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ADHESION IMPROVEMENT OF FIBRES BY CONTINUOUS PLASMA TREATMENT AT ATMOSPHERIC PRESSURE

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ABSTRACT

Carbon fibres and ultra-high-molecular-weight polyethylene (UHMWPE) fibres were continuously treated by a dielectric barrier discharge plasma at atmospheric pressure for adhesion improvement with epoxy resins. The plasma treatment improved wettability, increased the oxygen containing polar functional groups at the surface, and subsequently improved adhesion to the epoxy and fracture resistance of epoxy composites. Hansen solubility parameters (HSP), quantitatively describing physical interactions among molecules, were measured for the UHMWPE fibre surfaces. The result identifies two distinct types of surfaces in both the plasma treated and the untreated fibres. One type is typical of polyethylene polymers while the other is characteristic of the oxygenated surface at much higher values of HSP.

1. INTRODUCTION

Carbon fibres and ultra-high-molecular-weight polyethylene (UHMWPE) fibres are extensively used for improving the mechanical properties and reducing the weight of fibre reinforced polymer (FRP) composites. In order to achieve high mechanical strength of the FRP composites, fibre distribution, alignment, damage, and interface between fibre surfaces and a polymer matrix need to be understood and properly controlled. In particular strong adhesion between the fibre surfaces and the polymer matrix is one of the key issues for improving the longitudinal tensile strength of FRPs (Dilsiz 2000). An epoxy resin is often preferred for the host matrix due to excellent electrical properties, high mechanical strength, high resistance against aging/hydrolysis, and high bond strength to many polymer materials (Jones 1991). However, the non-polar nature of many fibres means that they are difficult to wet and almost impossible to chemically bond to generally used polymer matrices. Adhesion can be improved by surface treatment of many fibres, mainly by oxidation of the surfaces, introducing reactive polar functional groups onto the fibre surfaces.

Extensive research has been devoted to the surface treatment of carbon fibres and UHMWPE fibres in order to improve their bonding to the polymer matrix. Among various surface treatment techniques, plasma treatment is attractive due to its environmental friendliness and high treatment efficiencies without affecting the textural characteristics of the bulk material. These plasmas are often generated at low pressures. Plasma surface modification at low pressures, however, suffers from the drawbacks that they require expensive vacuum systems, and methods are only well-developed for batch or semi-batch treatments. To overcome these drawbacks an atmospheric pressure plasma treatment system can be used. This not only avoids the need for vacuum equipment but also permits the treatment of large objects, and continuous treatment on production lines (Kogoma, Kusano and Kusano 2011).

After the plasma treatment, there is a major change in the surface morphology accompanied by the inclusion of large amounts of oxygen, chain scission and local elimination of crystallinity. Surface characterization of the treated fibres is important in order to understand the effect of the treatment and the mechanism of the interaction with the polymer matrix. X-ray photoelectron spectroscopy (XPS) is a good candidate and widely used for this purpose, since it is surface-sensitive, and provides the quantitative information on atomic composition and chemical structure at the surface. The noticeable disadvantage of the XPS is that it is a localized analysis and does not give information on the uniformity and the overall character of the surfaces by a single measurement. XPS cannot tell exactly where the analysis took place, and in order to obtain a full understanding, one has to repeat the expensive and time-consuming analyses and then rely on statistical methods. On the other hand, Hansen solubility (cohesive energy) parameters (HSP) can be used to characterize the surface and can give the macroscopic information (Kusano, Teodoru and Hansen 2011). Here HSP are thermodynamic quantities that can quantitatively describe physical interactions among molecules. The HSP consist of three parameters; δ_D (dispersion), δ_P (polar) and δ_H (hydrogen bonds). More detailed discussions of the HSP concept are found elsewhere (Hansen 2007). Matching the HSP of fibres and matrix polymer will optimize the physical adhesion (Teodoru et al. 2009). Therefore, it is important to know the HSP of the oxygenated surfaces of the fibres. It is reported that HSP of an epoxy resin are δ_D, δ_P, and δ_H being 20.0, 10.0, and 8.0, while those of oxidized, unsized, chopped carbon fibres are δ_D, δ_P, and δ_H being 21.3, 8.7, and 11.5, all in $MPa^{½}$, respectively, and that they are very similar, thus contributing to good physical adhesion in such systems (Launay, Hansen and Almdal 2007).

In the present study, carbon fibres (Kusano, Andersen and Michelsen 2008, Kusano et al. 2012) and UHMWPE fibres (Teodoru et al. 2009, Kusano et al. 2011) were continuously treated by a dielectric barrier discharge (DBD) plasma at atmospheric pressure. Adhesive properties of treated and untreated fibres were evaluated and the fibre surfaces were characterized.

2. EXPERIMENTAL METHODS

Poly(acrylonitrile) (PAN) based unsized electrochemically-treated carbon fibres (TOHO TENAX HTA5001, 800tex) were used without pre-cleaning. UHMWPE fibres (1300 filament yarn with a tex number of 145, 12 μm diameter of a monofilament) were purchased from Goodfellow, UK, and were ultrasonically cleaned in acetone twice for 5 minutes and in methanol for 5 minutes to remove the silicon containing contaminants from the surfaces. After the cleaning, the Si content at the UHMWPE fibre surface was typically less than 1 atomic % measured by XPS.

The atmospheric pressure DBD was used to continuously treat fibres as shown in Figure 1. The feed speed of carbon fibres was 150 or 300 cm $minute^{-1}$, corresponding to 2- or 1-s treatment,

while that of UHMWPE fibres was 10 cm minute^{-1}. The high feeding speeds were chosen for carbon fibres so as to manufacture fibre reinforced composites which require several hundred metre carbon fibres. The DBD consists of parallel plate water cooled metal electrodes (50 mm × 50 mm) covered with alumina plates (100 mm × 100 mm × 3 mm). The DBD was generated by an alternating current power supply (Generator 6030. SOFTAL Electronic GmbH). The driving frequency was approximately 40 kHz and the average power was approximately 100-110 W. He gas was fed into the DBD at a flow rate of 1 L minute^{-1}. It is noted that contamination and the leakage of N_2, O_2, and H_2O from ambient air to the discharge is often inevitable, resulting in the introduction of oxygen and/or nitrogen at the exposed surfaces in a discharge, even if no oxygen or nitrogen containing gas is apparently supplied. In fact such a leakage sometimes plays an important role in oxidizing and nitriding the surface. The reproducibility of the treatment associated with the level of the leakage was indirectly ensured by confirming that the measured voltage and power were reproducible under the same conditions.

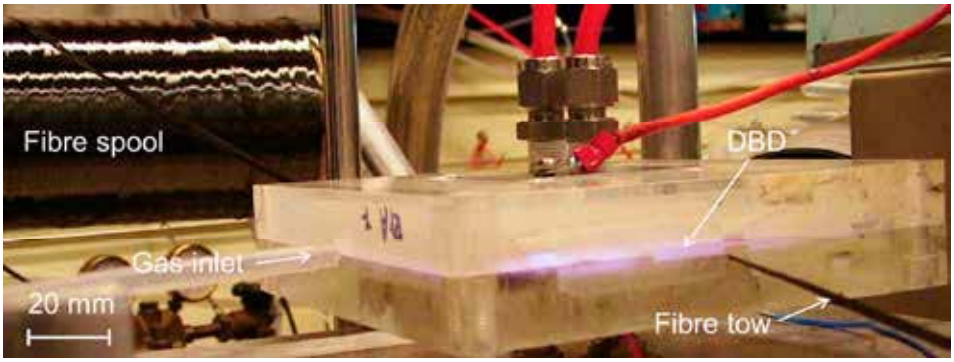

Figure 1. The atmospheric pressure DBD plasma treating carbon fibres continuously.

Carbon fibre reinforced epoxy (CFRE) plates for double cantilever beam (DCB) specimens were manufactured by filament winding followed by vacuum infusion, using untreated, 1- and 2-s plasma-treated carbon fibres with an epoxy resin (Prime 20. SP Systems) (Kusano et al. 2008). The thickness of the CFRE plate was 2 mm. Steel beams were glued to the outside of each composite plate with epoxy adhesive (Scotch Weld 460). The DCB specimens were loaded by pure bending moments and the fracture resistance was calculated using the J integral. The fibre adhesion of the CFRE plates was evaluated using fracture resistance values at steady state.

Another simple mechanical test was performed for the preliminary evaluation of the plasma treatment effect on adhesion of UHMWPE fibres with another epoxy (Strong Epoxy Rapid 2806, Casco). The 200-mm long fibres were aligned in parallel on a metal plate. Approximately 3-mm thick mixture was applied onto the plate so that it covered the fibre surfaces completely. After curing 90º peeling test was performed to evaluate the adhesive property of the fibres with the epoxy by gently pulling the fibres from the epoxy composites manually (Teodoru et al. 2009).

XPS was performed for the measurement of the oxygen/carbon (O/C) ratio of the carbon-fibre and UHMWPE-fibre surfaces using a SPECS Sage 100 and K-Alpha, ThermoFischer Scientific, respectively.

The basis of the HSP characterizations was to determine differences in interactions when fibre samples were immersed in a suitable set of test solvents. The fibre samples used for these characterizations were taken from a short piece of a much longer fibre either as supplied or after

plasma treatment. Interactions with the fibres were visually rated based on the extent to which the filaments were removed from each other thus increasing their apparent volume. The scale used for the rating was "1" for strongest interaction to "6" for very little interaction (Kusano et al. 2011). The interaction evaluated was the extent to which the fibres expanded in the vials. The fibre samples immersed in the solvents were stored at room temperature for at least 20 days after which there was no further change. 20 mg sample was placed in 13 mL of liquid in small vials such that the height of the liquid was approximately 5 cm. The fibres expanded to completely fill the vials when the interactions were strongest.

3. RESULTS AND DISCUSSION

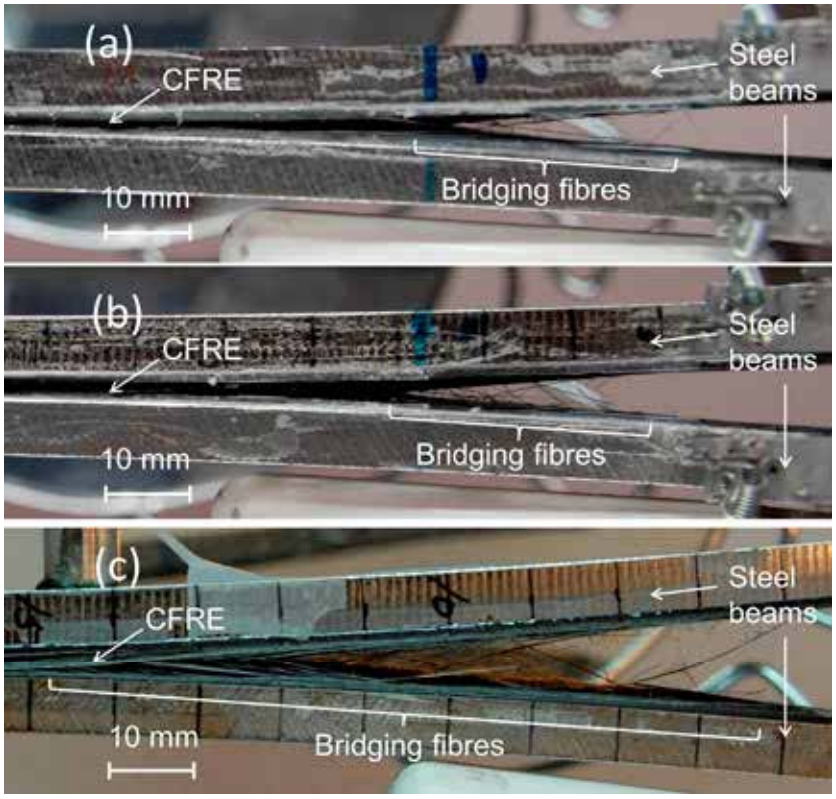

Figure 2. Photos of CFRE plates during the adhesion test. Untreated (a), 1-s (b) and 2-s (c) plasma treated.

Figure 2 shows photos of representative DCB specimens during the fracture mechanics test. All specimens show fibre bridging, which is a known toughening mechanism. The number of bridging fibres increases as the treatment time is longer. The fracture resistance of the CFRE with untreated and 1-s treated carbon fibres initially increased as the end-opening increased, and approached steady-state values. The CFRE with 1-s treated ones shows higher steady-state values (1700-2200 J m^{-2}) than those of the untreated ones (1400-1800 J m^{-2}) (Kusano et al. 2012). The fracture energy of the 2-s treated specimens steadily increased as the end-opening increased (1700-2400 J m^{-2} at the end opening of approximately 5 mm). It is therefore concluded that the plasma treatment improved the fracture resistance of the CFRE composites,

and that the longer treatment further improved them.

It is tempting to speculate that since the number density of bridging fibres increases as the treatment time is longer, the increase in macroscopic fracture resistance is due to a change in the adhesion properties of the fibre/matrix interface (Kusano et al. 2008, 2011).

The simple adhesion test for the UHMWPE fibres indicated that the untreated fibres were easily pulled off from the epoxy, showing a low adhesion between the fibres and the epoxy. The plasma treated fibres showed high interaction with the epoxy and were difficult to pull off (Teodoru et al. 2009).

The major effect of the conventional electrochemical treatments on carbon fibres for fibre/resin adhesion is believed to be the removal of weakly bound crystallites at the fibre surfaces, while the number of functional groups introduced onto the fibre surfaces by those treatments is too small to have a significant effect (Farrow and Jones 1994). They are less effective when they are applied to highly graphitised surfaces (Montes-Morán, Martínez-Alonso, Tascón and Young 2001). It is therefore interesting to know whether the plasma treatment can effectively oxygenate the fibre surfaces. The elemental composition of the carbon fibre surfaces before and after the plasma treatments was analyzed using XPS. The typical O/C ratio at the carbon fibre surface before plasma treatment is approximately 0.16, while it increases to approximately 0.18 after the treatment for 1 or 2 s. On the other hand, the O/C ratio of untreated UHMWPE fibre is 0.01, while that of the treated one is approximately 0.15, indicating that plasma treatment can efficiently oxidize the UHMWPE surface.

HSP correlations showed that there were two distinct regions of interaction on the untreated UHMWPE fibres. There was one region at high δ_P and moderately high δ_H characteristic of oxygenated species. The strong interaction, that is, a similar and clear effect of separating the fibres, is found in three solvents with very close HSP, N,N-Dimethyl formamide, N,N-Dimethyl acetamide, and N-Methyl-2-pyrrolidone. The oxygenated surface has δ_D, δ_P, and δ_H equal to 15.8, 13.4, and 6.0, all in $MPa^{½}$. There is a second distinct region characteristic of general polyethylene (PE) at higher δ_D and low δ_P and δ_H shown by the strong interaction with aromatic solvents. This PE surface has δ_D, δ_P, and δ_H equal to 18.0, 1.2, and 1.4, all in $MPa^{½}$. These HSP for the PE-type surface are based on literature values and could not be confirmed in this study because of too few data points in this region (Kusano et al. 2011).

Strong aromatic-solvent interaction with the UHMWPE fibres is characteristic of interaction with PE surfaces. This was also found for the plasma treated fibres. The data for benzene, toluene, and trimethylbenzene have therefore been deleted in the further analysis, since the primary interest here is the nature of the oxygenated surfaces and the simultaneous consideration of the two distinctly different surfaces only leads to a confusing result from the optimization software used to evaluate the HSP. There is a very good correlation with a high data fit for the strong interaction of solvents with the oxygenated surface of the plasma treated UHMWPE fibres. This correlation confirms a region with high δ_P and moderately high δ_H on the surface of the plasma treated UHMWPE fibres. For the plasma treated surface, this region is characterized by δ_D, δ_P, and δ_H being 16.5, 15.3, and 8.2, all in $MPa^{½}$. The differences between these HSP and those of the surface on the untreated samples are not large. However, the HSP of the treated fibres is higher than those of the untreated ones, indicating that the treated fibres contain more oxygen in basically the same functional groups of the untreated surfaces (Kusano et al. 2011).

4. CONCLUSIONS

Carbon fibres and UHMWPE fibres were continuously treated by atmospheric pressure DBD plasma for adhesion improvement with epoxy resins. Plasma treatments oxygenated the fibre surfaces, significantly increased the adhesion between fibres and epoxy resins and enhanced the fracture resistance of the fibre/epoxy composites. HSP characterizations appeared to be a useful technique to evaluate the potential fibre surfaces for wetting and physical adhesion.

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