PINE

INTERFACIAL STRUCTURE AND PROPERTIES OF WOOD/ POLYPROPYLENE COMPOSITES

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INTRODUCTION

Composite wood products have traditionally relied on thermosetting polymers like phenol-formaldehyde and urea-formaldehyde resins as binders. The continuing need to effectively utilize lignocellulosic fiber from low-quality hardwoods and from recycling streams has prompted consideration of new composites based on thermoplastic polymers [1,2]. Much of the development effort has focused on commodity polymers like polyethylene and polypropylene as the matrix or binder. Substantial progress has been made toward circumventing many of the processing challenges presented by this type of material. This work has consistently demonstrated the limited interaction that is established between the dissimilar phases, highlighting the need to better define factors influencing adhesion [3].

Several viable approaches to improve the properties of cellulose fiber/polypropylene composites have been studied [4,5]. Of these, fibers grafted with maleic anhydride modified polypropylene have shown the most potential [6-8]. Very little consideration has been given to high-yield pulp fibers or solid wood, however. This work describes the effect of wood fiber surface structure on interaction with polypropylene, and its influence on composite morphology and properties.

EXPERIMENTAL

Materials. Wood fibers were generated from Southern red oak chips with a pressurized disk refiner after a 2 minute steam pre-treatment at 100 psig. The fibers were drained, washed 3 times with hexane and air-dried to constant weight. The fibers were modified with commercial silane (Dow Corning, Z-6030) and titanate (Kenrich, LICA-12) compatibilizers in hexane. Modified fibers were also prepared with a commercial blend of fatty amines through a condensation reaction with formaldehyde. The fibers were characterized by x-ray photoelectron spectroscopy and dynamic contact angle analysis (CAHN Model DCA-322). A commercial isotactic polypropylene was used in all material formulations. Composites (50 weight percent) were prepared by first compression molding the fiber/polymer mixture into a small plaque. This was then cut for feeding into a Brabender %-inch laboratory extruder with a 3 mm strand die. The extruder speed was 35 rpm, and the barrel temperature was set at 195° C. Izod impact and tensile test specimens were prepared by injection molding the pelletized material at 200° C.

Methods. ***Thermal*** properties of the composites were determined with a Perkin-Elmer, Model DSC-7 calorimeter. The samples (ca. 15 mg) were scanned at 10 deg/min after first heating to 220” C for 5 minutes to erase thermal history effects. Composite morphology was evaluated on fracture surfaces of the composites using an Amray (AMR-900) scanning electron microscope.

RESULTS AND DISCUSSION

Each of the chemical treatments were shown to be effective modifiers of surface composition by x-ray photoelectron spectroscopy. The greatest increase in hydrocarbon character was found for the fatty amine compatibilizer. Table 1 shows the effect of modification on fiber surface energy characteristics. Both the fatty amine and silane compatibilizers significantly reduced the total surface energy of the fiber from approximately 36 mJ/m^2 to 29 mJ/m^2. Each of the modifications increased the contribution of the dispersive component to surface energy while minimizing the influence of specific forces. The data clearly reflect an increased hydrocarbon character as suggested by XPS, although the fatty amine and silane modifiers appear to be slightly less efficient.

Table 1. Effect of fiber modification on the surface energy of southern red oak fibers.

Treatment	Van Oss' Surface Energy, γ (mJ/m^2)		
	Total	Dispersive	Acid/Base
Control	35.60	29.56	6.04
Fatty Amine	29.19	27.90	1.29
Silane	26.31	26.60	1.51
Titanate	34.36	34.27	0.09

The effect of fiber modification on the crystallization behavior of polypropylene composites is shown in Figure 1. The onset of crystallization occurs near 120” C and varies only slightly for the different fiber composites. The unmodified and fatty amine composites exhibit a very similar' profile, with the peak temperature found at 112" C. This compares with a peak temperature of 115° C for the unfilled polypropylene (not shown). In contrast, a much broader crystallization exotherm that is centered at a slightly lower temperature is observed for the titanate- and silane-modified fiber composites. It is somehwat surprising that despite different surface properties the fatty amine-modified fiber is comparable to the control fiber in its influence on crystallization of the polypropylene matrix. While this suggests other factors may be important in determining matrix morphology, it clearly reveals different levels of interaction between the wood fiber and polypropylene that can be expected to influence composite performance.

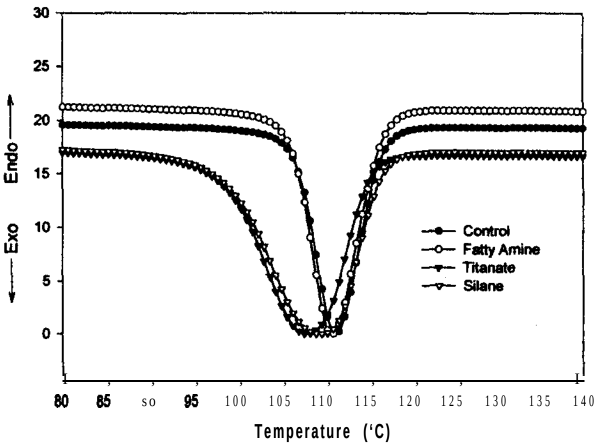

Figure 1. Crystallization peak of polypropylene (50 wt.%) composites prepared with red oak fibers: unmodified (•), fatty amine (o), silane (A), titanate(Δ).

The variation in mechanical properties of the wood fiber composites is compared to the untilled polypropylene in Table 2. As expected the modulus of elasticity is significantly higher for all of the fiber composites, increasing from almost 300 MPa for the unfilled polymer to approximately 840 MPa for the unmodified and titanate-modified fiber systems. The stiffness of composites prepared with the fatty amine and silane modifications was dramatically lower than the other composites. While this may arise from process variables like poor dispersion, it more likely reflects a plasticizing effect of the treatment on the lignin component. The strength properties of the fiber composites are consistently lower than the unfilled polypropylene. The same is true for elongation, although that is to be expected. This suggests that active reinforcement of the polypropylene matrix is virtually absent and very little stress transfer to the fiber is achieved.

Table 2. Mechanical property data for polypropylene/ red oak fiber (50/50) composites.

Property	P P	Fiber Treatment			
		Ctl	Ami	Sii	Tit
Elastic Modulus (MPa)	294	839	623	652	834
Tensile Strength (MPa)	35.3	29.2	24.1	25.4	26.9
Elongation (%)	67	6.5	7.4	6.4	5.7
Impact Strength (J/M)		17.3	20.0	16.6	17.1

It is worth noting that the composite prepared with the fatty amine-modified fibers exhibits the highest impact strength and elongation, as well as the lowest modulus and tensile strength. While this behavior is consistent with improved polypropylene compatibility and adhesion, it probably also reflects differences in the fiber properties as a result of chemical modification. Penetration and reaction with the bulk of the fiber (i.e., lignin) would disrupt the internal structure, reducing fiber strength and stiffness. Evidence of bulk modification may be indirectly available from the surface energy data. The wood fibers modified with the fatty amine and silane compatibilizers still have a considerable acid/base component relative to the titanate system. The target levels of modification were the same for all of the approaches. As such, the incomplete surface coverage may result from loss of the molecules into the fiber cell wall.

Figure 2 shows the freeze-fracture surface of composites prepared from the unmodified red oak fibers, and from fibers modified with the fatty amine and titanate compatibilizers. All three images illustrate the continuing limitations associated with fiber damage and dispersion in the polymer matrix. The basic issue of poor adhesion between wood fiber and polyolefins is readily evident from even a cursory evaluation of the unmodified fiber composite. There is no indication of adhesion on the clean fiber surfaces. A sharp contrast is offered by the fatty amine-modified fiber composite. Although fiber pull-out is extensive in this sample, improved fiber/polymer interaction is evident from regions where the fiber was embedded. The fracture surface of the titanate-modified composite reveals a completely different morphology. Improved interaction between the components is apparent; however, the extensive array of circular domains is of particular interest. Similar structures were found in the silane-modified system, but they were not as extensive. Although speculative in nature, this may result from nucleation of crystallites along the longitudinal axis of the fiber. Analysis of single-fiber specimens by polarized optical microscopy support the contention that transcrystallization [6] is significant in these composites. These observations further indicate that surface chemical structure and properties of the wood fibers dramatically influence composite morphology, which would further impact composite behavior.

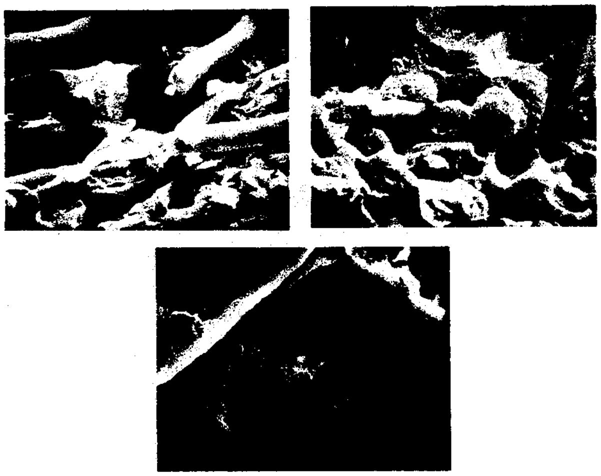

Figure 2. Scanning electron micrographs of freeze-fracture surfaces of polypropylene/red oak fiber composites: unmodified (top, *left*), fatty amine compatibilizer (*top, right*), titanate compatibilizer *(bottom).*

Conclusions

The properties of wood fiber/polypropylene composites develop from a complex interaction of several variables. Fiber wettability and interaction with polypropylene can be improved by modification with conventional silane and titanate compatibilizing agents. Similar improvements in fiber/polymer interaction are available using a fatty amine to increase the hydrophobic character of the fiber surface.

Chemical modification of the fiber with fatty amine and silane compatibilizers were detrimental to the mechanical properties of the composites. This can be attributed to diffusion and reaction in the bulk of the wood fiber, which effectively plasticizes the amorphous polymers of the fiber. Also, surface modification defines the nature of the interaction that is established between the fiber and polypropylene matrix. This can dramatically influence polymer crystallization, and ultimately composite properties. Research is continuing to establish the complex relationships between fiber characteristics and processing conditions (e.g., thermal history) on crystalline morphology and composite performance properties.

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