Interface and Mechanical Properties of Poly(methyl methacrylate)–Fiber Composites

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ABSTRACT: Long-fiber pellets were made by an *in situ* pultrusion process. Fiber-reinforced composites were prepared by an injection-molding process and an extrusion/injection-molding method with pellets, respectively. SEM observations showed that the strong interface was maintained during the injection process for low shearing forces, although polymer adhesion to the fiber surface was completely delaminated in the process of extrusion/injection molding for very high shearing forces. Enhanced adhesion of composites promoted substantial improvement of mechanical properties compared to those with poor adhesion. However, the enhanced adhesion between the fiber and the matrix also sacrificed the impact resistance properties. Longer fibers substantially enhanced the properties of composites. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2478–2483, 2004

Key words: poly(methyl methacrylate) (PMMA); pultrusion process; fibers; composites, adhesion

INTRODUCTION

Fiber-reinforced thermoplastics (FRTPs) show substantial improvement in such characteristics as tensile strength, flexural strength, and stiffness, for example, compared with those of the pure plastic matrix. In general, FRTP includes a continuous matrix phase of thermoplastic and a discontinuous filler phase of fibers. The properties of these materials depend not only on the intrinsic characteristics of the polymer matrix and the fiber, but also depend on fiber content, fiber length distribution,[1,2] interfacial adhesion,[3,4] fiber orientation distribution, and void volume.[5]

With the development of pultrusion technology, long-fiber–reinforced thermoplastics can be made by an injection or a thermal melt pressing process with long-fiber pellets. In these processes, the length of fiber would be destroyed, but the average length of fiber is also much longer than that produced by the extrusion process with a twin-screw extruder.[6,7] With long fibers, materials can obtain some benefits, such as improved mechanical properties, better impact resistance, and enhanced creep performance.[8–12]

The interface between a polymer matrix and inorganic filler such as glass fiber plays a critical role in the performance of polymer-reinforced composites. To effectively transfer a load from the matrix to a reinforced fiber, the interface between the two different materials in the composites should be highly adhesive. The treatment of glass fiber is necessary. In general, glass fiber is treated with size agents and a silane coupling agent. The silane coupling agent confers good adhesion between the polymer matrix and the fibers. The chemical bonds between the interface can more effectively improve the mechanical properties of composites.[13]

Poly (methyl methacrylate) (PMMA) has many outstanding properties, including high strength, good weatherability, transparency, and excellent biocompatibility. Fiber-reinforced PMMA may have many potential applications. This work was undertaken to investigate the mechanical properties of long glass fiber–reinforced PMMA, and the interfacial effects on the properties of long-fiber–reinforced composites.

EXPERIMENTAL

Materials

Long glass fiber–reinforced PMMA pellets of 8 mm were prepared in our laboratory.[14] In preparation of the long-fiber–reinforced composite, two kinds of glass fiber, F-266 and F-988 (Jushi Group, Zhejiang Province, China), were used. The long-fiber pellets were designated as P-266 and P-988, respectively. F-266, with methacrylic groups on the surface, was used for unsaturated polyester; F-988, with amide groups, was used for nylon resins. Each glass fiber

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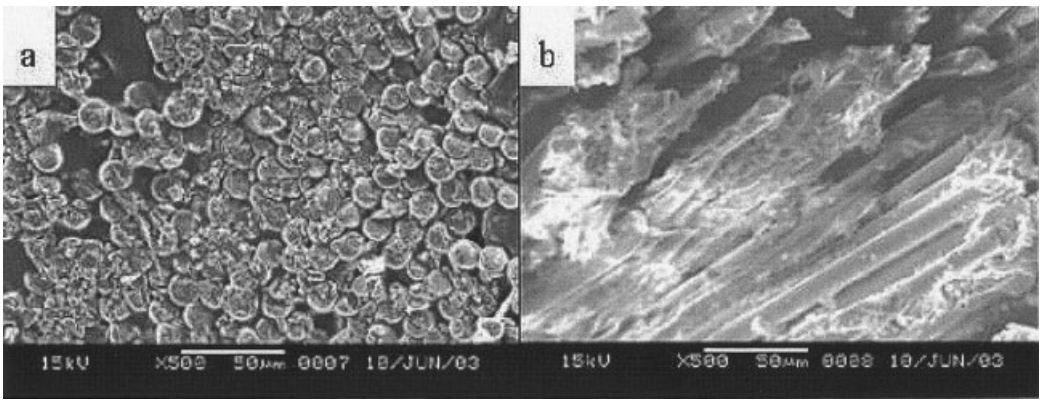

Figure 1 SEM microphotographs of long-fiber pellets of P-266: (a) cross section; (b) fracture surface.

was classified as E-glass, with a diameter of 13 μm. PMMA (Shanghai PEN Manufacture Factory, Shanghai, China) was dried at 90°C for 8 h before use.

Preparation of composites

A Φ35 twin-screw extruder (TE-35, Jiangsu Keya Chemical Engineering Co., Ltd.) was used to prepare the short-fiber–reinforced composites. These two kinds of 8-mm pellets and PMMA resin were mixed and dried at 90°C before use. The barrel temperatures were set at 200–210–220°C. The pelletized materials were then dried and injection molded into standard specimens on an injection-molding machine (J80M2V, Zhende Plastics Machinery, China). The specimens were designated as 266(S) and 988(S), respectively.

The homogeneous mixture of long-fiber pellets and PMMA resin was dried and directly injected into long-fiber testing samples on the injection-molding machine as above. The materials were designated as 266(L) and 988(L), respectively.

Apparatus and measurement

Tensile and flexural tests were carried out on a universal testing machine (Instron 1122, Canton. OH). Impact strength was measured on an XLU-22 impact tester. All mechanical properties were tested following ASTM standards. Bent fracture surfaces were observed on a JSM-5600LV scanning electron microscope (SEM; JEOL, Tokyo, Japan). Surfaces of fracture specimens were gold-sputtered before observation.

RESULTS AND DISCUSSION

Description of long-fiber pellets

The long-fiber pellets were prepared by an *in situ* pultrusion process that was developed in our laboratory.[14] The prepolymer of MMA with low viscosity was used to impregnate continuous glass fibers. The process was similar to that of Ma and Chen,[15–18] with some modifications. The low viscosity allowed good wettability of glass fibers, which can be seen from SEM microphotographs of cross sections of pellets [Figs. 1(a) and 2(a)]. These figures also show that glass fibers disperse very well in the polymer matrix, although voids are also observed. Figure 1(b) and Figure 2(b) are the SEM microphotographs of the fracture surface of long-fiber pellets. The surfaces of fibers in P-266, prepared with F-266 glass fiber, are rough, although the glass surfaces are

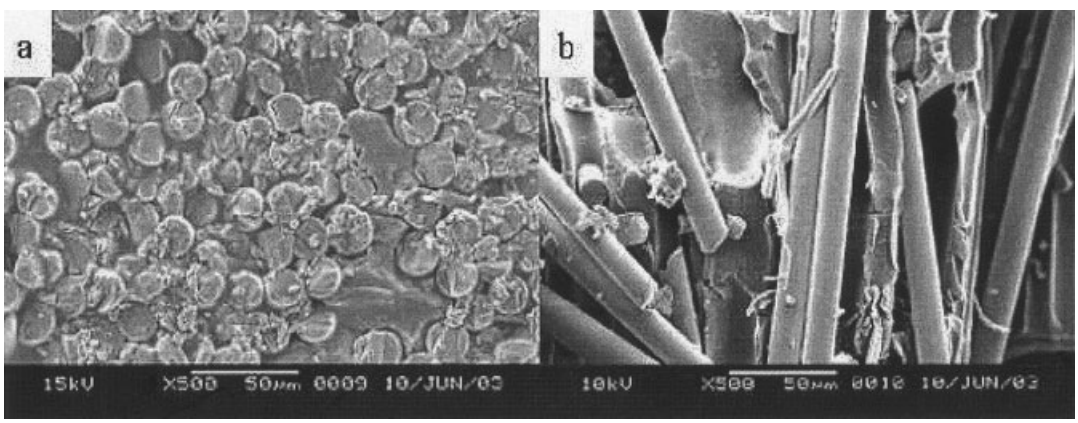

Figure 2 SEM microphotographs of long-fiber pellets of P-988: (a) cross section; (b) fracture surface.

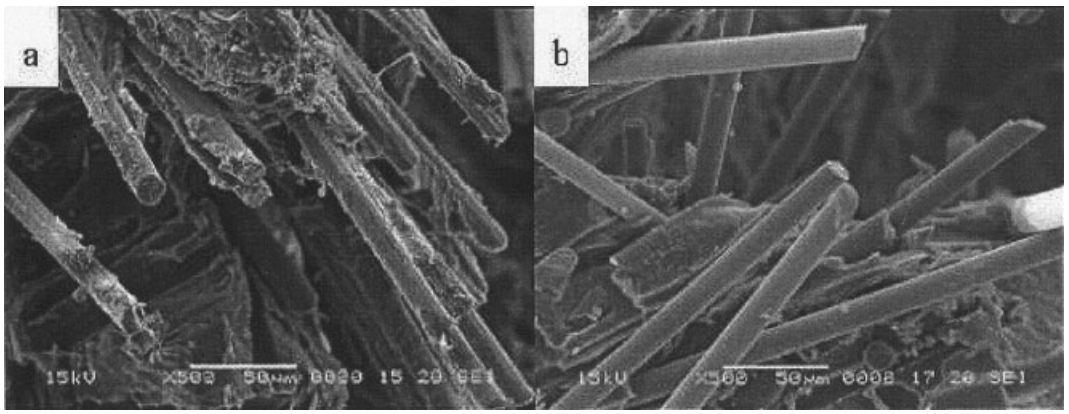

Figure 3 SEM microphotographs of long-fiber–reinforced PMMA prepared by the injection-molding process: (a) 266(L); (b) 988(L).

smooth in pellets of P-988 that are made from glass fibers of F-988. These results were also found by other researchers.[13,19,21] Fyfe and Niu[19] reported a covalent bond formation in a PMMA/silica composite at the interface between the vinyl (or acrylic) silane coupling agent and PMMA matrix. Jo and Blum[13] also observed chemical bonds formed between glass fibers that were treated with a silane coupling agent of APMS and PMMA matrix at the interface. Results of investigation by Lin et al.[20] indicated that the glass fiber surfaces were smooth at the break at temperatures lower than 75°C, but became rough when temperatures were above 75°C. Compared with the results in the above-cited literature, the roughness of glass surfaces in P-266 indicates that the methacrylic groups react with monomer to form chemical bonds at the interface of composites during the pultrusion process for F-266 glass fibers. The smoothness of glass fiber shows no polymer graft on the surface of fiber for P-988.

Fracture morphology

The scanning electron micrographs of the bent fracture surfaces of fiber-reinforced composites are shown in Figures 3 and 4. Figure 3(a) is the microphotograph of 266(L) prepared with long-fiber pellets of P-266 by the injection-molding process. The rough surfaces of glass fiber indicate that the polymer adhering to the fibers can be maintained without damage during the injection-molding process for low shearing forces; moreover, the surfaces of fibers in composites of 988(L) are still smooth, thus promoting poor adhesion between fibers and matrix in P-988, as shown in Figure 3(b).

Figure 4 shows the fracture surfaces of short-fiber–reinforced composites prepared with long-fiber pellets by the extrusion-molding method. Figure 4(a) is the microphotograph of 266(S) and Figure(b) is that of 988(S). It can be seen that the surfaces of fibers are all smooth in these two composites. The smoothness of fibers in 266(S) indicates that the polymer adhering to the surfaces of fibers in P-266 pellets is completely delaminated during the extrusion process at very high shearing forces. This result indicates that the chemical bonds formed at the interface can be destroyed under high shearing forces.

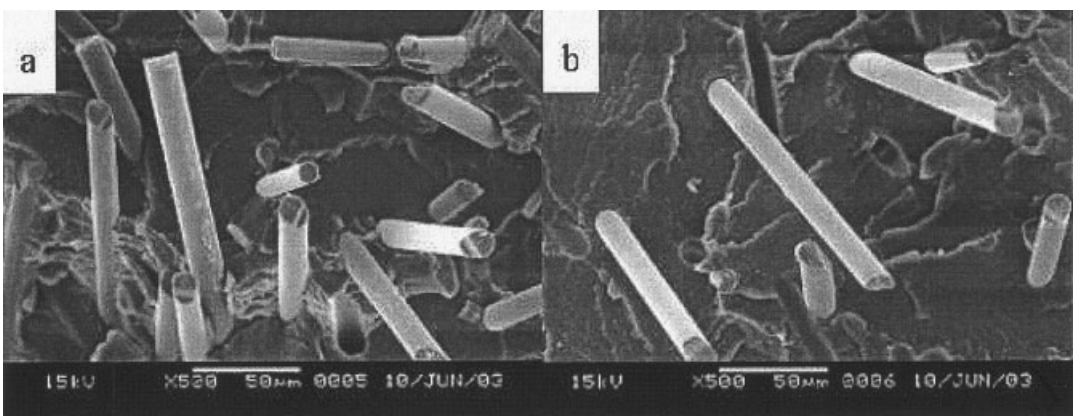

Figure 4 SEM microphotographs of short-fiber–reinforced PMMA prepared by the extrusion/injection-molding process: (a) 266(S); (b) 988(S).

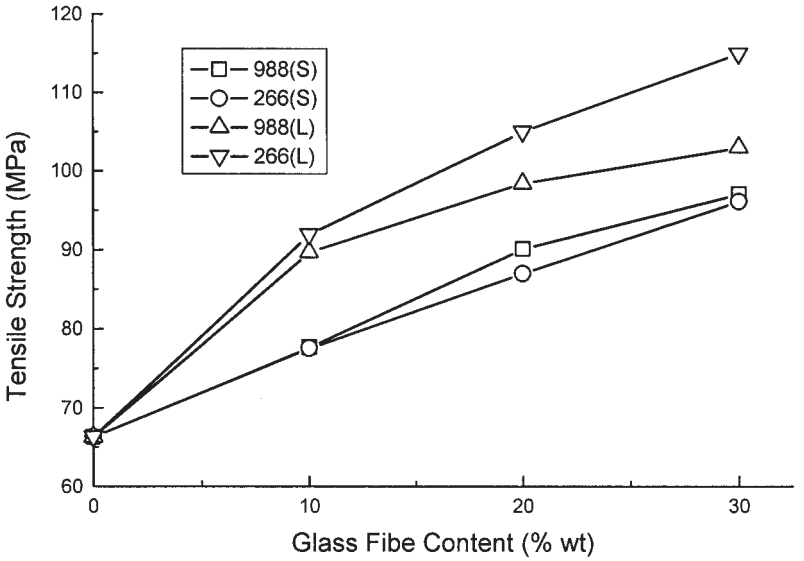

Figure 5 Tensile strength as a function of glass fiber content in composites.

Mechanical properties of fiber-reinforced PMMA

Figure 5 shows the relationship between tensile strength and fiber contents. It can be seen that the tensile strength of composites is higher than that of the pure resin, and long-fiber–reinforced composites have a much greater degree of enhancement than that of short-fiber–reinforced composites with corresponding fiber content. For short-fiber–reinforced composites, 266(S) and 988(S), the tensile strengths are identical at the same degree of adhesion of composites observed from Figure 4. However, the tensile strength of 266(L) is greater than that of 988(L) for long-fiber–reinforced composites. The enhanced properties are attributed to the greater degree of adhesion in 266(L) composites, as shown in Figure 3.

The flexural strengths and moduli of composites are illustrated in Figure 6 and Figure 7, respectively. Flexural strength follows a pattern similar to that of tensile strength. The flexural strength of the 266(L) composites is greatly improved compared with that of the 988(L) and the short-fiber–reinforced composites. On the other hand, the flexural moduli of composites are nearly the same. Studies conducted by Stoffer and coworkers[20,21] indicated that the covalent bonds formed at the interface enhanced the mechanical properties of composites. Bajaj et al.[22] and Jo and Blum[13]

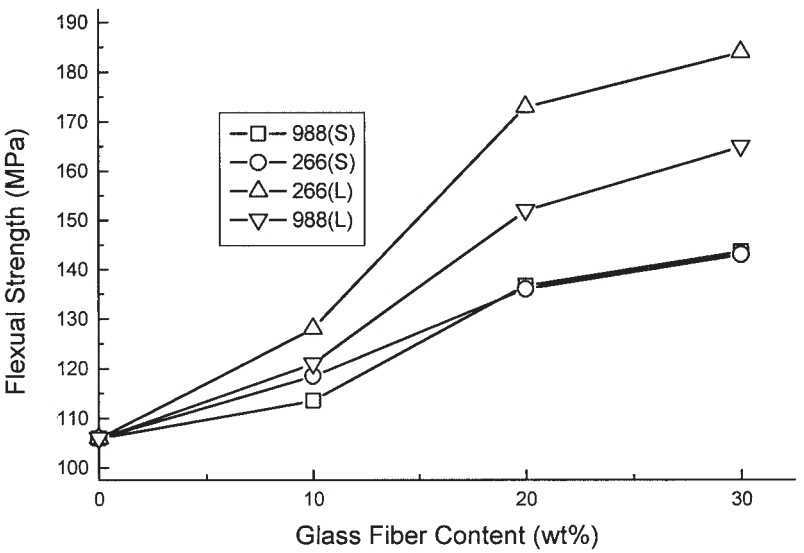

Figure 6 Flexural strength as a function of glass fiber content in composites.

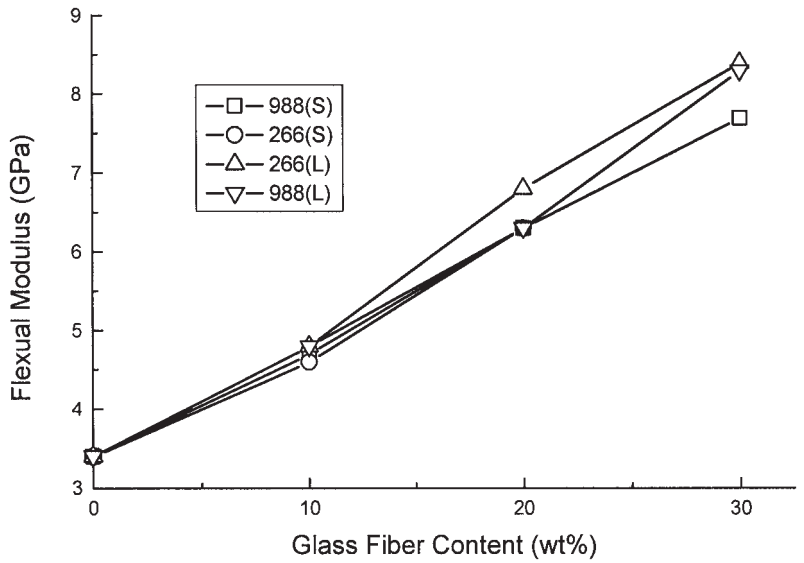

Figure 7 Flexural modulus as a function of glass fiber content in composites.

showed that, although the flexural strength of continuous-fiber–reinforced composites containing silane coupling agents was increased over that of untreated composites, their flexural moduli remained unchanged with silane coupling agent treatment. Our results are in accordance with theirs.

Composites containing long fibers have substantially improved impact resistance, whereas, in contrast, the impact strength of short-fiber–reinforced composites remain unchanged. This can be seen from Figures 8 and 9. Unlike the relationships of the tensile and flexural strengths with interface adhesion, the impact strength of both the notched and the unnotched of 988(L) composites are increased over that of 266(L) composites. This demonstrates that the enhanced adhesion of a fiber-reinforced PMMA composite will sacrifice the impact resistance properties.

The above results show that the lengths of fibers and enhanced adhesion, attributed to the chemical bonds that formed at the interface, promote the improvement of mechanical properties of composites.

CONCLUSION

The dispersion of fibers in matrix was relatively thorough in long-fiber pellets prepared by the *in situ* pultrusion process with prepolymer of MMA. The adhesion of composites was enhanced for glass fibers of

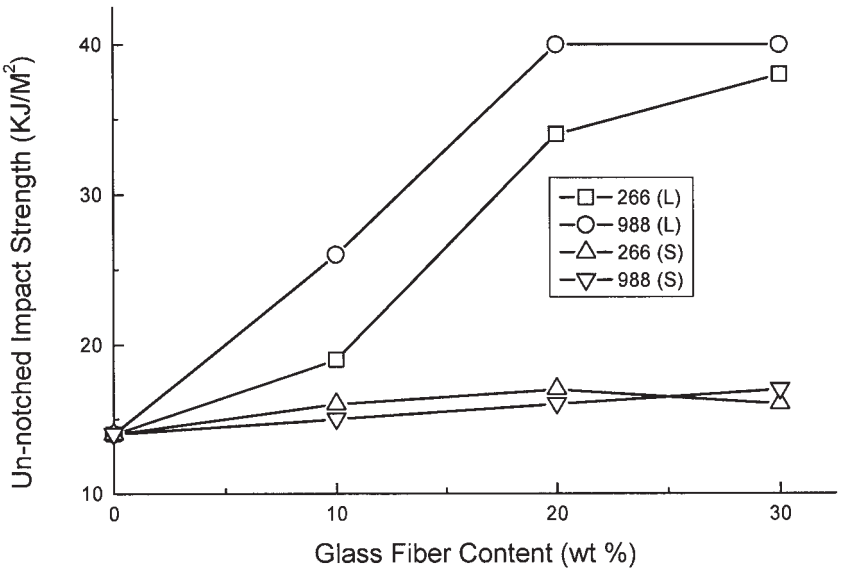

Figure 8 Unnotched Izod impact strength as a function of glass fiber content in composites.

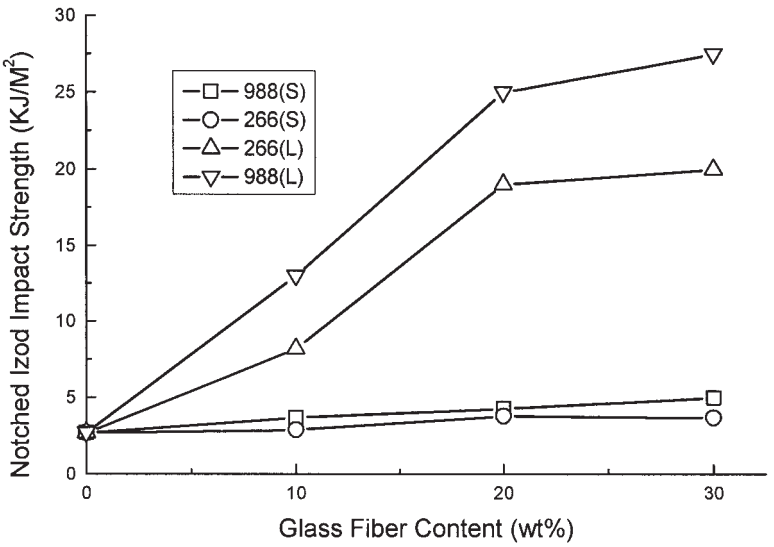

Figure 9 Notched Izod impact strength as a function of glass fiber content in composites.

F-266, but poor for F-988. The polymer adhering to the surface of fibers with covalent bonds was delaminated at high shearing forces during the extrusion/injection-molding process, but maintained at low shearing forces in the injection-molding method. Mechanical properties of composites with enhanced adhesion were much greater than those of composites with poor adhesion. Longer fibers were significantly more effective than short fibers at improving the physical properties of composites. With respect to impact resistance, however, the enhanced adhesion of the composites causes lower impact strengths.

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