Applied Surface Science 328 (2015) 241–246

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Effect of plasma surface treatment of recycled carbon fiber on carbon fiber-reinforced plastics (CFRP) interfacial properties

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ARTICLE INFO

Article history:
Received 10 July 2014
Received in revised form
30 November 2014
Accepted 1 December 2014
Available online 9 December 2014

Keywords:
Recycled carbon fiber
Plasma surface treatment
CFRP
Interfacial properties

ABSTRACT

We studied the effects of plasma surface treatment of recycled carbon fiber on adhesion of the fiber to polymers after various treatment times. Conventional surface treatment methods have been attempted for recycled carbon fiber, but most require very long processing times, which may increase cost. Hence, in this study, plasma processing was performed for 0.5 s or less. Surface functionalization was quantified by X-ray photoelectron spectroscopy. O/C increased from approximately 11% to 25%. The micro-droplet test of adhesion properties and the mechanical properties of CFRP were also investigated.

1. Introduction

Global energy consumption increases every year. In particular, energy consumption by the transport sector has grown exponentially. Most energy for transport has been provided by oil for a long time. Hence, it is necessary to develop energy-efficient vehicles. Carbon fiber-reinforced plastics (CFRP) are among the most effective solutions, and they reduce the weight of vehicles. The use of CFRP is growing in various applications: not only aircraft but also automobiles. This is because of its low density and high mechanical strength compared to steel [1,2]. However, CFRP is not suitable for general industrial usage because of its high price, long processing times and difficulties in both secondary processing and recycling [3]. To reduce the price of CFRP for manufacturing, the use of recycled CF would be the most promising approach [4,5].

Despite the advantages of recycled CF, there are differences from freshly produced CF. While fresh CF is sized by the polymeric component, recycled CF loses the sized layer. Additionally, recycled CF generally forms a bundle of fibers. In particular, changes in the surface characteristics of recycled CF impair the mechanical properties of the resulting CFRP due to reduced interfacial adhesion between recycled CF and the polymer matrix [6–8]. Adhesion between CF and the polymer matrix in a composite is a primary factor in stress transfer from matrix to fiber. Poor adhesion results from the chemically inactive surface of the fiber. Thus, surface treatment of recycled CF may improve adhesion, and thus the mechanical properties of CFRP. Various modifications of CF have been studied: chemical oxidation [9–11], electrochemical treatments [12–17], high temperature atmospheric oxidation [18–20], surface functional group grafting procedures [20–22] and plasma treatments [23–29].

Here, plasma treatment was used to improve adhesion between recycled CF and the polymer matrix. Plasma is a quasi-neutral gas of charged and neutral particles [30] containing cations and electrons. These charged particles activate or react with the CF surface. Modified polypropylene (PP) was used as a matrix polymer to define the interfacial properties of CFRP. Homo-PP and maleic anhydride grafted polypropylene (MAPP) were mixed to give 0.5% by volume (% v/v) maleic acid. Because there is no interfacial adhesion between recycled CF and homo-PP, the differences before and after CF surface treatment depend on the conditions [31,32].

2. Experimental

2.1. Materials

2.1.1. Recycled carbon fiber

Recycled CF supplied by Hitachi Chemical Co. (Tokyo, Japan) was used in this study (Fig. 1.). This recycled CF was regenerated from CFRP aircraft components using depolymerization under ordinary pressure [33]. The origin of this recycled CF was PAN-based carbon fiber (Torayca T700SC, Toray Industries, Tokyo, Japan).

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http://dx.doi.org/10.1016/j.apsusc.2014.12.012
0169-4332/

Fig. 1. Recycled CF from aircraft components.

2.1.2. Polypropylene

Homo PP (J3000GP, MFR = 30) was manufactured by Prime Polymer Co. (Tokyo, Japan). The other PP was maleic anhydride grafted polypropylene (MAPP) (Yumex 1010) supplemented with 10% v/v maleic anhydride from Sanyo Chemical Industries (Kyoto, Japan). To create pellets for the microdroplet and CFRP specimens, homo-PP and MAPP were mixed to give 0.5% v/v maleic acid modification ratio using a mixer (Labo Plastomill 10C100S90, Toyo Seiki, Japan). Kneading conditions were 10 rpm at 200 °C for 5 min.

2.2. Plasma surface treatment

The principle of plasma surface treatment is to insert dielectric insulation between metal electrodes, applying high frequencies and voltage. Electrons emitted from the electrodes by corona discharge are accelerated in an electric field [28,34]. In the high-energy space between electrodes during discharge, various gas phase reactions occur. In this study, the plasma treatment machine for the recycled CF was from E-square Corporation Ltd. In this experiment, a radio frequency (RF) power supply and alternating-current (AC) source were used at 0.8 kW. As shown in Fig. 2, this process has the advantage that many samples, or very long samples, can be treated reliably because of the continuous conveyor belt. Samples can be plasma processed in a steady stream by semi-automated conveyor belt.

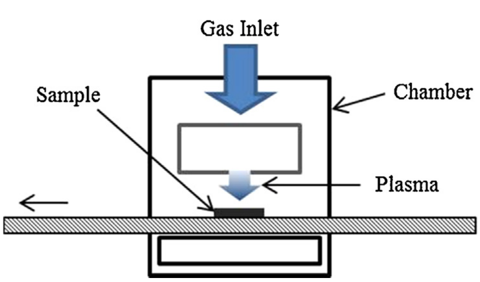

Fig. 2. Schematic illustration of the plasma process for surface treatment of samples.

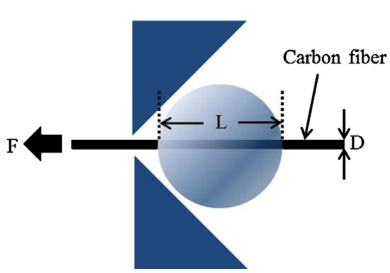

Fig. 3. Schematic of the microdroplet test.

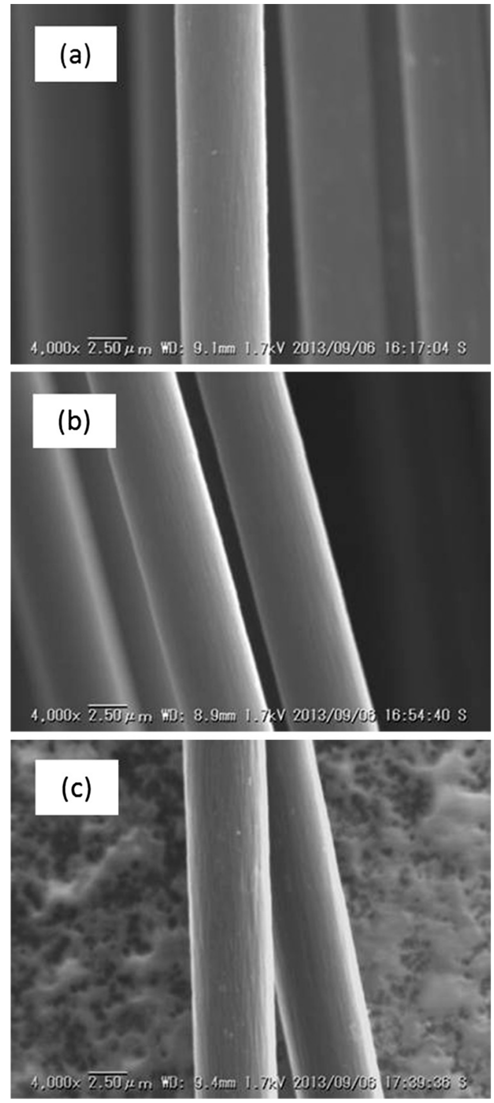

Fig. 4. Surface morphologies of carbon fibers: (a) fresh CF, (b) recycled CF and (c) after treatment.

The dry air flow rate was set at 0.34 L/min with N_2 carrier gas (100 L/min). Samples were treated with plasma for six irradiation times (0, 0.167, 0.333, 0.500, 5, and 10 s).

2.3. Characterization

2.3.1. Scanning electron microscopy (SEM)

The CF surface and the fractured surface of CFRP were examined by SEM (VE-8800, Keyence, Japan). Fiber samples were secured on the copper plate with conductive adhesive.

Table 1
Effects of plasma treatment on surface elemental composition (plasma treatment time: 0.500 s).

Samples	Atomic percent				
	C	O	N	Si	O/C ratio
Fresh CF	75.18	23.03	0.97	0.82	0.31
Before treatment	87.72	10.22	1.57	0.49	0.12
After treatment	78.19	19.76	1.64	0.41	0.25

Table 2
The surface elemental composition of plasma-treated recycled CF treated in the longitudinal direction (plasma treatment time: 0.500 s).

Distance (d) μm	Atomic percent				Atomic ratio O/C
	C	O	N	Si	
0	78.56	19.30	1.72	0.42	0.25
500	77.56	20.25	1.67	0.52	0.26
1000	77.07	20.76	1.73	0.44	0.27
1500	77.70	20.52	1.58	0.20	0.26
2000	76.53	21.62	1.75	0.10	0.28
2500	77.32	20.62	1.59	0.46	0.27
3000	76.44	21.41	1.65	0.50	0.28
3500	78.41	19.54	1.72	0.33	0.25
4000	80.46	17.58	1.43	0.52	0.22
4500	80.02	17.84	1.62	0.53	0.22
5000	80.04	17.92	1.58	0.46	0.22

2.3.2. X-ray photoelectron spectroscopy (XPS)

XPS was undertaken using a K-Alpha (Thermo Fisher Scientific Inc.). XPS spectra were obtained using an Al-Ka (1486.7 eV) monochromatic X-ray source. Operating vacuum was approximately 5.0×10^{-8} mbar with a detection angle of 0°.

2.3.3. Microdroplet test

Micro-mechanical experiments are important for evaluation of adhesion between fiber and polymer matrix [35,36]. To evaluate adhesion between plasma-treated recycled CF and polymer, a microdroplet test was conducted as shown in Fig. 3. After making spherical modified PP microdroplets on a single CF at 180 °C, the specimen was loaded between two blades at 25 °C. At this time, two-dimensional measurement software (AR-U120P3MF, ARTRAY

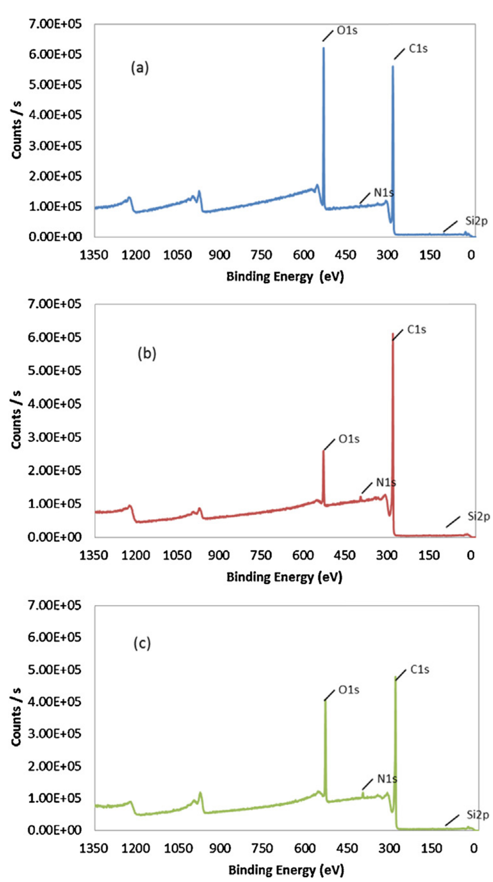

Fig. 5. XPS survey spectra of fibers: (a) fresh CF, (b) before treatment and (C) after treatment.

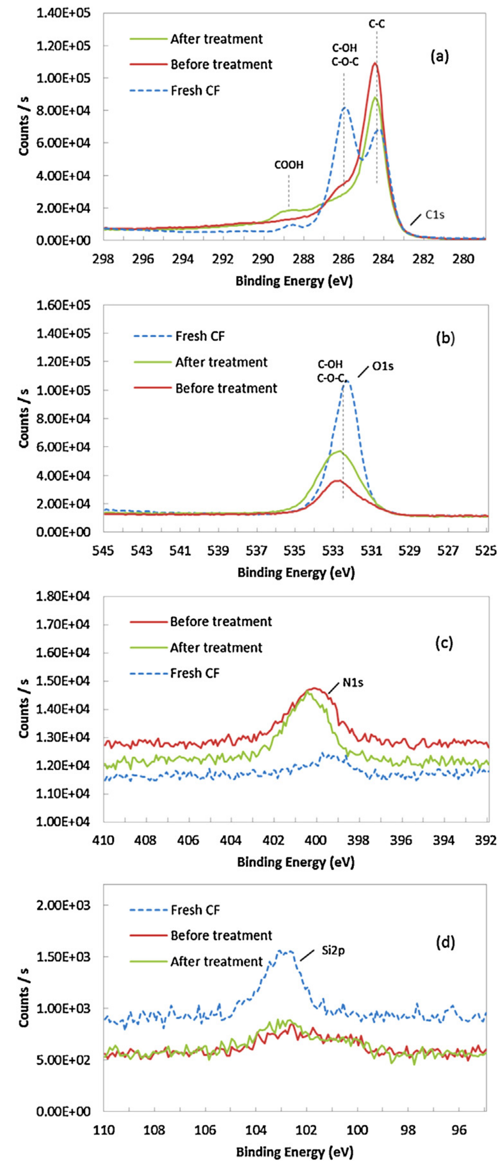

Fig. 6. XPS spectra of CF: (a) C 1s, (b) O 1s, (c) N 1s and (d) Si 2p.

Co., Ltd., Japan) measured the length (L) of the embedded CF. Interfacial shear strength was then measured during a unidirectional pulling process at a speed of 0.12 mm/min. Interfacial shear strength (τ) was calculated using the following equation.

$$\tau = \frac{F}{\pi DL} \quad (1)$$

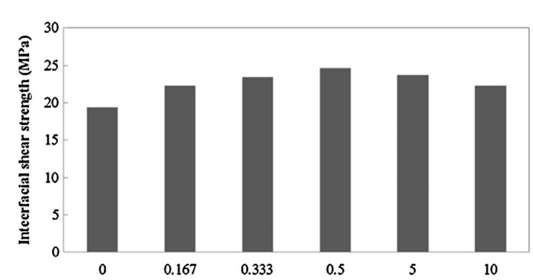

Fig. 7. Interfacial shear strength of recycled CF after various irradiation times.

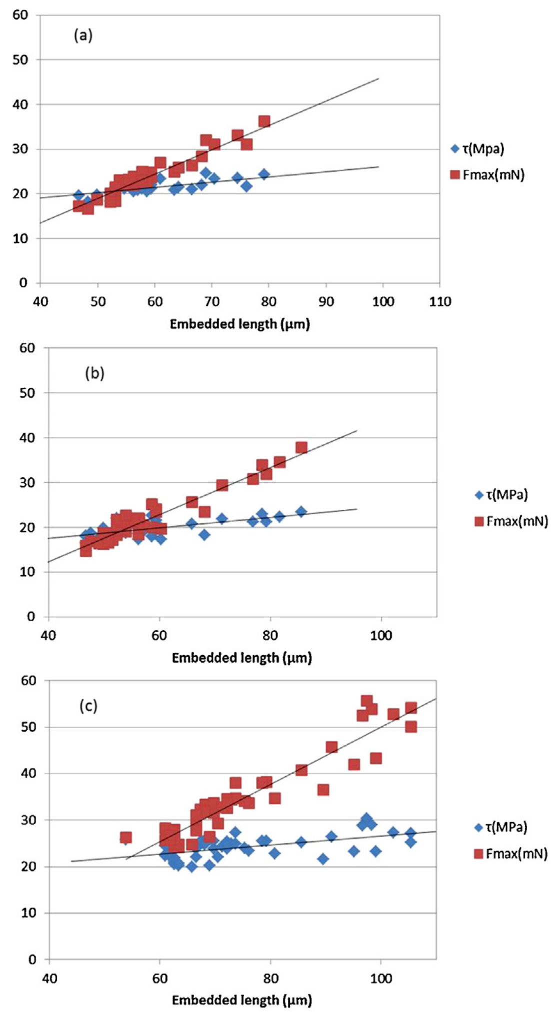

Fig. 8. Interfacial shear strength under different conditions: (a) before treatment, (b) 0.167 s treatment and (c) 0.500 s treatment.

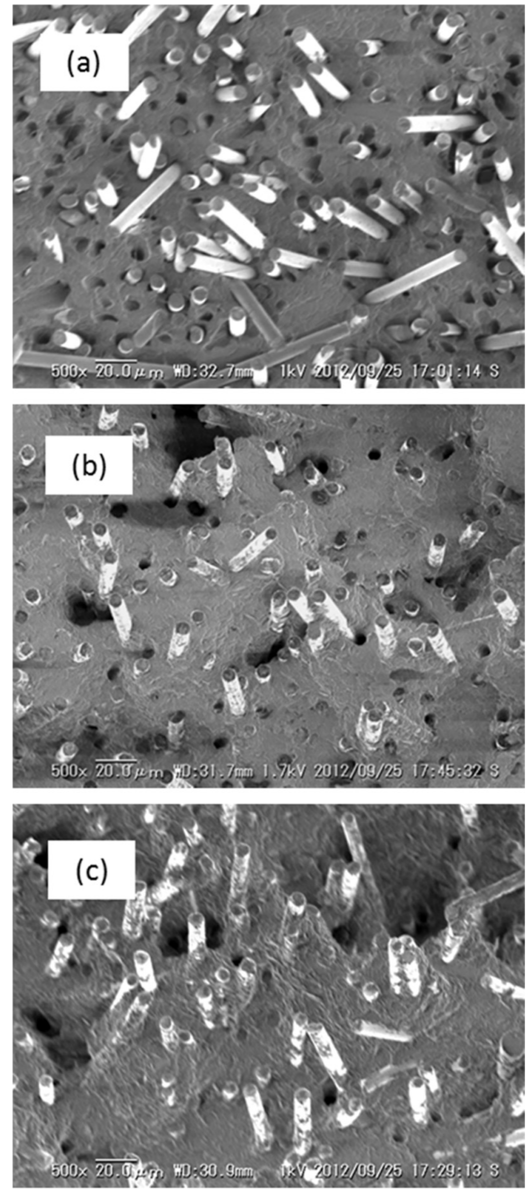

Fig. 9. Scanning electron micrographs of the fractured surfaces of CF/PP composites containing 15% v/v CF: (a) before treatment, (b) after treatment and (c) fresh CF.

2.4. CFRP specimen preparation

To create specimens for mechanical testing, the volume fraction of CF was 15% v/v in CFRP. Kneading conditions to make CFRP intermediates were 10 rpm at 200 °C for 5 min. Furthermore, recycled CF was cut to 7 mm using a cutter, making it equal in length to the fresh CF (T700SC). Injection molding (PM1 by Toyo Seiki) was conducted to prepare a test piece for a 3 point bending test. CFRP resin was injected through a cylinder after heating to 200 °C in a mold (85 mm × 10 mm × 2 mm) at 100 °C. To confirm the mechanical properties of CFRP specimens, a bending test was performed using an AGS-X (Shimadzu Autograph). The ratio of thickness to span length was 1:16. Crosshead speed was 2 mm/min.

3. Results and discussion

3.1. Surface morphology

The surface morphologies of fresh CF (Fig. 4a), recycled CF (Fig. 4b) and recycled CF treated with plasma for 0.500 s (Fig. 4c) were examined by SEM at 4000× magnification. Fresh CF and recycled CF showed comparatively smooth surfaces (Fig. 4a). Compared with Fig. 4b, Fig. 4c shows that the surface grooves have been slightly deepened, and more superficial grooves generated, by plasma surface treatment. Plasma-treated CF has a slightly roughened surface, which may be caused by the etching effects of plasma. However, fiber surfaces were not etched drastically with plasma treatment. Plasma treatment may not have caused deep etching because of the short exposure times. Therefore, under these experimental conditions, the predominant effect of plasma treatment was not on surface morphology, but rather on chemical composition.

3.2. Surface analysis

The elemental surface composition of the fibers by XPS analysis is presented in Table 1. The O/C level after treatment was two times higher than before treatment. Despite only 0.500 s of plasma treatment, a significant increase of O/C level was achieved in recycled CF. Table 2 shows O/C levels and detailed atomic percentage measured along the longitudinal direction on surface. The purpose of the measurements in Table 2 is to test continuous plasma treatment in a longitudinal direction. The O/C ratios of 11 points in the sample imply that the conveyer system enables consistent treatment of long or multiple samples in a short time.

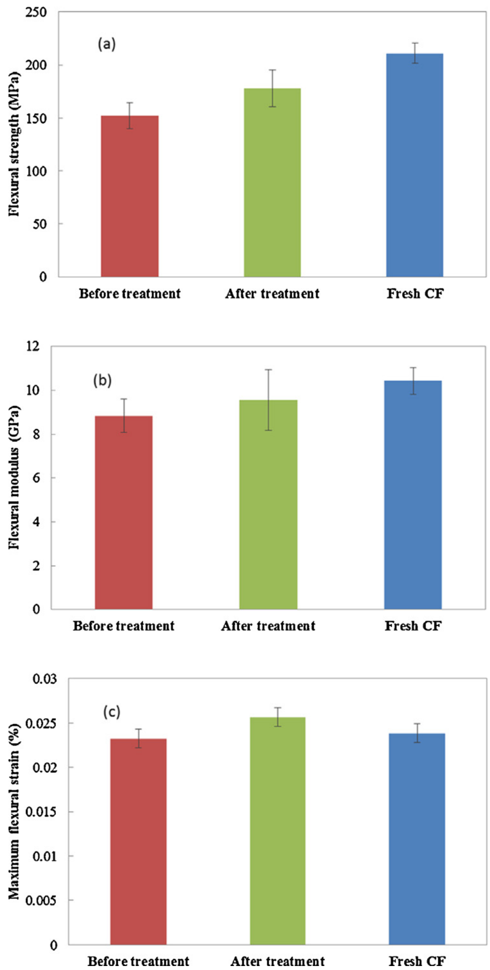

Fig. 10. Flexural properties: (a) strength, (b) modulus and (c) maximum strain.

Fig. 5 shows wide-scan spectra obtained for the elements in CF. For fresh CF (Fig. 5a), the high intensity of the O 1s peak is due to the polymeric sizing layer. Following plasma treatment of recycled CF, a significant increase was observed at 531 eV, providing evidence of increased oxygen on the fiber surface (Fig. 5b and c).

Fig. 6a shows the broad carbon peaks of CF observed from 280 to 298 eV. These peaks can be attributed to several surface functional groups, for instance C—C (284.7 eV), C—OH (286.5 eV), C=O (287.5 eV) and COOH (288.9 eV). Fig. 6a indicates that plasma treatment introduced polar oxygen-containing functional groups on to the recycled CF. In particular, after treatment samples showed significantly more COOH groups, which are removed during recycling [37]. Moreover, the oxygen spectra in Fig. 6b are consistent with the surface functional groups in the plasma-treated samples. Both before and after treatment, CF exhibited a single broad O 1s peak at 532.6 eV, which falls in the fingerprint region for both hydroxide and ether groups. The O 1s peak was lower after recycling than in fresh CF, but rose again after plasma treatment. On the other hand, the N 1s and Si 2p peaks showed no significant differences (Fig. 6c and d). This implies that plasma treatment introduces oxygenated functional groups on recycled CF, which may enhance adhesion between polymer and CF in CFRP.

3.3. Adhesion

Fig. 7 shows the interfacial shear strength of recycled CF after various plasma treatment times. Interfacial shear strength increased up to 0.500 s processing. Beyond 0.500 s, the interfacial shear strength slightly decreased after 10 s treatment. This may be due to the etching effect reducing the surface area for adhesion between CF and PP after processing times over 0.500 s.

Fig. 8 shows interfacial shear strength under different conditions by microdroplet testing. From the scatter plot of interfacial shear strength and embedded length, interfacial shear strength appears to depend on embedded length. The distribution of embedded length after treatment (Fig. 8b and c) is broadened, and interfacial shear strength is improved, relative to before treatment (Fig. 8a). A cross-sectional picture of the CFRP confirms that microstructure is influenced by plasma treatment. As shown in Fig. 9, adhesion is better after treatment (Fig. 9b) than before (Fig. 9a). Many holes formed in the composite by pulling CF out of the matrix resin, as shown in Fig. 9a. Furthermore, it is not easy to discern attached matrix resins on the CF surface. This suggests that adhesion between CF and PP is worse before than after treatment (Fig. 9b). Thus, these adhesion results imply that interfacial adhesion between CF and PP is improved by treating CF with plasma.

Fig. 10 shows the results of three point bending tests of CFRP. Flexural strength (Fig. 10a) after treatment was approximately 17% higher than before treatment. Flexural modulus also increased after treatment (Fig. 10b). The mechanical properties of the treated specimen were close to those of fresh CF.

4. Conclusion

In this study, plasma treatment of the surface of recycled CF was investigated. The most significant result was that, even after very brief plasma treatment, this process generated oxygenated functional groups on the surface and resulted in better adhesion between recycled CF and the polymer matrix. The results of surface analysis suggest that this process can enhance the surface activity of recycled CF. These characteristics may help to overcome the drawbacks of recycled CF by restoring mechanical and chemical properties to levels approaching those of fresh CFRP.

Acknowledgments

This study was conducted as part of the Japanese METI project “Future Pioneering Projects/Innovative Structural Materials Project” from financial year 2013. The authors would like to express sincere appreciation to the project members, who provided valuable information and useful discussions.

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