Study of interlaminar shear strength of rare earths treated aramid fiber reinforced epoxy composites

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Aramid fiber is a good candidate for the reinforcement for polymer composites owing to its low density and high specific strength. However, because of high crystallility, the surface of aramid fiber is chemically inert and smooth, thus its adhesion with the resin matrix is poor. Therefore, surface-modification is essential to enhance its reinforcing effect [1–3].

In order to improve the adhesion to epoxy matrices, the surface of aramid fibers can be modified chemically to increase the concentration of reactive functional groups or to roughen the surface of the fiber to increase the physical interface with the resin matrix [4–6].

In this study, aramid fibers were treated with rare earth modifier solutions (RES) and the effects of RES concentration on interlaminar shear strength (ILSS) of aramid/epoxy composites were investigated in detail. Short-beam-shear (SBS) tests were used to determine the ILSS and the fracture surfaces of ILSS specimens were analyzed by scanning electron microscopy (SEM). A series of single fiber tensile tests were carried out to determine whether damage to the fiber have been caused by the surface treatment. RES surface modification is an entirely new method for aramid fiber surface modification and it has some advantages, such as little pollution to environment, low cost, high efficiency and so on.

The fibers used in this study are F-12 aramid fibers. Rare earth compound $LaCl_3$ purchased from Shanghai Yuelong New Materials Co., Ltd. Ethylenediamine tetraacetic acid (EDTA), ammonium chloride, and hydrogen nitrate were commercially obtained without further purification. E-51 epoxy resin and 593 curing agent were manufactured by Shanghai Resin Factory Co., Ltd.

Before surface treatment, F-12 aramid fibers were circumfluent extracted by toluol, acetone, and deioned water for 3 hr in sequence to eliminate the organic impurity on the fiber surface. Then the fibers were dried in a vacuum oven at 110 °C for 6 hr.

For the preparation of the RES, $LaCl_3$, EDTA, ammonium chloride, and hydrogen nitrate were added to ethanol. The final pH of solution was 5. The $LaCl_3$ content in the solution was varied from 0.1 to 0.9 wt%.

F-12 aramid fibers were immersed in the RES at room temperature for 1 hr, and dried in a vacuum oven at 110 °C for 6 hr.

There are several methods for the determination of the ILSS, such as the short-beam-shear (SBS) tests, the four-point shear test, the tensile test, the double notch shear test and so on. The SBS test has the advantage of being a simpler test arrangement [7].

F-12 aramid/epoxy unidirectional laminated composites were manufactured. The content of F-12 aramid fibers was fixed at 65% by volume for all composite specimens. The ratio of E-51 epoxy resin to 593 curing agent was 100:25 by weight. This mixture can be cured at room temperature. The ILSS specimens were prepared according to ASTM D-2344. The distance between supports divided by the thickness of the specimens, $L/d = 5$. The experiments were performed with a Zwick/Roell Z020 Material Testing Machine, at a cross-head speed of 1 mm/min. An average value was obtained from the 5 specimens tested for each RES composition. The fracture surfaces of the ILSS specimens were coated with gold then observed using a SEM (Model: CSM950, made by OPTON Co., Ltd. Germany).

Single aramid fiber tensile specimens were prepared by attaching a single fiber to a paper frame using epoxy resin. The fibers were tested using a Single Fiber Strength Testing Machine (Model: HD009, made by Tsingdao Shanfang Instrument Co., Ltd. China) at a cross-head speed of 1mm/min. The gauge length was 10 mm. For each group at least 20 specimens were tested.

Fig. 1 shows the effect of RES concentration on the interlaminar shear strength of aramid/epoxy

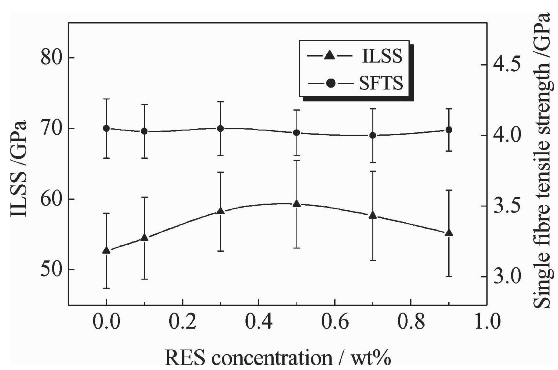

Figure 1 The effect of RES concentration on ILSS and single fiber tensile strength.

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composites and the tensile strength of single fibers. The RES concentration was varied from 0.1 to 0.9 wt%. It can be seen that the ILSS values of composites increased with increasing RES concentration to a maximum at about 0.5 wt% RES concentration. Above this RES concentration, the ILSS of aramid/epoxy composites decreased gradually. The improvement of ILSS can be attributed to improved composites interfacial adhesion caused by the effects of rare earth elements in the RES. Rare earth elements have the special physicochemical characteristics owing to their electronic structures. They can bond with polymers having coordinate groups [8–9]. First the rare earth elements were adsorbed onto the fiber surface through chemical bonding and physical adsorption. These adsorbed rare earth elements can act as active centers due to their large coordinate numbers and this can improve the interfacial adhesion between aramid fiber and epoxy resin matrix [10]. As a result, the ILSS of composites was improved. However, excess rare earths may result in the formation of rare earth salt crystals on the aramid fiber surface. These can be seen as white powder on the fiber surface. Consequently, a decrease in the tensile properties of aramid/epoxy composite occurred because these salt crystals act as impurities which can influence the interfacial adhesion between aramid fiber and epoxy matrix.

Fig. 1 also shows that the tensile strengths of single fibers are not changed significantly. Thus the tensile properties of single fibers are not affected by the RES concentration and little damage was done by the RES treatment.

The SEM micrographs of fracture surfaces of RES treated F-12/epoxy composites at various concentrations are shown in Fig. 2. The surfaces of untreated

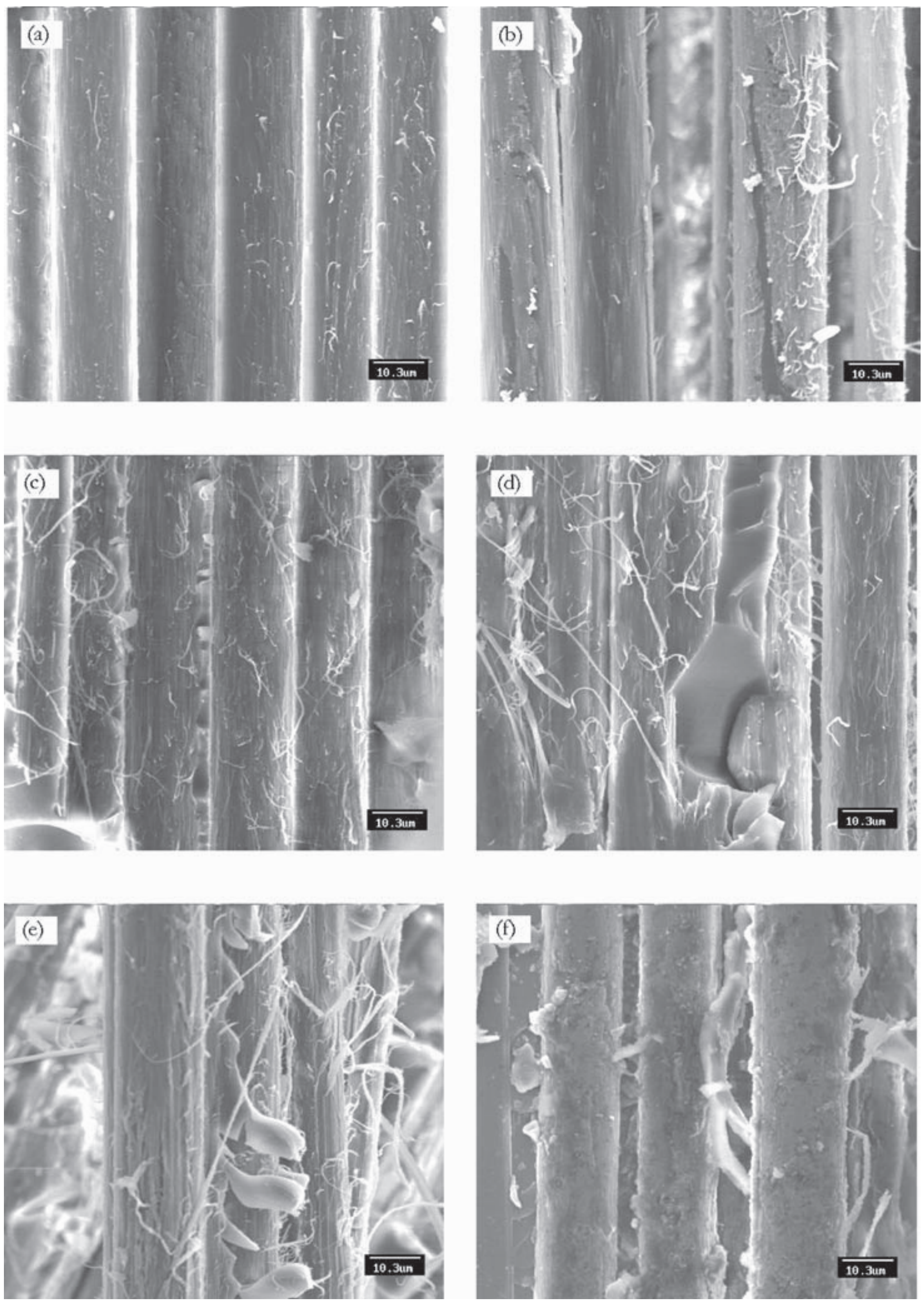

Figure 2 SEM micrographs of the fracture surface of F-12/epoxy composites vs. RES concentration. (a) Untreated; (b) 0.1 wt%; (c) 0.3 wt%; (d) 0.5 wt%; (e) 0.7 wt%; (f) 0.9 wt%.

fibers are smooth and little epoxy matrix adhered to the fiber surface as shown in Fig. 2a. This means that the interfacial adhesion between untreated fiber and epoxy resin is relatively poor, and the interface is more likely to be subject to debonding damage. The fracture surfaces of the RES treated specimens are shown in Figs 2b–2f. The interfacial adhesion is improved by RES treatment; however, the effects are not same at the different RES concentration. Good results were obtained at the concentrations of 0.3, 0.5, and 0.7 wt%. A large amount of epoxy resin adhered to the fiber surface as shown in Fig. 2c–2e. This is especially evident in Fig. 2d, where a mass of epoxy matrix has adhered to the fiber surface and internal cracks in the epoxy matrix were observed. This reveals that the interfacial adhesion was greatly improved by the formation of chemical bonds between aramid fiber and epoxy resin. Comparing Fig. 2c–2e with Fig. 2f, it can be seen that the amount of adhered polymer decreases and the effect of RES surface treatment at the concentration of 0.9 wt% is not as good. This indicates that excess rare earths give rise to the poor adhesion between the aramid fiber and epoxy resin. It can be reasonably concluded that the interfacial adhesion between the aramid fiber and epoxy resin depends on the RES concentration and shows a maximum value at 0.5 wt%. The above results are consistent with the ILSS of aramid/epoxy composites.

In conclusion, the ILSS of the F-12 aramid/epoxy composites can be improved considerably by RES surface treatment. The optimum performance of the aramid/epoxy composites is obtained at 0.5 wt% RES concentration. Little damage was done by RES treatment to the fiber.

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