**Development of Carbon Fiber Fabric Reinforced Polypropylenes
- Part 1 : Effect of Content of Maleic Acid and Removal of Sizing Agent -**

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Abstract: Carbon fiber fabric reinforced polypropylene (CFRPP) was prepared by press molding. The mechanical properties of the CFRPP samples were measured by means of a three-point flexural test. An evaluation was carried out on how press molding conditions, maleic acid content in the PP film, and removal of sizing agent adhered to carbon fiber affected the flexural properties of CFRPP. The flexural strength and flexural modulus increased with increasing press temperature, and the impregnation of melted PP into the carbon filaments improved. However, the arrangement of carbon fiber was disarranged by the flow of melted PP when the press molding temperature was too high. Therefore, it is necessary to determine the optimal press molding temperature along with the press molding pressure. The mechanical properties of CFRPP were improved by increasing the content of maleic acid and removing sizing agent. Through observation of failure mode and apparent volume fraction of void, it was estimated that the improvement of mechanical properties was due to improvement of interfacial adherence between carbon fiber and PP. The maximum flexural strength of CFRPP was 453 MPa and the maximum flexural modulus was 58.2 GPa in this study.

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1. Introduction

Global warming caused by an increase in CO₂ is an environmental problem that has been attracting more and more attention. As one means of reducing CO₂ emissions, Kitano *et al.* [1] have proposed reduction of the weight of automobile parts to improve fuel consumption. They calculated 8,050×10⁶ kg/year of reduction in CO₂ in the case of metal automobile parts being substituted by lightweight carbon composite materials. Takahashi *et al.* [2] have suggested that carbon fiber reinforced thermoplastics are suitable for automobile parts as compared with carbon fiber reinforced thermoset plastics, which are now aggressively used in the field of aerospace, because carbon fiber reinforced thermoplastics are advantageous in terms of price, productivity, and recycling efficiency as compared with thermoset plastic.

Polypropylene (PP) is a lightweight, low-cost thermoplastic, of which there are stable supplies in the market. Therefore, PP is one of the best possible materials for developing carbon fiber reinforced thermoplastics. However, there is a technical problem; interfacial adherence of carbon fiber with an olefin polymer, such as

PP or polyethylene, is critically low [3]. Therefore, existing studies on carbon fiber reinforced plastics have targeted mainly thermoset composites [4-7]. However, recently Takahashi *et al.* reported having improved interfacial adherence between carbon fiber and PP by removing sizing agent from carbon fiber and by modifying PP with maleic acid [2].

On the other hand, the general configuration of continuous carbon fiber used for composites is uniaxially aligned or fabric forms. Carbon fiber fabric is particularly suited to work such as stacking [8]. There is another merit of using the fabric form of carbon fibers. It is easy to separate the textile manufacturing process (weaving) and the matrix polymer impregnation process. The division of work makes it easy for small and medium-sized enterprises to cooperate, and to develop carbon fiber reinforced plastic.

In accordance with the above, we think that PP is a useful matrix for carbon composite material, and that the use of carbon fiber fabric is conducive to cooperation among companies for the development of carbon composite materials. Therefore, we have been developing carbon fiber fabric reinforced PP (herein CFRPP) and have been improving the mechanical properties of CFRPP. The aim of this study was to improve the flexural

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properties of carbon fiber fabric reinforced polypropylene. Therefore, the paper reports the effects of press molding conditions, the content of maleic acid in PP film, removal of sizing agent from carbon fiber fabrics and disorder of fiber alignment in the pressing process. The flexural properties were estimated using the three-point flexure test, which is a simple evaluation method.

2. Experiments

2.1 Melt mixing

PP (Japan Polypropylene Co., Ltd., i-PP, MFR=75) was mixed with maleic acid (Kanto Chemical Co., Inc. purity : min 98.0%) using a co-rotating batch kneader (Musashino Kikai Co., Ltd.). The kneader has two mixing rotors and a $\phi 45$ mm extruder screw. The volume of the cavity is 3 L.

First, PP pellets were fed to the kneader and melted at 180°C for 10 min by rotation of rotors at 15 rpm. Next, maleic acid was put in the kneader and mixed with PP for 20 min under the above-mentioned conditions. Finally, the PP modified by maleic acid was extruded in strand form, and then pelletized. The PP pellets obtained by means of this process had 20% weight fraction of maleic acid.

2.2 Film molding

PP film was molded using a film molding extruder (Research Laboratory of Plastics Technology Co., Ltd.), which has a $\phi 40$ mm screw and 300 mm T-die. PP film was extruded at 180 to 225°C. The touch roll temperature was 100°C, and the take-up speed was 2 m/min. The thickness of the PP film was 100 μ m. PP films containing maleic acid of 0.1 to 1.0% weight fraction were made from virgin PP pellets and PP pellets containing maleic acid of 20% weight fraction.

Fig. 1 Press molding process diagram

2.3 Carbon fiber fabric

Carbon fiber (Toray Co., Ltd., T700SC, 12,000 filaments) was woven using a rapier loom (Toyoshima Business System Co., Ltd.). The fabric configuration was plain weave, in which both warp and weft densities were 5.9 yarns/5 cm, and the weight was 230 g/m².

When the sizing agent was removed from carbon fiber fabric, the carbon fiber fabric was heat-treated at 400°C for 10 minutes.

2.4 Press molding

11 PP films and 10 carbon fiber fabrics were piled up alternately, and pressed using a pressing machine (Tester Sangyo Co., Ltd.), which had a flat metallic mold. Table 1 shows press molding conditions, and Fig. 1 shows a typical press molding process diagram in this study. First, the metallic mold was heated up to various temperatures over the melting temperature of PP. Pressure was increased up to 1.5 MPa at the same time. Then the temperature and pressure were held for 10 minutes (herein this process is called the pre-heating process). Next, the pressure was increased to 14.6 MPa after the temperature was decreased to 180°C or 160°C. Then the temperature and pressure were held for 10 minutes

Table 1 Press molding conditions

Sample No.	Pre-heating Temperature		Hot-press Temperature		Maleic Acid Content in the PP %	Removing Process of Sizing Agent	Density / g cm ⁻³	V_f %
	Pressure / MPa	Temp. / °C	Pressure / MPa	Temp. / °C				
1	1.5	180	14.6	180	0	None	1.36	54
2	1.5	180	14.6	160	0	None	1.34	51
3	1.5	200	14.6	160	0	None	1.37	54
4	1.5	220	14.6	160	0	None	1.36	51
5	1.5	240	14.6	160	0	None	1.36	54
6	1.5	220	14.6	160	0.1	None	1.39	56
7	1.5	220	14.6	160	0.5	None	1.40	57
8	1.5	220	14.6	160	1	None	1.39	55
9	1.5	220	14.6	160	0	Done	1.33	52
10	1.5	220	14.6	160	1	Done	1.37	54

(herein this process is called the hot-press process). Finally, while the pressure was maintained, the mold was cooled down less than 90°C with a cooling rate of 5.9 K/min. The thickness of CFRPP samples was about 2 mm.

2.5 Evaluation method for PP film and CFRPP

The thermal properties of PP film were measured by DSC (SII Nano Technology Inc. DSC7200). The sample was measured from -100°C to 240°C in the heating process, and then measured from 240°C to -100°C in the cooling process. Both heating and cooling rates were 10 °C/min.

The flexural properties of CFRPP samples were measured by means of the three-point flexure test [9] using a universal test machine (Shimadzu Co., Ltd. AG-100KNplus). The dimensions of the sample were 15 mm in width, and 100 mm in length. The distance between fulcrums was 80 mm, and the test speed was 5 mm/min. All samples were curing more than 48 hour at room temperature of 23°C and 50% humidity. And the tests were conducted at the same atmosphere.

The volume fraction of carbon fiber V_f in a CFRPP sample was evaluated based on equations (1) and (2) [10].

Fig. 2 DSC curve of neat PP film in heating and cooling process.

$$W_f = \frac{m_1}{m_0} \times 100 \quad (1)$$

$$V_f = \frac{W_f \times \rho_c}{\rho_f} \quad (2)$$

Here, W_f is the weight fraction of carbon fiber in the CFRPP sample, m_0 is the weight of the CFRPP sample, m_1 is the weight of the CFRPP sample after heating at 400°C for over 16 hours, ρ_c is the density of the CFRPP sample, and ρ_f is the density of the carbon fiber (1.8 g/cm³). The apparent volume fraction of void V_v in a CFRPP sample was evaluated based on equations (3) and (4) [10].

$$V_r = \frac{(100 - W_f) \times \rho_c}{\rho_r} \quad (3)$$

$$V_v = 100 - (V_f + V_r) \quad (4)$$

Fig. 3 Photographs of surface of CFRPP samples.

Fig. 4 Effect of press molding conditions on flexural properties of CFRPP samples.

Here, V_r is the volume fraction of PP in the CFRPP sample, and ρ_r is the density of PP film.

The density of the PP film and the CFRPP sample, the sample size was 15 mm × 15 mm, were measured with the underwater substitution method. The value of ρ_r and ρ_c used the average measured 10 times of the PP film and the CFRPP, respectively.

3. Results and Discussion

3.1 Thermal properties of PP film

The DSC curve of neat PP film is shown in Fig. 2. In the heating process, the melting point of neat PP film was measured at 168°C, and endothermic change was completed above 180°C. In the cooling process, crystallization of PP began from about 130°C. The crystallization temperature was 118°C.

Therefore, the pressing temperature was set above 180°C so that PP would melt completely. In the confirmation test, once PP was molten over 180°C, the

molten state of PP was maintained until 130°C in the cooling process.

3.2 Effect of press molding conditions

Fig. 3 shows photographs of the surface of CFRPP samples. No. 1 was the sample prepared by press molding with pre-heating and hot-pressing process at 180°C. The arrangement of carbon fiber was disarranged by the flow of melted PP in the press molding. No. 2 was prepared by press molding with pre-heating process at 180°C and with hot-press process at 160°C. The arrangement of carbon fiber was not disarranged under these conditions. The results suggest that the arrangement of carbon fiber strongly depends on the relationship between temperature and pressure in the press molding process, and the relationship between viscosity and fluidity of melted PP. In other words, in order to keep the arrangement of carbon fiber, it is necessary to suppress the fluidity of melted PP. Conversely, low viscosity and high fluidity of PP are required for impregnation of melted PP into the carbon filaments. Therefore, the optimal press molding condition which is compatible with both the arrangement of the carbon fiber and the resin impregnation should be determined. In this study, we focused on the condition of pre-heating temperature.

Fig. 4 shows apparent V_v of CFRPP samples with various pre-heating temperatures and a fixed hot-pressing temperature of 160°C. Apparent V_v decreased with increasing temperature from 180°C to 220°C in the pre-heating process (Nos. 2 - 4). The apparent V_v of No. 4 was less than 2%. The results suggest that the impregnation of melted PP into carbon filaments was improved by increasing the pre-heating temperature. However, the arrangement of carbon fiber of No. 5 was disarranged as indicated in Fig. 3. And apparent V_v of No. 5 was higher than No. 4 inversely. Therefore, the optimal press molding temperature had to be determined along with the press molding pressure.

Fig. 5 shows the flexural strength and flexural modulus of Nos. 1 - 5. Flexural strength and flexural

Fig. 5 Effect of press molding conditions on flexural properties of CFRPP samples.

modulus increased with increasing temperature in the pre-heating process. Samples Nos. 3 - 5 with over 200°C pre-heating showed higher flexural modulus. Both the flexural strength and flexural modulus increased with decreasing V_v . The impregnation of PP improving into carbon filaments, cohesive force of the PP / carbon fiber fabric system itself increases. Therefore, the improvement in impregnation of PP contributes to improvement in the flexural properties, especially the flexural modulus.

From the results, the press molding conditions were determined as those used in sample No. 4. Subsequent experiments followed condition No. 4 : 220°C in the pre-heating process and 160°C in the hot pressing process.

Fig. 6 Effect of maleic acid content on flexural properties of CFRPP samples.

3.3 Effect of the content of maleic acid

Fig. 6 shows the flexural strength and flexural modulus of No. 4 and Nos. 6 - 8. Both flexural strength and modulus increased with the content of maleic acid. The flexural strength of No. 8, which contained 1 wt% maleic acid was 453 MPa.

Fig. 7 shows photographs of the side view of No.4 and Nos. 6 - 8 after the three-point flexure test. The arrow of a figure shows the part where compressive force was added by a three-point flexural test. No.4, which contained no maleic acid, showed delamination between carbon fiber fabric and PP. On the other hand, shear failure associated with oblique cracks was dominant in Nos. 6 - 8. If the interfacial adherence of carbon fiber and PP is bad, delamination will take place in the flexural test. Conversely, the transition of failure mode changing from delamination to shear failure was caused by the improvement in interfacial adherence between carbon fibers and PP. Therefore, the interfacial adherence of carbon fiber and PP was improved with the addition of maleic acid, and the mechanical property of CFRPP increased with improved interfacial adherence.

3.4 Effect of removing sizing agent from carbon fiber fabric

Generally, sizing agent is applied to commercial

Fig. 7 Photographs of side-view of CFRP samples after three-point flexural test.

carbon fibers. Sizing agent often contains a coupling agent such as silane, and it fortifies the interfacial adherence between fibers and matrix, especially epoxy resin. However, such sizing (coupling) agents often function inversely for thermoplastic matrix. Therefore, in our material system consisting of carbon fiber fabric and PP, the sizing agent should be removed from carbon fiber fabrics.

In order to study the effect of the presence of sizing agent, we conducted a heating process to remove sizing agent from carbon fiber fabrics. Heating the carbon fiber fabric at 400°C and more than 10 minutes, weight reductions of the carbon fiber fabric were saturated with about 1 wt%. The weight reduction is caused by ablation of a sizing agent on the carbon fiber fabric. Therefore, the sizing agent was removed from carbon fiber fabric; we heat-treated the carbon fiber fabric at 400°C for 10 minutes.

Fig. 8 shows the flexural strength and flexural modulus of No. 4, No. 8, and Nos. 9 - 10. First, when No. 4, which did not contain maleic acid, and No.9 were compared, both the flexural strength and flexural modulus of No. 9, from which the sizing agent had been removed,

Fig. 8 Effect of sizing agent removal from carbon fiber fabric on flexural properties of CFRPP samples.

were higher than the values for No. 4, from which the sizing agent had not been removed. Next, when No. 8 and No. 10 containing 1wt% of maleic acid were compared, the flexural modulus of No. 10, from which the sizing agent had been removed, was higher than that of No. 8, from which the sizing agent had not been removed; although the flexural strength was almost equivalent. The maximum flexural modulus in the study was 58.2GPa in sample No. 10. These results showed that the content of maleic acid was of no concern; the mechanical property improved through the removal of sizing agent.

4. Conclusion

The aim of this study was to improve the flexural properties of carbon fiber fabric reinforced polypropylene. CFRPP samples were prepared under several press molding conditions. The flexural properties of the CFRPP samples were measured by three-point flexural test. The effects on flexural properties caused by the press molding conditions, the content of maleic acid in the PP film, and the removal of sizing agent from carbon fiber fabrics were evaluated. The flexural properties increased with increasing temperatures in the pressing process, although the arrangement of carbon fibers was disarranged by the flow of PP resin when the press molding temperature was high. Therefore, it is necessary to determine the optimal press molding temperature along with the pressure in molding process. The interfacial adherence between the carbon fiber and the PP was improved by adding maleic acid to the PP. The impregnation of the PP into the carbon filaments was improved by removing sizing agent. As a result, the effects on the mechanical properties of CFRPP caused by maleic acid and removal of sizing agent were confirmed.

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