Curing of Low Level Melamine-Modified Urea-Formaldehyde Particleboard Binder Resins Studied with Dynamic Mechanical Analysis (DMA)

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ABSTRACT: Effects of resin formulation, catalyst, and curing temperature were studied for particleboard binder-type urea-formaldehyde (UF) and 6 ~ 12% melamine-modified urea-melamine-formaldehyde (UMF) resins using the dynamic mechanical analysis method at 125 ~ 160°C. In general, the UF and UMF resins gelled and, after a relatively long low modulus period, rapidly vitrified. The gel times shortened as the catalyst level and resin mix time increased. The cure slope of the vitrification stage decreased as the catalyst mix time increased, perhaps because of the deleterious effects of polymer advancements incurred before curing. For UMF resins, the higher extent of polymerization effected for UF base resin in resin synthesis increased the cure slope of vitrification. The cure times taken to reach the vitrification were longer for UMF resins than UF resins and increased with increased melamine levels. The thermal stability and rigidity of cured UMF resins were higher than those of UF resins and also higher for resins with higher melamine levels, to indicate the possibility of bonding particleboard with improved bond strength and lower formaldehyde emission. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 377–389, 2005

Key words: urea-formaldehyde (UF) resins; urea-melamine-formaldehyde (UMF) resins; DMA curing and thermal stability of UF and UMF resins

INTRODUCTION

Urea-formaldehyde (UF) resins (Fig. 1)[1–8] are currently the major binders of wood composite boards, such as particleboard (PB), medium density fiberboard (MDF), and hardwood plywood,[9] but they have drawbacks of low water resistance and high formaldehyde emission.[10–13] The overall formaldehyde/urea (F/U) mole ratio of UF resins has been the key parameter used in lowering the formaldehyde emission, and is currently at a low value of about 1.15. Lowering the F/U ratio further would decrease the formaldehyde emission but it also reduces the bond strength and water resistance of boards due to the resultant limited crosslinking. Melamine, which has functionality of 3 or higher, is used with minor amounts of urea in manufacturing melamine-urea-formaldehyde (MUF) resins widely used in bonding specialty wood composites (Fig. 1).[14] On the other hand, low levels of melamine have been added to UF resins in manufacturing urea-melamine-formaldehyde (UMF) resins to improve the water resistance and/or decrease the formaldehyde emission.[15–18] Although the chemistry of melamine-formaldehyde resins is similar in general to that of UF resins, significant differences were reported recently[19] as well as new details on UF resin chemistry.[20–25] Melamine costs significantly more than urea and therefore the resin synthesis optimization of UMF resins was studied[19] and their curing efficiency investigated using the dynamic mechanical analysis (DMA) method reported in this article.

In syntheses of UF resins, on which syntheses of most UMF resins are based, the urea is added in two parts, the first urea (U_1) and the second urea (U_2).[20] First, the first urea and formaldehyde are reacted in a weak alkaline pH at F/U_1 mole ratio of about 2.10 to form mono-, di-, and trihydroxymethylureas. Secondly, the reaction, after adjusting the pH to 4 ~ 5, is continued at 95°C, where hydroxymethylureas polymerize by forming methylene (~ 80%) and methylene-ether (~ 20%) bonds. In this step, some hydroxymethyl groups split off as formaldehyde due to the reverse hydroxymethylation reaction and the decreasing urea amide group sites within the resin system. This polymerization reaction is normally carried out to viscosity V-X (Gardener-Holdt) (~ 32 P) at a resin solids level of 60–65% and ended by increasing the pH to about 8.0, resulting in a mixture of polymeric methylene/methylene-ether hydroxymethylureas. In the third step, the reaction mixture is cooled to about

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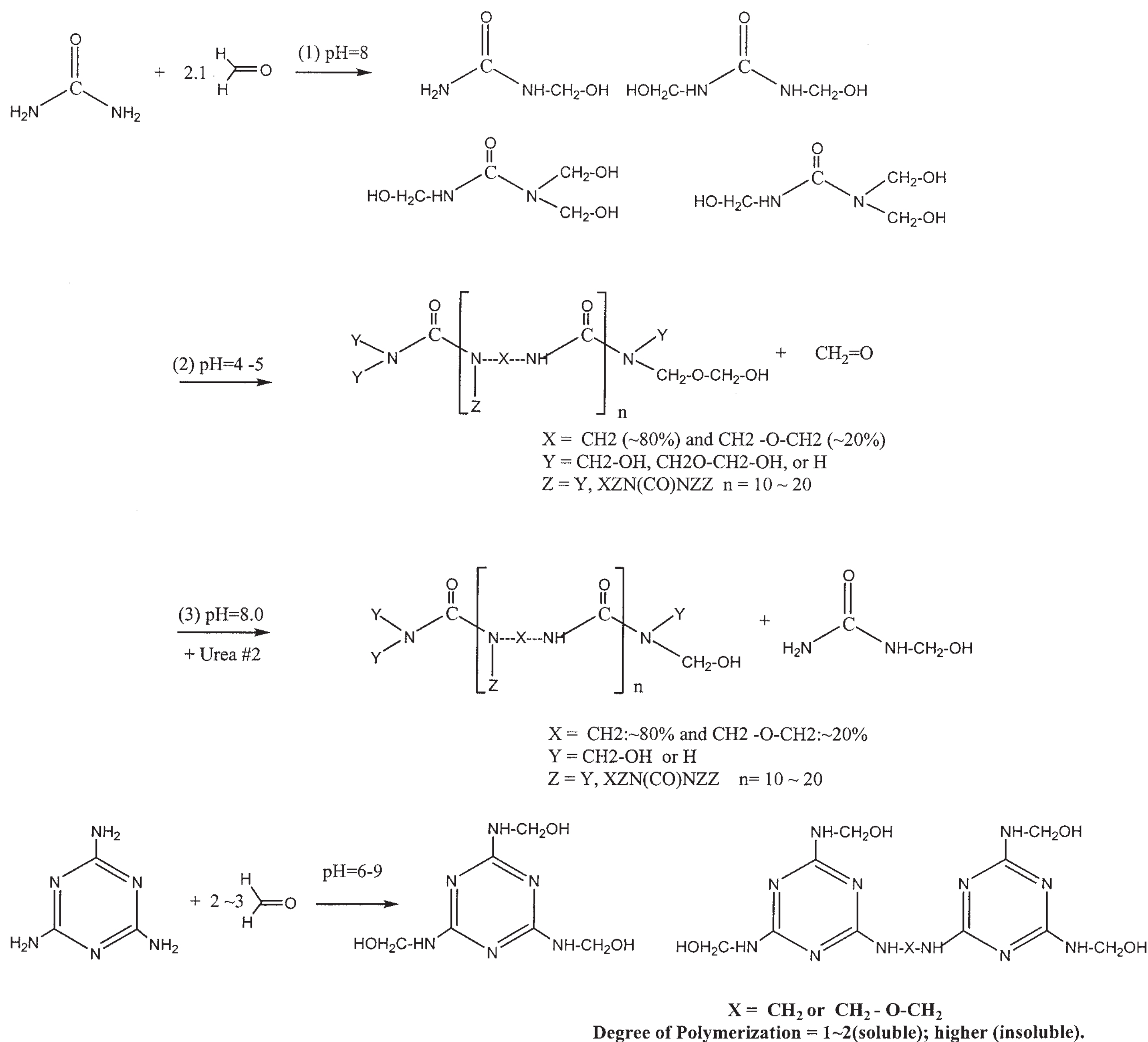


Figure 1 Schematic representation of (A) urea-formaldehyde (UF) and (B) melamine-formaldehyde (MF) resin systems.

60 ~ 70°C and the second urea is added to the final $F/(U_1+U_2)$ of about 1.15, followed by cooling to room temperature. Some of the second urea reacts with the free formaldehyde present in the reaction mixture to form monomeric hydroxymethylureas, normally leaving less than 0.5% free formaldehyde in the resin. About 25% of the urea used in the resin synthesis remains as free urea and the rest as monomeric and polymeric hydroxymethyl methylene/methylene ureas (Fig. 1).

Past research on UMF resins made with 4 ~ 35% melamine levels showed that the PB or MDF strength and formaldehyde emission performances often varied a lot and did not necessarily improve with the melamine levels,[15–18,26] nor were the underlying resin parameters clarified. One report on bonding plywood with UMF resins indicated improved durability, which the authors ascribed to the melamine's higher basicity than urea.[27] Current MUF resins, made by using melamine levels of 50% or more, need stronger acid catalysts,[28] and UMF resins may need stronger acid catalysts and/or higher press temperatures or longer press times in comparison to UF resins.

The solubility of melamine-formaldehyde (MF) resin components, those formed in MUF and UMF resin syntheses, decreases rapidly with molecular weight and, therefore, UMF resins may contain insoluble MF resin components as suspended particles with unknown thermosetting quality. Furthermore, the MF resin system reacts optimally at pH 6 ~ 9 but is too fast at pH 4 ~ 5 and, on the other hand, the UF resin system polymerizes at an optimal speed at pH 4

~ 5 and too slowly at pH 6 ~ 9.[14] These reaction rate differences were delineated in our study on UMF resins.[19] In the study, the UF base resin was reacted to various different extents of polymerization at pH 4 ~ 5 and, after adjusting the pH to 6 ~ 9, low levels of melamine were added and reacted further to a target viscosity of resin. Adding melamine early with the first urea and formaldehyde and reacting at pH 6 ~ 9, a common procedure used in prior research, resulted in a very high extent of polymerization for MF resin components and only a little extent of polymerization for UF resin components. On the other extreme, adding melamine after the UF base resin has been advanced to a high extent resulted in a very low extent of polymerization for MF components. It was found that the optimum extent of polymerization for UF base resin was D ~ K viscosity. The various UMF resins showed different handling and wood bonding characteristics because of the different molecular weight distributions attained, as well as different melamine levels. UF resins are commonly cured using latent catalysts, such as ammonium salts of strong acids, which react with free formaldehyde present in resins to produce free acids. The wood composite board mats are cured in industry at 150 ~ 170°C for about 3min for 1.25-cm thick boards,[9] but the hot pressing can often cause precure/over-cure problems in surface layers and under-cure problems in core layers, to cause deterioration of bond strength and water resistance properties of the board. These cure problems can become more problematic for UMF resins since the MF components might cure slower than UF components. Therefore, curing of these UMF resins was studied to delineate the melamine level and catalyst level effects using DMA before evaluating them as particleboard binders.

Thermosetting resins go from a liquid stage to a viscous stage and gelation and to vitrification resulting in crosslinked polymers in curing.[29] The DMA method based on TA Model 983 DMA has been used effectively to monitor the curing of thermosetting wood composite binder resins. The DMA method continuously measures the storage and loss moduli and tan δ (the ratio of loss modulus to storage modulus) of a resin sample as the sample chamber temperature is increased and/or maintained. Although the DMA method does not accurately simulate the hot pressing conditions of boards, useful resin curing parameters have been obtained. For example, Follensbee and colleagues found that phenol-formaldehyde (PF) wood composite resins' storage moduli decreased as the extent of the precuring of resin was increased.[30] Kim and colleagues reported that the curing rate of PF wood composite binder resins increased with the curing temperature, the extent of polymerization and formaldehyde/phenol mole ratio of resins.[31] Kim and colleagues also found that the urea commonly added to PF resins lowered the curing speed of resins but resulted in minimal deleterious effects on the bond strength of boards.[32] Ebewele claimed that certain modified UF resins cure to give an improved polymer structure based on DMA results.[33] However, no groundwork has been reported on the general curing parameters of UF or UMF resins, such as gel time, cure time, and curing rate, using the DMA method. In this study, UMF resins were synthesized at two melamine levels with UF base resins of two optimum extents of polymerization and their curing was compared with a UF resin control. Catalyst level, catalyst mixing temperature and time, and DMA curing temperature and time, as well as thermal stability of cured resins, were examined.

METHODS

Resins

Syntheses of all resins, reported previously,[19] are described briefly (Fig. 1). Resin UFA, typical PB binder-type UF resin control, was synthesized by reacting formaldehyde (F_1) and urea (U_1) at an F_1/U_1 ratio of 2.1, first at pH 7.0–8.0 and then at pH 4.6. The second urea (U_2) was added at pH 8.0 and at 60°C, attaining $F/(U_1+U_2)$ ratio of 1.15, and the resultant resin cooled to room temperature. Resins UMF6D, UMF6K, UMF12D, and UMF12K were similarly synthesized, named with number to indicate the melamine level and letter to indicate the viscosity of UF base resin at the melamine addition point. Thus, a UF base resin was synthesized with an F_1/U_1 ratio of 2.1 and pH 8.0 in the first step and further advanced at pH 4.6 in the second step until a D or K viscosity was reached. After adjusting the pH to 8.0, 6 or 12% melamine and the second formaldehyde (F_2) were added for an $(F_1+F_2)/(U_1+M)$ ratio of 2.1 and the reaction mixture was reacted initially at the same pH, then at pH 6.3 ~ 6.7 until ~ V viscosity, adjusted pH to 8.0 and cooled to 60°C. Finally, the second urea was added and the resin mixture cooled to room temperature to obtain resins with an $(F_1+F_2)/(U_1+U_2+M)$ ratio of 1.15. Resins $UFA_{1.05}$ and $UFA_{1.25}$, $UMF12D_{1.05}$ and $UMF12D_{1.25}$, and $UMF12K_{1.05}$ and $UMF12K_{1.25}$ were synthesized using the same procedures except the final $(F_1+F_2)/(U_1+U_2+M)$ ratio was adjusted to 1.05 and 1.25, respectively, by increasing or decreasing the second urea.

DMA sample preparation and runs

Resin UFA was mixed with 0.3, 0.5, or 0.8% ammonium sulfate based on liquid resin weight and the resin mix placed in water baths at four different temperatures (0, 15, 25, and 35°C). Resin mixes were taken from the water baths after 15, 90, and 180min, and

approximately 25 mg of mixed resin were evenly spread on fiberglass braid (16.15 × 10.95 × 0.12mm dimension). The resin-impregnated braid was clamped horizontally between the two DMA arms, the rigidity reading was zeroed for cancellation of braid effect, and curing was initiated (TI Instruments, DMA Model 983).[34] A fixed displacement mode with 0.80mm amplitude and 0.4Hz oscillation frequency were used. The temperature program started with an equilibration wait at 30°C, followed by increasing the temperature at a rate of 50°C/min to 120, 150, or 170°C and holding for 25 min. Duplicate runs were made but usually no significant differences in curves were observed for most runs. After cooling, cured samples were weighed and the thicknesses of samples measured for verification. Data from too high or low resin weights or thicknesses were discarded, and samples were rerun. Using the DMA instrument analysis software, the rigidity (storage modulus, G′), loss modulus (″), and tan delta (δ, G″/G′) curves were obtained. For UMF resins, the catalyst level was set at 0.5% ammonium sulfate, and resin mixes were kept for 15 min at 25°C; DMA runs were made similarly.

RESULTS AND DISCUSSION

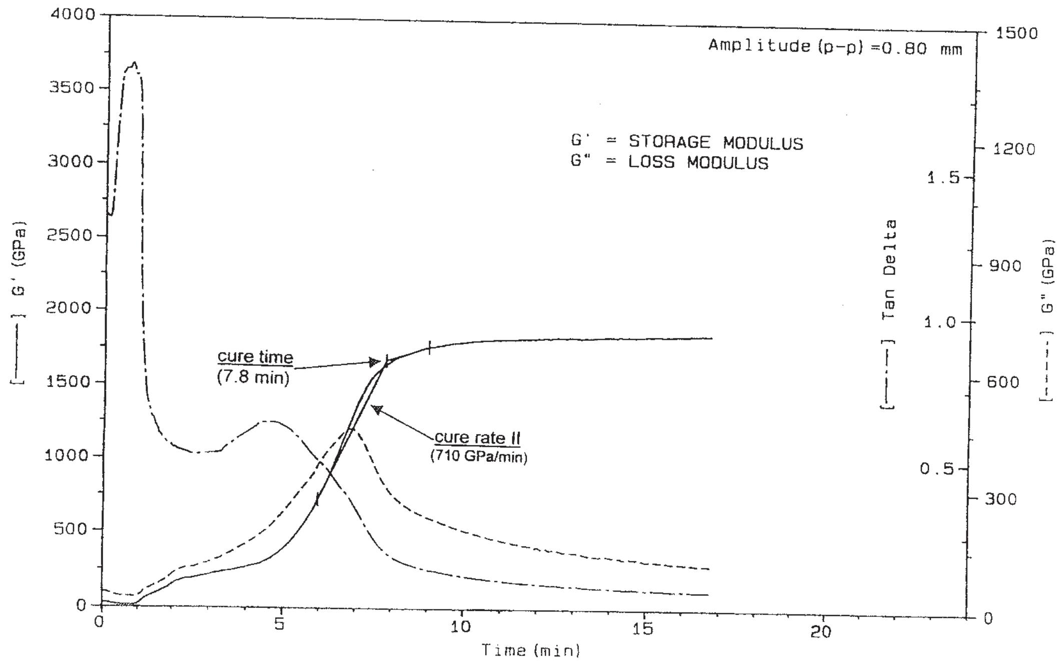
General DMA curing pattern of Resin UFA

DMA results of Resin UFA obtained at 120°C with 0.5% ammonium sulfate as catalyst are shown in Figure 2a. The rigidity curve started at a very small value (dried resin) and initially decreased to a lower value due to thermal softening (Fig. 2b). The rigidity curve then began to increase rapidly at about 60s during the temperature ramping period to reach a small value while the tan delta curve was rapidly decreasing toward 0.5, indicating that the gelation of the resin had occurred from the incipient formation of an infinite polymer network.[29] The time to reach the rigidity increasing point was defined as *gel time*. The rigidity increase continued until about 130s, with the rate of increase in this first segment defined as *cure rate I*. The curing temperature reached 120°C at about 110s and, therefore, the rigidity increase entailed the rigidity decreasing effect of the increasing temperature. In this early segment of cure, the loss modulus also increased due to the infinite polymer network being formed and expanded, and the tan delta curve decreased rapidly due to the more rapid increase in the rigidity than in the loss modulus. The loss modulus increase reflects the increased energy lost from the infinite polymer network being formed to uncured resin components that are thermally coupled to it. The amount of uncured resin components coupled to the infinite polymer network would increase as the polymer network grows, reflected as increasing loss modulus. The rigidity value attained in the first segment is small compared to the final rigidity value, and the significance of cure slope I to the overall curing is unknown. The second segment of cure began and continued until about 260s, a relatively long time, where both the rigidity and loss modulus increases were small, indicating a minimal expansion occurring in the infinite polymer network initially. The tan delta curve ranged between 0.6 and 0.7, reflecting the rubbery state of the sample at the measuring temperature.[35]

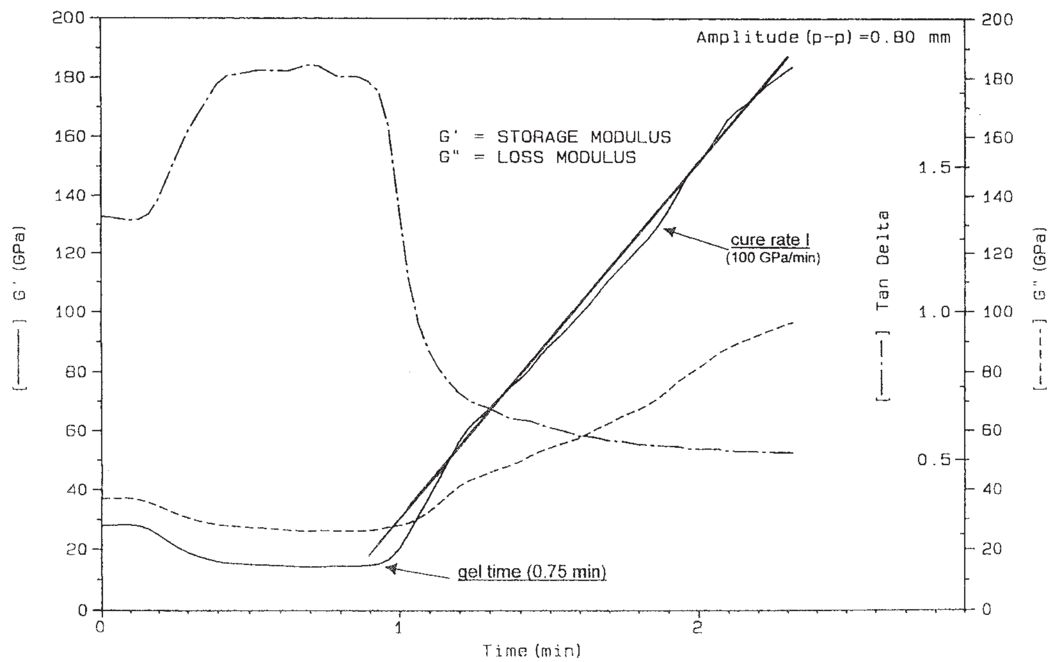
The third segment then began with rapidly increasing rigidity and rapidly decreasing tan delta curves and completed at about 480s, passing through the vitrification and further advancing to the highly elastic state. The rigidity and loss modulus curves reached the final values and the tan delta curve reached a very low value, indicating that most low molecular weight resin components were consumed. The rate of rigidity increase in this final segment was defined as *cure rate II*. Both the rigidity and loss modulus increased in the first part of this segment, and then the loss modulus reached the maximum at about 420s and then began to decrease. The loss modulus decrease reflects the decreasing level of uncured resin components remaining in the sample. At the loss modulus maximum, the rigidity value reached 1600GPa and the tan delta value decreased to 0.4, indicating that the vitrification point of resin at the measuring temperature had been passed.[35] The resin curing continued, and the rigidity reached a high plateau value (∼ 2800GPa) and the loss modulus a low plateau value (∼ 250GPa), with the tan delta decreasing to about 0.09 at the measuring temperature. The tan delta value was less than 0.05 when the cured sample was cooled and the DMA rerun at room temperature, indicating that a highly glassy state of resin was attained. The *cure time* of resin was defined as the time when the rigidity rise ended in this segment, as shown in Figure 2a. Furthermore, it is noted that the rigidity curve remained stable for the next 15 min, indicating that no appreciable degradation of the polymer network occurred.

The gelation and first segment of curing of Resin UFA

The DMA curing profile of Resin UFA (Fig. 2a) was generally similar to those of other UF and UMF resins studied in this work and represented by the three segments of rigidity development. That the second segment is relatively long and entails only a small increase in rigidity makes the gelation and first segment of curing stand out as an early gelation compared to DMA curing results of PF resins.[31,32] This early gelation, which implicates an appropriate hot pressing procedure in wood composites manufacturing, appears to arise from the presence of a minor fast-reacting component. In the curing of thermoplastic polymers to crosslinked products, such as in rubber



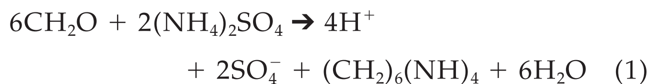
(a)



(b)

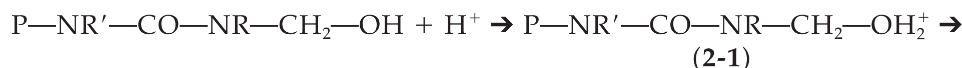
Figure 2 DMA results of Resin UFA (a) and (b) early curing stage at 120°C.

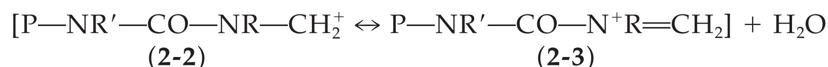
products, it has been shown that crosslinking at about 1–2% monomer level, or one out of 50–100 monomer units, would give the typical infusible rubbery products.[36] UF resins are composed of the first urea-derived polymeric components (~ 55%) with a broad molecular weight distribution and the second urea-derived monomeric components (~ 45%). UF resins are cured only in acidic pH, and ammonium salts of strong acids are commonly used as latent catalysts. Formaldehyde present in UF resins in small amounts[6] reacts with ammonium salts to generate free acid species and weakly basic hexamethylenetetramine (eq. (1))[14]:

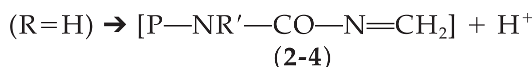


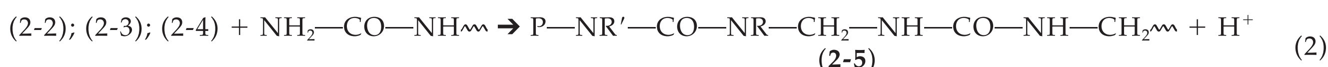
$$6CH_2O + 2(NH_4)_2SO_4 \rightarrow 4H^+ + 2SO_4^- + (CH_2)_6(NH)_4 + 6H_2O \quad (1)$$

The free acid activates hydroxymethyl groups of UF polymers by forming an acid complex (**2–1**), dissociates into the cationic methylene intermediate (**2–2**), resonance stabilized to an amidinium ion (**2–3**) and, when the substitutent on the nitrogen is hydrogen, convertible to an imine group (**2–4**).[14,25,37] The reaction intermediate reacts with a urea amide group to form methylene bonds (**2–5**) (eq. (2)):

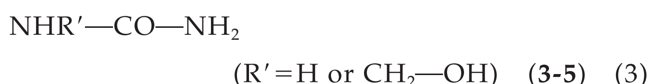








The early gelation in curing of UF and UMF resins appears to be traced to certain polymeric UF resin components and structures. Polymeric UF resin components are branched at every three or four urea units via methylene and methylene-ether groups and harbor ample amounts of Type I (**3–1**) and Type IIt and IIi hydroxymethyl groups (**3–2**, **3–3**).[23,24,25] The branching includes gem di-substituted urea units (**3–4**), located in the middle of polymer chains, with concentration increasing as resins are aged due to the reverse reaction of hydroxymethyl groups. The free amide groups of monomeric UF resin components (**3–5**) are present in high concentration due to the second urea addition.[6]



It was shown that Type I hydroxymethyl groups, in acidic pH of resin synthesis, react fast with (monomeric) free urea amide groups (**3–5**) but very slowly with imide groups (eq. (2)).[20] On the other hand, Type IIt/IIi hydroxymethyl groups (**3–2**, **3–3**) are relatively unreactive since the cationic methylene intermediate to be formed would not be resonance-stabilized compared to Type I hydroxymethyl groups because the amidinium ion intermediate (**2–3**, R=CH_2OH) would not be as readily formed, nor converted to the imine intermediate (**2–4**). In the first stage of curing, Type I hydroxymethyl groups of high molecular weight fractions would react not only with monomeric urea amide groups (**3–5**) to extend linear polymer structures, but also with the unsubstituted amide groups of gem di-substituted urea units (**3–4**). The latter type of reactions will result in a fast molecular weight increase and crosslinking, such as the early gelation of UF resins observed. The concentration of gem di-substituted urea groups (**3–4**) in fresh resins can be low because amide groups of polymeric resin components are mostly bonded to hydroxymethyl groups, but it would increase by the reverse hydroxymethylation reactions after the second urea addition. This reversal occurs relatively slowly at room temperature but faster at elevated temperatures, and one UF resin that was post-treated at 60°C in alkaline pH for several hours was found to have the gem di-substituted urea group increased to 0.17 group per mole of the first urea (U_1), 1 out of about 6 urea units.[24] The early gelation tendency of UF resins might be the cause of the precuring problems often occurring in industry when the wood acid level in board mat or the ambient temperature exceeds the norm, gelation of resin before the hot press is completely closed. Further study by varying the branching extent of UF polymers and minimizing the gem di-substituted free amide group content would be useful in efforts to minimize the precuring tendency of UF resins.

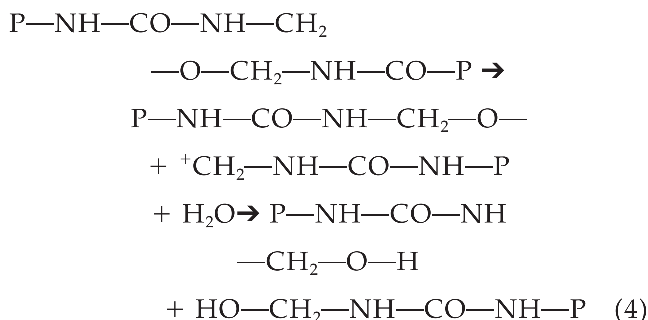
Curing of Resin UFA in the second segment

In the second segment of curing (Fig. 2a), both the rigidity and loss modulus increased very slowly in comparison to those in the first or last segment. The underlying mechanism for this segment remains unclear, but it may be that the small resin molecules react

TABLE I
DMA Results of Resin UFA Obtained with Ammonium Sulfate Catalyst and Various Mix Parameters

Catalyst mixing parameters			DMA results			
Catalyst (%)	Mix. temp (°C)	Mix. time (min)	Gel time (min)	Cure rate I (GPa/min)	Cure rate II (GPa/min)	Cure time (min)
0.5	0	15	0.75	150	787	5.8
		90	0.75	150	784	5.9
		180	0.75	67	520	5.8
	15	15	0.76	290	667	7.5
		90	0.76	150	427	7.8
		180	0.73	180	400	7.9
	25	15	0.74	100	710	6.9
		90	0.72	120	674	7.0
		180	0.7	140	867	7.8
	35	15	0.59	200	767	7.4
		90	0.65	250	467	8.0
		180	NA	NA	NA	NA

among themselves or with larger polymers only to extend the linear polymer structures. Alternatively, the reaction that occurs in the first segment may have slowed down because of depletion of the reactive fractions discussed above. It is also possible that polymers are forming while other polymer structures are breaking down. UF polymer chain structures consist of methylene (~ 80%) and methylene-ether (~ 20%) bonds, and the latter group is known to break down at elevated temperatures, such as during the curing of resins (eq. (4))[14]:



Such breakdown would delay the development of rigidity. Investigation on ways to vary the methylene-ether group content and resultant curing behavior would be worthwhile in efforts to shorten the overall curing time.

Curing of Resin UFA in the third segment

In this segment, the rigidity rises rapidly to a high value, and the loss modulus peaks and then decreases to a low plateau value, reaching the typical highly glassy state (Fig. 2a). This characteristic is similar to that observed with other highly crosslinking thermosetting resins, such as phenol-formaldehyde resins,[31,32] and suggests that crosslinking (**5–1**) by methylene groups occurs extensively (eq. (5)). Reactions between Type IIi hydroxymethyl groups and imide groups appear to occur primarily in the final curing stage (eq. (5)):

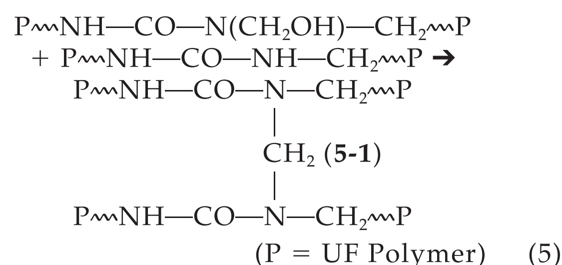


TABLE II
DMA Cure Time, Cure Rate II, and Gel Time of Resins Obtained at Various Temperatures

	Cure temp (°C)	Resins				
		UFA	UMF6K	UMF6D	UMF12K	UMF12D
Cure time (min)	120	8.5	12.4	13.7	16.2	18.3
	150	5.7	8.5	10.8	9.2	10.8
	170	4.5	7.5	8.5	6.3	6.5
Cure rate II (GPa/min)	120	258	188	191	123	89
	150	525	291	253	295	256
	170	180	240	206	330	266
Gel time (min)	120	0.67	1.05	1.12	1.15	1.17

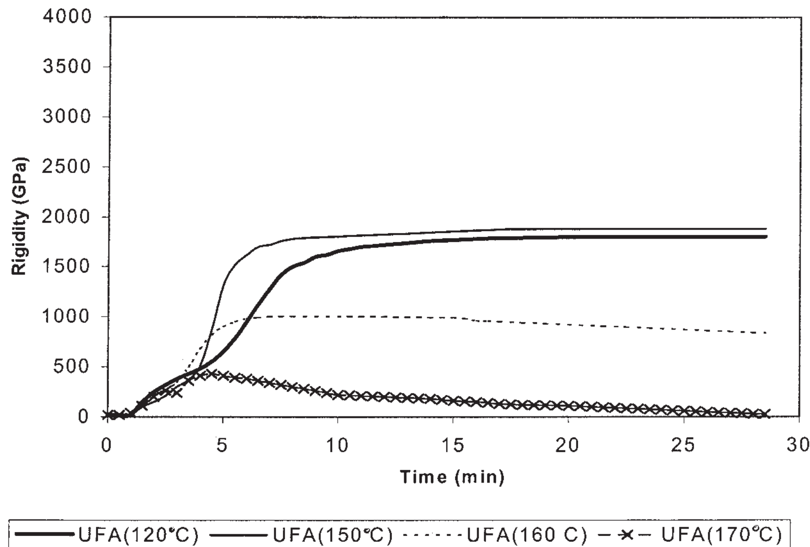


Figure 3 DMA rigidity curves of Resin UFA obtained at different curing temperatures.

Although UF resins are the main cause of formaldehyde emission from particleboard, the amount of formaldehyde lost in curing of boards constitutes only a very small fraction of the total formaldehyde used in resin manufacture.[38,39] Therefore, the current F/U mole ratio, about 1.15, can be reasonably equated with the methylene group content in cured resins, which corresponds to a crosslinking level of about 30%, or 1 crosslinking methylene-bond (**5–1**) for every 3.3 urea units. This level of crosslinking is relatively very high for a thermosetting resin,[35] and the characteristics shown in the third segment of curing of Resin UFA appear to be in accord with the relatively high crosslinking level expected from this F/U mole ratio. On the other hand, the strength of boards and the durability in water soak tests only slowly improve when the F/U mole ratio of resins is increased from 1.15. However, it appears that the higher the crosslinking extent, the better the cured resins' performance, perhaps up to 1.5.

Catalyst level, mix time, and temperature effects on DMA curing of Resin UFA

Gel time, cure slope I and II, and cure time obtained for Resin UFA at 0.5% ammonium sulfate catalyst level with mix time of 15, 90, and 180min at 0, 15, 25, and 35°C are reported in Table I. Similar data obtained at 0.3 and 0.8% catalyst levels (not reported) indicated that the 0.3% level was short but the 0.8% level did not

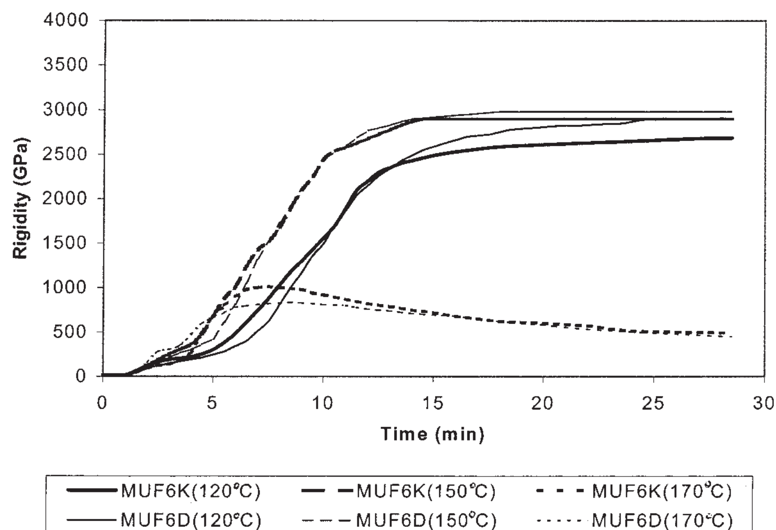


Figure 4 DMA rigidity curves of Resins UMF6D and UMF6K at three different temperatures.

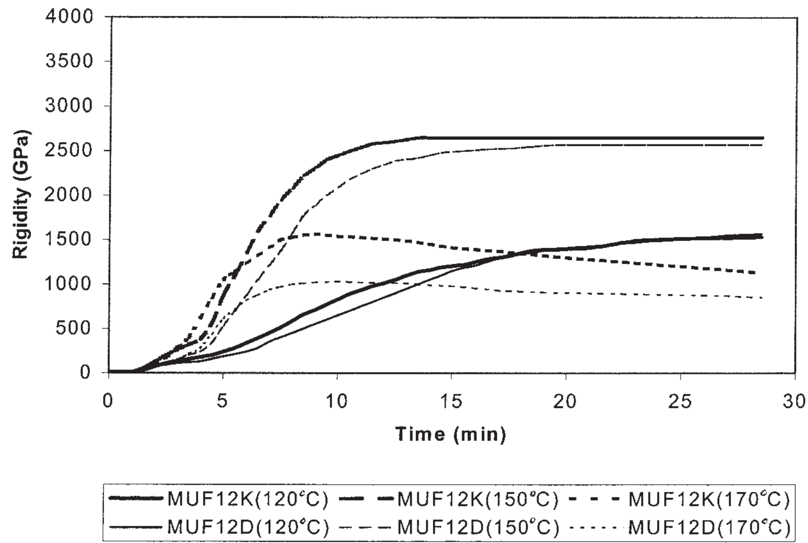


Figure 5 DMA rigidity curves of Resin UMF12D and UMF12K at three different temperatures.

show much effect from the increased catalyst amount. Gel times generally shortened with increasing mix times except at 0°C and did not change significantly at different temperatures except at 35°C. All resin mixes made with 180-min mix time at 35°C gelled before the DMA run. Cure rate I increased as the mix time and catalyst level increased, except at mix temperature 0°C, similar to the shortening of gel times. It may be that the polymer components that cause gelation continue to react in the first segment of curing. Therefore, the precuring tendency of UF resins may be predicted from gel time and cure rate I.

Cure rate II values decreased as the resin mix time increased from 15 to 180min at all temperatures except at 0°C, indicating that the resin advancement occurring in resin mixes hampers rigidity development in the final segment. The reason for this is unclear. It may be that the polymer fraction that advances in resin mixes and perhaps also in the early part of curing appears to have different, less optimal polymer structures in comparison with those obtained in the final segment of curing. On the other hand, higher catalyst levels generally resulted in higher cure rate II values. Cure time values were shortest for the resin mixes made at 0°C, a result of higher cure rate II values ascribable to the little advancement incurred in resin mixes. Wood composites binder resins that cure fast in the final curing stage would be desirable for process reasons. Overall, the results indicate that UF resins tend to advance in resin mixes by catalysts that can engender precure problems and hamper the proper curing in

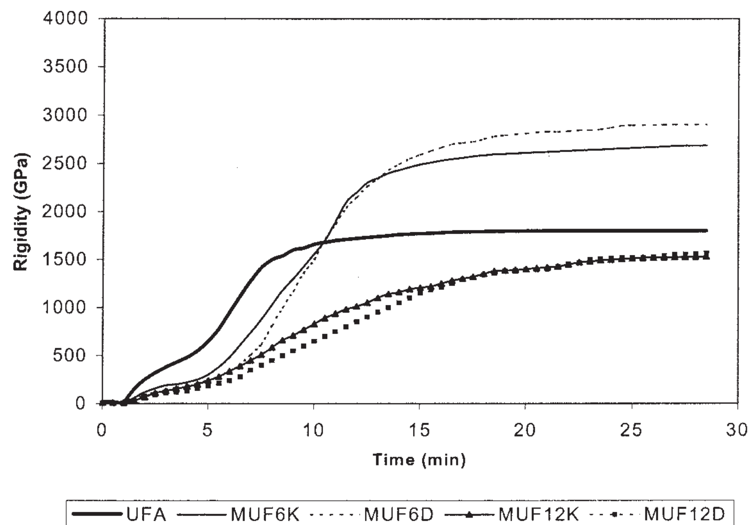


Figure 6 Comparison of DMA rigidity curves of UFA and various UMF resins at 120°C.

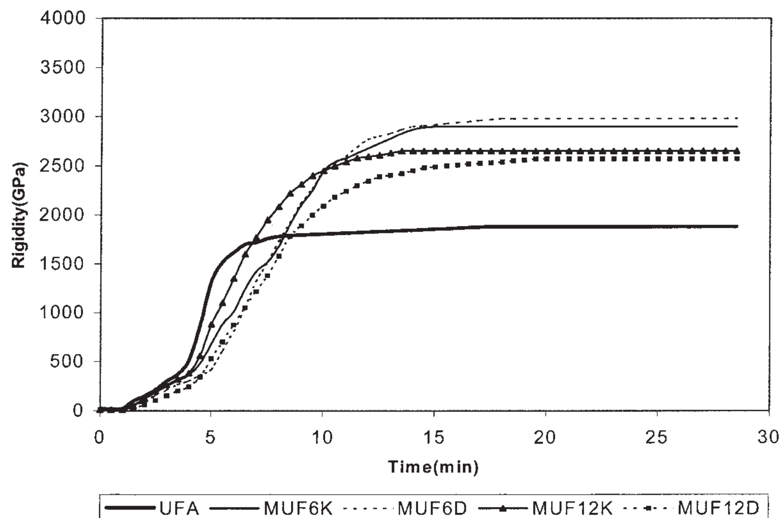


Figure 7 Comparison of DMA rigidity curves of Resin UFA and various UMF resins obtained at 150°C.

the final segment. The low mix temperatures and short mix times preferred in industry thus appear proper.

DMA of Resin UFA and UMF resins at various temperatures

DMA of UF and UMF resins were isothermally conducted at 120°C, 150°C, and 170°C to compare the curing parameters. Resins were mixed with 0.5% ammonium sulfate catalyst at room temperature for 10 min (Table II). The cure rate II values of UF and UMF resins increased as the temperature increased from 120 to 170°C, with the latter resins increasing to lower values at all temperatures. Furthermore, the cure rate II values of UMF12K and 12D were lower than those of UMF6K and 6D, a slower curing by increasing melamine levels from 6 to 12%. This melamine level effect was most pronounced at 120°C. The reason for melamine's cure retarding effect has been ascribed to the higher basicity of melamine than urea to tie up the acid catalyst generated.[27] On the other hand, Resins UMF6K and 12K showed higher cure slope values than Resins UMF6D and 12D, reflecting the base UF resins' extent of polymerization increased from D to K viscosity. The cure times of these resins also led to the same conclusions. This observation may be useful in synthesizing UMF resins, especially at relatively low levels of melamine usage: the urea components, present in large proportions, need to be preadvanced to appropriate extents before melamine addition.

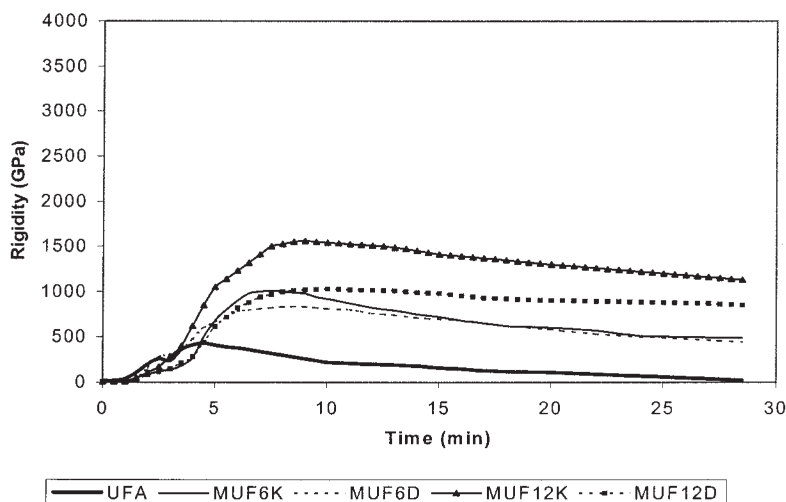


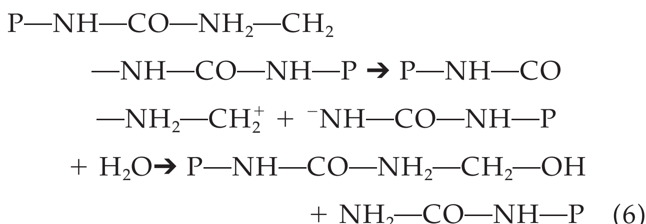
Figure 8 Comparison of DMA rigidity curves of Resin UFA and various UMF resins obtained at 170°C.

TABLE III
DMA Cure Rate II and Cure Time of Resins at Different {F/(U + M)} Mole Ratios

F/(U + M)	Cure rate II (GPa/min)			Cure time (min)		
	UFA	UMF6D	UMF12D	UFA	UMF6D	UMF12D
1.05	340	270	150	5.7	9.2	10.9
1.15	500	320	260	4.5	8.7	9.5
1.25	900	520	510	4.3	5.7	8.0

Final rigidity values attained and optimum curing temperatures

The final rigidity values of Resin UFA (Fig. 3) were very high at 120 and 150°C ascribable to the optimum curing temperatures used. However, the rigidity value decreased at 160°C and more significantly at 170°C and when kept for 25min at 170°C it decreased to zero, reflecting the cured resin's complete degradation. In industry, particleboard bond strength decreases are often observed and traced to over-cure of resins. Thus, methylene bonds of cured UF resins appear to begin to break down at an appreciable rate at 160°C (eq. (6)):



$$\mathrm{P{-}NH{-}CO{-}NH_2{-}CH_2{-}NH{-}CO{-}NH{-}P} \rightarrow \mathrm{P{-}NH{-}CO{-}NH_2{-}CH_2^+} + \mathrm{{}^-NH{-}CO{-}NH{-}P} + \mathrm{H_2O} \rightarrow \mathrm{P{-}NH{-}CO{-}NH_2{-}CH_2{-}OH} + \mathrm{NH_2{-}CO{-}NH{-}P} \quad (6)$$

In industry, hot pressing is usually conducted at 150–170°C for about 3 min for 0.5″ thick boards, with the temperature and time often adjusted for different furnish characteristics and ambient temperature to maximize the production and performance properties. Over-cure of resin occurs more often in the hotter surface layers, and the potential degradation is minimized by cooling boards shortly after the hot pressing.[9]

The final rigidity values of UMF resins varied significantly with the curing temperature and melamine level (Figs. 4 and 5). Resins UMF6D, 6K, 12D, and 12K all showed higher rigidity values at 150°C than 120°C, a more complete cure at the higher temperature, but the rigidity values all decreased at 170°C. If comparing the results at 120°C (Fig. 6), Resins UMF6D and 6K showed higher rigidity values than Resins UMF12D and 12K, a less effective cure due to the higher melamine content at the low temperature. At 150°C (Fig. 7), all UMF resins cured well and the final rigidity values of Resin UMF12 were higher than Resin UMF6, reflecting the higher melamine level and an adequate temperature. This result is expected from the higher functionality of melamine, 3.0 or higher, in comparison to the lower functionality of urea, about 2.3, as well as other molecular characteristics. Furthermore, although the final rigidity value of Resin UMF6D was similar to UMF6K at 150°C, the rigidity of Resin UMF12K was higher than that of UMF12D. Thus, the extent of polymerization of the UF base resin also affects the final rigidity value, indicating that the UF base resin needs to be advanced to an appropriate level for optimum strength, as well as for faster cure

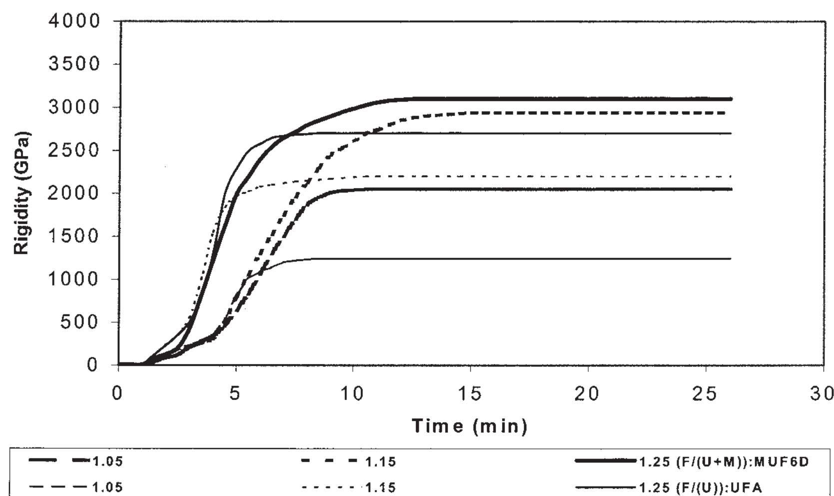


Figure 9 DMA rigidity curves of Resins UFA and UMF6D at three different F/(U+M) mole ratios.

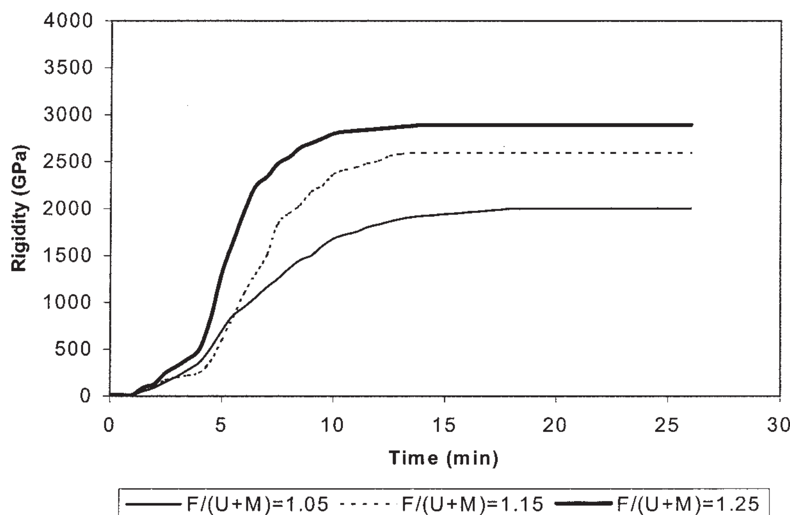


Figure 10 DMA rigidity curves of Resin UMF12D at three different F/(U+M) mole ratios.

rate as discussed above. If the UF resin components in UMF resins were under-advanced, an overall incomplete cure might result, especially in the presence of melamine with its higher basicity that lowers the activity of the acid catalyst. These final rigidity results, which can be considered contradictory if considered without the curing temperature, appear to explain the fluctuating strength values of UMF resin-bonded boards observed in past research.

As discussed above, all resins showed degradation at 170°C. However, UMF resins resisted the degradation increasingly better with increasing melamine levels (Fig. 8). While Resin UFA cured and held at 170°C for 25 min lost all rigidity value, Resin UMF6D and 12D degraded to 25 and 65%, respectively, under the same condition, in comparison to the strength value of Resin UFA obtained at 120°C. Thus, the MF components lessen the over-curing of resin. It may be that the higher basicity of melamine reduces the activity of acid catalysts remaining in cured resins and/or the methylene bonds of MF polymers are more resistant to heat degradation. This degradation resistance of UMF resins would be the parameter that needs to be investigated in depth in efforts to maximize the beneficial effects of the higher cost melamine.

Resins made with different final F/(U+M) mole ratios cured at 150°C

Resins UFA, UMF6D, and UMF12D made at F/(U+M) ratios of 1.05, 1.15, 1.25, respectively, were cured at 150°C for F/(U+M) mole ratio effects (Table III, Figs. 9 and 10). The results indicate that Resins UMF6D and 12D have longer cure times than Resin UFA for all mole ratios, indicating the melamine's cure-retarding effect is not overcome by the mole ratio increase. However, the cure times of all resins decreased slightly as the mole ratio increased from 1.05 to 1.25, and the cure times for UMF resins decreased somewhat more than Resin UFA. Similarly, the cure rate II values of all resins increased as the mole ratio increased from 1.05 to 1.25, as expected by the higher functionality. The cure rate II values of Resin UMF6D and 12D were lower than that of Resin UFA at all mole ratios (Table III), and the cure rate II value of UMF12D was lower than that of UMF6D at all mole ratios. These melamine level and base UF resin effects agree with the discussion made above with the mole ratio of 1.15, although the cure rate II value differences were smaller at higher mole ratios, indicating that the delay of resin cure due to melamine is partly compensated by higher mole ratios. The final rigidity values for all resins were higher at higher mole ratios, and the rigidity values of Resin UMF6D and 12D were higher than that of Resin UFA at all mole ratios. Overall, the final rigidity values of UMF resins at mole ratio of 1.05 are comparable with those of Resin UFA with a mole ratio of 1.15. Thus, UMF resins might be useful at lower F/(U+M) mole ratios than UF resins to give particleboard with similar strength but have reduced formaldehyde emission.[16]

CONCLUSIONS

DMA gel time, cure time, and cure rate values of UF and UMF resins measured at 120 ~ 170°C were found to be useful in optimizing resin formulation, catalyst level and mix time, and curing temperature and time. DMA curing of UF and UMF resins showed a distinctive three-segment curing pattern: gelation with a small increase in rigidity; rubbery state over a relatively long period of time; and a rapid increase in rigidity to vitrification and to high modulus state.

Each stage was characteristic of various resin syntheses and catalyst mixing parameters. Higher temperatures shortened the overall cure of resins. Optimum catalyst levels were between 0.5% and 0.8% based on liquid resin weight. With this level of catalyst, the gel time decreased but the cure rate II slowed as the catalyst mix time increased, indicating that the advancement of resins incurred in resin mixes could degrade the final modulus development. For UMF resins, the higher advancement of the UF base resin increased the cure rate II and shortened cure time. The cure times of UMF resins were longer than UF resins and increased with melamine levels, suggesting that higher temperatures are needed to cure UMF resins in practice. The final rigidity and thermal stability of cured UMF resins were higher than those of cured UF resins and increased with increasing melamine levels and, therefore, the thermal degradation often observed in UF resin-bonded particleboard would be lessened with UMF resins. The resultant higher rigidity values of UMF resins would allow the F/(U+M) ratio to be lowered to reduce formaldehyde emission of particleboard compared to UF resins, without lowering the strength properties.

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