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## ADHESION IMPROVEMENT OF CARBON FIBRES BY PLASMA SURFACE MODIFICATION

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### ABSTRACT

Plasma surface modifications are attractive for the application of adhesion improvement because they avoid the use of toxic chemicals, only the surface is treated while the bulk properties remain unchanged, oxygen and/or nitrogen containing functional groups are easily introduced into the surfaces, surface cleaning and weak-layer elimination can be performed simultaneously with the surface modification, and physical and chemical micro-etching is expected, improving the mechanical interlocking with adhesives. Plasma surface modification of carbon fibres has been studied for adhesion improvement with polymer matrices for enhancing longitudinal tensile strength of carbon fibre reinforced polymer (CFRP) composites.

In the present work, atmospheric pressure dielectric barrier discharge is used to treat unsized electrochemically-treated carbon fibres in various gas conditions. An x-ray photoelectron spectroscopic analysis indicated that oxygen-containing polar functional groups are effectively introduced onto the carbon fibre surfaces by He, He/O<sub>2</sub> and Ar plasma treatments. CFRP composite plates were prepared using both untreated and He plasma-treated carbon fibres with an epoxy resin for the adhesion test. Improved wetting to the uncured epoxy resin was observed for the plasma treated ECFs. The plasma treated specimens showed a higher fracture resistance, indicating that adhesion between the fibres and the epoxy was improved by the plasma treatment.

### 1. INTRODUCTION

Carbon fibres have been extensively used for improving mechanical properties of polymer composite materials due to their high strength, high toughness and light weight. 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 other polymer materials (Jones 1991).

In order to achieve high mechanical strength of the composites, fibre distribution, alignment,

fibre damage, and interface between fibre surfaces and a polymer matrix need to be considered. 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 carbon fibre reinforced polymers (CFRP) (Dilsiz 2000). However, due to the non-polar nature of carbon fibres they are difficult to wet and almost impossible to chemically bond to general polymer matrices. It is noted that for adhesion improvement the chemical effect of oxygen containing polar functional groups such as -OH, =O, and -COOH at the carbon fibre surfaces is known to be more important than the mechanical effect of rough surfaces (Fukunaga 2000). Proper surface modification thus should be chosen so that carbon fibre surfaces can be wettable by the polymer matrix and bond to it tightly. Adhesion can be improved by surface treatment of the fibres, mainly by oxidation of the surfaces, introducing reactive groups onto the fibre surfaces so that they can react with matrices as well as increase the surface energy for improved wetting.

Extensive research has been devoted to the surface modification of carbon fibres in order to improve their bonding to the resin matrix, including dry or wet oxidation, electrochemical methods, polymer coatings, plasma treatment, plasma polymerization, and plasma enhanced chemical vapour deposition (PECVD) (Dilsiz 2000, Fitzer 1981, Hughes 1990). The wet oxidation and electrochemical methods use nitric acid,  $\text{KMnO}_4$ ,  $\text{H}_2\text{SO}_4$ , sodium hypochlorite, chromic acid, and electrolytic NaOH, while the dry methods use oxygen, ozone, and catalysis. However, these kinds of chemical methods may be least preferable. For example, when the carbon fibres are oxidised in concentrated nitric acid, the equipment used must have good corrosion resistance and the acid absorbed on the fibre surfaces must be properly removed by subsequent washing, which is time-consuming and inevitably damages and tangles the carbon fibres (Dilsiz 2000, Hughes 1990). These methods can also produce environmental pollution. On the other hand, plasma surface modification techniques are attractive for this application, because they can be operated at room temperature, they do not require any use of solvents and toxic chemicals (environmentally friendly process), the bulk properties are retained, oxygen and/or nitrogen containing functional groups are easily introduced into the surfaces, which is often required for the application of adhesion improvement, a surface can be cleaned and weak-layers can be eliminated simultaneously with the surface modification, and physical and chemical micro-etching is expected, improving the mechanical interlocking with adhesives.

Plasma surface modification can usually be divided into two categories with opposite effects, depending mainly on the process gas(es) used. The first one mainly ablates the surfaces, and is usually called "plasma treatment", "plasma surface modification", "plasma ablation", or "non-polymer-forming plasma". The second one is usually called "plasma polymerization", "polymer-forming plasma" or "PECVD". In the following "plasma surface modification" is meant to cover both types while "plasma treatment" is used for the first one. If the used gas(es) has high proportions of carbon and hydrogen atoms, double- or triple- bonds in its composition such as methane, ethylene, acetylene and ethanol, or if they are precursors such as metal-organic (organometallic) gas(es), the plasma often results in plasma polymerization or PECVD. Here, metal-organic gases are those which contain a metal, particularly compounds in which the metal atom has a direct bond with a carbon atom. Otherwise, the plasma will have a tendency of ablation (plasma treatment). These techniques have been studied for adhesion improvement of carbon fibres (Dilsiz 2002).

It is argued, however, that to date none has changed the performance of the finished CFRP composite significantly enough to warrant large-scale development (Mason 2004). This kind of plasma is generally obtained at low pressure. These plasma surface modifications at low pressures, however, suffer 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, plasma surface modification at atmospheric pressure has been developed, avoiding expensive vacuum equipment, it permits the treatment of large objects and continuous treatment on production lines can readily be designed. Atmospheric pressure plasma has already been used to treat glassy carbon plates, which are thought to be ideal model specimens for fundamental studies of adhesive properties of carbon fibres due to the structural similarity and easier handling than carbon fibres (Mortensen 2006, Kusano 2006, 2007a).

In the present work, carbon fibres are treated by atmospheric pressure dielectric barrier discharge (DBD) plasma for adhesion improvement with an epoxy resin.

## 2. EXPERIMENTAL METHODS

An atmospheric pressure DBD has been used to treat the unsized electrochemically-treated carbon fibres (TENAX HTA5001, 800tex). It was generated between parallel plate water cooled metal electrodes (50 mm × 50 mm) covered with alumina plates (100 mm × 100 mm × 3 mm) by an AC (ca. 40 kHz,  $V_{pp} \sim 13$  kV) power supply (Generator 6030. SOFTAL Electronic GmbH, Germany). The average power input was 80-100 W corresponding to a power density of 6.5-8 W cm<sup>-2</sup>, obtained by measuring voltage and current with a high voltage probe and a 50 Ω current viewing resistor.

He, Ar, a mixture of He with O<sub>2</sub>, N<sub>2</sub> or NH<sub>3</sub>, or a mixture of Ar with NH<sub>3</sub> was fed into the DBD. O<sub>2</sub> gas was used for enhanced surface oxidation, while NH<sub>3</sub> were attempted for introducing amino groups onto the carbon fibre surfaces. The gas conditions are summarized in Table 1. The carbon fibres were also treated with the DBD in an ambient air without feeding gas (air plasma).

Table 1 Condition of plasma treatments.

	Gas flow rate [sccm]					Treatment time [s]
	He	Ar	O <sub>2</sub>	N <sub>2</sub>	NH <sub>3</sub>	
Untreated	-	-	-	-	-	-
He plasma	1000	-	-	-	-	1
						2
						100
He/O <sub>2</sub> plasma	1000	-	100	-	-	100
He/N <sub>2</sub> plasma	1000	-	-	100	-	100
He/NH <sub>3</sub> plasma	1000	-	-	-	1	100
Ar plasma	-	1000	-	-	-	100
Ar/NH <sub>3</sub> plasma	-	1000	-	-	1	100
Air plasma	-	-	-	-	-	100

X-ray photoelectron spectroscopic (XPS) analysis were employed to study the changes of the functional groups on the carbon fibre surfaces using a Sage 100 (SPECS, Berlin, Germany) instrument operated at a pressure of <math>10^{-5}</math> Pa. All the samples were analyzed using an unmonochromated Mg K $\alpha$  X-ray source operated at a power of 300 W at a take-off angle of 90°, resulting in a maximum probe depth of  $\approx 10$  nm. The number of scans was minimized in order to prevent X-ray induced sample damage, and kept constant for all the samples. Atomic concentrations of each element were calculated by determining the relevant integral peak intensities using a linear background. The systematic error is estimated in the order of 5 – 10 %.

A regional analysis was performed on the carbon 1s (C1s; pass energy 23 eV). The C1s binding energies at 284.8 and 286.2 eV correspond to C-C, hydrocarbons and C-N, C=N, C-O, respectively.

Plates for double cantilever beam (DCB) specimens were prepared for the adhesion test. At the end of the plate, a slip foil was inserted in the mid-plane to act as crack starter. Composite plates were prepared using both untreated, 1- and 2-s He plasma-treated carbon fibres with an epoxy resin (epoxy resin [Prime 20. SP Systems] mixed with diethylenetriamine / polyoxypropylamine). Steel beams were glued to the outside of each composite plate with an epoxy adhesive (Scotch Weld) which was cured for 24 h at room temperature. The fracture mechanics test was performed by applying pure bending moments to the DCB specimens using a dedicated test machine (Sørensen 2006).

### 3. RESULTS AND DISCUSSION

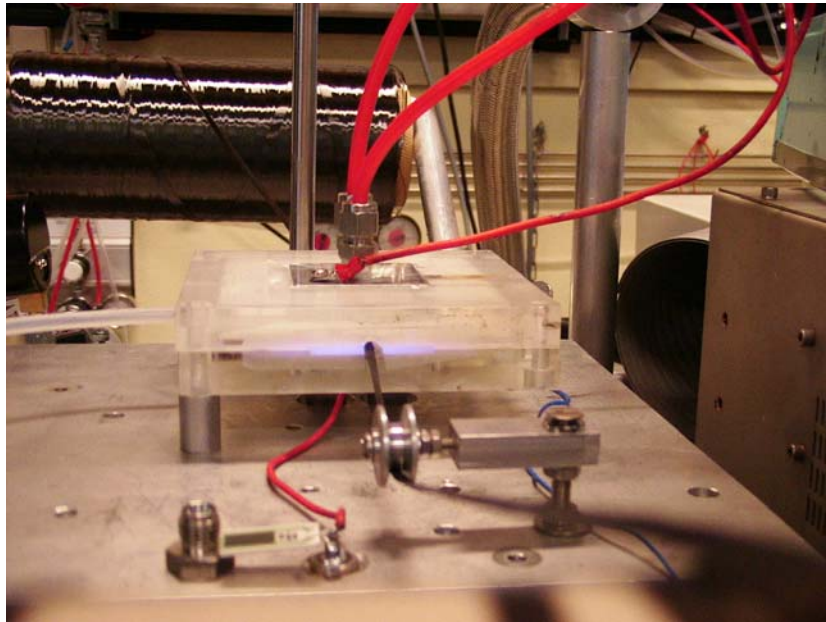


Fig. 1. Plasma treatment of carbon fibre surfaces using atmospheric pressure DBD.

Carbon fibre surfaces were continuously treated using the atmospheric pressure DBD as shown in Fig. 1.

XPS was used to analyse the elemental composition of the carbon fibre surfaces before and after the plasma treatments. The surfaces are dominated by carbon, oxygen and nitrogen. Fig. 2 shows ratios of O/C and N/C for each specimen. It is found that oxygen can be effectively introduced by He, He/O<sub>2</sub>, and Ar plasmas. Additionally the He plasma treatment for 1 s resulted in significant oxidation, while the longer treatments did not improve oxidation drastically. However, further investigation is necessary for understanding the effect of treatment time. Regional analysis on carbon 1s spectra shows decrease in the binding energy peak at 284.8 eV and increase in that at 286.2 eV after each plasma treatment, indicating that a surface density of the C-O single bond increases after the plasma treatments.

CFRP plates were prepared using untreated, 1-s and 2-s He plasma treated carbon fibres for the adhesion test. Improved wetting to uncured epoxy resin was observed for the plasma treated carbon fibres.

## Adhesion improvement of carbon fibres by plasma surface modification

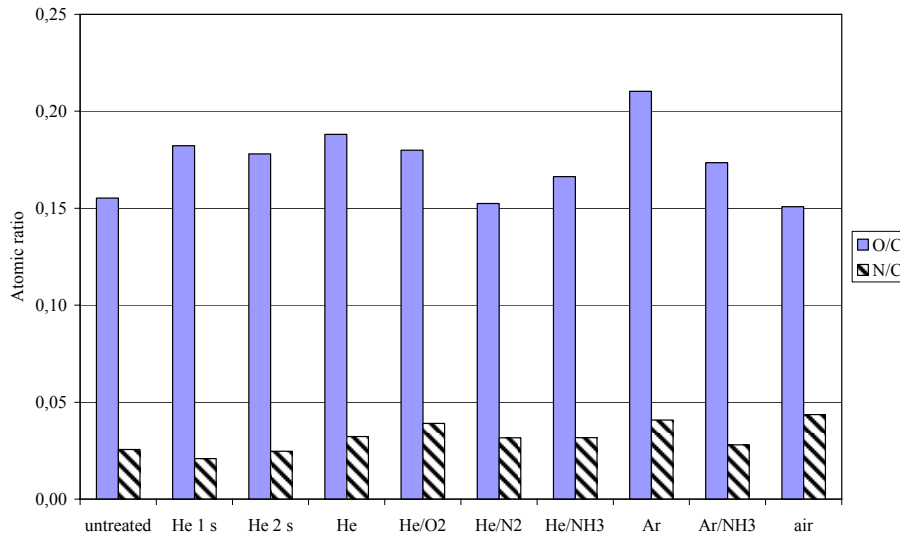


Fig. 2. O/C and N/C ratios of the carbon fibre surfaces.

Adhesive property was evaluated using fracture resistance values at the crack growth initiation and at the steady state. Data are taken when the stable crack growth is seen in the mid plane of the CFRP plates so that the adhesive property between the carbon fibre surfaces and the epoxy matrix can be properly evaluated. The results are summarized in Table 2.

Table 2

Treatment time [s]	Fracture energy [ $\text{J m}^{-2}$ ]	
	Crack initiation	Steady state
0	160 – 260	1400 – 1800
1	160 – 280	1700 – 2200
2	230 – 310	1700 – 2400 (*)

\* The fracture energy at the end-opening of about 5 mm.

The mechanical property of the CFRP composite plates improved after the He plasma treatment, indicating that adhesion of the carbon fibres to the matrix is improved with the treatment. In the case of untreated and 1-s treated specimens, the fracture energies reached steady state values at the end-opening of about 3.5 mm. On the other hand, as the crack growth proceeds, the fracture energies of 2-s treated specimens steadily increased without approaching to a steady state due to their better adhesion than the others. Since the oxygen content of 1- and 2-s treated carbon fibre surfaces are almost the same, a possible explanation of this adhesion improvement is enhanced surface roughness after longer plasma treatment (Kusano 2007b).

## 4. CONCLUSIONS

Carbon fibres were treated by atmospheric pressure DBD plasma for adhesion improvement with epoxy resin. He, He/O<sub>2</sub> and Ar plasma treatments increased oxygen containing polar functional groups on to the carbon fibre surfaces. He plasma treatment improved the wettability by the uncured epoxy resin, and increased the adhesion energy. It is suggested that longer He plasma treatment might increase the surface roughness

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