RECENT ADVANCES IN AGRO-FIBER/THERMOPLASTIC COMPOSITES

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ABSTRACT

Flexural strength, tensile strength, and unnotched Izod toughness were much higher for aspen-PP composite with 2% MAPP compatibilizer as compared with the composite with no compatibilizer. Flexural modulus, tensile modulus and notched Izod toughness are about the same for both sets of composites. Rockwell hardness and abrasion resistance was higher in the compatibilized composite as compared to the noncompatibilized composite. Flexural creep is greater in noncompatibilized composites than there was in the compatibilized composites. Water soaking for 24 hours give an increase in weight of about 1% regardless of compatibilizer content. Increasing the time to 30 days did not cause any additional moisture uptake. Cyclic humidity testing between 30 % RH and 90% RH showed that there was a small but steady increase in moisture sorption with each humidity cycle. Thermogravametric analysis showed little differences in the thermal properties of the two types of composites charred under nitrogen and air. The major weight loss, under nitrogen, for both composites, occurred at 460°C with a minor weight loss peak at 351 °C. There was slightly more char formation in the noncompatibilized composite (19.2%) as compared to the char formation in the compatibilized composite (17.7%). Weathering of both composites was restricted to the outer 0.5 mm of the surface. Weathering gave rise to a loss in surface smoothness and the development of a white chalky surface layer. A slight weight loss occurred during the brown-rot fungus test on the two aspen-PP composites showing that a small attack, probably in the surface aspen fibers, may occur on the surface of the composites. No attack was observed in either composites by the white-rot fungus.

INTRODUCTION

The field of natural fiber reinforced thermoplastic composite materials is now rapidly growing both in terms of industrial applications and fundamental research. The breadth of the interest in the subject and its worldwide aspect was reflected in the participation at the fourth international Woodfiber-Plastic Composites Conference held in Madison, Wisconsin, May 11-14, 1997. This conference was sponsored by the United States Department of Agriculture, Forest Service, University of Wisconsin, University of Toronto, American Plastics Council, American Chemical Society, and the Forest Products

Society and was hosted by the Forest Products Laboratory in Madison There were a total of 278 registrants with representation from 17 countries [1].

The conference covered both fundamental and applied aspects of the fiber-plastic composite field. The fundamental sections covered topics such as fiber analysis, optimizing particle size, characterizing woodfiber-plastic composites, surface interactions, interface and compatibilization, adhesion, structural-property relationships, failure mechanisms, and property improvement effects. The application sections covered topics such as processing issues, compounding equipment, materials requirements, design, codes and standards, marketing, construction applications, and transportation issues. There were keynote presentations on the role of design in industrial materials technologies, the role of renewables in the global raw materials picture, and opportunities in the automotive industry for filled and reinforced plastic materials.

The use of lignocellulosics as fillers and reinforcements in thermoplastics has been gaining acceptance in commodity plastics applications in the past few years. It is interesting to point out that the use of the lignocellulosics in commodity thermoplastics to reduce cost and/or to improve mechanical performance is not new, and there are plenty of published papers, including patents dating back to the 1960's and 1970's. The resurgence of interest in the 1990's is probably due to increasing plastic costs and environmental aspects of using renewable materials.

The lignocellulosics that can be used in thermoplastics can be obtained from several sources, both from forestry and agricultural resources. The physical form can vary from fine wood flour (particulate) to kenaf, flax, sisal and other agro-based fibers. The cost and performance of the final composite products dictates the type of lignocellulosic to be used in the plastics. Literature also cites the use of typical plastics such as polyethylene, polypropylene, polyvinyl chloride and also some elastomeric co-polymers for blending with the lignocellulosics.

Blending of the plastics with the lignocellulosics may require compatibilization to improve the dispersion, flow and mechanical properties of the composite and has been reported as far back as the late 1960's. Extrusion of lignocellulosics-filled plastics for the automotive industry is well known and has been used for more than twenty years. Typical blending involves the plastic-filler/reinforcement to be shear mixed at temperatures above the softening point of the plastics. The heated mixture is then typically extruded into "small rods", that are then cut into short lengths to produce a conventional pellet. The pellets can then be used in typical injection or compression molding techniques. To reduce the cost of this blending process, direct injection molding of wood bark fibers in plastics have also been reported in the 1960's. The direct injection molding process probably has limitations on the amount of filler/fiber that can be used in the composite, and is also likely to be limited to particulate or shorter fiber. The chemical characteristics of the surface and bulk of the lignocellulosics are also important in the blending with plastics. The ability of the matrix of the lignocellulosic (hemicellulose and lignin) to soften in the presence of moisture at plastic processing temperature may give these renewable materials unique characteristics to develop novel processing techniques.

There is still a great deal of basic research going on in many parts of the world in the area of natural fiber/thermoplastic composite materials. This research includes the use of many different types of agro-based fibers, expanding the amount of agro-based fibers in the composites, developing better

compatibilization systems, developing testing procedures, and understanding performance through modeling. Equipment development is going forward to produce more efficient mixing systems, faster through put, and new methods of molding/injection.

One of the research areas of interest in the fiber/plastics composite area is performance of these materials in outdoor applications. Issues of weathering, moisture up take, creep, and decay resistance are important properties to study to determine the change in properties as a function of environmental stresses.

The purpose of this paper is to describe recent results on environmental testing of fiber/ thermoplastic composites from a cooperative study between the Forest Products Laboratory, the University of Wisconsin, and the University of Toronto.

EXPERIMENTAL

MATERIALS

Two sets of specimens were prepared: 30% aspen fiber:70% polypropylene (PP) (by weight) with no additives and 30% aspen fiber:68% polypropylene:2% maleic anhydride grafted polypropylene (MAPP) (by weight). The PP homopolymer had a melt flow index of 12 g/10 min. as measured by ASTM D-1238. The MAPP had a number average molecular weight of 20,000, a weight average molecular weight of 40,000 and about had 6 % by weight of maleic anhydride in the polymer.

The aspen fiber, MAPP and PP (the latter two in pellet form) were compounded in a high intensity thermo-kinetic mixer where the only source of heat is generated through the kinetic energy of rotating blades. The blending was accomplished at 4600 rpm and then automatically discharged at 190°C. The total residence time of the blending operation averaged about 2 min.

The mixed blends were then granulated and dried at 105°C for 4 hours. Test specimen were injection molded at 190°C using pressures varying from 2.75 MPa to 8.3 MPa depending on the constituents of the blend.

PHYSICAL PROPERTIES

Test specimen dimensions were according to the respective ASTM standards. The specimens were stored under controlled conditions (20 % Relative Humidity and 32 °C) for three days before testing. Tensile tests were conducted according to ASTM 638-90, Izod impact strength tests according to ASTM D 256-90, and flexural testing using the ASTM 790-90 standard. The cross-head speed during the tension and flexural testing was 12.5 mm/min. Six specimens of each type were tested and the results averaged.

Rockwell hardness was measured using a 0.625 mm ball and 60 Kgf (588.4N) of indent force (Rockwell scale L). Specimens were conditioned at 27°C 30% RH prior to hardness testing. Six measurements were taken at different parts of 4 specimens and the results averaged.

Taber abrasion was measured using a H-18 abrasion wheel. Two wheels, each with 1 Kg weight,

rotate on the surface of the specimen causing sliding and scuffing abrasion. After 1000 cycles, the Taber Wear Index (TWI) was calculated as follows:

$$TWI = \frac{\text{Specimen weight loss (mg) x 1000}}{\text{number of cycles}}$$

The lower the wear index, the better the abrasion resistance of the material

Flexural creep tests were conducted using a load of 35% of the flexural failure load for specimens with no coupling agent (3.1 kg). Tests were conducted at a single loading at either 23°C Or 40°C. Total creep strain was reported as the strain in mm on the specimen. It is the sum of the instantaneous (elastic) strain plus the creep deformation with time (plastic).

MOISTURE SORPTION

Liquid water sorption tests were conducted by submerging the specimens in water for 24 hours and measuring the increase in weight as compared to the original oven dry weight of the specimens. The specimens were then re-submerged in water and left for an additional 30 days. Again, the increase in weight was determined as compared to the original oven dry weight.. Five specimens of each type were tested and the results averaged.

Cyclic humidity tests were conducted by first measuring the weight of the specimens at 27°C, 30% RH and then placing the specimens in a 27°C 90% RH room for 15 days. After weight was measured under these conditions, the specimens were again placed in the 27°C, 30% RH room for another 15 days. This cycle was repeated 5 times. Thirty specimens of each type were tested and the results averaged.

THERMAL PROPERTIES

Thermogravimetric analysis (TGA) and derivative (DTG) analysis were done either in nitrogen or air. Samples of 4.1 mg were charred at 20°C/min to a temperature of 600°C using a nitrogen or air flow rate of 200 ml/min. Furnace temperature was programmed by the data system through a digital-to-analog converter.

WEATHERING

The faces of all test specimens were exposed to a 6500-watt xenon arc light source (which closely approximates natural sunlight spectrum in the visible and ultraviolet (UV) regions) in an enclosed chamber at 45 to 50°C. Half of each specimen was covered with aluminum foil so only half of each specimen was exposed to UV light. Exposure to UV radiation alternated with a spray of distilled water for 18 minutes followed by 102 minutes of UV light without water spray. Exposure time is expressed as hours of exposure to light. All specimens were oven dried, weight and thickness measured

before the test. Specimens were removed at approximately 200 hour intervals and changes in brightness measured. Brightness is a measure of bleaching or whiteness of the specimen. Twenty-five of each type of composite were tested and the results averaged.

At the end of 2100 hours, the specimens were re-oven dried and their thickness and weight measured. The thickness of the weathered end of each specimen was measured, the white chalky surface was removed and thickness measured again to determine the depth of surface degradation.

DECAY TESTS

A 12 week soil-block test was run according to specifications outlined in ASTM Standard D 1413. Specimens were sterilized and placed in test with either the brown-rot fungus *Gloeophyllum trabeum* (Madison 617)or the white-rot fungus *Coriolus versicolor* (Madison 697). Twelve specimens of each type of composite were tested and the results averaged. Specimens were conditions at 27°C, 30% RH before and after test. Extent of fungal attack was determined by weight loss.

RESULTS AND DISCUSSION

The mechanical properties of the aspen fiber-polypropylene composites with and without compatibilizer are shown in Figure 1. Values for flexural strength, tensile strength, and unnotched Izod toughness are much higher for the composites with 2% MAPP compatibilizer as compared with composites with no compatibilizer as has been shown before [2-4]. Flexural modulus, tensile modulus and notched Izod toughness are about the same for both sets of composites. Rockwell hardness is higher in the compatibilized composite indicating that the compatibilizer improves hardness. The Taber Wear Index is higher for the noncompatibilized composite indicating that abrasion resistance is higher in the compatibilized composite than in the noncompatibilized composite.

Table 1 - Mechanical properties of aspen fiber-polypropylene composites

Property	30% aspen 70% PP	30% aspen 68% PP 2% MAPP
Flexural strength (MPa)	53.7 (+/- 0.4)	76.6 (+/- 0.5)
Flexural modulus (GPa)	3.1 (+/- 0.1)	3.4 (+/- 0.1)
Tensile strength (MPa)	29.6 (+/- 0.1)	48.2 (+/- 0.3)
Tensile modulus (GPa)	2.5 (+/- 0.4)	2.7 (+/- 0.1)
Izod-notched (J/m)	28 (+/- 1)	27 (+/- 6)
Izod-unnotched (J/m)	119 (+/- 11)	149 (+/- 11)
Rockwell hardness	79.1	92.3
Taber Wear Index	152	102

The results of the flexural creep tests are shown in Figures 1 and 2. At both temperatures tested, there is more creep in the noncompatibilized composites than there is in the compatibilized composites. As expected, there is less creep at 23°C as compared to 40°C in both types of composites.

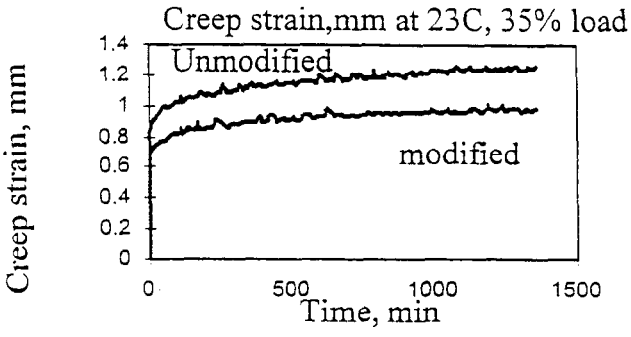

Figure 1 - Creep strain of aspen-polypropylene composites at 23°C at 35% of flexural failure load.

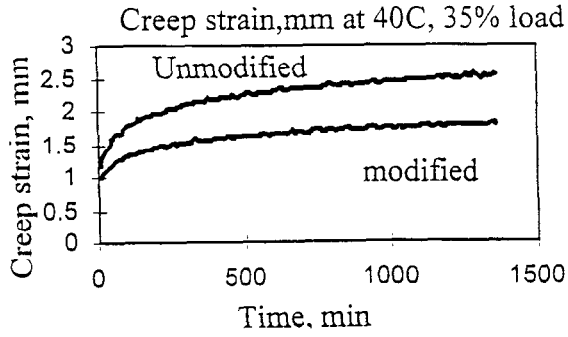

Figure 2 - Creep strain of aspen-polypropylene composites at 40°C at 35% of flexural failure load.

Both composite types soaked in water for 24 hours give an increase in weight of about 1% regardless of compatibilizer content. After an additional 30 days of water soaking, the in crease in weight was still about 1% for both types of composites. The fibers at the surface of the composite can sorb a small amount of water but the data suggests that water is not wicked from fiber to fiber within the composite even after long periods of time. If wicking occurred, a higher level of water sorption would be expected after the 30 day period.

Table 2 shows the results of cyclic humidity tests. Both composites give an EMC of about 0.13 at the first 30% RH condition. The composite containing the compatibilizer shows a slightly higher EMC at 90% as compared to the composite containing no compatibilizer. The noncompatibilized composite shows slightly lower EMC values at each 30%-90% cycle, however, both composites show an EMC under 2% in the final 90% RH cycle. It is interesting to note that the EMC for both types of composites slowly increases with each cycle which indicates that each time the composite swells from 30% RH to 90% RH, the composite does not return to the EMC at 30% RH from the previous cycle. The data indicates that five cycles of humidity cycling may not be enough to determine the ultimate swelling and moisture sorption of these composites in actual exterior applications.

Table 2 - Cyclic humidity testing of aspen-polypropylene composites

Specimen	Equilibrium moisture content (EMC) at 27°C at two different relative humidities										
	30%	90%	30%	90%	30%	90%	30%	90%	30%	90%	30%
	<———				%					———>	
30% Aspen 70% PP	0.13	0.78	0.39	1.17	0.52	1.43	0.78	1.43	0.91	1.69	1.17
30% Aspen 68% PP 2% MAPP	0.13	0.89	0.51	1.28	0.77	1.41	0.90	1.66	1.15	1.91	1.28

The results of the cyclic testing shows that there is a small but steady increase in moisture sorption with each humidity cycle. No increase in weight due to moisture sorptioin was seen in the long non-cyclic water soaking test. Perhaps a water test of wetting and drying cycles might give different results as compared to the continuous soaking test results.

Figures 3 and 4 show the thermogravimetric analysis of both types of composites charred under nitrogen and Figures 5 and 6 show the thermogravimetric analysis of both types of composites charred under air. The TGA data in Figure 3 and 4 shows that the major weight loss, under nitrogen, for both composites, occurs at 460°C which must be the decomposition of the PP. The minor weight loss peak at 3.51 °C is the aspen component of the composites. There is slightly more char formation in the noncompatibilized composite (19.2%) as compared to the char formation in the compatibilized composite (17.7%).

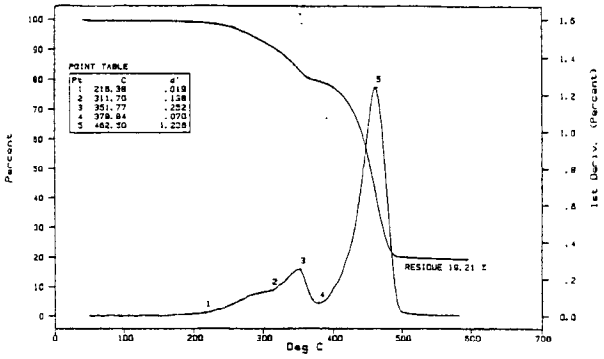

Figure 3 - Thermogravametric testes in nitrogen on noncompatibilizes aspen-polypropylene composites

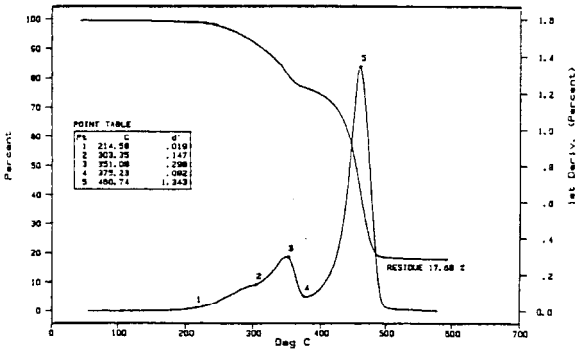

Figure 4 - Thermogravametric testes in nitrogen on compatibilizes aspen-polypropylene composites

The data in Figures 5 and 6 show that the major weight loss, in air, for both composites, occurs at about 355°C with a small weight loss peak at about 435°C. Very little char remains at 500°C in air.

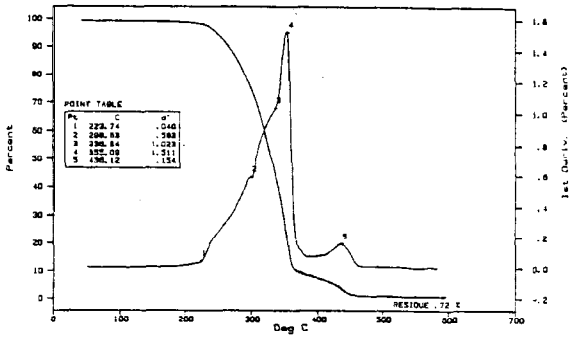

Figure 5 - Thermogravametric testes in air on noncompatibilizes aspen-polypropylene composites.

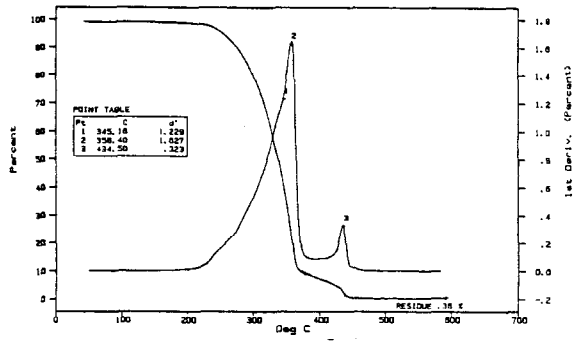

Figure 6 - Thermogravametric testes in nitrogen on compatibilizes aspen-polypropylene composites.

Table 3 shows the increase in brightness or whiteness as the surface of the composites degrade in UV radiation. The surface of both composites shows some bleaching and water spotting at 200 hours of UV exposure. At 400 hours, a slight surface roughness is noted and at

Table 3 - Weathering of aspen-polypropylene composites

Specimen	Increase in brightness at: (Hrs)*										Weight loss after test
	200	400	600	800	1000	1200	1400	1600	1800	2000	
	<———				%				———>		
30% Aspen 70% PP	15.7	32.5	40.2	43.7	45.1	48.3	49.0	50.5	50.6	49.3	3.9
30% Aspen 68% PP 2% MAPP	10.5	36.0	42.1	46.4	47.2	50.0	51.4	51.8	53.3	52.2	2.9

* Compared to the original unexposed surface

600 hours the surfaces start to turn white. By 1400 hours, the surfaces are rough and a white powder can be removed from the surfaces with mild abrasion. At 2000 hours, the surfaces are very rough and chalky.

Slightly more weight loss occurs during weathering in composites with no compatibilizer as compared to the compatibilized composites but the rate of surface degrade is about the same for both composites. After 2000 hours of UV exposure, about 0.3 mm of the surface of both composites has been lost to degradation. Measuring the thickness of the specimens after scraping the white degraded material from the surface down to original color shows that the degradation has occurred in the top 0.4 mm. This shows that while weathering is restricted to the outer 0.5 mm, the loss of surface smoothness and the development of a white chalky surface layer may restrict this type of composites from some exterior applications.

Table 4 shows the results of the 12 week soil-block test using a brown- and white rot fungi. Aspen alone losses over 50% of its weight due to brown-rot decay and over 25% of its weight due to white-rot decay. Pure PP shows no decay by either fungi in the test. A slight weight loss occurs during the brown-rot fungus test on the two aspen-PP composites showing that a small attack, probably in the surface aspen fibers, may occur on the surface of the composites. No attack is seen in either composites by the white-rot fungus.

Table 4 - Weight loss after 12 weeks soil-block test of aspen fiber-polypropylene composites

Specimen	Weight loss due to attack by:	
	G. trabeum	C. versicolor
	<——— %	———>
100% Aspen	54.2	27.3
100% PP	0	0
30% Aspen 70% PP	0.23	0
30% Aspen 68% PP 2% MAPP	0.08	0

CONCLUSIONS

Using agro-fiber-polypropylene composite in outdoor environments raises questions about their performance in adverse conditions. Long term exposure to micro organisms, moisture, ultraviolet radiation, heat, load, and abrasion may limit their use for some exterior applications. Flexural creep, especially as the temperature and load increases, will be a concern. Problems associated with creep by increasing the percentage of agro-fiber, however, the thermoplastic matrix in these composites will always result in some plastic creep.

Composites submerged in water for long periods of time did not result in an continual increase in moisture content, however, under cyclic humidity conditions, the composites showed a small but steady increase in moisture sorption with each humidity cycle. Once the surface fibers are wetted under static moisture conditions, little additional moisture is sorbed by the composite with time. As the agro-fiber content increases in these composites, more fiber to fiber wicking is possible so moisture gain may increase with time.

Thermogravametric analysis showed that at 30% agro-fiber, pyrolysis is mainly due to the PP component. As the agro-fiber content increases, the pyrolysis reactions will change. At very high levels of agro-fiber, it may be necessary to add a fire retardant to the composites.

While weathering of these composites is limited to the outer 0.5 mm of the surface, it results in a loss in surface smoothness and the development of a white chalky surface layer. Direct exposure to sunlight may not be desirable to maintain color stability.

A slight weight loss occurred during the brown-rot fungus test on the two aspen-PP composites showing that a small attack, probably in the surface aspen fibers, may occur on the surface of the composites. No attack was observed in either composites by the white-rot fungus. Biological attack may increase as the agro-fiber content increases.

Environmental testing of agro-fiber-thermoplastic composites will continue on composites with higher agro-fiber content, different additives, and different thermoplastics.

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