Thermoplastic Modification of Urea–Formaldehyde Wood Adhesives to Improve Moisture Resistance

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ABSTRACT: Urea–formaldehyde (UF) resins are prone to hydrolytic degradation, which limits their use to indoor applications. This study examined the modification of UF resin with various thermoplastics as a means to increase the moisture resistance of the adhesive. UF adhesives were modified *in situ* with various hydrophobic and hydrophilic thermoplastic formulations, using either polar or nonpolar initiators. Unmodified and modified UF resins were characterized in terms of viscosity, pH, and gel time in their prepolymer suspension state. Cured solid UF resin plaques were prepared to isolate moisture sorption effects of the cured UF resin from that of the wood component in composites, which dominates their moisture uptake. Relative crosslink density and moisture sorption tests were run on cured UF resin plaques. Results indicated that viscosity increased after modification in most cases, with higher viscosities resulting from formulations using an acidic (polar) initiator. In all cases, activation energies of the curing reactions of thermoplastic-modified UF suspensions were lower than the unmodified UF. High relative crosslink density compared to the unmodified UF was found for one sample, which correlated well with lower overall moisture sorption. Higher relative crosslink density of cured UF resin plaques appeared to be an indicator of lower moisture uptake. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4222–4229, 2006

Key words: urea–formaldehyde resin; thermoplastic; modification; moisture resistance; gel time; viscosity; crosslink density; activation energy

INTRODUCTION

Urea–formaldehyde (UF) is an inexpensive thermosetting adhesive that is used extensively in wood composite products, including particleboard and medium density fiberboard (MDF).[1–5] In 1998, over 14 million cubic meters of particleboard and MDF were produced in North America, with UF resin as the primary adhesive.[5] Urea–formaldehyde is the least expensive of the commercial adhesives used in wood composite products, and thus is desirable for wood bonding.[1–4] However, UF resin also has the lowest moisture resistance of the major wood adhesives, which limits its practical use to indoor products only.[1–5] The limited ability of UF to resist moisture is caused by: (i) the brittleness of the adhesive, which allows the cured resin to crack and allow moisture to penetrate into the bonded product, and (ii) chemical breakdown at the amino bonds within the cured thermoset.[2,3] Heat and moisture together further accelerate the hydrolysis process.[1,4] An effective modification of UF resin to improve moisture resistance would greatly increase the market for these adhesives.

Improving the moisture resistance and toughness of UF-bonded wood composites has been a focus of research for several decades.[2,4,6] Improvements in both moisture resistance and overall composite toughness have been demonstrated through the manipulation of process variables, such as resin content, wood type and moisture content, wood particle geometry, etc.,[7–10] or through increasing the formaldehyde-to-urea molar ratio of the UF adhesive itself.[1,4,11] Greater moisture resistance has also been reported when additives, such as amines or thermoplastics, were incorporated into the UF resin.[12–16]

Rachtanapun and Heiden investigated the effect of hydrophilic and hydrophobic thermoplastic additives on the properties of UF adhesives to improve both toughness and hydrolytic resistance of UF-bonded wood composites.[17,18] Acrylic thermoplastic copolymers with different degrees of hydrophilicity were first prepared by free-radical polymerization, then isolated and added to the UF resin at 8% w/w UF suspension. Wood composites manufactured with the thermoplastic-modified UF adhesives had greater impact strength than unmodified control specimens. However, the polymerization, isolation, and blending of the thermoplastics with the UF resin was time-

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consuming, and only a few thermoplastic polymers could be successfully blended into the UF.

Das found the thermoplastic monomer and initiator could be added directly into a concentrated UF slurry to polymerize the monomers *in situ*.[19] After polymerization, the UF solids concentration was restored, resulting in modified resins that had lower viscosities than those reported by Rachtanapun. The impact strength of wood flour composites prepared with thermoplastic-modified UF resin increased, compared to those prepared from unmodified UF. Some formulations also showed greater moisture resistance than the control under controlled humidity tests. However, both time and energy were expended in concentrating the UF resin, which would likely be too costly to be industrially viable. In addition, the data indicated a need to isolate the moisture effects on the thermoplastic-modified UF resin from the moisture effects on the wood flour composites.

Carlborn improved upon the method of Das by eliminating the concentration step and simply adding the acrylic monomers and initiator into the UF adhesive as received from the manufacturer. An effective cure cycle was also developed to prepare solid UF resin plaques (2–3 mm thick) from modified and unmodified UF, which allowed moisture effects on the UF to be studied separately from the wood composite.[20] The moisture uptake of wood composites is dominated by the effects of the hygroscopic wood component, which comprises 80–90% of the composite. Curing the resin separately into solid, thick plaques of reproducible size allowed the moisture uptake behavior of the resin itself to be evaluated. Several formulations of thermoplastic-modified UF plaques absorbed less moisture than the unmodified control. However, only one type of thermoplastic-modified UF resin outperformed the control in mechanical property tests on particleboard made with thermoplastic-modified UF resin.[20] Although significant improvements in moisture resistance of the UF resin were observed, no attempt was made to study the curing kinetics of the resins. In addition, increased crosslink density of the cured resin was suggested as a possible reason for superior moisture resistance in the formulations that outperformed the control samples, but this relationship was not fully explored.

To study the effects of thermoplastic modification on the curing kinetics of modified UF resins and to further investigate the moisture resistance of the cured resin plaques, three formulations with high-moisture resistance, including the one with improvements in mechanical properties of particleboard, from Carlborn's work were chosen for further investigation. The objective of this research is to investigate the curing kinetics of the modified UF resins, and to develop relationships between relative crosslink density of cured UF plaques and their moisture sorption behavior.

MATERIALS AND METHODS

Materials

The liquid UF resin used in this study was Dynea Prefere^{TM} UF resin, donated by Dynea, Inc (Springfield, OR). The solid content, pH, and viscosity at 25°C were 62.4%, 7.72, and 140 cP, respectively. Acrylic monomers used for thermoplastic modification included acrylamide, 97% (AM), and methyl methacrylate, 99% (MMA). The 2,2′-azobisisobutyronitrile, 98% (AIBN), and 2,2′-azobis(2-methylpropionamidine) dihydrochloride, 97% (V-50), were used as free-radical initiators and ammonium persulfate (98%) was utilized as a catalyst. Ammonium chloride (99%) was used to prepare a saturated solution for moisture sorption tests. All of these chemicals were purchased from Sigma-Aldrich Chemical Company (Milwaukee, WI). A silane-containing monomer, ureidopropyltriethoxysilane, 50% (U-Si) was purchased from Gelest Inc. (Tullytown, PA) and also used as a thermoplastic modifier. All chemicals were used as received unless otherwise mentioned.

Modification of UF resin with thermoplastics

As mentioned, formulations used in this work were selected because of superior reduced equilibrium moisture sorption compared to the UF control and increased mechanical properties of particleboard observed by Carlborn.[20] Thermoplastic-modified UF resins were prepared by polymerizing acrylic monomers *in situ* in the presence of UF resin as received. Both hydrophilic (acrylamide or AM) and hydrophobic (methyl methacrylate or MMA and ureidopropyltriethoxysilane or U-Si) monomers were used. On the basis of the total amount of thermoplastic, AM and MMA were combined in a 10:2 weight ratio for AM:MMA (10:2). AM, MMA, and U-Si were mixed at 4:2:2 weight ratio for AM:MMA:U-Si (4:2:2). A third formulation consisted only of U-Si. Thermoplastic formulations for each modification in 200 g of UF prepolymer suspension are summarized in Table I.

The thermoplastic content of the modified UF resin was set at 5% by weight of UF solid in the UF resin suspension. In formulations with initiator, either polar V-50 (acidic) or nonpolar AIBN was added to the system at 2 mol % of the total thermoplastic monomers to initiate polymerization and to impart either polar or nonpolar end groups to the thermoplastic polymer. While formulations containing AM and MMA were polymerized using free-radical initiators, the U-Si was expected to react into the UF network itself during crosslinking, and thus did not need an

TABLE I
Thermoplastics and Initiators Used for the Modification of UF Resins

Monomer formulations	Initiators	Thermoplastic modifiers		
		AM	MMA	U-Si
AM:MMA (10:2)	V-50, 0.0017 mol	5.20 g; 0.0732 mol	1.11 mL; 0.0104 mol	
	AIBN, 0.0017 mol	5.20 g; 0.0732 mol	1.11 mL; 0.0104 mol	
AM:MMA:U-Si (4:2:2)	V-50, 0.0013 mol	3.12 g; 0.0439 mol	1.67 mL; 0.0156 mol	3.12 g; 0.0059 mol
	AIBN, 0.0013 mol	3.12 g; 0.0439 mol	1.67 mL; 0.0156 mol	3.12 g; 0.0059 mol
U-Si	None			12.48 g; 0.0236 mol

initiator.[20] The monomers and initiators were blended together if they were soluble, or if the initiator was insoluble in the monomers, it was first dissolved in water and then the aqueous solution was blended with the monomers. The monomer/initiator mixture was then added to UF resin (200 g of 62.4% solid) that had been preheated at 65°C in a 400-mL flask. The mixture was stirred at 300 rpm with a mechanical stirrer and maintained 65°C for 1.5 h to polymerize the monomers in the presence of the UF resin.

Viscosity measurement

In the commercial manufacture of particleboard, UF is spray-applied to wood particles before mat forming and compression molding. This process requires that the UF resin viscosity not exceed 500 cP at 25°C.[21] The viscosity of unmodified and modified UF resin suspensions were recorded to determine whether the modified resins met this requirement. A Brookfield LVDV II+ Pro programmable viscometer (Brookfield Eng. Lab., Inc., Middleboro, MA) with Wingather software (version 2.1) and Thermosel system was used to measure the viscosity of unmodified and thermoplastic-modified UF resins at 25°C. An 8 g aliquot of UF resin was tested using the Thermosel system to control sample temperature at 25 (± 0.1)°C. An SC4–18 spindle was used for all viscosity measurements. Viscosity was measured four times per minute for 15 min at 4 rpm, and average viscosity was calculated.

Solids content and pH

Approximately 2 g of unmodified or modified UF resin suspensions were weighed into a preweighed aluminum weighing dish and placed in a convection oven at 105°C. The samples were maintained at this temperature until equilibrium mass was achieved. The solids content was calculated as the weight of the dry sample divided by the initial weight of the sample, multiplied by 100. An Oakton pH CON 510 pH meter was used to measure the pH of unmodified and modified UF resin suspensions at 25°C. Three replicates were made for each resin type under both tests.

Determination of gel time and activation energy

Gel time depends on the rate of the curing reaction, and can be an indication of how quickly the resin will begin to cure in composites under a given pressing condition. Gel times of all thermoplastic-modified UF resins were determined using a Sunshine gel time meter (Davis Inotek, Philadelphia, PA) at temperatures of 110, 120, 130, and 140°C. Ammonium persulfate curing catalyst (0.1 wt % based on the weight of UF resin) was dissolved in 1 mL of water and added to 100 g of UF resin. A 5 g portion of this mixture was then used to measure the gel time. Three replicates were run for each unmodified and thermoplastic-modified UF resin sample.

Gel time data were used to calculate the activation energy of the crosslinking reaction for unmodified and thermoplastic-modified UF resins. A preliminary assumption was made that the curing process of the resin at a given temperature would be a linear function until the gel point was reached. Since the reaction rate is a function of increasing temperature, the activation energy (E_a) can be calculated on the basis of the Arrhenius equation:

$$\ln k = \ln A - \left(\frac{E_a}{R}\right)\frac{1}{T} \tag{1}$$

where k is the rate constant (1/s or 1/gel time); A is the pre-exponential constant; E_a is the activation energy (J/mol); R is the gas constant (J/mol/K); and T is the absolute temperature (K).

Molding of neat resin plaques

To explore moisture sorption kinetics and the crosslink density of cured UF resin, unmodified and thermoplastic-modified UF resins were cured into solid resin plaques with dimensions of 38 × 38 mm^2 and 3 mm thickness. A curing catalyst, ammonium persulfate (0.1 wt % of UF resin), was first dissolved in a 2 mL of water and added to 200 g of modified UF, followed by mixing with a mechanical stirrer for 5 min at 250 rpm. Aluminum molds (38 × 38 mm^2 and 3 mm thick) were filled with UF resin and placed in a convection oven preheated to 40°C. After 2 h, an aluminum plate weighing 2 kg was placed on the samples to compress the resin and yield a flat surface. The molding was continued for an additional 14 h at 40°C, so that samples precured for a total of 16 h at that temperature. After 16 h, temperature was increased to 100°C and held for 1 h, and then raised to a final curing temperature of 135°C for 2 min. Heat was then discontinued and the samples remained in the oven until they had cooled to room temperature. The cooled resin plaques were removed from the molds and conditioned in a desiccator for 5–7 days before being used for the moisture sorption tests and crosslink density measurements.

Relative crosslink density

Crosslink density is an important factor, which governs the physical properties of cured thermoset resins.[22] In Carlborn's work, high relative crosslink density was suggested as a means to increase moisture resistance of cured UF resin plaques, although the correlation was not investigated fully.[20] Higher crosslink density would simply provide more bonds within a given area, which must be hydrolyzed to break down the UF structure, allowing moisture to penetrate into the sample.

Several methods exist to measure crosslink density of cured thermosets.[23] Two of the most commonly used methods are to (i) measure the equilibrium swelling of the cured thermoset in a solvent and (ii) measure the modulus of the cured resin above the glass transition temperature. Solvent swelling data can give absolute values for crosslink density only when accurate values of the Flory-Huggins polymer–solvent interaction parameter are available. When this parameter value is not known, equilibrium swelling can be used only as a measure of the relative crosslink density. Since no polymer–solvent interaction parameters for cured UF were available, relative crosslink density was measured on unmodified and thermoplastic-modified UF resin plaques using an equilibrium swelling method.

UF plaques were weighed and placed in a jar of methyl alcohol. Samples were removed and wiped dry with a tissue and then reweighed. This process was repeated regularly until equilibrium mass was reached. The initial mass and the equilibrium mass after swelling were used to calculate the swell ratio, which is indicative of the relative crosslink density. Equilibrium swelling of the cured UF plaques was calculated using eq. (2):

$$Q = \left[\left(\frac{W_s - W_0}{W_0}\right)\right]100 \qquad (2)$$

where W_s and W_0 are the weights of the fully swollen and unswollen UF plaques, respectively. The inverse of Q represented relative crosslink density. Three replicates were made for each resin type.

Moisture sorption study

Moisture sorption tests were performed on cured UF resin plaques to explore the kinetics of moisture uptake for thermoplastic-modified UF resins. This test was intended to separate moisture effects of the adhesive from the effects of the hygroscopic wood component in the composite, since the wood component comprises 80–90% of typical UF bonded wood composites.[20] For the moisture sorption test, a saturated ammonium chloride solution was placed in a sealed chamber to provide a constant 79.5% relative humidity (RH) at 20°C, which is equivalent to equilibrium moisture content of ~16%. Samples, which had been weighed before being placed in the chamber, were removed from this chamber and weighed at various intervals until equilibrium mass was obtained. At least four replicates were tested for each resin type.

From the mass values, percent moisture content (MC) of each sample at time t was calculated by eq. (3):

$$\mathrm{MC} = \left[\left(\frac{M_t - M_0}{M_o}\right)\right]100 \qquad (3)$$

where M_t is the mass of the sample at time t, and M_0 is the initial mass of the dry sample.

Moisture uptake curves were derived from the data obtained with eq. (3). From these curves, a moisture uptake rate was defined to quantify how quickly the moisture sorption process occurred in the samples. Thus, the rate of moisture uptake (MU) was defined as:

$$\mathrm{MU} = \frac{\Delta \mathrm{MC}}{\Delta t} \qquad (4)$$

where ΔMC is the change in moisture content (%) and Δt is change in time (hours). Values for moisture uptake rate (%/h) were calculated from the initial slope of a plot of MC% versus time. Only the straight line region below equilibrium moisture content was used for this calculation. Initial weighing intervals were closely spaced to accurately quantify the rate of moisture sorption.

RESULTS AND DISCUSSION

Viscosity, solids content and pH

As mentioned, viscosity is one of the most important resin properties when manufacturing particleboard and must be kept under 500 cP at 25°C if the resin is to be sprayed using current manufacturing equipment.[21] Since both solids content and pH can affect resin vis-

TABLE II
Properties of Unmodified and Thermoplastic-Modified UF Resin Suspensions

		UF suspensions				
Formulations	Initiators	Viscosity (cP)[a]	Solids content (%)	pH[b]	Activation energy (kJ/mol)	ln *A*
Control	None	140	62.4	7.72	30.71	4.88
AM:MMA:U-Si (4:2:2)	V-50	443	63.4	6.53	18.98	0.66
	AIBN	343	63.4	6.76	26.02	2.72
AM:MMA (10:2)	V-50	493	63.6	6.98	15.57	0.15
	AIBN	269	63.4	8.04	24.38	2.66
U-Si	None	118	63.1	7.83	26.08	3.31

[a] Viscosity measured at 25°C and 4 rpm.
[b] Measured at 25°C.

cosity, these properties were monitored for both unmodified and thermoplastic-modified UF resins. Table II summarizes the viscosity at 25°C, solids content, and pH for unmodified and thermoplastic-modified UF resins.

Compared to the unmodified UF resin, viscosity was higher for both AM:MMA:U-Si (4:2:2) and AM:MMA (10:2) modified UF resins, regardless of the initiator used. Similar trends have been observed for UF resin modified with thermoplastics in prior studies.[19,20] The increase in viscosity upon thermoplastic modification was likely due to the presence of a thermoplastic polymer phase within the UF resin. In addition, heating the modified UF resin during radical polymerization may have advanced the resin cure, resulting in higher viscosity. In both formulations, the increase of viscosity was greater with V-50 than when AIBN was the initiator, possibly because of the greater acidity of the V-50 initiator itself. This is discussed along with pH below. A different mechanism for the reaction of the U-Si was expected to occur, where the U-Si could undergo a condensation reaction directly with the UF network instead of forming a separate polymer phase within the UF resin structure. This difference may account for the lower viscosity of this formulation as the relatively low temperatures used during thermoplastic modification were likely not high enough to drive a significant degree of crosslinking. The U-Si formulation would be expected to undergo most of its reaction and subsequent viscosity increase during the precuring and final crosslinking stages of cure of the UF resin.

Solids content of the modified UF resins was nearly the same, regardless of formulation (Table II). This was expected, as the same amount of thermoplastic was added to each formulation. These results indicate that there was no significant loss of water from the UF resin during thermoplastic modification, as the solids content is nearly at the theoretical value for the addition of 6.24 g of thermoplastic per 200 g of UF resin. Since these values remained nearly the same while viscosity varied over the different formulations, solids content was clearly not a factor in the viscosity of the modified UF resins.

The pH of the modified UF resins likely played a larger role in the viscosity. As listed in Table II, the formulations with the lowest pH (most acidic) had the highest viscosity values. The buildup of the UF network has been reported to increase faster at lower pH, resulting in higher viscosity.[1,4] The lower pH and resulting viscosity increase when V-50 was the initiator could be attributed to the chemical nature of V-50, which is an acidic salt. In both AM:MMA (10:2) and AM:MMA:U-Si (4:2:2), the viscosity was higher in each formulation with V-50 than when AIBN was used. Increases in viscosity were also reported by Carlborn and Das when V-50 was used as an initiator.[19,20] However, the AM:MMA:U-Si (4:2:2) with AIBN initiator also had a low pH, but only moderately high viscosity value, which indicated that pH is not the only factor affecting the thermoplastic-modified UF resin viscosity.

All of the thermoplastic-modified UF formulations studied were below the target viscosity of 500 cP at 25°C, which would allow them to be incorporated into the current particleboard manufacturing process.

Gel time and activation energy

The gel times of thermoplastic-modified UF resins were used to assess the relative activation energy of the crosslinking process of the unmodified and thermoplastic-modified UF resins. Figures 1 and 2 show Arrhenius plots of the gel time data, while the effects of thermoplastic modification and types of initiator on activation energy of the UF crosslinking process are summarized in Table III. Regardless of the thermoplastic formulation used, activation energy of all thermoplastic-modified UF resin formulations decreased compared to unmodified UF, which indicated less of an energy barrier to begin crosslinking (Table III). However, the V-50 initiator caused the greatest reduction in activation energy, possibly because the acidic nature of the V-50 caused the crosslinking to accelerate

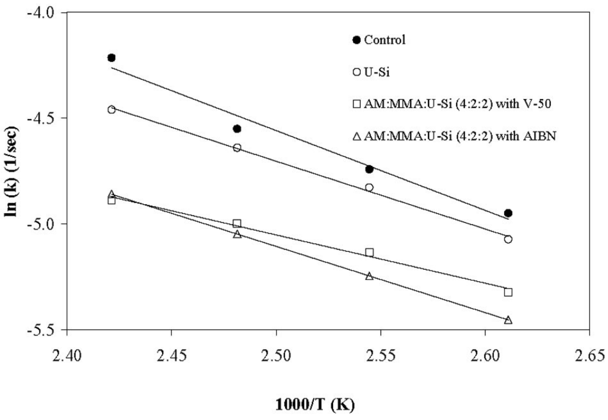

Figure 1 Arrhenius plots derived from gel time data of unmodified, U-Si modified, and AM:MMA:U-Si (4:2:2) modified UF resins.

in those formulations. Reduced activation energy of crosslinking could be beneficial for the commercial use of these modified UF resins in particleboard manufacture as less energy would be required to begin the curing process.

Crosslink density study

Crosslink density results are also summarized in Table III. The relative crosslink density of AM:MMA modified UF with V-50 initiator and of U-Si modified UF was higher than the control. In particular, AM:MMA modified with V-50 initiator had the highest relative crosslink density, possibly due to the acidity of the V-50 itself accelerating the curing in this formulation (Lower Ea). The next highest crosslink density was observed for the U-Si formulation, which was expected to react with the UF network itself during curing. Conversely, AM:MMA modified UF resin with AIBN initiator had lower crosslink density than the control. The samples with high crosslink density would be expected to have lower moisture sorption rates and equilibrium moisture uptake than those with low crosslink density, mainly due to the extra bonds within a given area that would need to be hydrolyzed to allow moisture to penetrate the sample.

Moisture sorption of cured UF plaques

Moisture uptake rate and equilibrium moisture content are indications of the affinity of the cured UF resins for water. Since moisture sorption in the cured UF resin plaque affects the hydrolysis of UF resin, both moisture uptake rate and equilibrium moisture content of unmodified and modified UF resin plaques were monitored to assess the effects of thermoplastic composition and initiator on moisture sorption. Figures 3 and 4 illustrate the moisture sorption curves of unmodified and modified UF resin plaques at 79.5% RH, while average moisture uptake rate and equilibrium moisture content values are summarized in Table III.

Figure 3 shows the moisture sorption of UF plaques modified with U-Si, with AM:MMA:U-Si (4:2:2) (with both V-50 and AIBN initiators), and unmodified UF plaques. Although all AM:MMA:U-Si modified UF resin plaques had initial moisture uptake rates that were higher than the control, they ended up with approximately the same equilibrium moisture content as the control (16%). The formulations containing AIBN initiator absorbed moisture at a faster rate and had higher values of equilibrium moisture content than those with V-50. Carlborn also observed this trend for cured UF resin plaques.[20] Only U-Si modified resin plaques had significantly lower equilibrium moisture content, approximately 14%. The U-Si modified UF resin plaque also absorbed moisture at a slower rate than the control UF, likely due to the hydrophobic nature of U-Si in the formulation. These results correlated well with the crosslink density, since this formulation showed slightly higher crosslink density than the unmodified UF resin. The additional bond density within this cured resin may explain its ability to resist moisture better than the unmodified UF sample.

Figure 4 illustrates the moisture sorption curves of UF plaques modified with AM:MMA (10:2) with AIBN and V-50 initiators and the control UF plaques. The UF plaques modified with AIBN again absorbed moisture much faster than the control. Interestingly, AM:MMA modified plaques with V-50 displayed a significantly slower rate of moisture uptake than the control. Equilibrium moisture contents of AM:MMA modified UF with AIBN and the control UF plaques were about 16%. By contrast, the equilibrium moisture content of AM:MMA with V-50 was about 11%, which was the lowest found for any of the thermoplastic-

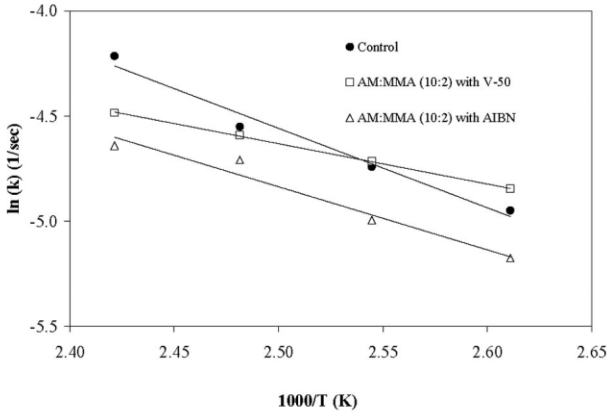

Figure 2 Arrhenius plots derived from gel time data of unmodified and AM:MMA (10:2) modified UF resins.

TABLE III
Properties of Unmodified and Thermoplastic-Modified UF Resin Plaques

		UF plaques			
Formulations	Initiators	*Q* (%)	Relative crosslink density	Moisture uptake rate (%/h)	Equilibrium moisture content (%)
Control	None	17.86	0.05	0.33	16.3
AM:MMA:U-Si (4:2:2)	V-50	–	–	0.36	15.5
	AIBN	–	–	0.49	16.0
AM:MMA (10:2)	V-50	5.35	0.19	0.10	10.6
	AIBN	23.44	0.04	0.57	15.6
U-Si	None	14.61	0.07	0.22	13.9

modified UF samples. This observation may be explained by the significantly higher relative crosslink density of this sample, compared to the other formulations tested. This formulation resisted moisture even better than the U-Si modified UF, possibly resulting from its increased crosslink density relative to the U-Si. Higher relative crosslink density appears to be an important factor in the moisture resistance of the cured UF resin.

CONCLUSIONS

UF resins were modified *in situ* with three thermoplastic formulations and both polar and nonpolar initiators. Viscosity, solids content, and pH of the unmodified and thermoplastic-modified UF resin suspensions were measured to document differences in thermoplastic formulations and to assess whether the modified resins could be used in typical particleboard manufacturing equipment. In addition, gel times were measured at four different temperatures and activation energy was derived from the gel time data. UF resin plaques were made to explore moisture sorption of the cured UF resin, which could separate the moisture effect on UF from the effects of the wood component in the composites. Relative crosslink density was also determined for some formulations to correlate moisture resistance to increased bond density in the cured UF resin formulations.

Viscosity was found to increase in most cases after modification with thermoplastics. This was likely due to a separate thermoplastic polymer phase forming within the UF network. One formulation, U-Si, had lower viscosity after the modification, likely because of the different mechanism of reaction and the likelihood that the reaction had not yet occurred under the low temperatures used in modification. Solids content was not found to affect the viscosity of modified UF resins. Except for one formulation, AM:MMA (10:2) with AIBN, decreased pH values were observed in thermoplastic-modified UF resins, regardless of initiator. With the same thermoplastic formulation, pH was lower with V-50 initiator than when AIBN was used. Viscosity of all modified resins was below 500 cP, which would allow their use in conventional industrial spraying equipment. For all thermoplastic-modified UF resins, activation energy was decreased compared to the unmodified UF. For both AM:MMA:U-Si and AM:MMA modified resin, the most significant decrease of activation energy was observed when V-50 was used as initiator. AM:MMA (10:2) modified UF with V-50 was found to have both the highest

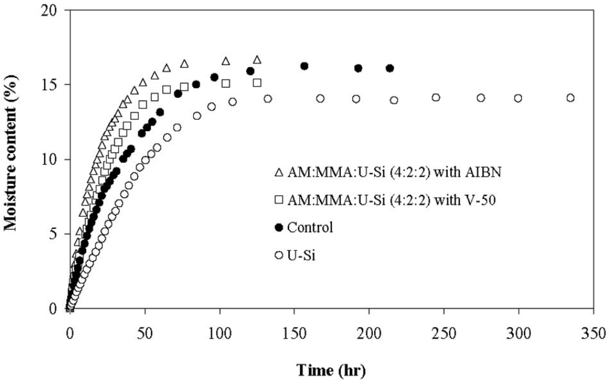

Figure 3 Moisture sorption curves of unmodified, U-Si modified, and AM:MMA:U-Si (4:2:2) modified UF resin plaques at 79.5%RH and 20°C.

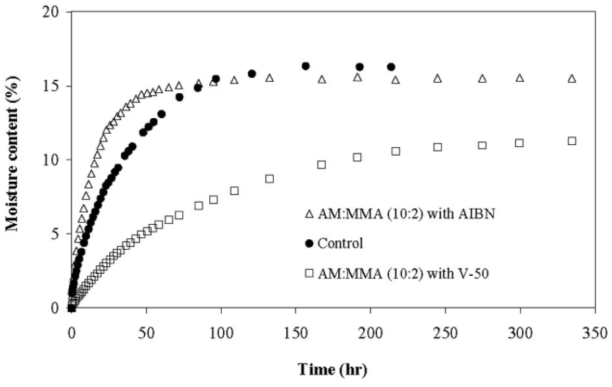

Figure 4 Moisture sorption curves of unmodified and AM:MMA (10:2) modified UF resin plaques at 79.5% RH and 20°C.

relative crosslink density and the lowest moisture sorption of the formulations tested. The U-Si formulation was also found to have high relative crosslink density and low moisture sorption, which suggested that crosslink density was a factor in the lower moisture sorption of cured thermoplastic-modified UF resin.

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