Thermoplastic Polymers as Modifiers for Urea-Formaldehyde (UF) Wood Adhesives. I. Procedures for the Preparation and Characterization of Thermoplastic-Modified UF Suspensions

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ABSTRACT: Acrylic thermoplastic copolymers with different degrees of hydrophilicity were prepared and introduced into a commercial aqueous urea-formaldehyde (UF) suspension at 5–10% w/v. The most hydrophilic acrylic thermoplastic was introduced into the UF suspension as an aqueous solution, whereas the most hydrophobic acrylic was introduced as a surfactant-stabilized suspension. Acrylics with intermediate hydrophilicity were introduced into the UF suspension as a self-dispersed aqueous suspension. The thermoplastic-modified UF suspensions with 5% thermoplastic (58% solids) had a viscosity at 30°C of ~ 114 cP, compared with a viscosity of ~112 cP for the original UF suspension (60% UF solids). At 10% thermoplastic (63% solids), all the thermoplastic-modified UF suspensions exceeded 200 cP. The viscosity of the UF suspension modified with self-dispersed thermoplastic was reduced by ~ 50% by reducing the thermoplastic molecular weight. SEM micrographs of cured thermoplastic-modified UF showed phase-separated thermoplastic domains in a continuous UF phase for the UF modified with self-dispersed and surfactant-stabilized thermoplastic, but UF modified with the water-soluble thermoplastic showed a single phase. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 890–897, 2003

Key words: thermoplastic; composite; adhesive

INTRODUCTION

Urea-formaldehyde (UF) adhesive is the least expensive of the most commonly used wood adhesives and is the dominant adhesive for particleboard, accounting for ~ 90% of the adhesive used in the particleboard industry.[1] The uses for UF are, however, limited by the fact that it is very brittle and has the least moisture resistance of all the major wood adhesives.

Most efforts to improve UF wood-composite properties have investigated altering UF ratios and process variables, possibly because such approaches are easy to apply industrially and are likely to be low cost. Process modifications studied include controlling the grain angle of the wood,[2] fillers,[2] surface roughness,[3] spraying conditions,[4] cure-cycle modification,[2] and varying the adhesive bond-line thickness.[2] These modifications yield improvements in toughness, although greater improvements are desirable, but do not improve the moisture resistance of the adhesive. Increasing the bond-line thickness improves the durability of bonded wood, but only because it takes longer to degrade the bond, not because the moisture resistance of the UF itself is altered. To improve the toughness and moisture resistance of the UF, the adhesive needs to be modified, ideally with a single modifier to accomplish both tasks.

Only a few investigations have studied chemical modification of the adhesive formulation.[5–9] This may be because any modification of UF resin must be low cost and also allow the adhesive to be processed by using conditions (spray equipment, cure time, and temperature) that are similar to those used with unmodified UF or the modifications will not be practical.

The most successful attempt to modify the adhesive itself appears to be the work of Ebewele et al., who modified the UF with reactive diluents to improve both the toughness and the moisture resistance of UF.[7–9] They replaced ~ 30+% of the urea in the UF adhesive with hexamethylene diamine, bishexamethylenetriamine, and triethylaminetriamine, or their urea derivatives. The fracture toughness, G_{1C}, of the wood composites produced by using the modified UF, was nearly doubled. The moisture resistance was evaluated by measuring the internal bond (IB) strength before and after 10 soak/dry moisture exposure cycles. The IB strength of the unmodified composite

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control was reduced from an initial value of 850 to 0 kPa after this treatment. The wood composites prepared with the modified UF had initial IB strengths that were typically ~ 50–100% greater than the unmodified UF, and after exposure to the soak/dry moisture cycles, typically possessed an IB strength between 100 and 300 kPa. This reactive diluent approach apparently has not been commercialized, possibly because it uses large amounts of reactive diluent that may make the approach too costly.

The overall objective of this project is to improve both the toughness and the hydrolytic resistance of UF wood composites without significantly altering the processing or excessively increasing the cost of the product. The first part of the research is reported here and describes investigations into the types of thermoplastic modifiers that can be introduced into UF suspensions, methods for introducing them, and their effect on the viscosity of the thermoplastic-modified UF suspension. The desired viscosity range for the modified UF suspensions was ~ 75–200 cp at 30°C. Initially very low molecular weight imides, urea end-capped hyperbranched polyester, and acrylic-based copolymers were investigated as thermoplastic additives. Imides were investigated because they are hydrolytically stable and are step-growth polymers, and so the molecular weight is easy to control, and at very low molecular weight do not substantially increase viscosity and can still improve toughness.[10] Hyperbranched polyesters were investigated because they also do not increase viscosity significantly, and, although they are more expensive, can be effective tougheners in small amounts.[11] Acrylic thermoplastics were investigated because they are commodity polymers and so are low cost relative to most other polymers; their composition is easy to vary with numerous low-cost commercially available monomers, and compositions that are similar to exterior paints should have hydrolytic resistance. The most hydrophobic acrylic thermoplastics would need to be stabilized in water with the aid of surfactant to afford a stable suspension in the aqueous UF suspension, whereas a water-soluble thermoplastic can simply be dissolved in water and added to the UF suspension as a solution. Acrylic thermoplastics with intermediate hydrophilicity could be prepared that might be able to form stable self-dispersions in water without the aid of a surfactant and so be blended into the UF suspension as a self-dispersion. The general procedures for the synthesis of each of these types of thermoplastics are presented in this article. The procedures describe thermoplastics that were studied here as well as some thermoplastic compositions that are not otherwise discussed until the second article in this series, where they are studied in wood flour composites.

METHODS

Materials

Imide oligomers were prepared from the diamines 1,6-hexamethylenediamine (HMDA) and diaminobenzoic acid (DABA), purchased from Aldrich (Milwaukee, WI), and 5-(2,5-dioxotetrahydrol)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride, that was purchased from Chriskev (Leawood, KS). Hyperbranched polyester (HBP, G4), urea, and *p*-toluene sulfonic acid (*p*-TSA) were purchased from Aldrich. The following monomers were purchased from Aldrich Chemical Co.: methylmethacrylate (MMA), acrylamide (AM), acrylic acid (AA), 1-vinyl-2-pyrrolidinone (VP), ethyl acrylate (EA), and vinyl acetate (VA). The initiator 2,2-azobis(2-methylpropionamide dichloride) (V50), and the surfactant, Tween40, were purchased from Aldrich. Acetone, dimethylsulfoxide (DMSO), and dimethylacetamide (DMAc) were purchased from Fisher Chemical Fisher Scientific (Fair Lawn, NJ). UF was donated by Southeastern Adhesives Co. (Lenoi, NC) and received as a 60% (w) solids resin with a U : F ratio of 1 : 1.18, and a density of 1.25 g/mL, that increased to 1.5 g/mL after cure.

Instrumentation

Viscometry was performed by using a Brookfield LV DV-11 viscometer (Brookfield Engineering Laboratories, Inc., Stoughton, MA). FTIR spectroscopy was performed by using a Galaxy Series FTIR 3000 (Mattson Instruments, Inc., Madison, WI). ^{1}H-NMR spectroscopy was performed by using a Varian XL 400 NMR (Varian, Palo Alto, CA). Scanning electron microscopy (SEM) was done on neat specimens by using a JEOL 35 C electron microscope (JEOL Ltd., Tokyo, Japan) at 20 kV. The SEM specimens were gold coated by using an E5000 sputter coater (Edwards High Vacuum, BOC Ltd., Crawley, Sussex, U.K.) prior to observation.

Preparation of thermoplastic and thermoplastic-modified UF

Low molecular weight imides

Diamine and dianhydride (molar ratios of 2 : 1, 3 : 2, and 4 : 3) were blended together with DMAc and heated at reflux for 1 h. The product was isolated by precipitation into ethanol and collected by filtration. In the case of the 3 : 2 DABA-containing imide, the pendant acid group dispersibility was also evaluated after esterification of the carboxylic acid with ethylene glycol, using *p*-TSA catalyst and heating an additional 1 h.

Urea-terminated HBPs

Excess urea (~ 2 equiv per theoretical hydroxyl equivalent) was added together with HBP into DMSO and heated at reflux. The product was isolated by removal of the solvent under reduced pressure.

Self-dispersible and water-soluble acrylics

A representative procedure is described. V50, a water-soluble initiator (2 mol % based on mol of monomer), was added to a preheated solution of water (200 mL) and acetone (400 mL) at 65–75°C in a round-bottomed flask equipped with a condenser. MMA (100 mL, 0.93 mol) and AM (13.29 g, 0.187 mol) were dissolved in acetone (100 mL) and placed in an addition funnel. This was added dropwise over a 1-h period to the initiator that was already dissolved in a water–acetone solution and then stirred for an additional 1 h. The acetone was then removed from the reaction solution under reduced pressure, which sometimes caused the product to separate into two components, a water-dispersible component, that remained as a milky dispersion in the water, and a second, solid component, which was soluble in acetone but insoluble in water. The VP : AM (2 : 10) copolymer was completely water-soluble. Only water-soluble or water-dispersible components were used to modify the UF. Variations on this procedure included altering the amount of initiator used (4 and 1% mol/mol monomer) or amount of acetone.

Surfactant-stabilized emulsion polymerization

Three copolymers were prepared via conventional surfactant-stabilized emulsion polymerization, by using Tween40 as a surfactant. Copolymers were prepared from EA : AM : VA (80 : 10 : 10, w), EA : AM : VA (65 : 25 : 10, w), and MMA : EA : AM : VA (30 : 35 : 25 : 10, w). A representative procedure is given for EA : AM : VA (80 : 10 : 10).

Tween40 (2.49 g, 9% w/w water), EA (5.0 mL, 5.1×10^{-4} mol), AM (1.226 g, 1.717×10^{-4} mol), and VA (0.65 mL, 7.1×10^{-3} mol) were added into water (22 mL) in a kettle and heated at 65–75°C while stirring. V50 (0.646 g, 3.174 mol % based on mol of monomer) was dissolved in water (10 mL), transferred to an addition funnel, and added dropwise to the reaction kettle. The addition was completed in ~ 1 h, and the product was stirred for an additional ~ 1 h.

Modification of UF suspension with self-dispersible or water-soluble thermoplastic

Thermoplastic (5 or 10 g for each 100 mL of UF suspension) was suspended or solubilized in hot water (12.5 mL) and cooled to room temperature (RT) before adding to the UF suspension (100 mL) into which ammonium chloride catalyst (0.1 g, 0.1% w/v UF suspension) had already been mixed. If the thermoplastic could not be dispersed directly in hot water, it was dissolved in water (12.5 mL) and acetone (15 mL) for each 5 g of thermoplastic. The mixture was blended with the UF suspension containing the catalyst and then subjected to reduced pressure to obtain the desired solids content (58 and 63% solids for 5 and 10 g of thermoplastic, respectively).

Modification of UF suspensions by using surfactant-stabilized thermoplastic

The latex (sufficient to provide 5 g of thermoplastic) was placed in a vacuum oven to evaporate ~ 15 mL water (~ 0.5–1 h). The concentrated latex was added to the UF suspension (100 mL) along with ammonium chloride catalyst (0.1 g, 0.1% w/v UF suspension). The final volume was adjusted as needed to maintain the same solids content as the self-dispersed system.

Measurement of the viscosity of UF and modified UF suspensions

The viscosity of the thermoplastic-modified UF prepolymer suspension was measured at 30°C by placing an aliquot (0.1 mL) of the suspension on the plate of a Brookfield LVD-11 viscometer and measuring with plate rotations of 10 rpm. The viscosity of unmodified UF resin as received and with 0.5 mL water added to 4 mL of the as-received suspension (the same ratio of added water used in the thermoplastic-modified UF suspensions) was measured for controls.

Determination of UF solids content and thermoplastic content in UF

The UF is supplied commercially as a UF methylolurea prepolymer dispersed in water. An aliquot of this suspension was placed in an aluminum dish of known mass and reweighed. The resin-containing aluminum dish was placed in a vacuum oven and heated to constant weight and reweighed. The UF solids mass was found to be 60.0% w/v of aqueous suspension.

Thermoplastic was added to this suspension at a level of 5 g for each 100 mL (5% w/v), which corresponds to 8% w based on UF solids, and at 10 g thermoplastic for each 100 mL (10% w/v), which corresponds to 16% w based on UF solids.

Neat resin cure and SEM observation

The UF prepolymer with or without the thermoplastic modifier, but in all cases without the cure catalyst, was poured in an aluminum dish (~ 1-mm-thick) and then placed in an oven that had been preheated to 55°C and maintained at that temperature under reduced pressure for 3 h. The pressure was then returned to atmospheric pressure and maintained at 55°C overnight (~ 12 h). The specimen was then transferred to a convection oven that had been preheated to 100°C and was maintained at that temperature for 2 days. Heat was then discontinued and the samples were allowed to cool to RT. The specimens were fractured with a hammer and the fracture surface was observed with SEM.

RESULTS AND DISCUSSION

Preparation of thermoplastics used as modifiers

Three classes of thermoplastics were initially investigated to identify suitable thermoplastic types and methods for introducing thermoplastic modifiers into the aqueous UF suspension. Very low molecular weight thermoplastic imides were evaluated that were prepared from a single dianhydride capped with two diamines. It was thought that the amine end groups might provide enough hydrophilicity so that the imide could be dispersed in water. When this failed with simple diamines such as hexamethylenediamine, then diaminobenzoic acid was used to provide additional hydrophilicity from the carboxylic acid group and possibly from zwitterions formed between the acids and amines. The imides were dispersible at 5–15% in water at pH ~ 9 but not at pH 7 or pH 5. Additional modification of the imide structure might have imparted water dispersibility but likely monomers were too expensive, so imides were not studied further.

A commercially available hydroxy-terminated G4 HBP was modified to possess urea end groups (from ^{1}H-NMR ~ 30% of the hydroxyl groups were converted to urea groups). The HBP was not dispersible in water at any pH and was not further investigated.

Thermoplastic acrylic copolymers were prepared by radical polymerization. MMA is a low-cost monomer and polymethylmethacrylate (PMMA) has good exterior durability, so acrylic thermoplastic additives based on MMA should be low cost and improve the moisture resistance of UF. Acrylic polymers with different degrees of hydrophilicity were prepared by copolymerizing MMA with vinylic monomers having different degrees of hydrophilicity. In some cases, MMA was copolymerized with monomers such as EA and VA, with the intention of making the thermoplastic softer while maintaining the hydrophobicity. In other cases, hydrophilic copolymers were prepared with hydrophilic comonomers AM, VP, and AA, with the intention of making the thermoplastics easier to disperse in water without the aid of surfactant. The monomers' structures are shown in Figure 1.

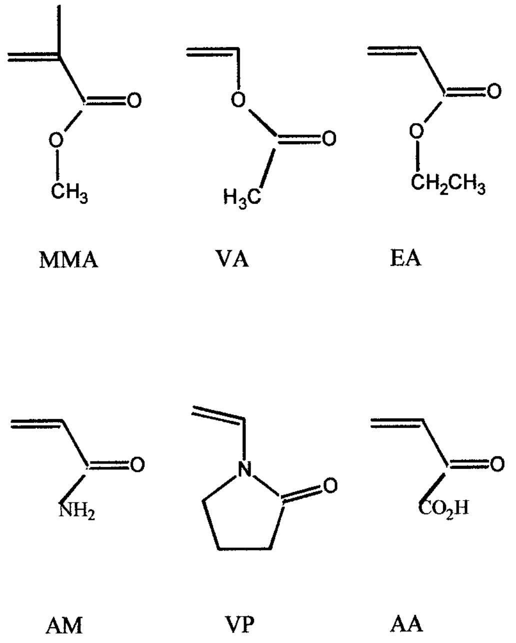

Figure 1 The monomers used in the synthesis of acrylic thermoplastic modifiers.

The most hydrophilic copolymer prepared was VP : AM (2 : 10), and this copolymer was water-soluble, so there was no difficulty in mixing it with the UF suspension. Several hydrophobic thermoplastics were prepared including PMMA, MMA : EA : AM : VA (30 : 35 : 25 : 10), EA : AM : VA (65 : 25 : 10), and EA : AM : VA (80 : 10 : 10, w). These formulations were varied to range from hard (PMMA) to soft (EA : AM : VA 80 : 10 : 10), but were very hydrophobic and so surfactant (Tween40) was used to help form a stable suspension in water. Tween40 only kept the latex stable for 24 h before coagulation, so it was not a particularly good surfactant for these thermoplastics, but because the latex was used immediately after preparation, a better surfactant for these systems was not investigated. There was no difficulty in mixing the surfactant-stabilized suspensions into the UF suspension, but it is unlikely that the thermoplastic ever forms an intimate mixture with the UF resin. The thermoplastic probably remains as individual particles stabilized in the UF suspension.

Use of surfactant to stabilize the thermoplastic in water has the advantage that it allows any thermoplastic, regardless of how hydrophobic it might be, to be introduced into the aqueous UF suspension. However, it was also thought likely that surfactant would be detrimental to the properties of composites prepared by using it to stabilize the thermoplastic. Therefore, more hydrophilic thermoplastics that can disperse in water without surfactant were also considered. A series of copolymers of MMA and AM, in which the AM component was systematically increased, was prepared and studied for the ability to be dispersed in water. The MMA : AM copolymers were as follows: 10 : 2, 10 : 4, 5 : 10, and 2 : 10. The copolymers were prepared by using 2 mol % V50 initiator. The effect of thermoplastic molecular weight on the water dispersibility was also studied for MMA : AM 2 : 10 by preparing a low molecular weight copolymer (LMW MMA : AM) with 4 mol % V50 initiator, and a

TABLE I
Water Stability of Self-Dispersed Thermoplastics in UF Suspension

Thermoplastic[a]	Water-dispersible fraction (%)	Stable in UF[b]	
MMA : AM (10 : 2)	8	pH 7 pH 8	No No
MMA : AM (10 : 4)	10	pH 7 pH 8	No No
MMA : AM (5 : 10)	100	pH 7	Yes
MMA : AM (2 : 10)	100	pH 7	Yes
MMA : AM (2 : 10) HMW	100	pH 7	Yes
MMA : AM (2 : 10) LMW	100	pH 7	Yes
MMA : AA (10 : 2)	5	pH 7	No
MMA : AA (10 : 4)	8	pH 7	Yes

[a] The benchmark thermoplastic is prepared with 2 mol % initiator; LMW thermoplastic is prepared with 4 mol % initiator; HMW is prepared with 1 mol % initiator.

[b] The suspension contains 5% w/v thermoplastic and was observed for ~ 1 h.

high molecular weight copolymer (HMW MMA : AM) with 1 mol % V50 initiator. The results of this study are summarized in Table I, in which the yield of the water-dispersible fraction from the thermoplastic synthesis step is reported and the thermoplastic-modified UF suspension is identified as stable or unstable.

The actual amount of AM actually incorporated in the thermoplastic was not measured, but the product produced with theoretical MMA : AM contents of 10 : 2 and 10 : 4 afforded only 8–10% of self-dispersed thermoplastic (the fraction that stayed dispersed in water after all the acetone and ~ 25–50% of the water from the synthesis step was removed), yet even that hydrophilic fraction of thermoplastic failed to stay completely dispersed within the UF suspension after standing for ~ 1 h. Thermoplastic with a theoretical ratio of MMA : AM of 5 : 10 had a higher water-dispersible fraction and showed no sign of aggregation in the UF suspension over the observation period (~ 1 h). When the AM component was further increased, the thermoplastic was completely dispersible in water and formed a stable UF suspension at the benchmark molecular weight (from 2 mol % V50) as well as at low and high molecular weight (from 4 and 1 mol % V50). To determine if AA could promote a higher degree of water-dispersibility than the AM comonomer, MMA : AA 10 : 2 and 10 : 4 were prepared. No statistically significant difference was observed in the fraction of water-dispersible thermoplastic that was obtained, although the water-dispersible component of the MMA : AA 10 : 4 copolymer did form a more stable suspension in the UF than did MMA : AM 10 : 4.

These data show that MMA : AM copolymers with a ratio of 5 : 10 or higher in AM can be dispersed in water without surfactant over the range of molecular weights produced with V50 at 1–4 mol % initiator.

Effect of thermoplastic on UF suspension viscosity

The viscosity of the thermoplastic-modified UF prepolymer suspensions was evaluated at 5 and 10% thermoplastic content (w/v UF suspension) to determine if the viscosity of the modified suspension remained in a range that was suitable for spraying with conventional industrial spray equipment. The actual viscosity range desired varies with the spray equipment used, the desired application temperature, and the resin type, but for most particleboard applications a viscosity of ~ 200–300 cp is probably preferred, but anywhere between ~ 100 and 500 cp at 21°C (70°F) is generally acceptable ([1]). Here we sought a viscosity for the thermoplastic-modified UF suspensions of no more than 200 cp at 30°C because this should ensure that a modified UF would be processible with conventional spray equipment and conventional spray conditions.

The viscosity of selected thermoplastic-modified UF suspensions and also of two unmodified UF control suspensions was measured at 30°C. The results are shown in Table II. The first control (C_{AR}) is the as-received UF prepolymer suspension (60% UF solids w/v), whereas the second control (C_{DIL}) is the unmodified UF suspension after it has been diluted with the same amount of water that is introduced into the UF suspension with the thermoplastic additive, making this control ~ 53% solids. Therefore, this control has the same amount of water as the thermoplastic-modified suspensions, but is of lower solids content. The thermoplastic-modified suspensions having 5% thermoplastic are ~ 58% solids and the suspensions with 10% thermoplastic are ~ 63% solids.

The viscosity was measured for thermoplastic-modified UF suspensions that were selected to represent the three methods of introducing thermoplastic into the UF suspension. The VP : AM (2 : 10) thermoplastic was the only water-soluble thermoplastic. The MMA : AM (2 : 10) thermoplastic was selected as the self-dispersed thermoplastic, and EA : AM : VA (65 : 25 : 10) was selected as the surfactant-stabilized latex. The viscosity of the soluble and self-dispersed thermoplastics was studied at both 5 and 10% thermoplastic loading. The viscosity of the surfactant-stabilized thermoplastic was measured at 5% only to determine if the surfactant-stabilized thermoplastic-modified UF was in the processible range. The viscosity of a surfactant-stabilized suspension is controlled not only by solids content but also by the particle size of the dispersed phase, and this is easily controlled by the amount and identity of the surfactant used, so if required, the

TABLE II
Effect of Thermoplastic Type and Loading on Prepolymer Viscosity

Thermoplastic	Thermoplastic form	Thermoplastic loading (%)	Viscosity[a] (cP at 30°C)	Δ Viscosity[b] (%) C_{AR}/C_{DIL}
C_{AR}	—	0	111.5	—
C_{DIL}	—	0	47.9	—
VP : AM (2 : 10)	Soluble	5	88.5	−21/85
VP : AM (2 : 10)	Soluble	10	222.1	99/363
MMA : AM (2 : 10)	Self-dispersed	5	114.3	3/139
MMA : AM (2 : 10)	Self-dispersed	10	373.2	235/679
EA : AM : VA (65 : 25 : 10)	Latex	5	166.8	50/248

[a] Viscosity, except for the C_{AR}, is of the UF suspensions that contained additional water. The total solids (w/v) for these suspensions is 60% for C_{AR}, 53% for C_{DIL}, and 58% for the thermoplastic modified suspensions.

[b] The first number is the % change in viscosity relative to the viscosity of the C_{AR} (Final − Initial/C_{AR}), and the second number is the % change in viscosity relative to the viscosity of the C_{DIL} (Final − Initial/C_{DIL}).

modified UF suspension viscosity can be reduced by increasing the amount of surfactant used during the thermoplastic synthesis.

The data in Table II show that the viscosity of the thermoplastic-modified UF suspensions with a thermoplastic loading of 5% was below the 200 cp target and was close to the viscosity of the C_{AR} control. At 10% thermoplastic loading, the UF suspensions modified with soluble and self-dispersed thermoplastic were above the 200 cp target, and the suspension modified with the surfactant-stabilized thermoplastic would have been above this target. It is preferable to use as little thermoplastic as possible to modify the UF because the thermoplastic adds cost. However, if 10% thermoplastic is needed, then the suspension viscosity can be reduced. This can be done with surfactant-stabilized thermoplastic by changing surfactant or increasing the amount used to produce smaller particles. The viscosity of the UF suspension modified with water-soluble or self-dispersed thermoplastic can be reduced by reducing thermoplastic molecular weight. This can be accomplished with a higher initiator concentration. Lowering the molecular weight of a thermoplastic that is in solution or self-dispersed (a fraction of the self-dispersed copolymer is very likely to be water-soluble and entangled) will lower the viscosity because of reduced entanglements, which in turn reduces viscosity.

To confirm that the viscosity of a self-dispersed thermoplastic can be controlled by controlling the molecular weight of the thermoplastic, a low and high molecular weight thermoplastic was prepared. The data in Table III show that the viscosity is nearly halved with the LMW MMA : AM (2 : 10) and is close to doubled when the molecular weight of the thermoplastic is increased. These data confirm that controlling the molecular weight of the thermoplastic at 5 or 10% thermoplastic loading offers enough control over the modified suspension viscosity to keep the viscosity in the range that is desired to allow it to be sprayed out of conventional processing equipment.

TABLE III
Effect of Molecular Weight of MMA : AM (2 : 10) on UF Suspension Viscosity

Thermoplastic	Initiator (mol %)	Thermoplastic loading (%)	Viscosity[a] (cP at 30°C)	Δ Viscosity[b] (%) C_{AR}/C_{DIL}
C_{AR}	—	0	111.5	—
C_{DIL}	—	0	47.9	—
Low MW MMA : AM (2 : 10)	4	5	59.9	−47/25
MMA : AM (2 : 10)	2	5	114.3	3/139
High MW MMA : AM (2 : 10)	1	5	188.0	69/292

[a] Viscosity, except for the C_{AR}, is of the UF suspensions that contained additional water. The total solids (w/v) for these suspensions is 60% for C_{AR}, 53% for C_{DIL}, and 58% for the thermoplastic modified suspensions.

[b] The first number is the % change in viscosity relative to the viscosity of the C_{AR} (Final − Initial/C_{AR}), and the second number is the % change in viscosity relative to the viscosity of the C_{DIL} (Final − Initial/C_{DIL}).

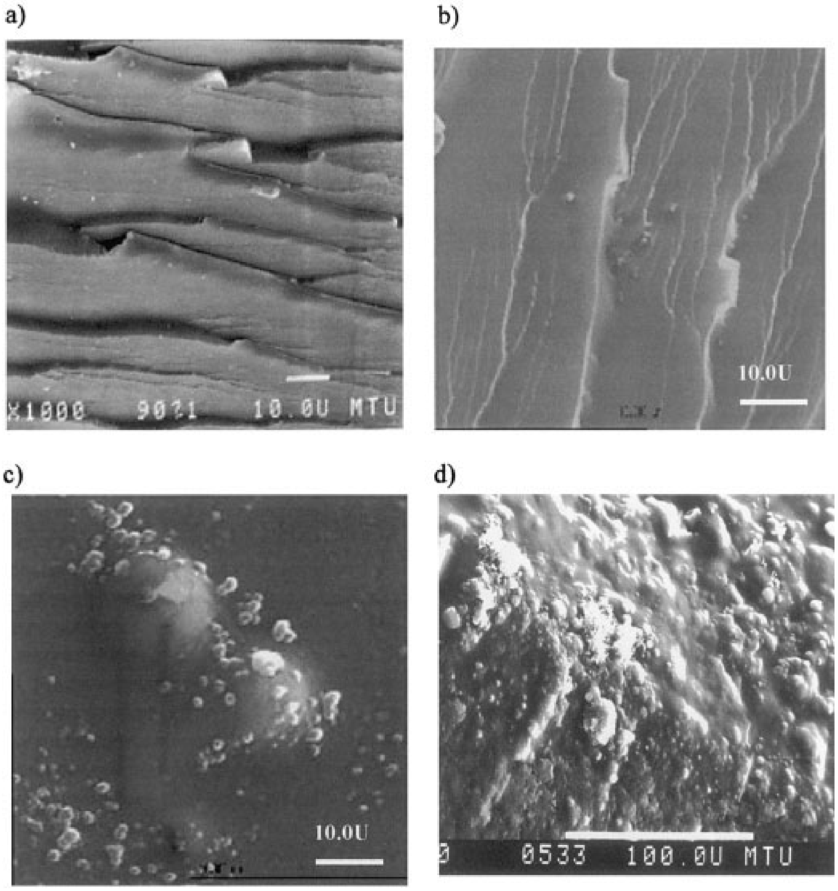

Figure 2 SEM micrographs of (a) unmodified UF observed at ×1000 magnification; (b) UF modified with 5% of VP : AM 10 : 2 observed at ×2000 magnification; (c) UF modified with 5% of self-dispersed MMA : AM 2 : 10, prepared with 2 mol % V50, observed at ×2000 magnification; and (d) UF modified with 5% surfactant-stabilized MMA : AM, prepared with 2 mol % V50, observed at ×390 magnification.

Neat resin morphology

The morphology of neat resin specimens was investigated to determine if the thermoplastic phase separated from the UF and to observe the effects of the methods of introducing thermoplastic into UF on morphology. The morphology of a neat resin might differ from that in the wood composite (reported in the next article in this series) but SEMs of wood–flour composites are more complex so an initial observation was made with neat resin specimens that were fractured with a hammer. The SEM micrograph of unmodified UF [Fig. 2(a)] shows the typical brittle fracture pattern associated with thermosets. The micrograph of the UF modified with 5% of the water-soluble thermoplastic, VP : AM (10 : 2), also shows a brittle surface but no obvious fractures or phase separated thermoplastic domains are evident [Fig. 2(b)]. The micrograph of the UF modified with the self-dispersed thermoplastic MMA : AM (2 : 10) shows clear signs of phase-separated thermoplastic in a continuous UF phase [Fig. 2(c)]. Phase separation of a thermoplastic phase in the thermoset is often associated with increased toughness in a thermoset,[12] so this morphology might be associated with increased toughness for a wood composite prepared with this modified suspension. To determine the effect of surfactant on morphology, this same resin was prepared as a surfactant-stabilized latex. The micrograph of that modified UF is shown in Figure 2(d). Phase separation is observed, but the appearance is distinctly different from that observed in the specimen shown in Figure 2(c). It is possible that the continuous UF domain is not adhering well to the thermoplastic domains due to the surfactant, because several of the white thermoplastic domains appear to be aggregated and sitting on the surface of the UF.

CONCLUSION

Different thermoplastics were prepared and introduced into aqueous UF suspensions to determine if they formed stable dispersions in the aqueous suspension and if the viscosity was maintained in a range that would permit the thermoplastic-modified UF to be sprayed from conventional wood composite spray equipment. Low molecular weight amine-terminated imides and urea and hydroxyl-terminated HBPs did not form stable suspensions in the aqueous UF suspension. Different acrylic thermoplastics were prepared and introduced into the aqueous UF suspension by using different approaches. The most hydrophobic thermoplastics were introduced into the UF suspension as surfactant-stabilized latices and the most hydrophilic were introduced into the suspension as an aqueous solution. Acrylics with intermediate degrees of hydrophilicity were introduced into the aqueous UF suspension as self-dispersed suspensions in water. All three methods produced stable thermoplastic-modified UF suspensions at 5 and 10% (w/v) thermoplastic loading in the UF suspension. At 5% thermoplastic loading, the viscosity of the modified UF suspensions was below the maximum viscosity target of 200 cp at 30°C. At higher thermoplastic loadings, the modified suspensions were above this target. Lowering the molecular weight of the self-dispersed thermoplastic reduced the viscosity by nearly half, so molecular weight control is effective for controlling the viscosity of suspensions modified with water-soluble or self-dispersed thermoplastic. The thermoplastic-modified UF suspensions were cured and fracture surfaces were observed by SEM microscopy. The UF modified with water-soluble thermoplastic showed no sign of phase separation, although the fracture surface did not show the brittle fracture patterns of the unmodified UF. The self-dispersed thermoplastic showed phase-separated thermoplastic domains within a continuous UF phase. The UF modified with surfactant-stabilized thermoplastic also showed phase-separation but the surface was rough and differed from the self-dispersed thermoplastic-modified UF.

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