A new surface treatment method of carbon fibre – liquid-phase–gas-phase double effectiveness method (LGDE)

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Liquid-phase coating and gas-phase oxidation surface treatment are considered as a new surface treatment method of carbon fibres. The tensile strength of carbon fibres and the interlaminar shear strength of carbon fibre-reinforced plastic are improved by the method. The effectiveness and the mechanism of action have been studied. © *1998 Kluwer Academic Publishers*

1. Introduction

It has been demonstrated by many authors that composites of carbon fibres (CF) without any surface treatment have a low interlaminar shear strength (ILSS) [1, 2]. It is well known that the success of a composite material depends on the properties of the fibre–matrix interface. The mechanical performance of a composite material strongly depends on the chemical, physical and mechanical phenomena which occur at the interface. Optimization of the phenomena will improve the final properties of the composite material.

A number of surface treatments have been developed which could improve the fibre–matrix interfacial bonding (see the comprehensive reviews [3, 4]). All these methods, such as gas-phase oxidation, liquid oxidation and catalytic oxidation, which serve to increase the surface area and the number of functional groups, lead to an improvement of mechanical interlocking and chemical bonding between the fibre and the matrix. The ILSS of CFRP is ultimately improved, but the tensile strength of CF is affected by the oxidation methods. The tensile strength of CF is another key factor to the mechanical properties of composite material. In this work, a new surface treatment method of CF, liquid-phase coating and gas-phase oxidation, was studied.

2. Experimental procedure

The fibres studied were HT PAN-CF with different tensile strengths which were produced by JiLin Carbon Factory, People's Republic of China. The average diameter of these CFs is approximately 7 μm. The fibres were acquired without a sizing finish and they were used as-received. A diagrammatic sketch of the LGDE method for surface treatment of CF is shown in Fig. 1. Pitch was dissolved with tetrahydrofuran (THF) as a coating solution. The fibres were coated by the solution with a certain concentration in the liquid-phase coating process. The coated fibres were oxidized in air at 400–600 °C in the gas-phase oxidation process, the oxidized fibres being called treated fibres. The thickness of the coating agent on the surface of CF was controlled by the concentration of pitch solution and coating time. In order to evaluate the mechanical properties of the interfacial adhesion of carbon fibre-reinforced plastic (CFRP) made from the three samples (as-received, coated or treated CF), the interlaminar shear strengths (ILSS) of UD-CFRP composites were investigated. The UD-CFRP composites with fibre volume fractions of 60%–65% were made from the three CF samples. The matrix resin system used was (AG-80 epoxy resin + diaminodiphenyl sulphone(DDS) hardener + dissolvant acetone). The chemical structural formulae of AG-80 epoxy resin and hardener DDS are shown in Fig. 2. The temperature and pressure cycles of the fabrication of the UD-CFRP composites are shown in Fig. 3. ILSS tests were conducted in our laboratory. The test system was a Shimadzu Autograph (Japan), which was controlled by a DCS-500 computer system. The tensile strength of treated CF was determined with the test method for tensile properties of CF strands, according to GB3362-82 (China). The interlaminar shear strength of the UD-composites was investigated with the short-beam shear test method, according to GB3357-82 (China).

The new surface treatment method, liquid-phase coating and gas-phase oxidation, is called the LGDE method, because of the double effective improvement of the tensile strength of CF and the ILSS of the UD-composites.

3. Results and discussions

CF is a brittle material which there is a complex interlinking of layer planes both longitudinally and laterally. In brittle solids the defects are small cracks
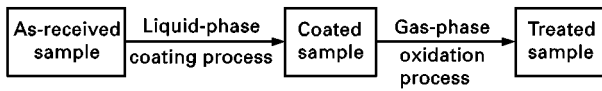
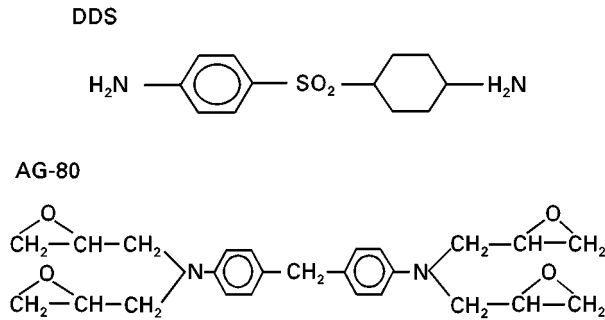Figure 1 The schematic diagram for LGDE method of surface treatment of CF.

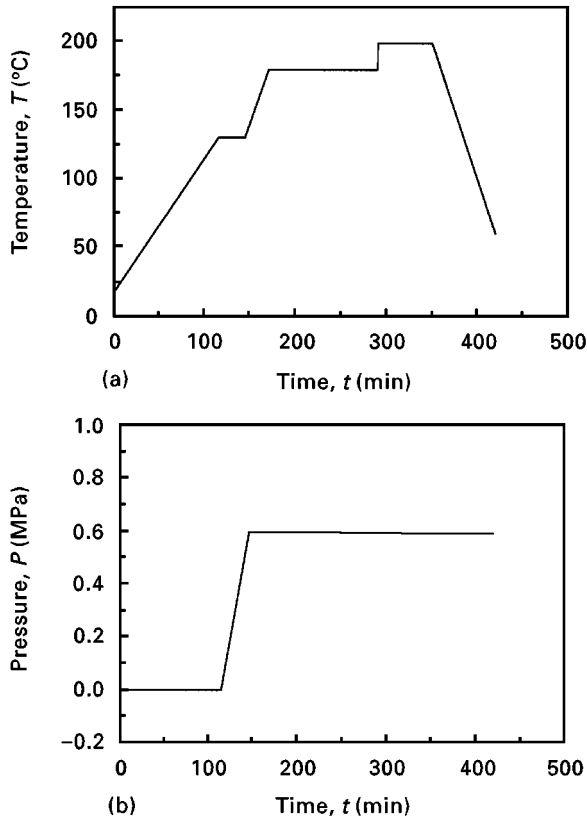Figure 2 Hardener DDS and cpoxy resin AG-80 chemical structure formulae.

Figure 3 Temperature and pressure program during fabrication of UD-CFRP composites.

which act as stress concentrators. Failure of CF has been observed to initiate from both surface and internal flaws [5]. Internal flaws which did not initiate failure were seen to have walls containing crystallites arranged mainly parallel to the fibre axis. Internal and surface flaws which did initiate failure showed evidence of large misoriented crystallites in the walls of the flaws [6]. Nevertheless, surface flaws are a problem in relatively low-strength CF. There is some interesting evidence for the improvement of the tensile strength of CF by the dual liquid-phase–gas-phase method by

means of the reducing effect of the surface flaws on tensile strength.

The liquid-phase coating process of the LGDE surface treatment method increases the tensile strength of CF by improvement of the defects. After liquid-phase coating of CF, the flaws and the holes of CF were mended by the coating agent, firstly due to the difference of surface free enthalpy. The degree of stress centralization of the flaws and the CF holes were weakened because of the interaction between the coating agent and the CF defects. The interaction included both physical and chemical action forces, but the physical one was main factor.

During the gas-phase oxidation process of the LGDE surface treatment method, the low molecular compounds of pitch coating agent also underwent polymerization. The pitch coating agent and the CF surface were oxidized by air. Not only were oxygen-containing functional groups added to the CF surface, but the joint between the CF surface and the coating agent was also strengthened due to the increased chemical bonding to each other. The gas-phase oxidation process will result in a further increase in the tensile strength of CF due to the increased chemical interaction force between the CF surface and the coating agent, and further weakening of the stress centralization of the CF surface defects.

Fig. 4. shows the change in the tensile strength of the coated CF in comparison with that of as-received CF. C_i ($i = 1$–4) represents the concentration of the coating agent solution, and C_{i+1} is larger than C_i. The thickness of the coating on the surface of the CF was so thin that it could not be determined by scanning electron microscopy. The tensile strength of the coated CF was increased by 8%–18%, in comparison with that of as-received CF. Although the effectiveness of a low concentration of coating agent solution is better than a high-concentration solution in the improvement of the tensile strength of CF, according with these data, there must be an optimum concentration of coating agent solution for the healing of the surface flaws of CF. The effectiveness is achieved by improvement of the CF surface flaws which greatly affect the tensile strength of CF. The combination of the CF surface with a coating agent is mainly a physical action.

After the coated CF was oxidized in air at 400–600 °C, the tensile strength of the treated CF was increased further (treated CF sample). The chemical action between the CF surface and the coating agent was strengthened by air oxidation and the effectiveness of the tensile strength was further increased.

Fig. 5 shows the dependence of tensile strength on the air oxidation time. After coating and air oxidation, a maximum tensile strength is obtained at an air oxidation time of 130 s. For the certain concentration of coating agent solution, the tensile strength of the coated PAN-CF oxidized at different times from 10–200 s was increased by 4%–40%. Therefore, the concentration of the coating agent solution and the oxidation time are the most important factors which determine the increased effectiveness of the tensile strength of CF.
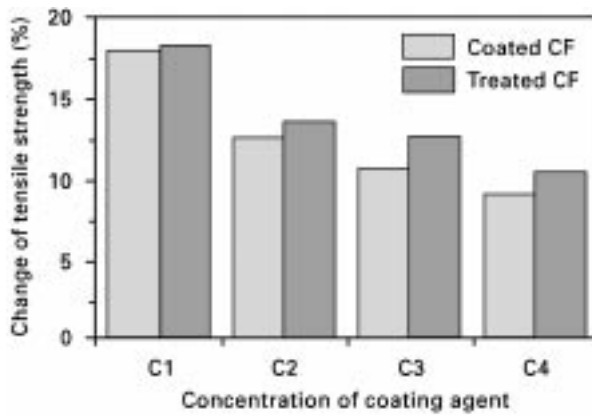
Figure 4 The change of tensile strength of coated and treated CF by comparison with as-received sample.
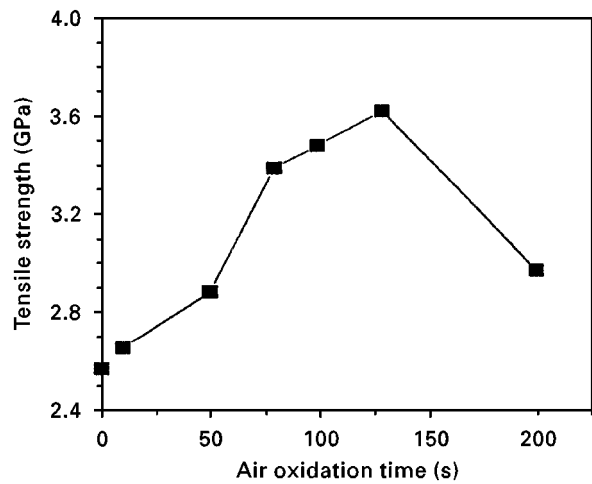

Figure 5 The effectiveness of air oxidation time on tensile strength of coated PAN-CF.
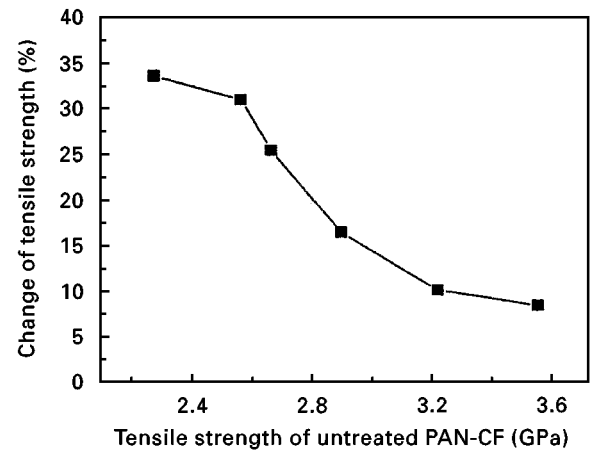

Figure 6 The comparison of treatment effectiveness of as-received PAN-CF with different tensile strength.

For CF with different tensile strengths, this surface treatment method varies in effectiveness. The results are shown in Fig. 6. The lower the tensile strength of PAN-CF, the more effective is this method. After surface treatment of PAN-CF, the original tensile strength of 2279 MPa, is increased by 33.60%. However, for PAN-CF with a tensile strength 3560 MPa, the improvement in effectiveness is only 8.35%, because there are more defects on the surface of the CF with lower tensile strength. There is a greater
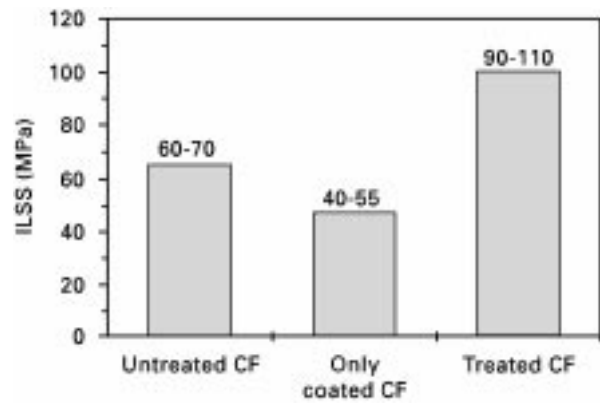

Figure 7 The value of ILSS of UD-CFRP composites made from as-received or coated or treated PAN-CF.

improvement in effectiveness for this kind of CF by the LGDE surface treatment method.

If the gas-phase oxidation process was not conducted, the ILSS value of UD-CFRP composites made from this kind of coated CF sample would decrease in comparison with the as-received sample, although the tensile strength of coated CF would increase. Because the weak joint between the CF surface and the coating agent would form a weak interface layer in UD-CFRP composites, the stress could not be transferred successfully from the matrix resin to the reinforcing CF at the interface. The interfacial layer would be destroyed due to peeling of the weak joint layer. After the gas-phase oxidation process, strengthening of the bonding between the CF surface and the coating agent and the addition of the oxygen-containing functional groups on the CF surface, increased the interfacial adhesion of the UD-CFRP composites. The ILSS value of the UD-CFRP composites made using this kind of treated CF, was increased greatly.

The ILSS values are shown in Fig. 7. The ILSS of the composites produced from as-received PAN-CF is only 60–70 MPa. After coating, on the other hand, the ILSS decreases to 40–55 MPa. This is caused by the relatively weak adhesion between the agent, the CF surface and the matrix resin. However, the air oxidation treatment not only improves adhesion between the coating and the CF surface but also modifies the surface characteristics of the coated CF. In particular, more oxygen-containing functional groups on the CF surface are obtained which are beneficial to improving the adhesion between the CF and the matrix resin. Therefore, the ILSS of the composites produced from treated PAN-CF is increased to 90–110 MPa, and the shear fracture toughness of the composites is improved as a result of the intermediate layer formed from the CF surface, the coating agent and the matrix resin.

4. Conclusion

A remarkable development potential of the new surface treatment method of CF has been demonstrated. The surface treatment method (LGDE) has a double effectiveness, with a great improvement in the tensile strength of treated PAN-CF and in the ILSS of the composites. The double effectiveness is attributed

largely to a combination of liquid-phase coating and gas-phase oxidation. The former can improve CF surface flaws and protect from excessive oxidation etching, the latter can improve the surface characteristics of CF, especially by producing more oxygen-containing functional groups on the CF surface which are beneficial to the adhesion between the CF and the matrix resin.

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