Interfacial Properties of PP/PP Composites

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ABSTRACT

The interface structure of polypropylene (PP/PP) composites, consisting of homo-PP fibers and propylene-ethylene random copolymer matrix, was investigated. Generally, in the case of increasing the relative nucleus concentration on the fiber surface, transcrystalline structure grows at the interface instead of spherulitic growth. In this study, PP fibers with nucleating agent were prepared in order to increase the relative nucleus concentration. As a result, it was found that the amount of fiber surface nucleation in PP/PP composites gradually increases with the increase of nucleating agent, and transcrystalline structure grows on the PP fiber. Mechanical properties of PP/PP composites, consisting of homo-PP fibers and propylene-ethylene random copolymer matrix, were measured. While the modulus of PP fiber decreases with increasing amounts of nucleating agent, the modulus of the PP/PP composites remained relatively stable. The effects of the transcrystalline region on the macroscopic mechanical properties were discussed using the law of mixtures. It was shown that the presence of the transcrystalline structure at the interface enhances the mechanical properties of the PP/PP composites.

1. INTRODUCTION

In recent years, composites with excellent properties have been achieved. The adhesive properties of the fiber-matrix interface especially have been a subject of interest, because the presence of interfaces strongly influences the mechanical properties of composites. For example, the combination of inorganic fibers and organic matrices makes high performance composites such as CFRP and GFRP However, the adhesion between these two types of materials is essentially not good due to the completely different natures of both substances. Composites that consist of the same type of material, especially thermoplastic materials, but with different roles such as reinforcing fiber and matrix phase, do not require that attention be paid to its interface /1,2/.

Several studies have looked at thermoplastic materials of the same kind in both fiber and matrix; these materials were focused and evaluated /3-8/. In these thermoplastic composites, the improvement in mechanical properties is due to the interface structures. Accordingly, surface modifications of fibers by plasma treatment, chemical etching, etc., for improvement adhesion of fiber and matrix polymer, have been tried in several studies /1,2,9/.

Furthermore, it has been indicated that a transcrystalline interface between fiber and matrix polymer is produced under certain conditions and the presence of this interface improved the mechanical properties of the composites /10/. However, it has been shown that a transcrystalline interface has little effect on the stress transfer ability of the interface /11/. Thus, it is uncertain how the transcrystalline structure on the fiber surface improves the mechanical properties of the composites. In these studies of single polymer composite, the material used for fiber and matrix polymer was polyethylene (PE). Therefore it is difficult to produce a transcrystalline interface. Generally, in the case of increasing the relative nuclei concentration on the fiber surface, the transcrystalline structure grows on the

interface instead of the normal spherulitic growth /9/. By using polypropylene fiber, increasing the relative nucleus concentration is possible, because there are many nucleating agents for PP. That is to say, we think it is easy to produce a transcrystalline interface by using PP fibers with a suitable nucleating agent.

In this study, PP fibers which contained nucleating agent were prepared by changing the relative nuclei concentration. The unidirectional PP fiber reinforced PP composites were fabricated by the aid of a film stacking and press molding process. The effects of a nucleating agent on interfacial structures and properties of composites were studied by using single-filament fragmentation tests and tensile tests of the PP/PP composites.

Fig. 1: DSC curves of PP fiber and PP matrix film.

2. EXPERIMENTAL

The materials used were a homo-polypropylene fiber and a propylene-ethylene random copolymer matrix (Sumitomo Chemical Industry Co., Ltd.). The material used as a nucleating agent was poly-vinyl-cyclo-hexane (PVCH) dispersed in a butene-propylene random copolymer (1000 ppm) (Sumitomo Chemical Industry Co., Ltd.) /12/. The PP fibers were obtained with the following concentrations of PVCH: 0, 35 and 50 ppm.

In PP/PP composites, the molding temperature is important for maximizing adhesion and for keeping the fiber shape because the reinforcement and matrix are of the same material. Differential Scanning Calorimeter (DSC) measurements were thus carried out on the reinforcement and matrix. According to these DSC results, the melting temperature of the PP film was 135°C and that of the PP fiber and also the PP fiber filled with nucleating agent was 165°C as shown in Figure 1 (3.5 wt%, 5.0 wt%), so that 163°C was selected as the molding temperature.

Specimens for single-filament fragmentation tests and tensile tests were fabricated by means of the film stacking and press molding process as shown in Figure 2. The press mold holding time was 1 minute for both specimens. The fiber volume content of PP/PP composites for the tensile tests was 12%. Tensile tests were performed using an Instron universal testing
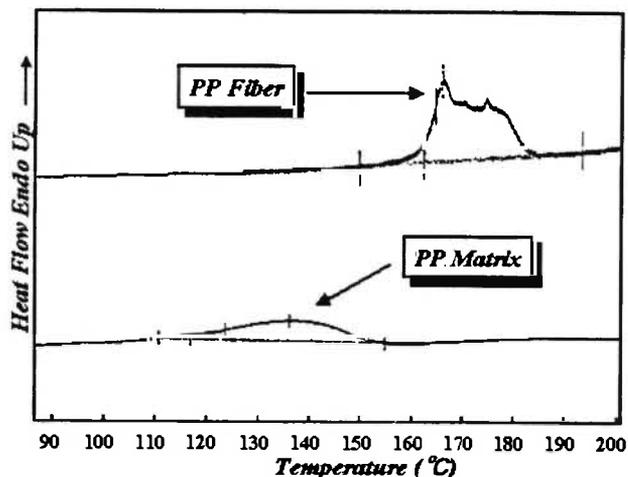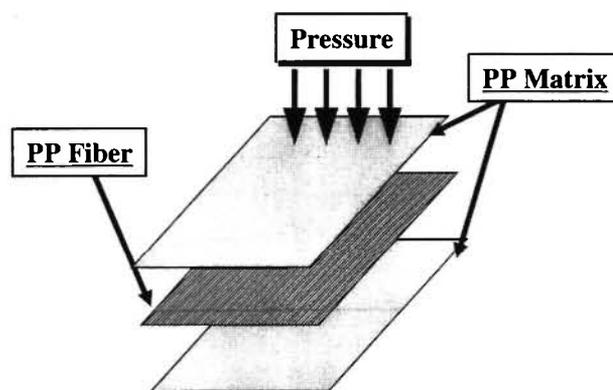

Fig. 2: Film stacking.

machine (type 4206) at room temperature. The test condition was 10 mm/min crosshead speed in all cases.

Single-filament fragmentation tests have been employed to evaluate interfacial shear strength /13,14/. Figure 3 indicates the specimen shape for the single-filament fragmentation test. In this technique a critical fiber length has to be measured. When tensile strain is applied to the specimen, a number of fractures of embedded fibers occur. Then the fragment lengths and fracture position along the fiber were measured by a polarization microscope (Nippon Kougaku, S-Po). The average length of fiber <L> was calculated using the average of the fragment lengths. The fiber-matrix
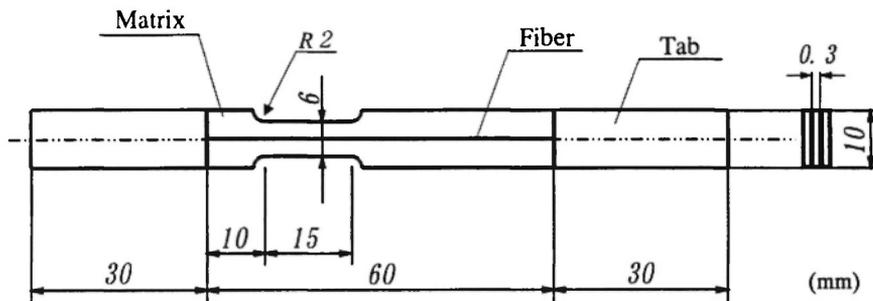
Fig. 3: Specimen shape for single-filament fragmentation test.

interfacial shear strength, τ_i, was evaluated by equation (1):

$$\tau_i = \frac{3D\sigma_f}{8 < L >} \qquad (1)$$

where <L> is the average length of fiber in fracture, D is the diameter of fiber and σ_f is the tensile strength of the fiber.

In the single-filament fragmentation test, the relationship between the fiber-matrix interfacial shear strength and the amount of nucleating agent in PP fibers was evaluated. In the tensile tests of PP/PP composites, the relationship between tensile modulus and the amount of nucleating agent in PP fiber was evaluated.

3. RESULTS AND DISCUSSION

Figure 4 shows the optical micrographs of specimens after the single-filament fragmentation test. It is clear that a number of fractures of the embedded fibers has occurred. The critical fiber lengths were evaluated by averaging the fractured fiber lengths.

Figure 5 presents the relationship between the fiber-matrix interfacial shear strength and the PVCH concentrations in the fibers. The fiber-matrix interfacial shear strength increased with increasing concentration of PVCH. The adhesive properties of the fiber-matrix interface are improved by using PP fibers with added nucleating agent.
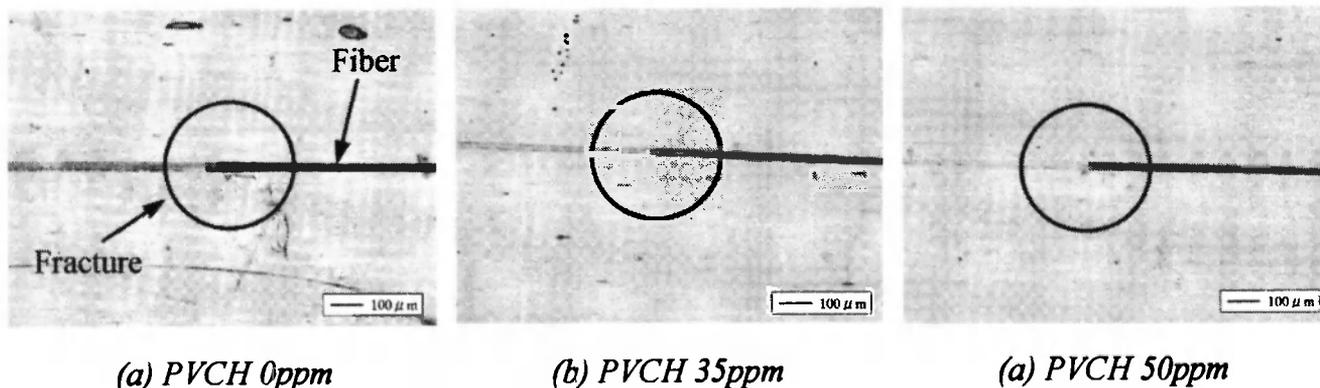

(a) PVCH 0ppm   *(b) PVCH 35ppm*   *(a) PVCH 50ppm*

Fig. 4: Micrographs of specimen after single-filament fragmentation test.
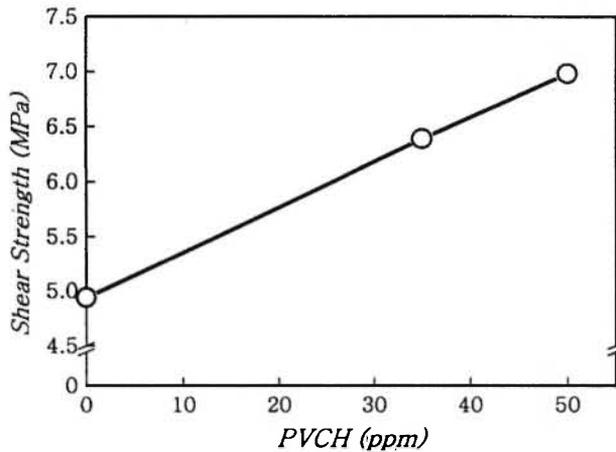
Fig. 5: Shear strength in single-filament fragmentation test.

In PE/PE composites, it has been observed that crystallization of the matrix occurs at first on the fiber surface and then in the bulk /7/. The crystallization behavior of the PP/PP composite is similar to that of the PE.PE composite. If the fiber surface has many nucleation sites that can grow matrix polymer crystallites, a transcrystalline layer on the fiber surface is produced.

Consequently, the growth of this transcrystalline layer on the fiber surface was observed using a polarized light optical microscope. Figure 6 shows the optical micrographs of cross-sections of PP/PP composites which have fibers containing PVCH as the nucleating agent.

When using fibers containing PVCH, which had concentrations of 35 ppm and 50 ppm, transcrystalline growth was clearly observed on the fiber surface. The thickness of the transcrystalline layers in PP/PP composites, filled with PVCH, was about 8~10 μm. On the other hand, in the case of using fibers without PVCH, the thickness of the transcrystalline layers when observed was about 5~8 μm. This result indicated that increasing the concentration of PVCH in fibers increased the extent of the transcrystalline layer.

Figure 7 presents the relationship between the mechanical properties of PP/PP composites and the PVCH concentrations in the fibers. In the case of the 0 degree direction, the tensile modulus and strength of PP/PP composites remained relatively constant with increasing concentration of PVCH. In these experiments, the nucleating agent was PVCH, dispersed in butene-propylene random copolymer to improve the dispersion of PVCH. By adding the butene-propylene
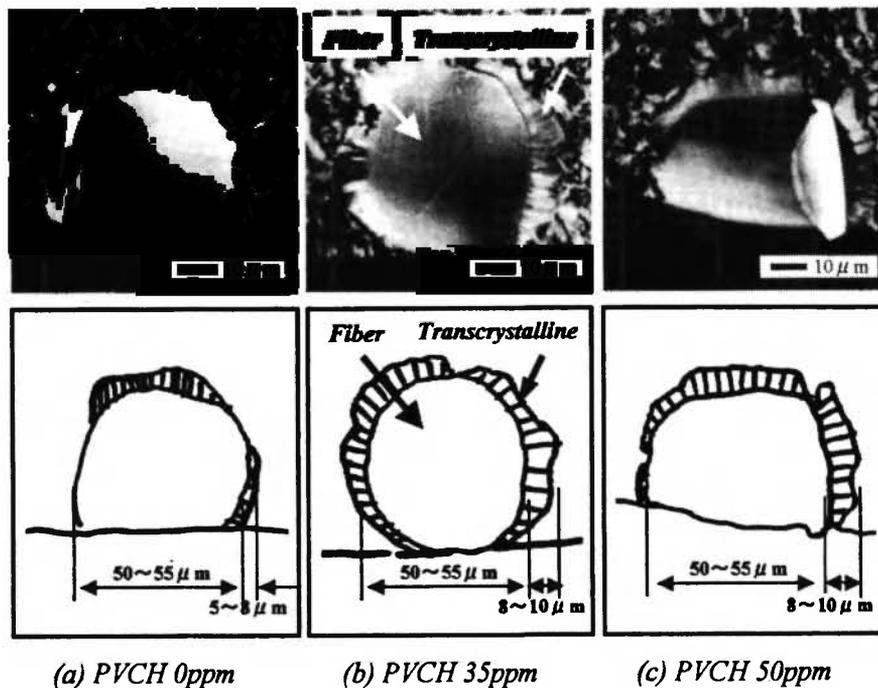

(a) PVCH 0ppm   *(b) PVCH 35ppm*   *(c) PVCH 50ppm*

Fig. 6: Optical micrographs of cross-sections for PP/PP composites.

(a) Modulus in 0 degree direction

(b) Strength in 0 degree direction

(c) Modulus in 90 degrees direction

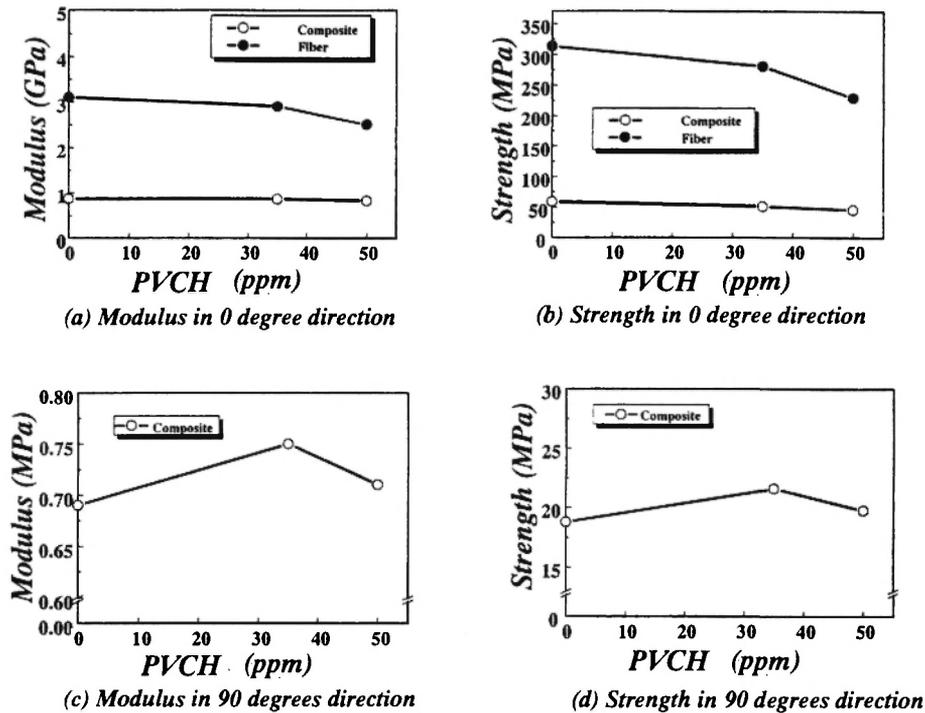(d) Strength in 90 degrees direction

Fig. 7: Tensile moduli and strengths of PP/PP composites.

random copolymer to the fiber, the tensile modulus and the strength of the fibers decreased. Mechanical properties of the composite show behavior similar to those of fiber as shown in Figure 7.

In the 90 degree direction, the tensile modulus and the tensile strength of the composite increased upon increasing the concentration of PVCH in the fibers. This behavior in the 90 degree direction is similar to that reported in the literature for PE/PE composites /8,15/, and, as can be seen, growth of the transcrystalline layer enhances the mechanical properties.

Figure 8 shows scanning electron micrographs of the fiber surface of the PP/PP composite after tensile tests in the 90 degree direction. As can be seen, the fibers with PVCH seem to be surrounded by some matrix layers, which exhibit transcrystalline layer features. However, the fibers without PVCH in PP/PP composite do not appear to have this matrix layer. These results indicate that the interfacial strength between the fibers with PVCH and the matrix is stronger than that between the fibers without PVCH and matrix.

The Laws of Mixtures for the modulus in the 0 and 90 degree directions were evaluated. The Laws of Mixtures are given as follows:

$$E_{exp} = \alpha_0 \left\{ a\,E_f + (1-a)\,E_m \right\}$$

$$E_{exp} = \alpha_{90} \left\{ \frac{E_f\,E_m}{E_f\,(1-a) + aE_m} \right\}$$

where E_{exp} : tensile modulus of PP/PP composite
E_f : tensile modulus of fiber
E_m : tensile modulus of matrix
A : volume content of fibers
α_0 : coefficient in 0 degree direction
α_{90} : coefficient in 90 degree direction

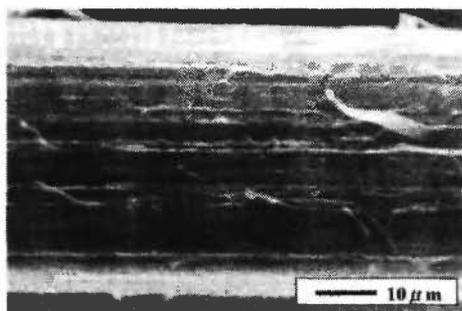(i.e. α indicates experimental value/theoretical value)

Table 1 shows the relationship between the concentration of PVCH in the fibers and the value of α in the 0 degree (α_0) and 90 degree (α_{90}) directions. The value of α_0 and α_{90} increases with an increase in
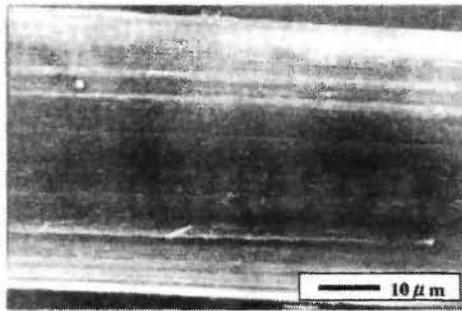
(a) PVCH 0ppm
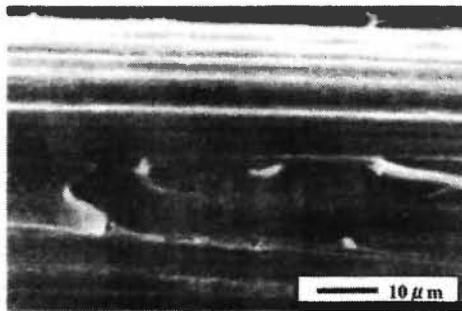
(b) PVCH 35ppm

(c) PVCH 50ppm

Fig. 8: SEM micrographs of fiber fracture surfaces for PP/PP composites in 90 degree direction.

concentration of PVCH. Furthermore, the value of α_{90} was increased much more markedly than the value of α_0 for the same increase in concentration of PVCH. From this result, the transverse modulus of the PP/PP composites increased with an increase in PVCH due to an increase in the extent of the transcrystalline layer. In the 0 degree direction, the mechanical properties of the PP/PP composite were little affected by the presence of the transcrystalline layer. However, in the case of the 90 degree direction, the mechanical properties of the PP/PP composite were much affected by the presence of the transcrystalline layer. As shown in Table 1, the values of α_0 and α_{90} were over 1. The transcrystalline grows in a straight line on the surface of the fiber. However, normal spherulitic grows radially. Therefore, it is possible to think that the crystallinity of the transcrystalline was higher than that of the normal spherulitic structure. The matrix structure consists of the transcrystalline layer and the spherulitic structure. Consequently, the values of E_m increased due to the increase in extent of the transcrystalline layer.

4. CONCLUSIONS

In this study, a fiber with a nucleating agent, PVCH, was selected as reinforcement, and the fiber-matrix interfacial shear strength of single-filament fragmentation specimens and the mechanical properties of PP/PP composites were investigated. As a consequence, good adhesion between a fiber with a nucleating agent and the matrix was realized by producing a transcrystalline layer at the interface of single-filament fragmentation

Table 1
Mechanical properties and law of mixture

	PVCH (ppm)	E_{exp} (GPa)	E_f (GPa)	α
0 degree	0	0.87	3.1	0.99
	35	0.86	2.9	1.00
	50	0.82	2.5	1.01
90 degree	0	0.73	3.1	1.04
	35	0.67	2.9	1.13
	50	0.69	2.5	1.10

$E_m = 0.58$ (GPa), a = 0.12

specimens and PP/PP composites was demonstrated by the increase in fiber-matrix interfacial shear strength of single-filament fragmentation specimens and the mechanical properties of PP/PP composites. Especially in the transverse direction, the mechanical properties of PP/PP composites increased with increasing concentration of the nucleating agent. From this result, it is concluded that the mechanical properties, especially in the 90 degree direction, were affected by the presence of the transcrystalline layer.

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