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The effect of surface treatment on the interfacial properties in carbon fibre/epoxy matrix composites

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Carbon fibres with different degrees of surface oxidation, as well as epoxy-sized fibres, were used to prepare epoxy composites in order to compare the effects of the fibres surface chemistry on the interfacial properties. X-ray photoelectron spectroscopy, water vapour adsorption measurements and contact angle examination were applied to characterize the carbon fibre surfaces. A correlation was found between the content of primary adsorption sites on the fibre surface and interlaminar shear strength (ILSS) of the composites. Higher values of ILSS obtained for the oxidized fibres containing composites are proposed to be due to the higher concentration of carboxylic groups created on the oxidized fibres surface and to the creation of chemical bonds at the fibre/epoxy matrix interface. Enthalpy of cure, reaction peak temperature and glass transition temperature of the composites were determined by differential scanning calorimetry.

1. Introduction

The role of the interphase region in the fibre-reinforced composites is a subject of considerable research activities, because the fibre/matrix interface has long been recognized as a key factor strongly affecting the composite properties.

It is well known that the surface oxidation of carbon fibres improves the overall composite properties [1, 2]. This effect is usually related to one or several of the following parameters. First, the fibres may contain specific morphology after oxidation, giving rise to a new zone in the vicinity of the fibre surface, different from the bulk composition [3]. On the other hand, oxygen-containing groups, developed at the surface after oxidation, are proposed to be important for better fibre-to-matrix adhesion, because they are able to react with the matrix, creating chemical bonds at the interface [4, 5]. The reactive groups on the fibre surface may also exert a catalytic effect when the network is being formed [6]. The influence of the oxygenated groups on the wettability of the fibre is indisputable [3, 5].

However, the nature of the interfacial bond, as well as the interphase phenomena in general, in carbon fibre composites, are still a subject of debate and controversy, and the exact role of the interface in determining the overall properties of composites is still poorly understood.

In our previous work [7], carbon fibres which have undergone an oxidative treatment were found to influence the cross-linking reaction of DGEBA-based epoxy resin, when dipropylenetriamine was used as a hardener, increasing the cross-linking degree in the interphase.

The objective of the present study was to investigate the effect of the carbon fibre surface oxidative treatment on wettability and on the epoxy resin curing reaction when a hardener other than an amino-hardener is used, and to compare the effects obtained when commercially epoxy-sized carbon fibres instead of oxidized fibres are used.

2. Experimental procedure

Carbon fibres with a nominal diameter of 7 μm (supplied by Akzo) and different surface treatments have been used. The CO refers to fibres which had undergone different degrees of dry oxidative treatment (1, weakly; 2,3,4, strongly, in order of increasing degree of oxidation), while CE represents the commercial epoxy-treated (sized) fibres. To exclude the effect of fibre surface morphology, CO fibres without any pronounced roughening of the surface within the resolution range of the SEM (0.1 μm) were analysed.

To characterize the chemical composition of the carbon fibre surface, X-ray photoelectron spectroscopic (XPS) analysis was applied. The XPS studies were performed using a Riber spectrometer with an MgK_α X-ray source (28 mA, 12.5 kV). The instrument

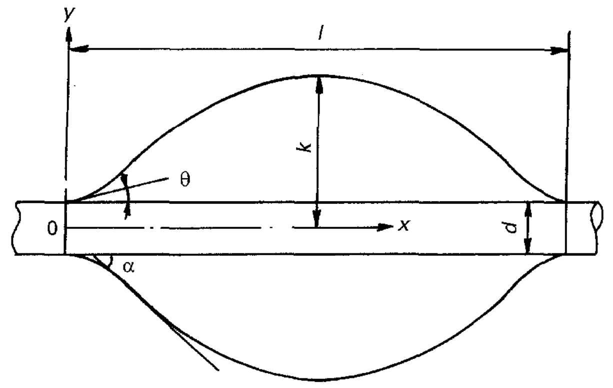

Figure 1 Cross-section of a drop on the fibre and its parameters.

was calibrated using the C 1s photoelectron peak, which was assumed to be 284.6 eV.

High-resolution XPS were analysed by performing background substraction and iterative line shape decomposition, based on summed gaussian lorentzian functions (80%/20%). The full-width-at-half-maximum of each decomposed C 1s line is 1.85 ± 0.075 eV. The relative concentration of the present functional groups on the carbon fibre surface was calculated from the ratio of the area under the corresponding group with respect to the total area of the C 1s signal. On the basis of XPS the O 1s/C 1s atomic ratio (A_O/A_C) was also estimated from the peak area ratio.

Contact angle measurements were performed using the static-droplet-on-a-single-fibre technique, as described elsewhere [8]. Droplets of glycerol and uncured bisphenol A-based epoxy were placed on each filament using a fine needle and efforts were made to keep the droplet diameter to 80–90 μm. To provide a representative value of contact angle, values from 20–30 replicate specimens from each sample were averaged. The measured values of apparent contact angle are reported as α_{meas}, and the calculated values, evaluated by measuring the relative dimensions of the droplet (as illustrated in Fig. 1) and applying elliptical integrals [9], are reported as θ.

In order to determine the content of primary adsorption centres, created on the fibre surface after the oxidative treatment, the adsorption values of water vapour were measured at 298 K by the gravimetric method. Prior to adsorption, the carbon fibre samples were dried for 5 h at 453 K. The adsorption value of water vapour at a relative pressure of 0.25 is assumed to cover the primary adsorption centres.

Differential scanning calorimetry (DSC) was performed with Mettler TA-3000 under a nitrogen atmosphere at a heating rate of 10 K min^{-1}. The measurement was followed by rapid cooling, and a second heating run was made on the same sample to obtain the glass transition temperature of the network.

Commercial-grade bifunctional epoxy resin with an anhydride of phthalic acid as a hardener and dimethylaniline as accelerator, were used to prepare unidirectional composite specimens by an impregnation and lay-up procedure with a nominal carbon fibre volume fraction of 0.6. The specimens were first cured at 80 °C for 1 h and then post-cured at 140 °C for 2 h.

Interlaminar shear strengths (ILSS) were obtained using the standard short-beam shear test (crosshead speed of 1 mm min^{-1}).

3. Results and discussion

In our previous work [7], applying the single-fibre pull-out technique, the values of the interfacial shear strength of epoxy matrix/carbon fibre micro-composites for CE (46.4 MPa), CO-3 (51.9 MPa) and for untreated unsized carbon fibres (CU) (37.2 MPa) were determined. Increased impact resistance was found for CE- compared to CO-containing bulk composites, obviously due to the stronger interfacial bonding between the oxygenated groups at the CO surface and the epoxy matrix.

In order to characterize the role of the carbon fibre surface chemistry in epoxy composites, CO fibres with different degrees of oxidative treatment were analysed. The results of the water vapour adsorption values, contact angle data and ILSS values of the composites are reported in Table I.

The surface and adsorption properties of carbon fibres depend on their crystal structure and chemical composition. Disturbance in the elementary microcrystalline structure, for example, by the presence of imperfect graphitic layers and the presence of non-carbonic substances, influence the adsorption properties of carbon fibres. The oxidized carbon fibres

TABLE I Adsorption values of water vapour at a relative pressure of 0.25, the contact angle data for carbon fibres with different surface treatment and ILSS of the corresponding composites

Fibre	a (mol kg^{-1})	Epoxide				Glycerol	ILSS (MPa)
		α_{meas} (deg)	θ (deg)	CV (%)[a]	S.D.[b]	α_{meas} (deg)	
CO-1	0.1161	56.5	62.8	3.95	2.13	57.5	51
CO-2	0.2349	52.5	57.3	3.31	2.77	49.5	58
CO-3	0.2895	48.0	47.1	6.85	3.26	46.0	69
CO-4	0.2999	47.7	42.0	7.50	4.50	45.0	69
CE	0.1432	55.3	59.5	3.66	1.96	44.0	56
CU	–	62.8	71.5	2.90	2.10	59.8	37

[a] CV, coefficient of variation.

[b] S.D., standard deviation.

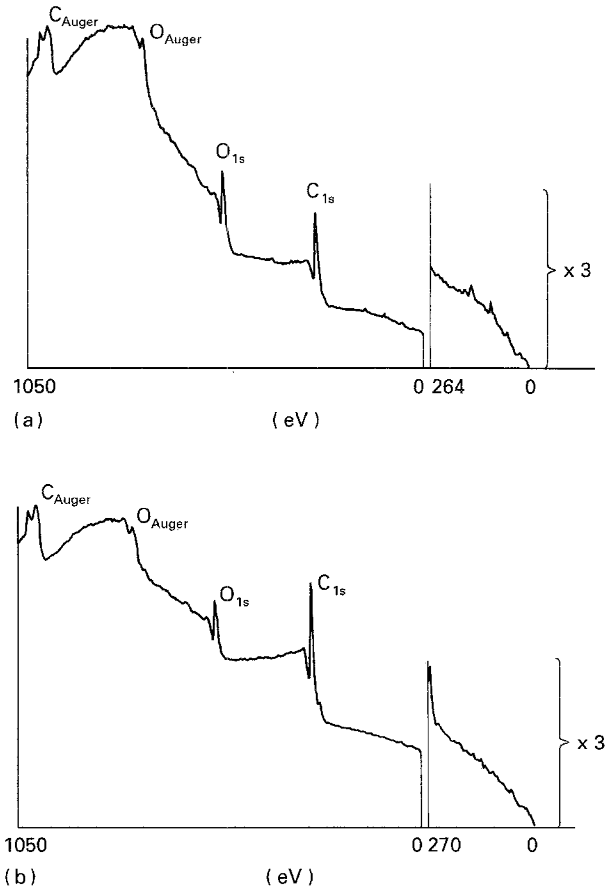

Figure 2 XPS survey spectra for (a) CO-3 and (b) CE fibres.

possess oxygen-containing groups on their surfaces which form polar (more active) adsorption centres. The polar centres can be regarded as the primary active sites for adsorption of polar substances [1, 10], which lead to adsorption of water molecules either as single molecules or perhaps with some cluster formation.

The results in Table I show that the oxidized fibres 2, 3 and 4 contain a greater number of primary adsorption centres than the epoxy-treated fibres, and the a-value increases with the degree of oxidative treatment. The results of the liquid droplet contact angle experiments reveals that the oxidative treatment produces a decrease in the average contact angle (i.e. a better wettability is achieved both for glycerol and an epoxy system), which is obviously due to a rise in the total surface free energy and especially its polar component [11]. There is a clear correlation between the observed adsorption values (i.e. primary active sites) and the measured glycerol (epoxy)/carbon fibre contact angle.

A survey of XPS of CO-3 and CE fibres is shown in Fig. 2. The increase in surface oxygen content as a result of oxidation is clearly demonstrated by the relative peak intensities.

Active sites, present at the fibre surface, are potentially important in the formation of an adsorptive bond with epoxy-matrix molecules [3]. The oxidized fibres exhibit a higher content of carbonyl and especially carboxyl functional groups (Fig. 3, Table II) which obviously serve as primary adsorption sites for water vapour, as determined by adsorption measurements, and also as reaction sites with the epoxide molecules, i.e. carboxyl and ester groups are proposed to be far more important for fibre/matrix adhesion [12], because they are able to react with matrix molecules, creating chemical bonds at the interface. Thus, the higher values of ILSS, observed for CO fibres containing composites (see Table I), should be related to a higher degree of oxygen-containing groups at the CO fibre surface and to the reaction between the carboxylic acid groups with the epoxy-end groups.

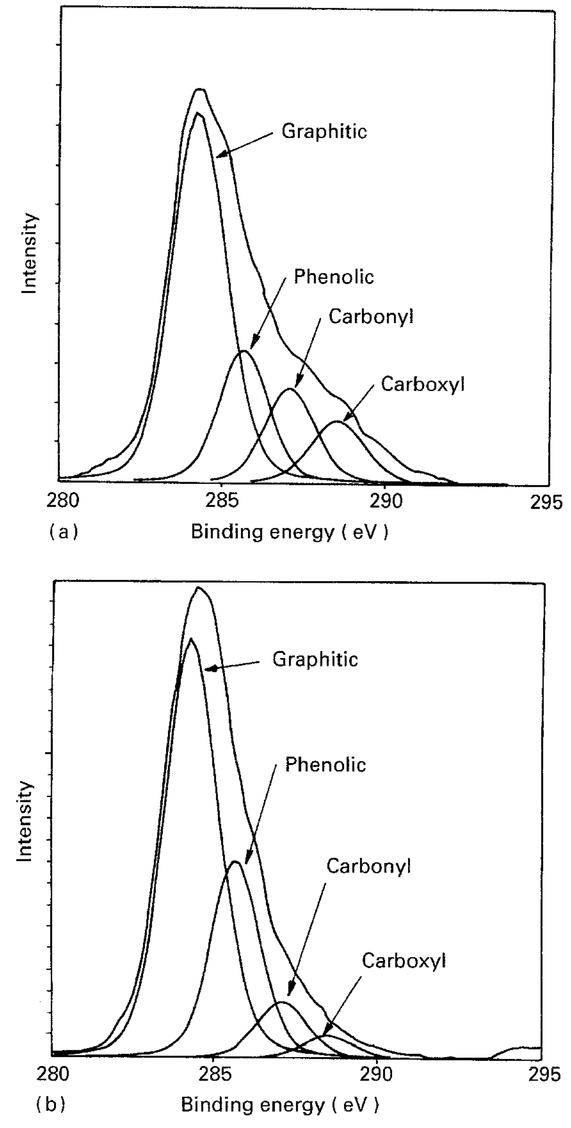

Figure 3 Curve-resolved C 1s XPS spectra of (a) CO-3 and (b) CE fibres.

TABLE II The relative concentration of the functional groups on the carbon fibre surface and O 1s/C 1s atomic ratio, as determined by deconvolution of high-resolution C 1s spectra

	Binding energy ± 0.1 eV	Concentration of functional groups in C 1s spectrum (%)	
		CO-3 fibre	CE fibre
Graphitic	284.4	57.6	62.0
Phenolic	285.8	18.9	27.5
Carbonyl	287.1	13.6	7.8
Carboxyl	288.7	9.8	3.0
A_o/A_c		0.79	0.43

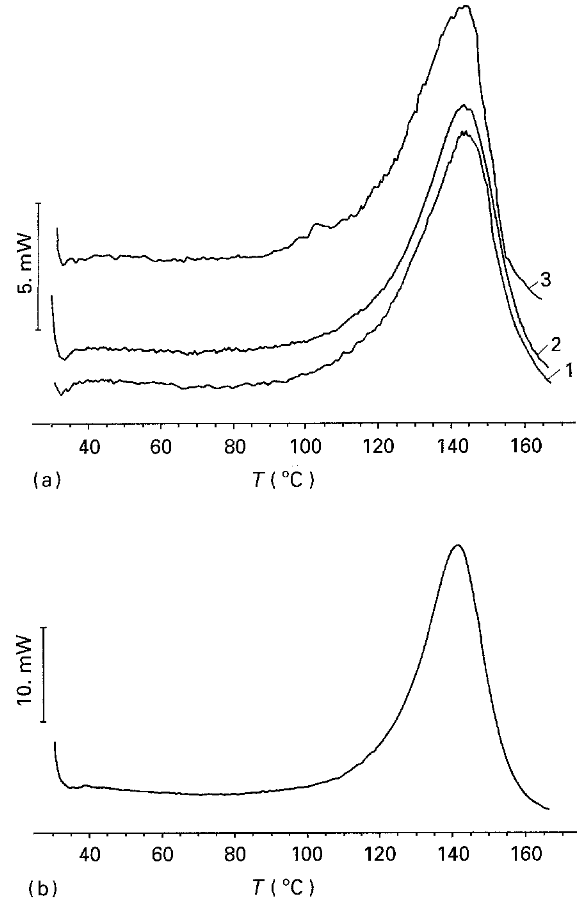

Figure 4 DSC scans of the fibre/epoxy resin mixtures (1:1 wt/wt) prepared from (a) CO and (b) CE fibres.

TABLE III DSC analysis data of carbon fibres/epoxy resin mixtures (1:1 weight ratio)

Fibre	ΔH (J g^{-1})	T_r (°C)	T_g (°C)
CO-1	123.0	144.0	142.0[a]
CO-2	120.0	143.2	142.0
CO-3	122.6	143.8	143.5
CE	169.8	141.7	135.8

[a] T_g of cured epoxide is 130 °C.

It should be pointed out that some correlation between the ILSS and the corresponding values of previously determined interfacial shear strength [7] for CO-, CE- and CU-fibres containing microcomposites, exists. Similar correlations were found for glass fibre-reinforced composites, when the pull-out test was applied for calculating the interfacial shear strength of microcomposites and a symmetrically notched tensile shear test was used for macroshear strength determination [13].

In the case when DGEBA-based epoxide/dipropylenetriamine were used to prepare CO- and CE-fibre-reinforced composites, the oxidized fibre-containing system was found to undergo a more intensive cross-linking reaction during the cure [7]. Among the factors affecting this phenomenon was proposed to be the selective adsorption of an epoxy component of the resin in the vicinity of the fibre surface. In order to compare the effects of the fibre surface chemistry on the cross-linking reaction of the epoxide, DSC analysis of uncured mixtures of carbon fibres and epoxy resin (1:1 weight ratio) was performed. DSC data are shown in Fig. 4 and Table III.

Similar values for the heat of cure, as well as for the reaction peak temperature, are found for the oxidized fibre-containing mixtures. The heat of cure of the system with epoxy-sized fibres is higher, but the corresponding glass transition temperature, T_g is lower compared to oxidized fibres/epoxy system. The higher T_g could be attributed to the interphase region, where the mobility of the resin is restricted by carbon fibres, proposing a higher degree of cross-linking of the matrix in the vicinity of the oxidized fibre surface.

4. Conclusion

Comparing the effects of the carbon fibres surface chemistry on the interfacial properties of epoxy composites, it is obvious that there is no simple conclusion to be drawn for the optimum interphase state. However, both the oxidative treatment and epoxy-sizing of the fibres are found to influence the ILSS of the UD-composites. Increased values of ILSS are obtained for the oxidized fibre-containing composites, probably due to the higher concentration of carboxyl groups created on the fibre surface, which act as primary polar adsorption sites at the interface. The heat of cure and the epoxy cross-linking reaction peak temperature do not change significantly with the degree of oxidative treatment when an anhydride-curing agent is used; this is somewhat conflicting evidence when compared with our previous results concerning epoxy/amine systems [7].

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