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An Influence of Nanofiller Size on the Joining Strength of Injection Overmolded Component by Insert of Nanofiller-Filled Thermoplastics Films at Interface.

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Abstract. Injection overmolding process is promising process for fabrication of thermoplastic composites which has excellent mechanical properties and complex shapes. Concretely, the continuous fiber-reinforced thermoplastic composites are fabricated by stamping process as substrate. Followed by the melt polymer is overmolded onto the substrate by injection molding for fabrication the ribs and bosses. Therefore, in this process, joining strength between two materials is a major factor in the mechanical strength of a product. As the new approach to improve the joining strength, nanofiber-filled thermoplastic film is inserted between the substrate and overmolded polymer for reinforcing the interface directly in nanoscale. In our previous works, we revealed that multi-walled carbon nanotubes (MWCNTs) filled polypropylene (PP) films could improve the interlaminar shear strength. However, it is still unclear cause why interlaminar shear strength increased by adding the films. In this study, to clarify the influence of nanofiller size on the adhesion strength, two kinds of nanofillers, CNTs and vapor grown carbon fibers (VGCFs) were used. As a quantitative evaluation method of adhesive strength, a tensile overlay shear strength test was performed. As a result, it improved the joining strength at CNT contents of 0.5wt% of CNTs film the best. CT scan images confirmed that CNT tangled with polymer chains. This indicated that entanglement between CNTs and injection resin has effect on the adhesion. By diffraction scanning calorimetry (DSC) data, the crystallinity of nanofiller-filled thermoplastic film was lower than PP film and it was considered that addition of nanofiller distracted crystallization PP. Therefore, although the crystallinity of substrate surface decreased by adding nanofibers, CNT contents of 0.5wt% was the best contents for joining strength. Consequently, the relationship between crystallinity and joining strength requires detailed investigation, such as focusing on crystallization behavior during cooling.

Keywords: Injection over-molding, Carbon nanotube

INTRODUCTION

The injection over-molding process for thermoplastics has attracted attention for automotive mass production as a promising direct joining method for fabricating hybrid fiber-reinforced thermoplastics (FRTP) parts. This process is a combination of stamping and injection molding (IM) for manufacturing complex three-dimensional (3D) parts. The continuous FRTP in laminate form (Organo sheet) is used as a substrate of hybrid composite parts. Preheated organo

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sheet are inserted into the mold of IM and thermoformed to a specific shape. Moreover, thermoplastics reinforced with fibers are injected onto the inserted parts by IM for structuring multiple rib parts. [1] Due to the integration of optimal processes for each material, this methodology provides new ultra-light weight parts that have high mechanical properties, recyclability, and short-cycle manufacturing.

Meanwhile, in this process, joining strength between two materials is a major factor in the mechanical strength of a product. It is generally known that adhesive strength is affected by injection conditions. [2] It has also been reported that the joining strength is highly dependent on the maximum temperature of the interface and that the cylinder temperature is the molding condition that affects the interface temperature. [3] However, increasing the cylinder temperature increases the cooling time, leading to a decrease in the molding cycle. Therefore, to improve the joining strength, a technique of adding multi-walled carbon nanotubes (MWCNTs) filled polypropylene (PP) film to the substrate surface was developed as our previous study. This approach improved the interlaminar shear strength (ILSS). [4] However, it is still unclear cause why the strength improved by adding CNTs.

In this study, to clarify the influence of nanofiller size on the joining strength, two kinds of nanofillers, CNTs and vapor grown carbon fibers (VGCFs) were used. In addition, this study focuses on the melt state of substrate surface during injection molding when nanofibers are added to the interface and examines a method for quantitatively evaluating the effect of nanofibers on joining strength.

EXPERIMENTAL

Method of making films containing nanofibers

The materials are MWCNTs (NANOCYLSA, NC7000™) and VGCFs (Showa Denko K.K., VGCF®-H) for the nanofibers and PP (Japan Polypropylene Co. NOVATEC MA04) for the matrix. The fiber length and diameter of CNTs were 9.5nm and 1.5μm, VGCFs were 150nm and 6μm. A co-rotating intermeshing twin-screw extruder was used to mix the materials, producing pellets of PP/CNTs and PP/VGCFs. The pellets were formed into nanofiber-containing films (150μm) using a servo press.

Tensile lap-shear strength test

The specimens were prepared using hybrid molding. Unidirectional prepreg sheet (TAFNEX CF/PP, Mitsui Chemicals, Inc.) was used for the substrate, and PP (NOVATEC MA04 Japan Polypropylene, Corp.) was used for the injection resin. For the base, a total of 20 prepreg sheets were stacked in a configuration of $[0°/90°]_5$ and a film containing nanofibers was placed at the joints of the injection resin and autoclaving the sheets using a servo press. The molding conditions of the injection molding machine were as follows: cylinder temperature 240°C, injection speed 100 mm/min, holding pressure 40 MPa, and mold temperature 70°C. **Figure 1.** shows the outline of the test specimen produced. The test was conducted in accordance with JIS k6850, and the tensile shear bond strength occurring at the interface was calculated from the following **Equation (1)**.

$$\tau = \frac{N}{A} \tag{1}$$

τ : Tensile lap-shear strength [MPa], N : Break force [N], A : Joining area

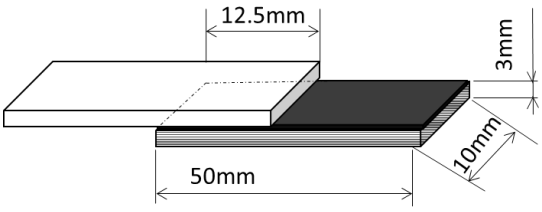

FIGURE 1. Specimen of tensile lap-shear strength test

DSC and XRD

To reproduce the condition of the nanofiber-containing film after injection molding, the specimens of DSC and XRD were heat-treated at 210°C using a servo press and then quenched with 10°C water. The DSC measurement conditions were as follows: temperature was increased from 40°C to 210°C at a rate of 10°C/min, maintained at 210°C for 5 minutes, and cooled to 40°C at a cooling rate of 25°C/min. **Equation 2.** was used to calculate the crystallinity [5], and the heat of melting of the complete crystalline material was set to 209 J/g [6].

$$X_c = \frac{\Delta H_m}{(1-\omega_t)\Delta H_m^0} \tag{2}$$

X_c : Crystallinity [%], ΔH_m : The experimental heat of fusion [J/g], ω_t : The weight fraction of fiber, ΔH_m^0 : The heat of fusion of the complete crystalline[J/g]

RESULTS AND DISSCUSSION

First, the relationship between nanofiber content and tensile lap-shear strength is shown in **Figure 2.**. From this graph, the joining strength is most improved at CNT contents of 0.5wt%

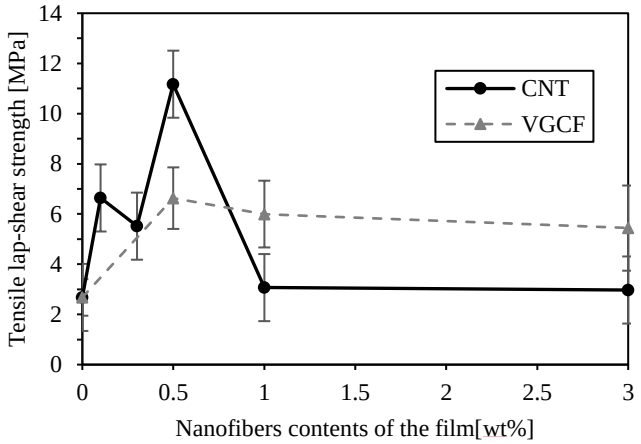

FIGURE 2. Relationship between nanofiber contents and tensile lap-shear strength

The fracture morphology after testing shown **Figure 3.** by X-ray CT. Firstly, in CNTs, the PP(0.0wt%), 0.1wt%, and 0.3wt% are all debonded between substrate and injection resin. On the other hand, 0.5wt% shows debonding in the laminate substrate. Also, the 1.0wt% and 3.0wt% show delamination between the injection resin and the substrate due to the decrease in joining strength. Secondly, in VGCFs, debonded interface was observed at all content rates. Therefore, we found that the fracture morphology changes depending on the joining strength.

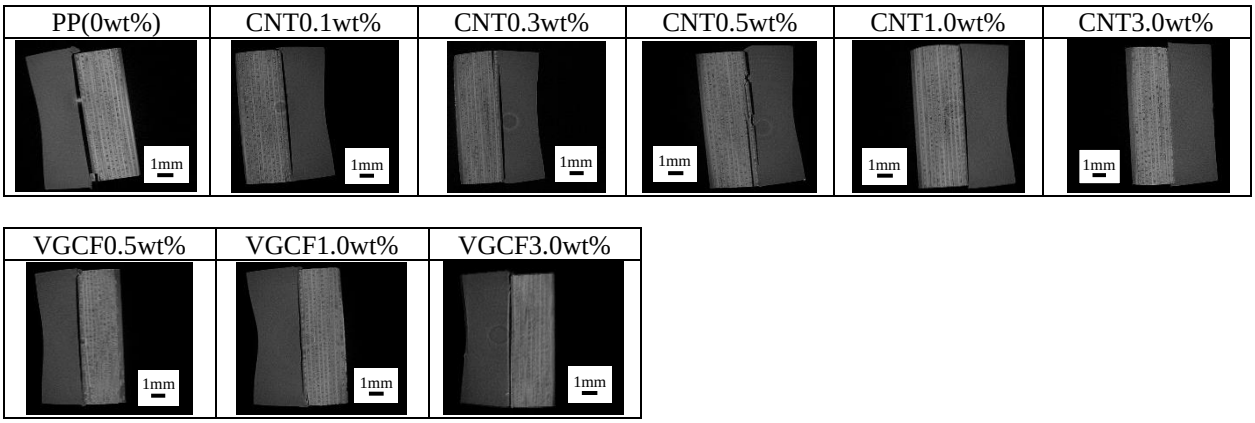

FIGURE 3. X-ray CT scan images of tested sample

DSC and XRD results are shown in **FIGURE 4.** and **FIGURE 5.** . Figure 4 shows that the crystal structure was not significantly changed regardless of the content or the size of the nanofibers, all of which were α-crystalline. Figure 5 shows that crystallinity decreases with increasing nanofiber content. Therefore, although the crystallinity of substrate surface decreased by adding nanofibers, CNT0.5wt% was the best contents for joining strength. Therefore, 0.5wt% CNT was the best content for joining strength, even though the crystallinity of the substrate surface decreased with increasing nanofiber content and there was no change in crystalline structure. From the data of this study, the crystallinity of the substrate surface of the specimen (nanofiber-containing film) is not considered to be an influential factor on the joining strength improvement. However, the fracture configuration of the X-ray CT image indicates that nanofibers have some influence between the two materials, so it is necessary to investigate the cooling behavior of the nanofiber-containing film in the future.

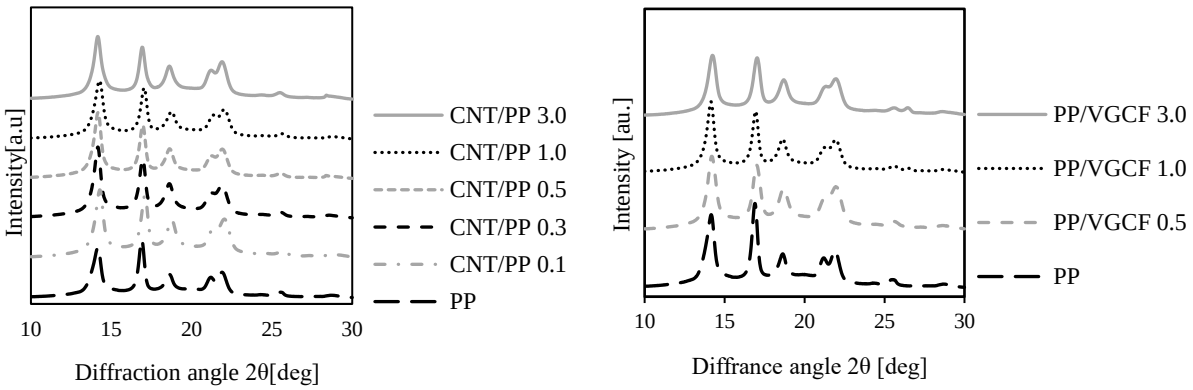

FIGURE 4. XRD Patterns of isothermal crystallized (a) PP/VGCF film and (b) PP/CNT film

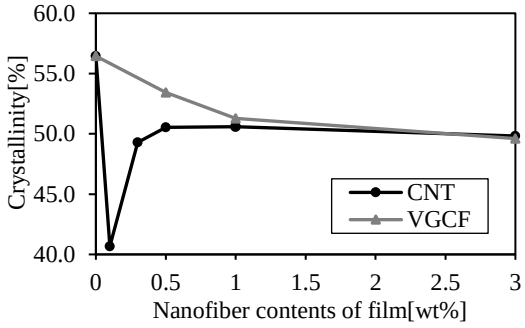

FIGURE 5. Relationship between Crystallinity of film and nanofiber contents of film

CONCLUSIONS

In this study, a tensile lap-shear strength test was used as a method of evaluating joining strength in order to investigate the influence of nanofiber size on a joining strength. In addition, the melting behavior of the substrate surface (nanofiber-containing film) was investigated to determine the cause of the increase in joining strength due to the addition of nanofibers. From these results, the following conclusions were drawn.

- At a content of 0.5wt%, the tensile lap-shear strength of the CNT containing film is about 1.6 times higher than that of the VGCFs film.
- In the tensile lap-shear strength test, delamination was observed in the laminate substrate when CNT content of 0.5wt% were added.
- The crystallinity of the substrate surface (nanofiber-containing film) decreased as the nanofiber content of the nanofiber-containing film increased.

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