249°C at 0.01 MPa and vapor pressure 0.001 MPa at 180°C
Triethylaminetriamine (TEATA)	Organic Chemicals Division, W. R. Grace & Co., Lexington, MA	High purity grade with < 2% ethylene amine
Triethyleneoxidediamine (TEODA)	Texaco Chemical Co., Bellaire, TX	Liquid, viscosity 8 cP at 25°C, total amine 13.5 meq/g
Poly(propyleneoxide)triamine (PPOTA)	Texaco Chemical Co.	Pale yellow liquid, viscosity 70 cP at 25°C, total amine 6.4 meq/g
Paraformaldehyde	Aldrich Chemical Co., Milwaukee, WI	95%, mp 163–165°C
Urea	J. T. Baker Chemical Co., Phillipsburg, NJ	mp 134°C
Ammonium chloride	J. T. Baker Chemical Co.	Reagent grade
Formic acid	J. T. Baker Chemical Co.	88% aqueous solution

stant weight. Adding ethanol to the reaction mixtures for triethylaminetriurea (TEATU) and triethyleneoxidediurea (TEODU) did not yield precipitates immediately. Consequently, for those derivatives and for poly(propyleneoxide)triurea (PPOTU), water was distilled from the reaction mixture until the temperature began to rise above 100°C. Subsequently, crystals formed in the TEATU and TEODU systems after 1 and 3 weeks, respectively, at ambient conditions. The crystals were washed thoroughly with ethanol and dried at 80°C to a constant weight in a vacuum oven (about 0.1 MPa). For PPOTU, the mixture remained as a clear viscous liquid. Synthesis of the urea derivative of BHMTA was carried out in the presence of the total urea to be used in the resin synthesis, without isolation of the derivative.

The hydrochloride derivatives of hexamethylenediamine (HMDA · 2HCl) and triethylaminetriamine (TEATA · 3HCl) were prepared according to the procedure described by Farlow.<sup>38</sup>

### Resins

Our resin synthesis procedure evolved during the course of the study, with the result that the resins were not prepared identically. The control (unmodified) resin and the resins modified with urea-capped TEATA, TEODA, and PPOTA (TEATU, TEODU, and PPOTU) were all prepared at a final F/U mole ratio of 1.6. Those syntheses were carried out as follows. The required amount of formaldehyde (Ta-

ble III) was charged as an approximately 45% aqueous solution into a resin kettle previously heated to about 60°C, and the pH was adjusted to 7 with triethanolamine (TEA). All the modifier was then added slowly along with sufficient urea to produce an initial F/U ratio of 2.0. When all the urea and modifier were in solution, the pH was adjusted to 7.5 with 50% NaOH solution. The temperature was increased to reflux, and the reaction mixture was refluxed for 30 min while holding the pH constant. Viscosity buildup was monitored at regular intervals by withdrawing an approximately 5-mL sample of the reaction mixture into a test tube, which was placed immediately in a water bath at 25°C. After the test tube was 5 min in the bath, viscosity was read on a Gardner–Holt bubble viscometer scale.<sup>†</sup> If Gardner viscosity *E* was not reached after 30 min, the temperature was reduced to 80–90°C, and the pH was dropped first to 6.5–6.0 and then to 5.5–5.0 if necessary. These reaction conditions were maintained until the reaction medium reached *E* viscosity. The pH was then adjusted to 6.5 (as necessary), and the second urea addition was made to yield a final F/U ratio of 1.6. The reaction mixture was held at 90°C and pH 6.5 until reaching *H* viscosity. At *H* viscosity, the mixture was cooled to 60°C, held for 20–30 min, and then cooled to room temperature.

<sup>†</sup> The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

**Table III** Composition of Resins<sup>a</sup>

Modified Resin	Total Modifier <sup>b</sup>	HCHO	Weight Fraction		
			Urea/Amine		
			Addition 1	Addition 2	Addition 3
Control	0	0.449	0.449/0	0.102/0	0
TEATU <sup>c</sup>	0.211	0.375	0.338/0.211	0.076/0	0
TEODU <sup>c</sup>	0.186	0.386	0.349/0.186	0.079/0	0
PPOTU <sup>c</sup>	0.357	0.305	0.276/0.357	0.062/0	0
BHMTU <sup>d</sup>	0.178	0.368	0.371/0.145	0.083/0.033	0
HMDU <sup>c</sup>	0.098	0.349	0.332/0.059	0.047/0.008	0.174/0.031
HMDA <sup>e</sup>	0.132	0.346	0.313/0.132	0.045/0	0.164/0
TEATA <sup>e</sup>	0.139	0.345	0.310/0.139	0.044/0	0.162/0

<sup>a</sup> Final F/U mole ratio 1.6 for resins identified as control, TEATU, TEODU, PPOTU, and BHMTU; 1.2 for HMDU, HMDA, and TEATA.

<sup>b</sup> Weight fraction of amine as amine. Overall mole ratio of amine to urea 1.9.

<sup>c</sup> Amine was urea-capped prior to resin synthesis, using approximately stoichiometric amounts of urea and amine.

<sup>d</sup> Amine was urea-capped prior to resin synthesis, using total of urea required for resin.

<sup>e</sup> Amine added directly to formaldehyde and urea during resin synthesis.

The pH was adjusted to 7.5–8.0, and the resin was allowed to sit overnight at ambient temperature before storing in a refrigerator.

For the resins modified by adding the uncapped amines TEATA and HMDA, the procedure was similar to the procedure described for urea-capped resins, except for the use of a third addition of urea to yield a final F/U ratio of 1.2. The procedure for the HMDU-modified resin also involved three urea additions and a final F/U ratio of 1.2; however, the modifier was added proportionately in all three urea additions. For the BHMTU-modified resin, the urea capping was carried out in the presence of all the urea for the resin synthesis; BHMTU was therefore added along with the urea in two steps to a final F/U ratio of 1.6.

Resin solids content was measured by drying triplicate samples (2.5 g each) to constant weight at 105–110°C. Resin viscosity was measured using a Brookfield cone/plate digital viscometer (Model LVT DCP) maintained at 25°C. Free formaldehyde in the resin was determined by a modified sodium sulfite procedure.<sup>37</sup>

### Resin Characterization and Curing Behavior

The <sup>13</sup>C- and <sup>1</sup>H-NMR spectra were obtained with a Bruker WM250 spectrometer on the amines, the urea-capped amines, and several samples extracted from the reaction mixture during resin synthesis. The resin samples were frozen immediately after extraction and until analysis. Usually, deuterated

dimethylsulfoxide (DMSO) was used as solvent, but occasionally deuterated chloroform was substituted. Typical instrument parameters for quantitative <sup>13</sup>C spectra were 30 kHz sweep width, 7.8 μs (45°) pulse width, 30 s pulse delay, inverse gating, and 500–1000 scans. Typical parameters for <sup>1</sup>H spectra were 3 kHz sweep width, 5 μs (30°) pulse width, 2 s pulse delay, and 1 or 2 scans.

Infrared spectra were obtained on cured resins in potassium bromide pellets using a Nicolet Model 6000 Fourier transform infrared spectrometer.

Differential scanning calorimetry (DSC) thermograms were obtained with a Perkin-Elmer DSC-2 at a heating rate of 10 K/min over a temperature range of 300–480 K. Ten grams of resin were weighed accurately in a beaker, an appropriate amount of curing agent was added, and the mixture was stirred vigorously by hand for 3–5 min. A small amount (5–20 mg) of the mixture was placed in a Perkin-Elmer DSC large volume capsule, and the capsule was hermetically sealed before scanning.

### Internal Stress Development

The internal stress developed by neat resins during cure at 23°C and 44% relative humidity (RH) was measured using a procedure modeled after that described by Perera and Vanden Eynde.<sup>39</sup> After mixing with 5% curing agent, the resin was carefully brushed on one surface of a 146 × 12.5 × 0.48 mm aluminum strip freshly etched with a chromic acid-sulfuric acid mixture (Method A, Ref. 40). The ad-

hesive was brushed on only a 120-mm length of the aluminum strip to permit clamping the uncoated portion in the deflection measuring device. Using a doctor blade, the film thickness was reduced to 0.15 mm. Extreme care was taken to ensure that no adhesive was deposited on the back side or the edges of the strip. The uncoated end of each strip was clamped in a metal block assembly and placed in a controlled 23°C/44% RH room. The unbalanced internal stresses that developed during resin cure caused the strips to bend, and the relative amount of internal stress could therefore be determined by measuring the deflection at the end of the strips.

### Formaldehyde Liberation from Cured Resins

Resin samples were cured with 5% curing agent by heating thin films between Teflon-coated platens in a press at 0.14 MPa for 10 min. The heating rates and final temperatures approximated those used for bonding the solid wood specimens. After cure, the resins were ground and sieved. The material passing an 80-mesh sieve was collected, pumped under vacuum for several days, and stored over phosphorus pentoxide.

Formaldehyde liberation was measured as described previously.<sup>41</sup> Briefly, about 10 mg of the powder was weighed into a weighing bottle, a glass cross placed on the bottom, and a small beaker containing 5.00 mL of 27% sulfuric acid placed on the cross. After being sealed with greased caps, the bottles were stored in a cabinet at 27°C. The formaldehyde subsequently liberated from the powder at that temperature and at 80% RH was absorbed by the sulfuric acid. At intervals, the sulfuric acid was removed and analyzed for formaldehyde.

### Resistance of Bonded Wood Joints to Cyclic Stress

Ten grams of the UF resin solution was mixed thoroughly with curing agent (usually 0.5 g). The curing agents were ammonium chloride, formic acid, HMDA · 2HCl, and TEATA · 3HCl. Preliminary investigation had shown that mixing formic acid directly with UF resin results in a rapid increase of resin viscosity, which makes proper and uniform spread of adhesive on the wood substrate difficult. Therefore, for resins cured with formic acid, the resin was applied to one adherend and formic acid to the mating adherend.

For each resin, one hard maple (*Acer saccharum* Marsh) panel (230 × 127 × 6 mm) was bonded under the following conditions: 0.95–1.26 g/m<sup>2</sup> glue spread, 10-min open assembly time, 2-min closed assembly

time (except for formic acid curing where open and closed assembly times were zero), 10-min press time, 0.7-MPa bonding pressure, and 95–100°C bonding temperature (approximately at the DSC exotherm peak of each system). After bonding, the panels were reconditioned to 6% moisture content and cut into reduced-size (645 mm<sup>2</sup>) ASTM-D905-type compression shear specimens.<sup>42</sup> Twenty specimens were obtained from each panel.

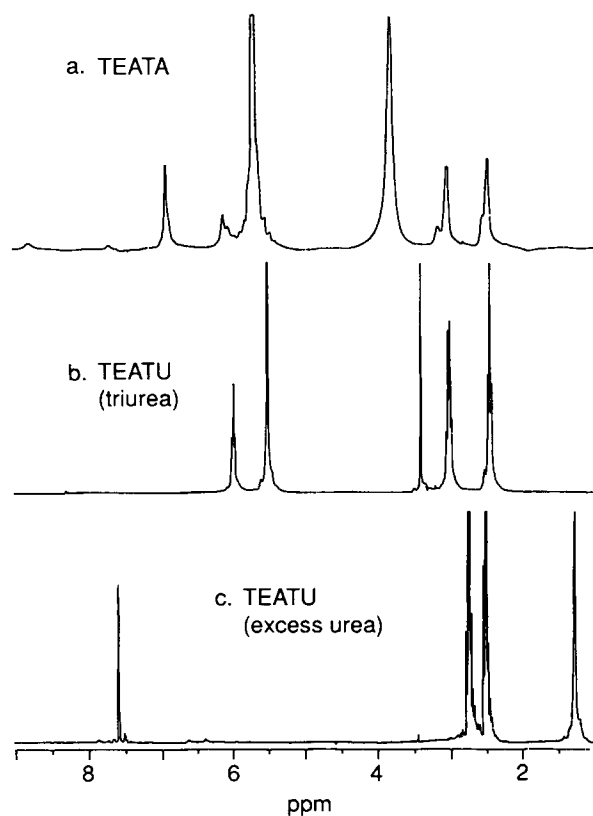
Test specimens from each panel were randomized into five groups. One group was tested dry (6% moisture content), and the other groups were subjected to 1, 3, 5, or 10 vacuum-pressure soak-dry (VPSD) cycles. Each cycle consisted of submerging the specimens in cold tap water for 30 min at about 0.1-MPa vacuum and 30 min under pressure at 0.4 MPa, followed by 20 h drying in a forced-draft oven at 43–45°C. The cycled specimens were equilibrated to 6% moisture content before testing on a Riehle Ametek testing machine at a crosshead speed of 5 mm/min.

## RESULTS AND DISCUSSION

### Structure and Characterization of Amine Derivatives and Resins

#### Amine Derivatives

The amine derivatives isolated as crystalline compounds possessed the following melting points (°C): HMDU, 197–200; TEATU, 165; TEODU, 135; HMDA · 2HCl, 258; and TEATA · 3HCl, > 300. The NMR spectra for the higher molecular weight amines and their urea derivatives, e.g., PPOTA and PPOTU, were complex and difficult to interpret definitively. However, the spectra for the simpler materials were more easily interpreted. In Figures 1 and 2, we use TEATA to illustrate the probable situation for all the systems. For TEATA itself (see Table I for structure), the proton [Fig. 1(c)] and carbon [Fig. 2(c)] spectra show approximately equal amounts of two methylene groups; the proton spectrum has a peak at 1.3 ppm for the amine group. The triurea-capped amine has no detectable unreacted amine in the proton spectrum [absence of 1.3 ppm peak, Fig. 1(b)] but essentially equal amounts of the two different methylene hydrogens (2.4 and 3.0 ppm) and of primary amide hydrogens (=NCONH<sub>2</sub>; 5.5 ppm); the triurea-capped amine also has half as many secondary amide hydrogens (—NHCONH<sub>2</sub>; 6.0 ppm). The unquantified carbon spectrum for the triurea-capped amine [Fig. 2(c)] has two slightly shifted methylene peaks and a single



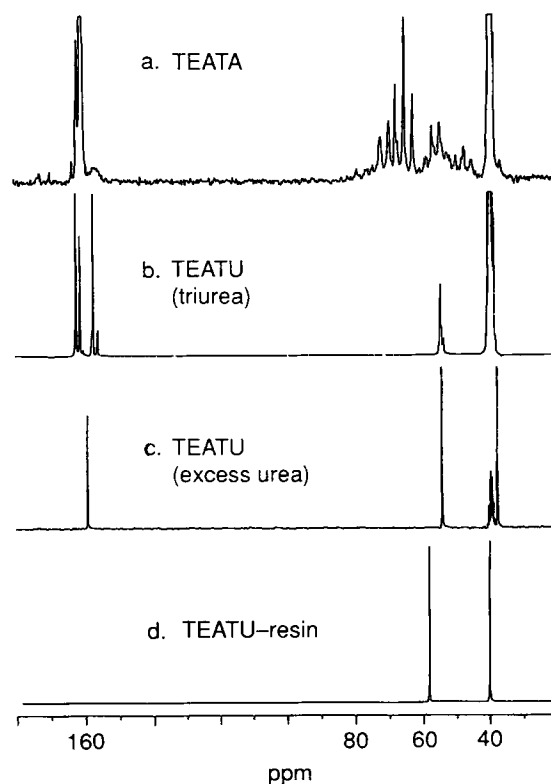
**Figure 1** Proton NMR spectra of TEATA and TEATU (ML90 5416).

amide carbonyl peak (159 ppm). Thus, this derivative is clearly the desired triurea-capped TEATA. However, when the capping reaction was conducted in the presence of all the urea planned for the resin synthesis (16.1 mole ratio of urea to TEATA), multiple urea substitution on the amine appeared to occur. This is evidenced by the proton peaks at 6.9 ppm and above [Fig. 1(a)] and the multiple carbonyl carbon peaks near 160 ppm [Fig. 2(a)].

### Resins

The initial standard properties (Table IV) of the control and modified resins are similar, with the exception of the two resins made by direct addition of amines (HMDA and TEATA).

The NMR spectra of unmodified UF resins are themselves rather complex, reflecting the variety of structures that are typically present. In general, the only clear distinction between spectra for unmodified resin and resin modified with urea-capped amine is the presence of small peaks for the methylene groups of the amines; e.g., the 37-ppm peak in Figure 2(a). Consequently, the spectra are not informative



**Figure 2**  $^{13}\text{C}$ -NMR spectra of TEATA and TEATU (ML90 5417).

about how or whether the amines were chemically incorporated into the resin chains.

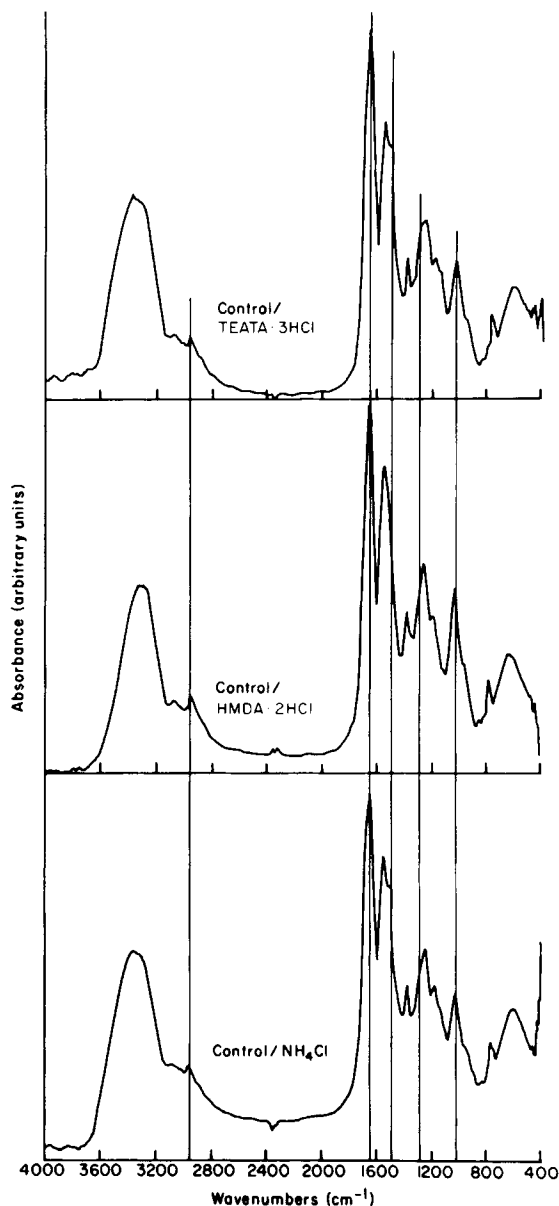
### Resin Curing Behavior

#### Infrared Spectroscopy

Figures 3 and 4 illustrate the major differences observed in the infrared spectra of cured resins. Those

**Table IV** Initial Resin Properties

Modified Resin	pH	Viscosity at 25°C (Pa s)	Solids Content (%)	Free $\text{CH}_2\text{O}$ (%)
Control	8.49	0.319	63	0.48
TEATU	8.10	0.375	61	0.29
TEODU	8.15	0.322	62	0.33
PPOTU	8.28	0.658	64	0.23
HMDA	7.81	0.042	60	0.06
TEATA	5.05	0.029	55	0.11
HMDU	7.55	0.260	63	—
BHMTU	7.66	0.718	61	0.57



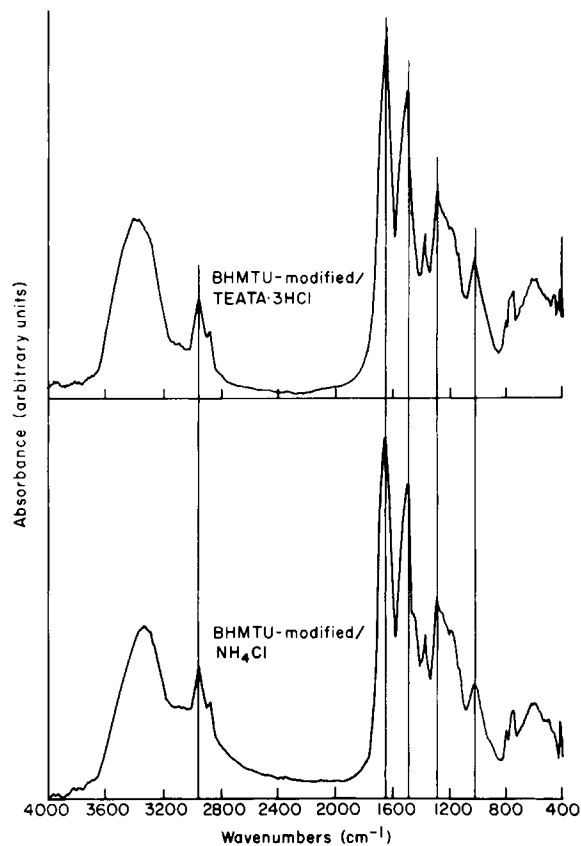
**Figure 3** Infrared spectra of control resin after cure with different curing agents (ML90 5304).

differences occur in three regions: (a) around  $2900\text{ cm}^{-1}$ , where the CH-stretching absorption of the methylenes from some of the modifiers is very evident (Fig. 4); (b) at  $1510$  and  $1290\text{ cm}^{-1}$ , where bands tentatively assigned to tertiary amide<sup>43</sup> are strongest in the systems containing the potentially trifunctional modifiers as either urea derivatives or hydrochlorides (Table V and Figs. 3 and 4); (c) at approximately  $1030\text{ cm}^{-1}$ , attributable to residual hydroxymethyl groups, which are generally weak in the ammonium-chloride-cured systems (Table V) and PPOTU-modified systems, and are by far the

strongest in the formic-acid-cured HMDU-modified system, despite the lower F/U mole ratio of the HMDU resin. Because UF cure is acid catalyzed, we might have expected that resins with the lowest pH would possess the lowest residual hydroxymethyl content and the highest trifunctional amide content. However, no general correlation is evident from the data in Table V; one notable exception is the high hydroxymethyl content and high pH of the formic-acid-cured HMDU-modified resin.

### Differential Scanning Calorimetry

Figures 5–10 present the DSC thermograms for some of the resin and curing agent combinations. Table VI summarizes the effects of resin and curing agent on cure rate and cure activity in terms of four parameters: the exotherm heat per gram of resin solids ( $H_c$ ), the exotherm peak temperature ( $T_p$ ), the time span between initiation and completion of the exotherm ( $t_c$ ), and the ratio of exotherm heat to time span ( $R_c$ ).



**Figure 4** Infrared spectra of BHMTU-modified resin after cure with different curing agents (ML90 5303).



**Table V Infrared, pH, and Formaldehyde Liberation Rates of Cured Resins**

Modified Resin	Curing Agent	Infrared Intensity <sup>a</sup>		pH	Formaldehyde Liberation Rate <sup>b</sup>	
		1030 cm <sup>-1</sup>	1510 and 1290 cm <sup>-1</sup>		$\frac{1}{2}$ day	25 days
Control	NH <sub>4</sub> CL	0.32	W	2.0	26	2.1
	TEATA · 3HCl	0.32	W to M	2.1	16	1.2
	HMDA · 2HCl	0.41	VW	2.1	20	1.1
HMDU	NH <sub>4</sub> Cl	0.25	W to M	2.1	NA	NA
	TEATA · 3HCl	0.35	M	2.5	NA	NA
	HMDA · 2HCl	0.36	W	2.2	NA	NA
	Formic acid	0.67	W	3.1	NA	NA
BHMTU	NH <sub>4</sub> Cl	0.18	S	2.0	40	1.9
	TEATA · 3HCl	0.22	S	2.1	24	1.3
PPOTU	NH <sub>4</sub> Cl	0.07	M	2.0	34	1.4
	TEATA · 3HCl	0.07	M	2.1	19	0.9
	HMDA · 2HCl	0.16	W to M	2.1	21	0.9
	Formic acid	0.09	M	—	NA	NA

<sup>a</sup> For the 1030-cm<sup>-1</sup> values, peak height was divided by 1610 cm<sup>-1</sup> peak height; assigned to hydroxymethyl group. For the 1510 and 1290 cm<sup>-1</sup> peaks, W is weak, M medium, S very strong; tentatively assigned to tertiary amide.<sup>26</sup>

<sup>b</sup> In mg HCHO/g resin/day.

Figure 5 compares the thermograms of the resins at mole ratio 1.2 that were modified by the direct addition of amines to urea and formaldehyde during resin synthesis (HMDA and TEATA) or modified by adding a urea-capped amine (HMDU). The first two resins possessed no significant cure activity within the temperature range of interest (310–480 K), whereas the HMDU-modified resin exhibited strong cure activity. During resin synthesis, we observed that addition of either HMDA or TEATA to the formaldehyde-urea reaction mixture produced a violent reaction that resulted in fairly insoluble material. Because of the poor solubility and lack of cure activity of these two resins, the approach of direct amine addition was not pursued.

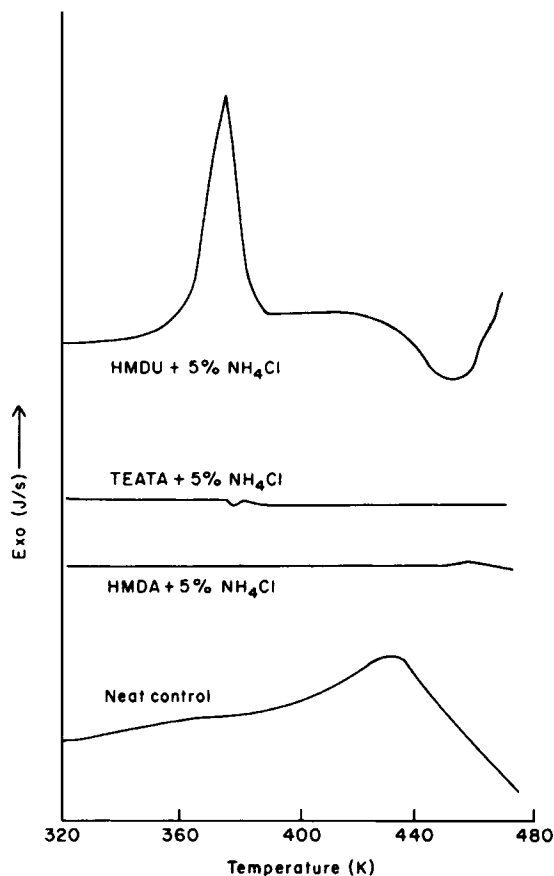
Figure 6 shows the thermograms of resins at mole ratio 1.6 cured with 2% ammonium chloride (total adhesive basis). All resins except the TEATU-modified resin showed high cure activity. Note that the cure exotherm for the TEODU-modified resin was not only relatively broader but mostly occurred at a higher temperature than the exotherms for the control and TEATU-modified resins. For resins cured with 2% HMDA · 2HCl and TEATA · 3HCl (thermograms not shown), cure activity was virtually nonexistent except for PPOTU-modified resin, and, to some extent, for the control resin.

Figures 7–10 and Table VI compare the thermal behavior of resins cured with 5% of three different curing agents with the thermal behavior of corresponding neat resins (no curing agent). The rela-

tively broad cure exotherms occurring between 380 and 470 K for the neat resins shifted to lower temperatures (363–373 K) and were much sharper when the resins were cured with 5% curing agent. The cure peaks were also about 10 K lower when the resins were cured with either ammonium chloride or TEATA · 3HCl than with HMDA · 2HCl. On the other hand, resins cured with TEATA · 3HCl had relatively broader cure exotherms. For TEODU-modified resin (Fig. 9), the exotherms peaked at higher temperatures and were broader than the exotherms for the PPOTU-modified (Fig. 7) or control (Fig. 8) resins. For TEATU-modified resin (Fig. 10), the thermogram with ammonium chloride showed a fairly broad exotherm, with the peak appearing at about 379 K; thermograms with either HMDA · 2HCl or TEATA · 3HCl showed two cure exotherms, a very small one at about 370 and 377 K, and a broad one at 397 and 400 K, respectively.

The following observations about the cure activity of these systems are apparent from the thermograms (Figs. 5–10) and the DSC parameters (Table VI).

1. Cure activity was minimal with 2% amine hydrochloride curing agents, but increased significantly as the amount of curing agent was increased to 5%. In contrast, ammonium chloride was active at the lower level, except for the TEATU-modified resin.
2. The cure exotherm heat for the PPOTU-modified resin was much higher than the



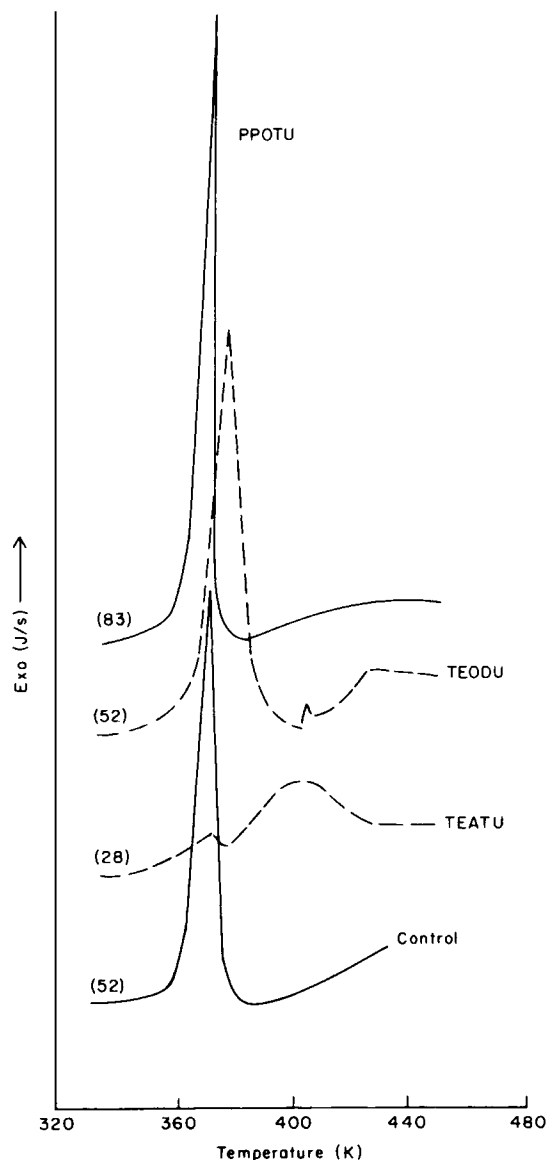
**Figure 5** DSC thermograms comparing the cure activity of neat control resin with that of  $\text{NH}_4\text{Cl}$ -cured resins modified by direct addition of amines (HMDA and TEATA) and resin modified with urea-capped amine (HMDU) ( $\text{NH}_4\text{Cl}$  amount is wt % total resin) (ML90 5418).

exotherm heat for the other resins, despite the fact that the PPOTU resin contained significantly more chemically inert material (the higher molecular weight amine necessitated higher weight fraction to achieve the same mole ratio; Table III).

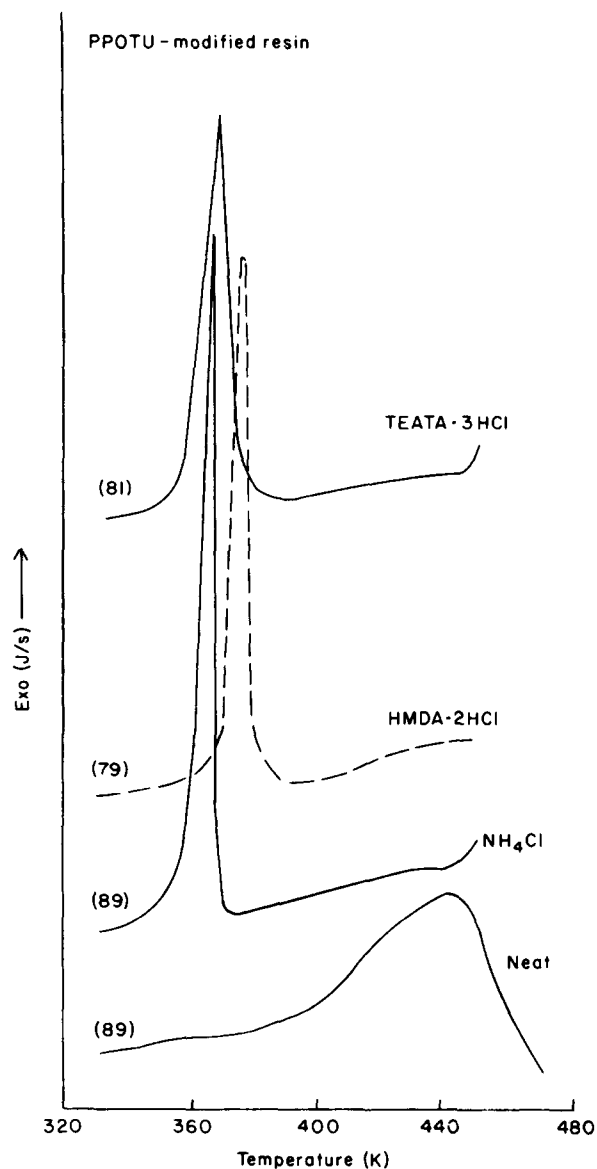
3. For a given curing agent, the order of reactivity of the resins was approximately in the order PPOTU (usually) > control > TEODU > TEATU.
4. For a given resin, the ability to hasten cure was approximately in the order  $\text{NH}_4\text{Cl}$  > TEATA · 3HCl (usually) > HMDA · 2HCl.

These observations can be partially rationalized by recognizing that UF resin cure may be enhanced by two factors:

1. Greater chain mobility and greater accessibility of reactive groups. This may account for the faster cure, higher exotherm heat, and lower final methylol content of the PPOTU-modified resins (Tables V and VI).
2. High acidity: The UF resin cure is catalyzed by acid. In resins containing ammonium chloride or amine hydrochloride, the pH at any moment is greatly influenced by the rate

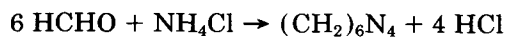


**Figure 6** DSC thermograms of control and modified (TEATU, TEODU, and PPOTU) resins with 2%  $\text{NH}_4\text{Cl}$  curing agent (numbers in parentheses are exotherm heat values in J/g;  $\text{NH}_4\text{Cl}$  amount is wt % total resin) (ML90 5419).



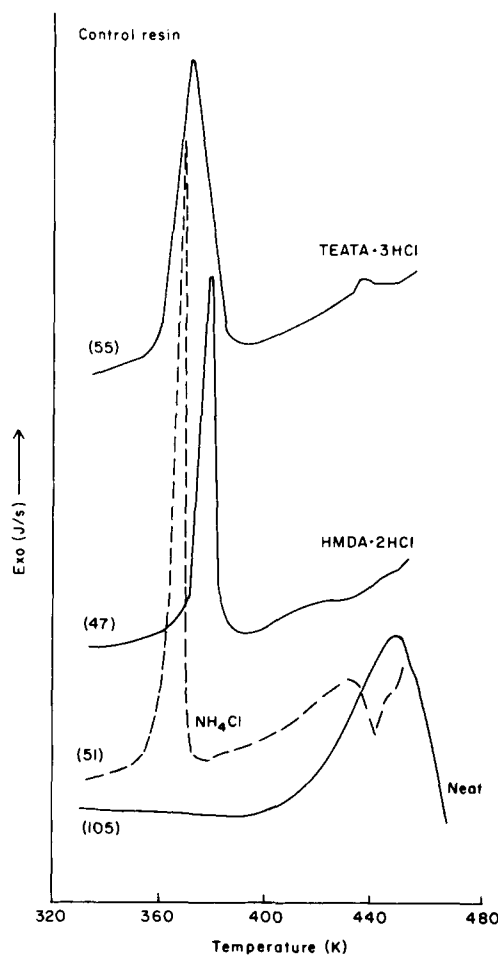
**Figure 7** Effect of different curing agents on DSC thermograms of PPOTU-modified resin (numbers in parentheses are exotherm heat values in J/g; curing agents present at 5 wt % total resin) (ML90 5420).

and extent of resin reaction with formaldehyde to liberate hydrogen chloride, as illustrated by the following reaction for ammonium chloride:

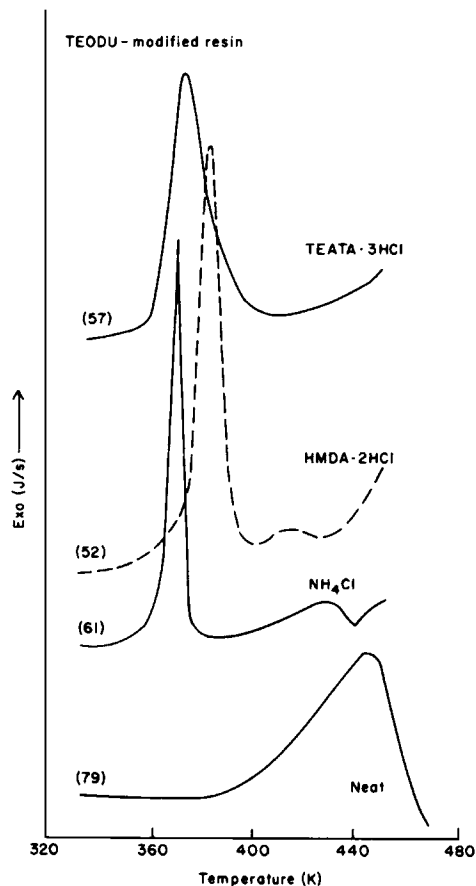


Higuchi and Sakata<sup>17</sup> examined the change in pH over time in mixtures of formaldehyde and ammonium chloride, with and without UF resin. They

concluded that the liberation of hydrogen chloride is not instantaneous but continues during resin gelation and cure, and that UF resin has a buffering character that changes as gelation and cure proceed. Therefore, it is likely that complex differences exist among our unmodified and amine-modified resins (both urea-capped and amine hydrochloride) in the rate and extent of acidification during gelation and cure. Moreover, a more direct difference resulted from using a constant weight percentage of curing agents with different equivalent weights (53, 85, and 94 g/eq for NH<sub>4</sub>Cl, TEATA·3HCl, and HMDA·2HCl, respectively). In view of these factors, the small difference in final pH of the cured resins (Table V) is rather surprising. However, the somewhat lower pH of the ammonium chloride systems compared to the amine hydrochlorides is qual-



**Figure 8** Effect of different curing agents on DSC thermograms of control resin (numbers in parentheses are the exotherm heat values in J/g; curing agents present at 5 wt % of total resin) (ML90 5421).



**Figure 9** Effect of different curing agents on DSC thermograms of TEODU-modified resin (numbers in parentheses are the exotherm heat values in J/g; curing agents present at 5 wt % total resin) (ML90 5422).

itatively consistent with the slower cure rates of the latter (see Table VI).

#### Formaldehyde Liberation by Cured Resins

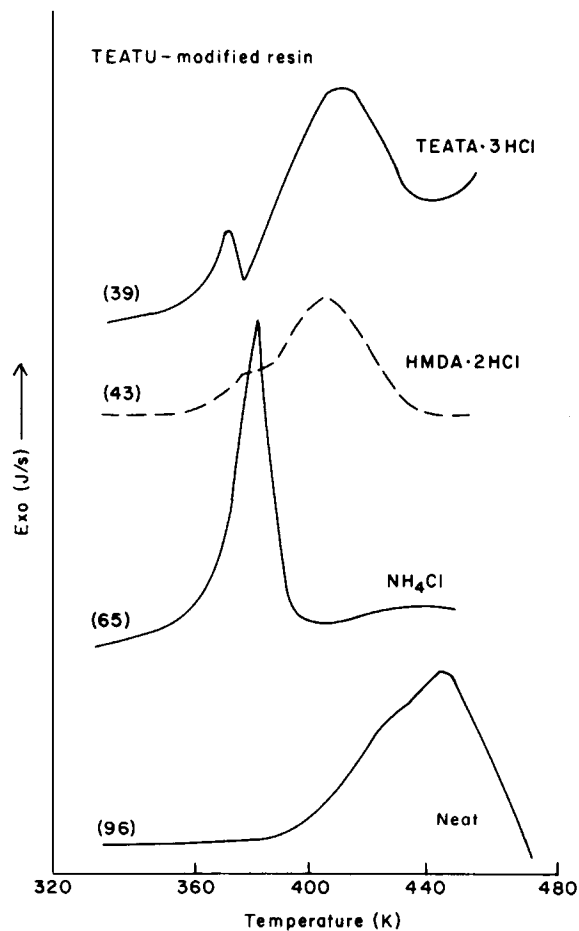
Figures 11–13 compare the formaldehyde liberation at 27°C and 80% RH for control, PPOTU-modified, and BHMTU-modified resins, all at mole ratio 1.6 and cured with  $\text{NH}_4\text{Cl}$ ,  $\text{HMDA}\cdot 2\text{HCl}$ , or  $\text{TEATA}\cdot 3\text{HCl}$ . Table V includes average liberation rates over the initial and final sampling periods (0–1 and 20–30 days, respectively). For a given resin, the formaldehyde liberation was clearly greatest in magnitude and rate when the curing agent was ammonium chloride; differences between the two amine hydrochlorides arose primarily in the first sampling period, where liberation was greater with  $\text{HMDA}\cdot 2\text{HCl}$ . For a given curing agent, the magnitude of formaldehyde liberation increased in the

order  $\text{BHMTU} > \text{control} > \text{PPOTU}$ ; however, during the final sampling period, the rate for the modified resins was either lower than that for the control (PPOTU) or about the same as that for the control (BHMTU).

Although acidity is known to increase formaldehyde liberation from conventional UF resins,<sup>10,16,17</sup> there is at most a weak correlation between resin pH and liberation rate for these systems (Table V). One might also expect that formaldehyde liberation would be greater for the less cured resins—as measured by higher residual hydroxymethyl content and lower tertiary amide; however, these expectations are not met (Table V).

#### Resistance of Wood Joints to Cyclic Stress

Figure 14 shows the effect of cyclic stress (VPSD) on the shear strength of joints bonded with control



**Figure 10** Effect of different curing agents on DSC thermograms of TEATU-modified resin (numbers in parentheses are the exotherm heat values in J/g; curing agents present at 5 wt % total resin) (ML90 5423).

**Table VI Exotherm Parameters from Differential Scanning Calorimetry**

Modified Resin	DSC Parameter	Curing Agent <sup>a</sup>		
		NH <sub>4</sub> Cl	TEATA · 3HCl	HMDA · 2HCl
Control	$t_c^b$	6.5	9.5	7.8
PPOTU		7.0	7.8	9.2
TEODU		7.9	12.7	12.1
TEATU		11.4	17.7	20.5
Control	$T_p^c$	365	366	374
PPOTU		363	365	373
TEODU		369	370	380
TEATU		379	370	402
Control	$H_c^d$	51	55	47
PPOTU		89	81	79
TEODU		61	57	52
TEATU		65	39	43
Control	$R_c^e$	7.9	5.8	6.0
PPOTU		12.7	10.4	8.6
TEODU		7.7	4.5	4.3
TEATU		5.7	2.2	2.1

<sup>a</sup> Five percent of total resin.

<sup>b</sup> Time (min) between initiation of exotherm and return to baseline.

<sup>c</sup> Exotherm peak temperature (K).

<sup>d</sup> Exotherm heat (J/g resin solids).

<sup>e</sup>  $H_c/t_c$  (J/g/min).

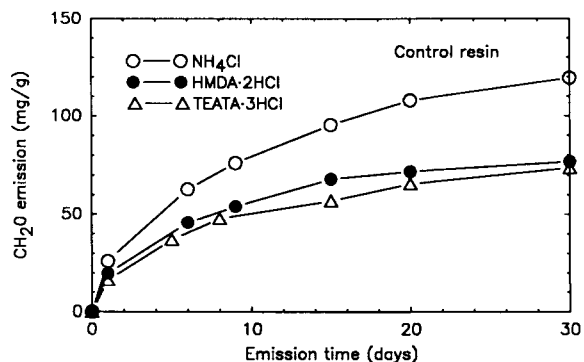
and PPOTU-modified resins using different curing agents. Figure 15 gives the relative internal stress developed by the same systems during ambient cure. Preliminary bonding tests suggested that the performance of joints made from TEATU- and TEODU-modified resins cured with NH<sub>4</sub>Cl, HMDA · 2HCl, and TEATA · 3HCl was inadequate; this is consistent with the low reactivities determined from DSC. However, joints prepared from these resins and cured with formic acid exhibited strength properties (wet and dry) comparable to those of the control and PPOTU-modified resins. The resistance to strength decay during cyclic stressing and the internal stress development during ambient cure for these systems cured with formic acid are given in Figures 16 and 17, respectively.

The following observations are pertinent for these results:

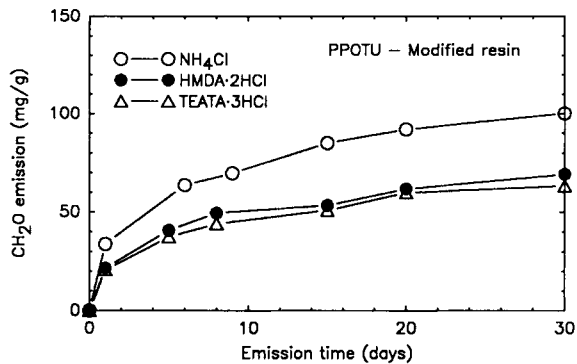
1. With the ammonium chloride curing agent, joints made using the resin modified with trifunctional PPOTU had excellent resistance to cyclic stress, whereas joints made with unmodified resin (control) degraded significantly (Fig. 14).
2. When unmodified and PPOTU-modified resins were cured with TEATA · 3HCl and HMDA · 2HCl, the joints had excellent and

essentially equal resistance to cyclic stress (Fig. 14).

3. With formic acid curing agent, joints made with resins modified with trifunctional comonomers (TEATU and PPOTU) showed excellent resistance to cyclic stress, whereas joints made with either unmodified resin or difunctional monomer (TEODU) degraded relatively faster (Fig. 16).
4. The internal stress (deflection) developed by resins containing different curing agents (100 days at 23°C/44% RH) generally followed the order NH<sub>4</sub>Cl > formic acid



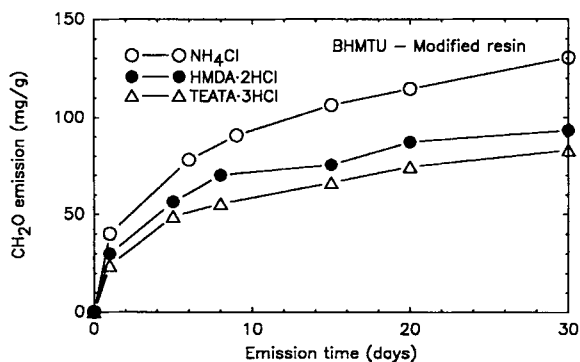
**Figure 11** Effect of curing agents on formaldehyde liberation from control resin.



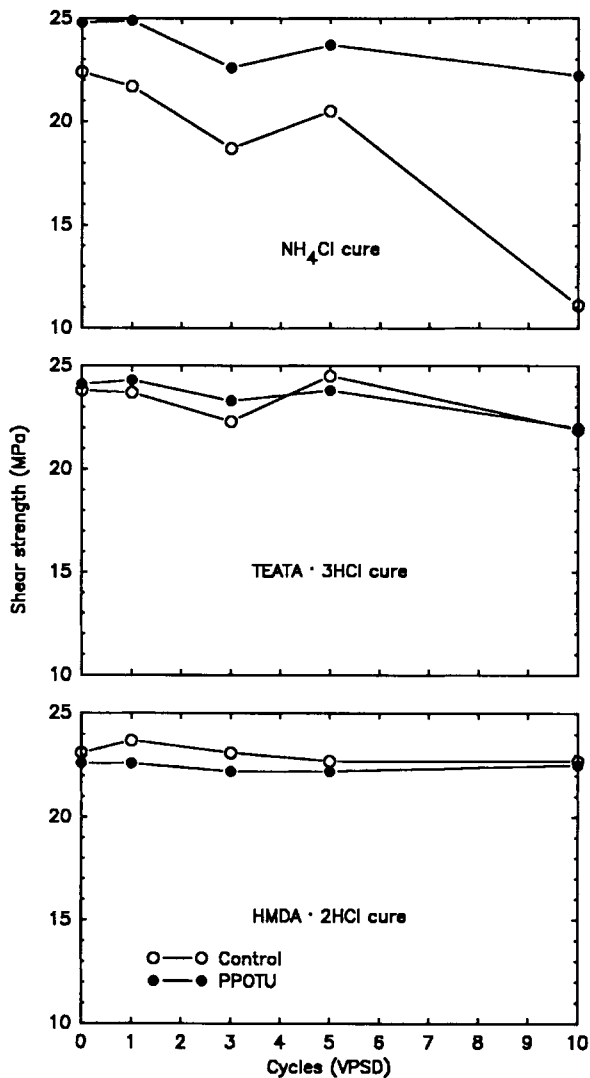
**Figure 12** Effect of curing agents on formaldehyde liberation from PPOTU-modified resin.

> TEATA · 3HCl > HMDA · 2HCl (Figs. 15 and 17). The maximum in the internal stress–time curve for the control resin cured with ammonium chloride (Fig. 15) was due to stress relief caused by spontaneous film fragmentation at that point. Several of the cyclic stress-resistant systems exhibited low internal stress values, but a clear and direct correlation between cyclic stress resistance and internal stress is not apparent.

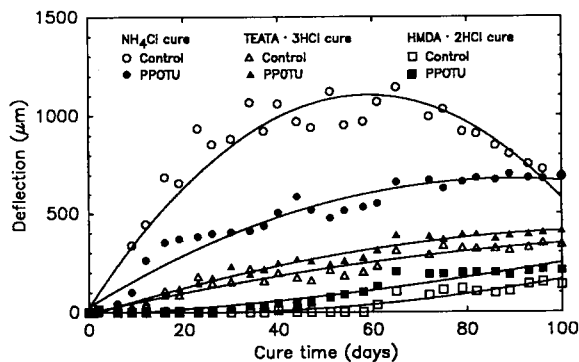
We suggest that lower internal stress development, lower stress concentrations, and higher resistance to cyclic stress are fostered by both slower gelation and flexible polymer chains. In systems with intrinsically stiff chains, rapid gelation leads to regions in which molecular mobility is highly hindered and structures are frozen. The product is then expected to be incompletely cured, to possess a non-uniform crosslink density, and to be inherently stressed. Consequently, it will be susceptible to rapid loss of integrity under aggressive environments. The control resin cured with ammonium chloride typifies



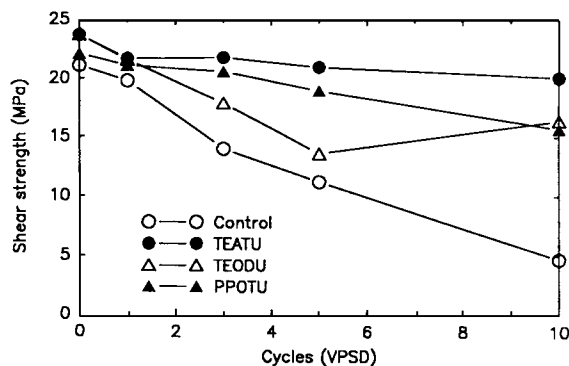
**Figure 13** Effect of curing agents on formaldehyde liberation from BHMTU-modified resin.



**Figure 14** Effect of curing agents on the cyclic stress resistance of joints bonded with control (○) and PPOTU-modified (●) resin.



**Figure 15** Effect of curing agents on the internal stress developed during cure (23°C/44% RH) of control (open symbols) and PPOTU-modified (closed symbols) resin.



**Figure 16** Cyclic stress resistance of several resins cured with formic acid.

this behavior; its polymer structure is stiff, it cures rapidly (Table VI), and it possesses poor cyclic stress resistance (Fig. 14) and high internal stress (Fig. 15).

In contrast, the amine hydrochlorides brought about slower cure (Table VI), allowing greater molecular mobility and greater and more efficient crosslinking. Assuming the amine hydrochlorides were directly incorporated into the resin structure, they also provided greater inherent chain flexibility. Thus, the control resin cured with HMDA · 2HCl or TEATA · 3HCl showed much greater resistance to cyclic stress and lower internal stress than the control resin cured with ammonium chloride (Figs. 14 and 15). Although the PPOTU-modified resin cured rather rapidly (Table VI), the great flexibility and large weight fraction of that modifier (Table III) apparently provided sufficient molecular mobility to ensure efficient crosslinking and a stress-resistant joint (Figs. 14–16). The TEATU- and TEODU-modified resins cured relatively slowly (Table VI) and imparted some degree of flexibility to the joint (Fig. 16).

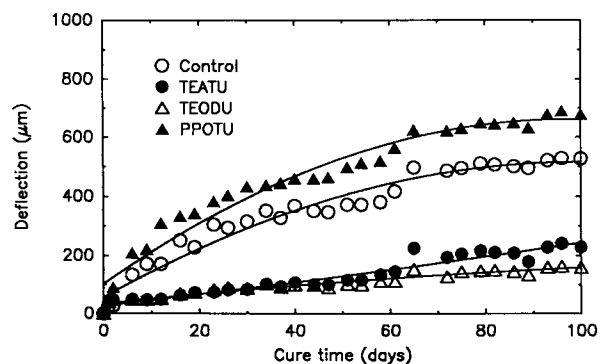
Finally, we note that the above rationale is consistent with several observations reported by other investigators. For example, Steiner and Chow<sup>30</sup> observed that small amounts of melamine, furfural, or resorcinol caused significant improvements in the durability of UF-bonded wood joints and suggested that the UF system was very sensitive to minor changes that altered the configurational and conformational character of the cured resin. Ross<sup>29</sup> argues that UF resins tend to react intramolecularly, leading to hydrophobic molecules that are only weakly bound together. Hse<sup>44</sup> found that UF resins formulated at low pH gave poor performance; he suggested that this might be due to fast condensation. Ezaki et al.<sup>31</sup> found that adding furfuryl alcohol to UF resins delayed the drop in pH and enhanced

the resistance of the resin to cracking. Bolton and Irle<sup>21</sup> were able to prepare thin, cured UF films only by curing slowly at moderate temperature; at higher cure temperatures, the films cracked.

## CONCLUDING REMARKS

The work reported here focused on UF systems that were modified in two ways: (a) by substituting 10 mol % of urea during synthesis with urea-capped amines or (b) by adding 5 wt % (total resin) amine-hydrochloride curing agents. We observed the following:

1. Modifying UF resins by adding di- and tri-functional amines directly to urea and formaldehyde during resin synthesis destroyed resin cure activity.
2. Incorporating urea-capped di- and trifunctional amines into UF resins during synthesis produced resins with usable but varying cure reactivity. TEATU- and TEODU-modified resins were less reactive than the unmodified resin. On the other hand, the PPOTU-modified resin was comparable to the unmodified resin in reactivity.
3. Resistance of UF-bonded joints to cyclic stress was substantially improved by modifying the resins through (a) incorporating trifunctional urea-capped amines into the resin during synthesis or (b) curing the resins with di- and trifunctional amine hydrochlorides.
4. Resins cured with ammonium chloride had a much greater tendency to craze and fracture than those cured with the amine hydrochlorides. In our study, crazing was also reduced



**Figure 17** Internal stress developed during cure (23°C/44% RH) of several resins cured with formic acid.

by modifying the resin with urea-capped amines.

5. Resins cured with either TEATA·3HCl or HMDA·2HCl had lower formaldehyde liberation than those cured with ammonium chloride.

Overall, the results support our hypothesis that the stability of UF-bonded wood products can be enhanced by altering the resin structure to produce a more flexible, random, 3-dimensional cured network. Our work further indicates that flexible di- and triamines show good promise as modifiers.

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