

Wood-Fiber Reinforcement of Styrene–Maleic Anhydride Copolymers

JOHN SIMONSEN,¹ RODNEY JACOBSEN,² ROGER ROWELL²

¹ Oregon State University, Corvallis, Oregon 97331-7402

² U.S. Forest Products Lab, Madison, Wisconsin 53705

Received 31 October 1996; accepted 31 January 1997

ABSTRACT: Styrene–maleic anhydride (SMA) copolymers containing either 7 or 14% maleic anhydride were filled with either pine flour or dry-process aspen fiber from a medium density fiberboard (MDF) plant. Material properties of the filled and unfilled SMA plastics were compared with those of aspen-fiber-filled and unfilled polystyrene (PS). The fiber-filled SMA composites were equivalent or superior to unfilled SMA in strength, stiffness, and notched Izod impact strength. Filled PS composites outperformed or matched the performance of filled SMA composites in the parameters tested. Unnotched Izod impact strength of filled polymers was generally inferior to that of the unfilled polymers. Water absorption from a 90% relative humidity exposure, a 24-h soak, and a 2-h boil showed mixed results when compared to the unfilled polymers. Dynamic mechanical analysis showed no change in glass transition temperature (T_g) after the addition of filler for either SMA or PS composites. The presence of the anhydride functionality on the polymer backbone did not appear to improve the strength of the composite. No evidence was found for chemical bond formation between the SMA and wood fiber. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1567–1573, 1998

Key words: composites; copolymers; polymers; styrene–maleic anhydride; wood

INTRODUCTION

Wood–polymer composites, wherein the wood is dispersed as particles in a thermoplastic matrix, have received much research attention in recent years. Such interest is merited because these materials hold promise for low cost, improved performance composites that may be produced from recycled materials.^{1–4} Research on wood–polymer composites has led to commercial products for a variety of markets. However, the usefulness of these materials remains limited by their mechanical properties. This is especially true for those materials intended for use in construction and in other areas where strength and stiffness are important considerations. Consequently, much re-

search has been directed toward the development of compatibilizers, which are compounds that reduce the initial interphase incompatibility present in the composites.⁵ Compatibilizers can significantly improve the material properties of the resulting composite. One of the more successful compatibilizers is maleic anhydride modified polypropylene (MAPP), which has been shown to substantially improve the properties of wood-filled polypropylene composites.⁶

Styrene–maleic anhydride (SMA) copolymers, both unfilled and filled with glass fiber, are used extensively in the automotive industry for the injection molding and thermoforming of interior parts. SMA is preferable to PS in automotive applications because of its higher heat distortion temperature.⁷ The presence of the maleic anhydride group on the polymer backbone is of interest because it may react with the hydroxyl group on the wood filler, thus enhancing the material prop-

Correspondence to: J. Simonsen.

Journal of Applied Polymer Science, Vol. 68, 1567–1573 (1998)
© 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/101567-07

erties of the composite, analogous to MAPP.⁸ The use of low-cost wood fillers to improve the properties of the final composite might provide impetus to the recycling of these potentially useful plastics.

This study was undertaken to evaluate the effectiveness of wood fillers in SMA polymers. A secondary objective was to acquire information regarding the question of interphase bonding between the SMA and the wood filler.

EXPERIMENTAL

Materials

Dry-process mixed hardwood fiber, mostly aspen (*Populus* spp.), from a medium density fiberboard (MDF) plant was used as the fiber filler. Pine (*Pinus* spp.) flour was contributed by American Wood Fiber (Schofield, WI) as their standard 40-mesh pine #4020. ARCO Chemical Company (Newtown Square, PA) contributed SMA copolymers Dylark 232 (SMA-7) and Dylark 332 (SMA-14), which contained 7 and 14% maleic anhydride, respectively. Polystyrene (PS) was contributed by Dow Chemical Co. (Midland, MI) as product Styron 685D. Material properties for the plastics were taken from the suppliers' literature.

Sample Preparation

Separate composites were made of aspen fiber at 20, 30, and 40% (weight) and SMA-7, SMA-14, and PS. Pine flour at 20, 40, and 50% (weight) was combined with SMA-7. Unfilled control samples were made from SMA-7, SMA-14, and PS alone. All compounds were blended in a high-intensity kinetic mixer (Synergistics Industries Inc., St. Remi-Napierville, Quebec, Canada) where the only source of heat was that generated through the kinetic energy of rotating blades. An initial trial of various mixer speeds and discharge temperatures was performed on SMA-7 containing 20, 40, and 50% pine flour. The discharged samples were observed visually for fiber dispersion and filler degradation. The resulting processing schedule was selected as the optimum compromise between maximum mixing time at high temperature and minimum degradation of the wood filler, as measured by discoloration. Each compound was blended at 5500 rpm until its temperature reached 149°C, at which point the mixer speed was reduced to 4500 rpm. When the temper-

ature reached 232°C, the batch was automatically discharged from the mixer. The total blend time varied with the proportions of the batch, but averaged about 2 min.

The compounds were granulated and dried at 105°C for 4 h, then formed into test specimens of approximately 3 × 12 × 100 mm with a Cincinnati Milacron Molder. The specimens were injection molded at 218°C; injection pressures varied from 8.3 to 12.4 MPa, depending upon the compound.

Mechanical Properties

Five 3 × 12 × 100 mm samples for each test and for each compound were used to determine modulus of rupture (MOR) and modulus of elasticity (MOE). Tests were performed in accordance with American Society for Testing and Materials (ASTM) standards.^{9,10} The crosshead speed during testing was 1 mm/min. Densities were determined by weighing and manually measuring the dimensions of rectangular samples, then dividing weight by volume. 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 standards.¹⁰

Water Sorption

For each compound, three 3 × 10 × 10 mm samples were cut from pieces of the molded specimens. The smaller samples were subjected to one of the following tests to determine their susceptibility to moisture. Samples were either (1) placed in an environmental chamber maintained at 90% relative humidity (RH) for 19 days, (2) submerged in distilled water and soaked for 24 h at room temperature, or (3) submerged in boiling water for 2 h. The samples were weighed before and after each treatment, and the percent weight gain (PWG) was calculated as

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

where W_o is the initial weight of the sample; and W_f is the final weight of the sample.

Dynamic Mechanical Thermal Properties

Dynamic mechanical thermal analysis (DMTA) of samples was conducted with a Rheometrics, Inc.,

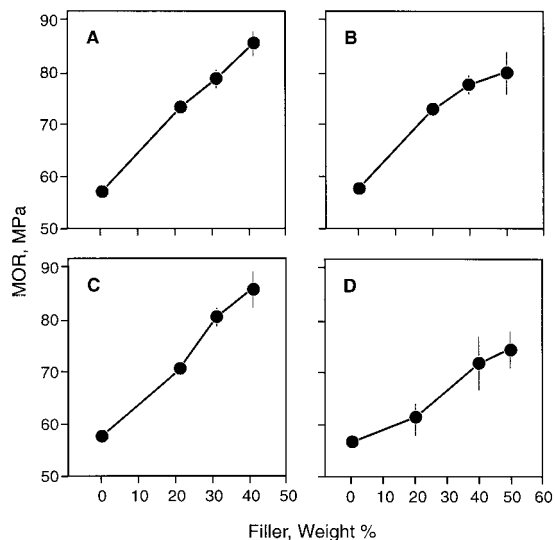


Figure 1 Flexural strength (MOR) of (A) aspen-fiber-filled SMA-7, (B) aspen-fiber-filled SMA-14, (C) aspen-fiber-filled PS, and (D) pine-flour-filled SMA-7.

RSA-II Solids Analyzer. One $3 \times 12 \times 48$ mm sample was tested for each aspen-fiber composite and unfilled control. The samples were tested at 5° intervals over the temperature range of from 30 to 80°C and at 1° increments from 80 to 140°C , using a three-point bending geometry and a constant frequency of 1 Hz.

Microscopy

Images were obtained with an AmRay 1000A scanning electron microscope operated at 10 kV on Polaroid type 55 positive-negative film.

RESULTS AND DISCUSSION

Mechanical Properties

MOR

Both aspen fiber and pine flour added reinforcement to SMA-7 and SMA-14 (Fig. 1); however, composites of SMA-7 and aspen fiber were substantially stronger than those of SMA-7 and pine flour. The specific strength of flour-filled SMA-7 was dramatically lower than that of the fiber-filled samples (Fig. 2); the strength properties of fiber-filled SMA-7 and PS were essentially equal. The flour-filled SMA-7 showed a lower slope of strength versus fiber content in comparison to the fiber-filled plastics. The lower aspect ratio of the flour filler is probably responsible for the weaker

reinforcement compared with that of the fiber filler.¹¹

The strength of fiber-filled SMA-14 composites leveled off as a function of fiber content, in contrast to that of SMA-7 and PS (Figs. 1 and 2). This may be due to incomplete wetting of the filler by the plastic; if that were the case, however, we would then expect to see similar behavior in the other plastics. A second possible explanation is that the mixing properties of SMA-14 are different from those of SMA-7 and PS due to its higher T_g . In that case, the leveling off of strength would be explained by a lack of dispersion of the fiber in the matrix. If there were bonding between the anhydride functionality of the copolymer and the wood surface, the interphase between the two should be strengthened and the properties of the final composite might be expected to improve. The lack of improvement in strength suggests that either there is no bonding between the anhydride and the wood surface, or the bonding that exists does not affect the strength of the final composite. Further studies are needed to reach a firm conclusion on this matter.

MOE

The flexural moduli of all samples increased with increasing filler content, regardless of type. In fact, the increase was within the experimental error of the measurements for all samples. This supports the hypothesis that the relationship of MOE

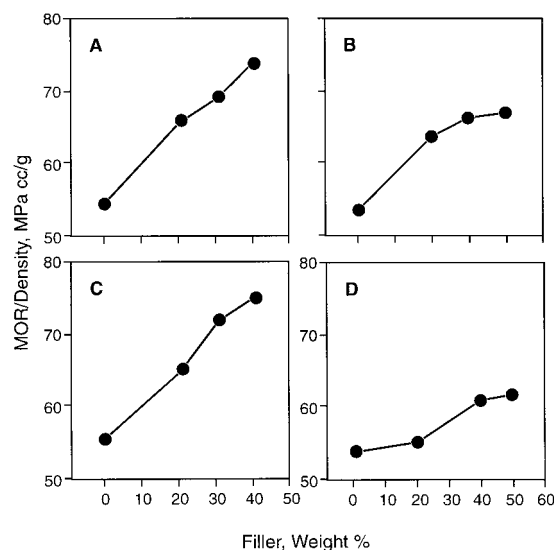


Figure 2 Specific strength (MOR/density) of (A) aspen-fiber-filled SMA-7, (B) aspen-fiber-filled SMA-14, (C) aspen-fiber-filled PS, and (D) pine-flour-filled SMA-7.

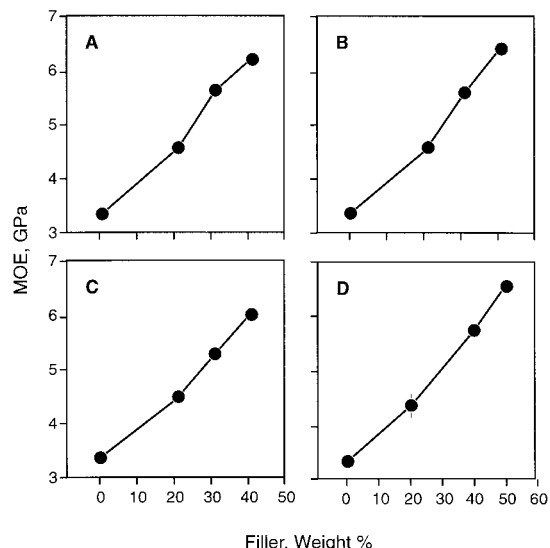


Figure 3 Flexural modulus (MOE) of (A) aspen-fiber-filled SMA-7, (B) aspen-fiber-filled SMA-14, (C) aspen-fiber-filled PS, and (D) pine-flour-filled SMA-7.

to fiber content is not a strong function of the aspect ratio of the filler (Fig. 3).

Impact Strength

Notched Izod impact strength increased for SMA-14 and PS as the percent of filler increased (Fig. 4). The notched Izod impact strength of fiber-filled SMA-7 at all content levels was not greatly different from that of unfilled SMA-7. The SMA-7 composite with pine-flour filler showed a decrease in notched Izod impact strength for 20 and 40% filler contents, and then a slight increase from 40 to 50% filler. Although SMA-14 showed an increasing impact strength where SMA-7 showed no increase, SMA-14 at 0% filler showed a lower impact strength than SMA-7. Thus, the absolute value of impact strength was higher for SMA-7, even though it did not increase with filler content. PS showed the best notched Izod impact strength performance, increasing to 24.1 J/m at 40% filler content.

There appeared to be little difference in unnotched Izod impact strength between wood-fiber- and flour-filled SMA-7 samples. All composites tested showed decreasing unnotched impact strength as the amount of filler increased (Fig. 4). This may be due to small particles in the wood creating points of weakness for crack propagation. In the notched samples, the notch determined the point where the crack initiated. The presence of fibers at the notch may have absorbed some of the

impact energy, whereas in the unnotched samples, the crack was free to propagate at the weak points in the composite. The biggest drop in impact strength occurred at low filler contents, but increasing the amount of filler had little additional effect. Careful screening or washing of the filler to remove small particles might mitigate the decrease somewhat. The impact strength, which is proportional to the work of fracture, for short fibers with aspect ratios below the critical aspect ratio (the aspect ratio required for fiber to break at its ultimate stress), is proportional to the square of the fiber length.¹² Removing small particles would thus be expected to increase the average aspect ratio of the filler and thereby perhaps improve the impact strength. This is a subject for future research.

Water Sorption

For most of the samples tested, weight gain upon exposure to water increased with increasing filler content for all three water absorption tests. For all samples, the weight gains were less than 4%. The water absorptions for the unfilled plastics were about 0.5% in the 90% RH test, and 1.5% in both the 24-h soak and 2-h boil. The standard deviations of the measurements were typically about $\pm 1\%$; thus, quantitative comparisons were difficult. Water absorptions increased to about 2 to 3% at the highest filler

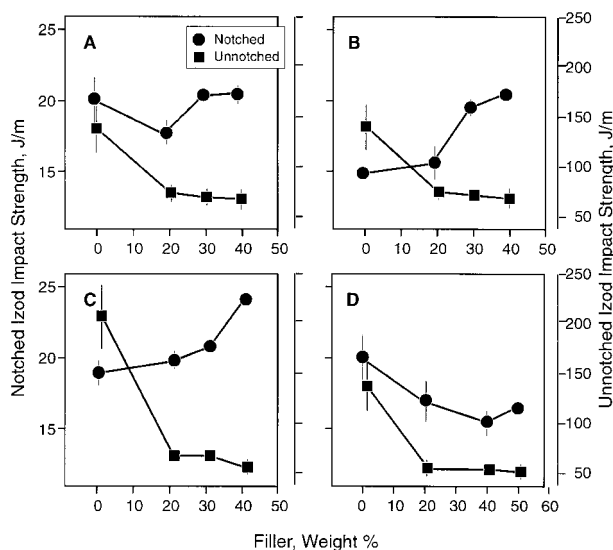


Figure 4 Notched and unnotched Izod impact strength of (A) aspen-fiber-filled SMA-7, (B) aspen-fiber-filled SMA-14, (C) aspen-fiber-filled PS, and (D) pine-flour-filled SMA-7.

content in the 90% RH test, 1.5 to 2.5% in the 24-h soak, and 2.5 to 4.0% in the 2-h boil. Thus, the greatest weight gains, and the greatest variability in weight gains, were observed with the 2-h boil. The 90% RH test showed weight gains as great or greater than the 24-h soak. This indicates that water vapor was diffusing into the composite and being absorbed by the wood filler. Although that process was probably slower than the infusion of liquid water, especially at high filler contents where interfiber interactions are greater, it was ultimately just as effective for water absorption by the composites. There were no statistically significant differences among the various compositions.

Both the 90% RH and the 2-h boil tests resulted in higher water absorptions than the 24-h soak. This may indicate that the wood fillers in the former two tests were closer to equilibrium than were those in the 24-h soak. If so, the 24-h soak may be a less reliable indicator of water absorption than the other tests, even though it is far more frequently reported in the literature.

If we assume that all of the water absorption of the composite occurs in the wood component, and use a rounded figure of 4% for the maximum weight gain of a typical 40% filled sample, we can calculate the maximum weight gain of the wood component to be 10%. The moisture content of green aspen solid wood is approximately 100%.¹³ Therefore, the samples in these tests were probably far from equilibrium, but the weight gains observed were much less than would be expected from solid wood samples. We concluded that the plastic matrix formed a strong, but not impenetrable, barrier to moisture absorption by the wood component.

Dynamic Mechanical Thermal Properties

The DMTA scans revealed no changes in glass transition temperature (T_g) for either the PS or the SMA composites. In addition, the shape of the T_g curve showed only the decreasing and upper temperature broadening typical of reducing the proportion of a polymer in a composite (Fig. 5).¹¹ This lends further support to the contention that the maleic anhydride moiety does not interact with the wood-fiber component. Certainly, if there were actual chemical bonding between the SMA backbone and the wood fiber that represented any significant proportion of the SMA in the composite, we would expect the T_g to be effected. Chemical bonding to the wood fiber should reduce the mobility of the polymer backbone and, if so, would

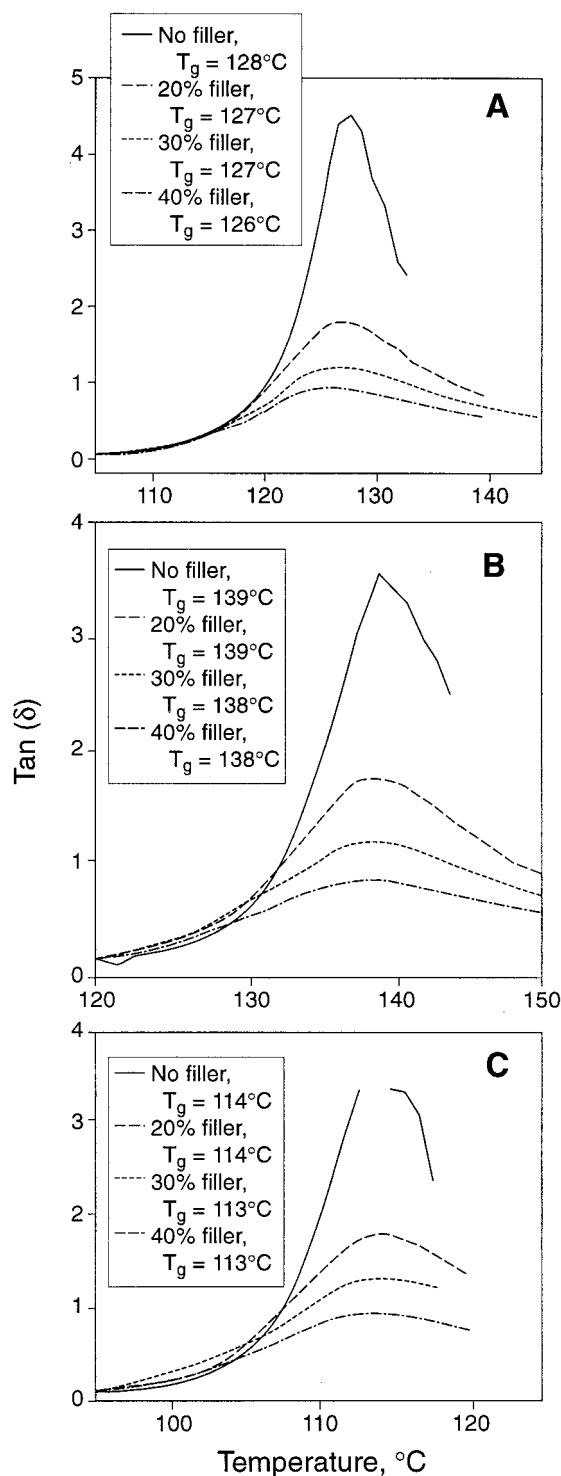


Figure 5 $\tan(\delta)$ versus temperature from dynamic mechanical thermal analysis scan for aspen-fiber-filled (A) SMA-7, (B) SMA-14, and (C) PS.

increase the T_g . Because this was not observed, we conclude that there was no evidence of significant chemical bond formation between the anhydride and the wood fiber.

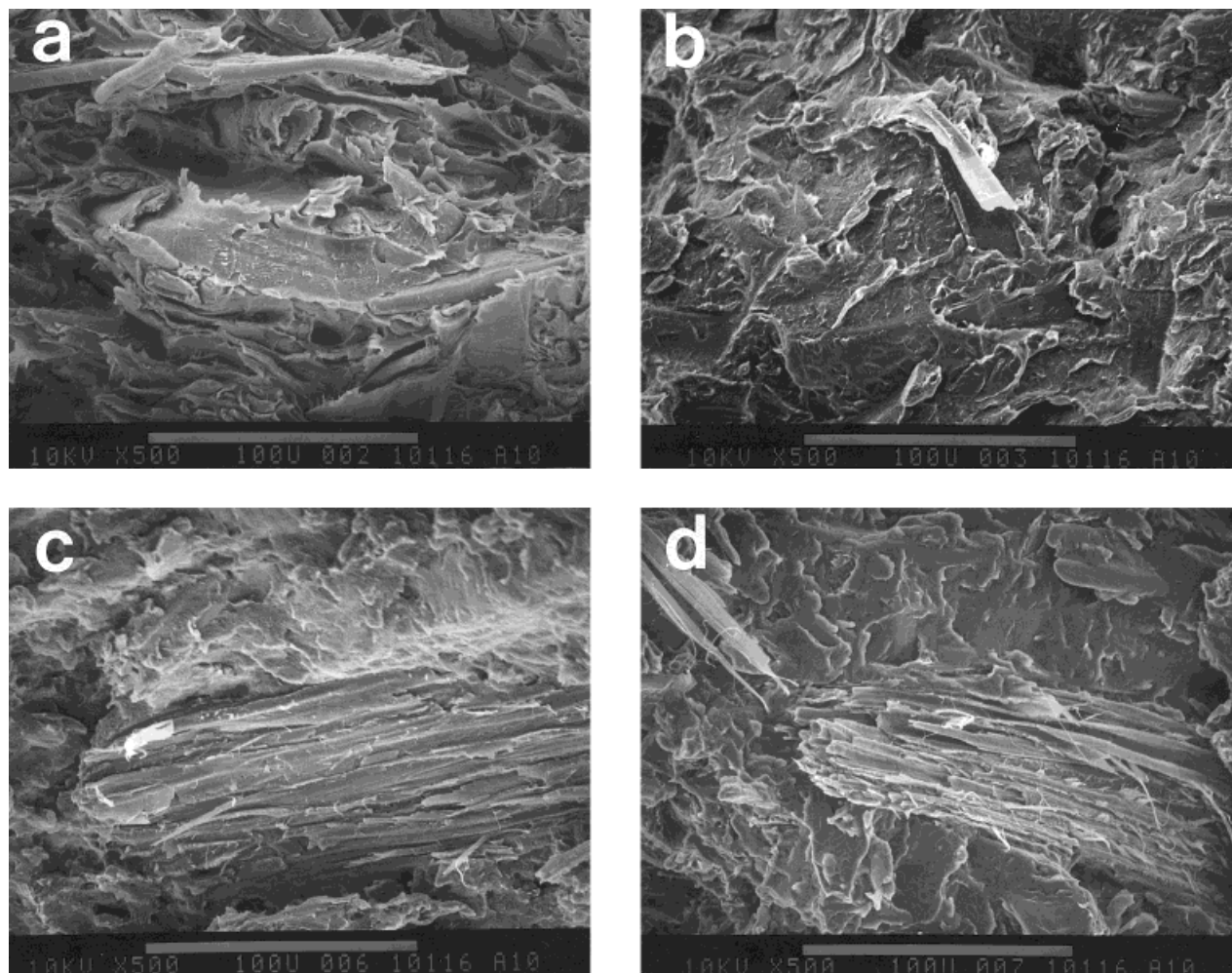


Figure 6 Scanning electron microscope photographs of (a) 40% aspen-fiber-filled PS, (b) 40% fiber-filled SMA-7, (c) 50% pine-flour-filled SMA-7, and (d) 40% fiber-filled SMA-14.

Microscopy

Images of samples fractured in tension were obtained in the SEM at 500 \times (Fig. 6). Greater flow was observed in the PS fracture than in the SMA-7 and SMA-14 samples. This is indicative of the greater brittleness of the SMA-based polymers. Fiber bundles were found in all samples [Fig. 6(c,d)], indicating that mixing was not complete at the level of individual fibers. The pine-flour-filled SMA-7 showed a greater abundance of small particles and fiber bundles. All images revealed evidence of fiber pullout and generally poor adhesion between the fiber surface and the surrounding matrix, although the PS sample also showed examples of fiber breakage during fracture [Fig. 6(a)].

CONCLUSIONS

The mechanical properties of wood-filled polymers were superior to those of the unfilled polymers. There was no apparent relationship between the maleic content of the polymer and the properties of the final composite. In fact, the mechanical properties of PS composites were equivalent to or better than those of SMA composites. Impact properties varied among composites. Notched Izod impact strength improved with increasing filler content for SMA-14 and PS, held steady for fiber-filled SMA-7, and decreased for flour-filled SMA-7. Unnotched Izod impact strength decreased with increasing filler content for all samples. The water absorption of the samples varied, but in all cases was much lower than that of solid

wood under the same conditions.¹¹ The presence of the plastic matrix formed an effective, but not perfect, barrier against water absorption by the wood component. Dynamic mechanical thermal analysis showed no evidence of chemical bond formation between the anhydride functionality and the wood fiber.

Wood-filled SMA composites appear to offer several advantages over SMA alone and should be considered in appropriate applications.

REFERENCES

1. H. Kishi, M. Yoshioka, A. Yamanoi, and N. Shiraishi, *Mokuzai Gakkaishi*, **34**, 133 (1988).
2. R. T. Woodhams, G. Thomas, and D. K. Rodgers, *Polym. Eng. Sci.*, **24**, 1166 (1984).
3. D. Maldas, B. V. Kokta, R. G. Raj, and S. T. Sean, *Mater. Sci. Eng.*, **A104**, 235 (1988).
4. K. Yam, B. Gogoi, C. Lai, and S. Selke, *Polym. Eng. Sci.*, **30**, 693 (1990).
5. S. L. Rosen, *Fundamental Principles of Polymeric Materials*, John Wiley & Sons, Inc., New York, 1993.
6. A. R. Sanadi, R. A. Young, C. Clemons, and R. M. Rowell, *J. Reinforced Plastics Compos.*, **13**, 54 (1994).
7. ARCO Chemical Company, *Dylark Engineering Resins*, Brochure #ACC-P102A-907, ARCO Chemical Co., 3801 West Chester Pike, Newtown Square, PA 19073 (1990).
8. S. Takase and N. Shiraishi, *J. Appl. Polym. Sci.*, **37**, 645 (1989).
9. American Society for Testing and Materials (ASTM), ASTM D 790-86, Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials, ASTM Annual Book of Standards, Philadelphia, 274-283 (1986).
10. American Society for Testing and Materials (ASTM), ASTM D 256-93, Standard test methods for determining the pendulum impact resistance of notched specimens of plastics, Annual Book of Standards, Philadelphia, 1-18 (1993).
11. L. E. Nielsen, and R. F. Landel, *Mechanical Properties of Polymers and Composites*, Marcel Dekker, Inc., New York, 1994.
12. M. J. Folkes, *Short Fibre Reinforced Thermoplastics*, Research Studies Press, a division of John Wiley & Sons, Ltd., New York, 1982.
13. U.S. Forest Products Laboratory, *Wood Handbook: Wood as an Engineering Material*, U.S. Government Printing Office, Washington, DC, 1974.
14. A. J. Panshin and C. de Zeeuw, *Textbook of Wood Technology*, 4th ed., McGraw-Hill Book Co., New York, 1980, p. 207.