Atmospheric pressure plasma surface modification of carbon fibres

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Abstract. Carbon fibres are continuously treated with dielectric barrier discharge plasma at atmospheric pressure in various gas conditions for adhesion improvement in mind. An x-ray photoelectron spectroscopic analysis indicated that oxygen is effectively introduced onto the carbon fibre surfaces by He, He/O\textsubscript{2} and Ar plasma treatments, mainly attributed to an increase in the density of the C-O single bond at the carbon fibre surfaces. The O/C ratio increased to 0.182 after 1-s He plasma treatment, and remained approximately constant after longer treatment. After exposure in an ambient air at room temperature for a month the O/C ratio at the plasma treated surfaces decreased to 0.151, which is close to that of the untreated ones. It can be attributed to the adsorption of hydrocarbon contamination at the plasma treated surfaces.

1. Introduction
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 [1]. However, the non-polar nature of carbon fibres makes them difficult to wet and chemically bond to general polymer matrices. 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. Plasma surface modification technique is attractive for this application due to its environmental compatibility and high treatment effect without affecting the textural characteristics of the bulk materials, and thus has been extensively studied [2]. For example, carbon fibres were batch-treated using atmospheric pressure dielectric barrier discharge (DBD) for adhesion improvement [3]. In addition, atmospheric pressure plasmas have 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 [4-6]. On the other hand, carbon fibres were continuously treated using low pressure plasmas [7], showing higher interfacial shear strength with epoxy resin than batch-treated fibres, possibly because moving the fibres in the plasma gives a more uniform level of treatment [8]. However, for continuous treatment atmospheric pressure plasmas are greatly preferred, as vacuum equipment is avoided, and it permits large-scale development more easily than low pressure plasmas.

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In the present work, carbon fibres are continuously treated by atmospheric pressure DBD plasma. The treated and untreated carbon fibre surfaces are characterized using an x-ray photoelectron spectroscopy (XPS), and the results are compared with those in the literature.

2. Experimental methods
Poly(acrylonitrile) (PAN) based unsized electrochemically-treated carbon fibres (TOHO TENAX HTA5001, 800tex) were used for the study. They were continuously treated with atmospheric pressure DBD. The average power input was ca. 100 W corresponding to a power density of 8 W cm\(^{-2}\). He, Ar, a mixture of He with O\(_2\), N\(_2\) or NH\(_3\), or a mixture of Ar with NH\(_3\) was fed into the DBD. The flow rates of He, Ar, O\(_2\), N\(_2\) or NH\(_3\) are 1, 1, 0.1, 0.1, and 0.001 l min\(^{-1}\), respectively. The carbon fibres were also treated with the DBD in an ambient air without feeding gas (air plasma) [9].

The changes of the elemental compositions and functional groups on the carbon fibre surfaces were characterized using XPS (Sage 100, SPECS, Berlin, Germany). The systematic error is estimated in the order of 5 – 10 % of the measured values. 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 [10].

3. Results and discussion
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 [11]. They are less effective when they are applied to highly graphitised surfaces [12]. It is therefore interesting to know whether the plasma treatment can effectively add oxidative functional groups onto the carbon fibre surfaces.

![Graph showing O/C and N/C ratios at the carbon fibre surfaces before and after plasma treatments as determined by XPS.](image)

Figure 1. O/C and N/C ratios at the carbon fibre surfaces before and after plasma treatments as determined by XPS. The treatment time is 100 s unless it is stated. Aging conditions: ambient air, room temperature, one month.

The elemental composition of the carbon fibre surfaces before and after the plasma treatments was analysed using XPS. The surfaces are dominated by carbon, oxygen and nitrogen. Figure 1 shows
ratios of O/C and N/C for each specimen. It is found that oxygen can be effectively introduced by He, He/O₂, and Ar plasmas, while the nitrogen content increased slightly after He/O₂, Ar and air plasma treatments. Additionally the He plasma treatment for 1 s resulted in significant oxidation, while the longer treatments did not enhance oxidation. A regional analysis on C1s 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 and that the surfaces can be potentially further oxidised to generate carboxyl groups.

After one month exposure in an ambient air at room temperature, the O/C ratio at the He plasma treated carbon fibre surfaces decreased to 0.152, which is close to the O/C ratio of the untreated carbon fibre surfaces. However, the regional analysis on C1s spectra shows that the binding energy peak at 284.8 eV remains almost unchanged after the aging, indicating that the chemical structure at the carbon fibre surfaces before the treatment and after the treatment with the subsequent aging is different. Unsized carbon fibres are known to be almost insensitive to aging in air due to their rigid graphitic structures [13]. It is therefore suggested that the decrease in the O/C ratio by aging in air could be due to the adsorption of hydrocarbon contamination at the carbon fibre surfaces.

Table 1 compares O/C ratios (in %) at carbon fibre surfaces characterized using XPS (HM: high modulus fibre (type I), HS: high strength fibre (type II)).

| Pressure [Pa] | Gas          | Plasma Frequency [Hz] | Power [W] | producer Type | Carbon fibre Treatment time [s] | O/C ratio | Ref |
|--------------|--------------|-----------------------|-----------|---------------|---------------------------------|-----------|-----|
| 100          | O₂           | 2.45G                 | 150       | Sigri PAN, HS | 0 1 2 20 30 60 100 180         | 0.4       | [14] |
| 75           | Clemson      | University Pitch, HM  | 75        |               |                                 | 0.3       | [12] |
| 150          | Amoco        |                       | 150       |               |                                 | 0.2       |     |
| 100          | Ar           | 12.6                  | 75        |               |                                 | 0.1       |     |
| 26.7         | Ar           | 35M                   | 75        | Amoco         | 1.7                             | 0.7       | [16] |
| 133          | Ar           | 13.56M                | 50        | Courtauld PAN | 3.0                             | 1.9       | [17] |
| 66.7         | Ar           | 13.56M                | 30        | Taekwang PAN  | 12.0                            | 1.7       | [18] |
| 53.3         | Ar           | 13.56M                | 50        | Hercules PAN, HS | 11.2                            | 1.5       | [19] |
| 2            | Ar           | 13.56M                | 100       | Hercules PAN, HS | 11.7                            | 1.5       | [20] |
| 10           | Ar           | <300                  | Courtauld PAN, HM | 2.6 | 1.8       | [21] |
| 40           | He/ Oz       | 5k                    | 100       | Toho PAN, HS  | 13.5                            | 1.9       |     |
| 100          | He           | 40k                   | 100       | Toho Tenax PAN, HS | 18.2                            | 1.8       | This work |
ca. 0.2, which is significantly higher than those by the atmospheric pressure plasma treatments in refs.[3, 21], while comparable to those observed in the present study.

Untreated, 1-s and 2-s He plasma treated carbon fibres were used to prepare carbon fibre reinforced epoxy plates for the adhesion tests. The result indicates that adhesion of the carbon fibres to the matrix is improved with the treatment [9].

4. Conclusions

Carbon fibre surfaces were continuously treated by atmospheric pressure DBD plasma for adhesion improvement with epoxy resin. He, He/O₂ and Ar plasma treatments increased oxygen containing polar functional groups on to the carbon fibre surfaces.

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