Improved Mechanical Properties of PMMA Composites: Dispersion, Diffusion and Surface Adhesion of Recycled Carbon Fiber Fillers from CFRP with Adsorbed Particulate PMMA

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Abstract

In this study, composite materials were fabricated using the thermoplastic resin poly(methyl methacrylate) (PMMA) and recycled carbon fibers obtained by pulverizing carbon fiber reinforced plastics (CFRP). PMMA particles were adsorbed on the carbon fiber surfaces *via* electrostatic interactions, to promote the interfacial adhesion between the carbon fibers and the PMMA resin and thereby improve the dispersion of the fibers in the resin. This enhanced the mechanical properties of the composites; the yield stress and elastic modulus of the composite. As a result, the yield stress and elastic modulus of the composite improved owing to the prevention of void formation in the composite resulting from the chemical incompatibility between the filler and the resin and better dispersion of the PMMA-adsorbed carbon fibers in the resin compared to that in the unmodified fibers. This method can be applied to fabricate high-quality composites consisting of a combination of other resins and fillers.

Keywords: Recycled Carbon Fiber, Surface Adhesion, Composite, Dispersion, Diffusion

1. Introduction

Carbon fiber reinforced plastics (CFRP) are light, strong, and one of the most well-known composite materials used in industrial fields, especially the space industry. The scale of their production is increasing. Because most of its waste is used as an earth filling, it is essential to conceive novel and useful methods for using recycled carbon fibers. Various techniques have been developed for obtaining recyclable carbon fibers from CFRP [1]. Particularly, pulverization has been a preferred method to obtain short fibers from longer carbon fibers [2] or CFRP [3]. Further, one of the methods for using recycled milled carbon fibers is as a filler in polymer resins [4, 5]. In this case, the interaction or surface adhesion between the fibers and the resin matrix, and the dispersion of the filler in the resin significantly affect the mechanical properties of the composite materials [6-9]. The stress concentration induced by poor dispersion of the filler in the resin matrix deteriorates its mechanical property [10, 11].

In a recent study, we showed that the adsorption of poly(methylmethacrylate) (PMMA) particles on carbon fiber surfaces through electrostatic interaction could enhance the surface adhesion between the carbon fibers and the PMMA resin [12, 13]. Recycling of a thermoplastic resin like PMMA is advantageous [14]. Therefore, the objective of this study is to use a surface modification method similar to that used in our previous report to disperse the recycled, short carbon fibers in the PMMA matrix to enhance its mechanical properties.

The fiber distribution in each portion of the composite was observed by optical microscopy to evaluate the dispersion and diffusion of the carbon fibers in the matrix resin. Furthermore, we investigate the influence of the adsorption of the PMMA particles on the surface of the recycled carbon fibers, through electrostatic interaction, on the mechanical properties of the composite using a tensile test apparatus.

2. Experimental

2.1 Materials

Recycled carbon fibers were obtained from CFRPs by pulverizing them using a microfine grinder drive (MF 10 basic, IKA). The lengths of the obtained fibers were measured using an optical microscope (KH-8700, HiROX). The fiber length distribution is shown in **Fig. 1**.

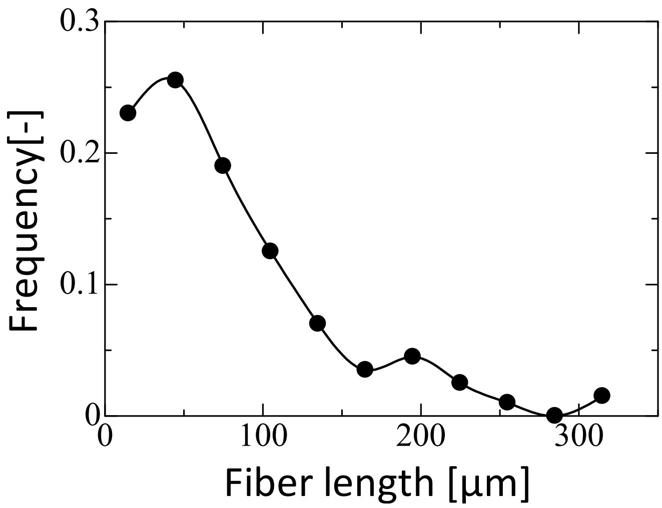

Fig. 1. Distribution of the fiber lengths of the recycled carbon fibers.

Water used for soap-free emulsion polymerization reactions was purified using a purification system (WG250, Yamato Scientific) followed by bubbling with nitrogen gas, to remove any dissolved oxygen. Methyl methacrylate (MMA, Tokyo Chemical Industry) was used as the monomer in the polymerization process. 2,2'-azobis(2-methylpropionamidine) dihydrochloride (V-50, Sigma Aldrich) was used as the radical initiator without further purification and this enabled the particles to be positively charged [15, 16]. The experimental conditions employed in the polymerization process [17] are listed in Table 1. The temperature of the reactor and the rotation speed of the impeller in the reactor were controlled by a magnetic stirrer equipped with a heater (RCH-20L, EYELA). The polymerization reaction time was set to 6 h. The average size and zeta potential of the synthesized PMMA particles were measured to be 170 nm and + 42.8 mV, respectively.

The recycled carbon fibers were immersed in the polymer colloid using water solvent to allow the polymeric particles to adsorb onto their surfaces, through electrostatic interactions [12].

Table 1. Experimental conditions of polymerization

Water	Initiator	Monomer	Reaction temperature	Rotation speed	Reaction time
75 g	8.12 mmol/L	66.7 mmol/L	70 ^{o}C	130 rpm	6 h

2.2 Analysis and evaluation of the mechanical properties of the composite

Morphologies of the carbon fibers modified with PMMA particles and cross-sections of PMMA composites containing the carbon fibers were examined by a field emission scanning electron microscope (FE-SEM, JSM-7500FA, JEOL). The specimens were coated with thin osmium films by vapor deposition (Osmium Plasma Coater OPC60A, Filgen), before FE-SEM observations.

To evaluate the dispersion and diffusion of the recycled carbon fibers in the PMMA composite, the location of the fibers sandwiched between thermoplastic PMMA films (HBS006, Mitsubishi Rayon) was investigated. First, a 2 μL droplet of a carbon fiber suspension (40 mg in 1 mL of ethanol) was placed at the center of the PMMA film as shown in **Fig. 2,** and ethanol was evaporated at 75 ^{o}C. Then, the recycled carbon fibers sandwiched between the PMMA films were heated at 250 ^{o}C for 50 min, and pressed at 81.8 MPa for 40 min by a heat press machine (II-S, ESTER SANGYO CO,. LTD.). The composite film was then quenched by placing it between two water-cooled steel plates at 25 ^{o}C. Before fabricating the composite by hot pressing, the recycled carbon fibers were located at the center of the film, as shown in **Fig. 3a**. After hot pressing, the recycled carbon fibers in the film had diffused to a wider area due to pressing. When the hot pressing process for short time was examined, the recycled carbon fiber stayed at the initial position and the bubbles were generated in the composite. Shear stress effect by pressing could not make the carbon fibers widespread throughout the composite. Hence, in the present study, the heating process required longer time to promote the diffusion of the recycled carbon fiber and prevent the generation of the bubbles in the composite.

To measure the translation distance of the recycled carbon fibers in the resin after hot pressing, the surface of the composite was divided into three areas as shown in **Fig. 3b**. Each area was composed of small cells of 3 mm × 3 mm. The lengths of the carbon fibers in each cell were measured using an optical microscope (KH-8700, HiROX) and the fiber length distribution in each area was evaluated.

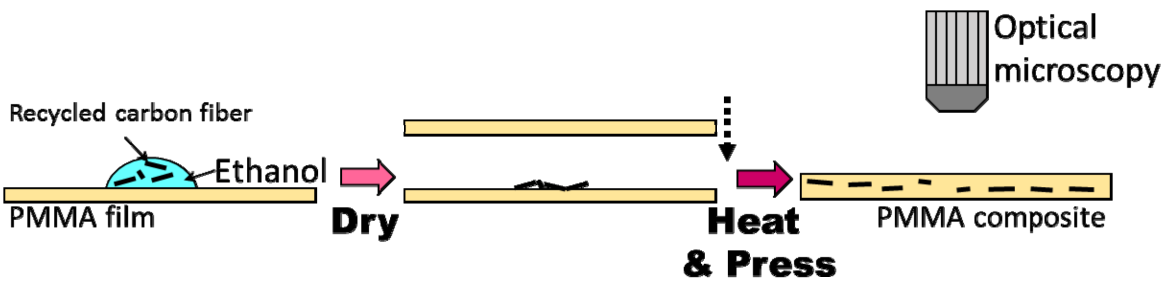

Fig. 2. Schematic of the fabrication of a PMMA composite for the analysis of the dispersion and diffusion of the recycled carbon fibers in the PMMA matrix.

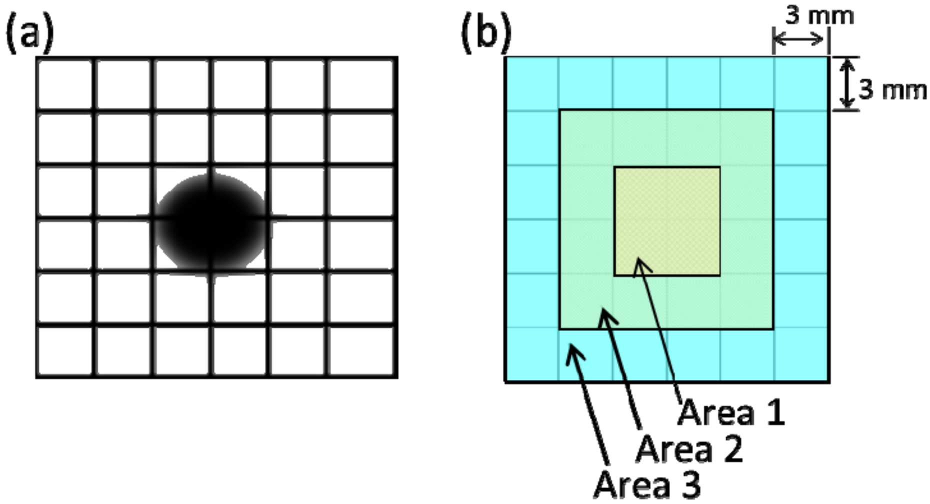

Fig. 3. Evaluation of the distribution of the fibers in the PMMA resin: (a) recycled carbon fiber on the film before hot pressing the composite; (b) definition of different areas on the PMMA composite.

To evaluate the mechanical properties of the PMMA composites, tensile tests for five samples were performed using a tensile testing machine (10073B, JAPAN HIGH TECH). The testing machine was operated at a crosshead speed of 8 μm/min for calculating the yield stress and elastic modulus. The specimens were prepared as follows: Recycled carbon fibers (1 wt% for keeping high transparency of the PMMA film) sandwiched between two PMMA films was hot-pressed under the same conditions for the evaluation of the dispersion and diffusion of the recycled carbon fibers. The composites were then cut into strips with a gauge length of 10 mm and a width of 3 mm using a cutting machine (SDL-200, DUMBBELL CO., LTD).

3. Results and Discussion

3.1. Adsorption of the PMMA particles on the recycled carbon fibers

The SEM image of the recycled carbon fibers was show in **Fig. 4**. This fiber was PAN-based carbon fiber. Some epoxy resins from CFRP were remained on the surface of the recycled carbon fiber. The effect of the residual epoxy resin was so small because the tensile strength of it was much smaller than that of the carbon fiber. In the present study, the influence of the epoxy resin on mechanical properties of the composite was negligible.

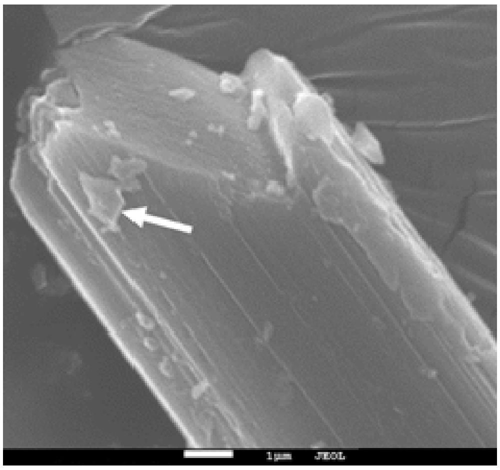

Fig. 4. SEM image of the recycled carbon fibers. The white arrow indicates the residual epoxy resin from CFRP. The scale bar corresponds to 1 μm.

SEM was used to investigate the adsorption of the PMMA particles on the recycled carbon fibers. SEM images of the carbon fibers modified with PMMA particles are shown in **Fig. 5**. In our recent studies, the interfacial shear strength between the carbon fiber and PMMA resin was shown to improve by the adsorption of particles [12, 13]. This result implies that the surface modification would be beneficial to improve the surface adhesion between the recycled carbon fibers and PMMA resin.

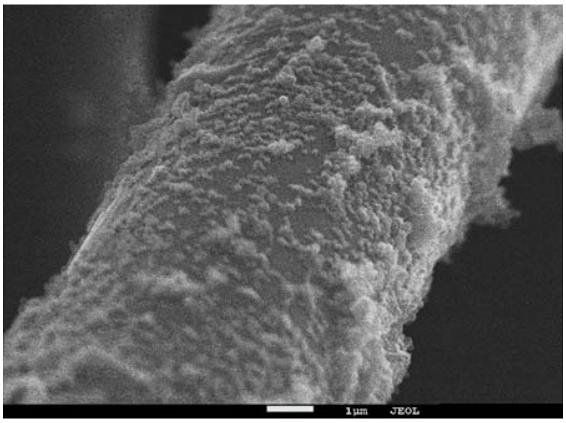

Fig. 5. Modification of the recycled carbon fibers with PMMA particles.
The scale bar corresponds to 1 μm.

3.2. Dispersion and diffusion of the recycled carbon fibers in the PMMA and surface adhesion between the fibers and resin

Optical microscopy was used to evaluate the dispersion and diffusion of the recycled carbon fibers, with their lengths < 90 μm, in the PMMA composites. The photos of the PMMA composite before and after the hot pressing process by optical microscope were shown in **Fig. 6** and analyzed. As shown in **Fig. 7,** most of the fibers were at the center of the PMMA composite, defined as Area 1, which indicated that they remained at the initial position with only a slight diffusion. When the carbon fibers with lengths < 30 μm were modified with the PMMA particles, the number of fibers observed in Area 3 was the largest because the smaller sized fibers diffused faster and the adsorbed PMMA particles lubricated the fiber surface in the PMMA film under the shear stress exerted by pressing. Hence, shorter fibers moved farther from the center during hot pressing. For each fiber size range, shorter fibers exhibited the largest diffusion distance (Fig. 7). On the other hand, the unmodified fibers did not show large changes in each fiber length. To clarify this, cross-sections of the PMMA composites were observed by FE-SEM. **Fig. 8** shows the effect of the PMMA particle adsorption on the recycled carbon fibers on the nature of the interface between the fiber and resin. The formation of voids between the unmodified carbon fibers and the resin was clearly observed in the optical micrograph as shown in **Fig. 8a**. It is well-known that the surface adhesion between carbon fibers treated by sizing agents containing the main component of the epoxy resin and a thermoplastic resin such as PMMA is very poor [18]. The poor surface adhesion between the recycled carbon fiber with small amount of epoxy resin and PMMA resin prevented the recycled carbon fiber from moving easily in the composite. Voids similar to that shown in Fig. 8a prevented the fibers from diffusing easily because the shear stress exerted by the pressing was not completely transferred to them because of the slippage owing to the voids [19].

In case of the carbon fibers adsorbed with PMMA particles, there was no void between the fibers and the resin. These results indicate that the fibers navigated easily within the resin matrix upon the adsorption of the PMMA particles. Thus, the surface modification of the recycled carbon fibers was effective in enhancing their dispersion in the matrix.

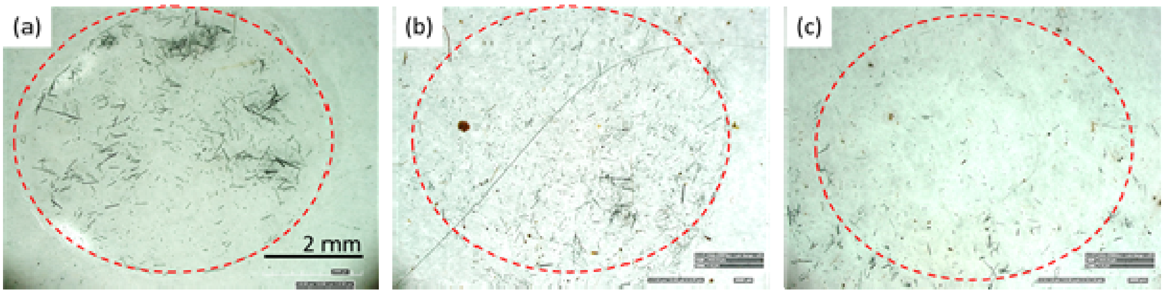

Fig. 6. Optical microscope photos of (a) the initial position, the positions of (b) the recycled carbon fibers and (c) the recycled carbon fibers with surface modification after heating in the PMMA composite. The circles surrounded with red dash lines indicate the position of the sample droplet with the recycled carbon fibers.

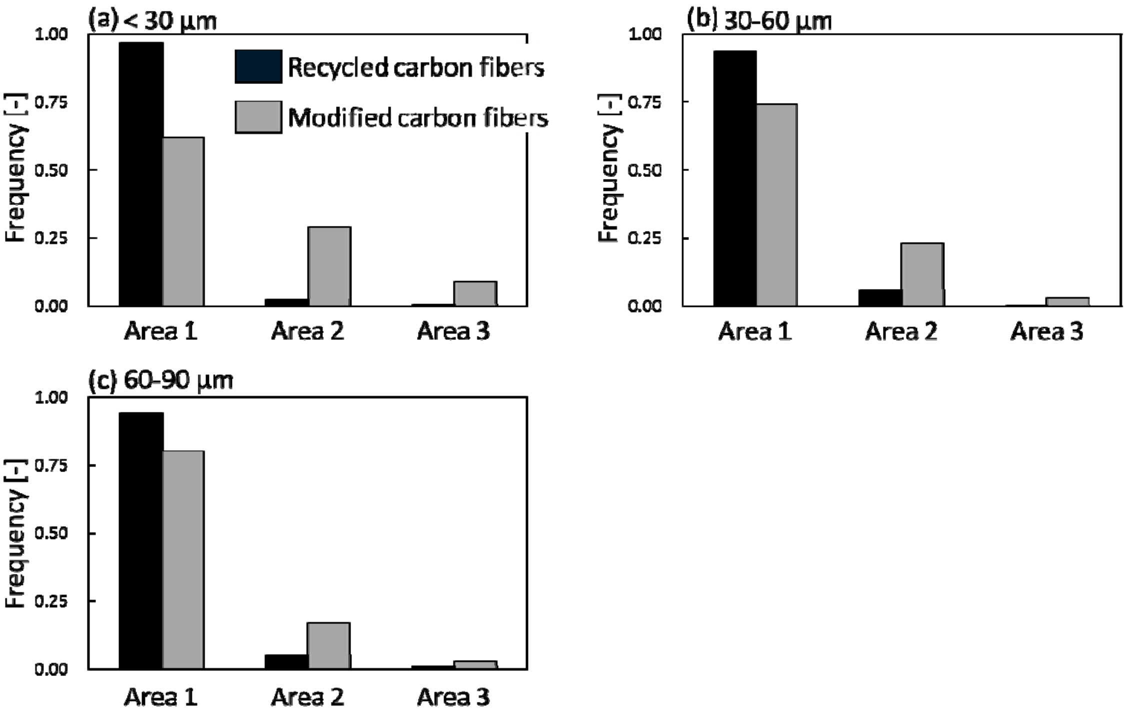

Fig. 7. Frequency of existence of the filler in the three defined areas of the PMMA composite for the following fiber lengths: (a) < 30 μm, (b) 30–60 μm, and (c) 60–90 μm.

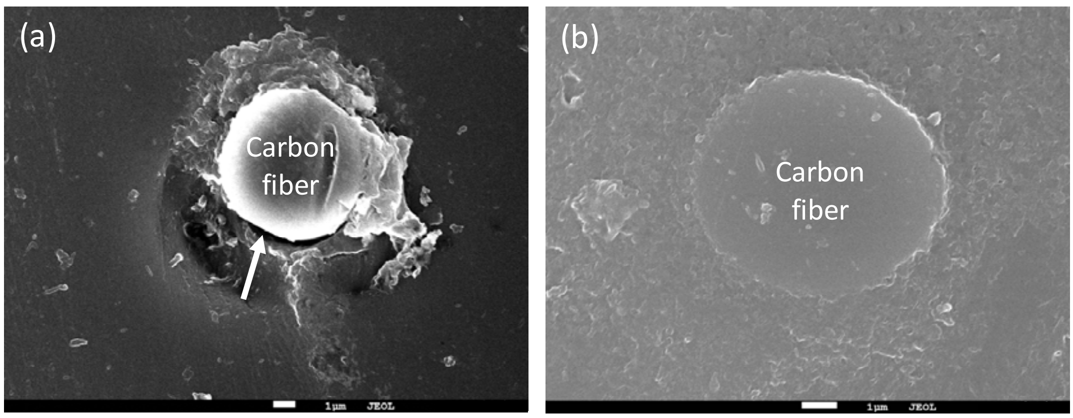

Fig. 8. Comparison of the surface adhesion between the fibers and resin in: (a) fillers without modification, and (b) modified fillers. The scale bars correspond to 1 μm. The white arrow in Fig. (a) points at the voids in the composite.

3.3. Effect of the carbon fibers on the mechanical properties of the PMMA composites

To evaluate the mechanical properties of the PMMA composites, tensile tests were performed. S-S curves were shown in **Fig. 9**. PMMA film with recycled carbon fibers was fractured at the small strain because the recycled carbon fibers were not dispersed throughout the composite. On the other hand, the surface modification made the recycled carbon fibers widespread in the composite and The yield stress and elastic modulus shown in **Fig. 10** depended on the composition of the PMMA resin. Both the yield stress and the elastic modulus of the PMMA composites with PMMA particle-adsorbed carbon fibers were enhanced compared to those of PMMA with no filler and PMMA composites with the unmodified carbon fibers. The surface modification of the recycled carbon fibers with the PMMA particles improved the mechanical properties of the composite and reduced their standard deviations to enhance the homogeneity of the composite because it improved the dispersion and diffusion of the carbon fibers in the matrix. Improvement in the surface adhesion between the fiber and matrix leads to efficient stress transfer [20]. Preventing the formation of voids in the composite *via* the adsorption of the PMMA particles could prevent the stress concentration, thereby improving the mechanical properties of the composite [21, 22].

Thus, the mechanical properties of the composite significantly affected the surface adhesion and hence the dispersion of the recycled carbon fiber fillers, in the matrix.

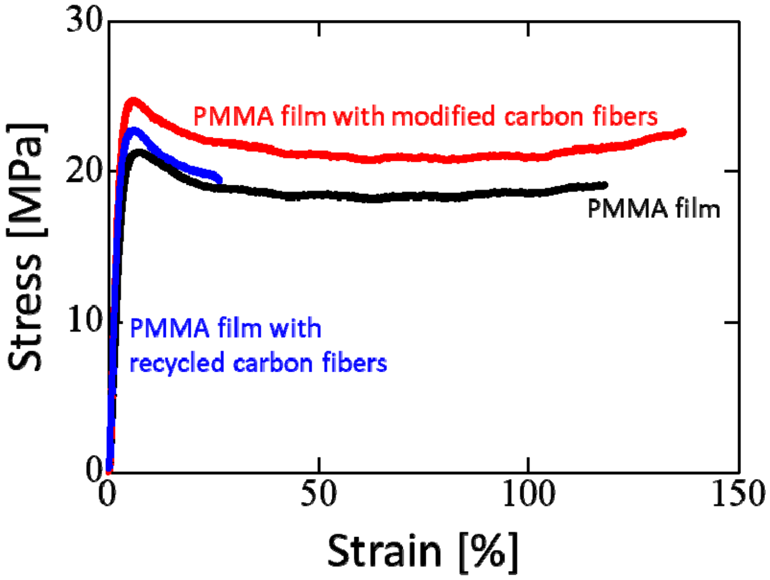

Fig. 9. S-S curves of the PMMA film and the PMMA composite films

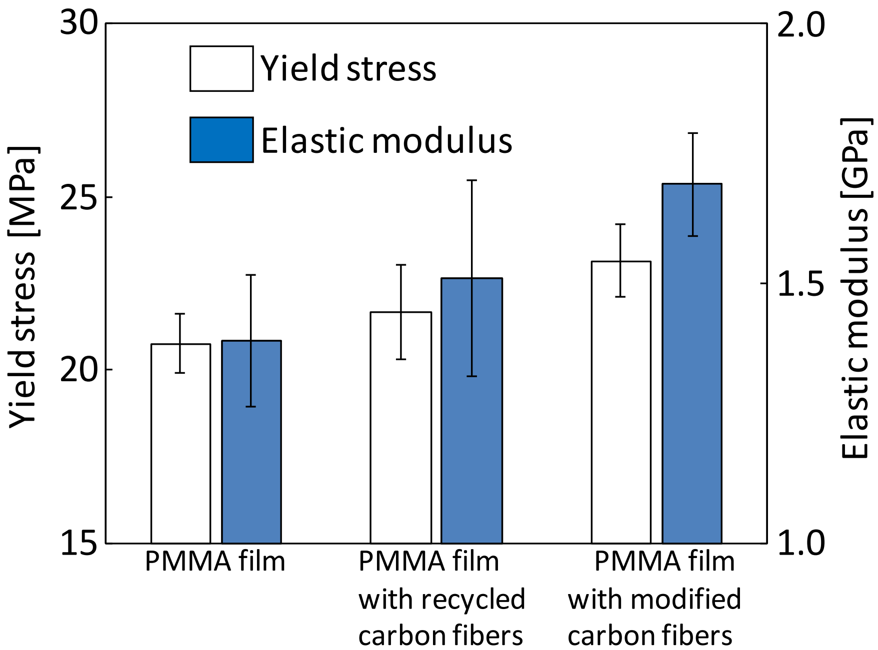

Fig. 10. Effect of the carbon fiber fillers on the mechanical properties of the PMMA composites. Error bars mean the standard deviations.

4. Conclusions

PMMA composites were synthesized using a PMMA resin and recycled carbon fiber fillers. The recycled carbon fibers were obtained by the pulverization of the CFRP. In order to enhance of the mechanical properties of the composite materials, the adhesion properties of the fillers were improved by the adsorption of PMMA particles on their surfaces through electrostatic interactions. Shorter recycled carbon fibers were found to diffuse through the entire PMMA resin owing to their surface modification with the PMMA particles. The good dispersion and diffusion of the carbon fibers in the PMMA resin combined with the improved surface adhesion of the fibers to the resin contributed significantly to the improvement in the mechanical properties, such as the yield stress and elastic modulus, of the composites.

The adsorption of particles consisting of the resin component on the fillers is a useful strategy for enhancing the performance of the composite materials by kneading method [23, 24].

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