

Differential Scanning Calorimetry and Dynamic Mechanical Analysis of Amine-Modified Urea-Formaldehyde Adhesives

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SYNOPSIS

Urea-formaldehyde (UF) resins are susceptible to stress rupture and hydrolytic degradation, particularly under cyclic moisture or warm, humid conditions. Modification of UF resins with flexible di- and trifunctional amines reduces this problem. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were used to study the thermal behavior of modified and unmodified adhesives to identify the physical and morphological factors responsible for the improved performance. A UF resin modified by incorporating urea-capped poly(propyleneoxidetriamine) during resin synthesis exhibited a higher cure rate and greater cure exotherm than the unmodified resin. Resins cured with a hexamethylenediamine hydrochloride curing agent had slower cure rates than those cured with NH_4Cl . DMA behavior indicated that modified adhesives were more fully cured and had a more homogeneous crosslink density than unmodified adhesives. DMA behavior changed with storage of specimens at 23°C and 50% relative humidity, after previous heating for approximately 20 min at 105°C to 110°C. The initial changes were postulated to occur because of physical aging (increase in density) and continued cure. These were followed by physical breakdown (microcracking) and possibly cure reversion. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The use of urea-formaldehyde (UF)-bonded wood products is normally confined to interior, nonstructural applications because UF resins are susceptible to stress rupture and/or hydrolytic degradation under cyclic moisture or warm, humid environments. The sensitivity of UF-bonded wood products to hydrolysis or stress rupture of bonds is attributable to a number of underlying structural factors, which include the following:

1. The presence of hydrolytically sensitive bonds both within the resin and between the resin and wood
2. Strong interchain bonding due to the highly polar nature of the urea linkages, which can promote brittleness, insolubility, and even crystallinity
3. Low crosslink density resulting from low

reactivity of secondary amides, which increases sensitivity to losses in crosslink density in stress-bearing applications

4. Inherent rotational stiffness of the urea structure, which creates a brittle polymer.

In addition, there is increasing evidence indicating (1) that the conventional concept of a three-dimensional, infinite network in a crosslinked thermoset may not always apply to UF resins,^{1,2} and (2) that the rigidity of cured UF resins detracts from the load-bearing ability of UF-bonded wood products.^{3,4} All of these factors suggest that the durability and stability of UF-bonded wood products can be enhanced by modifying the resin structure to produce a more flexible cured adhesive. Our approach to meeting this requirement involves incorporating flexible di- and trifunctional amines into the resin structure either as urea-capped derivatives during synthesis, as their amine hydrochloride salts used as curing agents, or both.

The effectiveness of this approach in enhancing the resistance of UF-bonded solid wood joints and

particle board to cyclic stress and moist heat aging was reported earlier.⁵⁻⁸ The objective of the present study was to clarify the physical and morphological factors responsible for the improved performance with modified adhesives by using differential scanning calorimetry (DSC) to determine relative cure reaction rates and dynamic mechanical analysis (DMA) to determine the changes in storage and loss moduli during cure.

EXPERIMENTAL METHODS

Materials and Synthesis

The chemicals employed are described in Table I. As in previous reports, code names are used. For example, hexamethylenediamine is HMDA; purified bis (hexamethylene) triamine is BHMTA; and crude BHMTA is C-BHMTA (Table I). For urea-capped amines, the final A in the code name is replaced by U. For example, HMDA becomes HMDU, and C-BHMTA becomes C-BHMTU. The hydrochloride salts of the amines are designated, for example, as HMDA · 2HCl and TEATA · 3HCl. The word *resin* refers to uncured polymer, while the word *adhesive* refers to the resin with a curing agent.

Hydrochloride Derivatives of Amines

The synthesis of the hydrochloride derivatives of amines was reported previously.⁷

Resins

The urea derivatives of amines (urea-capped amines) were made in the presence of the total urea to be used in a particular resin synthesis. All laboratory resins were synthesized by adding the urea

(or the combined urea and urea-capped amine) in two steps. The first step yielded an effective formaldehyde to urea mole ratio (F/U) of 2.0, and the second step yielded a final effective F/U ratio of either 1.6 or 1.4. Procedures for making the urea-capped amines and synthesis and characterization of resins were reported earlier.⁵⁻⁷ A commercial resin of F/U 1.6 (Neste Resins Springfield, OR) was used in some of the DMA experiments.

Differential Scanning Calorimetry

Five grams of resin solution were weighed accurately into a beaker, 0.25 g of curing agent (5 wt % of resin) was added, and sample was mixed vigorously for 3 to 5 min. Six to ten milligrams of the mixture were placed in a Perkin-Elmer DSC large-volume capsule, and the capsule was sealed hermetically. DSC thermograms were run immediately with a Perkin-Elmer DSC-2 at heating rates of 10, 20, 40, or 80 K/min over a temperature range of 300 to 450 K.

Dynamic Mechanical Analysis

Ten grams of resin and 0.5 g of curing agent were weighed accurately and mixed thoroughly in a beaker. The adhesive was transferred to a Petri dish, and strips (0.2 mm × 12 mm × 70 mm) of glass cloth (Whatman GF/C microfibre filter) were weighed and thoroughly soaked in the adhesive. The adhesive-soaked strips were laid flat on a clean glass plate, and the excess adhesive was squeezed out by slowly moving a teflon-coated roller over the entire length of the strips. This produced strips of uniform thickness. The strips were carefully removed from the glass plate and suspended for 3 h with metal clips in a forced draft oven at 30°C to remove excess moisture and preclude bubble formation during oven

Table I Experimental Materials

Material	Source	Remarks
Hexamethylenediamine (HMDA)	DuPont Petrochemicals Wilmington, DE	Anhydrous white solid, melting point 41°C
Bis(hexamethylene)triamine (BHMTA)	DuPont Petrochemicals	Brown viscous liquid with boiling point 249°C at 13.33 kPa and vapor pressure 0.93 kPa at 180°C
Poly(propylenedioxide) triamine (PPOTA, Jeffamine T-403)	Texaco Chemical Company Bellaire, TX	Pale yellow liquid, viscosity 0.07 Pa·s at 25°C, total amine 6.4 meq/g, molecular weight about 440
Ammonium chloride	Aldrich Chemical Company Milwaukee, WI	Moist white crystals, 97%, melting point 119 to 121°C

heating. The partially dried strips were sandwiched between two teflon sheets, which were, in turn, placed between two cauls. A 2-kg weight was placed on the cauls, and the entire assembly was placed in an oven at 105 to 110°C for 10 min. The resultant, flat, bubble-free, partially cured resin strips were removed from the caul assembly and cured further for 10 min in the oven at 105 to 110°C. Each strip was reweighed, placed in a paper envelope, and stored at 23°C and 50% relative humidity (RH) until DMA tests were run.

Strips prepared as just described had a resin loading of about 0.230 g. Their weights did not change with storage, indicating no change in moisture content. Three DMA specimens of approximate dimensions 11.00 × 0.40 × 12.00 mm were obtained from each strip. Initially, DMA runs were performed after 2 to 3 weeks of storage. Subsequently, however, the effects on DMA behavior of storage times from 1 to 69 days were investigated. After all DMA scans, the specimens were examined visually and under an optical microscope for evidence of changes in physical structure.

DMA scans used a DuPont Instrument 983 DMA unit, connected to a 9900 computer/thermal analyzer. Scans were performed at resonance frequencies with a peak-to-peak amplitude of 0.10 mm and a heating rate of 2°C/min. Duplicate tests were run for each adhesive, and no significant differences were observed between duplicates.

All DMA measurements were made on samples that had already been cured in an oven at 105 to 110°C for a total of 20 min. This treatment was at the approximate temperature used for pressing solid wood joints and particle boards with these adhesives, but at times that were about twice as long.⁵⁻⁸

RESULTS AND DISCUSSION

Differential Scanning Calorimetry

Figures 1 and 2 are DSC thermograms for various adhesive systems at F/U 1.4. An Arrhenius plot of heating rate (β) versus the reciprocal of the absolute peak exotherm temperature, T_p , for various adhesives is shown in Figure 3. The apparent activation energies, E_a , were calculated from the following relationship⁹:

$$E_a = -0.951R \left(\frac{\Delta \ln \beta}{\Delta(1/T_p)} \right)$$

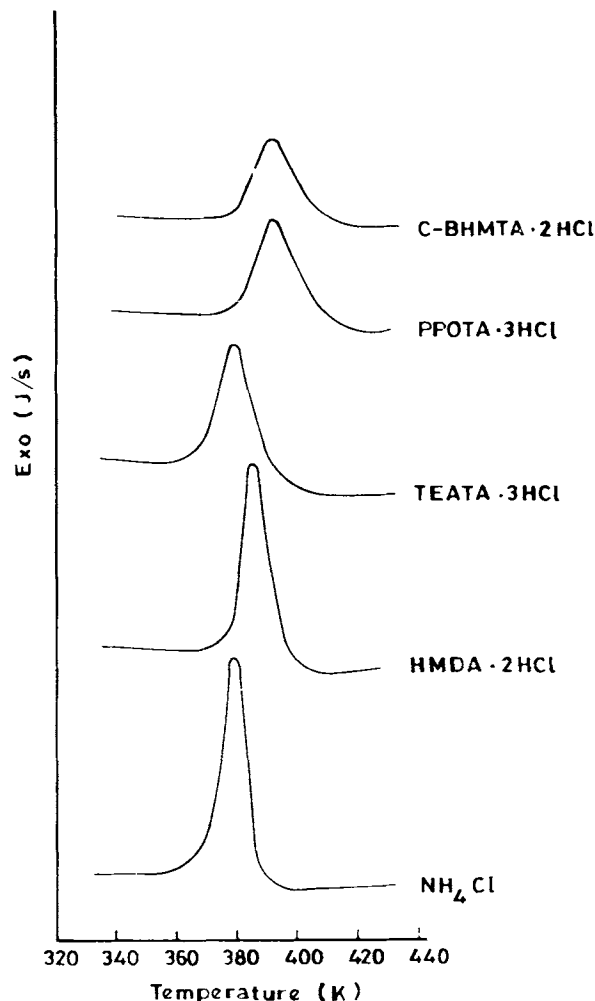


Figure 1 DSC thermograms for the unmodified control resin cured with different curing agents at a heating rate of 20°C/min.

Using the apparent activation energies and apparent frequency factors determined from the Arrhenius plots, the rate constants for the cure reactions at 120°C were estimated for various adhesives. Values of these parameters are shown in Table II.

Cure rates were faster for adhesives cured with NH_4Cl than for adhesives cured with $\text{HMDA} \cdot 2\text{HCl}$, and faster for PPOTU-modified adhesives than for the control adhesive. These differences were clearly due to differences among the apparent frequency factors. The greater apparent frequency factor with NH_4Cl compared to $\text{HMDA} \cdot 2\text{HCl}$ probably reflects a higher catalytic hydrogen ion concentration with NH_4Cl . The greater apparent frequency factor with PPOTU-modified adhesive compared to control adhesive may be the result of the greater flexibility imparted by PPOTU. More flexible polymer chains

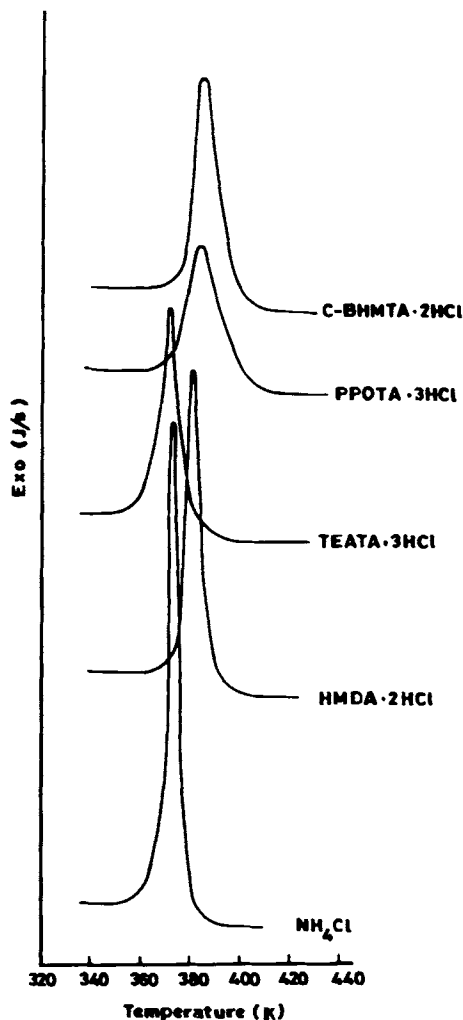


Figure 2 DSC thermograms for the PPOTU-modified resin cured with different curing agents at a heating rate of 20°C/min.

may also permit a greater extent of reaction, thereby accounting for the greater cure exotherm heat of the PPOTU adhesive compared to that of the control adhesive (Fig. 4).

Dynamic Mechanical Analysis

Figures 5 through 7 present the storage modulus (E') and loss modulus (E'') spectra from approximately 25 to 200°C for several adhesives after they had already been exposed to oven heating at 105 to 110°C plus storage at 23°C/50% relative humidity for 14 to 21 days. Figure 5 compares the effects of Neste (unmodified) resin cured with four different curing agents. We note several distinctive features of these data.

1. The low-temperature (below 100°C) storage modulus of the oven-heated Neste commercial resin with NH_4Cl curing agent was clearly higher than those of the Neste resin with the hydrochloride salts of amines as curing agents (Fig. 5) or those of the PPOTU- or C-BHMTU-modified resins with NH_4Cl as curing agent (Fig. 6). Similarly, with HMDA·2HCl as curing agent, the low-temperature storage modulus of the Neste resin was above those of the PPOTU- and C-BHMTU-modified resins (Fig. 7). Such reductions in stiffness for the modified adhesives could partially account for their improved performance in solid wood joints and particle board.
2. The storage modulus spectra for all of the Neste adhesives, whether cured with NH_4Cl or amine hydrochloride (Fig. 5), are more complex than those for adhesives made with modified resins (Figs. 6 and 7). The Neste adhesives show a rapid drop in E' above 120°C to a minimum at about 155°C or higher, a subsequent rise, and a second drop at temperatures about 165°C or higher. The temperatures at which these changes occurred were all greater for Neste/amine hydrochloride adhesives than for the Neste/ammonium chloride adhesive (Fig. 5).
3. The greater complexity of the storage modulus for the Neste adhesives is paralleled by a greater complexity in their loss modulus spectra. The loss modulus of the

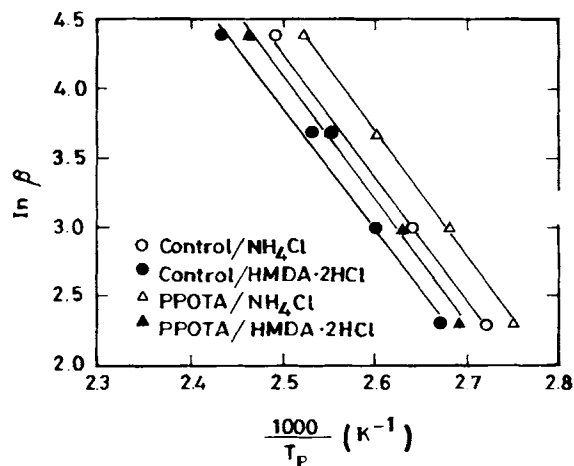


Figure 3 Arrhenius plot for unmodified (control) and PPOTU-modified resins cured with either NH_4Cl or HMDA·2HCl.

Table II Kinetic Parameters from DSC Measurements

Resin ^a	Curing Agent	Apparent Activation Energy E_a (kcal/mol)	Apparent Frequency Factor, A (min^{-1})	Cure Rate at 120°C, k_{120} (min^{-1})
Control	NH_4Cl	16.7	2.64×10^{11}	143
	$\text{HMDA} \cdot 2\text{HCl}$	16.5	1.31×10^{11}	88
PPOTU	NH_4Cl	17.0	5.88×10^{11}	202
	$\text{HMDA} \cdot 2\text{HCl}$	16.9	2.92×10^{11}	120

^a F/U = 1.4.

Neste/ NH_4Cl adhesive is especially complex. It appears to have overlapping peaks between 120 and 155°C and between 170 and 190°C; the most intense peak appears at 155°C, which is approximately the position of the minimum in the storage modulus of that material.

4. In strong contrast to the Neste systems, the storage and loss modulus spectra of the adhesives made from PPOTU- and C-BHMTU-modified resins (Figs. 6 and 7) exhibit only a single peak in the region studied. The temperatures of the storage modulus drop and loss modulus peak are higher than those for the first drop in storage modulus for the Neste adhesives when comparisons are made with identical curing agents.

Thus, there are major differences between the dynamic mechanical behavior of adhesives made from unmodified Neste resin and from the amine-modified resins, and also between Neste/ NH_4Cl and

Neste/amine hydrochloride adhesives. We provide a rationale for the observed behavior in the following discussion.

According to current views,¹⁰⁻¹⁴ two molecular phenomena occur as most liquid thermosetting polymers cure. The first is gelation, which corresponds to incipient formation of an infinite network. The second is vitrification, which occurs when the

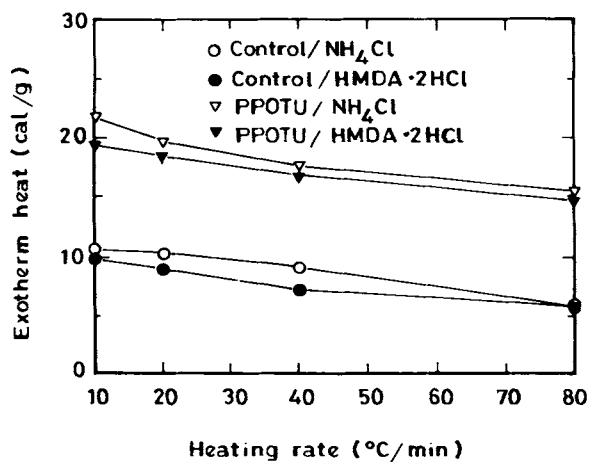


Figure 4 Exotherm heats during DSC cure of control resin and PPOTU-modified resin cured with either NH_4Cl or $\text{HMDA} \cdot 2\text{HCl}$.

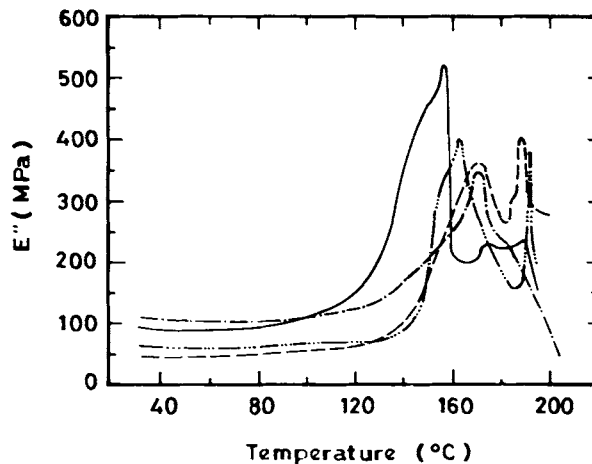
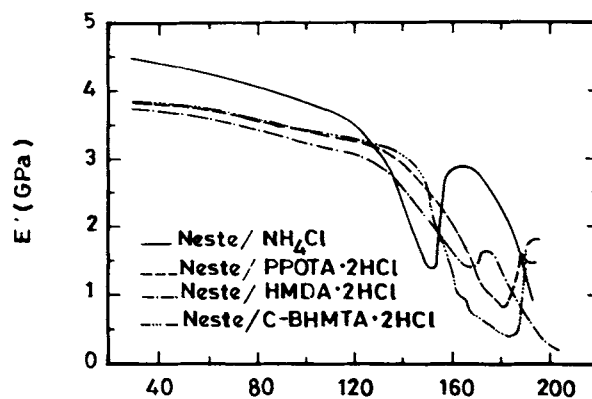


Figure 5 Storage modulus, E' (top), and loss modulus, E'' (bottom), for the unmodified Neste resin previously oven cured with different curing agents (F/U = 1.6).

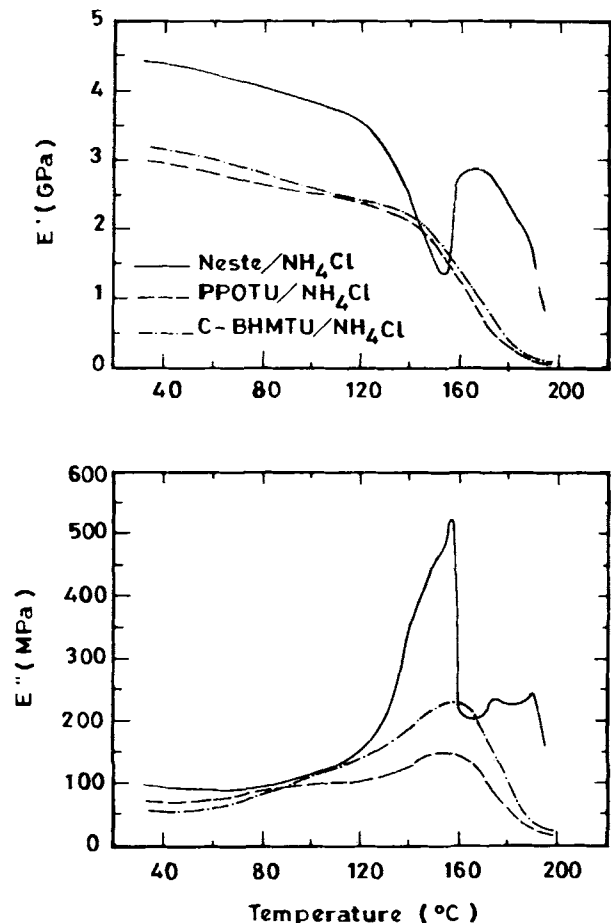


Figure 6 Storage modulus, E' (top), and loss modulus, E'' (bottom), for the unmodified Neste and the PPOTU- and C-BHMTU-modified resins previously oven cured with NH_4Cl ($F/U = 1.6$).

glass transition temperature (T_g) of the reacting mixture rises to the cure temperature. At gelation, resin fluidity decreases substantially. However, conversion is far from complete, and the reaction rate is still kinetically controlled. With continued cure, the T_g reaches the cure temperature, and vitrification occurs. At that point, the reaction rate becomes diffusion controlled and is drastically reduced. If the temperature is later raised above the initial cure temperature, the material softens and the cure rate again accelerates until the T_g increases to that new cure temperature.

Before examining the DMA results in this light, however, we need to consider whether the observed drops in storage modulus and the accompanying peaks in loss modulus were indeed due to devitrification at a glass transition or whether they were caused by physical or chemical degradation of the adhesives. The following points are relevant:

1. The relatively high contents of acidic curing agents employed here would certainly foster resin hydrolysis. However, the moisture content of the DMA specimens undoubtedly was very low by the time the specimens exhibited any drop in storage modulus.
2. It is extremely unlikely that degradation (thermal or hydrolytic) could have caused the drops in storage modulus in those cases in which the drop was immediately succeeded by a modulus rise due to further cure (i.e., the Neste adhesives in Fig. 5). It is very difficult to conceive of a mechanism whereby additional cure could or should follow degradation, especially within a thin specimen exposed to inert gas flow such that low-molecular-weight degradation products would readily be lost. This argument, of course, does

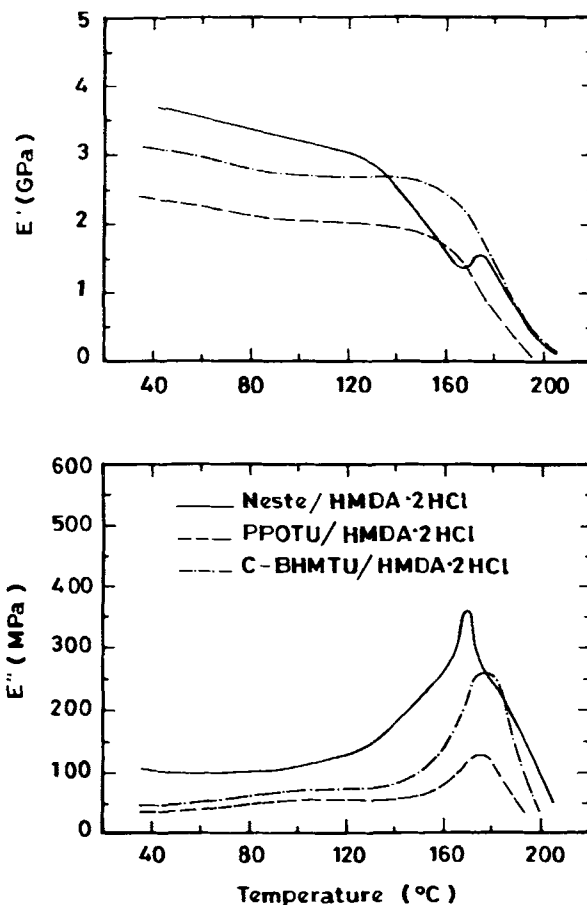


Figure 7 Storage modulus, E' (top), and loss modulus, E'' (bottom), for the unmodified Neste and the PPOTU- and C-BHMTU-modified resins previously oven cured with $\text{HMDA}\cdot 2\text{HCl}$ ($F/U = 1.6$).

Table III Estimated Glass transitions of Adhesives Before DMA Scan

Resin	Curing Agent	Estimated Glass Transition (°C)	
		From First Loss Modulus Peak	From Inflection in First Storage Modulus Drop
Neste	NH ₄ Cl	154	144
	PPOTA · 3HCl	171	173
	HMDA · 2HCl	169	162
	C-BHMTA · 2HCl	162	160
PPOTU	NH ₄ Cl	160	165
	HMDA · 2HCl	176	177
C-BHMTA	NH ₄ Cl	158	168
	HMDA · 2HCl	173	185

not apply to the second storage modulus drop for the Neste resins (Fig. 5) or to the modified resins (Figs. 6 and 7), in which no rise in storage modulus was seen after the initial drop.

3. After the scan in Figure 5, the Neste adhesive specimens, particularly the Neste/NH₄Cl, were visibly degraded (bubbles, cracks, dark brown coloration) and were very weak and friable when probed with a pointed tool. The post-DMA specimens of the modified adhesives (Figs. 6 and 7) were much lighter in color and did not contain bubbles or cracks; however, they were noticeably weaker than pre-DMA counterparts when probed with the pointed tool.

We suggest, therefore, that during oven heating, the glass transition temperature of the unmodified adhesive rose quickly to the oven temperature; that is, vitrification occurred at a point at which the adhesives were not completely cured. In subsequent DMA scans, the Neste adhesives exhibited an initial drop in storage modulus at the T_g achieved in the total pre-DMA history (e.g., approximately 150°C for the Neste/NH₄Cl adhesive; Fig. 5). This softening allowed further cure to take place, as evidenced by the rise in storage modulus (e.g., at 150 to 160°C for the Neste/NH₄Cl adhesive), leading to further vitrification and ultimately to a second storage modulus drop above 170°C. Whether those second, high-temperature drops in storage modulus with the Neste adhesives were due to exceeding a second T_g or to sample degradation cannot be stated with certainty, although the specimens were clearly degraded at termination of the scans. Possibly, the high-temperature drops in storage modulus reflected the ini-

tiation of a glass transition, which was followed by degradation as the samples approached 200°C.

In contrast to the Neste adhesives, each of the urea-capped amine adhesives in Figures 6 and 7 exhibited only a single drop in storage modulus and no subsequent rise due to additional cure. Therefore, we must accept the possibility that those drops were not due solely to exceeding the transition attained in the pre-DMA treatment but that they were at least partially due to resin degradation. However, in view of the absence of obvious degradation—as judged by the post-DMA inspection, we assume that the storage modulus drops and accompanying loss modulus peaks of these materials do indeed reflect the glass transitions attained in the pre-DMA treatment, with the possibility of some contribution from degradation at the final temperatures. Accepting this interpretation, we are led to suggest further that the absence of additional cure within the softened adhesives argues for their having achieved essentially complete cure during their pre-DMA history.

Adopting this interpretation of the observed DMA behavior, it is of interest to compare the T_g 's resulting from the pre-DMA treatment of the various adhesives. Because the complexity of some of the spectra make it difficult to select T_g values unequivocally, we used two criteria for that selection: the lowest temperature loss modulus peak and the inflection point of the lowest temperature storage modulus drop (Table III). Although the T_g 's from the two procedures differ significantly in some cases, the relative values within each procedure suffice to illustrate some interesting patterns. We note first that all the T_g 's are well above the oven-heating temperature (105 to 110°C), indicating that considerable cure must have occurred within the glassy materials after removal of the specimens from the

oven. (Additional evidence for this postoven cure is given in the later discussion of aging.) Second, we note that for all three resins, the T_g with NH_4Cl as curing agent is below those with the amine hydrochloride salts as curing agents; moreover, with a particular curing agent the T_g with the Neste resin is generally below those with urea-capped amine resins. At the same degree cure, we would expect the modified adhesives to be more flexible and exhibit lower glass transitions. Therefore, we take this contradiction as additional evidence that unmodified Neste resin vitrified more rapidly during the oven heating and consequently was unable to achieve as complete a cure as the modified systems.

A lower degree of crosslinking in the pre-DMA Neste/ NH_4Cl system is also indicated by the greater amount of relaxation processes associated with the intense loss modulus peak (Fig. 5). Furthermore, the lower initial storage modulus of the PPOTU- and C-BHMTU-modified adhesives relative to the un-

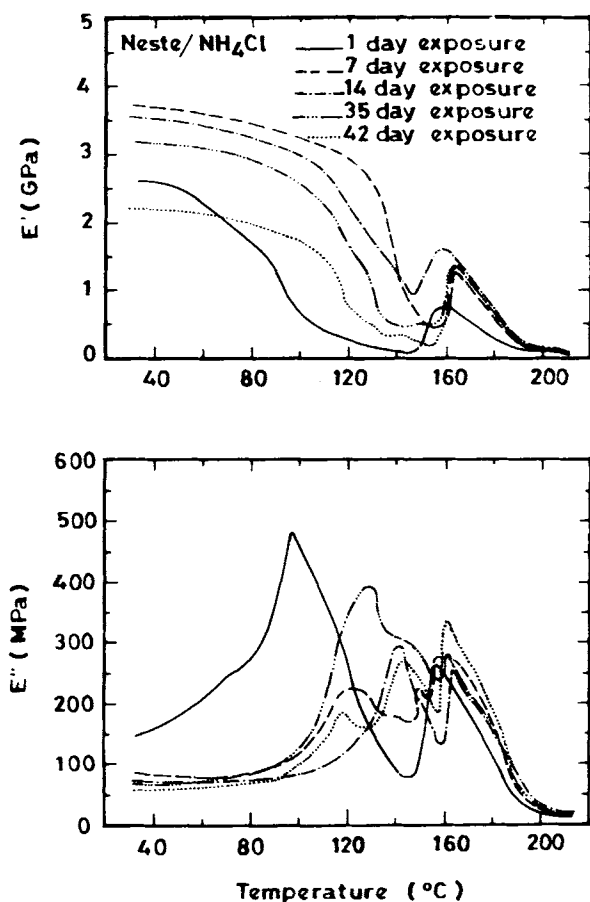


Figure 8 Effect of aging time at 25°C and 50% RH on the DMA spectrum of the unmodified control resin previously oven cured with NH_4Cl ($F/U = 1.6$).

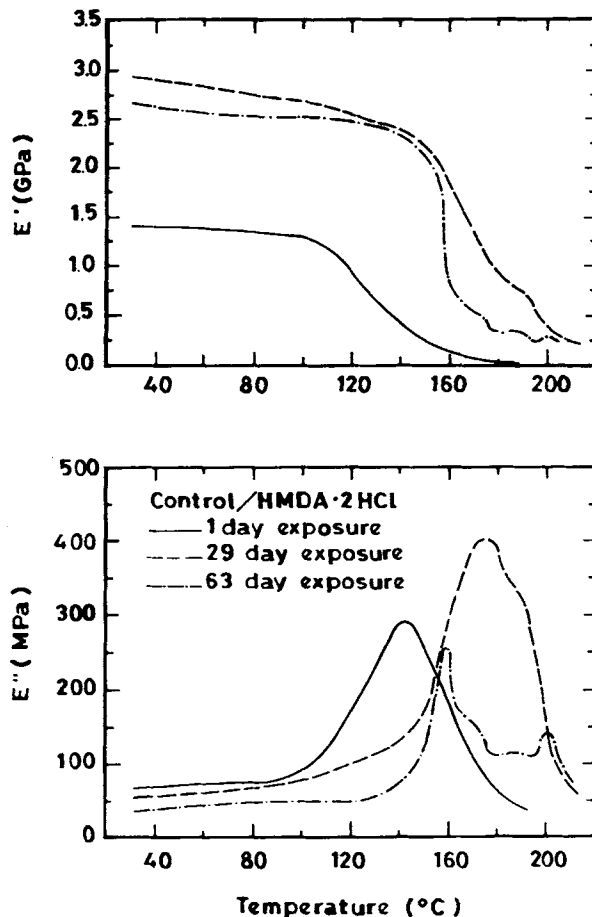


Figure 9 Effect of aging time at 25°C and 50% RH on the DMA spectrum of the unmodified control resin previously oven cured with $\text{HMDA} \cdot 2\text{HCl}$ ($F/U = 1.4$).

modified/ NH_4Cl adhesive (Figs. 6 and 7) means that the modified adhesives have more molecular flexibility after vitrification.

DSC data are consistent with the preceding arguments. For example, the calculated reaction rates at 120°C were less with $\text{HMDA} \cdot 2\text{HCl}$ curing agent than with NH_4Cl curing agent (Table II). In addition, DSC measurements also indicated that the PPOTU-modified resin reacted faster than the laboratory-synthesized unmodified resin (Table II). We rationalize this ability of the modified adhesives to achieve full cure during their pre-DMA history on the basis that the urea-capped amine moieties interfere with hydrogen bonding between polymer chains and provide greater flexibility, thus slowing the increase in the T_g during cure.

Finally, we speculate on the reasons for the complex loss modulus peaks of the Neste adhesives (Fig. 5). For a long time, the concept of an infinitely large

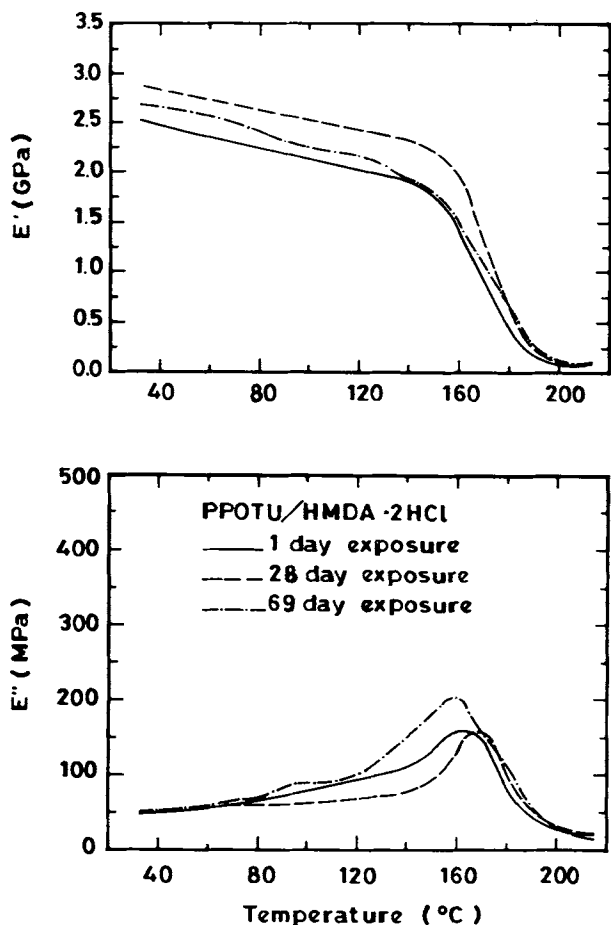


Figure 10 Effect of aging time at 25°C and 50% RH on the DMA spectrum of PPOTU-modified resin previously oven cured with HMDA · 2HCl (F/U = 1.4).

molecule with a homogeneously crosslinked network has been used to describe the morphology of crosslinked thermosets. However, the presence of inhomogeneities in the crosslink density has been documented by electron microscopy,¹⁵⁻¹⁷ thermo-mechanical measurements,¹⁸ and swelling experiments.¹⁵⁻¹⁹ Today, it is generally recognized that morphology of thermosets is more properly described in terms of a two-phase system of higher crosslinked regions immersed in a less crosslinked matrix. Extending this view to the present systems, we suggest, for example, that the complex loss modulus peak at approximately 155°C for the Neste/ammonium chloride adhesive is due to the presence of regions having different crosslink densities and T_g 's after oven heating. Additional cure in the DMA above those glass temperatures perpetuates this morphological inhomogeneity, producing the overlapping loss modulus peaks at approximately 170 to 190°C.

Perhaps the simpler loss modulus spectra of the adhesives with urea-capped amines (Figs. 6 and 7) derives from the greater flexibility of these polymer chains, which permits more random crosslinking and delays freezing-in of configurations, leading ultimately to cured adhesives with a more homogeneous morphology.

Effect of Storage Time on DMA Behavior of Precured Adhesives

The DMA tests just discussed were conducted two to three weeks after the specimens were heated in an oven. Although no changes were observed in the weight of the specimens during storage at 23°C and 50% RH, we felt it necessary to verify that the observed differences in DMA spectra did not arise from small differences in storage times. Therefore, a number of DMA specimens were prepared with the unmodified Neste/ NH_4Cl adhesive at F/U 1.6. An-

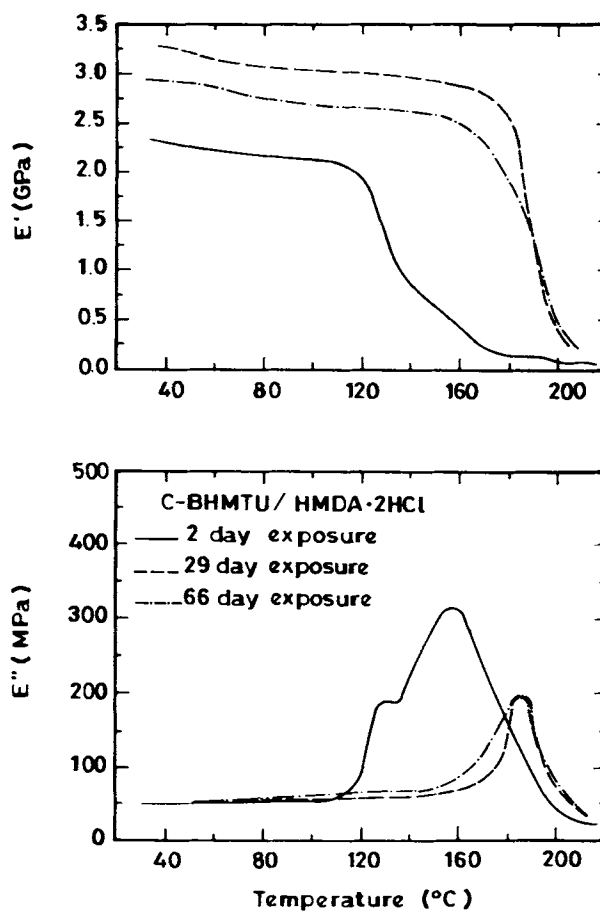


Figure 11 Effect of aging time at 25°C and 50% RH on the DMA spectrum of C-BHMTU-modified resin previously oven cured with HMDA · 2HCl (F/U = 1.4).

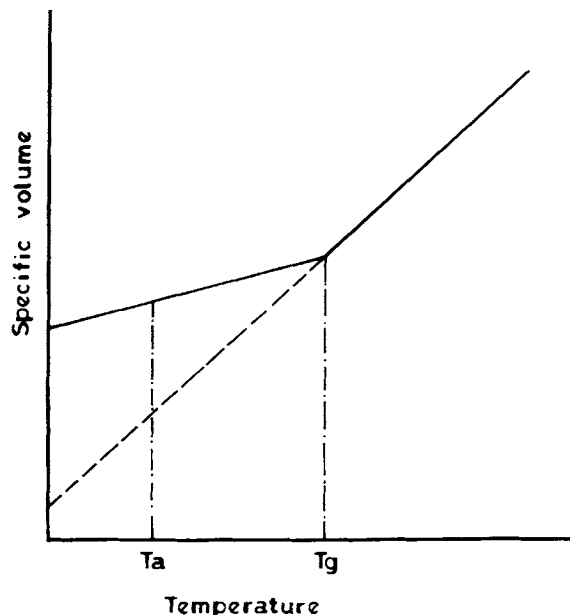


Figure 12 Schematic plot of specific volume-temperature relationship for thermosetting resins.

other series was prepared with laboratory-synthesized unmodified and modified resins at F/U 1.4 with HMDA · 2HCl as the curing agent. DMA scans were run after different storage times at 23°C and 50% RH. Prior to storage, all specimens were cured in an oven at 105 to 110°C for 20 min, approximately twice the normal cure time used in our wood-bonding experiments.^{5,6}

Marked changes occurred in the DMA spectra of some adhesives during the storage period of 1 day to nearly 10 weeks (Figs. 8-11). In general, during early storage both the low-temperature storage modulus and T_g increased, while both parameters decreased during later storage periods. These changes were particularly noticeable for the Neste/NH₄Cl adhesive. The loss modulus for this system exhibited multiple peaks whose intensities decreased while their complexity increased with increasing aging times (Fig. 8). Only slight changes occurred in the location and intensity of the peaks in the loss modulus of the PPOTU-modified adhesive. The loss modulus peak for the C-BHMTU-modified adhesive (Fig. 11) was broad, with a small shoulder at 130°C. With longer aging, the peak size decreased substantially and shifted to a higher temperature, and the shoulder disappeared.

We believe the early increases in low-temperature storage modulus and T_g are due to one or both of two processes. The first is continued cure in the glassy state (chemical aging); the large changes

shown for Neste/NH₄Cl and the small changes for PPOTU/HMDA · 2HCl are consistent with the relative degrees of cure achieved by these two systems during oven heating, as discussed in the previous section. The second process which may contribute to the early DMA changes is often referred to as physical aging. Here, initially produced glassy polymer is in a low-density state (solid line, Fig. 12) caused by the freezing-in of nonequilibrium conformations as the material is cooled below its T_g .¹⁴ The drive toward thermodynamic equilibrium (dashed

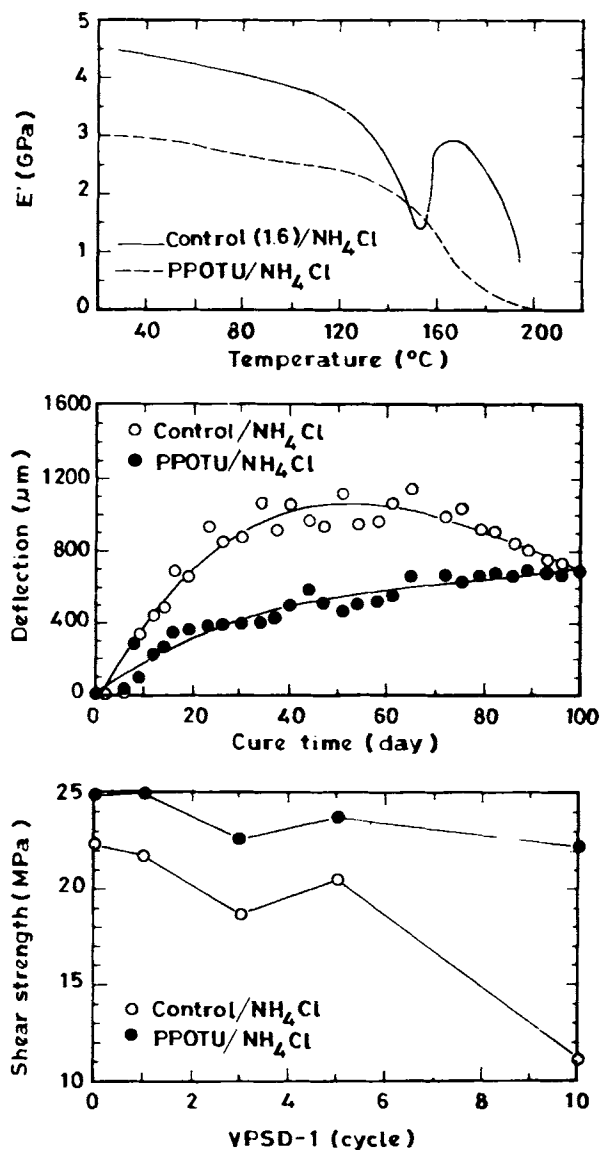


Figure 13 Interrelationship between cured adhesive modulus (top), internal stress developed during cure (middle), and the cyclic soak-dry stress resistance of UF-bonded solid wood joints (bottom).

line, Fig. 12) leads to time-dependent increases in density and modulus.^{14,20,21} In UF systems, an increase in equilibrium conformations and density could also enable more hydrogen bonding, which, in turn, could increase T_g .

We believe further that the later decreases in storage modulus and T_g are also due to one or both of two processes, different from but related to the aforementioned. In this case, the first process is the well-established reversion of UF cure brought about by acidic curing agents; this could account for reductions in both storage modulus and T_g . However, we observe that this is more probable under humid conditions. The second process is microcracking within the adhesive or at the adhesive/glass cloth interface as a result of internal stresses induced by the increase in modulus and the shrinkage during cure and early storage. The greater the inhomogeneity in the crosslink density, the greater would be the magnitude of the internal stress and hence the adhesive's tendency to fragment. Extensive fragmentation is common in unmodified UF adhesives after prolonged ambient aging. During cure, the internal stress-time curve for unmodified/ NH_4Cl adhesive film goes through a maximum at the point at which fragmentation of the film occurred.⁵ Microscopic examination of unused DMA specimen revealed the presence of microcracks, especially with unmodified adhesives. Microcracking could cause apparent loss of stiffness but no reduction in T_g . These changes in DMA behavior should have had only minor influence on the DMA data discussed earlier (Figs. 5 to 7) because those experiments were all performed within 14 to 21 days after the oven treatment, a period of relatively small change.

As we reported previously, modified adhesives generate less internal stress during cure and are more resistant to cyclic soak-dry stress than unmodified adhesives.⁵ It is evident from the present study that the improved performance of joints bonded with modified adhesives is a result of morphological changes in cured adhesive and the associated changes in properties (e.g., modulus and internal stress; Fig. 13).

CONCLUSION

The overall conclusion emerging from the observed thermal and dynamic mechanical behavior of unmodified and amine-modified UF adhesives is that adhesive structure and cure rate and resulting morphology of the cured state have a profound influence

on the properties of the cured system. The unmodified resin, with its inherent stiff structure and strong tendency to form hydrogen bonds between chains, undergoes early vitrification during cure, thereby preventing full cure. The resulting partially cured adhesive has low fracture toughness and is internally stressed; it is therefore susceptible to physical breakdown (microcracking).

Curing unmodified resins with amine hydrochlorides, such as HMDA \cdot 2HCl, has several consequences: lower cure rate, delayed vitrification, increased extent of cure (conversion), more uniform crosslink density, and reduced cure-shrinkage stress. Therefore, the cured adhesive is inherently tougher and more durable than the unmodified UF adhesive.

Structural modification via incorporation of urea-capped flexible amines may or may not reduce the cure rate. However, modification apparently does interfere with hydrogen bonding and produces enough molecular flexibility to delay vitrification and promote improved cure and improved properties.

The original hypothesis of this study stated that the stability of UF-bonded wood products can be enhanced by modifying the resin structure to incorporate flexible comonomers into the polymer chains and to produce a more efficiently cured network with greater flexibility and greater ability to respond reversibly to applied stresses. The results reported here support that hypothesis.

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REFERENCES

1. T. J. Pratt, W. E. Johns, R. M. Rammon, and W. L. Plagemann, *J. Adhesives*, **17**, 275 (1985).
2. J. A. Koutsky, *Proceedings of Wood Adhesives in 1985: Status and Needs*, May 1985, Madison, WI, sponsored by USDA Forest Service, Forest Product Laboratory, and the Forest Products Research Society.
3. J. M. Dinwoodie, *Holzforchung*, **31**, 50 (1977).

4. M. A. Irle and A. J. Bolton, *Holzforschung*, **45**, 69 (1991).
5. R. O. Ebevele, G. E. Myers, B. H. River, and J. A. Koutsky, *J. Appl. Polym. Sci.*, **42**, 2997 (1991).
6. R. O. Ebevele, G. E. Myers, B. H. River, and J. A. Koutsky, *J. Appl. Polym. Sci.*, **43**, 1483 (1991).
7. R. O. Ebevele, G. E. Myers, and B. H. River, *J. Appl. Polym. Sci.*, **49**, 229 (1993).
8. R. O. Ebevele, B. H. River, and G. E. Myers, *J. Appl. Polym. Sci.*, **52**, 689 (1994).
9. R. B. Prime, in *Thermal Characterization of Polymeric Materials*, E. A. Turi, Ed., Academic Press Inc., Orlando, FL, p. 00.
10. G. Wisanrakkit and J. K. Gillham, *J. Appl. Polym. Sci.*, **42**, 2465 (1991).
11. J. B. Enns and J. K. Gillham, *J. Appl. Polym. Sci.*, **28**, 2831 (1983).
12. G. Wisanrakkit, J. K. Gillham, and J. B. Enns, *J. Appl. Polym. Sci.*, **41**, 1895 (1990).
13. G. Wisanrakkit and J. K. Gillham, *J. Appl. Polym. Sci.*, **42**, 2453 (1991).
14. S. Montserrat, *J. Appl. Polym. Sci.*, **44**, 545 (1992).
15. W. Funke, *J. Appl. Polym. Sci.*, **16**, 1497 (1967).
16. E. H. Erath and M. Robinson, *J. Appl. Polym. Sci.*, **C3**, 65 (1963).
17. R. E. Cuthrell, *J. Appl. Polym. Sci.*, **12**, 1263 (1968).
18. H. Batzer, F. Lohse, and R. Schmid, *Angew. Makromol. Chem.*, **29/30**, 349 (1973).
19. A. S. Kenyon and L. E. Nielson, *J. Macromol. Sci. Chem.*, **A-3**, 275 (1969).
20. A. J. Kovacs, *J. Polym. Sci.*, **30**, 131 (1958).
21. S. E. B. Petrie, *J. Polym. Sci.*, **10**, 1255 (1972).

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