

Effect of Rare Earth Elements' Surface Treatment on Tensile Properties and Microstructure of Glass Fiber-Reinforced Polytetrafluoroethylene Composites

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ABSTRACT: Three types of surface modifiers, *N*- β -aminoethyl- γ -aminopropyltrimethoxysilane coupling agent (SGS), a mixture of silane and rare earth elements (SGS/RES), and rare earth elements surface modifier (RES), were used to treat the glass fiber surface. Tensile tests of glass fiber-reinforced polytetrafluoroethylene (GF/PTFE) composites with different surface treatment conditions, surface modifiers, and glass fiber content were carried out. Finally, the fracture surface morphologies of GF/PTFE composites were investigated using scanning electron microscopy. Experimental results show that the tensile properties of the treated GF/PTFE composite increased compared with those of the untreated one. RES is superior to SGS/RES and SGS modifiers in promoting interfacial adhesion between the glass fiber and PTFE because of the effects of rare earth elements

on the compatibility. Meanwhile, the optimum contents of rare earth elements for the improvement of the tensile properties of GF/PTFE composite were obtained for RES and SGS/RES modifiers. The interfacial adhesion of the GF/PTFE composites treated with RES or SGS/RES modifiers was mainly controlled by the contents of rare earth elements. The tensile properties of the GF/PTFE composites improved considerably when the content of rare earth elements in surface modifiers was 0.2–0.4 wt %, and the optimum tensile performance of GF/PTFE composites was obtained at 0.3 wt % RE content. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1667–1672, 2002

Key words: polytetrafluoroethylene; composites; interfaces; adhesion; mechanical properties

INTRODUCTION

Polytetrafluoroethylene (PTFE) is a useful load-bearing material because it is characterized by a low friction coefficient, high thermal stability, and chemical resistance.^{1–3} Although PTFE has been considered as an attractive engineering material, its application has been greatly constrained because of its low mechanical properties, high thermal expansion, and excessive viscoelastic deformation under load.

Glass fiber (GF) has been widely used to improve the properties of polymer composites. Fiber-reinforced polymer composite often consists of two major components: an inorganic phase, such as glass fibers, and an organic polymer matrix, such as a PTFE resin. The interfacial adhesion between the fiber and the matrix is an important factor that controls the mechanical properties of polymer composites.

It is well known that the application of a silane coupling agent to a glass fiber surface will improve the fiber–matrix adhesion of composites, greatly enhancing its mechanical properties.^{4–8} The silane coupling

agent is used to improve the adhesion between the two constituents in the polymer composites and can act as a bridge between the glass fiber and the matrix. Two interfaces are found in the glass fiber-reinforced polymer composites: the glass fiber/silane coupling agents interface and the silane coupling agents/matrix interface. Chemical bonding theory and interdiffusion theory have been used to successfully explain most phenomena observed in silane-treated glass fiber-reinforced polymer composites.⁹ Saidpour et al.¹⁰ found that the mechanism of performance enhancement of glass fiber-reinforced vinyl ester composites was that the silane coupling agent could react chemically with both the hydroxyl at the glass surface and the resin. Jang et al.^{11,12} investigated the mechanical properties of glass fiber-reinforced polystyrene (GF/PS) composites and glass fiber-reinforced poly(phenylene sulfide) (GF/PPS) composites with variations of silane coupling agents and surface treatment conditions, and they concluded that the silane leads to the formation of the siloxane bond with glass fiber and an interpenetrating network (IPN) with the polymer. Generally, strong interfacial adhesion may be achieved through chemical bonding.

For glass fiber-reinforced thermoplastic polymer composites, the interfacial adhesion is usually not strong enough to counteract the lack of chemical bonds or specific interactions across the interface of

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the relatively immiscible components.¹³ To improve the interfacial adhesion, various techniques of fiber surface treatment have been studied for different resin matrices.^{13–15} In these studies, besides coupling agents, the pretreatment formulations applied to glass fibers varied widely and contained acid groups, binding agents, and surfactants. It is very important to consider the suitability of fiber surface treatment with the chosen thermoplastic matrix.

Aglan et al.^{16,17} investigated the fatigue fracture resistance of glass fiber-reinforced PTFE (GF/PTFE) composites. Wang et al.¹⁸ studied the influences of content of glass fiber on the tensile strength and dielectric properties of GF/PTFE composites. However, investigations on the effects of surface treatment of the glass fiber on the mechanical properties of GF/PTFE composites have not been intensively conducted.

Rare earth compounds have been widely used in optics, electronics, metallurgy, and chemical engineering because of their special characteristics. During the past several decades, effective research results were acquired in the investigation and application of rare earth elements (RE) as addition agent for the surface heat treatment of alloys.^{19–24} These investigations were focused on the effect and application of rare earth elements for the metal surfaces, and were not related to using rare earth elements as nonmetal materials (such as glass fibers) surface modifier. In particular, less information is available about applying the rare earth elements for the surface treatment of glass fiber, as well as the effect of rare earth elements on the mechanical properties of polymer composites.

The purpose of the present work was to investigate the surface treatment of glass fiber using RE-doped surface modifiers. The effects of different surface treatment conditions, RE surface modifiers, and glass fiber content on the tensile properties of GF/PTFE composites were evaluated. The fracture surface morphologies of GF/PTFE composites were also investigated. The optimum amount of rare earth elements for glass fiber surface treatment and its influence on the tensile properties of GF/PTFE composites were identified.

EXPERIMENTAL

The E-glass fiber (fiber diameter: 9–11 μm) used in the experiments was obtained from Nanjing Fiberglass Research and Design Institute (China). PTFE used as matrix resin of the composites was manufactured by Shanghai Chlor-Alkali Chemical Co. (China). *N*- β -Aminoethyl- γ -aminopropyltrimethoxysilane coupling agent SG-Si900 was procured from Nanjing Shuguang Chemical General Co. (China). Rare earth compound LaCl_3 was purchased from Shanghai Yuelong New Materials Co. (China). Three types of surface modifiers were used: an alcoholic solution of 1.0 wt % SG-Si900, identified as SGS; an alcoholic solution of LaCl_3 ,

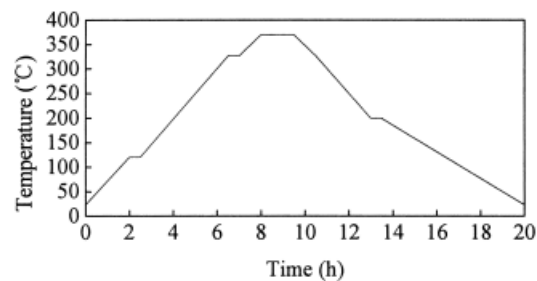


Figure 1 Sintering process of GF/PTFE composites.

marked as RES; and an alcoholic solution of 1.0 wt % SG-Si900 and LaCl_3 , labeled as SGS/RES. The LaCl_3 content in an alcoholic solution was varied from 0.1 to 0.8 wt %. The glass fibers were dipped into the surface modifiers for 1 h, and then dried for 4 h at 120°C.

GF/PTFE composites with a variation of glass fiber content from 5 to 30 wt % were manufactured. The pretreated glass fibers and PTFE resin were mixed in a glass container and stirred well so that they could be distributed uniformly and then put into a stainless steel mold (inner diameter: 120 mm). The mixed materials were then transformed into 2.0-mm-thick sheets by compression molding under 35 MPa for 5 min at room temperature. Finally, the materials were sintered in a high-temperature oven and carefully cooled down to room temperature to get GF/PTFE composites. The heat process of sintering GF/PTFE composites is shown in Figure 1.

The GF/PTFE composite plates were cut into narrow-waisted dumbbell-shape specimens in accordance with ASTM D638-89. The tensile test was carried out on an Instron tensile testing machine (Model 1186). The test was conducted on samples at room temperature using a crosshead speed of 5 mm/min. The fracture surfaces of the GF/PTFE composites were examined using a Hitachi S-520 scanning electron microscope (SEM; Hitachi, Tokyo, Japan). The samples were fractured in liquid nitrogen and then coated with gold.

RESULTS AND DISCUSSION

Tensile properties

Figure 2 represents the relationship between RE content in RES modifier and the fracture tensile strength, as well as elongation, of GF/PTFE composites. The GF/PTFE composites contained approximately 20% glass by weight. The RE content in RES modifier was varied from 0.1 to 0.8 wt %. It is seen that the fracture tensile strength and elongation of GF/PTFE composites increased with increasing RE content up to 0.3 wt %. The maximum values of the fracture tensile strength and elongation of GF/PTFE composites were obtained at 0.3 wt % RE content. Above the maximum

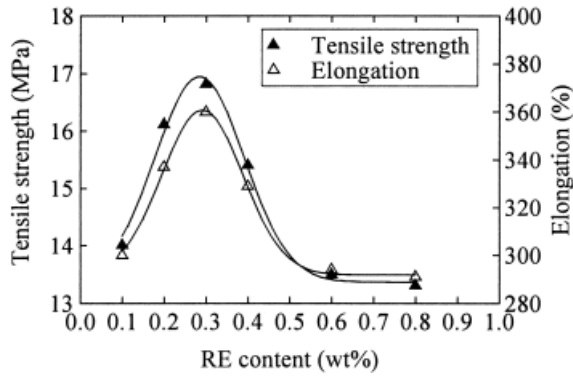


Figure 2 Relationship between RE content in RES modifier and tensile properties of GF/PTFE composites.

value, the tensile properties of GF/PTFE composites decreased gradually.

By use of earlier techniques, rare earth elements activated the steel surface and created a distorted region near the steel surface layer, which improved the properties of surface layers of steels.^{21,23} According to the chemical bonding theory and the interdiffusion theory, rare earth elements are adsorbed onto the glass fiber surface and create a distorted region near the fiber surface through chemical bonding and physical adsorption. These rare earth elements adsorbed on the glass fiber surface improve the glass fiber-PTFE interfacial adhesion. However, excess rare earth elements may hinder the formation of the distorted region near the fiber surface, so that the interfacial adhesion decreases, further resulting in the decrease of the tensile properties of the GF/PTFE composites.

Figure 3 represents the relationship between RE content in SGS/RES modifier and the fracture tensile strength, as well as elongation, of GF/PTFE composites. The GF/PTFE composites contained approximately 20% glass by weight. The RE content in SGS/RES modifier was varied from 0.1 to 0.8 wt %. The tensile properties of GF/PTFE composites were max-

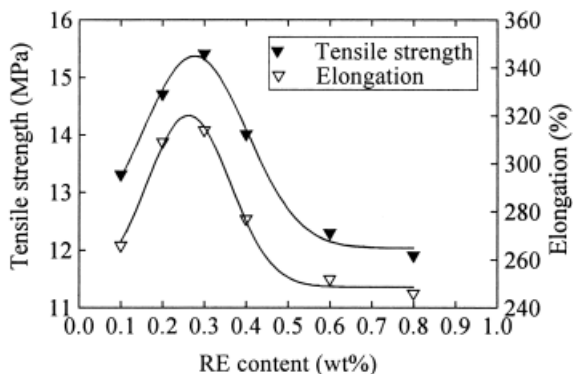


Figure 3 Relationship between RE content in SGS/RES modifier and tensile properties of GF/PTFE composites.

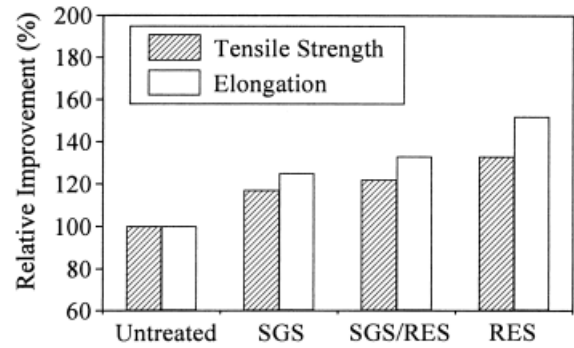


Figure 4 Effect of surface modifiers on tensile properties of GF/PTFE composites.

imum also at the 0.3 wt % RE content. The overall trend was similar to that of the GF/PTFE composite treated with RES modifier. The interfacial adhesion of the GF/PTFE composites treated with RES or SGS/RES modifier was mainly controlled by the content of rare earth elements. However, the fracture tensile strength and elongation of GF/PTFE composites treated with SGS/RES modifier were a little lower

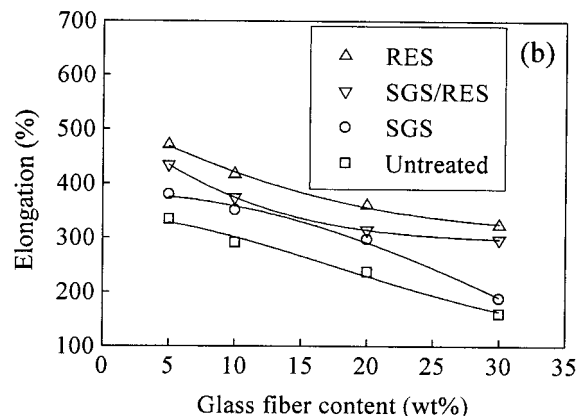
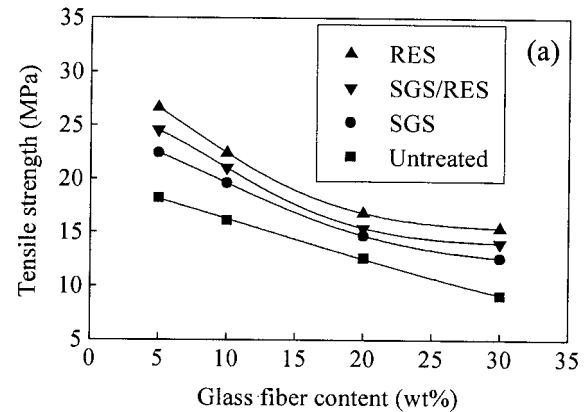


Figure 5 Tensile properties of treated GF/PTFE composites as a function of glass fiber content: (a) tensile strength; (b) elongation.

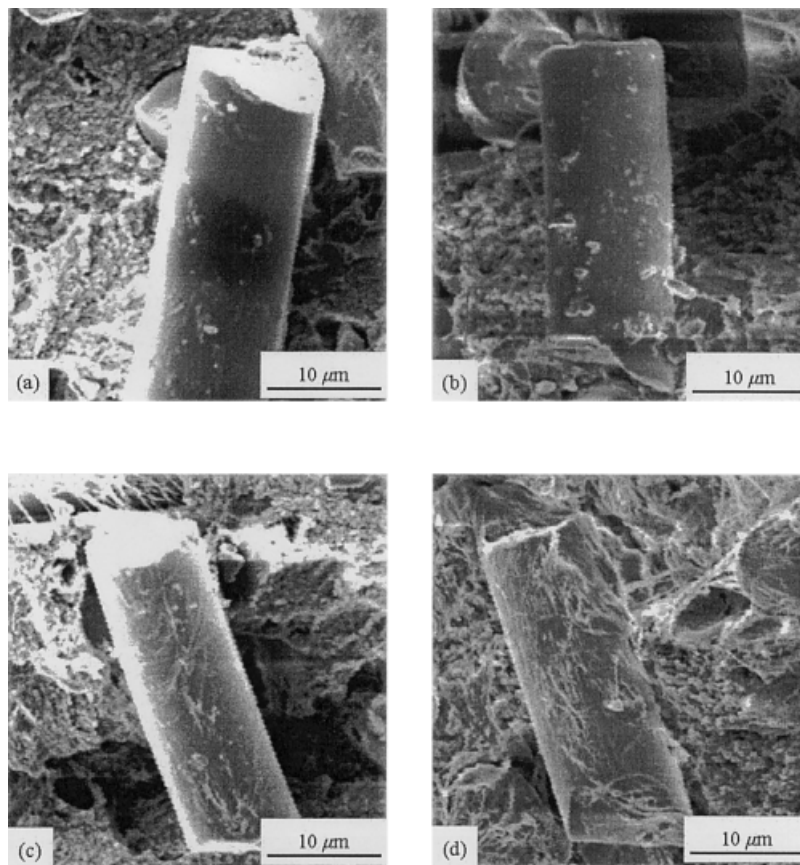


Figure 6 SEM micrographs of the fracture surface of GF/PTFE composites: (a) untreated; (b) SGS-treated; (c) SGS/RES-treated; (d) RES-treated.

than those of GF/PTFE composites treated with RES modifier at the same RE content, as represented in Figures 2 and 3. These results indicated that the formation of the distorted region near the fiber surface created by rare earth elements had been slightly influenced by introducing a silane coupling agent.

The effect of surface modifiers on the fracture tensile strength and elongation of GF/PTFE composites is represented in Figure 4. The GF/PTFE composites contained approximately 20% glass by weight. The RE content in RES and SGS/RES modifier was fixed at 0.3 wt %. The tensile properties of the GF/PTFE composites treated with SGS, SGS/RES, and RES modifier were superior to those of untreated GF/PTFE composites. Among these surface modifiers, RES modifier was the most effective in promoting the interfacial adhesion between the glass fiber and PTFE. SGS/RES modifier was more effective than SGS modifier in improving the interfacial adhesion of the GF/PTFE composites. It is obvious that RE is effective for improving the interfacial adhesion of the GF/PTFE composites.

Figure 5 represents the fracture tensile strength and elongation of GF/PTFE composites as a function of glass fiber content with different surface modifiers. The RE content in RES and SGS/RES modifier was fixed at 0.3 wt %. Among three types of surface mod-

ifiers, RES was still the most effective in promoting the interfacial adhesion between the glass fiber surface and PTFE. However, the tensile strength and elongation of GF/PTFE composites decreased with increasing glass fiber content from 5 to 30 wt % for the same surface modifier. These phenomena indicate that in the case of PTFE-based composites, the contribution of glass fiber should be investigated in detail.

SEM investigation of fracture surfaces

The SEM micrographs of the fracture surfaces of the GF/PTFE composites with different surface modifiers are shown in Figure 6. The RE content in RES and SGS/RES modifier was fixed at 0.3 wt %. It was found that the interface between untreated glass fiber and PTFE matrix showed a delamination morphology, as seen in Figure 6(a). This means that the interfacial adhesion between the glass fiber and PTFE is relatively poor. PTFE cannot react with the glass fiber and does not have compatibility with the inorganic fiber, which resulted in the poor adhesion between the glass fiber and PTFE. The interface between the glass fiber and PTFE of the GF/PTFE composite treated with SGS adhered with a little scattered PTFE, as shown in Figure 6(b). This reveals that the interfacial adhesion

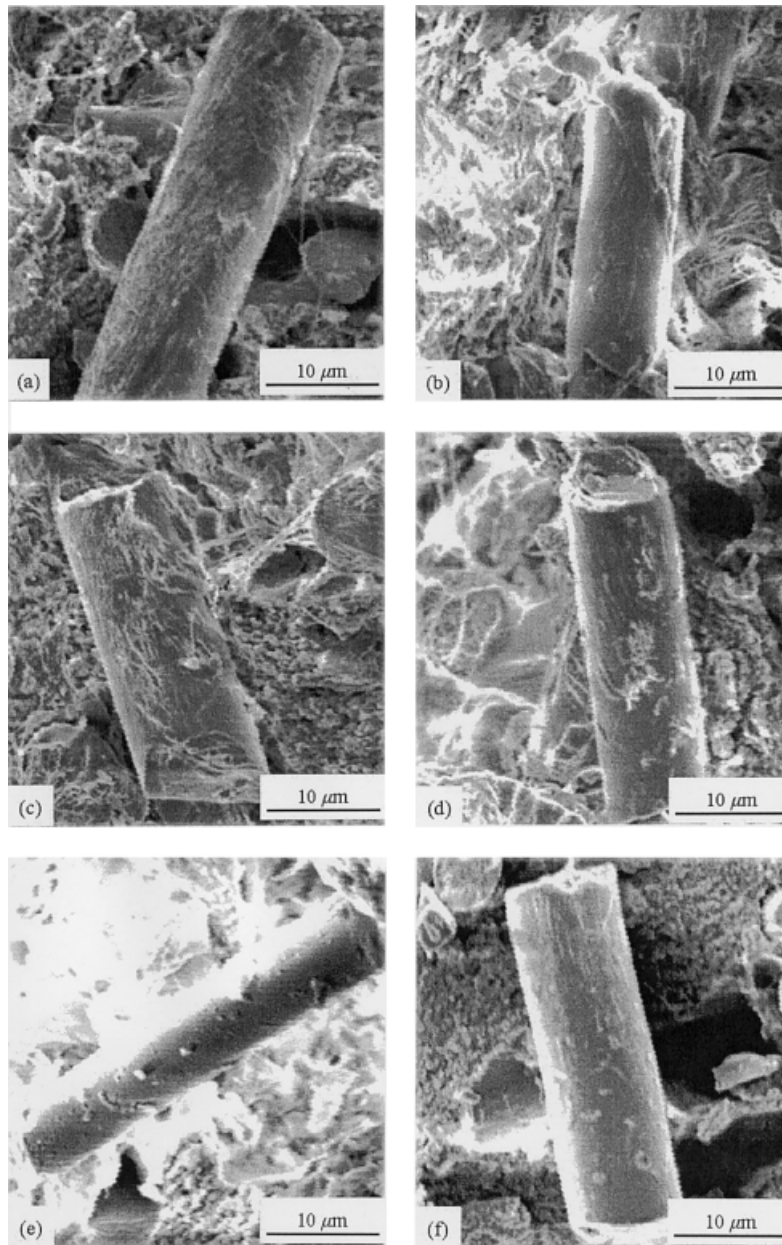


Figure 7 SEM micrographs of the fracture surface of GF/PTFE composites versus RE content: (a) 0.1 wt %; (b) 0.2 wt %; (c) 0.3 wt %; (d) 0.4 wt %; (e) 0.6 wt %; (f) 0.8 wt %.

between the glass fiber and PTFE was improved by SGS modifier. However, the interface between the glass fiber and PTFE of the GF/PTFE composite treated with SGS/RES showed a thin net-coating of adhered PTFE, as seen in Figure 6(c). The interface treated with RES showed a thicker net-coating of adhered PTFE, as seen in Figure 6(d), which is attributed to the improvement in interfacial adhesion by RE in the SGS/RES or RES modifier. It is reasonable to conclude that RE considerably improved the interfacial adhesion between the glass fiber and PTFE in the GF/PTFE composites. The above results are consistent with the fracture tensile strength and elongation data.

The SEM micrographs of the fracture surfaces of RES-treated GF/PTFE composites at various RE contents are shown in Figure 7. It is seen that the glass fiber is entwined with some polymers and the amount of entwined polymers varies with the content of RE in the RES modifier. This reveals that the interfacial adhesion of the GF/PTFE composite is improved compared with that of the untreated GF/PTFE composite. Figure 7(a)–(c) show that the amount of entwined polymers onto the glass fiber surface increases as RE content increases up to 0.3wt %. A comparison of Figure 7(d)–(f) with Figure 7(c) reveals that the amount of entwined polymers onto the glass fiber

decreases with further increase of the RE content. These results indicate that excess RE gives rise to the poor adhesion between the glass fiber and PTFE. It can be reasonably concluded that the interfacial adhesion between the glass fiber and PTFE depends on the RE content and shows the maximum value at 0.3 wt %. The above results are consistent with the fracture tensile strength and elongation data.

From the preceding results, it is evident that any variation in the structure or distribution of the rare earth elements and the silane coupling agent on the glass fiber surface will lead to the variation of interphase properties and thus the mechanical properties of the composites. It is well known that the silane chemisorbed and physisorbed onto the glass fiber surface will lead to the formation of the siloxane bond with glass fiber and an IPN with polymer. However, interfacial adhesion is largely affected by the chemical bond formation rather than by the IPN in the polymer composites.^{11,12} RES was the most effective modifier in promoting the interfacial adhesion between the glass fiber and PTFE, which can be attributed to the compatibility improvement caused by the effects of rare earth elements in RES modifier. Rare earth elements are characterized by chemical activity that is dependent on their special ($- - - 4f^{0-14}$) electron structure. Glass fiber is composed of ternary components SiO_2 , Al_2O_3 , and MgO . With low electronegativity and great activity, rare earth elements not only can clean and activate the glass fiber surfaces but can also generate $\text{Re}-\text{O}$ bands and a more stable hybrid state by decomposing $\text{Al}-\text{O}$, $\text{Mg}-\text{O}$, and $\text{Si}-\text{O}$ bands. The rare earth elements can permeate into the surface layer of glass fibers, and create distorted regions, given that the radius of ionized rare earths is equivalent to that of Al or Mg atoms. It is well known that the molecular chain structure of PTFE is $-\text{[CF}_2-\text{CF}_2\text{]}_n-$. These rare earth elements adsorbed on the glass fiber surface may break down the $\text{C}-\text{F}$ bonds to produce $\text{Re}-\text{F}$ or $\text{Re}-\text{C}$ bonds, and the distorted regions created by rare earth elements on the glass fiber surface may adsorb carbon atoms. These effects will improve the compatibility of glass fiber and PTFE. Therefore, the RE-treated glass fiber surface can enhance the interfacial adhesion between glass fibers and PTFE matrix, resulting in the optimum properties of the RE-treated GF/PTFE composites.

CONCLUSIONS

1. Rare earth elements modifiers (RES) are superior to SGS/RES and SGS modifier in promoting in-

terfacial adhesion between the glass fiber and PTFE because of the effects of rare earth elements on the compatibility. The interfacial adhesion between the glass fiber and PTFE depends on the RE content and shows the maximum value at 0.3 wt %.

2. The tensile properties of the GF/PTFE composites treated with RES or SGS/RES modifier are mainly controlled by the content of rare earth elements. The tensile properties of the GF/PTFE composites can be improved considerably when the content of rare earth elements in the surface modifier is 0.2–0.4 wt %, and the optimum performance of the GF/PTFE composites is obtained at 0.3 wt % RE content.

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References

1. Zhang, Z. Z.; Xue, Q. J.; Liu, W. M.; Shen, W. C. *J Appl Polym Sci* 1999, 72, 751.
2. Zhang, Z. Z.; Shen, W. C.; Liu, W. M.; Xue, Q. J.; Li T. S. *Wear* 1996, 196, 164.
3. Zhang, Z. Z.; Xue, Q. J.; Liu, W. M.; Shen, W. C. *Wear* 1997, 210, 195.
4. Wang, T. W. H.; Blum, F. D. *J Mater Sci* 1996, 31, 5231.
5. St John, N. A.; Brown, J. R. *Composites* 1998, 29A, 939.
6. Otaigbe, J. U. *J Appl Polym Sci* 1992, 45, 1213.
7. Miwa, M.; Horiba, N. *J Mater Sci* 1994, 29, 973.
8. Lee, N. J.; Jang, J. *Compos Sci Technol* 1997, 57, 1559.
9. Hirai, Y.; Hamada, H.; Kim, J. K. *Compos Sci Technol* 1998, 58, 91.
10. Saidpour, S. H.; Richardson, M. O. W. *Composites* 1997, 28A, 971.
11. Jang, J.; Lee, J. Y.; Jeong, J. K. *J Appl Polym Sci* 1996, 59, 2069.
12. Jang, J.; Kim, H. S. *J Appl Polym Sci* 1996, 60, 2297.
13. Pak, S. H.; Caze, C. *J Appl Polym Sci* 1997, 65, 143.
14. Hamada, H.; Fujihara, K.; Harada, A. *Composites* 2000, 31A, 979.
15. Jensen, R. E.; Johnson, C. E.; Ward, T. C. *J Polym Sci Part B: Polym Phys* 2000, 38, 2351.
16. Aglan, H.; Gan, Y.; El-Hadik, M.; Faughnan, P.; Bryan, C. *J Mater Sci* 1999, 34, 83.
17. Zhang, Z.; Aglan, H.; Faughnan, P.; Bryan, C. *J Reinf Plast Compos* 1998, 17, 752.
18. Wang, X. Q.; Han, J. C.; Du, S. Y.; Wang, D. F. *J Reinf Plast Compos* 1998, 17, 1496.
19. Wei, Y. D.; Liu, Z. R.; Wang, C. Y.; Fan, A. L.; Cheng, J. M. *Acta Metall Sinica* 1983, 19, B197 (in Chinese).
20. Liu, Z. R.; Zhu, F. Y.; Cui, Y. X. *J Rare Earths* 1993, 11, 196.
21. Cheng, X. H.; Xie, C. Y. *J Rare Earths* 1994, 12, 336 (in Chinese).
22. Peng, J.; Dong, H.; Bell, T. *Surf Eng* 1996, 12, 147.
23. Cheng, X. H. *Tribology* 2000, 20, 248 (in Chinese).
24. Wang, L. P.; Tang, B. Y.; Wang, X. F.; Wang, S. Y.; Paul, K. C. *J Rare Earths* 2001, 19, 40.