Effect of Rare Earth Elements Surface Treatment on Tensile Properties of Aramid Fiber-Reinforced Epoxy Composites

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ABSTRACT: Solutions of rare earth modifier (RES) and epoxy chloropropane (ECP) grafting modification method were used for the surface treatment of aramid fiber. Tensile properties of both the aramid/epoxy composites and single fibers were tested. The effects of RES concentration on tensile properties of aramid/epoxy composites were investigated in detail to explore an optimum amount of rare earth elements in solution for modifying aramid fiber. The fracture surface morphologies of tensile specimens were observed and analyzed with the aid of SEM. The experimental results show that rare earth treatment is superior to ECP grafting treatment in promoting interfacial adhesion between the aramid fiber and epoxy matrix. Meanwhile, the tensile strengths of single fibers were almost not affected by RES treatment. The optimum performance is obtained when the content of rare earth elements is 0.5 wt %. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1037–1041, 2004

Key words: composites; interfaces; adhesion; fibers

INTRODUCTION

Aramid fiber is a kind of high-performance organic fiber because it registers a high specific strength and modulus. Structures made of aramid fiber-reinforced (ARF) plastics are widely used in aviation and space engineering due to the low density and high specific strength of aramid fibers and composites based on them, which is important for aircraft industry.[1] The interfacial adhesion of fiber-reinforced composites plays a very important role in determining the composite mechanical properties. A better fiber/matrix interfacial adhesion/bond will impart better properties such as tensile strength, interlaminar shear strength, delamination resistance, fatigue, and corrosion resistance to a polymeric composite.[2] However, the surface of aramid fiber is chemically inert and smooth, and its compatibility with matrix resin is bad; thus, its adhesion with the resin matrix is poor. Therefore, to use aramid fiber as reinforcement, surface modification is essential to enhance its reinforcing effect.[3]

There are several fiber surface modification methods, such as chemical treatment (including coupling agent and chemically grafting methods) and plasma treatment used to improve the adhesion with the resin matrix.[4]

RES surface treatment had been applied to modify the surface of inorganic fiber (such as glass fiber),[5–7] and an obvious improvement of interfacial adhesion between glass fiber and resin was achieved, but has never been tried for organic fiber surface treatment. RES surface modification method has some virtues, such as no pollution to environment, low cost, high efficiency, simple process, and no damage to the fiber. In the present research, RES were used to modify the surface of aramid fiber and compared with the ECP grafting modification method.[8] Tensile properties of both the aramid/epoxy composites and single fibers were tested. The effects of RES concentration on tensile properties of composites were investigated.

EXPERIMENTAL

Aramid fiber used in this study is an F-12 aramid fiber. Rare earth compound $LaCl_3$ purchased from Shanghai Yuelong New Materials Co., Ltd (China). was used as the main component of the rare earth modifier. E-51 epoxy resin and 593 curing agent were manufactured by Shanghai Resin Factory Co., Ltd (China). ECP was produced by Shanghai Yonghua reagent factory (China).

Before surface treatment, F-12 aramid fibers were circumfluent extracted by toluol, acetone, and deioned water for 3 h in sequence to eliminate the organic impurity on the fiber surface, then dried in a vacuum oven.

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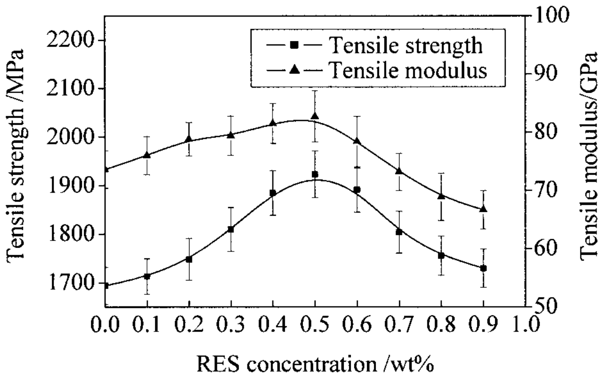


Figure 1 Relationship between tensile properties of F-12/epoxy composites and RES concentration.

Two types of fiber surface treatment have been applied in this research: RES treatment, and ECP grafting modification treatment.

For the ECP grafting modification treatment, F-12 aramid fibers were immersed in the solution of KOH (0.7%)/alcohol at 30°C for 2 h, then washed and dried. After that, these fibers were grafted in ECP at 90°C for 6 h, then washed with distilled water and dried.

For RES surface treatment, F-12 aramid fibers were immersed in the RES/alcoholic solution at room temperature for 1 h, and dried in a vacuum oven at 110°C for 4 h. The LaCl3 content in alcoholic solution was from 0.1 to 0.9 wt %.

F-12 aramid/epoxy unidirectional laminated composites were manufactured. The content of F-12 aramid fibers was fixed at 60% by volume for all composite specimens. The ratio of E-51 epoxy resin to 593 curing agent was 100 : 25 in weight. This mixture can be cured at room temperature. The tensile specimens were prepared according to Chinese national standards (GB3354-82), with a size of 230 mm × (12.5 ± 0.5 mm) × (2 ± 0.1 mm).

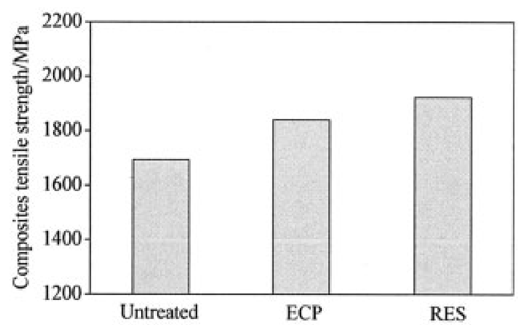
The tensile properties of composites were tested by AG-100kNA material tensile machine, at a crosshead speed of 5 mm/min. An average value was obtained of five specimens tested for each experimental data.

Single aramid fiber tensile specimens were prepared by attaching a single fiber to a paper frame using epoxy resin. It was tested using an INSTRON Tensile Testing Machine (Model 2211), at a crosshead speed of 2 mm/min. At least 20 specimens were tested in each group.

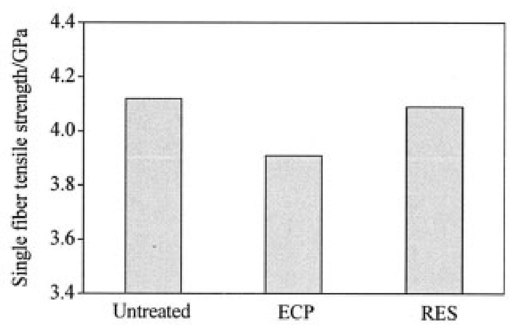
RESULTS AND DISCUSSION

The effects of RES concentration on tensile properties of F-12/epoxy composites

Figure 1 represents the tensile strength and tensile modulus of F-12/epoxy composites as a function of RES concentration. The content of rare earth elements was varied from 0.1 to 0.9 wt %. It can be seen that the tensile strength and tensile modulus of F-12/epoxy composites increased with the increase of RES concentration when RES concentration is less than 0.5 wt %. The maximum values of tensile strength and modulus were obtained at 0.5 wt %. Above the maximum value, the tensile properties decreased gradually. The improvement of tensile properties of composites can be attributed to interfacial adhesion improvement caused by the effects of rare earth elements in RES. Rare earth elements have the chemical activity, which depends on their special electron structure (- - - $4f^{0-14}$). The rare earth compounds are capable of coordinating and ionic combination reacting with some functional groups of polymers.[9] According to the chemical bonding theory, it is suggested that rare earth is adsorbed onto the aramid fiber surface through chemical bonding, which increases the concentration of reactive functional groups due to the chemical activity of rare earth elements.[10] These reactive functional groups can improve the compatibility between aramid fiber and epoxy matrix and form a chemical combination between the aramid fiber and epoxy matrix.[11] As a result, the interfacial adhesion of the aramid/epoxy

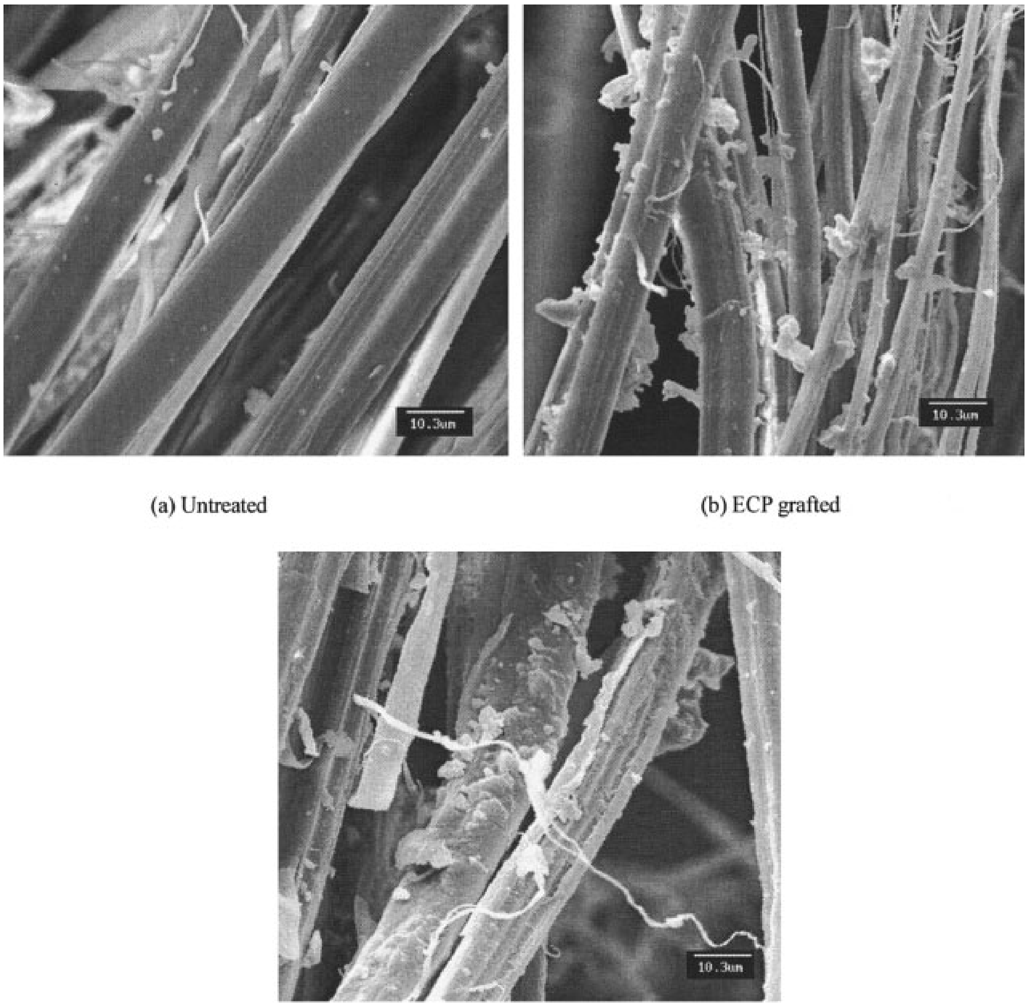


(a) Effect of surface treatments on tensile properties of F-12 / epoxy composites



(b) Effect of surface treatments on tensile properties of F-12 fibers

Figure 2 Effect of surface treatments on tensile properties of F-12 fiber and its epoxy composite. (a) Effect of surface treatments on tensile properties of F-12/epoxy composites. (b) Effect of surface treatments on tensile properties of F-12 fibers.



(a) Untreated (b) ECP grafted (c) 0.5wt% RES

Figure 3 SEM micrographs of the fracture surface of F-12/epoxy composites vs. surface modification. (a) Untreated; (b) ECP grafted; (c) 0.5 wt % RES.

composite is improved through RES surface treatment. However, excess rare earths may result in the formation of rare earth salt crystals on the aramid fiber surface. A little white power on the fiber surface can be seen. Consequently, a decrease of the tensile properties of the aramid/epoxy composite occurred because these salt crystals act as impurities that can influence the interfacial adhesion between the aramid fiber and epoxy matrix. The interfacial changes are still under investigation.

Comparison between the two treatments

According to above tensile experimental results, the concentration of RES was fixed at 0.5 wt %, while a comparison between RES treatment and the ECP grafting treatment was made, as shown in Figure 2. It is seen in Figure 2(a) that both surface treatments can improve the tensile properties of the aramid/epoxy composite, and RES-treated aramid fibers yielded better results. The tensile strength of the RES-treated aramid/epoxy composite has been improved about 13.5% compared with that of the untreated composite, and 8.6% improvement was achieved by the ECP grafting treatment.

From the single-fiber tensile test results shown in Figure 2(b), it is clear that the ECP grafting treatment does more damage to aramid fibers. The tensile strength of F-12 aramid single fibers treated with the ECP grafting method decreases about 5.1% compared with that of untreated aramid fibers, which is in accordance with the results in ref. 8. It is noticed that during ECP treatment aramid fibers were treated with KOH/alcohol solution to introduce —COOK groups to the surface of aramid fibers as grafting initiators, which may lead to hydrolyzation of aramid fiber sur-

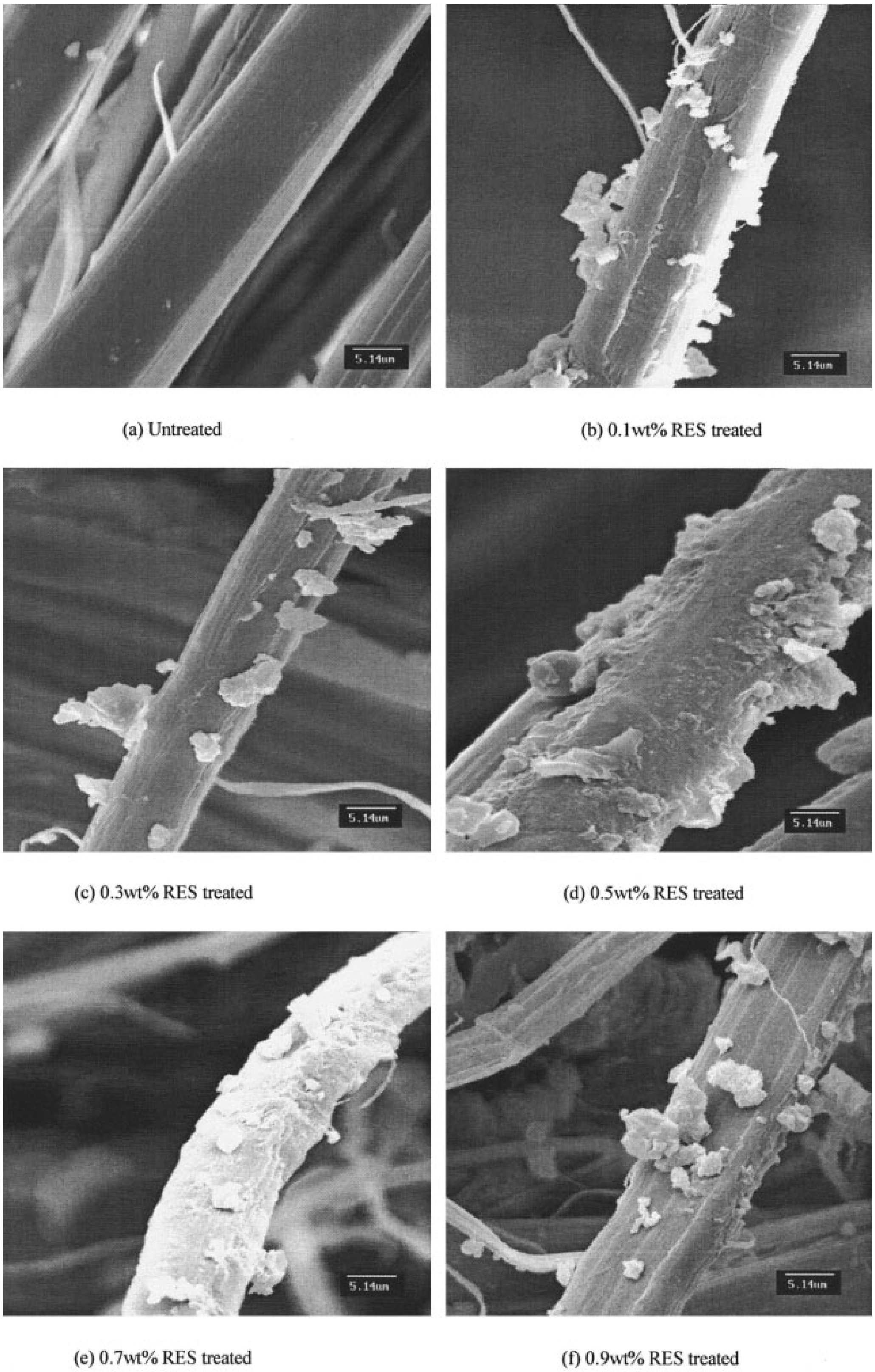


Figure 4 SEM micrographs of the fracture surface of F-12/epoxy composites vs. RES concentration. (a) Untreated; (b) 0.1 wt % RES treated; (c) 0.3 wt % RES treated; (d) 0.5 wt % RES treated; (e) 0.7 wt % RES treated; (f) 0.9 wt % RES treated.

face molecules. Excess hydrolyzation may result in damage to the fibers, and then affect the tensile properties of composites, whereas the tensile properties of RES-treated aramid fibers are not obviously changed, which reveals little damage done by RES treatment to F-12 aramid fibers.

Analysis of fracture surface morphology

The fracture surfaces of tensile specimens were coated with gold then observed using a scanning electron microscope (SEM) (Model: CSM950, made by OPTON Co., Ltd. Germany), as shown in Figure 3.

It was found that the surfaces of untreated fibers were smooth, and little epoxy resin was adhered to fiber surface as shown in Figure 3(a). Most fibers were pulled out from epoxy matrix owning to the poor adhesion with matrix. This means that composites reinforced with untreated fibers are more likely to subject to debonding damage. The interfacial adhesion between fiber and epoxy resin was improved by ECP grafting treatment because the fiber surface becomes rougher than that of the untreated fiber. Apparently there are a number of clusters of epoxy resin adhered to the fiber surface, as shown in Figure 3(b). Moreover, the interfacial adhesion became stronger with RES treatment. A large amount of epoxy resin adhered to the fiber surface and formed a thick layer, as shown in Figure 3(c). The above results are consistent with the tensile experimental data. All the results indicate that RES treatment is superior to ECP grafting treatment in promoting the interfacial adhesion between F-12 fiber and epoxy matrix; thus, the tensile properties of the F-12/epoxy composites can be improved considerably.

The SEM micrographs of the fracture surfaces of RES-treated F-12/epoxy composites at various contents of rare earth elements are shown in Figure 4. The amount of matrix resin adhered to the fiber surface varied with the concentration of RES. It increased with the increase of RES concentration [shown in Fig. 4(a)–(d)]. The maximum value was obtained at 0.5 wt % RES concentration [shown in Fig. 4(d)]. Epoxy resin covered most of the fiber surface and formed a thick layer. Above the maximum value, the amount of epoxy resin adhered to the fiber surface decreased gradually, as shown in Figure 4(d)–(f). It can be reasonably concluded that the interfacial adhesion is affected by RES concentration. The optimum performance is obtained when the content of rare earth elements is 0.5 wt %. These results are also in accordance with the tensile experimental results of composites.

CONCLUSION

1. RES treatment is superior to ECP grafting treatment in promoting interfacial adhesion between the F-12 aramid fiber and epoxy matrix due to the effects of rare earth elements on the compatibility.
2. RES treatment does hardly any damage to the fiber.
3. The tensile properties of the RES-treated F-12 aramid/epoxy composites are affected by the overall RES concentration. It can be improved considerably when the content of rare earth elements is 0.5 wt %.

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