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Influence of contents rate and dispersion of carbon nanotubes on interfacial adhesion between continuous fiber reinforced thermoplastics and injection resin

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Abstract. Fiber reinforced plastics have been expected as an alternative of metal materials in order to reduce the lightweight of the automotive and the environmental loading. Carbon fiber reinforced thermoplastics (CFRTP) have been studied from the view point of reducing cycle time and recycling of polymer materials. Prepreg compression molding (PCM) enables to provide the excellent mechanical property. However, PCM is difficult to form complex shape. On the other hand, hybrid injection molding (HIM) has attracted attention because HIM makes it possible to form complex shape. However, the mechanical property of molded parts are affected by the interlaminar shear strength between continuous fiber reinforced thermoplastics and injection molded parts. Some researchers reported interlaminar shear strength improve by use of carbon nanotubes (CNTs). Therefore, we aimed at improving interfacial adhesion by preparing a film with CNT added in matrix and inserting the film at the interface of hybrid injection molded parts. We conducted short beam test on specimens inserted films. When CNT/PP film was used, the interfacial shear strength was improved compared to when no film was used. When the CNT was in the low dispersion state, the interfacial shear strength rose gently up to 1.0 wt% and dropped greatly at 3.0wt%. On the other hand, when the CNT was in the highly dispersed state, the interfacial shear strength rose up to 0.5 wt%, and thereafter dropped. When the CNT content was 1.0 wt%, the CF entered deep into interface at low dispersion. However, the interface was smooth and entry of CF could not be confirmed on the peeled surface at high dispersion. There is an optimum value for the content and dispersibility of CNT in the film.

1. Introduction

Continuous fiber reinforced thermoplastics have excellent mechanical property. Among reinforcing fibers, specific gravity of carbon fiber is 1/4 times as heavy as that of iron. Specific strength of carbon fiber is 10 times as strong as that of iron. Specific modulus of carbon fiber is 7 times as large as that of iron. CFRTP is excellent in specific strength and specific rigidity. It is also expected as a substitute material for metals from the viewpoint of ease of formability, high productivity and recyclability. PCM is one of the process to produce the CFRTP parts. However, PCM is difficult to form the complex shape and it requires long time for molding. On the one hand, Injection Molding (IM) is used for produce the complex shape parts which is reinforced by short fiber and long fiber (i.e. carbon fiber, glass fiber, and natural fiber). HIM process is promising new method which is combined these PCM and IM process for

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producing the hybrid parts with excellent mechanical property. In HIM process, CF/PP organosheets are heated by infrared (IR) heater to melt the resin of these sheets and making shape of melted organosheet is done by mold of IM. However, the mechanical property of molded parts is affected by the adhesive strength between continuous fiber reinforced thermoplastics and injection molded parts. Some researchers reported interlaminar shear strength is improved by use of CNTs in case of thermoset resin. It is known that the aspect ratio (fiber length / fiber diameter) of the reinforcing fiber contributes to the mechanical properties of the fiber reinforced composite material. Since CNTs have higher aspect ratios than general scaled reinforcing fibers and microfibers, high adhesive strength can be expected. However, the adaption of CNTs in HIM process for improving the adhesive strength of thermoplastics hybrid parts has not reported yet. In this research, therefore, we newly devised a method of connecting interfaces at the nano level as a new approach. We aimed at improving adhesive strength by preparing a film with CNT added in matrix and inserting the film at the interface of hybrid injection molded parts. We assumed that adhesive strength was affected by the content of CNTs added and dispersion state and investigated them.

2. Experimental

2.1. Material

NOVATEC PP (manufactured by Japan Polypropylene Corporation, part number MA 04 A) was used as a matrix. Multi-walled carbon nanotube MWCNT (manufactured by NANOCYL SA, NC 7000 TM) was used as the CNT. CF / PP organosheet was used as an insert material. PYROFIL pellet PP-C-20A (manufactured by Mitsubishi Chemical Corporation) was used as an injection resin. PP (manufactured by Prime Polymer, product number J 108 M) was used as a matrix of CF/PP films and glass fiber (average fiber diameter 0.28 μm, aspect ratio 36) was used as reinforcing fiber of CF/PP films.

2.2. Fabrication of CNT/PP granules

For fabrication of CNT/PP granules, co-rotating twin-screw extruder ZSK18 MEGAlab (manufactured by Coperion) was used. At first, we prepared masterbatch (MB) of PP/CNT nanocomposite with 5.0 wt% content ratio of CNT by co-rotating twin-screw extruder. The used configuration for compounding MB is shown in figure 1. PP granules are fed into the main hopper and CNTs are fed into side feeder by volumetric feeder. The compounds are extruded as strand under the cooling water and cut into granules by pelletizer.

Second, the MB pellets and PP pellets were dry-blended at room temperature so as to have content ratio (0 / 0.5 / 1.0 / 3.0 wt%), and the blends were charged from the main hopper and kneaded. The screws were shown in figure 2. In screw I, the rotation speed was 150 rpm and the throughput was 3.8 kg/h. In screw II, the rotation speed was 500 rpm and the throughput was 5.0 kg/h. The barrel temperature was 200 ℃.

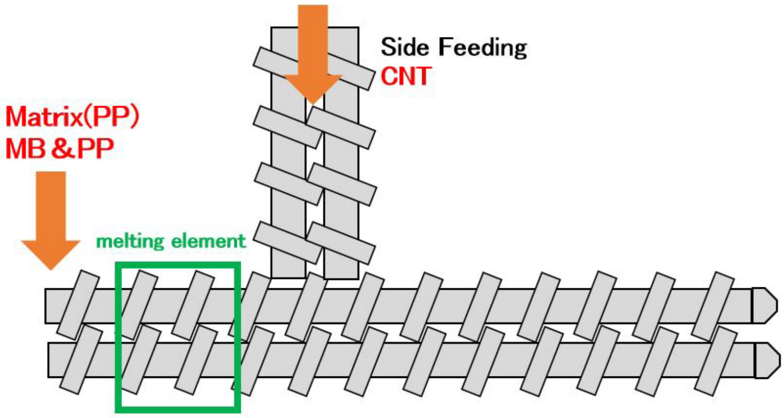

Figure 1. Screw configuration.

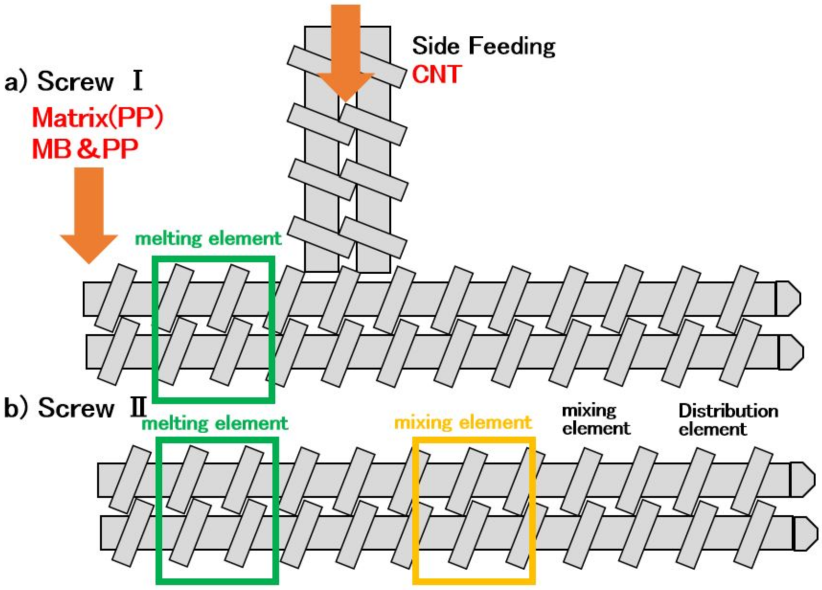

Figure 2. Screw configuration.

2.3. Fabrication of CNT/PP film

Equipment and process for producing CNT/PP films shown in figure 3. For fabrication of the film, granules were fed into a small twin-screw extruder (manufactured by Thermo Fisher Scientific, HAAKE Process 11) having a screw diameter of 11 mm. The thickness of the sheet was about 200 μm and width of the sheet was 16.5 mm. The film was taken up in a sheet winding device. The barrel temperature was 200 ° C, the rotation speed was 100 rpm, and the throughput was 1.0 kg/h.

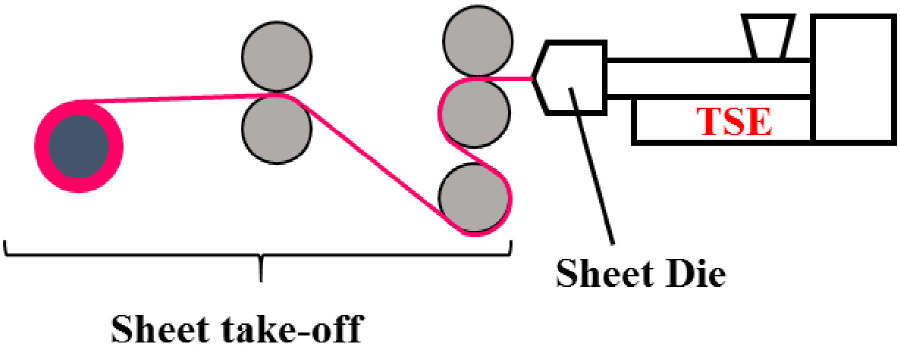

Figure 3. Overview of fabrication process for CNT/PP nanocomposite film.

2.4. Fabrication of insert material

Figure 4 shows a schematic diagram of the equipment and process of fabricating of insert material. As a method for molding a CNT-containing prepreg sheet used as an insert material, firstly 10 ply of a CF / PP organosheet was laminated with a configuration of [0 ° / 90 ° / 0 ° / 90 ° / 0 °] s. The CNT / PP film prepared was spot-welded to the surface portion. The laminate of the CF / PP organosheet and the CNT / PP films were heated and welded with a servo press (manufactured by TAIYO Corporation, product name: PQCS 2 - 60 kN - FC). The press pressure was 1.2 MPa. The molding temperature was 200 ℃. The width of CNT/CF/PP insert material was 70mm. The length of that was 120mm. The thickness of that was 1.2mm.

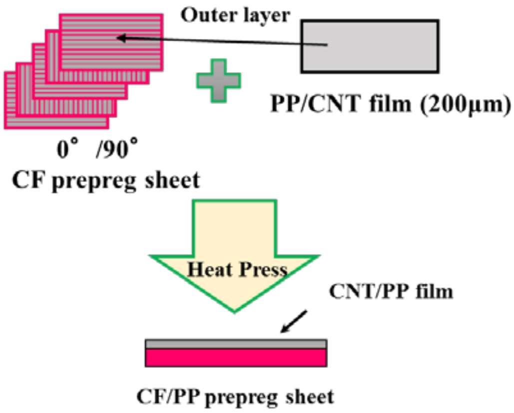

Figure 4. Overview of fabrication process of insert parts (CNT/CF/PP).

2.5. *Injection molding process*

The injection molding machine ET-40V (manufactured by Toyo Machinery Metals) was used. The thickness of the mold was 2.4 mm. The layer of CNT was molded at the center of thickness.

However, since the surface of the insert material is required to heat, a fully automatic vertical molding machine ET-80HR4 (manufactured by Toyo Machinery Metals) was used. Injection conditions were standard injection conditions (injection conditions: STD). The cylinder temperature was 240 °C, the holding pressure was 30 MPa.

2.6. *Evaluation of interlaminar shear strength*

Short beam three-point bending test was performed according to ASTM D 2344 standard. Autograph AG-1 (manufactured by Shimadzu Corporation) was used as a testing machine. Test speed was 1.0 mm/sec and distance between fulcrums was 9.6 mm. The insert side of the test piece was on the indenter side and the Injected side was on the fulcrum side. The interfacial shear strength τ was calculated by using equation (1). The point where the load was dropped slightly before fracturing of all materials during short beam testing was considered as the interfacial breaking load *F*. The test piece of width was *b*, that of thickness was *h*.

$$\tau = \frac{3F}{4bh} \tag{1}$$

2.7. *Dynamic viscoelasticity*

Dynamic viscoelasticity measuring device Rheogel-E 4000 (manufactured by UBM) was used. The CNT/PP film was cut into test pieces. The test pieces of thickness were 200 μm, that of length were 30 mm and that of width were 5.0 mm. The distance between fulcrums was 20 mm, the static load was 1.0 N, the displacement amplitude was 2.0 μm. The measurement temperature was 20 °C. The frequency range was 0.016 ~15.92 rad/sec.

3. Results and discussion

3.1. *Dispersion state of CNT*

The state of CNT dispersion in the CNT/PP pellets is evaluated from the viewpoint of melt viscoelasticity. Based on the results of the storage elastic modulus E ' in the melt viscoelastic properties, the state of dispersion of CNT in CNT/PP pellets is quantitatively evaluated. Elastic modulus E’ at frequency 0.1 rad/s is shown in figure 5. In the case of the storage elastic modulus E ', it is considered that the screw II exhibits a higher value under all the conditions. This result suggested that CNT dispersion was good in screwⅡ. From now on, CNT/PP pellets made with screw I are low dispersion and CNT / PP pellets made with screw II are made high dispersion.

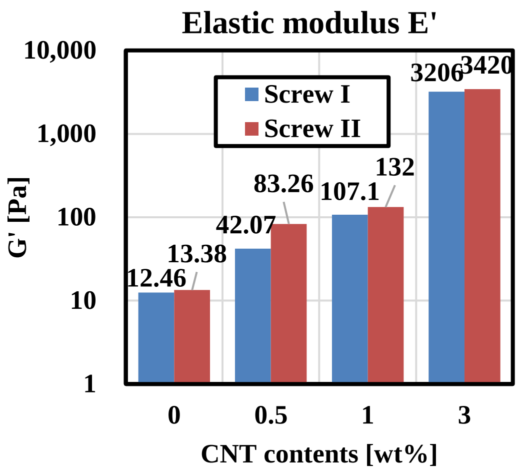

Figure 5. Comparison of elastic modulus E' between screw I and II process.

3.2. *Influence of CNT content and dispersion state on interfacial shear strength*

Figure 6 shows the relationship between the interfacial shear strength and the CNT content contained in the CNT/PP film. When CNT/PP film is used, the interfacial shear strength is improved compared to when no film is used. In addition, When CNT/PP film was used, the interfacial shear strength was improved compared to when no film was used. When the CNT was in the low dispersion state, the interfacial shear strength rose gently up to 1.0 wt% and dropped greatly at 3.0 wt%. On the other hand, when the CNT was in the high dispersion state, the maximum interfacial shear strength rose up to 0.5 wt%, and thereafter it dropped. From these results, it was revealed that the optimum content ratio exists to improve the interfacial shear strength. However, in the high dispersion state, the highest interfacial shear strength is shown at 0.5 wt%, but it is greatly reduced at 1.0 wt%.

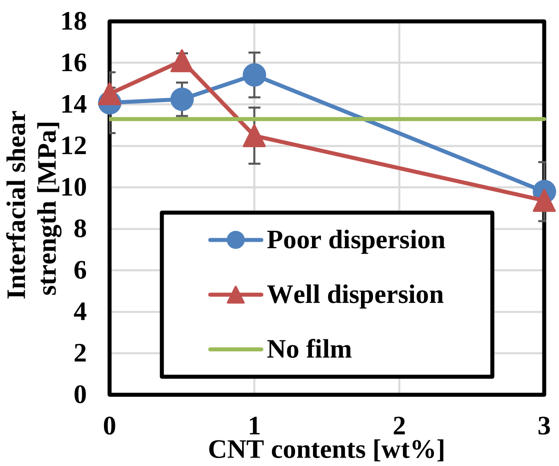

Figure 6. Correlation between CNT content and interfacial shear strength.

3.3. *Adhesion effect of the CNT at peeled surface*

SEM observation images of peeled surfaces of both the insert material side and the injection resin side after peeling under each condition are shown. The CNT content of 1.0 wt% is shown in figure 7. On the peeled surface at 1.0 wt%, a coarse interface can be confirmed at low dispersion showing the highest interfacial shear strength, and at high dispersion with reduced interfacial strength CNT has a twodimensional network structure confirmed. Moreover, as a result of comparing with low magnification images, the CF entered deep into the interface at low dispersion, whereas at high dispersion the interface was smooth and entry of CF could not be confirmed. Therefore, one of the causes of the decrease in interfacial shear strength is considered to be that the number of CF at the interface decreased. Furthermore, as the number of CNTs at the interface decreased due to the construction of the network, it could not play the role of the wedge effect and the interface shear strength decreased. From this, it can be easily imagined that a network structure is constructed in the highly dispersed state, but it is presumed that network construction is probably involved as a cause of lowering of interfacial shear strength. In other words, it is presumed that the number of CNTs and CFs playing the role of wedge effect decreases and the interfacial shear strength decreases as the CNTs establish a network.

These results suggested that CNT content and dispensability may affect CNT 's network construction and that the network construction influences the interfacial shear strength.

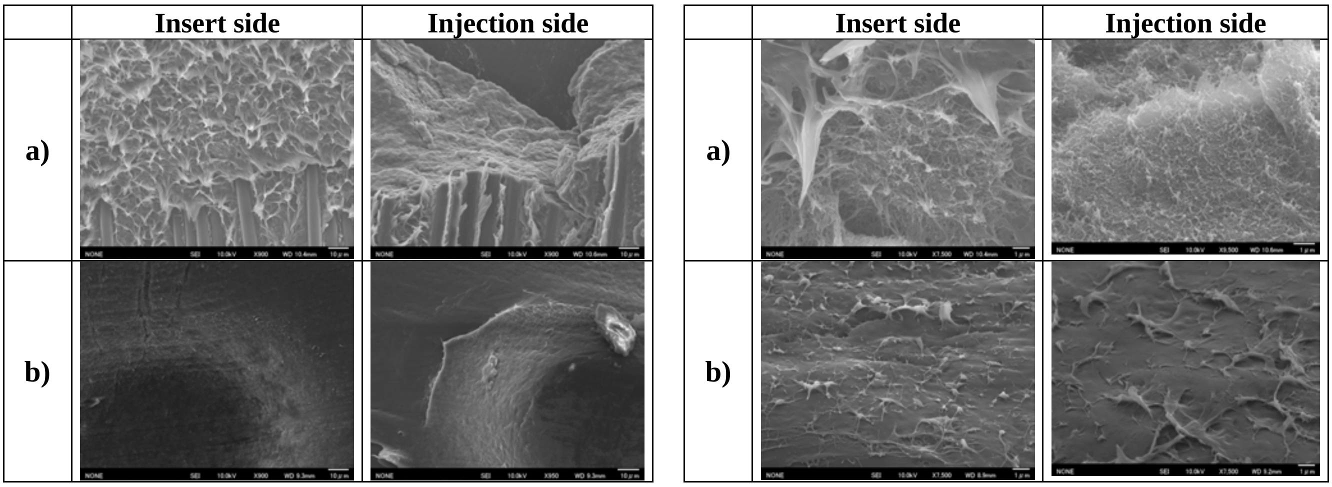

Figure 7. SEM micrograph of peeling surface between injection parts and insert parts at 1.0wt%, a) Poor dispersion and b) Well dispersion.

4. Conclusions

When CNT/PP film was used, the interfacial shear strength was improved compared to when no film was used. When the CNT was in the low dispersion state, the interfacial shear strength rose gently up to 1.0 wt% and dropped greatly at 3.0 wt%. On the other hand, when the CNT was in the high dispersion state, the interfacial shear strength rose up to 0.5 wt%, and thereafter it dropped. When the CNT content was 1.0 wt%, the CF entered deep into the interface at low dispersion. However, the interface was smooth and entry of CF could not be confirmed on the peeled surface at high dispersion. There is an optimum value for the content and dispensability of CNT in the film.

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