Thermoplastic Polymers as Modifiers for Urea–Formaldehyde Wood Adhesives. III. *In Situ* Thermoplastic-Modified Wood Composites

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ABSTRACT: Acrylic monomers and free-radical initiators were dispersed in an aqueous urea–formaldehyde (UF) suspension and polymerized *in situ* to afford a suspension containing 5 wt % thermoplastic (5 g of thermoplastic/100 mL of suspension). The viscosity of the thermoplastic-modified UF suspension (65 wt % solids at 25°C) ranged from 240 to 437 cP versus 121 cP for the unmodified UF control. Wood-flour composites (sugar maple and 50 wt % adhesive) were prepared with thermoplastic-modified UF suspensions and cured with the same cycle used for the composites prepared with the unmodified UF adhesive (control). The effect of the thermoplastic-modified UF adhesive was evaluated on the notched Izod impact strength and equilibrium moisture uptake of the wood-flour composites. The notched Izod impact strength of the composites prepared with modified UF adhesives increased by as much as 94% above that of the control. The increase depended on the initiator and the monomer composition. The modification affected the equilibrium moisture uptake and rate of moisture uptake in the wood-flour composites. Preliminary results for particleboard prepared with 10 wt % modified UF adhesive (5% thermoplastic in the UF resin) and unoptimized cure conditions confirmed a significant effect of the thermoplastic modification on both the internal-bond strength and thickness swelling of the particleboard. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3200–3211, 2008

Key words: crosslinking; impact resistance; thermosets; toughness

INTRODUCTION

Wood composites are increasingly being considered for use in new and more demanding applications that will impose greater demands on their properties. This has opened up the possibility of using more expensive wood adhesives if critical properties are improved. Which properties are deemed critical will depend on the specific application. Urea–formaldehyde (UF) adhesive is the least expensive of the major thermoset wood adhesives, but it has poor moisture-resistance and low mechanical properties. Despite its low cost, its use is restricted to applications in which these weaknesses are acceptable. Phenol–formaldehyde (PF), melamine–formaldehyde, melamine–urea–formaldehyde, and polymeric diphenylmethane diisocyanate adhesives have greater moisture-resistance and mechanical properties than UF adhesive but are also more expensive. A modified UF adhesive that retains a cost advantage over these adhesives but has

moisture-resistance and mechanical properties closer to theirs could find additional applications.

Thermoplastic polymers have been widely used for many years to modify the properties of thermoset resins,[1–5] although at the time this work was done our search of the literature found only two previous studies in which thermoplastic polymers were studied as modifiers for UF and PF adhesives.[6,7] Those researchers had some success, but the methods used in their research also had drawbacks.

The most successful effort to use thermoplastic additives to modify UF adhesive properties appears to be the work of Ebewele and coworkers,[8–11] who did not use polymeric additives but instead used lower molecular weight amine or urea-end-capped additives that probably functioned as reactive diluents. Their work resulted in significant improvements in the mechanical and moisture-resistance properties but used fairly significant amounts of amine modifiers, which possibly made the approach too expensive.

Our two earlier publications[12,13] investigated the feasibility of introducing premade thermoplastic into the UF adhesive and examined several different methods of adding thermoplastics to aqueous UF suspensions. In these studies, acrylic monomers and a free-radical initiator were premixed and added
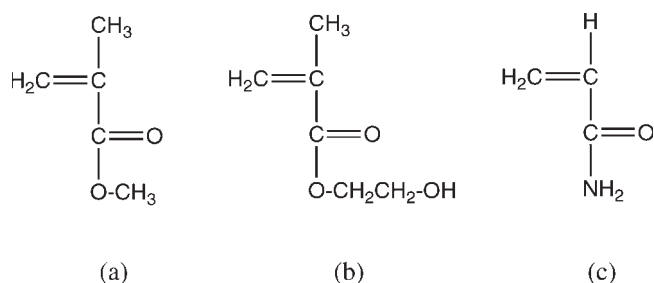
Figure 1 Chemical structures of the monomers: (a) MMA, (b) HEMA, and (c) AM.

directly to a commercial UF suspension (65% UF solids in water). The suspension was heated for ∼ 1.5 h to polymerize the monomer *in situ* with the intention of producing a semi-interpenetrating polymer network (S-IPN). An S-IPN is defined as ''a polymer comprising one or more networks and one or more linear or branched polymers characterized by the penetration on a molecular scale of at least one of the networks by at least some of the linear or branched macromolecules''.[14] S-IPNs can result when monomers are polymerized in the presence of either a pre-existing polymer network or a second reacting system that produces a thermoset network. Such network structures can improve properties, including moisture resistance, in comparison with a single network structure. However, in the case of a thermoplastic-modified UF, a highly complex system results because heating the system to effect the radical polymerization also can advance the UF cure. This can increase the viscosity and shorten the gel time, both of which can complicate the processing step. Although the addition of 5 wt % thermoplastic polymer to the UF suspension increased the suspension viscosity, our previous work showed that the viscosity of the modified UF resin generally remained at a level at which conventional equipment could spray between 20 and 30°C,[15] and the resin did not require increases in the mold time or temperature during composite manufacture. The notched Izod impact strength of wood-flour composites prepared with thermoplastic-modified UF adhesives was approximately twice that of UF controls. Despite these promising results, only water-soluble or extremely hydrophilic thermoplastics could be effectively dispersed within the aqueous UF suspension.

In this study, the modification route was simplified by the synthesis of the thermoplastic *in situ* in the UF suspension, which permitted both hydrophilic and hydrophobic thermoplastics to be investigated. The approach described in this article seeks to use thermoplastic polymers as modifiers, rather than reactive diluents, to develop a practical and effective method for thermoplastic modification of UF adhesives that can improve the moisture-resistance and mechanical properties.

EXPERIMENTAL

Materials

The UF adhesive (1.18 : 1.0 urea-to-formaldehyde molar ratio, 65% w/w in water) was donated by Southeastern Adhesives Co (Lenoir, NC). Wood flour (*Acer saccharum*, sugar maple, 40-mesh size) was donated by Horner Flooring Co. (Dollar Bay, MI). White oak particles (10-mesh size) were donated by American Wood Fibers (Schofield, WI). Methyl methacrylate (MMA), acrylamide (AM), and 2-hydroxethylmethacrylate (HEMA), shown in Figure 1, and two free-radical initiators, 2,2′-azobisisobutyronitrile (AIBN) and 2,2′-azobis(2-methylpropionamidine)dihydrochloride (V-50), shown in Figure 2, all from Aldrich Chemical Co. (Milwaukee, WI), were used as received.

General procedure for the preparation of the thermoplastic-modified UF slurry

The monomer(s) and initiator (0.42, 0.72, or 2 mol %, based on the total moles of the monomer) were combined and added to the slurry. In most cases, AIBN dissolved directly in the liquid monomers to afford a homogeneous solution. V-50, a water-soluble initiator, was dissolved in a minute quantity of water and then dispersed in the monomer mixture as an emulsion. The AM monomer, being a solid, was first dissolved in a minute amount of ethanol or water and then combined with other monomers. The monomer/initiator solution or emulsion was added at levels to deliver 5 g of the monomer for every 100 mL of the original suspension. The UF suspension was heated at 65–70°C for 1.5 h while being stirred at ∼ 300 rpm. Water was added as needed to restore the concentration of the suspension solids to 65 wt %
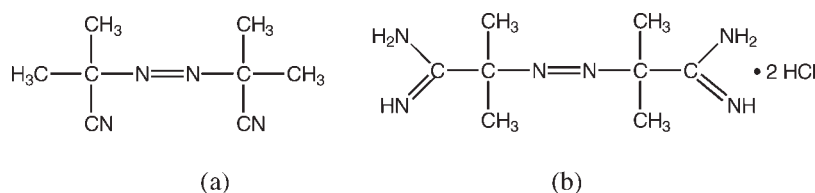

Figure 2 Chemical structures of the radical initiators: (a) AIBN and (b) V-50.

TABLE I
Thermoplastic Formulations and Designation

Thermoplastic designation	Initiator	Monomer molar ratio[a]		
		MMA (mmol)	AM (mmol)	HEMA (mmol)
V–PMMA	V-50	10	0	0
AIBN–PMMA	AIBN	10	0	0
V–AM : MMA-5	V-50	5	10	0
V–HEMA : MMA-5	V-50	5	0	10
AIBN–AM : MMA-5	AIBN	5	10	0
AIBN–HEMA : MMA-5	AIBN	5	0	10
V–AM : MMA-2	V-50	2	10	0
V–HEMA : MMA-2	V-50	2	0	10
AIBN–AM : MMA-2	AIBN	2	10	0
AIBN–HEMA : MMA-2	AIBN	2	0	10

[a] The comonomer ratios were constant at 10 mmol of the polar monomer to 5 or 2 mmol of MMA. The total monomer mass delivered into the suspension was kept at 5 wt %.

(60% UF and 5% monomer to 65% total solids). The modified suspension was used immediately.

Thermoplastic compositions

Five monomer formulations were polymerized with two radical initiators (V-50 and AIBN), and this gave a total of 10 thermoplastic formulations. The formulations and their designations are given in Table I. The designations give the initiator and monomer composition. For example, AIBN–AM–MMA-2 is the thermoplastic produced with AIBN as the initiator with 10 mmol of the AM monomer for each 2 mmol of MMA, whereas V–HEMA–MMA-5 is the thermoplastic produced with the V-50 initiator with 10 mmol of HEMA to each 5 mmol of MMA. The numerals 2 and 5 identify the millimoles of MMA used for every 10 mmol of the hydrophilic monomer (AM or HEMA). The numeral 10 is not used because the ratio of the hydrophilic monomer to MMA was kept at 10 : 2 or 10 : 5 mmol. The exception to this is the homopolymer of MMA, which is designated V–PMMA or AIBN–PMMA to identify the initiator. The initiator was used at 2 mol % with respect to the monomer unless stated otherwise, and the monomer was added to UF at 5 wt %. ^{1}H-NMR of the copolymer formulations, when prepared separately in water or organic solutions at the same monomer ratios used for UF, showed that the thermoplastic compositions were similar to the monomer feed. ^{1}H-NMR spectra, assignments, and calculations are given in detail elsewhere.[16]

Viscosity measurements

The viscosity of the UF suspension was measured (0.5 mL, 60% solids, 25°C) on a Brookfield LV DV-II viscometer (Brookfield Engineering Laboratories, Inc., Middleboro, MA) equipped with an S52 spindle at 10 rpm.

Preparation of the wood-flour composites

Thermoplastic-modified UF adhesives (65% total solids) were mixed with wood flour (50 g for every 125 g of the UF suspension) and NH_4Cl catalyst (0.1% w/w with respect to the UF solids in the suspension). The mixture was stirred for 2 min with a high-speed mechanical stir motor (300 rpm) and then apportioned approximately equally into 25 slots within a clean rectangular mold. The mold comprised an aluminum plate into which slots had been cut to afford Izod impact test specimens 64 ± 2 mm long, 12.7 ± 0.2 mm wide, and 3.8 ± 0.3 mm thick. This plate, resting on a second aluminum plate, was then covered with another aluminum plate, and the unit was transferred into a Wabash 12–101 T hydraulic hot press (Wabash Metal Products, Wabash, IN) that had been preheated to 135°C. All specimens were molded as follows:

- Pressure (1000 psi) was applied for 0.5 min.
- The pressure was released, and the specimens were allowed to degas for 0.5 min.
- Pressure (650–700 psi) was applied for 15 min.

Heating was discontinued, and the specimens were left under pressure to cool. The cooled specimens were removed, buffed (20-grit sandpaper), and notched with a CS-93E sample notcher (Custom Scientific Instruments, Cedar Knolls, NY) according to ASTM specifications. Impact tests were performed with a Tinius Olsen model 92 impact tester for plastics (Tinius Olsen Testing Machine Co., Inc., Willow Grove, PA) according to the procedure outlined in ASTM Standard D 256.

Preparation of the particleboard

Wood furnish (white oak) was oven-dried to a 4% moisture content. The UF suspension (10% w/w with

respect to the wood furnish) was carefully poured over the dried furnish, hand-mixed, and then stirred in a 20-L high-intensity mixer (type TGAHK20, Papenmeier, Germany) for 5 min to disperse the resin. The resin-coated wood furnish was formed into a mat by hand and compression-molded in a machine that had been preheated to 300°C. The mat was cured with the following cycle:

- The pressure was increased from 0 to 1000 psi over 15 s.
- The pressure was maintained at 1000 psi for 15 s.
- The pressure was decreased to 650 psi and held at that pressure for 3.5 min.
- The pressure was decreased from 650 to 0 psi over 30 s.

The board (14″ × 14″, pressed to a thickness of 7/16″) was removed from the press, allowed to cool, and trimmed to dimensions of 10″ × 10″ × 7/16″. The density of the board was 40 lbs/ft³.

Internal-bond (IB) strength of the particleboard

The IB strength of the particleboard samples (2″ × 2″) was determined according to the procedure outlined in ASTM Standard D 1037 (Applied Test Systems, Inc., Butler, PA). The tests were performed on an ATS machine at a crosshead rate of 0.3 in/min. At least 10 replicates were tested for each formulation.

Equilibrium moisture uptake of the wood-flour composites

Buffed wood-flour-composite specimens of known mass were placed in a plastic chamber maintained at 20°C and at 79.5% relative humidity by means of a saturated solution of ammonium chloride (prepared by the addition of 38 g of NH_4Cl to 100 g of water). The chamber, having a tight-fitting lid, contained a pump fitted with flexible tubing and pumped air through the saturated solution to maintain the humidity at that value. Composite specimens were removed at regular intervals to obtain their mass. The reported data points are averaged from three to five test specimens.

Thickness swelling (TS) of the particleboard

The thickness of the particleboard test pieces (3″ × 3″) was measured and then immersed in water at 20°C. Specimens were removed from water after 24 h, and then the thickness was measured again. The thickness was measured at a minimum of five places on all specimens. TS was reported as the percentage increase in the specimen thickness with the following equation:

$$TS = [(T_t - T_0)/T_0] \times 100 \qquad (1)$$

where T_0 and T_t are the thicknesses of the samples before and after 24 h of immersion, respectively.

Error analysis

Error analysis of the mechanical property data was used to verify the statistical significance of the data. Design Expert (version 5) software from Stat-Ease Corp. (Minneapolis, MN) was used. Design Expert uses an analysis of variance technique in which an F test determines the validity of an hypothesis made on three or more populations and a T test evaluates the significance of the difference between two means. Differences between data were considered statistically significant if the T test found ''Prob > $|t|$ < 0.0500'', whereas values of ''Prob > $|t|$ > 0.1000'' for a difference between two data was not statistically significant.

RESULTS AND DISCUSSION

Prior work[12,13,17] has demonstrated that a UF adhesive modified by 5 wt % thermoplastic gives up to a 95% increase in the fracture toughness of UF-bonded wood-flour composites. This article reports a continuation of that work and describes the effects of the monomer composition, relative molecular weight, and initiator type on the impact strength and moisture uptake of wood-flour composites. Some preliminary particleboard data are also presented.

The objective of this work is to characterize UF adhesive modifications that give low-viscosity suspensions, cure with a typical UF cure cycle, and give composites having substantially improved mechanical and moisture-resistance properties. In this approach, the selected radical initiators and acrylic monomers are combined, added to the UF prepolymer suspension, and polymerized *in situ*. This reactive blending method was initially expected to result in an S-IPN type product, but the results show a complex and dynamic system that is likely to form a conventional phase-separated, thermoplastic-toughened thermoset.

Thermoplastic compositions

The thermoplastic compositions are based on 2 or 5 mmol of nonpolar MMA for every 10 mmol of a polar comonomer (HEMA or AM). When these formulations are prepared in water or a mixed solvent, outside the UF suspension, the thermoplastic that is isolated possesses a composition that is similar to the monomer feed. However, neither the yield nor the composition of the thermoplastic that is produced within the UF suspension has been determined, and there is no expectation that this product will be similar

to that produced in isolation. It is also unlikely that a thermoplastic produced by AIBN initiation will be similar to that produced by V-50 initiation. It is not possible to extract a thermoplastic from UF and be certain that what is extracted is representative of what is produced *in situ*. It is also unlikely that we could reproduce the thermoplastic that is produced *in situ* because the radical polymerization is occurring in a polyphase system (water, MMA-oil phase, and UF dispersed phase) in which UF is also reacting during the radical polymerization, so the viscosity, polarity, and pH are changing during the radical polymerization. Furthermore, additional thermally initiated polymerization may be occurring during the molding process. For that reason, the actual composition, molecular weight, and other properties of the thermoplastic modifiers are unknown.

Although the product produced *in situ* was not isolated, some hypotheses about the thermoplastic have been made. AIBN is oil-soluble and will initiate radical polymerization within the suspended MMA-oil phase. This should yield a high-molecular-weight (suspension-type polymerization), MMA-rich thermoplastic having nonpolar alkyl end groups. Overall, the yield is probably relatively low because AIBN has a 10-h half-life at 67°C. Interfacial adhesion between the thermoplastic phase and UF is also low with AIBN initiation unless AM or HEMA copolymerizes with the MMA in the oil phase. However, both AM and HEMA are water-soluble. Therefore, a significant fraction of the polar comonomer could be in the aqueous phase, whereas AIBN is confined to the MMA-oil phase. As a result, this fraction of the comonomer is likely to be unpolymerized unless it undergoes thermally initiated polymerization during the molding stage. If any of the polar comonomer is present in the MMA-oil phase, it is likely to be incorporated into the thermoplastic. If this occurs to any significant extent, then some interfacial adhesion to the matrix can occur.

V-50 is water-soluble and will initiate the solution polymerization of a water-soluble acrylic monomer (AM and HEMA) or the emulsion polymerization of the MMA-oil phase, which may or may not contain some AM or HEMA. It will likely afford high-molecular-weight, MMA-rich chains having amidoimine end groups when it initiates the polymerization of the MMA-oil phase and give a low-molecular-weight, AM- and HEMA-rich thermoplastic having amidoimine end groups when it initiates the solution polymerization in the aqueous phase. Other differences may arise because V-50 is a hydrochloride salt, which alters the UF pH, accelerates its cure, and can alter the reactivity of AM.

All these differences are expected to result in different yields, different molecular weights, different compositions, and different polydispersities in ther-

moplastics produced by AIBN and V-50, both with respect to one another when prepared in UF suspensions and with respect to the product obtained from the identical formulation prepared in an isolated medium.

Although the molecular weight was not measured, we expected the different initiator concentrations (0.46, 0.72, and 2.0 mol % with respect to the monomer) to produce a systematic variation of the molecular weight, with the lowest relative molecular weight being produced with 2 mol % initiator and the highest relative molecular weight being produced with 0.46 mol % initiator.

Suspension viscosity

Practicality requires the viscosity of a thermoplastic-modified UF suspension to remain sufficiently low so that it can be sprayed from conventional equipment. Thermoplastic-modified UF suspensions are expected to be processable by conventional equipment if the suspension viscosity is in the range of 100–500 cP at 21°C (70°F), a range that is acceptable to most users.[15] The preferred upper limits of a suspension are a 5 wt % thermoplastic concentration and a viscosity below 300 cP at 25°C; these have been set by previous work that showed increasing the thermoplastic load from 5 to 10% significantly increased the viscosity but had little effect on the mechanical properties of the resulting wood composites.[13]

The viscosity of thermoplastic-modified UF suspensions (V-50 initiator) was close to the desired range except when they were modified by HEMA : MMA (Table II). The HEMA : MMA-modified suspensions might be processable at the current viscosity of $\sim$ 400 cP (25°C), but higher viscosity resins are less effectively distributed across wood surfaces during spraying. The higher viscosity is attributed to a larger fraction of the water-soluble polymer produced by HEMA : MMA versus AM : MMA.

The effect of increased water solubility on the suspension viscosity can be seen when we compare the viscosity of the modified suspensions (V–HEMA: MMA-2 and V–HEMA : MMA-5) with the viscosity measured for the V–HEMA : MMA-2-modified UF suspension (Fig. 3) that was prepared with an earlier route in which the formulation was made in an aqueous medium and only the components that remained in the solution or dispersion were used.[12,13] The suspensions were all prepared with a 5 wt % thermoplastic concentration.

The viscosity numbers are not compared directly because the earlier data were not measured at 30°C, but a difference in the slopes of the viscosity curves can also be seen. The *in situ* method gives modified suspensions having less dependence on the initiator amount (thermoplastic molecular weight) than the viscosity of suspensions modified by the dispersion

TABLE II
Effect of the Thermoplastic Composition on the Suspension Viscosity

Thermoplastic (5 g/100 g of UF solids)	Polar monomer (%)[a]		Viscosity (cP)[b]	Increase (%)
	Theoretical	Actual		
UF adhesive (control)			121	—
V–PMMA			223	84
V–AM : MMA-2	83	72	318	163
V–AM : MMA-5	67	42	241	99
V–HEMA : MMA-2	83	80	440	264
V–HEMA : MMA-5	67	63	414	242

[a] Prepared with 2 mol % V-50 initiator. The data were taken from ref. 16.
[b] Measured at 25°C with 60% solids.

of a premade thermoplastic that possess the same nominal formulation. This is attributed to the self-dispersed formulation containing a larger water-soluble fraction than the suspension having the same nominal formulation prepared *in situ*. This occurs because the self-dispersed method fractionates, so even though the same final mass of the thermoplastic is introduced into the UF suspensions, this method adds only the most polar fraction of the polymer that is soluble or remains dispersed within the aqueous phase. This fraction shows greater dependence on the initiator content because it is a solution viscosity.

The solution viscosity depends on the thermoplastic concentration and molecular weight. In radical polymerization, the molecular weight increases as the initiator concentration decreases, whereas the suspension viscosity depends on the volume fraction of the suspended polymer, but not the molecular weight. The relationship between the solution viscosity and molecular weight is[18]

$$\eta = KM^a \qquad (2)$$

where the intrinsic viscosity (η) of a solution depends on the thermoplastic molecular weight (M) and K and a are Mark–Houwink constants that depend on the polymer, solvent, temperature, and polymer geometry.

The thermoplastic molecular weight, in turn, shows an inverse dependence on the radical initiator concentration:[19]

$$\upsilon = \frac{k_p[M]}{2(f \times k_d \times k_t[I])^{1/2}} \qquad (3)$$

where υ is the kinetic chain length; [M] and [I] are the molar concentrations of the monomer and initiator, respectively; f is the initiator efficiency; and k_p, k_t, and k_d are the rate constants for chain propagation, chain termination, and initiator decomposition, respectively. The kinetic chain length is either the number-average degree of polymerization, X_n, or $2X_n$, depending on termination by disproportionation or combination.

The suspension viscosity dependence on the particle volume fraction is determined as follows (calculated for an ideal case that assumes a high concentration of monodisperse, spherical particles, without surface charge, under low shear in a Newtonian fluid):

$$\eta_o/\eta_f = \left(1 - \frac{\phi}{\phi_m}\right)^{-2} \qquad (4)$$

where η_o/η_f is the ratio of the viscosities of the suspension and suspending fluid, which is related to the particle volume fraction (ϕ) and the volume fraction of particles (ϕ_m) at which a fluid-to-solid transition occurs.[20–23]

Both modified UF suspensions show some dependence on the initiator content, and this shows that both suspensions contain a water-soluble thermoplastic fraction. The smaller initiator dependence shown by the *in situ* modification method indicates that a larger fraction of thermoplastic is present in the suspension as a macroscopically dispersed phase before the cure. Therefore, despite other advantages, given that some phase-separated thermoplastic is
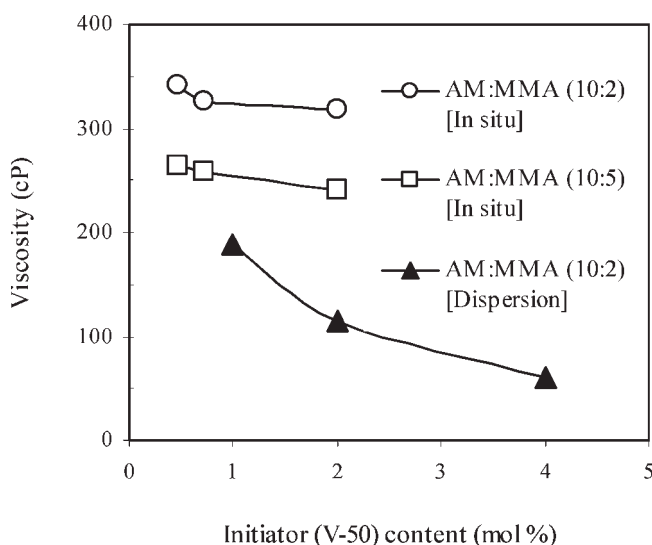

Figure 3 Effects of the modification method and initiator amount on the suspension viscosity.

TABLE III
Effect of the Blending Method on the Notched Izod Impact Strength
of the Wood-Flour Composites

Thermoplastic[a]	Impact strength (J/m)			
	Dispersed	Increase (%)	*In situ*	Increase (%)
UF adhesive (control)	3.1 ± 0.6	—	3.1 ± 0.6	—
V–AM : MMA-2	5.3 ± 0.9	71	4.8 ± 0.6	55
V–AM : MMA-5	4.0 ± 1.0	29	5.4 ± 0.5	74

[a] Initiated with 2 mol % V-50, which was introduced at a 5 wt % concentration with respect to the UF suspension.

present in the suspension before the cure, it is probable that the thermoplastic in the composite is in phase-separated thermoplastic domains rather than an S-IPN structure, as was originally intended.

Effect of the blending method on the impact strength

Wood-flour composites were prepared from 40-mesh maple flour and a UF adhesive modified with the *in situ* method. The notched Izod impact strength was measured, and the results were compared with earlier data for composites from UF modified with the same nominal formulation but prepared with the dispersion route.[12,13] The results are summarized in Table III.

The two control composites had the same impact strength, showing that there was no batch-to-batch variability in the UF starting material. Both modification methods gave statistically significant increases in the impact strength in comparison with the control. The *in situ* method appeared to give a bigger increase in the impact strength than the self-dispersed modification, but a statistical analysis showed that no significant difference existed between the two modifications. Therefore, although some differences in the copolymer compositions are likely, overall the *in situ* method appears to perform in a manner similar to that of the dispersion method.

Thermoplastic formulation and initiator amount: Comparison with the UF control

Five thermoplastic compositions—V–PMMA, V–AM : MMA-2 and V–AM : MMA-5, and V–HEMA : MMA-2 and V–HEMA : MMA-5—were used to modify UF suspensions, with the amount of the V-50 initiator varied between 0.46 and 2.0 mol % of the thermoplastic monomer. The molecular weight was not measured to verify a difference. All the compositions were prepared with the *in situ* reaction blending method. The results are summarized in Table IV.

A *T*-test analysis shows that the increases in the impact strength are statistically significant for all modified composites in comparison with the unmodified control, except for the following: V–PMMA (0.46 mol % V-50) and V–AM:MMA-2 (0.46 mol % V-50).

The lack of an effect of V–AM : MMA-2 (0.46 mol %) might be attributable to the low initiator amount (0.46 mol %), which, given the short polymerization time and mild temperature, might afford a polymer yield that is too low to be effective. V-50 has a 10-h half-life at 57°C, so it is more reactive than AIBN (10-h half-life at 67°C) but V-50 may initiate the solution polymerization of a water-soluble monomer and the emulsion polymerization of an oil-phase monomer (MMA). If the initiator initiates AM in the aqueous phase and MMA in the oil phase, possibly neither domain produces a thermoplastic at the molecular weight and in the amount that are required to improve the impact strength. If this is true, then the reason that V–AM : MMA-5 produced an increase in the impact strength might be the higher yield of the thermoplastic in the oil phase due to a higher MMA concentration.

The key factor that differentiates V–PMMA and V–AM : MMA-2 and V–AM : MMA-5 is likely to be the stability of the oil phase and interfacial adhesion

TABLE IV
Notched Izod Impact Strength of the Wood-Flour Composites
with a V-50-Initiated Thermoplastic-Modified UF Adhesive

Thermoplastic	Impact strength (J/m)			
	0 mol % V-50	0.46 mol % V-50	0.72 mol % V-50	2 mol % V-50
None (UF control)	3.1 ± 0.6	—	—	—
PMMA	—	3.3 ± 0.8	3.5 ± 0.7	5.2 ± 1.2
AM : MMA-2	—	3.2 ± 0.7	3.7 ± 1.0	4.8 ± 0.6
AM : MMA-5	—	4.0 ± 1.0	3.3 ± 0.9	5.4 ± 0.5
HEMA : MMA-2	—	5.3 ± 1.0	5.2 ± 0.9	5.1 ± 0.9
HEMA : MMA-5	—	5.9 ± 1.0	5.7 ± 1.2	5.3 ± 1.1

between the MMA-rich thermoplastic and the UF. The only interfacial stabilization between the oil and the UF suspension, and the only interfacial adhesion between the PMMA and UF matrix, will be from the amidoimine end groups of V-50. The poor stabilization likely leads to large domains with little interfacial adhesion. This would explain why the impact strength for V–PMMA rose with increasing V-50 concentration. This could also explain the different results with the HEMA : MMA formulations. If HEMA is more soluble in MMA than AM is, which is expected because HEMA : MMA formed a uniform solution whereas AM : MMA did not, then with 0.46 mol % V-50 initiation, the increase in the impact strength could be due to an increased yield of the thermoplastic that could interact with the UF. These data do not prove these hypotheses, but the results are consistent with them.

Thermoplastic formulation and V-50 amount: Comparison of the modified composites

No single monomer formulation appeared to be superior to any other under all conditions. At a 2 mol % V-50 initiator concentration, there was no statistically significant difference in the impact strength of any of the formulations (Table IV). The critical distinction between PMMA and the HEMA : MMA and AM : MMA formulations is that HEMA and AM are water-soluble. With AIBN, this means that the aqueous-phase monomer will remain unreacted unless thermally polymerized during molding, but with V-50 initiation, a thermoplastic is likely to be produced by two mechanisms: emulsion polymerization in the MMA-oil phase, which may contain some AM or HEMA, and solution polymerization of the water-soluble monomer.

It appears that V–HEMA : MMA-5 affords a greater increase in the impact strength than V–HEMA : MMA-2, but a T-test analysis of the impact strength shows no statistically significant difference among the HEMA : MMA composites at any level of V-50 between 0.46 and 2.0 mol %.

The AM : MMA formulations give the most complicated response to the V-50 amount. V–AM : MMA-2 gives little or no increase in the impact strength until 2.0 mol % V-50, whereas V–AM : MMA-5 shows a small increase in the impact strength at 0.46 mol % V-50, then a decline, and then a significant increase in the impact strength at 2.0 mol % V-50. This complicated response may be due to multiple competing effects in the system. AM was initially expected to perform in a manner similar to that of HEMA. That is, it was thought that despite the water solubility, some of the monomer would be in the MMA-oil phase to help stabilize the interface between it and the aqueous phase during radical polymerization and then between the MMA-rich thermoplastic and UF

phase after the composite preparation. The lack of effect of the V–AM : MMA-2 formulation on the impact strength until 2.0 mol % V-50 initiator suggests that either AM is entirely or almost entirely in the aqueous phase, but it apparently undergoes little solution-phase polymerization. AM and V-50, which are dissolved in water and dispersed within the MMA-oil phase before blending with the UF suspension, may form a complex within the aqueous phase. The rate of AM polymerization has been reported to decrease with an increased initiator concentration because of rapid termination.[24] The results may be affected by a very low-molecular-weight aqueous-phase AM homopolymer with little or no emulsion polymerization until, with 2.0 mol % initiator, a higher yield of the MMA-rich thermoplastic is produced. The data for the V–AM : MMA-5 formulation may reflect competing effects of a better yield of the MMA-rich polymer with increasing V-50 content but poor interfacial adhesion until, at 2.0 mol %, both the yield and interfacial adhesion are effective and are observed as an increase in the impact strength.

The data are not definitive, but it is likely that for the HEMA : MMA and AM : MMA formulations, some thermoplastic is formed by both mechanisms, and so both components might contribute to the composite properties as long as both have adequate interfacial adhesion. In a dynamic system with changing initiator amounts and monomer partitioning into different phases, as well as changing viscosities and cure rates, the relative yield and contribution of each type may change as well.

Thermoplastic formulation and initiator end groups

The V-50 initiator was selected because of its water solubility, activity at lower temperatures, and ability to bond to the UF matrix. However, its use also complicates understanding the system because it can polymerize by two mechanisms and because it is a hydrochloride salt and so can catalyze the UF cure. To clarify a possible contribution made by a solution-produced thermoplastic to the impact strength of modified composites, the AIBN initiator was used. AIBN will initiate only radical polymerization of the oil phase. The alkyl end groups of AIBN, however, will not promote interfacial stabilization or adhesion, and this initiator is less reactive than V-50, but this study can yield some useful comparisons. The impact strength of the composites prepared with UF modified by an AIBN-initiated thermoplastic and a V-50-initiated thermoplastic is given in Table V.

The impact strength of the AIBN–PMMA UF composite (2 mol % AIBN) showed a small but statistically significant increase in the impact strength in comparison with the UF control (3.6 ± 0.8 vs 3.1 ± 0.6 J/m,

Thermoplastic	Initiator	Initiator content (mL %)	Impact strength (J/m)	Increase (%)
Control	—	—	3.1 ± 0.6	—
PMMA	AIBN	2	3.6 ± 0.8	16
PMMA	V-50	2	5.2 ± 1.2	68
AM : MMA-2	AIBN	0.46	3.9 ± 1.5	26
AM : MMA-2	V-50	0.46	3.2 ± 0.7	3
AM : MMA-5	AIBN	0.46	4.9 ± 0.7	58
AM : MMA-5	V-50	0.46	4.0 ± 1.0	29
HEMA : MMA-2	AIBN	0.72	3.9 ± 1.3	26
HEMA : MMA-2	V-50	0.72	5.2 ± 0.9	68

respectively). The impact strength of the V–PMMA composite was 5.2 ± 1.2 J/m. The better result is certainly due to interfacial adhesion, although possible differences in the thermoplastic yield and molecular weight cannot be excluded.

The impact strength of AIBN–HEMA : MMA-2 (0.72 mol % AIBN) was 3.9 ± 1.5 J/m versus 5.2 ± 0.9 J/m for V–HEMA : MMA-2 (0.72 mol % V-50; Table V). Some HEMA should copolymerize with MMA in the oil phase to provide interfacial adhesion between the MMA-rich domains and the UF, in which case the impact strength of AIBN–HEMA : MMA-2 (0.72 mol % AIBN) should be closer to that of its V-50-initiated counterpart. Three possibilities can explain the lesser impact strength of AIBN–HEMA : MMA-2 (0.72 mol % AIBN). The first is less efficient polymerization by AIBN (10-h half-life at 67°C) than V-50 (10-h half-life at 57°C). This could be a contributing factor. In both HEMA : MMA formulations (with 0.72 mol % initiator), there is a statistically significant difference in the impact strength based on the initiator, although in the AM : MMA formulations, there is not.

A second contributing factor may be less interfacial adhesion, suggesting the HEMA is not polymerizing in the oil phase to the extent needed to overcome the lack of adhesion from AIBN end groups. However, we cannot exclude the possibility that insufficient HEMA is copolymerizing with MMA in the oil phase to provide the needed adhesion. In bulk polymerization, the reactivity ratios of HEMA and MMA have been reported to be $r_{HEMA} = 0.111$ and $r_{MMA} = 0.814$, and in dimethylformamide they have been reported to be $r_{HEMA} = 0.67$ and $r_{MMA} = 1.08$,[25,26] but they have not been found for aqueous-phase or emulsion polymerization. As stated previously, HEMA and MMA are added to UF as an initially homogeneous oil phase that also contains oil-soluble AIBN, which supports a likely HEMA–MMA copolymer, but the UF suspension is a multiphase system (aqueous, oil, and UF monomer/oligomer suspension), and so the concentration of HEMA depends on the partition that is not known.

The partitioning of the monomer exerts a strong influence on the thermoplastic produced, as shown by the results of Devi et al.,[27] who used a two-phase microemulsion of HEMA and styrene and found that the reactivity ratios of the monomers in the microemulsion differed from those in bulk and solution. They found $r_{styrene} = 3.79$ and $r_{HEMA} = 0.17$ versus literature values for bulk polymerization of $r_{styrene} = 0.27$ and $r_{HEMA} = 0.49$ and solution values of $r_{styrene} = 0.41–0.50$ and $r_{HEMA} = 0.53–1.65$. With a 50 : 50 monomer feed, the microemulsion product possessed an initial styrene molar fraction of 0.803 with 0.197 HEMA. The final composition was 0.941 styrene and 0.059 HEMA.

Given the data of Devi et al.[27] and the unknowns in our system, we cannot prove that *in situ* polymerization produces a HEMA–MMA copolymer for either AIBN–HEMA : MMA-2 or V–HEMA : MMA-2. Therefore, the possibility exists that the difference in the impact strength is due to a difference in the interfacial adhesion.

A third possible reason for the better impact strength for V–HEMA : MMA-2 versus AIBN–HEMA : MMA-2 is that the V-50 initiator successfully initiated a solution polymerization of HEMA and the solution product contributed to the increased impact strength. This seems possible, given that this formulation also resulted in a larger increase in the solution viscosity than the AM formulations.

Differences in polymerization efficiency, interfacial adhesion, and solution polymerization, could all be contributors to differences in impact strength of V–HEMA : MMA-2 and AIBN–HEMA : MMA-2.

Given all these possibilities, it is interesting that a *T* test showed that the impact strength measured for the wood composites from UF modified by V–AM : MMA-2 (0.46 mol % V-50) was not statistically different from that of its AIBN counterpart (3.2 ± 0.7 vs 3.9 ± 1.5 J/m). A *T*-test analysis did, however, show that the impact results from composites prepared with UF modified by V–AM : MMA-5 (0.46 mol % V-50) were different from the results

Effects of the Initiator Identity and Amount on the Notched Izod Impact
Strength of the Wood-Flour Composites (50 wt % maple and 40 mesh)
Bonded with a UF Adhesive Modified by HEMA:MMA-5

Initiator in HEMA : MMA-5 (mol %)	Impact strength (J/m)			
	AIBN	Increase (%)	V-50	Increase (%)
0 (control)	3.1 ± 0.6	—	3.1 ± 0.6	—
0.46	4.0 ± 1.0	29	5.9 ± 1.0	94
0.72	4.7 ± 0.8	52	5.7 ± 1.0	84
2	3.0 ± 1.0	0	5.3 ± 1.0	71

with its AIBN counterpart (4.0 ± 1.0 vs 4.9 ± 0.7 J/m; Table V).

Effect of the initiator identity and amount on HEMA : MMA-5

The system that is most likely to illustrate the effects of the initiator on the thermoplastic is HEMA : MMA-5 because the HEMA is both water-soluble and MMA-soluble. Thus, it is most likely to be able to provide interfacial adhesion to the MMA-rich thermoplastic in the absence of V-50 and also able to undergo solution polymerization in the aqueous phase.

As previously discussed, V–HEMA : MMA-5 (0.46, 0.72, and 2.0 mol % V-50; Table VI) showed an increase in the impact strength compared with UF, but a T-test analysis did not find a statistically significant difference in the impact strength of the composites when they were compared to one another. Conversely, the AIBN amount did effect impact strength, with 2 mol % giving no increase in strength. These results indicate with a lesser interfacial adhesion (AIBN initiation) thermoplastic molecular weight plays a role in impact strength, but molecular weight is less important with good interfacial adhesion (V-50 initiation).

The HEMA : MMA-5 formulation is the most likely to afford an MMA-rich thermoplastic from an oil phase that has sufficient polar comonomer to provide interfacial adhesion to UF. The aqueous-phase AM polymerizes, but to a very low molecular weight, which does not promote an increase in the impact strength. This in turn suggests that the impact strength depends on the emulsion-produced polymer. This supports a positive contribution to the increased impact strength primarily from an emulsion-produced polymer with interfacial adhesion from HEMA and end-groups, while with AIBN-initiated solution polymerization the importance of molecular weight and polar co-monomers is increased.

Moisture resistance of the wood-flour composites

We evaluated the effects of the thermoplastic composition, molecular weight, and end group (initiator) on the moisture uptake of the wood-flour composites by following the weight gain for 12 days in a controlled-humidity chamber. After 12 days, the control specimens absorbed 5 wt % moisture and appeared to have reached the equilibrium moisture content (EMC) by day 10 [Fig. 4(a)].

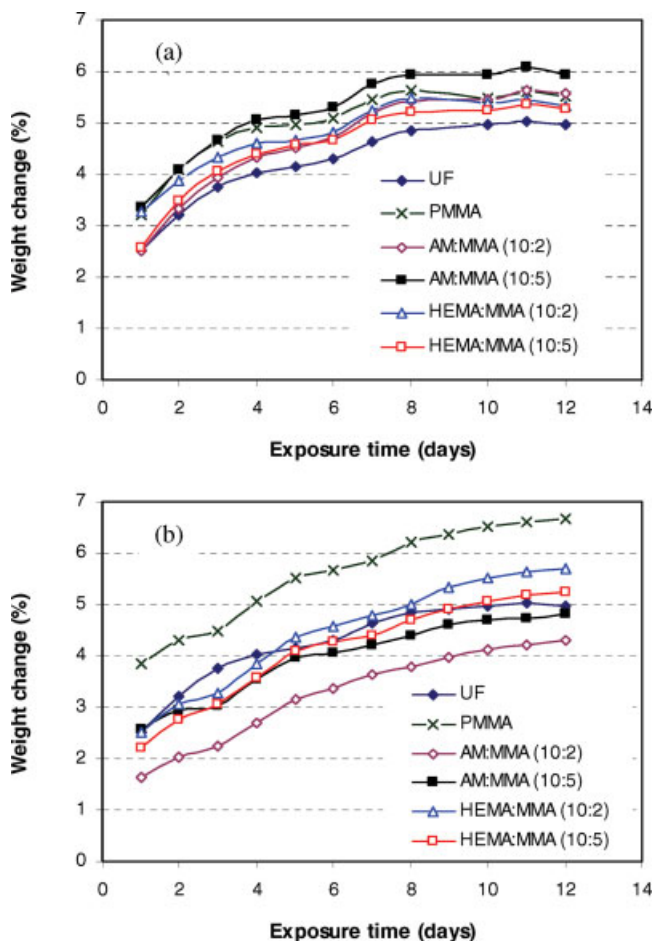Composites prepared with UF modified by an AIBN-initiated thermoplastic [Fig. 4(a)] reached

Figure 4 Equilibrium moisture uptake of the wood-flour composites modified by (a) AIBN- and (b) V-50-initiated thermoplastic-modified UF adhesives. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE VII
IB Strength of Particleboard

Thermoplastic	Initiator	V-50 initiator (mol %)	IB strength (psi)
None	—	—	9 ± 6
None	—	—	11 ± 10
V–AM:MMA-5	2		50 ± 24
V–AM:MMA-2	2		164 ± 49

The particleboard was white oak (10 mesh) with 10 wt % modified UF (5 wt % thermoplastic in the UF suspension).

EMC after $\sim$ 8 days, absorbing more moisture more rapidly than the controls. The V-50-initiated systems [Fig. 4(b)] were more complex. All but V–PMMA initially absorbed moisture more slowly than the controls, but after 10 days, all had absorbed the same or more moisture than the UF control, with the exception of V–AM : MMA-2.

V–AM : MMA-2 absorbed only $\sim$ 4 wt % moisture versus 5 wt % for the control specimens; however, the V–AM : MMA-2 specimens may not have reached equilibrium. Moreover, many of the specimens absorbed moisture in a steplike manner, appearing to reach equilibrium, then absorbing moisture in a rapid step, then appearing to reach equilibrium, then experiencing another step jump, and so on. The unmodified UF adhesive also appeared to take up moisture in two stages, with an initial uptake that leveled off after 4–5 days followed by a slower uptake until equilibrium. The thermoplastic-modified systems appear to follow a similar trend, except there appears to be significant differences in the rate of moisture uptake and the number of stages of uptake.

The steplike nature of the uptake is interesting, but assuming that the surface composition might be different from the bulk composition would allow for slope changes but should result in slope decreases as one phase approaches saturation and not sudden increases in the slope that level off. The increases in the slope suggest the fracture and exposure of a new surface. These tests were performed on small woodflour composites that had already been used in fracture studies and so already had at least one surface that had multiple exposed flaws. Consequently, the data generated in this test cannot be given much significance beyond being promising, in that they show that even a small amount of a thermoplastic modifier can affect the moisture uptake by some mechanism.

IB strength and TS of particleboard

The effect of the thermoplastic modification on the mechanical properties and on the moisture properties was verified by the preparation of thermoplastic-modified, UF-bonded particleboard and by the test-

ing of both the IB strength and TS tests on larger, unfractured particleboard specimens. Two modifications, V–AM : MMA-2 and V–AM : MMA-5, were used to prepare the particleboard (white oak particles) with 10 wt % adhesive and pressed to achieve a density of 40 lbs/ft^3. Control boards were prepared at each run in the preparation of the modified boards.

The IB strengths of the particleboards are given in Table VII. All the particleboards were cured with the same cycle. V–AM : MMA-5-modified particle board possessed an IB strength of 50 ± 24 psi, while V–AM : MMA-2 modified particle board was 164 ± 29 psi and unmodified UF particleboard was 9 ± 6 psi and 11 ± 10 psi. IB strengths for UF-bonded particleboard of a medium density (37–50 lbs/ft^3; specific gravity = 0.59–0.80) are typically in the range of 60–70 psi (0.41–0.48 MPa).[15] The IB strength is an indication of how well the particles are bonded in the panel, particularly in the core region. Therefore, the cure cycle used here was clearly inadequate to fully cure the unmodified UF, but nevertheless with the same cure cycle, the modifications afforded an improvement over the unmodified UF and produced IB strength values that are superior to those typically reported in the literature for well-bonded particleboards. The V–AM : MMA-2-modifed UF gave an IB strength of 164 psi, which was well above the IB strength found for the UF control composite and the composite from V–AM : MMA-5, at 50 psi.

The TS results for the particleboard specimens following a 24-h cold-water soak are shown in Figure 5. Each data point is the average of 18 test pieces. The unmodified control possessed a TS of $\sim$ 26%, the TS of the UF modified by AM : MMA-5 was only $\sim$ 16%, after 24 h, while the specimens modified with AM : MMA-2 had a TS of $\sim$ 38%. The data suggests a possible effect by a solution-polymerized AM, which benefits IB strength, but gives a complex effect on thickness swell. The obtained particleboard data are not sufficient to explain these results, but it is significant
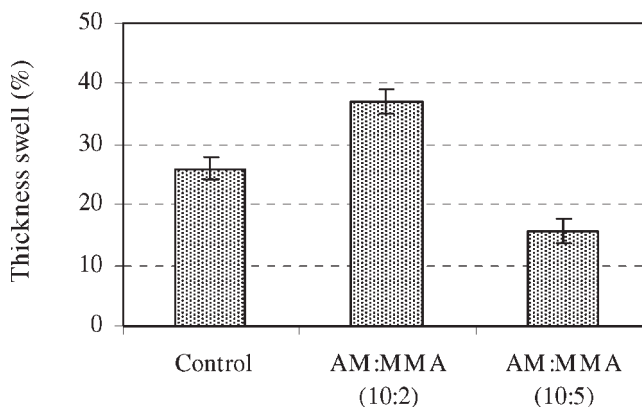

Figure 5 TS of particleboard specimens after 24 h of soaking in cold water.

that only 5 wt % thermoplastic in the UF suspension (8% with respect to the UF solid), is able to affect the mechanical and moisture-resistance properties of the composite. Consequently, the method is worthy of further investigation.

CONCLUSIONS

Acrylic monomers (MMA, HEMA, and AM) were combined with a radical initiator and were polymerized *in situ* in aqueous UF via heating at 65–70°C for 1.5 h. The modified UF suspension (5 wt % thermoplastic in UF) remained within a processable viscosity range and was used to bond wood-flour composites (50 wt % maple) and particleboard (10 wt % white oak).

A single cure cycle was used to mold unmodified and thermoplastic-modified wood-flour composites. The modified composites possessed a notched Izod impact strength as much as 94% greater than the unmodified controls. Differences in impact strength due to monomer formulation and initiator were attributed to multiple effects. Improvements in impact properties were due to phase-separated MMA-rich domains. Differences based on initiator and formulations were attributed to differences in thermoplastic yield, molecular weight, and interfacial adhesion of the dispersed MMA-rich phase. V-50 may have initiated some aqueous phase solution polymerization of AM but this does not appear to have had any significant effect on impact strength. IB strength was measured for AM-containing formulations with the greatest increase being found with the formulation having the greatest AM content, V-AM : MMA-2, while V-AM : MMA-5 also increased IB strength, but by a lesser amount. This may indicate a contribution to IB strength from an aqueous phase AM component. The V-AM : MMA-5 also gave a decrease in thickness swell while the V-AM : MMA-2 increased thickness swell compared to the control, which is attributed to differences in hydrophobicity of the resin effecting water transmission into the wood.

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