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Role of fibre surface–matrix combination in carbon fibre reinforced epoxy composites

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The effect of surface treatment of carbon fibres with concentrated as well as dilute nitric acid on the mechanical properties of carbon fibres has been reported. The role of the fibre–matrix interface in carbon fibre reinforced epoxy resin composites has been studied. Composites have been made both with untreated and surface treated carbon fibres and epoxy resin Araldite LY556 with different hardeners. Mechanical properties as well as fracture behaviour of these composites suggest that it is the physical interlocking between the fibres and the matrix, along with some chemical bonding between the two, and not the pure chemical bonding which yield better composites.

1. Introduction

Performance of fibre reinforced composites is predominantly governed by the mechanical properties of the reinforcing fibre, matrix system and the fibre–matrix interface, which decides the mode of transfer of stress from one fibre to another. Once the first two components have been fixed, attention is focused on the fibre–matrix interfacial properties. In case of carbon fibre reinforced composites, many studies have been made [1–4] to improve the surface so as to achieve maximum translation of fibre properties in composites. For structural engineers, it is more important to know the complete mechanical behaviour of a particular material, its various mechanical properties and the mode of fracture. The latter is purely dependent on the fibre–matrix interfacial properties, adhesion of carbon fibres with the matrix. A better adhesion of carbon fibres to the polymer matrix is firstly achieved by improving the surface of the carbon fibres so as to allow physical interlocking of the fibres with the matrix, and secondly by forming surface groups on the surface of carbon fibres which result in chemical bonding between carbon fibre surface and surface active resins [5]. Various methods employed to improve the surface of carbon fibres include polymer grafting to the surface [6, 7], etching of the fibres by air oxidation [8], anodic oxidation [5] and nitric acid treatment [1, 2, 9]. Since nitric acid can form surface groups on carbon fibre surfaces in short treatment times, this has received much attention from the academic point of view in order to study the effect of chemical bonding between fibre and matrix on the fracture of composites. A systematic study was carried out in this direction in this laboratory in order to examine the fracture behaviour of carbon fibre with different degrees of surface treatment and reinforced with different epoxy resin hardener systems. The results are reported in this paper.

2. Experimental procedure

2.1. Materials

Experiments were performed with Sigrafil HF carbon fibres without surface finish and surface treatment. Three commercially available surface treated carbon fibres, Modmor-IIIS from Morganite UK, Sigrafil HF_3 from Sigri Electrographite Gmbh West Germany and Torayaca T-300, were also used for comparison composite studies. Epoxy resin Araldite LY556, a condensate product of Bisphenol A and Epichlorohydrin, was used with hardeners HY951 (liquid aliphatic amine type) HT972

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(solid aromatic amine) and HY917 (liquid cycloaliphatic anhydride).

2.2. Treatment of carbon fibres with nitric acid

Sigrafil HF carbon fibres were treated with concentrated nitric acid and 35% nitric acid under reflux for different times. After treatment, the fibres were washed thoroughly for 16 h with distilled water and dried under vacuum. The mechanical properties of these fibres were measured with an Instron universal testing machine. Twenty fibre specimens were tested for each sample and the values reported are the average values. Thermogravimetric analysis (TGA) techniques were used to estimate surface groups on carbon fibres.

2.3. Composites

Unidirectional model composites were made by the pre-preg technique. Pre-pregs were made by impregnating untreated carbon fibres, nitric acid treated carbon fibres and commercially treated carbon fibres, with different resin–hardener systems, by the wet winding technique. Pre-pregs cut in the proper size were put into the mould and kept in a heated press. Ten samples could be made in one mould. Pressure was applied when the resin had just started gelling so as to keep the fibre volume to 60 to 65% in a composite of size 150 mm × 5 mm × 2 mm. Composites were cured under optimum conditions of heating rate and time, evaluated earlier [10].

2.4. Composite testing

Flexural strength, tensile strength as well as interlaminar shear strength (ILSS) of the composites were measured on an Instron universal testing machine. Flexural strength was measured by the three-point bending technique using span-to-thickness ratios of the composites of 40:1. Interlaminar shear strength was also measured using three-point bending with a span-to-thickness ratio of 5:1. For tensile strength measurement, composites were waisted in the middle as described earlier [11]. Ends were glued with aluminium tabs to avoid stress development and fracture within the grips. For each test, ten composite specimens were taken and the values reported are the average values.

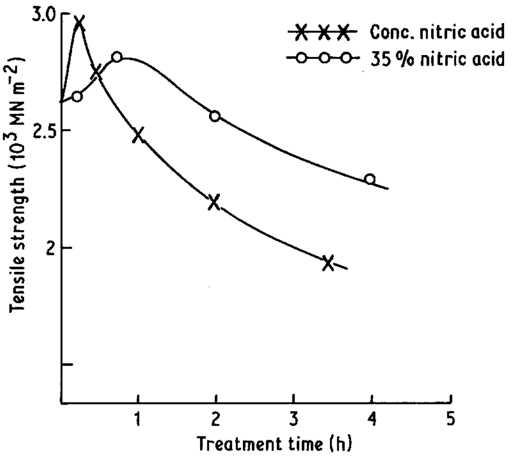

Figure 1 Change in tensile strength of carbon fibres after treatment with HNO_3.

3. Results and discussion

3.1. Effect of nitric acid treatment on carbon fibres

Surface flaws and proculements at the surface of carbon fibres introduced during processing or present in the precursor affect the ultimate mechanical properties of carbon fibres to a great extent. The strength of carbon fibres may be increased if these surface flaws are removed. This can be done by nitric acid treatment. Fig. 1 shows the variation of tensile strength of carbon fibres with treatment time in both concentrated and dilute nitric acid. As is seen from the figure, the strength of carbon fibres increases with initial treatments and decreases for long duration of treatment. The effect of time is more critical with concentrated acid. The outer surface of type II carbon fibres is very sensitive to nitric acid. For the initial treatments, the surface flaws are removed and the fibre surface is smoothed, resulting in an increase in tensile strength of the carbon fibres. Prolonged treatments with both concentrated and dilute nitric acid cause etch pits on the surface which account for the drastic decrease in strength of the carbon fibres.

When carbon fibres are treated with nitric acid, carboxylic, hydroxyl and carbonyl groups form on the surface of the fibres [9]. Thermogravimetric analysis is widely used to identify the surface groups on carbon products and carbon fibres [9, 12, 13]. Weight loss between 300 and 600° C is attributed to evolution of CO_2 due to decomposition of carboxyl groups, whereas between 600 and 1000° C, to carbonyl and hydroxyl groups forming CO. Fig. 2 shows the TGA curves of the above treated carbon fibres. As is shown in the Fig. 2, fibres treated for 15 min with

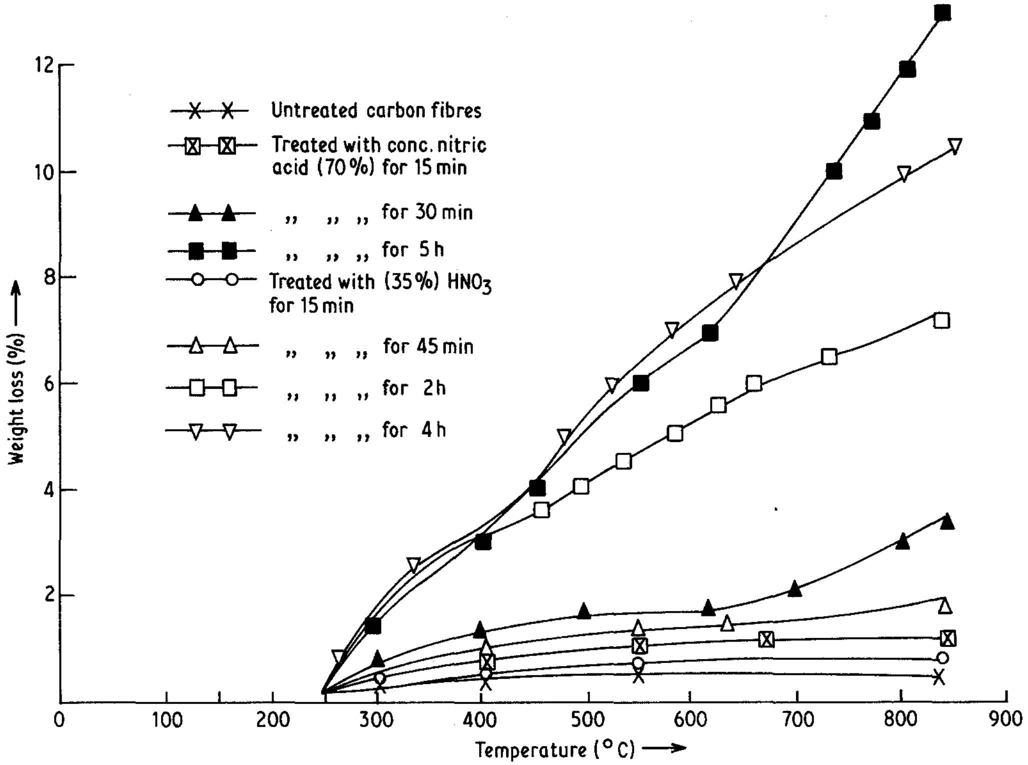

Figure 2 Thermogravimetric analysis of treated carbon fibres.

concentrated nitric acid and dilute nitric acid show a very small weight loss (1%), whereas fibres treated for longer times show a very large weight loss, indicating that in the first few minutes the surface is mainly being improved and it is for longer times that more surface groups are being formed.

3.2. Effect of different hardeners on the composite properties

Normal epoxy resins, except the ultra-high molecular weight resins, are polymerized with or by a cross-linking agent or hardener. The type of curing and the properties of the cured resin are greatly dependent on the type of hardener used. In the present studies three commercially available hardeners were used with the same basic resin system LY556. Table I shows the mechanical properties of the carbon fibres (Modmor, HF_3 and Torayaca) reinforced composites with three resin–hardener systems. It shows for two fibre types (HF_3 and Torayaca) that the mechanical

TABLE I Mechanical properties of composites with commercial carbon fibres and different resin–hardener system

Fibre type	Resin hardener system	Fibre volume (%)	Flexural strength ($MN\,m^{-2}$)	Tensile strength ($MN\,m^{-2}$)	ILSS ($MN\,m^{-2}$)	Mode of fracture
1. Sigrafil	LY556 + HY951	60	1200	1094	71.34	Shear
	LY556 + HT972	60	1680	1150	82.32	Tensile
	LY556 + HY917	60	1798	1167	87.2	Tensile with fibre pull out
2. Modmor	LY556 + HT972	60	1563	1270	63.54	Tensile
	LY556 + HY917	60	1780	1260	78.32	Tensile
3. Torayaca	LY556 + HY951	60	1870	1620	70.2	Shear
	LY556 + HY972	60	2150	1680	79.8	Tensile
	LY556 + HY917	60	2390	1710	84.3	Tensile

properties of composites with system B (LY556 + HT972, aromatic amine type hardener) are better than with system A (LY556 + HY951, cyloaliphatic amine type). Modmor fibres also showed a similar trend but the data were insufficient and have not been included in Table I. Though the flexural strength and ILSS of the composites are further improved by using anhydride type hardeners, system C (LY556 + HY917), tensile strength is hardly affected. The mode of fracture (flexural testing) also changes from pure shear to shear cum tensile. Fibre pull-out is also noticed, leading to the conclusion that fracture energy is increased. The fracture behaviour, along with the properties of the composites with anhydride as hardeners, shows that the nature of polymerization of the resin system is a more effective deciding factor in load transfer among the fibres within a composite.

3.3. Mechanical properties of composites with treated carbon fibres

To study the effect of interface in carbon fibre reinforced composites, unidirectional model composites were made with the forementioned surface treated fibres and the resin–hardener systems, system A (LY556 + HY951) and system B (LY556 + HY972). Fig. 3a and b shows the flexural strength, tensile strength and the ILSS (interlaminar shear strength) of composites with surface treated carbon fibres. As is shown in Fig. 3a, flexural strength, tensile strength and ILSS of system A composites initially increase with fibre treatment time, and fall off thereafter. There is a steep increase in flexural strength, tensile strength and ILSS of the composites made with carbon fibres treated for 15 min in concentrated nitric acid. For prolonged treatment, the flexural strength and tensile strength decrease sharply whereas ILSS decreases gradually. A similar effect is noticed with dilute nitric acid treated fibres as well, though the decrease is not as sharp as in case of concentrated nitric acid treated carbon fibres. The first increase in the properties of composites with concentrated nitric acid is attributed to the removal of surface flaws

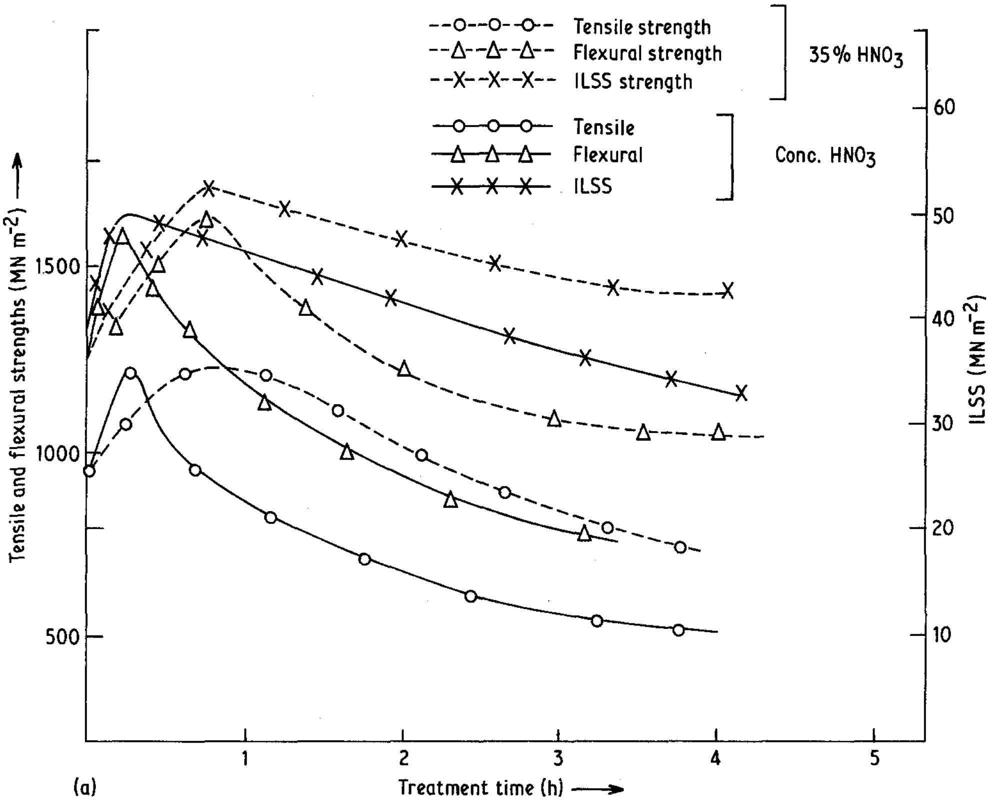

Figure 3 (a) Variation of tensile strength, flexural strength and interlaminar shear strength of composites with HNO_3 treatment time of carbon fibres. (LY556 + HY951) system). (b) Variation of tensile strength, flexural strength and interlaminar shear strength of composites with HNO_3 treatment time of carbon fibres (LY556 + HT972 system).

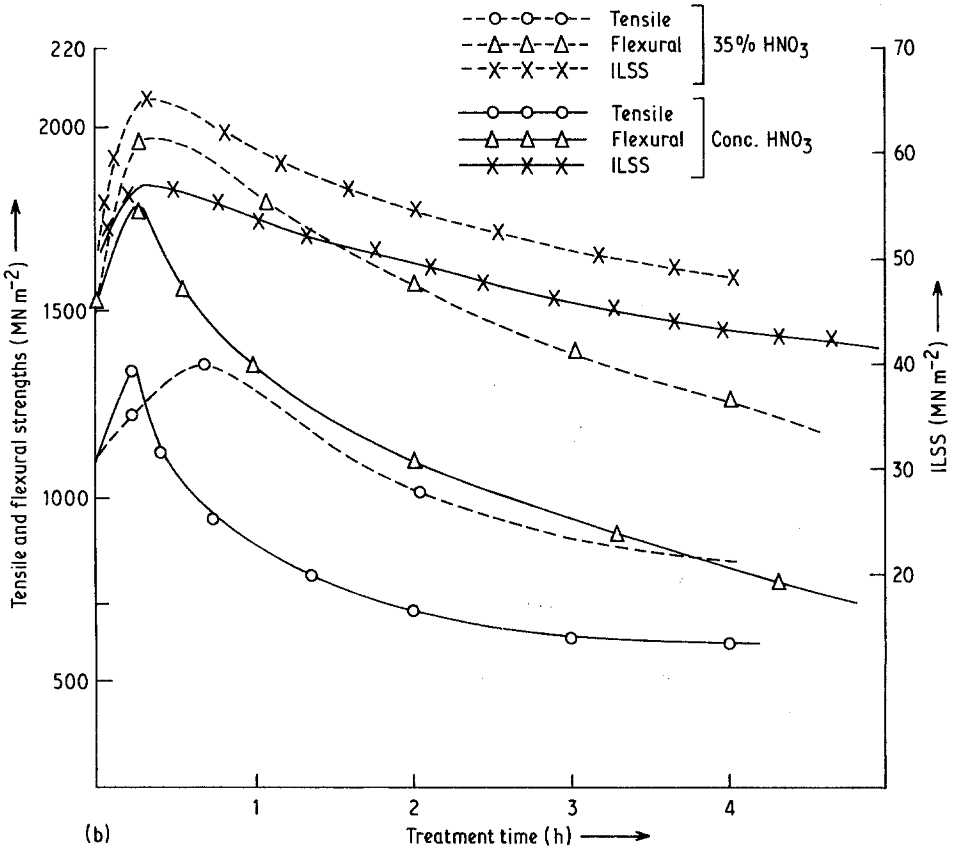

Figure 3 Continued

and modification of the surface. Both these effects increase the strength of the fibres, as is clear from Fig. 1, and also improve the physical interlocking of the resin with the fibres. Chemical adhesion is also improved, but to a small degree. With longer treatment time with concentrated HNO_3, although the number of the surface groups is increased, which increases the chemical bonding of the resin to the fibre, the fibre surface is damaged to a large extent and the fibre properties deteriorate. This accounts for the drastic decrease in the mechanical properties, especially the tensile strength of the composites.

Similar effects are also noticed with dilute nitric acid treated carbon fibres, the only difference being that the maximum percentage translation of fibre properties in composites is higher than for concentrated nitric acid treated fibres. Also, the ratio of flexural strength to tensile strength is not very large. ILSS of the composites is higher than of those made with concentrated nitric acid.

It is obvious that surface group concentration for dilute nitric acid etched carbon fibres will be lower than for those treated with concentrated acid. Even then the ILSS of the composites with the former fibres is higher than of those with the latter fibres. This confirms the hypothesis that fibre surface, which has become very sensitive to shear forces, plays a predominant role in deciding the fracture of the composites.

Fig. 3b shows the mechanical properties of the composites with resin–hardener system B (LY556/HT972). This shows similar behaviour to Fig. 3a. The values of the mechanical properties of the composites are higher than those with cyloaliphatic amine hardener. Better translation of fibre properties can be realized with this resin–hardener system. However, this system is relatively more sensitive to the surface of the fibres, and the decrease in composite properties with higher etching times is higher than in case of system A.

4. Conclusions

From the present studies it is concluded that the fibre–matrix interface, the deciding factor in the translation of fibre properties in the composites, is not only dependent on the surface groups present on the fibre but also on the structure of the fibre surface and the resin–hardener system. While giving surface treatments to the fibres one has to optimize the conditions in such a way that the surface structure of the fibre is not destroyed while modifying the number of surface groups. Both flexural strength and tensile strength of the composites are heavily affected by the former parameter. Therefore the flexural strength, tensile strength as well as ILSS of the composites should be kept in mind when modifying the interfacial bonding in carbon fibre composites.

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