EFFECT OF PLASMA SURFACE TREATMENT OF RECYCLED CARBON FIBER ON THE MECHANICAL PROPERTIES OF RECYCLED CFRP

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1 Introduction
The world energy consumption has been increased every year. Especially, the demand of energy consumption of transport sector has been grown exponentially. However, most energy consumption for transport is largely depended on oil for a long time. Hence it is necessary to develop effective measures for high-energy efficient vehicles as soon as possible. Although fuel cell technology is now under development, it will take long period to be in practical applications. Recently, the use of CFRP (carbon fiber reinforced plastics) is growing and diversifying because of low density and high mechanical performance compared with steel. Their use is increasing in various applications not only aircraft but automobiles [1, 2]. Therefore, we focused on the lightening weight of automobile by using CFRP [3-6]. However, current CFRP is not suitable for industrial uses because of high cost, long manufacturing time and difficulty of both secondary processing and recycling [7]. To reduce the energy consumption and the cost of CFRP in manufacturing, recycling of carbon fiber for high performance application is the most effective [8, 9].

In this study, plasma treatment was used to improve the surface characteristics of the recycled carbon fiber. Fiber surface treatment is a part of this study, as it is well known that the composites interfacial properties can be significantly enhanced by increasing surface activities [10-12]. In addition, we chose the two types of polypropylene to evaluate the adhesion between polymer and fiber. The adhesion property between the surface of plasma treated carbon fiber and a polypropylene was analyzed using micro droplet test. Furthermore, mechanical properties were compared with various conditions.

2 Materials
2.1 Carbon fiber
Carbon fibers show exceptional mechanical properties, low weight and make polymer composites reinforced. There are two kinds of carbon fibers, which are pitch-based and PAN-based carbon fibers. Generally PAN-based carbon fiber is used for structural materials in various industry and aerospace, which has properties to easily satisfy both high modulus and strength. In this study PAN-based recycled carbon fibers which are used were supplied by Hitachi Chemical Co., Ltd. The PAN-based recycled fiber was regenerated from the polymer composite materials in the parts of an aircraft (Fig. 1.). Moreover, the origin of the recycled carbon fiber was Toray (T700SC). In other words, the recycled fiber and fresh fiber are essentially the same in this experiment. As shown in Fig. 2. the diameter of PAN-based recycled carbon fiber was 6 micrometers measured by scanning electron microscope.

Fig. 1 A picture of recycled carbon fiber which was regenerated from the aircraft parts.
2.2 Polypropylene
As well known, polypropylene (PP) is produced in large quantities and commonly used material in the world. One of polypropylenes applied in this study was acid-modified PP which is manufactured by Sanyo Chemical Industries (Yumex 1010, supplemented with 10% maleic anhydride) and another polypropylene was homo-PP manufactured by Prime Polymer Co., Ltd. (J3000GP with melt flow rate of 30g/10min). We made the mixed compound as test samples, which are acid content 0.5%.

Recently, maleic anhydride grafted polypropylene has been tried for the purpose of improving interfacial adhesion of carbon fiber composite material.[13] As shown in Fig. 3, grafted maleic groups, polypropylene has a polar functional group on the surface of the interface between the fibers by interdiffusion, intermolecular entanglement, chemical adsorption, physical adsorption and hydrogen bond. In the same way, the phenomenon can be appears in the carbon fiber and related studies have been reported [14].

3 Experiments
3.1 Plasma surface treatment
We did plasma treatment on the recycled carbon fiber in clean dry air. The principle of the plasma surface treatment is to insert dielectric (insulation) between the metal electrodes applied to the high-frequency high voltage. Electrons emitted from the electrodes by the corona discharge are accelerated in an electric field [15, 16]. Fig. 4 shows that plasma treatment does not significantly affect the mechanical and surface properties. In this study, we used plasma treatment device for the surface treatment of recycled carbon fibers as shown in Fig. 5. We installed horizontally movable conveyer line. Prepared samples can be passed through in the plasma system by conveyer. Therefore we were able to investigate an influence of plasma sources and irradiation time on the carbon fiber surface.

Fig. 2 SEM image of the recycled PAN-based carbon fiber.

Fig. 3 Interfacial adhesion due to the addition of maleic anhydride.

Fig. 4 SEM image of the carbon fiber surface after plasma treatment.
As you can see in Figs. 6-7, through water droplets test, we conducted simple test to verify effects of the plasma treatment on the plasma treated carbon fibers. In the Fig. 7, we can see the water droplets that are easily absorbed in the plasma treated surface. It shows that the properties of specimen surface changed to hydrophilic properties. Even though experimental time was only 0.167 seconds, the surface modification was confirmed in this way. Since this plasma treatment can be used in dry atmosphere in a few second, it is quite promising way to recover the surface affinity of carbon fiber that is removed by resin removing processes during CFRP recycling.

3.2 Surface characterization by XPS
XPS analysis is to perform a surface analysis by irradiating X-rays to the sample in the air, and detects the emitted electrons (photoelectrons) and analyzing the photoelectron. The amount of O/C was calculated from elemental of O, C, N, of Si.

3.3 Micro droplet test
Micro-mechanical experiment is important for evaluating of adhesion property between fiber and polymer matrix. In addition, because it is difficult to measure, research is still in progress. [17, 18]. In order to evaluate the adhesion between plasma treated carbon fiber and polymer, we applied micro droplet tester as shown in Fig. 8-9. After immobilizing the carbon fiber in the chamber, we formed spherical shaped micro droplets on the carbon fiber by increasing chamber temperature up to 180℃. At this time, two-dimensional measurement software (AR-U120P3MF the supplied ARTRAY Co., Ltd.) measures the length L of the embedded fibers. When the spherical polymer droplets are loaded between two blades, interfacial shear strength is measured by pulling out the carbon fiber into one direction. The speed of measuring was 0.12mm/min and the tensile load cell was installed (Maximum load 200mN). After all, the spherical polymer droplets, which are not bearing the strain, come unstuck from the carbon fiber. Interfacial shear strength (τ) can be calculated by following equation.
\[
\tau = \frac{F}{\pi DL}
\]  

Where, \( F \) is a measured load, \( D \) is a diameter of the carbon fiber, \( L \) is an embedded length of the polymer sphere.

![Fig. 8 A schematic figure of micro droplet test.](image)

![Fig. 9 A picture of micro droplet on the carbon fiber, which is the range of 40-80μm in this experiment.](image)

3.4 Mixing
To create pellets for micro droplet test, homo-PP and acid modified PP were mixed to be 0.5% of acid modification ratio by using Toyo Seiki Labo Plastomill (10C100S90). Then the pellet was cut in 2-3mm angle. Kneading conditions are shown Table 1. In addition, volume fraction of recycled carbon fiber was made 15% in the composite. Kneading conditions to make CFRP intermediates referred to Table 2. Furthermore, plasma treated recycled carbon fiber was cut to be 7mm by using a cutter to make same with the fresh fiber's length. To leave the fiber length, rotational speed was changed to 10rpm.

3.5 Injection molding
We conducted injection molding test (PM1 machine made by Toyo Seiki). After cylinder heated to 200 °C, to prepare a test piece for 3 point bending test, CFRP resin was injected in mold (85 × 10 × 2mm) which temperature at 100 °C. General machine has integrated part with the cylinder and screw. But inlet part of this machine was made piston not screw type. Therefore, injection can be performed while maintaining the fiber length of the molding material as compared with the general injection mold machine.

3.6 Three point bending test
To confirm the mechanical properties of CFRP specimen, the bending test was performed using a Shimadzu Autograph AGS-X. The ratio of the thickness was 1:16. The crosshead speed was 2mm/min.

4 Results and Discussions
4.1 Surface properties
We measured the amount of O/C of the surface at the spot of 400μm specimens (plasma treatment time: without treatment, 0.167 seconds, 0.333 seconds and 0.500 seconds). The 400μm spot analysis can be measured by averaging the O/C distribution in a wide range [Table 3]. We found that the content of O/C can be increased by plasma treatment, and that the improvement is saturated in the processing time.

### Table 1 A kneading condition of homo-PP and modified-PP.

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### Table 2 Mixing condition of CFRP intermediates.

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### Table 3 A kneading condition of homo-PP and modified-PP.

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of 0.167 seconds. We measured the O/C while moving in the longitudinal direction of the fiber surfaces that comparing between without plasma treatment, plasma treatment (0.500 seconds), and fresh carbon fibers. The 10μm spot analysis, it is possible to measure the O/C distribution close to a single fiber. It is shown in Fig. 10.

Table 3 Difference in O/C of carbon fiber surface by plasma treatment time.

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<th>Times [sec]</th>
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<td>O/C</td>
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<td>0.180</td>
<td>0.172</td>
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Fig. 10 A result of XPS test about O/C of carbon fiber surfaces.

4.2 Adhesion properties

Fig. 11 shows the interfacial shear strength of PP on the carbon fiber by micro-droplet test. The interfacial shear strength increasing until the 0.5 seconds processing; however the interface shear strength was slightly decreasing from 5 seconds to 10 seconds. There was a dependency of embedded length in the interfacial shear strength of the micro-droplet. From the approximate line of the scatter plot of the interfacial shear strength and embedded length, the interfacial shear strength is tend to depend on the embedded length. Therefore we compared the interfacial shear strength of samples, which are point of 80μm of embedded length in a straight line. With the various sizes of Micro-droplets we applied interfacial shear strength test in three plasma treatment conditions [Fig. 12-4].

Fig. 11 The interfacial shear strength measured by micro droplet test.

Fig. 12 The interfacial shear strength between PP and recycled CF without plasma treatment.

Fig. 13 The interfacial shear strength between PP and recycled CF with plasma treatment of 0.500sec.
4.3 Mechanical properties

We confirmed that the strength of the specimen with the plasma treatment time was 0.5 seconds is improved about 17% higher than specimens without the plasma treatment [Fig. 15-17]. In addition, detailed results of the Strain-Stress curve are shown below [Fig. 18-20]. The Strain-Stress curve results have a slight difference due to the injection molding of fiber orientation. Despite the a little difference of results, we can identify the overall trend of influence. In other words, the surface treatment of plasma could make effective surface adhesion properties for recycled carbon fibers.
Fig. 19 Stress-strain curve of CFRP with plasma treatment.

Fig. 20 Stress-strain curve of fresh carbon fiber composite.

5. Conclusion
In this study, we investigated the plasma treatment on the surface of the recycled carbon fiber. Results of XPS experiments explained that plasma treatment could make enough surface activity even for a short period of plasma processing time. This result sounds quite attractive from a viewpoint of mass production. In addition, we found that plasma treatment improved adhesion between the recycled carbon fiber and polypropylene through micro-droplets testing. Furthermore, mechanical properties were also improved. Finally, these results mean that the physical properties of the recycled carbon fiber composites can be improved.

Acknowledgement
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References


