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Polystyrene/wood composites and hydrophobic wood coatings from water-based hydrophilic-hydrophobic block copolymers

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Abstract The combination of synthetic thermoplastic polymers and wood is normally problematic because wood surfaces are hydrophilic while typical thermoplastic polymers are hydrophobic. A possible solution is to use block copolymer coupling agents. In this work we show the use of a potentially useful synthetic method of producing hydrophilic-hydrophobic block copolymers as hydrophobic coatings and coupling agents in polystyrene/wood flour composites. In particular, wood veneers are coated with water-based emulsions of hydrophilic-hydrophobic block copolymers from styrene and methacrylic acid. Dried coated surfaces are shown to become hydrophobic through dynamic contact angle measurements. When wood flour is coated with the hydrophilic-hydrophobic block copolymer based on styrene and acrylic acid, significant improvement in the ultimate tensile properties of composites formed from coated wood flour/polystyrene mixtures is realized. Since no volatile organic compounds (VOCs) are used in coating wood surfaces and subsequent composite production, improvement in mechanical properties of thermoplastic/wood flour composites are shown to occur in environmentally responsible formulations.

Introduction

Beginning with plywood and moving through to oriented strandboard, the combination of wood and synthetic polymers has helped to maintain the competitive position of the forest products industry while enhancing the utilization of our forests in terms of both scope and efficiency. Today's environmental and social concerns have placed even greater demands on both the forest resource and the forest products industry; and once again, the combination of wood and synthetic polymers may help to ease that pressure. Synthetic plastics have become increasingly prevalent in traditional wood product markets over the years; yet through the technological advances responsible for this encroachment, new material systems and applications for wood/polymer materials have been presented. Such an opportunity can be found in the area of fiber-reinforced polymers (FRPs; Gerstle 1987), where some of the more dramatic technological advances have been made. The development of wood fiber-reinforced plastics continues to receive high priority as a long-term goal in wood product research.

In part, this priority stems from the growing resource present in the form of virgin fiber from low-value hardwoods and recycled fiber (Bentley 1989) from paper or pallets that is, in many respects, ideally suited for polymer reinforcement. Characterized by its light weight and high strength, this natural fiber offers a number of advantages over currently used reinforcing fibers in terms of cost and weight, as well as processing considerations (Kokta 1988). Unfortunately, the consolidation of wood fibers with thermoplastic polymers also presents a number of unique problems that must first be addressed. The most notable shortcoming of wood fiber/thermoplastic polymer systems is the lack of adhesion between the two components (Zadorecki and Flodin 1985; Seferis and de Ruvo 1986; Kokta 1988). Consequently, an inferior fiber/matrix interface is established that prevents the necessary stress transfer from the polymer matrix to the load-bearing fiber, reducing the function of the fiber to that of a poor filler or extender.

In spite of the widely recognized importance of the fiber/matrix interface, physico-chemical factors that determine its strength and quality remain poorly defined for the wood/thermoplastic polymer system. Certainly, the question has been extensively addressed through numerous reports on the effect of various compatibilizers and coupling agents on the mechanical properties of the composite (Woodhams et al. 1984; Dalvag et al. 1985). While these studies have focused on the problem and shed considerable insight into potential solutions, the interpretation of the results has been complicated by the use of secondary properties to evaluate fiber/polymer interactions, rather than the direct observation of interfacial performance or quality. In spite of the widely recognized importance of the fiber/matrix interface, the physio-chemical factors that determine its strength and quality remain poorly defined for the wood-thermoplastic polymer system. One unanswered question of particular significance to nonpolar polymer matrices, such as poly-

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ethylene and polystyrene, is the contribution of molecular entanglements to fiber/polymer compatibility and, subsequently, interfacial strength and quality.

Rather than using a coupling agent as a component of a mixture that also includes the wood fiber and thermoplastic (polystyrene), we have directly placed the coupling agent (hydrophilic-hydrophobic block copolymer) on the wood surface before being blended with the polystyrene. This should result in minimal waste of the coupling agent, inasmuch as micelle formation of the block copolymer can be virtually eliminated. Since the block copolymer has surfactant properties, it can be dispersed in an aqueous medium without the use of volatile organic compounds (VOCs). Upon drying of wood surfaces exposed to the aqueous emulsions of the hydrophilic-hydrophobic block copolymer, hydrophobic surfaces were obtained based on contact angle measurements. Polystyrene composites of treated wood flour further showed that an improvement in tensile properties is obtained over a similar composite of untreated wood flour.

Experimental

Preparation of hydrophilic-hydrophobic block copolymers

Materials used for polymerization

Methacrylic acid, acrylic acid, and styrene monomers were purchased from Aldrich Chemicals, and they contain the usual amount of inhibitors. They were purified using a double distillation technique under reduced pressure. The initiator, 2,2′-azobisisobutyronitrile (AIBN), was obtained from Eastman Kodak. It was used without further purification.

Size exclusion chromatography

Molecular weights of the dried polymer samples from the reactor fluid were measured using a size exclusion chromatograph (SEC). The chromatography system has refractive index and multi-angle light scattering detectors (Wyatt Technologies). Thus, measured molecular weights were absolute, and there was no need to calibrate molecular weights after injecting a few samples. For the analysis of intermediate polystyrene samples, we used a silica column (Supelco LC-1 Supelcosil) with liquid chromatography-grade toluene as the carrier fluid. For the analysis of the block copolymer samples, tertrahydrofuran (THF) was used as the carrier fluid and four styrene-divinylbenzene polymer columns were used as packing material.

Nuclear magnetic resonance

High-resolution proton and ^{13}C pulsed NMR spectroscopy of the copolymer materials was carried out using a 220-MHz Varian XL-200 and Varian 400-MHz NMR spectrometers. To minimize interference of proton signals for the ^{13}C spectra, proton noise decoupling was applied.

Block copolymer formation

Formation of the block copolymer was done by polymerizing styrene in ether through the so-called free-radical retrograde-precipitation polymerization (FRRPP) process (Caneba 1992). After four times the initiator half-life, live polystyrene radicals are reacted with methacrylic acid to form the hydrophilic block, which is presumably a random copolymer of styrene and methacrylic acid. A mixture of 1.5 ml inhibitor-free styrene, 10 ml ethyl ether and 0.0173 grams AIBN was charged into a thick-wall glass tube (10 mm in diameter), bubbled with nitrogen, and sealed with a Teflon cap (see Fig. 1). A very small magnetic stirrer bar was used. The tube was placed in an 80 °C water bath for about 10 hours and then removed and quenched in dry-ice for half an hour. A small quantity of sample was taken for conversion data. Under nitrogen protection, 3.0 grams methacrylic acid was added to the solution and immersed in the 80 °C bath for 8 hours before cooling to room temperature. The final product, which contains the polystyrene-*block*-poly(styrene-*co*-methacrylic acid) copolymer, was purified three times. SEC and NMR techniques were used to evaluate its molecular weight and segment ratio. The SEC analysis was done at Dow Chemical's analytical laboratory using THF as the solvent. Proton and ^{13}C NMR analyses were done using a Bruker 400-MHz instrument with THF-d_8 as the solvent.

For larger-scale work, we generated a polystyrene-*block*-poly(styrene-*co*-acrylic acid) polymer, which we think would offer better processability and economic characteristics compared to the polystyrene-*block*-poly(styrene-*co*-methacrylic acid) system. Since acrylic acid has a lower boiling point of 140–141 °C than that of methacrylic acid at 163 °C, unreacted acrylic acid is less difficult to strip from the reactor fluid and polymer product (Dean 1985). Also, the glass-transition temperature of poly(acrylic acid) at 106 °C is more appropriate for processing with polystyrene (glass transition at 100 °C). This is compared to the fact that poly(methacrylic acid) has a glass transition temperature reported at 228 °C (Brandrup and Immergut 1989). Finally, it should be noted that acrylic acid as a bulk material costs less than methacrylic acid[1].

Preparation and testing of coated wood and polystyrene-wood composites

Materials

Maple, oak, and ash veneers with 6% moisture content were used for contact angle measurements. Maple flour (60-mesh *Acer saccharum* from American Wood Fibers) was used to form the wood flour/plastic composites. Applied coatings and coupling agents, polystyrene-*block*-poly(styrene-*co*-methacrylic acid) (or PS-P(MAA-S)) and polystyrene-*block*- poly(styrene-*co*-acrylic acid) (or PS-P(AA-S)), were produced using the FRRPP process (Caneba 1992). Base polystyrene material used to generate the composites was obtained from Dow Chemical (Styron 685D, with number average molecular weight of 270,000 Da). The PS-P(AA-S) copolymer used in the

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[1] For example, it was reported in the April-May 1990 issue of the Chemical Reporter that the bulk price for acrylic acid is \$0.64/lb, while the bulk price for methacrylic acid is \$0.95–1.04/lb.

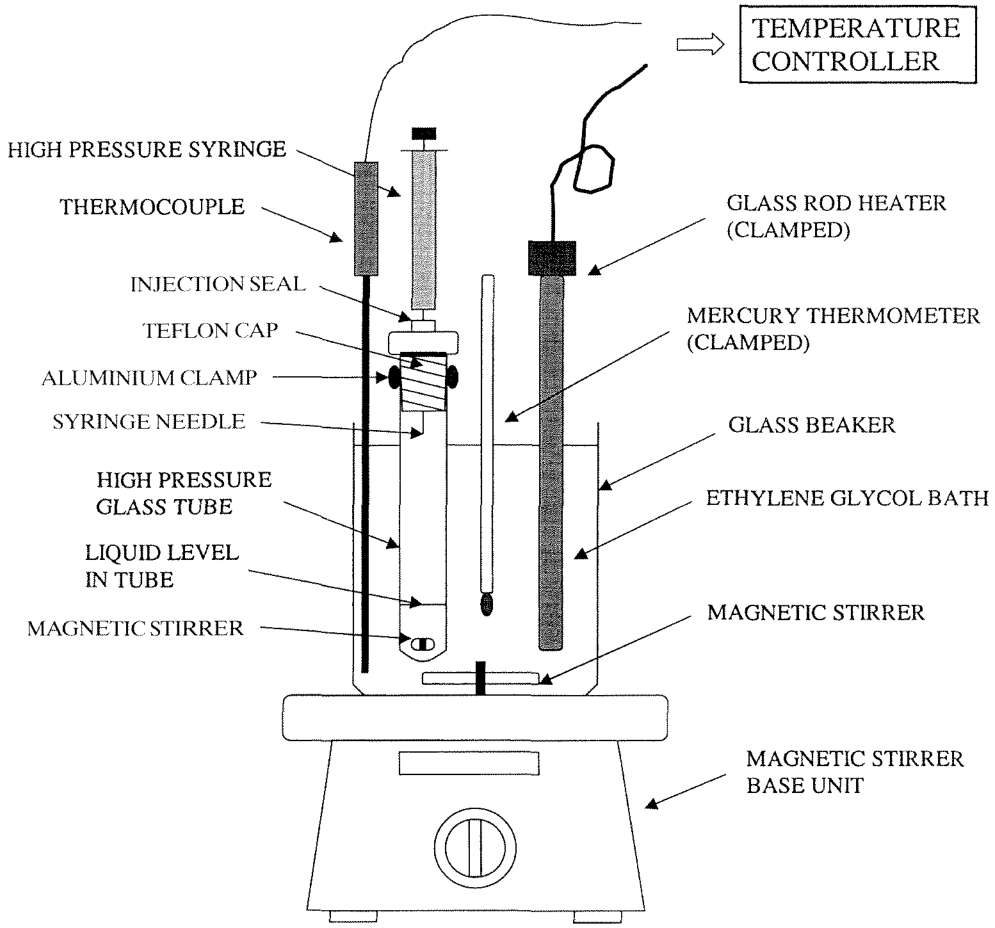

Fig. 1. Apparatus used in the synthesis of the PS-P(MAA-S) block copolymer

preparation of composites was brought to a pH of 6.5 with ammonia, in order to obtain a stable emulsion in water.

Contact angle measurements

Dynamic contact angle analysis of coated and uncoated (blank) veneer samples was performed using the following procedure:

1. Veneers were cut into 2-cm × 2-cm pieces.
2. Cut veneer samples were sanded to reveal fresh wood surfaces.
3. Exposed surfaces were coated with four different solutions (0.02, 0.1, and 0.2 wt% ammonia-water solutions at pH = 10 of the polystyrene-*block*-poly(styrene-*co*-methacrylic acid), and 0.2 wt% of ammonia-water solution at pH = 6 of polystyrene-*block*-poly(styrene-*co*-methacrylic acid) with 3 dip-dry cycles. Drying was done in air at room temperature.
4. After final air-drying, samples were allowed to air-dry for 10 more hours and kept in a desiccator.
5. Dynamic contact angle analyses of the coated samples were performed with a Cahn dynamic contact angle analyzer (model DCA-322), which is based on the Wilhelmy plate technique. High-performance liquid chromatography-grade water was used as the probe liquid, and the samples were immersed at a rate of 194 m/s to a depth of 15 mm.
6. Blank samples were analyzed after they were sanded.

Preparation of the composites

Water-based emulsions of the PS-P(AA-S) copolymer were mixed with wood flour that was dried to a moisture content of 0.3 wt%. The mixtures were dried in a vacuum oven for 48 h at 70 °C to a moisture content of 1 wt%. The base polystyrene material was ground into powder with the aid of liquid nitrogen. Then it was mixed with coated and uncoated wood (using a 20-liter mechanical mixer) at a 90/10 polystyrene/wood wt/wt ratio. The resulting solid mixture was then fed into a Brabender twin-screw extruder at 210 °C and 15 rpm, and the strands were immediately pelletized. To prepare the test samples, the pellets were flattened in a hot press at 200 °C for 5 min. The composite plate was cooled in a cold press for another 10 min to a thickness of 1.5–3.0 mm. From the resulting composite plate, tensile bars (with a gage length of approximately 114 mm and width of approximately 13 mm) were cut and allowed to stand for at least 8 h before stress-strain testing.

Aside from using uncoated wood to form the reference composite, we also prepared tensile bars from the base polystyrene using the same thermal history as that of the composites.

Testing of composites

Tensile testing measurements were done with a universal testing machine from SATEC Systems (capacity 120 cs – 120,000 lb). A strain rate of 0.2 in/min (0.085 mm/s) was used in testing the samples. Stresses were obtained from the measured force divided by the cross-sectional area of the samples. Strain was based on change in length relative to the sample gage length (approximately 114 mm).

Results: block copolymer formation

Figure 2 shows a refractive-index signal from a size exclusion chromatography system for the polystyrene material (PS intermediate) that was taken from the reactor just before the addition of methacrylic acid, as well as those of raw and purified copolymers (see Table 1 for the quantitative molecular weight results). The purified copolymer product is a polystyrene-*block*-poly(styrene-*co*-methacrylic acid) material, because the PS intermediate was at 60% conversion only. This means that unreacted styrene was present when methacrylic acid was added into the reactor.

The refractive index signal from the raw product (Fig. 2) clearly shows another peak of higher molecular weight (compared to that of the PS-intermediate peak) that can be attributed to the continuation of the propagation of live radicals. In the purified product, the PS-intermediate peak totally disappeared. The purification of the raw product was done with an investigation of the solubility of this material to various solvents. Table 2 shows that THF is a solvent for the raw and purified products.

With THF as the solvent for the raw copolymer product, we added water to precipitate homopolystyrene contaminant. The supernatant was dried and redissolved in THF. The addition of CH_2Cl_2 precipitated poly(methacrylic acid). Gravimetric analyses of solid materials in various solutions and precipitants gave us the following compositions of the raw product: 78 wt% polystyrene-*block*-poly(styrene-*co*-methacrylic acid) copolymer, 17 wt% polystyrene homopolymer, and 5 wt% poly(methacrylic acid) homopolymer. These gravimetric results translate to a 1:2.5 styrene-to-methacrylic acid weight ratio. Our NMR work gave a ratio of 1:2.4.

When the hydrophilic-hydrophobic block copolymer was placed in an ammonia-water solution of pH = 10, we were able to disperse it at the 0.2-wt% level. Subsequently, a slice of maple veneer was dipped into this copolymer solution and then air-dried. After a given number of dip-dry cycles, scanning electron micrographs of the coated surfaces were obtained. After the first dip-dry cycle, the wood surface seemed to change from a wetting to more of a nonwetting behavior. Micrographs of the dried surfaces of the wood showed that good coatings were obtained even after 10 dip-dry cycles. Continuous coats were applied onto individual fibers after 4 dip-dry cycles (Fig. 3). After 10 dip-dry cycles, there is very little indication of the polymer filling up spaces between wood fibers (Fig. 4).

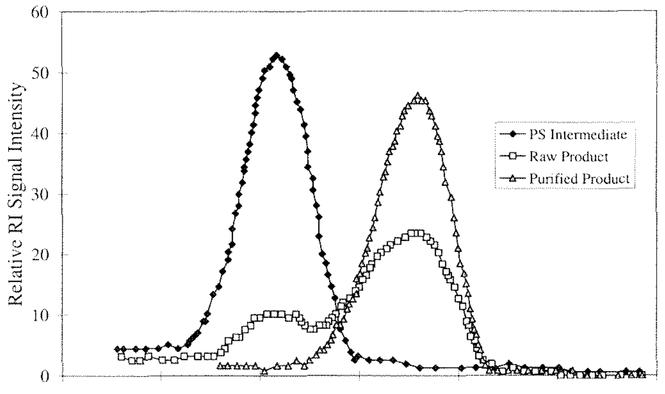

Fig. 2. Refractive-index (RI) signal from a size exclusion chromatography system for the polystyrene material that was taken from the reactor just before addition of methacrylic acid (PS intermediate), as well as RI from raw and purified copolymers

Table 1. Molecular weight data for the intermediate polystyrene and polystyrene-*block*-poly(styrene-*co*-methacrylic acid) copolymer

	PS intermediate	Raw copolymer product	Purified copolymer product
Number-average molecular weight, g/mol	10200	34500	228000
Polydispersity index	1.74	8.02	1.83

Table 2. Result of study of solubilities of the polystyrene-*block*-poly(styrene-*co*-methacrylic acid) copolymer and its components (+ means totally soluble; − means insoluble)

Solvent	PMAA	PS	Block product
THF	−	+	+
Toluene	−	+	−
Water	+	−	−
CH_2Cl_2	−	+	−
Methanol	−	−	Partially +

Advancing contact angle values of water (shown in Table 3) indicate that dip-dry cycles from ammonia solutions of polystyrene-*block*-poly(styrene-*co*-methacrylic acid) at pH = 6 and pH = 10 resulted in hydrophobic wood surfaces, i.e., the contact angles increased to more than 90°. The table also indicates that the system from the pH = 10 solution results in the same degree of hydrophobicity of the coated wood surfaces as the system from the pH = 6 solution.

Using a similar synthetic procedure, we produced the PS-P(AA-S) material to coat wood flour and generated polystyrene/wood flour composites from it. Figure 5 shows the plot of yield and ultimate stresses for the 90/10 polystyrene/wood flour wt/wt composites at 0, 1.5, and 3 wt% PS-P(AA-S) loadings on wood. For the base polystyrene used, we obtained a mean yield stress of 32 MPa and a standard deviation of 6 MPa. The ultimate stress was at 32 MPa with a standard deviation of 3 MPa. Figure 6 shows a plot of the yield and ultimate strains for the 90/10 polystyrene/wood flour wt/wt composites at 0, 1.5, and 3% PS-P(AA-S) loadings on wood. The mean value of the yield strain for the base polystyrene was 2.1% with a standard deviation of 0.4%. The mean value

Table 3. Dynamic contact angle measurements (advancing angle) of water on various uncoated surfaces (blank) and surfaces coated with ammonia-water solutions of polystyrene-*block*-poly(styrene-*co*-methacrylic acid) (PS-P(MAA-S)) at pH = 10 and pH = 6. Values are averages with standard deviations in parentheses

Coating	Maple	Cherry	Ash
Uncoated or Blank	84.0 (0.8)	87.7 (0.9)	82.5 (1.1)
0.02 wt% at pH = 10	92.6 (0.8)	95.2 (1.0)	92.0 (0.3)
0.1 wt% at pH = 10	92.4 (1.6)	94.0 (0.9)	92.7 (0.9)
0.2 wt% at pH = 10	93.4 (2.1)	94.0 (1.4)	91.9 (0.4)
0.2 wt% at pH = 6	91.1 (2.1)	95.9 (1.4)	90.0 (1.8)

of its ultimate strain was 2.4% with a standard deviation of 0.9%.

Discussion of results

We have demonstrated the possibility of forming block copolymers when we added methacrylic acid to the styrene reactor system in ether after most of the initiator molecules had decomposed into radicals. From Fig. 2, the block copolymer formation is apparently not efficient enough. In reality, the data for the raw product will have a bigger homopolystyrene peak at 10,200 g/mol because the block copolymer molecular weight is not as high as it looks. In fact, from the methacrylic acid-to-styrene ratio added of 2.0, intermediate polystyrene conversion of 60%, and second-stage conversion of 80%, the result is a block copolymer molecular weight of about 32,640 g/mol. This is lower than the value for the raw product (34,500 g/mol) and the purified product (228,000 g/mol) as shown in Table 1. One should realize that molecular weight measurements for the block copolymer are not accurate

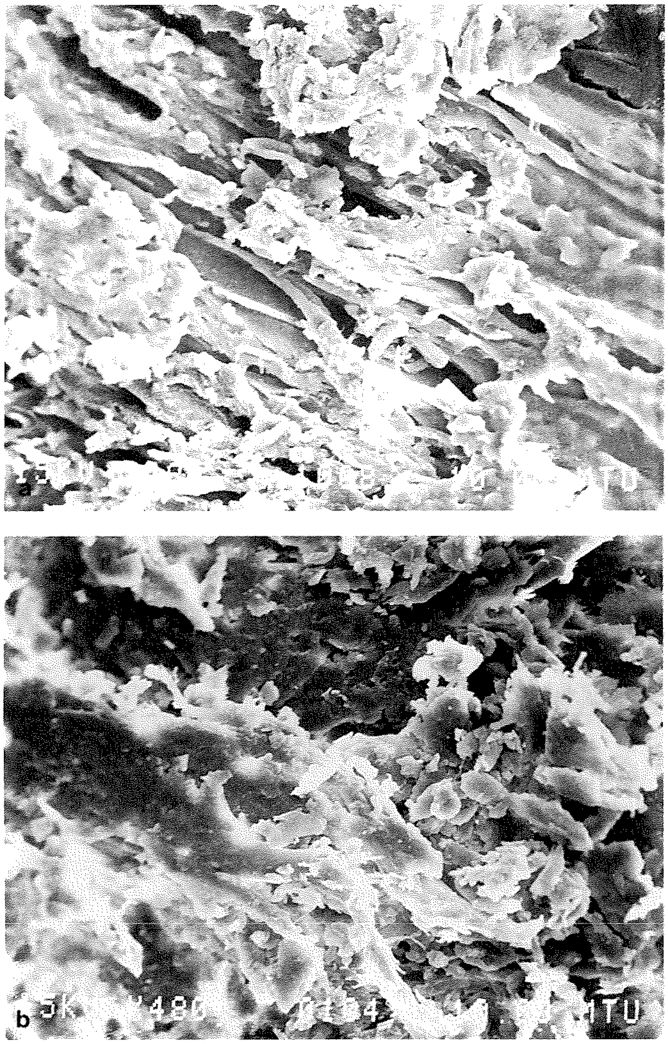

Fig. 3. Scanning electron micrographs of wood surfaces with (**a**) and without (**b**) coating from the PS-P(MAA-S) emulsion. The coated sample (**a**) was obtained from 4 dip-dry cycles. Magnification is 480 ×

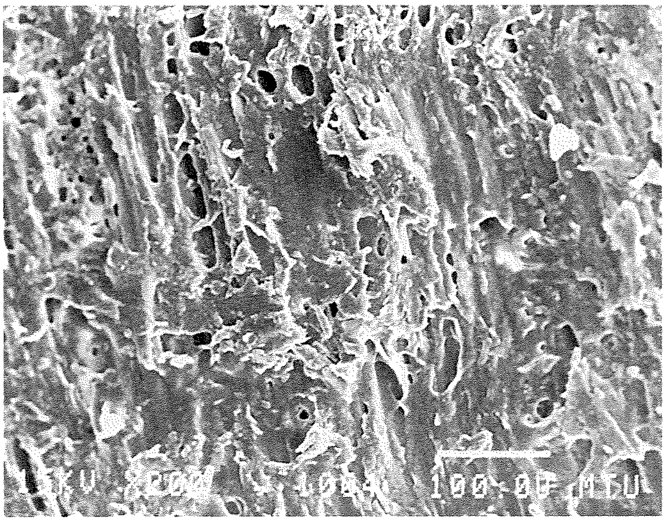

Fig. 4. Scanning electron micrographs of coated wood samples from 10 dip-dry cycles. Coating was done by cycles of dipping the wood into the PS-P(MAA-S) emulsion, and then air-drying for several minutes. Magnification is 480 ×

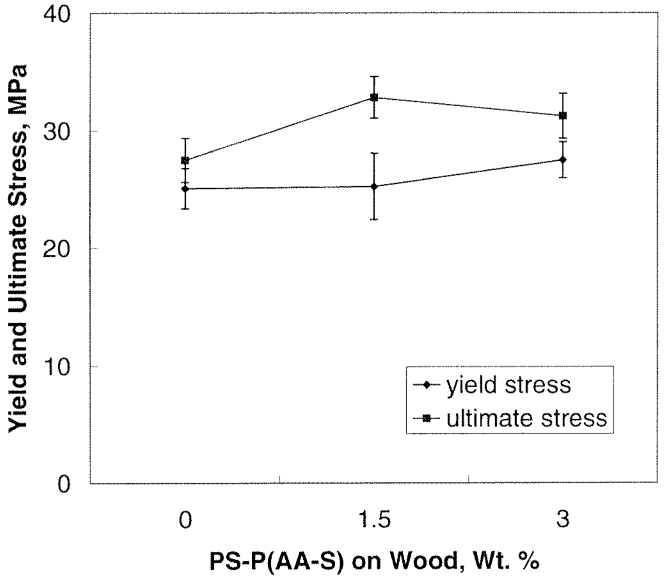

Fig. 5. Yield and ultimate stresses of 90/10 polystyrene/wood wt/wt composites at various PS-P(AA-S) loadings on the wood surface. Values can be compared with yield and ultimate stresses for the base polystyrene at 32 ± 6 and 32 ± 3 MPa, respectively

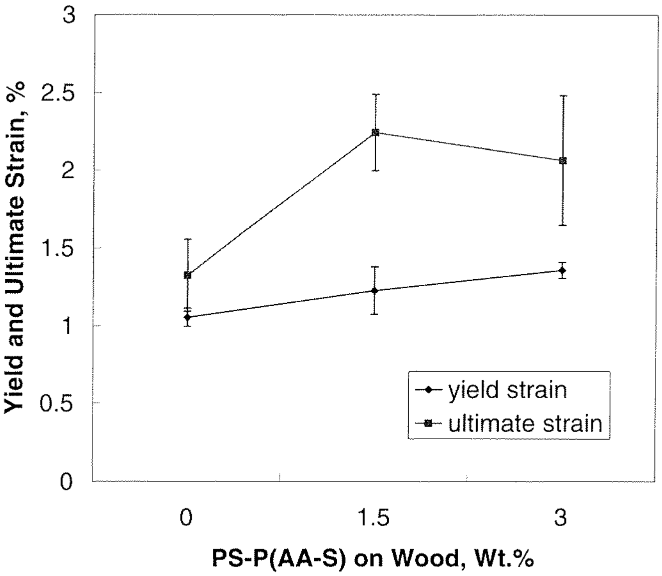

Fig. 6. Yield and ultimate strains of 90/10 polystyrene/wood wt/wt composites at various PS-P(AA-S) loadings on the wood surface. Values can be compared with yield and ultimate strains for the base polystyrene at 2.1 ± 0.4 and 2.4 ± 0.9%, respectively

considering that molecular weights were measured using polystyrene standards. Since the raw product has lost a great proportion (in mole numbers) of relatively short-chain molecules, it is no surprise that the purified product will have a higher average molecular weight than the stoichiometric value. Also, under the conditions used for block copolymerization, live polymer radicals in the interior of the particles would not be completely accessible to the monomers. This could explain why there is still some (insubstantial) amount of homopolystyrene contaminating the block copolymer in the raw product. On the other hand, short chain live radicals could also be present before the addition of the second monomer (methacrylic acid). This explains the small poly(methacrylic acid)-rich material extracted from the raw product. There is also the possibility that the methacrylic acid segments of the block copolymer could segregate in the size exclusion chromatography columns because THF is not a good solvent for poly(methacrylic acid). This possibility has been well documented by researchers who have done molecular weight measurements of low molecular weight carboxy-terminated polystyrene with known molecular weight distributions (Hirao et al. 1993). Finally, it was cited that a polymer with an ionizable group (-COOH in our case) could show a higher hydrodynamic volume for the same molecular weight, due to electrostatic repulsion, if the carrier fluid has a relatively low ionic strength, such as the THF used in our analysis (Barth 1986). Thus, the molecular weight of the copolymer seems to be higher than it really is.

Wood veneers of maple, cherry, and ash were coated with PS-P(MAA-S) from ammonia-water at different concentrations and with pH = 6 and pH = 10. In Table 3 it can be seen that the hydrophobicity of the veneer surface was increased after applying the polystyrene-*block*-poly(styrene-*co*-methacrylic acid) material. Without the coating, contact angles for all the species were between 82 and 88°, whereas after coating they were between 90 and 95°. It is also recognizable that contact angles did not considerably increase with the concentration (amount) of PS-P(MAA-S). Therefore, a good hydrophobic surface is obtained with low concentrations (0.02 wt%) of PS-P(MAA-S) at pH = 10.

In Fig. 5, yield-stress values of the composites are slightly lower than that of the base polystyrene at 32 ± 6 MPa, whereby a slight improvement was observed for the coated composite with 3 wt% copolymer on wood. On the other hand, definite improvements in ultimate stresses were obtained from the coated composites compared to the uncoated one. In fact, the composite with 1.5-wt% coating on wood exhibited a mean ultimate stress of 33 ± 4 MPa compared to that of the base polystyrene at 32 ± 3 MPa. For the composite coated with 3-wt% copolymer on wood, the ultimate stress was at 31 ± 4 MPa. All these above-mentioned data indicate good bonding between the wood and base polystyrene for the coated wood/polystyrene composites. One particular note of interest is the higher values of the ultimate strains for the coated wood-based composites at ultimate-stress values similar to that of the base polystyrene. This indicates that these composites should exhibit better impact properties than composites made from uncoated wood flour. As far as the mechanism of failure is concerned, the above data seem to indicate substantial cohesive failure in the coated wood-based composites. The exact sequence of events is still subject to debate, and it can only be resolved by a more detailed study of the fracture surfaces.

The significant improvement in composite properties using dilute emulsions of the coupling agent in water could be attributed to the efficiency of the application of the block copolymer. To promote adhesion between the hydrophilic wood surface and the hydrophobic polystyrene material, the coupling agent should be placed at the interface. The effectiveness of this placement of block copolymer coupling agents is always in question if the wood, thermoplastic, and coupling agent are mixed in a blending machine. Another factor that contributes to the efficiency of the use of the coupling agent in this study is that it is introduced within a liquid phase. This almost guarantees uniform dispersion of the block copolymer. Normally, one can always use organic solvents as the carrier liquid. However, in practical applications this is not only uneconomical but it is a pollution hazard. With the use of water as the carrier fluid for the hydrophilic-hydrophobic block copolymer as hydrophobic coating and composite coupling agent, we have achieved a significant improvement in material performance in an environmentally responsible and economical manner.

Inefficiencies in the production of the hydrophilic-hydrophobic block copolymers that we have observed should be surmountable enough for practical implementation, considering that effective coupling between the wood and polystyrene is obtained at less than 1.5 wt% on wood. We also found that removal of homopolymer contamination (polystyrene) is quite convenient through heating of the raw product in ammonia water. The homopolymer contamination separates out as a coagulant. As far as the cost of the synthesis method, all we can say is that it is the least costly of all the block copolymer formation methods around. It is also becoming increasingly efficient as we discover new solvents and process conditions. It is likely that process conditions will be discovered that can easily be implemented in a closed-loop solvent use and recycle operation.

Conclusions

We have shown that emulsions of neutralized polystyrene-*block*-poly(styrene-*co*-methacrylic acid) can be used to form hydrophobic coatings on wood surfaces. Through contact angle measurements, the emulsion was found to form a more hydrophobic surface on wood. When dilute emulsions of polystyrene-*block*-poly(styrene-*co*-acrylic acid) were used to coat wood flour surfaces, composites of polystyrene with coated wood flour exhibited slightly better yield stresses than composites from uncoated wood flour. Improvements that are even more significant were obtained in ultimate stresses and yield and in ultimate strains for coated-wood/polystyrene composites compared to their uncoated counterparts. In fact, ultimate stresses and strains of the coated wood/polystyrene composites have been found to be similar to those of the base polystyrene. All these indicate that the use of hydrophilic-hydrophobic block copolymers on wood surfaces can result in improvement to the mechanical properties of wood-thermoplastic composites in a manner that is both economical and environmentally responsible.

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