

INTERFACE ENHANCEMENT ON CFRP COMPOSITES BY EPOXIDATION OF CARBON FIBRES AT ROOM TEMPERATURE

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Abstract

Interface quality between the reinforcing and the host media plays a key role towards the fabrication of CFRP composites. In most cases, a strong interfacial bond is utilized by chemical or mechanical adhesion of the polymeric matrix to the surface of the reinforcing fibers. A chemical process involving untreated CF's functionalization via epoxidation reaction at room temperature (RT) has been proposed in this study. This contains the immersion of a given CF volume into an organic solution (chloroperoxybenzoic acid in dichloromethane) for different reagent concentration and timings. The functionalized CFs surface with oxygen moieties and especially epoxy rings at optimized grafting densities showed a noteworthy enhancement to the adhesion of the CF's with the epoxy-based matrix, through cross-linking reactions. Raman spectroscopy has been successfully adopted to study the stress-transfer characteristics in carbon fibre/epoxy systems, since the Raman lines of the reinforcing carbon fibres exhibit distinct and reproducible shifts when subjected to axial load in the fibre direction. Besides the obvious composite mechanical properties enhancement, we must highlight the ability to

recycle and re-use most of the solvent quantity and the effectiveness in RT conditions, something that classifies the process as energy-saving and environmental friendly.

1. Introduction

The properties of composite materials are essentially based on the microstructure and the performance of intermediate zone between a reinforcing fiber and polymer matrix. The so called interface is a region where the fiber and matrix phases are chemically or mechanically linked [1,2] and plays an important role in the stress transfer mechanism from the host medium to the fiber, determining the mechanical behavior of the resulting composites, such as interfacial shear strength (ISS), delamination resistance, fatigue life and corrosion resistance. A lot of work has been done on the modification of the fibre surface in order to improve the interfacial quality.[3-7]. Surface treatment mainly aims to remove a 'weak' outer layer from the fiber increasing the number of surface active groups. Generally, these methods either implant chemical groups onto the surface where free valences of the graphite carbon atoms have not been saturated or lead to surface roughening, resulting to interfacial strength enhancement when these groups are of sufficiently high concentration [8,9].

Most common methods are acid (gas or liquid) treatment, plasma treatment, rare earth treatment and gamma irradiation of CFs. Generally, oxidation etches the fiber surface and usually implant carbonyl and hydroxyl groups onto the surface. Plasma is an electrically conducting state of matter consisting of electrons, positively charged ions, and neutral atoms or molecules or both. The main purpose of plasma surface treatment of fibers or whiskers, that can be used as reinforcements in composite materials, is to modify the chemical and physical structure of the surface layer, tailoring fiber-matrix bonding strength, without influencing the bulk mechanical properties of the reinforcing phase. In gamma treatment method, CFs are exposed to high-energy gamma-irradiation or laser irradiation which leads to surface roughening, resulting in an improved fiber-matrix mechanical adhesion. Finally, according to the chemical bonding theory rare earth elements are adsorbed onto CFs' surface and the matrix through chemical bonding. In this way, the concentration of reactive functional groups increases due to the chemical activity of rare earth elements.

In this work, a novel, energy-saving, environmental friendly and easy to handle method of CF epoxidation at room temperature is proposed. The fibers are immersed into suitable chemical solution for a very short time (up to 5 minutes) resulting to the formation of epoxide rings on the surface of the CF. These generated epoxide rings can interact with the host polymer (especially with epoxy resins) and thus to enhance the adhesion between the fiber and the matrix. In this study, Raman spectroscopy has been successfully adopted to study the stress-transfer characteristics in carbon fibre/epoxy systems, since the Raman lines of the reinforcing carbon fibres exhibit distinct and reproducible shifts when subjected to axial load in the fibre direction. [10]. The interface investigation and the effect of

the surface treatment on the fibres were performed using a shear-lag based analysis [11]. The shear lag parameter and the shear stress were calculated, as originally proposed by Cox [12].

2. Experimental

2.1. Material preparation

Low Modulus PAN based Carbon Fibres provided by Courtaulds Grafil (EX-AIM) were used in this study. Fibres were unsized and untreated in 6k tows with a mean diameter of 4.8 μm . The host medium consisted of a two-part 'water clear' (base agent: R2820 / hardener: H8390, ratio: 2:1) system provided by Fibermax. The resin system is mixed and cured at Room Temperature (RT) and an additional post-curing at 40-80°C is implemented for achieving the final mechanical properties.

Carbon fibers were embedded in the matrix in such a way to be close to the outer surface of the coupon in order to be optically accessible to Raman Microscope. More detailed, the fabrication of CF reinforced resin 'model' composites was carried out by pouring a small quantity (in order to form a thin layer) of resin over the CFs, which were placed and aligned on a flat polished surface. The flat substrate was covered by stretched release film to ensure proper removal without damaging the cured coupon. The composite film was cured for 24 h at RT and then for 24 h at 40° C. The aforementioned procedure resulted to the fabrication of single fibre reinforced coupons, with a resin layer thickness in the range of 100 nm above the fibre. Two model composite types were prepared: i) short fibre coupons (CF fully embedded in an intermediate position, away from the edges) and ii) continuous fiber coupons (CF extends and covers the full length of the specimen). Rectangular specimens with dimensions 6cm x 5mm x 0.1 mm were used for testing.

3. Results and discussion

As mentioned above, in this work a chemical process involving untreated CFs' functionalization via epoxidation reaction at room temperature (RT) has been proposed. This involves the immersion of a given CF volume into an organic solution of 5 gr of 3-chloroperoxybenzoic acid in 125 ml dichloromethane for short times (1 to 5 minutes), subsequently washing with pure solvent and drying in mild temperatures (50°C). Straight after the drying, all samples were subjected to XPS analysis aiming to register the surface changes occurred due to the chemical treatment. The analysis focused on the monitoring of the present carbon and oxygen peaks, as derived from the sample surface. The C1s peak (figure 1) is analyzed into four components at binding energies 284.6 \pm 0.1, 286.2 \pm 0.1, 288.0 \pm 0.1 and 289.0 \pm 0.1 eV assigned to C-C bonds, epoxides (C-O) carbonyls (C=O) and carboxyls (O=C-OH) respectively. The O1s peak is analyzed into three components at binding energies at 532.5 \pm 0.1, 530.9 \pm 0.1 and 534.5 \pm 0.1 assigned to epoxides, carbonyls or carboxyls and adsorbed water

respectively. Using the total peak area of O1s and C1s peaks, in each sample and the appropriate sensitivity factors and equations, the average percentage of the relative atomic concentration in the analysed region, can determined and the results are shown in Table1. From the O1s spectra from the pristine sample the component assigned to C=O bonds is absent whereas as the epoxidation procedure time increases the C=O component is increased. In order to quantify the percentage of the surface concentration of epoxides the intensity of the C-O component to the total intensity of C1s peaks was calculated and presented in the last collum of Table 1. All results showed a significant increment on both oxygen and epoxides concentration on the CF's surface due to the epoxidation procedure for different times.

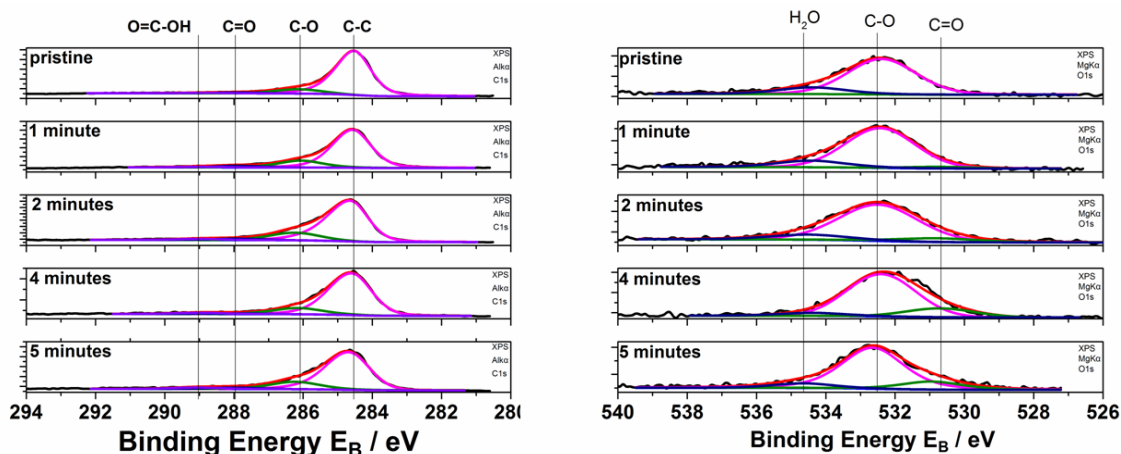


Figure1. XPS Deconvoluted XPS C1s (left) and O1s (right) peaks of pristine, 1min., 2min., 4min. and 5min. epoxidation time

Table1. % atomic Oxygen and Carbon on the fibre samples calculated from the total C1s and O1s intensities and the % epoxides calculated from the deconvolution of C1s peak.

Sample	% atomic O	% atomic C	% epoxides
Pristine	9.3	90.7	9.2
1min.	10.1	89.9	10.9
2min.	13.2	86.8	12.1
4min.	15.6	84.4	14.1
5min.	18.3	82.2	17.2

Furthermore, mechanical characterization by means of CF filament tensile testing before and after the treatment, demonstrated that the implemented epoxidation has no effect on the fiber mechanical properties, regardless of the treatment duration. As it is clearly presented in figure 2, the elastic modulus, the elongation to fracture and the strength values practically remained constant. In the light of the previous results, the epoxidation procedure on the one hand generated significant oxygen moieties and especially epoxy rings on the CF's surface that is expected to improve the adhesion with

epoxy-based matrices through cross-linking, and on the other hand did not affect the mechanical properties of the material.

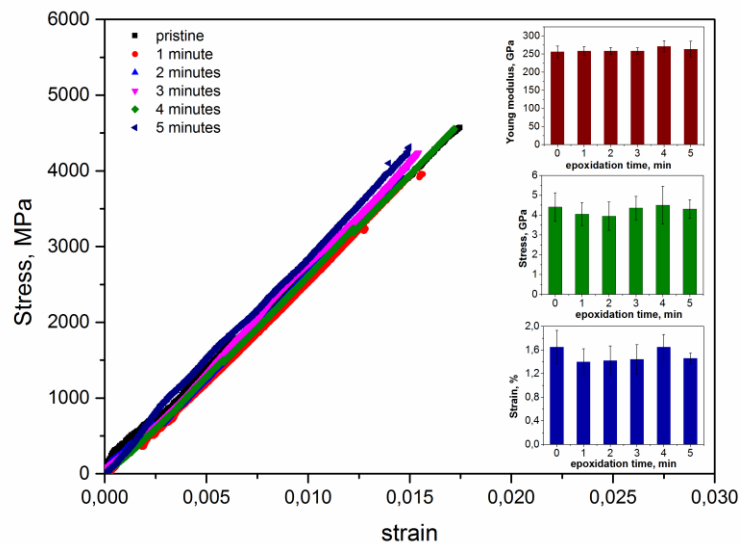


Figure 2. Single Carbon fiber fillament mechanical properties

Continuing, the main target of this study was the interface investigation of CF/epoxy based composites and its improvement due to the proposed epoxidation procedure. Raman spectroscopy has been adopted to study the stress-transfer characteristics in carbon fibre/epoxy systems, since the position of the D and G Raman peaks exhibit distinct and reproducible shifts when subjected to axial load in the fibre direction [13]. The Raman G peak corresponds to the in-plane, doubly degenerate E_{2g} phonon at the graphene Brillouin zone centre [14-16] and is present in all carbonaceous materials [17]. The D peak is due to the breathing modes of sp² rings and requires a defect for its activation. This basic principle (shift under applied strain) allows Raman spectroscopy to be used to measure stress or strain dependences of the CF's. Unique calibration curve was produced by stretching individual carbon fiber in 25 mm gauge length paper frames. Raman spectra were acquired at the middle of the fibre and three measurements were averaged at each step in the range of 1150–1750 cm⁻¹ and the strain sensitivity of the fibers found $\partial\omega_D/\partial\epsilon \approx -6.19 \text{ cm}^{-1}/\%$. The treated fibres did not exhibit any significant differences in their Raman calibration curves.

The interface investigation and the effect of the surface treatment on the fibres were performed using a shear-lag based analysis. Point by point Raman spectra of the embedded single fiber filaments under axial tension were acquired, starting from the break points or the edges (depending on the coupon type), until a total fibre length of approximately 2 mm was covered. Raman shift was converted to

strain and then subsequently to axial stress, as derived from the previously reported calibration and mechanical testing data. In Figure 3 it is presented the normalized axial stress for both treated (for 2 and 5 min) fibers, and the pristine ones. It is obvious that the stress build-up occurs faster as the epoxidation time increases and this is a definite indication that the interface quality improves with the epoxidation procedure.

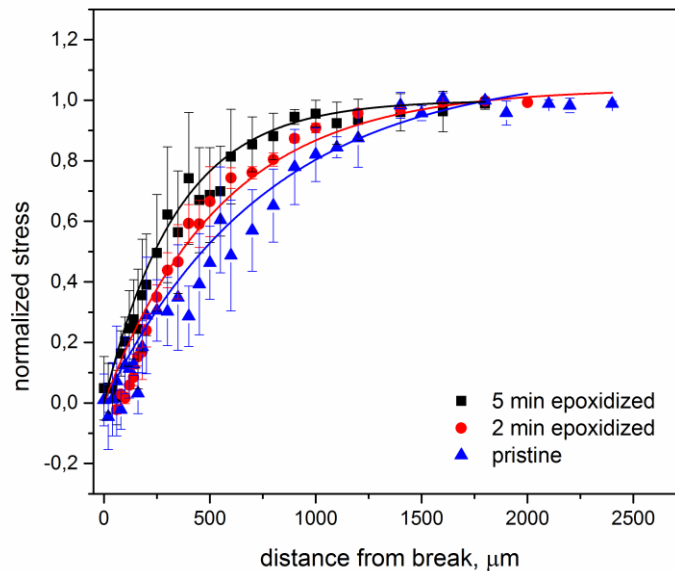


Figure 3. Normalized axial stress versus the distance from the discontinuity of CF embedded in the epoxy resin for different epoxidation time

The ISS values for the three different systems were also calculated and presented in Figure 4. As shown, the stress transfer response of the pristine and the two epoxidized CF/epoxy systems are considerably different. The 5 minutes epoxidized fiber/epoxy exhibits much higher ISS at the discontinuity ($x=0$) but also the decay in this case is more pronounced. The predicted values of the ISS for the maximum measured far field stress (table 2) found 3.3 MPa for the pristine, 4.7 MPa for the 2 minutes epoxidized and 7.7 for the 5 minutes epoxidized CF/epoxy composites respectively. Finally, the shear-lag parameter, β [11], that can be considered as the inverse length of the fitting parameter for the solution of the shear-lag differential equation [10] and can effectively serve as a stress-transfer efficiency index was also determined and presented in Table 2. The proposed method, using the β -parameter as a criterion, exhibited a significant improvement of 130 % in the interface strength. This, can be attributed to the additional chemical bonding of the generated epoxy rings due to the epoxidation procedure and the host resin, as expected.

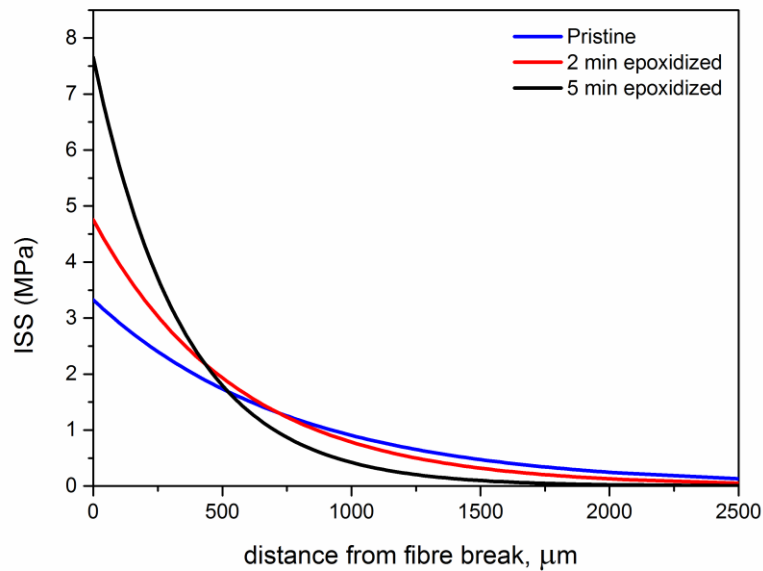


Figure 4. Interfacial shear stress versus the distance from the discontinuity of CF embedded in the epoxy resin for different epoxidation time

Table 2. Maximum interfacial shear stress and the the shear-lag parameter, β , at different treatment times.

epoxidation time	β	ISS (MPa)
pristine	0.0013	3.3228
2 minutes	0.0018	4.752
5 minutes	0.0029	7.656

3. Conclusions

The proposed epoxidation at room temperature method, exhibited a significant improvement of the interface strength between the CF filaments and the surrounding epoxy resin, which can be attributed to the additional chemical bonding by crosslinking reactions. The verification of the above was performed by using a combination of mechanical and spectroscopic methods. The main advantages of the proposed method, besides the obvious composite mechanical properties enhancement, are the ability to recycle and re-use most of the solvent quantity and the effectiveness in RT conditions (no external heating source is needed), which allows us to classify the process as energy-saving and environmental friendly.

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