PROPERTIES OF STYRENE-MALEIC ANHYDRIDE COPOLYMERS CONTAINING WOOD-BASED FILLERS

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ABSTRACT

Recycled newsprint (ONP) and dry process aspen fiber were combined with styrene maleic anhydride (SMA) copolymers containing either 7 or 14 percent maleic anhydride. The fiber-filled SMA composites were equivalent or superior to unfilled SMA in strength, stiffness, and notched Izod impact strength. ONP performed surprisingly well as a filler. Unnotched Izod impact strengths for filled polymers were lower than for unfilled polymers. Water sorption was similar among fillers, and was small compared with solid wood.

The use of wood as a reinforcing filler for thermoplastics has been receiving considerable attention from the research community and industrial manufacturers in recent years (4,5,8,9). The automotive industry uses styrene-maleic anhydride (SMA) copolymers for the injection molding and thermoforming of interior parts (3). The maleic anhydride functionality improves the properties of the copolymer. compared to polystyrene, especially the heat resistance. This class of polymers is interesting since the reaction of the maleic group with the hydroxyl group on a wood filler may be similar to that of maleic anhydride modified polypropylene (MAPP) (6). The SMA plastics used in automobiles may potentially be recycled as composites if economical wood-based fillers can be added to improve the final strength properties.

We investigated the effectiveness of recycled newsprint as a wood-based filler for SMA copolymers and compared its performance to aspen fiber and pine flour fillers.

MATERIALS AND METHODS

Old newsprint (ONP) was ground in a Szego mill (General Comminution Inc., Toronto, Ontario, Canada) and the resulting dark gray powder was stored in a fiberboard container. For the wood fiber filler, we obtained dry-process hardwood fiber (primarily aspen. *Populus* spp.) from a medium density fiberboard plant. American Wood Fibers (Schofield Wis.) contributed a standard 40-mesh pine (*Pinus* spp.) flour, #4020. Copolymers Dylark 232 (SMA-7) and Dylark 332 (SMA- 14), containing 7 and 14 percent maleic anhydride, respectively, were contributed by ARCO Chemical Company (Newtown Square, Pa.).

SAMPLE PREPARATION

Composites were made from SMA-7 and each of the following fillers: ONP at 0,20,30, and 40 percent (weight), aspen fiber at 0, 20, 30, and 40 percent (weight), and pine flour at 0,20,40, and 50 percent (weight). Separate composites were also made from SMA-14 and either ONP or aspen fiber at 20, 30, and 40 percent (weight).

A high-intensity kinetic mixer (Synergistic Industries Inc., St. Remi-Napierville, Quebec, Canada) was used to blend each compound. The kinetic energy of rotating blades generated the only heat used in the mixing process. Compounds were blended at 5500 rpm until the temperature reached 149°C; the blender speed was then reduced to 4500 rpm until the temperature reached 232°C, when the blender automatically discharged each batch. The total blend time averaged about 2 minutes, but varied somewhat, depending on the proportions of each compound.

A Cincinnati Milacron Molder was used to form test specimens from the compounds, which had been granulated and dried at 105°C for 4 hours. The specimens were injection molded at 218°C into three sizes; filler content determined the appropriate injection pressure, which varied from 8.3 to 12.4 MPa.

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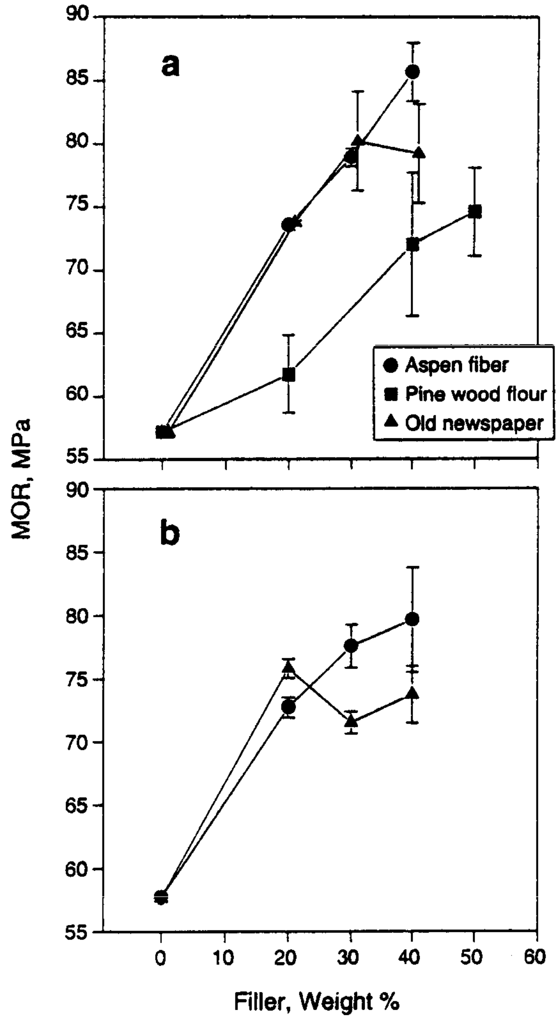

Figure 1. — Flexural strength (MOR) of filled copolymers: a. SMA-7; b. SMA-14.

Mechanical properties

For each type of test and for each compound, we used five 3- by 12- by 100-mm specimens. Modulus of rupture (MOR) and modulus of elasticity (MOE) were determined in flexure in accordance with American Society for Testing and Materials (ASTM) ASTM D 790-86 (2). The crosshead speed during testing was 1 mm/minute. Notched and unnotched Izod impact values were determined for each compound in accordance with ASTM D 256-93 (l).

Water absorption

Three types of tests were conducted to determine the water absorption of the composites. Three specimens for each filled and unfilled copolymer were either 1) placed in an environmental chamber for 19 days at 90 percent relative humidity (RH); 2) soaked for 24 hours in distilled water at room temperature; or 3) boiled in water for 2 hours. Before and after each treatment, the specimens were weighed and the percent weight gain (PWG) calculated as:

$$PWG = \frac{(W_f - W_0)}{W_0} 100\%$$

where:

W_0 = initial weight of the sample
W_f = final weight of the sample

Results and discussion

Mechanical properties

Modulus of rupture. — In composites with SMA-7, ONP filler yielded the same strength as aspen fiber at filler contents of 20 and 30 percent (Fig. 1a). This was surprising because ONP was a fine powder with an aspect ratio presumably close to 1. The pine flour, which also had a low aspect ratio, but appeared to have a larger particle size, showed inferior strength to both the ONP- and the fiber-filled samples. At the 40-percent tiller level, the strength of the ONP-filled sample dropped below that of the fiber-filled samples. This leveling off of MOR may perhaps be due to the presumably high-surface-area ONP filler that was not completely wetted by the matrix polymer. The leveling effect was even more evident in the ONP-filled SMA-14, wherein strength peaked at the 20 percent filler level (Fig. 1b).

Alternatively, this leveling effect may be due to the viscosity difference between SMA-7 and SMA- 14, SMA-7 and SMA- 14 have Vicat softening points of 118°C and 130°C, respectively (3). Thus, SMA- 14 may have a higher viscosity than SMA-7 at the same temperature, resulting in poorer mixing, or dispersion, of the filler in the matrix.

Modulus of elasticity. — MOE increased with increasing filler content for all systems (Fig. 2). There was little difference in stiffness between ONP, wood flour, or wood fiber-filled SMA copolymers. This suggests that MOE is not a strong function of the aspect ratio of the filler. The similar increases in MOE for ONP, aspen fiber, and pine flour also suggest that species differences were small in regard to stiffness.

Impact strength

Notched and unnotched Izod impact strengths were lower in ONP-tilled SMA-7 and SMA- 14 than in unfilled copolymer (Fig. 3). The diminution in impact strength seemed to be greatest as the filler content rose from 0 to 20 percent: the further decreases with increasing filler content were less severe. The impact strengths of wood flour-tilled samples were similar to those of ONP-filled samples. At filler content levels of 30 to 40 percent, however, the notched impact strength of aspen fiber-tilled SMA-7 stayed approximately the same. For fiber-filled SMA- 14, impact strength increased slightly with increasing filler.

Unnotched Izod impact strength was similar for all samples tested and showed the same trend of an initial sharp drop in impact strength as filler content increased, followed by a relatively constant level of impact strength as filler content increased further. The aspen fiber appeared to improve impact strength in comparison with the more particulate ONP and wood flour fillers. This was expected because fibers should be more resistant to crack propagation in the matrix.

Water absorption

Weight gain upon exposure to water increased as the percentage of filler increased for all composites tested, but the weight gains for all specimens were less than 4 percent (Table 1). The water absorption for the unfilled SMA-7 and SMA- 14 were about 0.5 ± 1 percent in the 90 percent RH test, and 1.5 ± 1 percent in both the 24-hour soak and 2-hour boil tests. The large standard deviations of the measurements made quantitative comparisons difficult. For both copolymers at the highest filler content, water absorption increased to about 2 to 3 percent in the 90 percent RH test, to 1.5 to 2.5 percent in the 24-hour soak and to 2.5 to 4 percent in the 2-hour boil. The 2-hour boil produced both the greatest weight gains and the greatest variation in weight gains. Weight gains in the 90 percent RH test were as much or more than those of the 24-hour soak; we therefore concluded that water vapor had diffused into the composite and was absorbed by the filler. Especially at high filler contents where interfiber interactions were greater, water vapor may have diffused more slowly, yet ultimately produced weight gains from water absorption just as effectively as did the ingress of liquid water. The various compositions did not differ significantly in water absorption.

Water absorption were higher for both the 90 percent RH and the 2-hour boil tests than for the 24-hour soak, perhaps because wood fillers were closer to equilibrium in those tests. If so, the RH and boil tests may be better indicators of water absorption than the 24-hour soak, although they are seldom used in other studies. In a typical tilled (40%) specimen, we estimated that the average maximum water absorption of the wood filler was about 10 percent: by contrast, green aspen solid wood has a moisture content of approximately 100 percent (7), which is considerably higher than that of our samples during the water absorption tests. Thus, the plastic matrix phase in the composites appeared to act as an effective, but not perfect, water repellant for the contained wood filler,

Conclusions

The strength and stiffness of ONP-filled SMA copolymers were higher than those of unfilled plastics, but were lower than those of wood fiber-filled copoly-

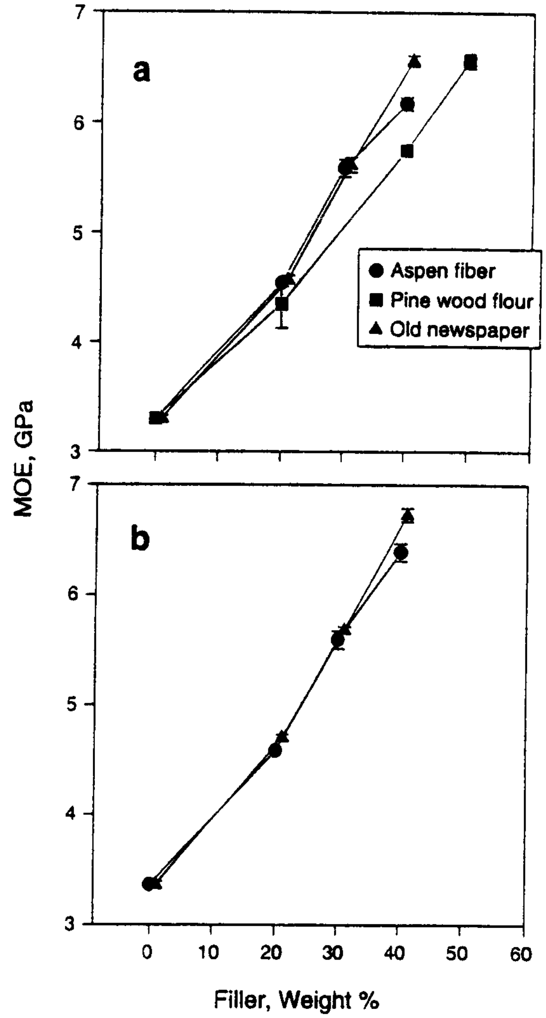

Figure 2. — Flexural modulus (MOE) of filled copolymers: a. SMA-7; b. SMA-14.

TABLE 1. Percent weight gain (moisture) of samples upon exposure to either 19 days at 90 percent relative humidity (RH), a 24-hour soak, or a 2-hour boil.

Filler/plastic	Filler	90% RH	24-hour soak	2-hour boil
	(weight %)	(% weight gain)		
Aspen/SMA-7	0	0.2	1.3	1.4
	20	1.5	1.4	1.4
	30	1.8	1.7	1.9
	40	2.4	2.1	3.7
Aspen/SMA-14	0	0.6	1.2	1.0
	20	1.4	1.8	1.4
	30	1.8	1.5	2.4
	40	2.1	1.9	3.0
ONP/SMA-7	0	0.2	1.3	1.4
	20	0.7	1.3	2.4
	30	-0.3	1.4	1.7
	40	2.9	1.6	2.7
ONP/SMA-14	0	0.6	1.2	1.0
	20	2.7	2.0	1.9
	30	3.7	1.2	2.0
	40	3.8	1.0	2.6
Pine flour/SMA-7	0	0.2	1.3	1.4
	20	1.4	1.2	1.9
	40	1.8	1.8	3.3
	50	2.8	1.3	2.3

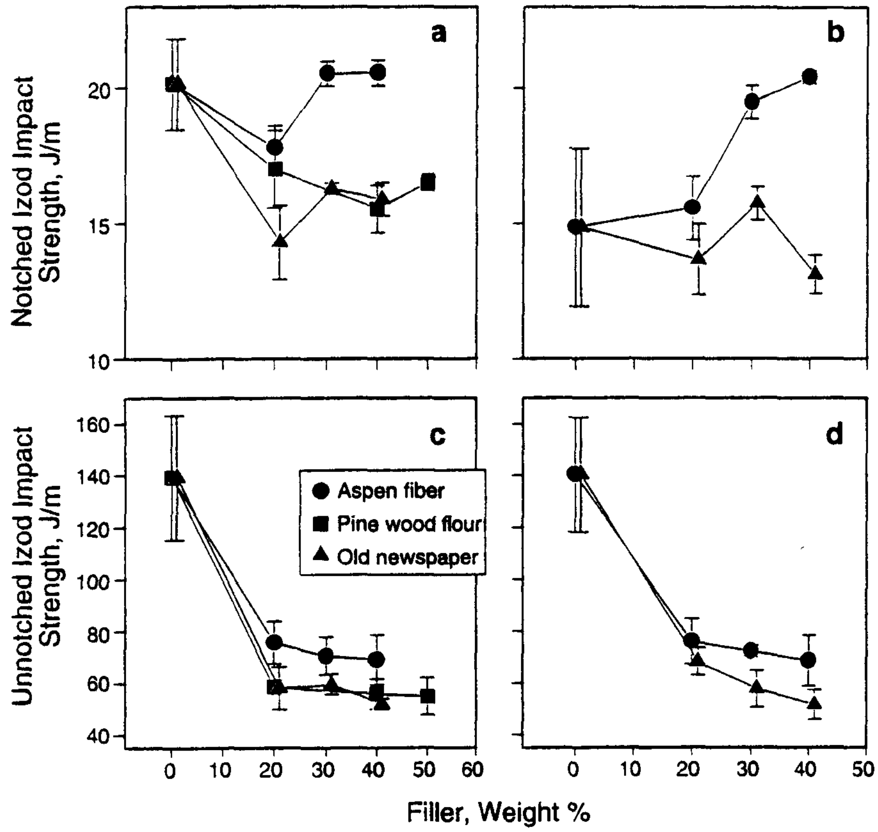

Figure 3. — Izod impact strength of filled and unfilled copolymers: a. SMA-7, b. SMA-14, c. SMA-7, and d. SMA-14.

mers. Impact strength was reduced by the presence of ONP fillers in SMA. Wood fiber fillers showed steady or improved impact strength, while wood flour fillers were similar in performance to ONP. Water absorption were relatively low in the composites in comparison to solid wood. The plastic matrix appeared to form a strong, but not impenetrable barrier to moisture.

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