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Effect of lanthanum on the tensile properties of carbon-fibre reinforced thermoplastic polyimide composites

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Rare earth (RE) La modification and air-oxidation methods were used to improve the interfacial adhesion of the carbon fibre reinforced polyimide (CF/PI) composite. The interfacial characteristics of composites reinforced by carbon fibres, treated with different surface modification methods, were investigated comparatively. Results showed that both RE modification and air-oxidation method improved the adhesion between the reinforcement and matrix, and that the RE modification method was superior to the air-oxidation method. For the CF/PI composite, optimum interfacial adhesion was obtained at 0.3 wt. % of La concentration. The fracture surfaces of samples were investigated by scanning electronic microscopy (SEM) to analyse the effects of various surface treatment methods.

Key words: *rare earth; carbon fibre; polyimide; composite*

1. Introduction

Polyimide and its composites attract extensive concern from tribological scientists world-wide because of their high mechanical strength, high wear resistance, good thermal stability, high stability under vacuum, good anti-radiation, and good solvent resistance [1, 2]. Carbon fibre reinforcement dominates in high-performance applications due to its outstanding mechanical properties combined with low weight. Strong interfacial adhesion strength must be achieved to improve the mechanical properties of composites, as it determines their mechanical properties [3]. Carbon fibre, however, often exhibits poor adhesion to polymers because its surface is chemically inert and smooth, and there are very few oxygen-containing functional groups. Much re-

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search has been devoted to enhance the adhesion between carbon fibre and polymer, hence it is well known that the surfaces of carbon fibres can be modified by surface treatment. Many approaches, such as electrochemical oxidation, plasma treatment, and liquid phase oxidation of carbon fibre, have been pursued in order to improve interfacial adhesion strength of carbon fibre reinforced composites [4].

RE surface modification has extensive application prospects due to its extraordinary properties, such as no environmental pollution, low cost, high efficiency, simple process, and no damage to the fibre. RE surface treatment has been successfully applied to improve the adhesion of glass fibre and PTFE, and aramid fibre and epoxy, respectively [5–7].

2. Experimental

In the present research, two types of methods of surface modification were used: RE modification and air-oxidation. The composites and the methods of treatment of carbon fibres are listed in Table 1. The effects of different surface treatment methods were comparatively investigated by the Erichsen test. The tensile fracture surfaces were observed by SEM. In addition, the effects of RE La concentration on the tensile properties of CF/PI composites were investigated in detail to explore an optimum amount of La in solution for modifying carbon fibre.

Table 1. Materials and surface treatments of carbon fibre

Material	Carbon fibre	Modifier
A	untreated	no modification
B	treated with RE	$LaCl_3$
C	treated with air (oxidation method)	air

Table 2. Main properties of PI (GCTP™)

Parameter	Value
Density (kg/m^3)	1350
Impact strength (kJ/m^2)	25
Tensile strength (MPa)	95
Thermal expansion (°C^{-1})	4.8×10^{-5}
Breaking elongation (%)	7
Glass transition temperature (°C)	260
Flexural strength (MPa)	150
Heat decomposition temperature (°C)	240

The reinforcements used in the present study were polyacrylonitrile (PAN)-based, unmodified, and unsized high strength (HS) carbon fibres (supplied by Shanghai Sxcarbon Technology Co. Ltd, China) with the following properties: tensile strength

2500 MPa, elastic modulus 200 GPa, density 1760 kg/m^3, diameter 7 μm, length 75 μm. $LaCl_3$, purchased from Shanghai Yuelong New Materials Co. Ltd. was used as the main component of the RE solution applied in surface modification. The matrix was a GCTP^{TM} TPI powder with a grit size of about 500 μm, provided by Nanjing University of Technology. Its main physical and mechanical properties are listed in Table 2.

Before the RE surface treatment of carbon fibres, RE solutions with the hot moulding technique was employed to prepare the composite specimens, which is the most common technique for the sintering of pure PI without sintering aids. In this process, the filler and resin were churned together in the mixer. Mixing was done for a few minutes after the addition of each component for about 20 minutes. The sintering powder was placed inside a stainless mould with its inner walls coated with a BN slurry to avoid any interaction between the powder and steel and also to facilitate the demoulding process. The compounds were put into the QLB–D170×170 vulcanising machine at 280 °C for 1 hour with a constant pressure of 12 MPa, then heated from 280 °C to 340 °C with the heating rate of 60 K/h in 1 hour. When the temperature reached 340 °C, it was kept constant for 1 hour. Afterwards, the compounds were cooled from 340 °C to 200 °C with the cooling rate of 120 K/h for 70 minutes. Pressure was kept constant during the whole process. The sintering cycle is shown in Fig. 1.

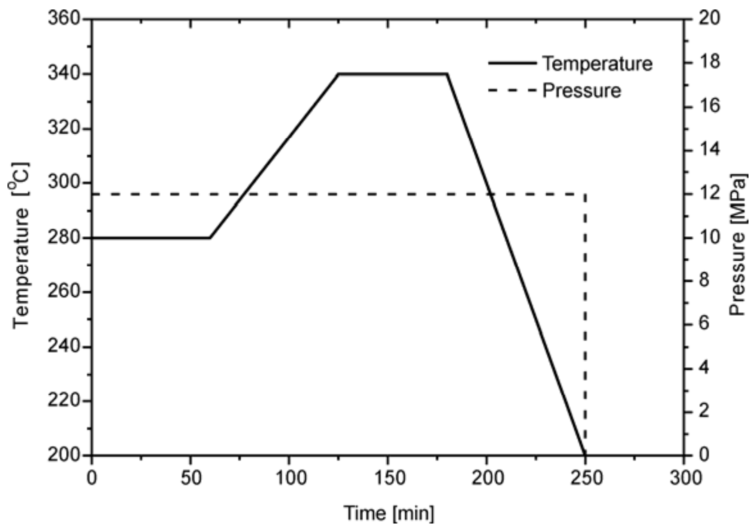


Fig. 1. Changes of temperature and pressure with time

The materials were then cooled to room temperature to get the composites. The CF/PI composite plates were cut into narrow-waisted dumbbell-shaped specimens in accordance with the Chinese standard GB/T1040–1992. The Erichsen tests were carried out on a computer-controlled Universal Testing Machine (made in China) at room temperature. The beam rate was 5 mm/min. For a more accurate determination of the material parameters and consideration of the possible scatter in the experimental data, the measurements were made at five constant loads for five specimens in tension. The obtained quantities were then averaged. All fracture surfaces were gold coated for 40 seconds using a Desk II Sputter-Coater (Denton Vacuum, New Jersey, USA) to reduce the incidence of surface charging in the SEM.

3. Results and discussion

The tensile strength and tensile modulus of CF/PI composite treated with RE as a function of La concentration is shown in Fig. 2. The La concentration was varied from 0.1 to 0.5 wt. %. It is seen that the tensile strength and tensile modulus increase with increasing La concentration, reaching the maximum value of 123 MPa and 3.3 GPa, respectively, at 0.3 wt. % La concentration. Above this maximum value, the tensile properties decrease gradually with increasing La concentration.

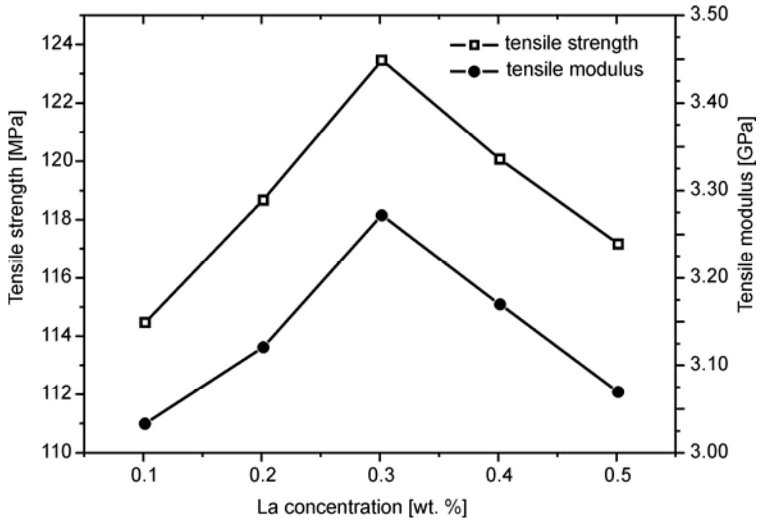


Fig. 2. The effect of La concentration on tensile properties

According to the chemical bonding theory, it is suggested that La atoms are adsorbed onto both the carbon fibre surface and PI matrix through chemical bonding, forming the effective bond between the reinforcement and matrix. The main component of the bond is the coordinate bond formed by functional groups (such as hydroxyl (C–OH), carbonyl (C=O), and carboxyl (COOH) groups) on the fibre surface and the PI matrix (such as the sulfuric group (–SO_2–) and carbonyl group (C=O)), with the concentration of reactive functional groups determined by the chemical activity of La [4]. These reactive functional groups can improve the interfacial adhesion between carbon fibres and the PI matrix. Excess La, however, may cause a decrease in the tensile properties of CF/PI through the formation of La salt crystals on the carbon fibre surface, which affects the effective bond between the fibre and matrix. This can be explained by monomolecular layer theory: when the monomolecular layer is formed (Fig. 3 b), the organic long-chains tangle with the functional groups on the two corresponding surfaces. When free La atoms are present at the interface (Fig. 3a), the adhesion force between macromolecules is reduced due to the existence of weak van der Waals forces. On the other hand, when the La atoms are too scarce to form a full monomolecular layer (Fig. 3c), there is no effective adhesion effect in the void, affecting the entire tensile strength. This monomolecular layer theory model is illustrated below.

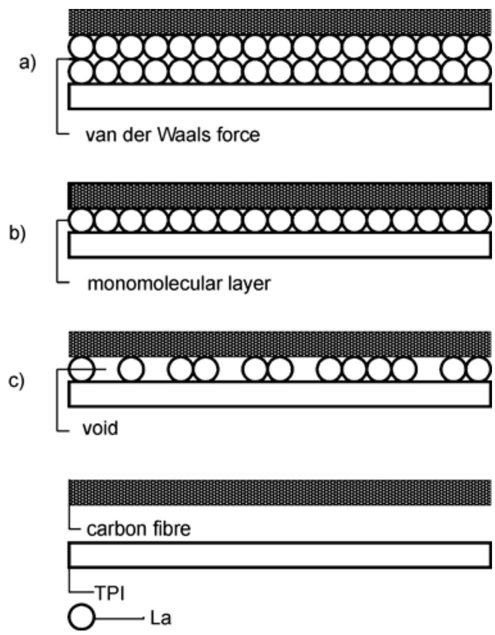
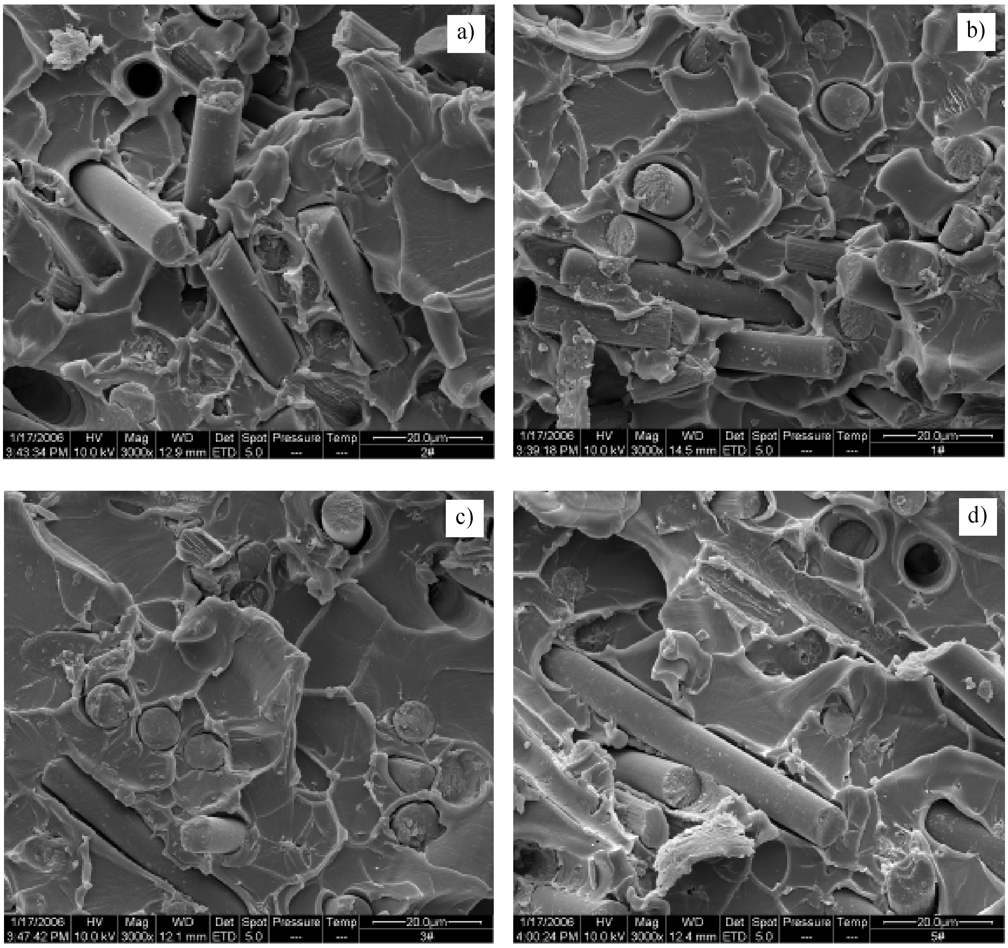


Fig. 3. The model according to monomolecular layer theory

SEM of the fracture surface is shown in Fig. 4 to illustrate the effect of La concentration on interfacial characteristics. Figures 4a, b show that the surfaces of carbon fibres are smooth and little resin is adhered to it. With an increase in La concentration, more resin becomes adhered to the carbon fibres and long carbon fibres are exposed on the fracture surface without forming effective adhesion with the resin. During the process of extraction, the fibres are easily separated from the matrix and the high strength of carbon fibres is not exerted. Thus, the composite showed poor tensile properties. Holes are found in Figs. 4d, e due to the extraction of carbon fibres, and the carbon fibres have the features of being extracted. The amount of resin adhered to the carbon is still small although La concentration increases, in accordance with the model shown in Fig. 3a. Only Fig. 4c shows effective adhesion between the carbon fibres and PI resin. The carbon fibres on the fracture surface are short and the surface is smooth. Nearly no gaps are found on the fracture surface in the case of strong adhesion between the reinforcement and matrix. The interfacial changes are still under investigation.



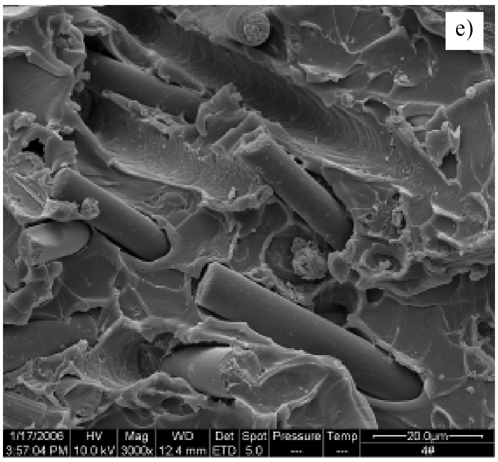


Fig. 4. The SEMs of fracture surfaces treated by RE La. Concentration of La: a) 0.1 wt. %, b) 0.2 wt. %, c) 0.3 wt. %, d) 0.4 wt. %, e) 0.5 wt. %

According to the tensile experimental results, the concentration of La was fixed at 0.3 wt. %, while a comparison between RE treatment and air-oxidation was made as shown in Fig. 5. It can be seen that although, both surface treatments improve the tensile properties of CF/PI composites, carbon fibres treated with RE yielded better results than the air-oxidized ones. The tensile strengths of CF/PI composites treated with RE and air-oxidation were improved by about 18.2% and 4.1%, respectively, compared to the untreated composite. The tensile modulus of the composite treated with the RE method had the highest value. Since the fibre types and fibre contents are identical in these specimens, the differences between the tensile properties shown in Fig. 5 must reflect the effects of the various treatment methods.

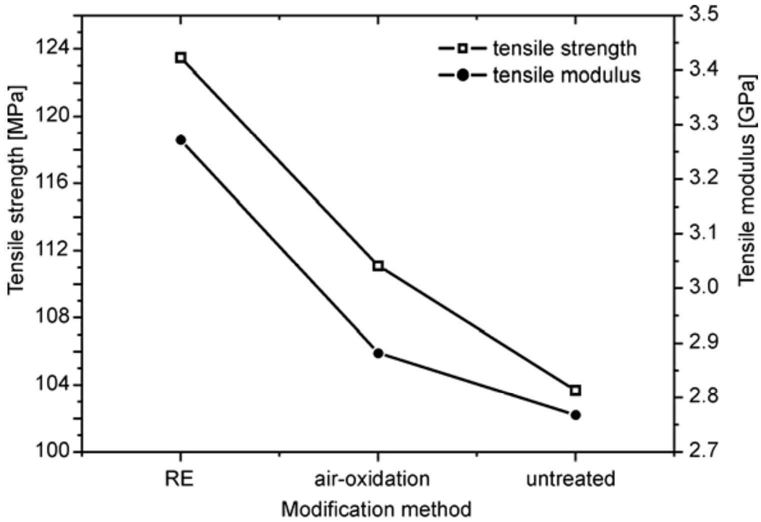


Fig. 5. The influence of the modification method on tensile properties

The details of the fracture surfaces are shown in Fig. 6. Figure 6a shows that the untreated carbon fibres are smooth and large gaps exist between the fibres and resin, which causes poor adhesion between the reinforcement and matrix, with obvious holes are scattered among the matrix. The fractures of the air-oxidized carbon fibres shown in Fig. 6b are rough due to the damage during the oxidation process. Small gaps can still be seen between the fibres and resin. The fractures of carbon fibres formed sharp slants, since the breaks on the carbon fibres introduced by air-oxidation caused non-uniform stress during tension. Air-oxidation mainly increases the surface functional groups of carbon fibres and roughness in order to improve the adhesion ability of the interface, which will do damage to the carbon fibre. The generation of voids and defects at interfaces affects the load transfer between the fibre and matrix, and finally affects the tensile properties of the composites. RE treatment, however, does no damage to the carbon fibres. The fracture shown in Fig. 6c is a flat surface compared to the one mentioned above. The carbon fibres on the fracture surface are short and broken along with the matrix, without leaving holes, which shows that the matrix and reinforcement a strongly adhered together.

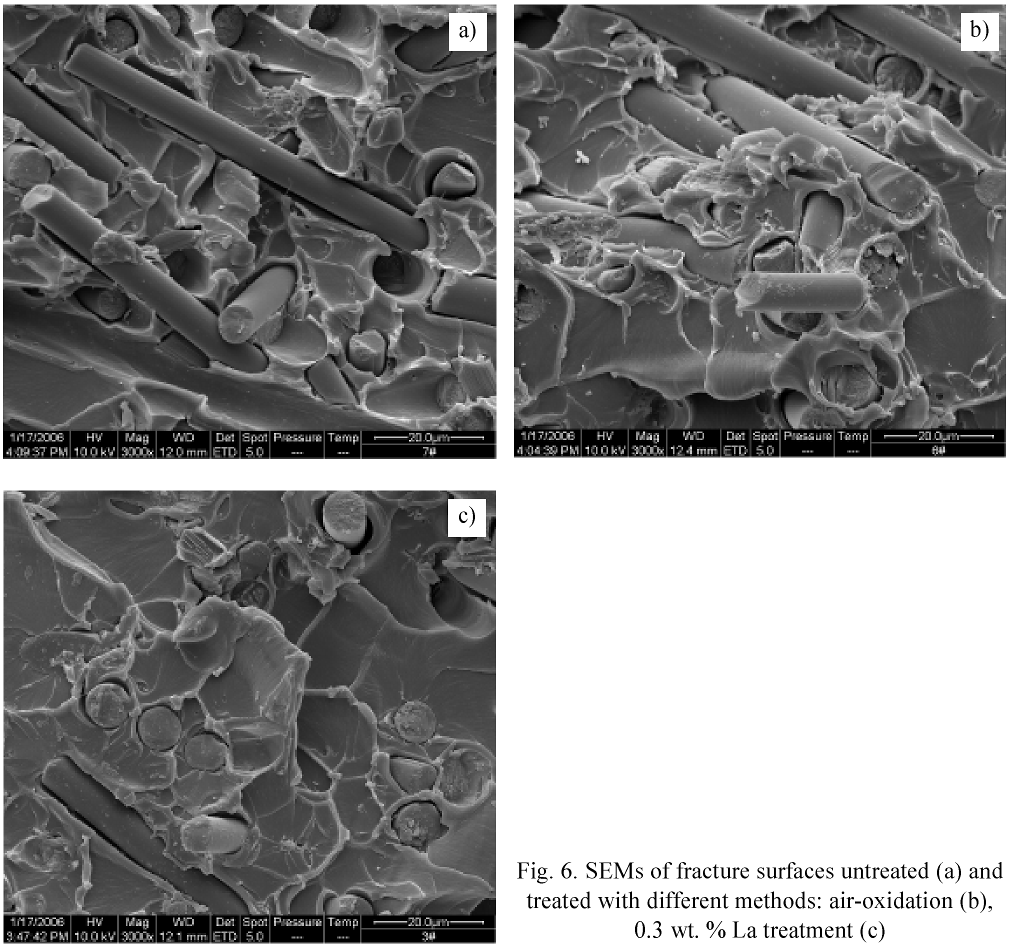


Fig. 6. SEMs of fracture surfaces untreated (a) and treated with different methods: air-oxidation (b), 0.3 wt. % La treatment (c)

4. Conclusions

La treatment is superior to air-oxidation in promoting interfacial adhesion between carbon fibre and the TPI matrix. The tensile properties of RE-treated CF/PI composites are affected by the La concentration in solution. The tensile properties of the CF/PI composite can be improved considerably when La concentration is in the range 0.2–0.4 wt. %. The optimum amount of La is 0.3 wt. %.

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