

# Wood Fiber Reinforcement of Styrene-Maleic Anhydride Copolymers

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## Abstract

Styrene-maleic anhydride (SMA) copolymers are used in the automotive industry, primarily for interior parts. The use of wood fillers may provide a more economical means of manufacturing these items and/or improve their properties. We made a preliminary study of the feasibility of utilizing wood-based fillers in SMA copolymers, comparing the mechanical properties of wood-filled SMA to wood-filled polystyrene. The fillers studied were fibers for aspen medium density fiberboard, pine wood flour, and milled recycled newsprint, which showed unusually high properties considering its size and aspect ratio.

We also investigated the thermal properties of the composites using differential scanning calorimetry. While the SMA molecule contains an anhydride group, we observed no evidence of chemical bonding between SMA and the wood filler.

## Introduction

The development of useful wood-filled thermoplastic products has received increasing attention from manufacturers and the research community recently. This is due to the low cost and easy processability of wood fillers. In addition, wood fillers can add reinforcement in some cases, improving the properties of the final composite over those of the unfilled plastic (6, 7, 10-12).

Styrene-maleic anhydride (SMA) copolymers are utilized in the automotive industry for the injection molding and thermoforming of interior parts. The superiority of SMA over polystyrene is due to its higher heat deflection temperature, which is required for automotive use (3).

The presence of the maleic anhydride group on the SMA polymer backbone suggests that it may react

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with the hydroxyl group on the wood filler. This sort of reaction has been postulated for polypropylene containing a compatibilizer consisting of maleic anhydride-modified polypropylene (MAPP), which has been shown to enhance the material properties of the composite (4, 8, 10).

In addition, SMA plastics are potentially recyclable from automobile parts. The motivation for recycling might be enhanced if wood fillers could provide expanded flexibility and property enhancement in these systems.

For these reasons we undertook an initial evaluation of wood-based fillers in SMA. We studied two different maleic anhydride levels and three types of fillers. These were compared to polystyrene-filled and unfilled systems.

## Experimental

### Materials

Fillers studied were:

- dry-process mixed hardwood fiber, mostly aspen (*Populus* spp.) from a medium density fiberboard plant (MDF fiber);
- 40-mesh pine (*Pinus* spp.) flour (no. 4020) from American Wood Fiber, Schofield, Wisconsin; and
- Szego milled old newsprint contributed by General Comminution Inc., Toronto, Ontario, Canada.

In addition, polystyrene filled with a thermomechanical pulp and a Douglas-fir flour were also included for comparison. These materials have been reported on elsewhere (9).

Plastics studied were:

- SMA copolymers from ARCO Chemical Company, Newtown Square, Pennsylvania, specifically Dylark 232 (SMA-7) and Dylark 332 (SMA-14), which contained 7 and 14 percent maleic anhydride, respectively and
- polystyrene 685D contributed by Dow Chemical Co., Midland, Michigan.

### Sample preparation

Two sample preparation processes were employed. A high-intensity kinetic mixer (Synergistic Industries Inc., St. Remi-Napierville, Quebec, Canada) was used to blend the samples. In this process, the only source of heat was that generated through the kinetic energy of the rotating blades. The blend protocol was an initial speed of 5,500 rpm until the bowl temperature reached 149°C, at which point the mixer speed was reduced to 4,500 rpm. When the temperature

reached 232°C the batch was automatically discharged from the mixer. The average blend time was about 2 minutes. The compounds were ground with a Wiley mill, then dried at 105°C for at least 4 hours. Test specimens were molded using a Cincinnati Milacron molder. The molder conditions were 218°C, and the injection pressures varied from 8.3 to 12.4 MPa depending upon the compound.

### Mechanical properties

Modulus of rupture (MOR) and modulus of elasticity (MOE) were determined in flexure in accordance with ASTM D 790-90 (1). The crosshead speed during testing was 1 mm/min. Specific strength was determined by dividing the MOR value by the density. Five samples each were used for notched and unnotched Izod impact tests for each compound. Tests were conducted in accordance with ASTM D 256-93 (2).

### Digital image analysis

The dimensions of the fillers were analyzed with an optical measuring system manufactured by Micro Motion Systems, Inc. Aspect ratio was calculated as the measured length divided by the average measured width of a two-dimensional image of each particle. At least 200 particles were measured for each filler and their distribution was plotted as a histogram.

### Water sorption

This property was determined using three different methods:

1. Small samples were placed in an environmental chamber maintained at 90 percent relative humidity (RH) for 19 days (90% RH).
  2. Samples were submerged in distilled water and soaked for 24 hours at room temperature.
  3. They were submerged in boiling water for 2 hours.
- The samples were weighed before and after each treatment, and the percent weight gain was calculated as:

$$\text{percent weight gain} = \frac{W_f - W_o}{W_o} 100\%$$

where:

$W_o$  = initial weight of the sample

$W_f$  = final weight of the sample

### Differential scanning calorimetry

A Perkin Elmer differential scanning calorimeter (DSC-7) interfaced to a model 1020 system controller was used to obtain temperature scans of the samples using 20 ml/min.  $N_2$ , a temperature gradient of 10°C/min. from 30° to 180°C, with the samples in open aluminum pans.

## Results and discussion

### Mechanical properties: comparison of plastics with thermokinetic mixing

All three plastics showed similar strength behavior when filled with MDF fiber and blended in the thermokinetic mixer (Fig. 1). The filler showed reinforcement, which is defined as a positive slope on the graph of strength (MOR) versus filler content. The MOR values did not appear to be correlated with maleic anhydride content, which might be expected if there were chemical bonding between the anhydride and the cellulosic filler. In fact, the strength of the SMA-14 appeared to drop at the higher filler content. We speculate this may be due to incomplete blending of the higher  $T_g$  SMA-14 as compared to polystyrene and SMA-7. The stiffness (MOE) of all three plastics were similar (Fig. 2). This was expected since the MOE values for the unfilled plastics are similar.

### Comparison of fillers

All three fillers tested (MDF fiber, pine flour, and newsprint) added reinforcement to the plastics tested (polystyrene, SMA-7 and SMA-14, Fig. 3). The MDF fiber was a better reinforcing agent than the pine flour filler. However, the newspaper filler was about equal to the MDF fiber except at the highest filler content (40%). A comparison of the geometry of the various fillers was undertaken to ensure that the aspect ratio of the newspaper was closer to flour than to fiber. Digital image analysis confirmed that the newsprint did not have a large aspect ratio in comparison to the

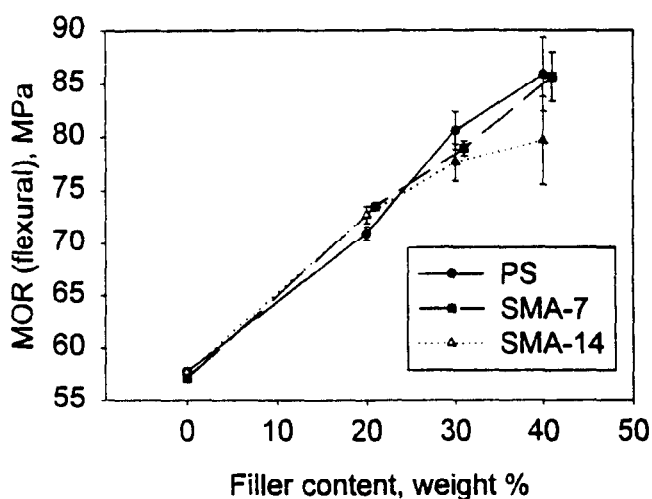


FIGURE 1. —Strength of plastics as a function of aspen MDF fiber content for samples blended in a thermokinetic mixer and then injection-molded.

MDF fiber (Fig. 4). The reason for the exceptional behavior of the newsprint filler is unknown and bears further investigation. Differences in the stiffnesses of the filled plastics were insignificant (Fig. 5). This was expected since the MOE of the plastics are similar, and the aspect ratio of the filler has related only poorly to stiffness in previous work (9).

### Impact properties

**Notched Izod impact strength.** —The results of studies were performed on all three plastics and three fillers were mixed. Polystyrene and SMA-7 strengths increased with increasing MDF fiber content, but decreased with increasing pine flour and newsprint contents (Fig. 6, top). SMA-14 notched Izods increased with increasing MDF content, but held steady with pine flour content (Fig. 6, bottom). Typically when a stiff filler is added to a relatively soft matrix, the impact strength decreases. These results may indicate that the wood-based fillers are not stiff in comparison to the matrices (polystyrene, SMA-7, and SMA-14), which are brittle plastics in comparison to polyethylene and polypropylene.

**Unnotched Izod impact strength.** —The unnotched Izod strengths consistently decreased with filler content for all three plastics tested (Fig. 7). The decrease appeared to occur at relatively low filler contents. After the initial drop, there was little further change in the impact properties. This behavior suggests the presence of small impurities, which may be dominating the fracture behavior of all the samples.

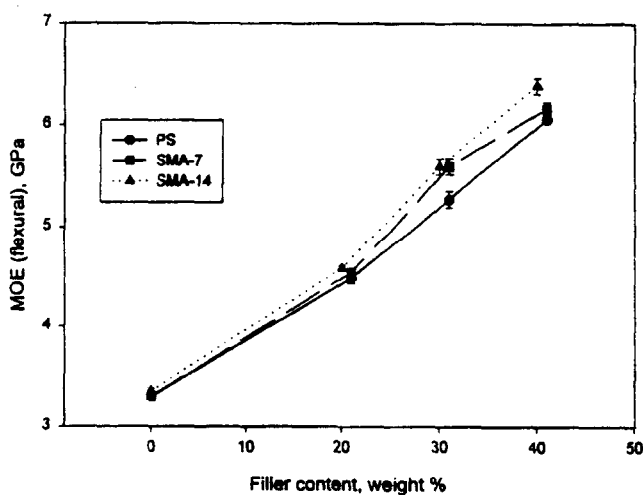
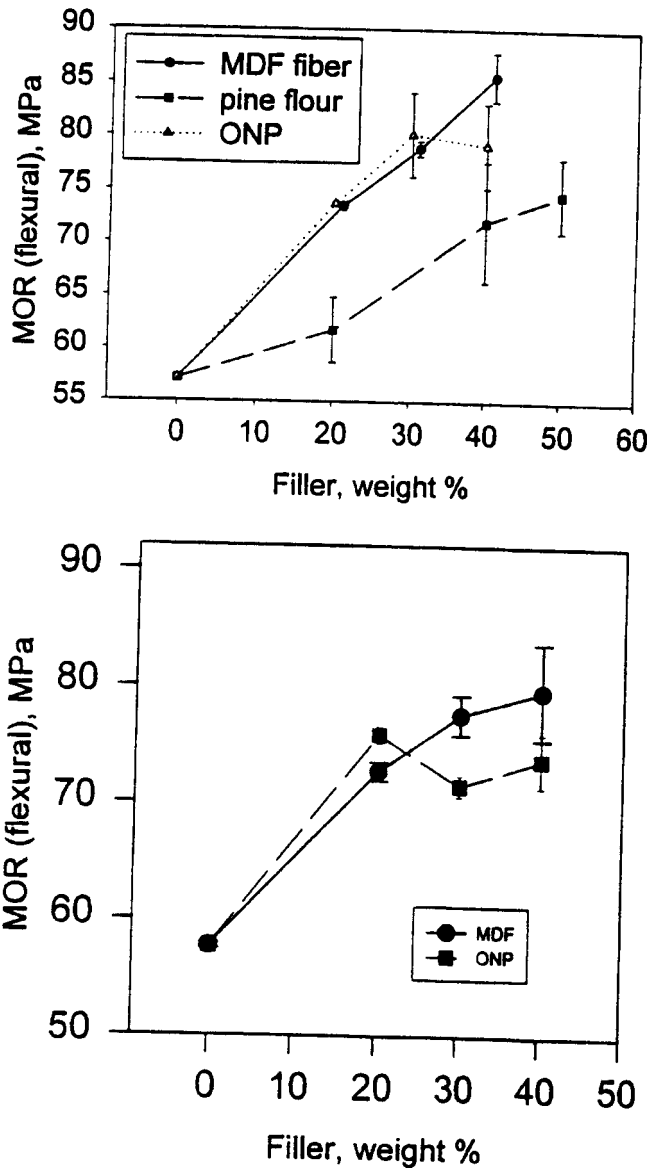
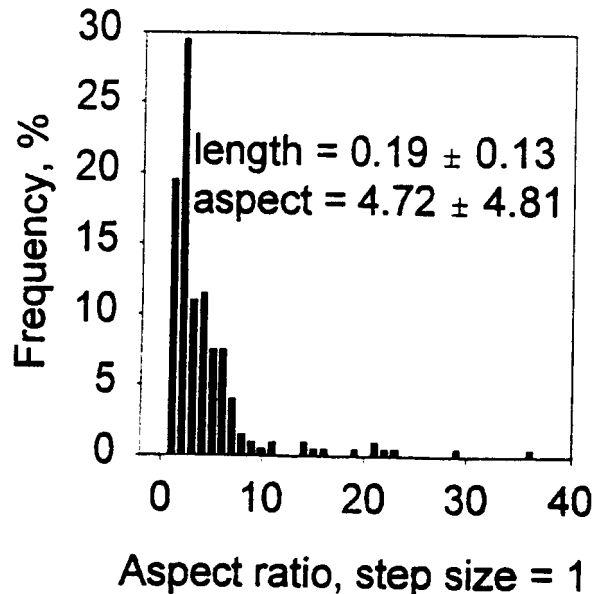
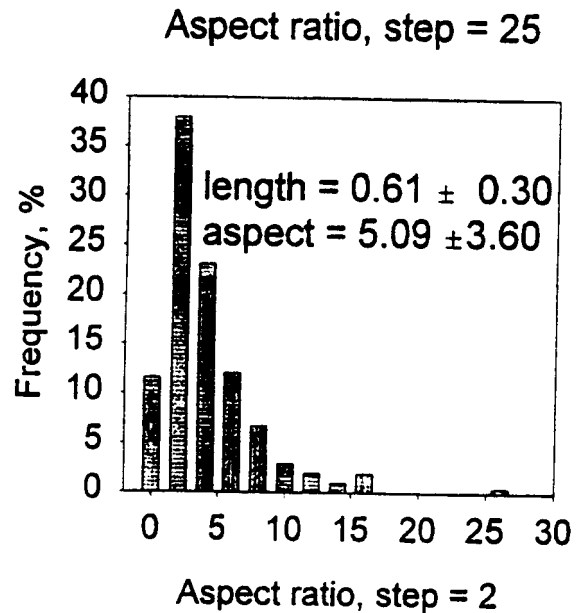
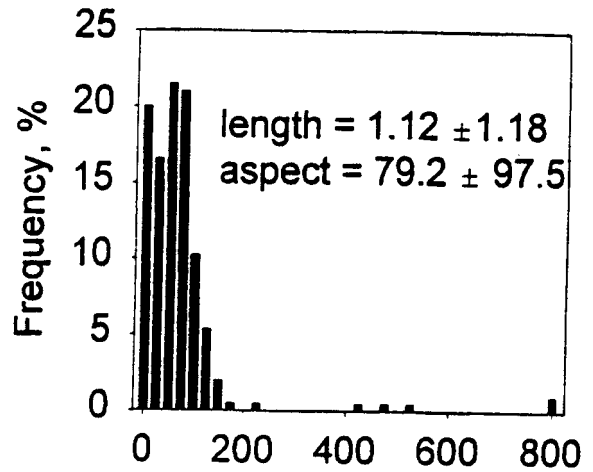


FIGURE 2. —Stiffness of plastics as a function of aspen MDF fiber content for samples blended in a thermokinetic mixer and then injection-molded.

**Water absorption.**—All the samples tested by the three different water sorption methods: 90 percent RH, soaking, and boiling showed small percent weight gains. The results were highly variable since the weight gains were a small difference between two relatively large numbers. The coefficients of variation were typically about 1 percent weight gain. The largest was 4 percent for SMA-7 filled with 40 percent aspen fiber (by weight). The smallest weight gains were for the unfilled plastics and clustered around 0.5 percent for the 90 percent RH test. There were no



**FIGURE 3.**—Strengths of various fillers in (top) SMA-7 and (bottom) SMA-14 for samples blended in a thermokinetic mixer and then injection-molded. MDF-filled polystyrene is included for comparison.



**FIGURE 4.**—Aspect ratio distributions of (top) MDF, (middle) pine flour, and (bottom) newsprint fillers.

statistically significant differences between the various compositions. The average percent weight gain for all the filled samples for all plastics and fillers were  $1.5 \pm 0.4$  percent for the soak test,  $1.9 \pm 1.1$  percent for the 90 percent RH test, and  $2.3 \pm 0.7$  percent for the boil test. The observation that the 90 percent RH test gave a higher average percent weight gain than the soak test may indicate that under the conditions of these tests water vapor is perhaps more effective than liquid water in permeating the composite. Even if we assume that all the gain was accounted for by

the filler, and that the initial moisture content of the wood fillers is about 10 percent, the percent weight gain of the harshest test increased the moisture content of the wood by only 10 percent (4% weight gain of 40% filler). Thus the total moisture content would still be 20 percent, which should be only marginally susceptible to decay (13). It therefore appears that the wood filler is relatively well protected from moisture in this system.

**Glass transition temperatures ( $T_g$ ).**—Differential scanning calorimetry was used to determine the  $T_g$  of the samples. A slight decrease was observed with the 40 percent filled samples in comparison to the unfilled samples (Table 1). The lowered  $T_g$  decreased

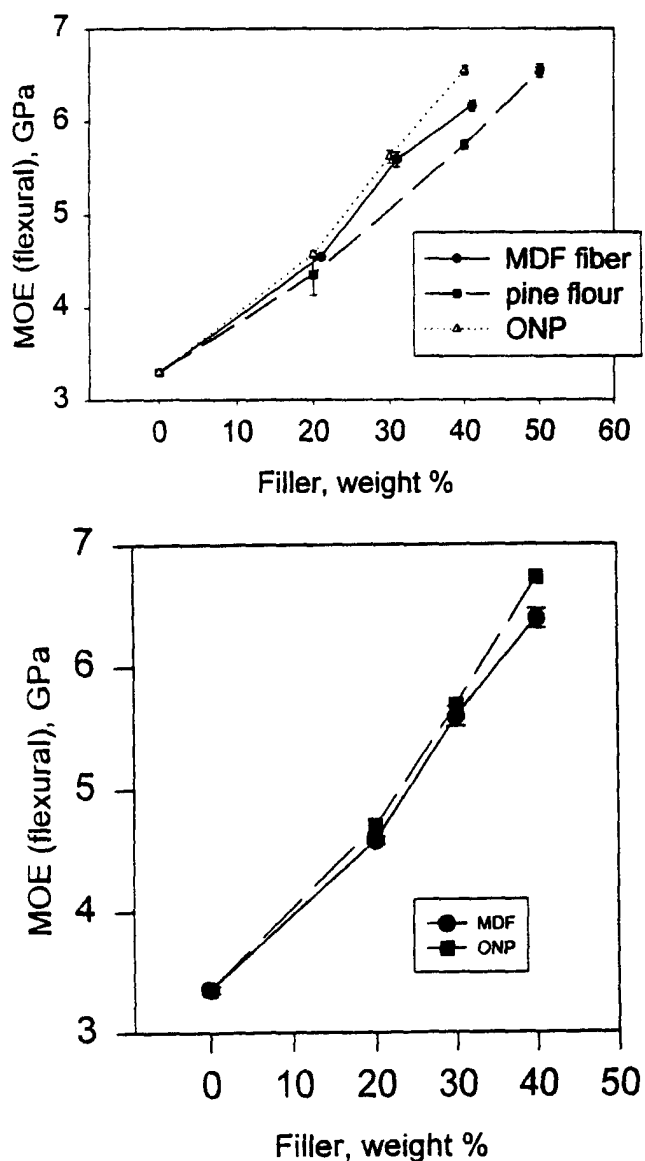


FIGURE 5.—Stiffness of various fillers in (top) SMA-7 and (bottom) SMA-14 for samples blended in a thermokinetic mixer and then injection-molded. MDF-filled polystyrene is included for comparison.

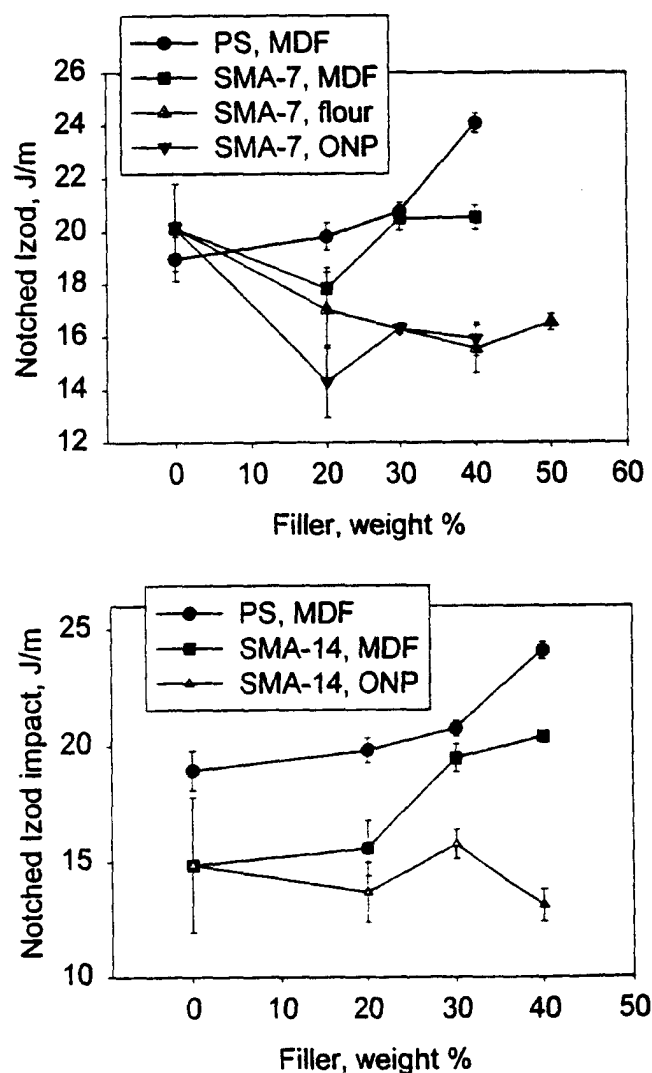


FIGURE 6.—Notched Izod impact strengths for various fillers in (top) SMA-7 and (bottom) SMA-14. MDF-filled polystyrene is included for comparison.

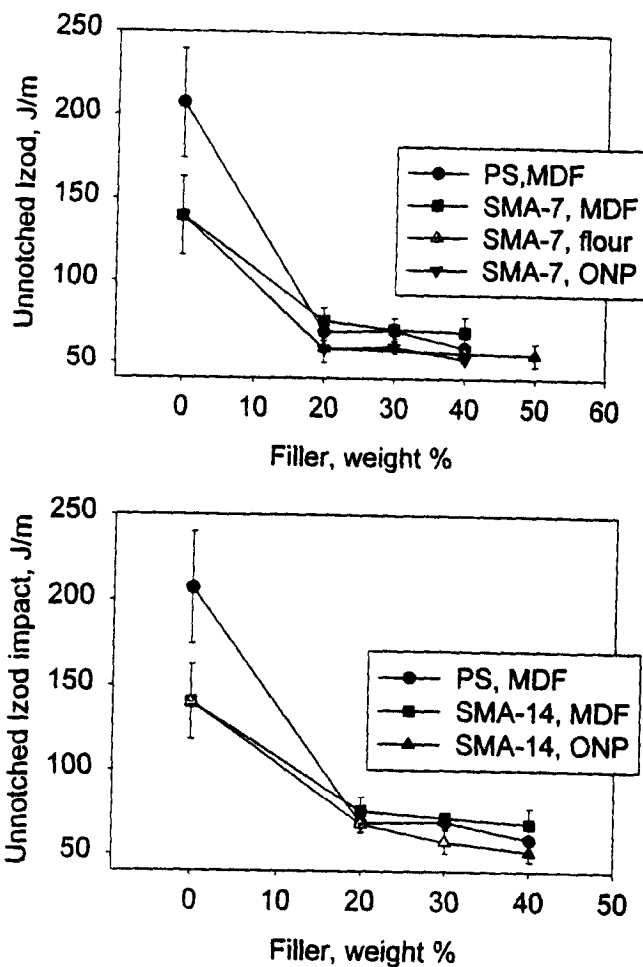


FIGURE 7. —Unnotched Izod impact strengths for various fillers in (top) SMA-7 and (bottom) SMA-14. MDF-filled polystyrene is included for comparison.

with increasing maleic content of the plastic. If there were chemical bonding between the matrix and the filler, we would expect the  $T_g$  to increase (5). While we cannot, on the basis of these data, conclude that there is no chemical bonding between the maleic anhydride group and the filler, these experiments do lend support to that hypothesis.

### Conclusions

The use of wood-based fillers improved the strength and stiffness of all the plastics studied. The fillers studied here were thus reinforcing fillers in this system. The newsprint filler showed unexpected strength in the three plastics studied. Notched Izod impact strengths were mixed. Unnotched Izod im-

TABLE 1.— $T_g$  comparisons for filled and unfilled plastics.

Sample	$T_g$	Drop in $T_g$
	----- (°C) -----	
Polystyrene, 0% filler	113	
Polystyrene, 40% MDF filler	109	4
SMA-7, 0% filler	124	
SMA-7, 40% filler	122	2
SMA-14, 0% filler	135	
SMA-14, 40% filler	134	1

pect strengths were consistently lowered in the filled composites. Water sorption indicated that the polystyrene and SMA plastics provided relatively good protection from moisture for the wood-based fillers. Differential scanning calorimetry studies showed a lowered  $T_g$  for filled plastics. The decreased  $T_g$  showed an inverse correlation with maleic anhydride content, which argues against the hypothesis that the maleic group chemically bonded with the filler.

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