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Interface improvement of carbon fiber/PMMA resin composites by fiber surface coating

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The surface of the carbon fiber (CF) has been pretreated by liquid phase deposition of microcrystalline cellulose (MCC). X-ray photoelectron spectroscopy, atomic force microscopy (AFM) and scanning electron microscopy (SEM) have been used to analyze and characterize the surface morphology and structure of carbon fiber, and the shear strength test and SEM observation of single fiber interface have been performed. The interfacial adhesion properties of carbon fiber composites have been investigated. The results have shown that the pretreated carbon fiber deposition increases the shear strength of the single fiber interface by 259.3%. The analysis results have shown that the improvement of interfacial shear strength has been related to the mechanical riveting between the fibers/resin and the force of the interface. Pretreatment has increased the carboxyl groups on the surface of carbon fibers and forms hydrogen bonds between carboxyl groups, thereby improving the interfacial properties of carbon fiber composites.

Keywords: Carbon fiber, Microcrystalline cellulose, Surface sizing treatment, Polymer-matrix composites (PMcs), Interfacial behavior, Impact property

1 Introduction

Carbon fiber has the advantages of high specific strength, high specific modulus, corrosion resistance and stability. Carbon fiber reinforced resin matrix composites are widely used in aerospace, marine and automotive industries[1-3]. The mechanical properties of carbon fiber composites depend not only on the inherent properties of the fibers and matrix, but also on the physicochemical properties of the interface between the fibers and the matrix. The non-polar and non-activated surfaces of carbon fibers[4] and the lack of chemical bonds and effective physical interactions between carbon fibers and the matrix prevent the interface from transferring loads from the matrix to the fibers. Therefore, the excellent mechanical properties of carbon fiber are not maximized[5-7]. In order to improve the bonding strength between the fiber and resin matrix in carbon fiber reinforced composites, the surface modification of carbon fiber has become a hot topic in recent years, such as strong acid treatment, electrochemical method, plasma treatment and oxidation method[8-16]. Meng *et al.*[17] used supercritical water and hydrogen peroxide to treat the surface of carbon fiber, and the interfacial shear strength (IFSS) and interlaminar shear strength (ILSS) of the composites were improved. This indicates that the interfacial strength between the treated carbon fiber/epoxy matrix is improved. Park *et al.* [18] performed anode surface treatment on carbon fibers and found that the increase in the number of oxygen-containing functional groups on the surface of the fibers is beneficial to the improvement of ILSS. Qian *et al.*[19] found that electrochemical anodizing in ammonium salt solution can improve the roughness of carbon fiber, and the relative content of polar elements such as oxygen and nitrogen also increased. After the electrochemical oxidation treatment, the ILSS value of the carbon fiber is greatly improved. Xie *et al.* [20] used He/O_2 to treat the surface of carbon fiber with ion, and found that plasma treatment can roughen the surface of the fiber. The dynamic water contact angle of carbon fiber decreases with the increase of treatment time. Among these carbon fiber treatment methods, plasma treatment methods have attracted great attention, mainly related to plasma damage to fiber damage. Polymethyl methacrylate (PMMA) is a biodegradable polyester material that can be completely degraded and has been used in food packaging, medical equipment and other fields. Due to the high price, low toughness and poor heat resistance of PMMA, its wider application is limited. Adding tough, degradable polymer materials to PMMA by blending[20-24].

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In order to improve the combination of PMMA and CF, current research focuses on CF surface treatment. For CF surface treatment, conventional methods include liquid phase oxidation, electrochemical oxidation, plasma oxidation, *etc*., but these methods have the disadvantages of complicated process flow and harsh reaction conditions. The effect on the combination is small. Therefore, there is a need to develop new methods for CF surface treatment and PMMA resin modification to improve the interface between PMMA and CF. In this study, Surface chemical elements of CFs were measured by X-ray photoelectron spectroscopy (XPS). The surface topographies of CFs before and after sizing treatment were observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The wettability and surface free energy of untreated CF and sized CF were characterized by dynamic contact angle (DCA). The fractured surface topographies of CFs/PMMA composites were observed by SEM.

2 Experimental Method

2.1 Materials

Carbon fiber was obtained by de-sizing commercial fibers. This is typically done by soxhlet extraction using acetone in the 80 °C with 72 h and thoroughly rinsed a couple of times with distilled water, and then dried in hot air.

2.2 Chemical Functionalization of CFs

The carbon fiber was first desmeared, washed with deionized water and placed in an oven (DZF-6020 vacuum drying oven) and dried at 40 °C for use as CF. The dried carbon fiber was pretreated with an oxygen plasma generated by a capacitively coupled RF glow discharge (HD-1A cold plasma modification processor) at a gas pressure of 27 Pa and a discharge power of 50 W. Then the CF was immersed in an aqueous $FeCl_3$ solution (catalyst, 2.5 mol/L) for 5 h, and then MCC for surface polymerization was added. After polymerization, the MCC coated carbon fibers were thoroughly washed with deionized water to remove monomer. MCC coating of the glass substrates was performed by spin coating from a MCC solution in chloroform (5% weight). A Chemat Technology, KW-4A spin-coater (Chemat Technology Inc.) wasused at 3000 rpm for 30 s. Coating of the stripped fiber by MCC was done by dip-coating into a MCC/chloroform solution (5%).

2.3 Characterization Techniques

XPS investigations were performed on a Kratos AXIS Ultra X-ray photoelectron spectrometer. The rubbers surfaces were analyzed with a monochromatic Al Kα X-ray source, operating at 1 keV and an emission current of 0.6 μA. The C 1s peak of each rubbers sample was analyzed by a peak synthesis procedure, which was estimated by a computer simulation.

Scanning electron microscopy (SEM) The surface of fracture morphology of carbon fibre/PI composite were studied using an AIS 2100 SEM (Seron technology, South Korea).

Before and after pretreatment by CSPM5500 full open microscopy processing platform (AFM) was used to characterize surface morphology of carbon fiber; surface morphology of carbon fiber after deposition and cross section of composite material were measured by S-4800 field emission scanning electron microscope (SEM). Tensile test along the fiber axis with WDW-20 microcomputer controlled electronic universal tester, tensile speed 0.2 mm/min, observation and statistics of fiber within 15 mm distance with YG002C fiber detection system.

The initial and the changes in static contact angle provide comparison of the spreading of MCC on different CFs. The fibers were placed on a horizontal stage and a water drop of 1 mm size was dropped on the CF using a syringe. The static contact angle of water was then measured using a reflecting microscope (AM4515, Anmo Electronics Co., Taiwan) in situ.

The test sample was prepared according to the single fiber crushing test standard: fix the single fiber before and after the modification to the two paper frames with the double-sided tape in advance, and place the paper frame on the glass plate. LY1534SP epoxy/Aradur3486 curing agent (weight ratio 10:3) was uniformly defoamed and then introduced into the paper frame. After 6 h at room temperature, press another glass plate and cure at 80 ° C for 3 h and then at 120 °C for 2 h. A single fiber composite is obtained.

The surface wettability of native and treated CF samples was measured by a contact angle measurement system in air at ambient temperature. The droplets of double de-ionized (DDI) water were applied on the sample surface by hand with a syringe.

Impact tests were performed on a drop weight impact test system (9250HV, Instron, USA). The specimen dimensions were 55 mm × 6 mm × 2 mm. The impact span is 40 mm. The drop weight was 3 kg, and the velocity was 1 m s^{-1}.

3 Results and Discussion

3.1 Element Analysis and Surface Topographies of CFs

Figure 1 shows the full spectrum of XPS for CF under different processing conditions. The surface elements and chemical composition of CF can be determined by X-ray photoelectron spectroscopy. Table 1 lists the surface element composition of the CFs at each step. As can be seen from Fig. 1, the untreated CF surface consists mainly of carbon, oxygen and a small amount of nitrogen (Fig. 1a). The height of the O1s peak relative to the C1s peak increased significantly after CF treatment (Fig. 1b), indicating that after the treatment of CF, oxygen was introduced into the CF surface to increase the oxygen content of the CF surface. Compared with CF (Fig. 1a) and p-CF (Fig. 1b), the height of the N1s peak (Fig. 1c) and (Fig. 1d) after MCC deposition polymerization is significantly increased. The introduction of nitrogen indicates that the CF surface has been successfully coated with MCC. The presence of the group on the surface of the carbon fiber was determined according to the position of the peak. The data in Table 1 shows that the content of oxygen-containing functional groups of CF fibers increased significantly after treatment, and the O/C ratio was 32.3%. The reason is that high-energy particles such as radicals, electrons, and excited atoms in the exchange intense energy with the surface of the carbon fiber, causing chemical bond cleavage and recombination on the surface of the carbon fiber to form an oxygen-containing functional group. The -COOH on the surface of the fiber after these treatments may form a hydrogen bond with the -NH.

SEM and AFM images of untreated CF and sized CF are shown in Fig. 2. As can be seen from Fig. 2a, the untreated carbon fiber CF has a smooth surface with a surface roughness of 10.0. It can be seen from Fig. 2b that a relatively small gully appears on the surface of the carbon fiber after treatment, which is

Table 1 — Surface element analysis of different CFs.

	element content (%)					
Samples	C	n	O	Si	O/C	Si/C
untreated CF	81.61	0.91	17.48	–	0.22	–
CF–COOH	70.01	2.38	27.61	–	0.38	–
CF–OH	74.18	1.53	24.29	–	0.32	–
sized CF	62.95	1.01	23.04	12.30	0.36	0.22

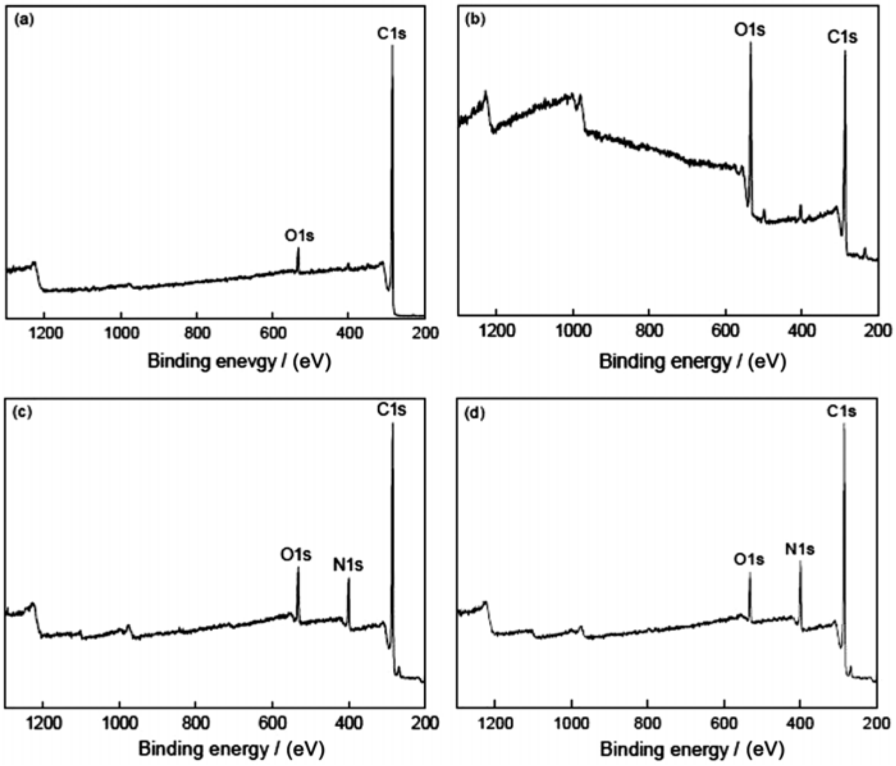

Fig. 1 — Wide-scan survey XPS spectra of different CFs.

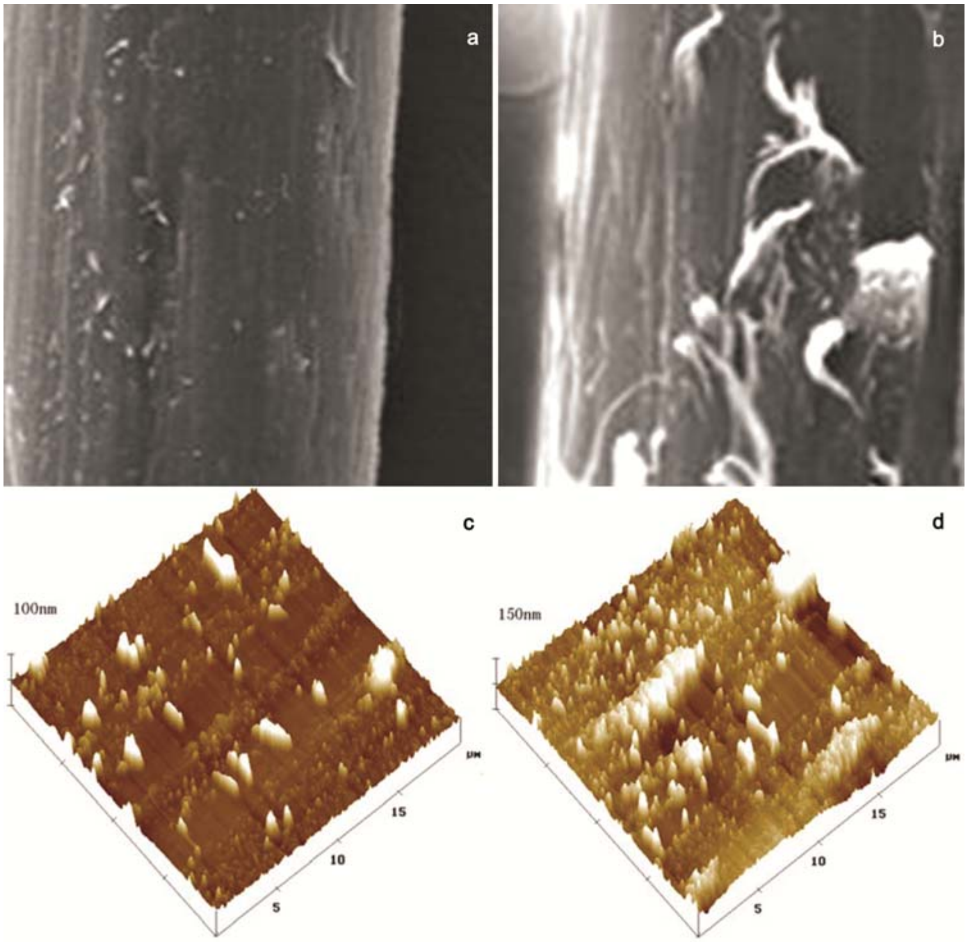

Fig. 2 — SEM, AFM images of different CF surfaces (a, c) untreated CF and (b, d) sized CF.

caused by the MCC surface treatment. The AFM topography of CF after MCC modification showed that the MCC layer was introduced on the surface of the fiber, and the surface roughness of the fiber increased. The MCC protrusion on the surface of the fiber greatly increases the surface roughness, so that the mechanical riveting between the fiber and the matrix resin is increased, thereby improving the interfacial bonding strength. This rough surface facilitates mechanical riveting with the matrix resin to improve the interfacial shear strength.

3.2 Dynamic Contact Angle and Wettability Analysis of CFs

The advancing contact angle (θ), the surface energy (γ), its dispersion component (γd), and polar component (γp) of untreated CF and sized CF are summarized in Fig. 3 and 4. As presented in Fig. 3, the surface energy of untreated CF was about 34 mN m−1. After sizing treatment, the surface energy of sized CF had a remarkable increase compared with untreated CF. The changes in chemical environment and topography of CFs surface affect fiber surface energy and its components[24]. Surface polar functional groups of CFs can enhance the polar component, while the dispersive component is dominated by the topography of the fiber. The CF samples were immersed in the resolution and etched, then the free radicals were produced at or near the CF surface which can interact to form the cross-links and unsaturated groups with the chain scission. The activated surfaces adsorbed the moisture and the radicals reacted with the oxygen.

Such enhancement indicated that after surface treatment, fibres became more hydrophilic and compatible with matrix. Given the nano sizing procedure, the fibre surface homogeneity was significantly improved compared to unsized fibres, hence one can say that sizing does not induce homogeneity which suggests that during sizing procedure the surface oxidation process can occur. Generally, the dispersive component is associated with van der Waals and other non-site specific interactions with epoxy sizing and epoxy matrix.

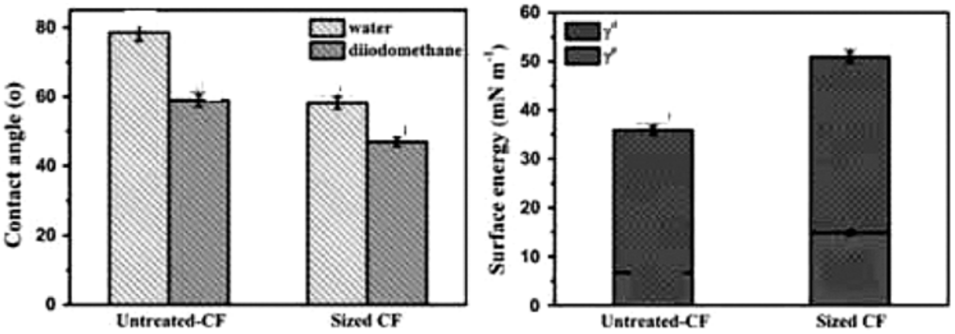

Fig. 3 — contact angles and surface energy of untreated CF and sized CF.

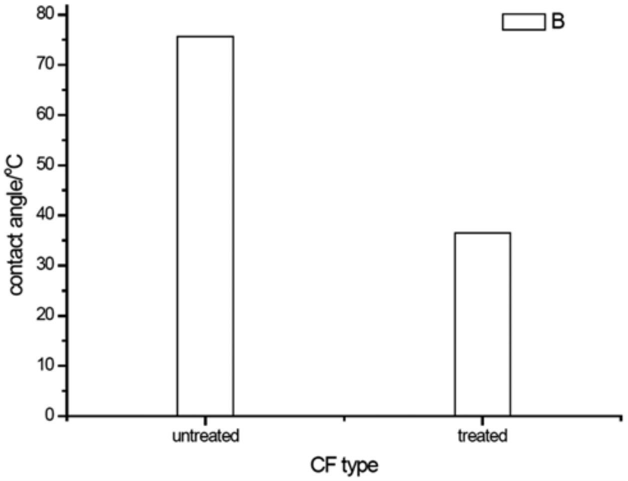

Fig. 4 — The water contact angle of CF sample.

Whereas, the polar component is correlated to dipole-dipole, dipole-induced, covalent/hydrogen bonding, and other site-specific interactions in which HNTs surface is able to form with epoxy sizing mainly through their aquaactivated hydroxyl groups on the surface.

3.3 Tensile Strength Testing of CFs

Figure 5 shows that the interlaminar shear strength values of the composites with surface treated carbon fiber are increased by 60% compared to that without treatment. It is proved that the better interfacial adhesion can be obtained through surface modification. The reasons attribute that the surface treatment was used as a method to bind oxygen functional groups on carbon fiber surfaces, which increase the interlock between the fiber and matrix, leading to the increase of the interlaminar shear strength of composites, which can effectively transfer the stress from matrix to the fiber, so the fiber can bring more reinforcement. Therefore, the ILSS of the composite reinforced by surface treated carbon fibers are considerably improved.

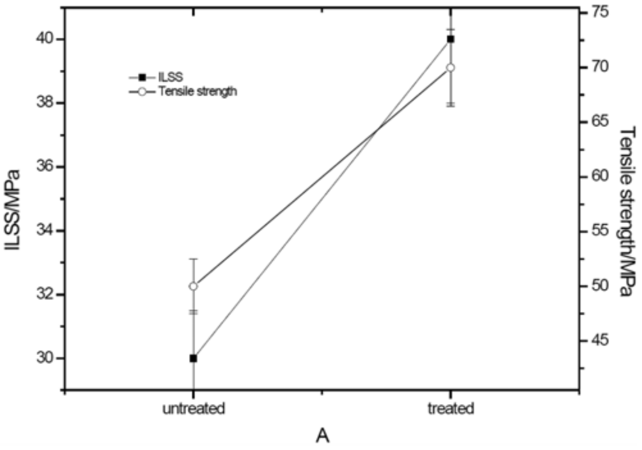

Fig. 5 — Tensile strength and ILSS of CF/PMMA composites.

It is seen in Fig. 5 that the surface treatments can improve the tensile properties of CF/PMMA composites, and surface treated carbon fibers yielded better results. The tensile strengths of surface treated CF/PMMA composites have been improved about 18 percent compared with that of untreated composite. Since the fiber types and fiber contents are identical in these specimens, the differences between the tensile properties shown in Fig. 5 reflect the effects of the different treatment methods.

3.4 Interfacial Property Testing of the Composites

Figure 6 shows a cross-sectional SEM image of a carbon fiber/PMMA composite treated by different methods. A SEM photograph of the CF/PMMA cross section (Fig. 6a) shows significant fiber debonding or adhesion failure, primarily related to the smooth and inert surface of CF. For the surface-treated CF/PMMA composite (Fig. 6b), the CF/PMMA composite interface also showed significant fiber pull-out. This is consistent with the above ILSS test results, and surface modification does not have a significant effect on the interfacial bond strength of the composite. From the cross-section of the

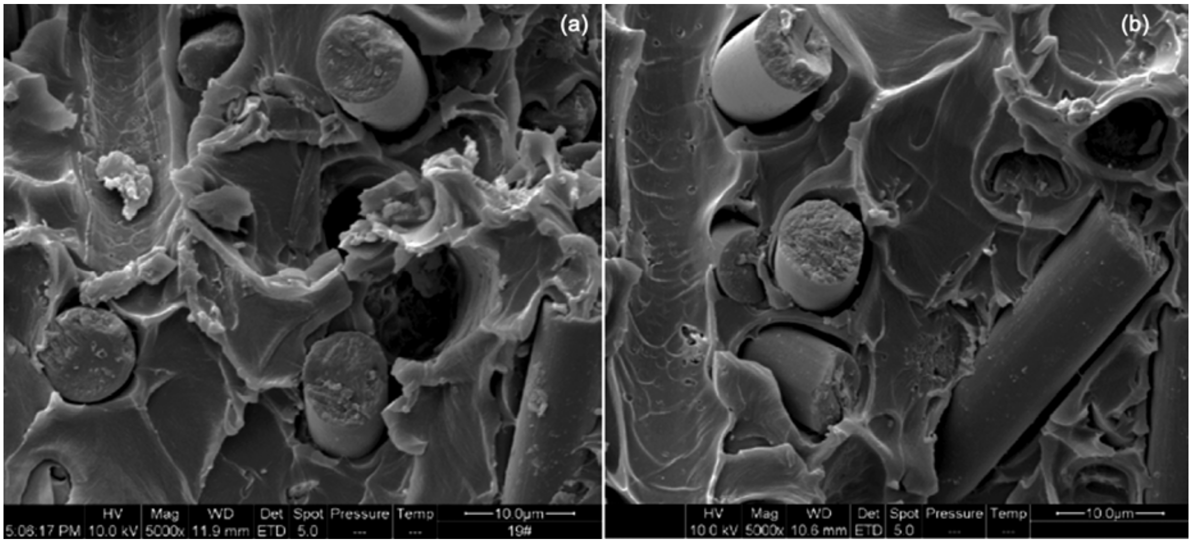

Fig. 6 — SEM morphologies of the fracture surface of composites reinforced with (a) untreated CF and (b) sized CF.

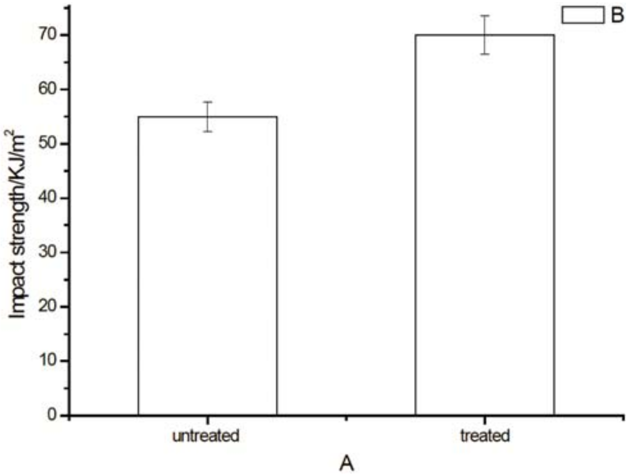

Fig. 7 — Impact test results of CF/PMMA composites.

CF/PMMA composite after modification (Fig. 6c), it can be seen that the phenomenon of fiber extraction is reduced. More importantly, for the SEM image of the modified CF/PMMA composite after pretreatment (Fig. 6d), not only the voids after fiber extraction but also the fibers are almost completely covered with PMMA resin. This indicates that the MCC treatment can significantly improve the interfacial adhesion between the fiber and the resin matrix, and the observation results are consistent with the single fiber ILSS results.

3.5 Impact Property Testing of the Composites

The treated composites exhibited good impact strength which is attributed to high crosslinking density composed of C-C bonds rendering the material more stable(Fig. 7). This behavior appears to be related to the difference in wettability and interfacial properties as reflected in IFSS.

4 Conclusions

Surface pretreatment improves the interfacial adhesion between the MCC coating and the carbon fiber, and is related to the mechanical lock between the fiber/resin and the interaction of hydrogen bonds between the interfaces. The MCC layer was introduced into the interface zone of the carbon fiber/PMMA composite after two-step treatment, which improved the interfacial shear strength of the carbon fiber and the matrix and the interfacial bond strength of the composite. On the one hand, the surface of the carbon fiber coated with the MCC layer is rough and the average roughness is improved, which is beneficial to mechanical riveting between the fiber and the resin, thereby improving the interface properties of the composite. On the other hand, surface pretreatment increases the number of polar groups, in particular the carboxyl group content. The carboxyl group forms a hydrogen bond with the introduced MCC macromolecule, which facilitates the transfer of stress at the interface, thereby greatly increasing the bond strength of the interface.

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