

Effect of surface treatment of carbon fibers with gamma-ray radiation on mechanical performance of their composites

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Gamma-ray radiation was used to surface treat PAN carbon fibers. The efficiency of gamma-ray radiation was compared with air oxidation in terms of variations in the surface structure of carbon fibers and the mechanical performance of their composites. It was observed that the composites reinforced with the gamma-radiated carbon fibers showed higher interfacial adhesion strength and thus better flexural and shear properties than the composites reinforced with air-treated fibers. The observed higher content of carboxyl group on the surface of the gamma-radiated carbon fibers is likely to be responsible for the stronger fiber-matrix bonding. It is concluded that gamma-ray radiation is an effective approach of tailoring surface properties of carbon fibers.

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The mechanical properties of carbon fiber-reinforced composites depend mainly on fiber properties and fiber-matrix adhesion. It is very well accepted that adhesion can be improved by surface treatment of carbon fibers. Various approaches have been developed, such as oxidation, coating, and grafting. Generally, oxidation etches fiber surfaces and generates hydroxyl and carbonyl groups that may react easily with matrices, and increases the surface energy for improved wetting. Methods used for the oxidation of such nonpolar carbon fiber surfaces include oxidation in various plasmas [1], oxidation in air [2], electrochemical oxidation in various electrolytes [3] and wet chemical methods [4] such as boiling in nitric acid, sulfuric acid, or phosphoric acid. Each of the methods mentioned above may cause loss of fiber strength if the treatment is excessively extended. Similarly, gamma-ray or neutron radiation changes the microstructure of carbon materials and causes losses of mechanical properties at high radiation doses [5]. It is recognized that radiation affects the crystal lattice by displacement of atoms within the lattice or electronic excitation [5, 6]. The electrons stripped from the atoms are believed to cause dimensional (topographical) change of carbon fibers and to create active

sites on fiber surfaces which may bind with functional groups of bulk polymers. Actually, gamma-ray radiation has been more widely used for radiation grafting by which reactive groups on the surface of polymers can be created [7]. Consequently, gamma-ray radiation seems an alternative technique for surface treatment of carbon fibers. The main objective of this preliminary study was to evaluate the efficiency of gamma-ray radiation by comparing it with air oxidation, with emphasis on variations in the surface structure of carbon fibers and the mechanical performance of their composites.

The reinforcement used in this study was high-strength PAN-based carbon fibers (T300) with the following specified properties: tensile strength, 3530 MPa; elastic modulus, 230 GPa; density, 1760 kg m⁻³; diameter, 6–8 μm. The preforms, three-dimensional (3D) four-directional fabrics, were prepared by the Nanjing Fibreglass R&D Institute, Nanjing, China. The matrix material used was home-made monomer casting (MC) nylon.

As-received carbon fibers were subjected to various surface treatments including desizing (immersed in an organic solvent), desizing plus air-oxidation, and desizing plus gamma-ray radiation, which are denoted as

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untreated, air-treated, and gamma-radiated, respectively. Radiation was performed in a Curie 30-model cobalt-60 gamma-ray machine (manufacturer: Research Institute of Atomic Energy, Shanghai, China). Fiber samples were irradiated to integral doses of 2 KGy (or 0.2 Mrad) at a dose rate of 67 Gy/h, in oxygen atmosphere and ambient temperature. For comparison, treatment in air at 450°C for an hour was also conducted in this investigation.

Various carbon fibers were characterized with X-ray photoelectron spectroscopy (XPS). Analyses were performed on a PHI 1600 model surface analysis system with a 250 W Mg K_{α} X-ray (1253.6 eV) source at a pressure range of 10^{-8} to 10^{-9} Torr. The morphology of the carbon fibers was studied using an XL30 model environmental scanning electronic microscope (ESEM).

As described previously [8], an RTM-aided vacuum solution impregnation plus *in situ* anionic polymerization technique was employed to prepare the 3D braided carbon fabric-reinforced MC nylon (C_{3D}/MC) composites. The preparation procedures were identical to those described elsewhere [9]. The composites reinforced with untreated, air-treated, and gamma-radiated carbon fibers are denoted as U- C_{3D}/MC , A- C_{3D}/MC , and G- C_{3D}/MC , respectively. The resulting composites were characterized in terms of flexural, shear, and impact properties. The measurement procedures were identical to those described in [10]. All specimens were tested along braiding tows. At least five samples were tested for each sample group from which the mean values and standard deviations were calculated.

Fig. 1 shows the SEM photos of carbon fibers subjected to various surface treatments. As depicted in Fig. 1a, the untreated carbon fibers showed relatively smooth surfaces. Only a few shallow grooves were found. The amount and depth of the crevices on the surface of the carbon fibers increased after air-oxidation (see Fig. 1b). Similar observations have been reported by other researchers [11, 12]. Fig. 1c presents the morphology of the gamma-radiated carbon fibers. Interestingly, the surface features of the gamma-radiated fibers were close to that of the air-treated fibers. The only slight difference was that certain deep crevices were noted on the surface of the gamma-radiated fibers. Though the mechanisms of 'carving' were different between air-oxidation and gamma-ray radiation, the former being etching and the latter bombardment, the surface features were similar, suggesting both etching and bombardment processes occurred preferably at defect-rich sites.

It is well known that surface treatment changes not only the morphology but also the chemical structure of fiber surfaces. The surface chemistry of the gamma-radiated carbon fibers was characterized by XPS and compared to that of the air-oxidized ones. Fig. 2 shows the wide scan spectra of various carbon fibers. Carbon, oxygen, and nitrogen were detected in all cases. Table I gives the contents of the three elements. Apparently, oxygen content increased by 95 and 69%, respectively after air-oxidation and gamma-ray radiation. It was also noted that the air-treated fibers showed an increase in ni-

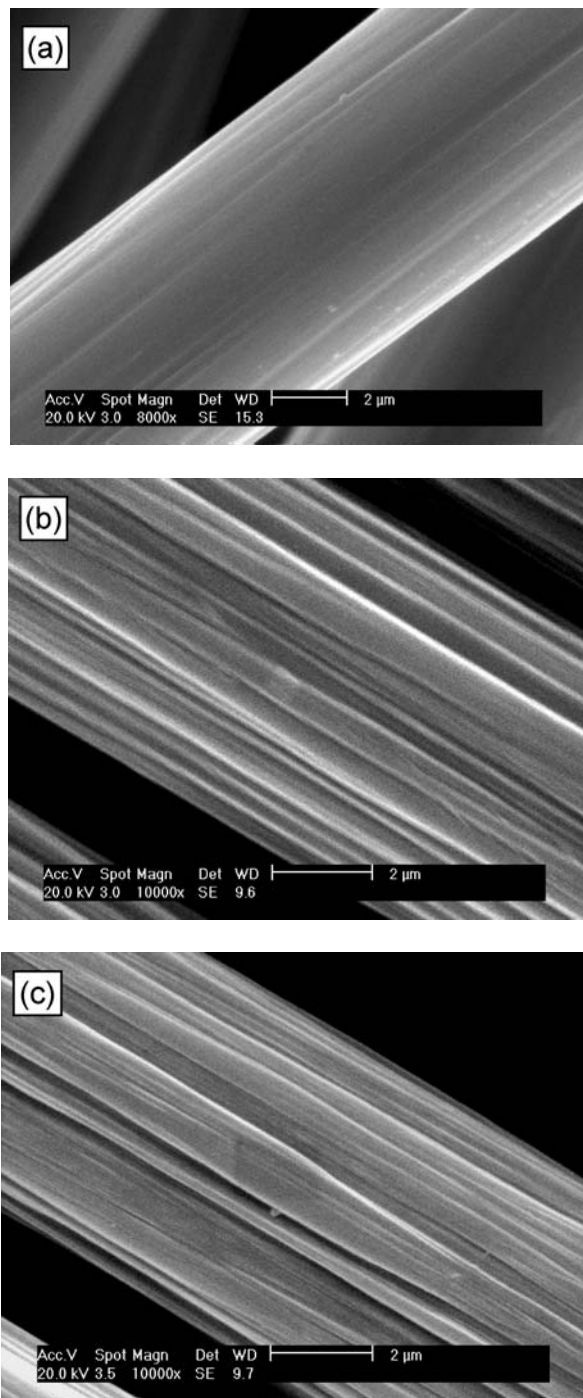


Figure 1 SEM photos of carbon fibers with different surface treatments: (a) untreated, (b) air-treated, and (c) gamma-radiated.

trogen content while the gamma-radiated carbon fibers showed a reduction.

Results of deconvolution of the C_{1s} spectra of the three carbon fibers are depicted in Fig. 3. Three peaks which represent graphitic carbon, (C-C, peak 1), hydroxyl group, (-OH, peak 2), and the carboxyl group (-COOH, peak 3) were found. Table II presents

TABLE I Elemental composition on various fiber surfaces

Fiber condition	C	O	N
Untreated	70.9 ± 1.5	22.8 ± 0.3	6.3 ± 0.1
Air-treated	47.2 ± 1.3	44.5 ± 0.1	8.3 ± 0.2
Gamma-radiated	55.6 ± 1.1	38.6 ± 0.3	5.8 ± 0.3

TABLE II Functional groups on different carbon fiber surfaces and their contents

Fiber condition	C—C	—OH	—COOH
Untreated	74.5 ± 5.2	23.0 ± 0.3	2.5 ± 0.2
Air-treated	55.7 ± 1.2	39.4 ± 0.6	4.9 ± 0.2
Gamma-radiated	80.2 ± 1.0	13.1 ± 1.0	6.7 ± 0.3

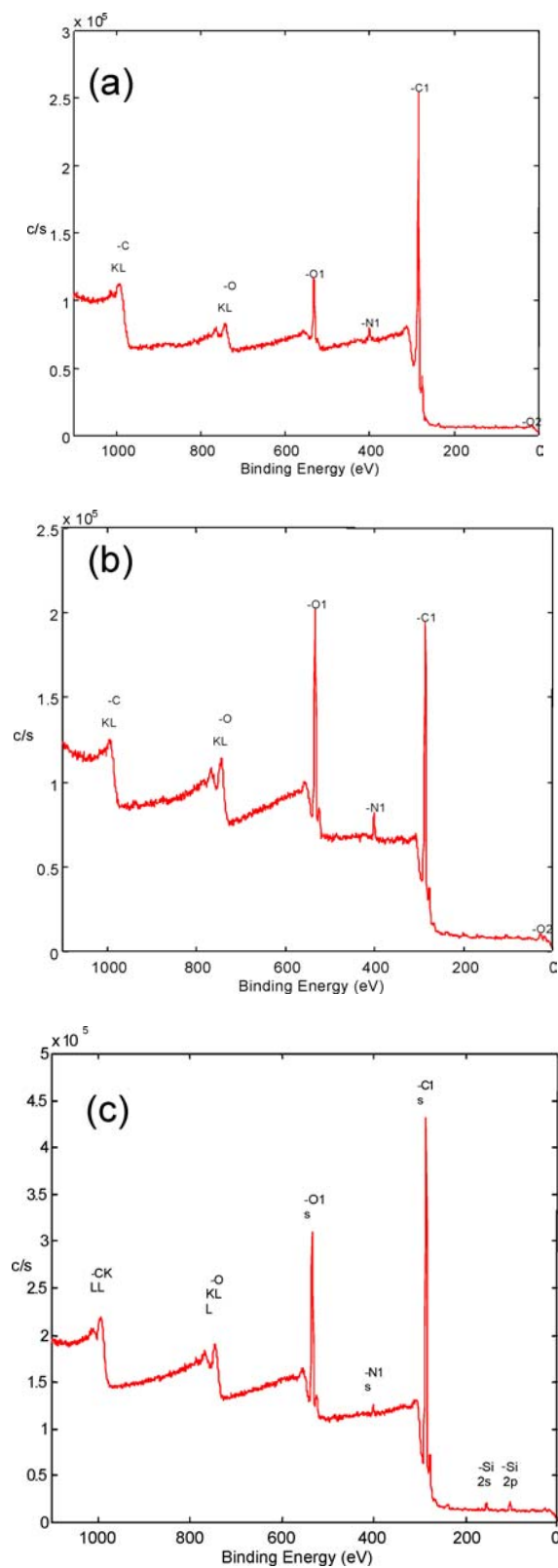


Figure 2 XPS wide scan spectra of carbon fibers: (a) untreated, (b) air-treated, and (c) gamma-radiated.

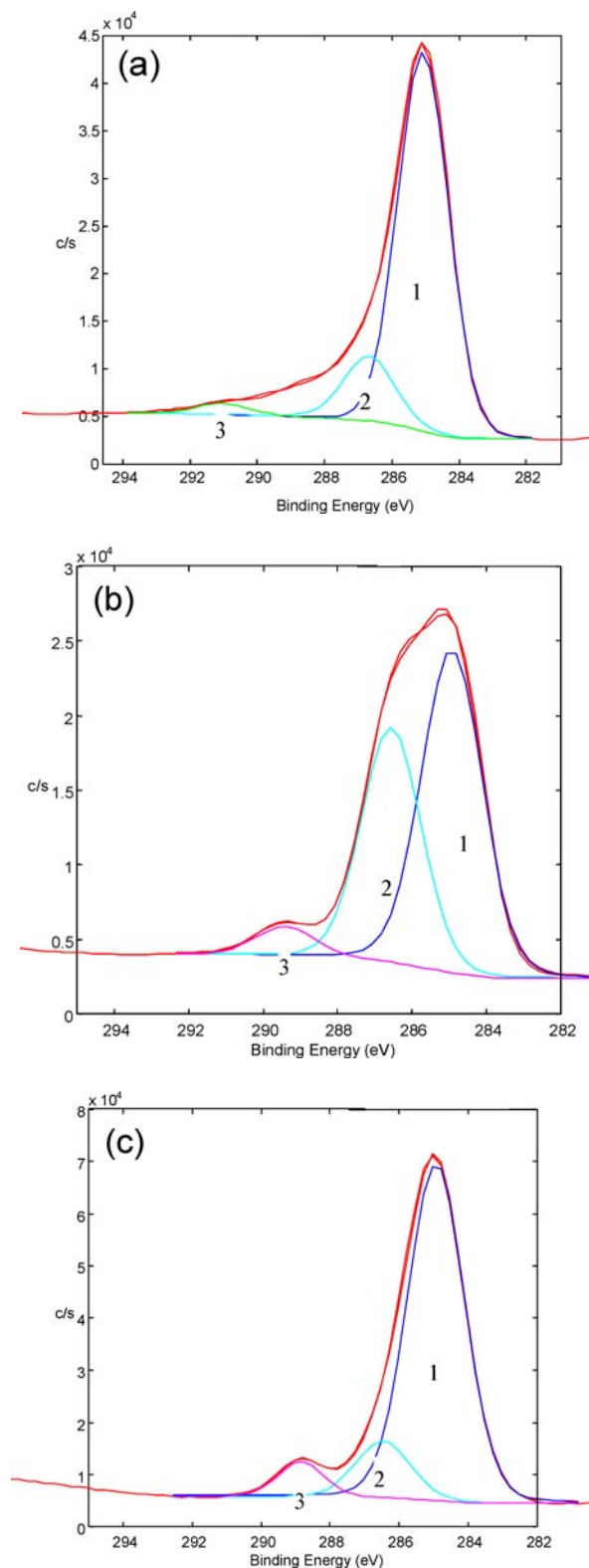


Figure 3 XPS spectra of C_{1s} region of carbon fibers: (a) untreated, (b) air-treated, and (c) gamma-radiated (1: C—C 2: C—OH 3: —COOH).

functional group contents measured by the deconvolution of the C_{1s} peak. The relative concentration of —COOH was increased by 96% from $2.5 \pm 0.2\%$ (untreated) to $4.9 \pm 0.2\%$ by air-oxidation and 1.68-fold from $2.5 \pm 0.2\%$ to $6.7 \pm 0.3\%$ by gamma-ray radiation. It was interesting to note that the changing pattern of the amount of —OH was opposite, the air-treated fibers showing an increase of 71% and the gamma-radiated ones a decrease of 43%.

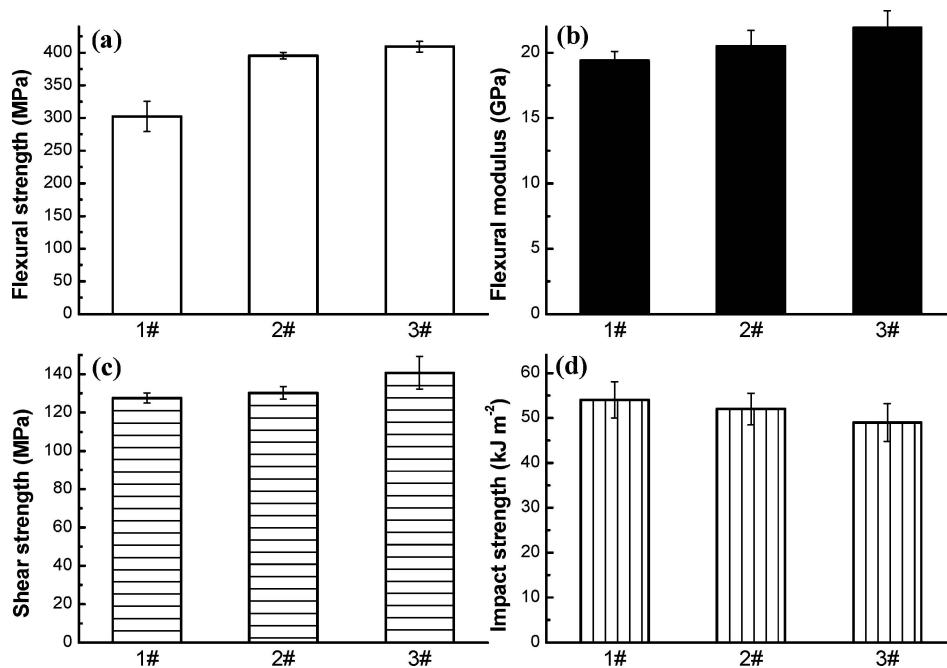


Figure 4 Mechanical properties of U-C_{3D}/MC (1#), A-C_{3D}/MC (2#), and G-C_{3D}/MC (3#): (a) Flexural strength, (b) Flexural modulus, (c) Shear strength, and (d) Impact strength.

Fig. 4 gives the mechanical properties (including flexural strength and modulus, shear and impact strengths) of the 3D MC nylon-based composites with various carbon fibers. The data in Fig. 4 demonstrate that after gamma-ray radiation, the flexural strength and modulus and shear strength increased by 36.2, 19.0, and 14.7%. The corresponding values for the composite samples reinforced with the air-treated carbon fibers were 31.7, 11.4, and 6.2%, respectively. The higher mechanical properties of the gamma-radiated fiber composites than the air-treated fiber composites are attributable to their higher interfacial adhesion (32 ± 2.9 MPa versus 24 ± 1.1 MPa [13] tested by an interlaminar shear test [2]). This suggests that gamma-ray radiation is more efficient in improving fiber-matrix adhesion than air-oxidation. SEM did not reveal any tremendous difference in morphology between the gamma-radiated carbon fibers and the air-treated carbon fibers. However, the contents of their functional groups differed considerably. As given in Table II, the gamma-radiated carbon fibers showed a higher content of the carboxyl group and a lower content of the hydroxyl group than the air-treated fibers. Hence, the higher interface adhesion strength of the G-C_{3D}/MC composites than the A-C_{3D}/MC composites may indicate that a reaction between the carboxyl group on the fiber surface and the amido group from the MC nylon matrix took place at fiber-matrix interfaces during the preparation process. Theoretically, the reaction between the carboxyl group and the amido group is possible [14]. The plausible reaction process is given in Fig. 5 [14]. However, direct evidence of the interface reaction requires further investigation.

It was noted that the G-C_{3D}/MC samples with higher interfacial adhesion showed lower impact strength than the A-C_{3D}/MC composites. This is understandable because a weaker interface usually produces greater toughness in composite materials [15]. This

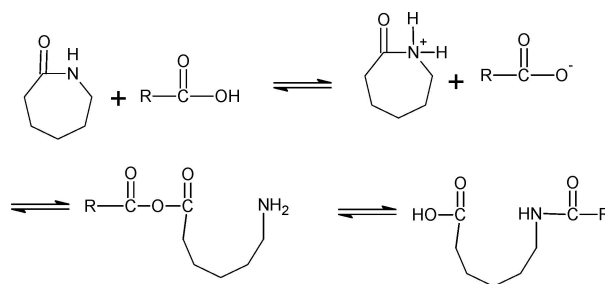


Figure 5 Reaction process between the carboxyl and the amido groups.

agrees well with results reported by various researchers [16].

It should be mentioned that the gamma-ray radiation process is far less widely employed than air-oxidation. More work is still needed to find optimum processing variables and to fully understand the mechanisms behind.

In conclusion, the composites with the gamma-radiated carbon fibers exhibited better flexural and shear properties than the composites with the air-treated and untreated fibers as a result of higher interfacial adhesion strength. The stronger fiber-matrix bonding is most likely due to the higher content of the carboxyl group on the surface of the gamma-radiated fibers. Our experimental results indicate that gamma-ray radiation is an effective approach of tailoring surface properties of carbon fibers.

Acknowledgements

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