유리섬유/PP 복합재료의 계면거동에 미치는 수지의 분자량 및 섬유직경의 영향

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The Effect of Molecular Weight and Fiber Diameter on the Interfacial Behavior in Glass Fiber/PP Composites

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요 약 : 유리섬유강화 열가소성 수지 복합재료의 계면거동 및 기계적 성질에 대한 연구의 일환으로 섬유직경이 다른 유리섬유와 분자량이 다른 polypropylene(isotactic)을 사용하여 유리섬유와 PP matrix의 계면조직에 섬유직경과 matrix의 분자량이 미치는 영향을 Hot stage와 편광현미경을 이용하여 검토하였다. 그 결과 polypropylene의 분자량 및 유리섬유의 섬유직경은 섬유축을 따라 형성되는 관상모양의 transcrystallinity의 morphorlogy에 영향을 미치며 matrix의 구정의 반경과 transcrystallinity의 두께는 같은 것을 알았다. 그리고 열가소성 복합재료에서 transcrystallinity의 형성은 matrix 에서 구정의 형성과 성장을 억제한다.

Abstract : The effects of fiber diameter and molecular weight of the matrix polymer in glass fiber reinforced polypropylene composites have been investigated on the interfacial microstructure. The influences of the surface state of fiber and the heat treatment condition on the interfacial morphology and the spherulitic formation process in matrix have also been investigated. From this study, it has been found that both fiber diameter and molecular weight of the polymer significantly influence the thickness of the transcrystalline layer. In addition, the radius of the largest spherulites in matrix has been found to be about the same as the thickness of transcrystalline region and to largely depend on the holding time at the crystallization temperature and cooling condition(or rate).

INTRODUCTION

The mechanical properties of fiber reinforced composites are generally known to be greatly affected by such factors as fiber length,[1,2] fiber orientation,[3~5] and the interfacial shear strength[6,7] bet-

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ween fiber and matrix.

In particular, an evaluation of interfacial structure and properties is essential for an understanding of composite properties, for the stress acting on the matrix is transmitted to the fiber across the interface between the fiber and the matrix. Hence, the interfacial bonding strength is mainly controlled by the physical and/or chemical bonding in case of the thermosetting matrix resin.

However, when semicrystalline thermoplastic resins are used as matrix systems, particular interfacial morphological features[8~10] may arise due to the direct influence of the fibers on the crystallization process. That is, a columnar growth of crystals corresponding to the lateral development of the spherulites, normally referred to as "transcrystallinity", is caused along the fiber axis due to the nucleating effect of fiber, thereby enhancing the interfacial bonding strength between fiber and matrix.[11~13]

The work reported here is a part of the research project concerned with the elucidation of the relationship between the interfacial microstructure and mechanical properties of glass fiber/thermoplastic resin composites. Hence, this paper focuses mainly on the effect of fiber diameter (D_f) and molecular weight (MW) of the matrix polymer on the interfacial microstructure in glass fiber (GF) reinforced polypropylene(PP) composites.

In addition, the influence of the surface state of fiber on the interfacial morphology and the variation of the spherulitic formation process in the matrix phase with the different heat treatment have been examined.

EXPERIMENTAL

Fiber

The glass fibers used for this study were supplied by Han Kuk Fiber Glass Co., Ltd., graded as "E-type" with a density of 2.54 g/cm^3, and had three different diameters of D_f=9.6, 12.1 and 19.5 μm. However, only a grade of fiber of D_f=12.1 μm was mainly used for the effective analysis and co-

mparison of the data obtained. In addition, carbon fiber of 7.43 μm diameter was also used for reference in the study.

The average fiber diameters have been estimated from the length and weight of the fiber using the value of fiber density for the glass fiber, and with the aid of the laser for the carbon fiber.

Matrix

The matrix material used for the preparation of composites was commercially available isotactic PP, supplied by Korea Petrochemical Ind. co., Ltd., with three kinds of melt flow index (MFI), i. e. MFI=3.5, 8, and 15. A grade of the polymer of MFI=15 has been mainly used, unless otherwise stated, throughout the study for the effective comparison among the data.

Surface-Treatment of Fiber

The glass fibers used in this study have been classified into three types, designated as the "treated", the "untreated, moistened", and the "untreated, dried" glass fibers, according to the condition of surface treatment as follows.

The first is obtained by washing the as-received (silane-treated) E-glass fiber in acetone for 30 min, followed by vacuum drying at 80 ℃ for 3 hrs to remove any spin finish or impurity.

The second type corresponds to the one made by allowing the untreated (without the silane-type coupling agent) GF to stand for a long time in the air so as to absorb sufficient (equilibrium) moisture.

Finally, the third is obtained by washing the untreated GF in acetone, followed by vacuum drying at 80℃ for 24 hrs to get rid of any moisture or impurity present. Unless otherwise noted, however, the E-glass fiber appearing in the text hereinafter will stand for the first type of GF.

In addition, carbon fibers used for reference were of two types : one is epoxy-treated, and the other, untreated.

Spceimen Preparation for Optical Observation

Test specimen for observation of the interfacial microstructure (or crystalline structure) of composites using a polarizing optical microscope were

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prepared according to the following procedure. A small amount of PP was placed onto a cover glass preheated to ca. 220℃ on a hot stage, then a single filament of GF was put on the melted PP, and finally another cover glass preheated was placed over the sample and pressed down using a weight of 300 g to ensure complete melting and constant film thickness,[14] subjected to the following heat-treatments appropriate for crystallization studies.

Heat-Treatment Condition

The samples thus obtained were heat-treated at a temperature of 220℃, above the melting temperature of PP by ca. 30℃, to ensure complete melting and to remove any thermal history. The melt holding (or annealing) times were varied as 5, 30, 60, and 120 min. The samples held in the melt for a prescribed period were cooled to room temperature of ca. 13℃ by three different procedures : the "water-super cooling", made by quick immersion into water, the "rapid cooling", where the cooling was carried out throught use of two sheets of steel plate containing the melt-held samples between them, and the "air cooling", made by standing in the air at ca. 13℃, where the wooden pincette was used to minimize the heat conduction effect. Among them, in particular, the rapid cooling method based on the use of steel plates has been taken as the standard cooling condition throughout the study in view of the optimum cooling rate.

Besides, several other heat treatment procedures have been employed for crystallization studies of PP composites in presence of reinforcing fibers. Typical examples among them will be given in the following. In the first case, the samples held for a given period at 220℃ were rapidly cooled to 130℃, corresponding to the crystallization temperature (Tc) of the maximum rate as found by observing the growth of spherulites of PP, where they were again held for different periods of 10, 60, and 120 min, followed by cooling to room temperature by the rapid cooling procedure.

In another case, the melt samples held at 220℃ were cooled to the final cooling temperature of 30, 50, 80, or 100℃ by the rapid cooling procedure

using the steel plates, and held for ca. 5 min at the respective temperatures, followed by cooling to room temperature rapidly.

Optical observations on the samples thus prepared were made using an Olympus microscope (PMG 3) with cross-polarizers in order to investigate the transcrystallinity developed on the fiber surface as well as spherulites in matrix for PP composites reinforced with GF or carbon fiber, the number of test specimen for a given type of experimental condition being 5 to 8, as required by the correct evaluation of the results obtained.

RESULTS AND DISCUSSION

From a series of studies on crystallization morphology (both the transcrystalline and spherulitic structures) of the PP composite samples obtained by varying the melt holding time at 220℃, it has been found that the melt holding of 30 min corresponds to the standard condition to differentiate among the interfacial microstructures of different experimental conditions under the present situation covered. Hence, this value has been taken as the standard melt holding time throughout the study.

Fig. 1 shows the variation of both the transcrystalline and spherulitic growths with the cooling condition (or rate) for PP with surface-treated glass fibers crystallized upon cooling from the melt held at 220℃ for 30 min according to the respective cooling procedures.

From this figure, we can easily understand that in case of the water (super) cooling condition the transcrystalline layer is not well developed along the fiber axis, and even any really distinctive spherulitic growth is hard to discern in the matrix phase, nearly similar to the amorphous state. In contrast, in case of the air cooling both the transcrystallinity and spherulites are well developed in composites.

In addition, the lateral extent (or thickness) of the transcrystalline layer and the size (or radius) of the largest spherulites for the rapid cooling con-

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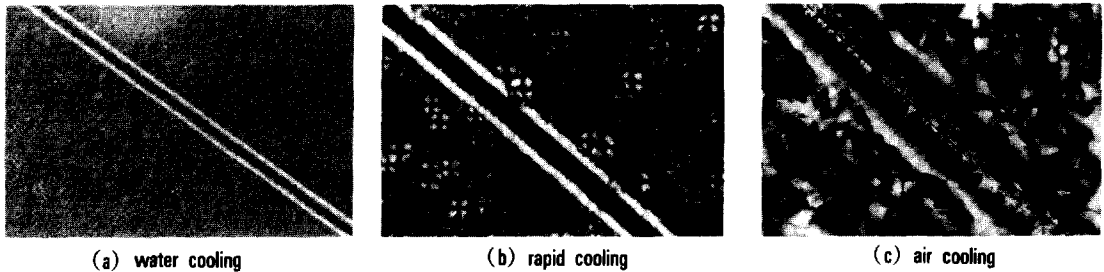(a) water cooling   (b) rapid cooling   (c) air cooling

Fig. 1. Transcrystallinity and spherulitic morphology of E-glass fiber/PP composites crystallized according to various cooling procedures from the melt held for 30 min at 220℃ (MFI = 15).
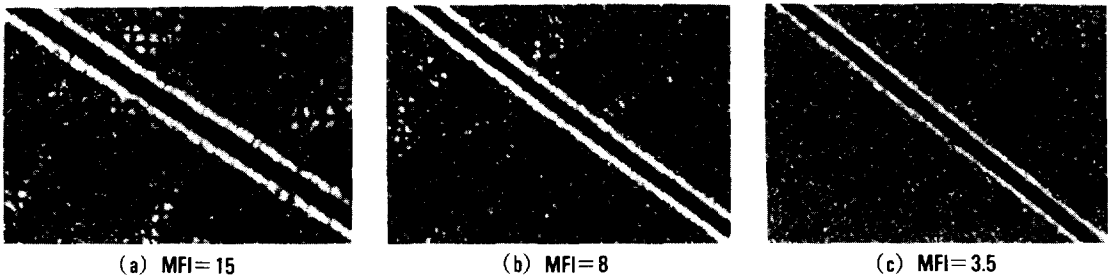

(a) MFI = 15   (b) MFI = 8   (c) MFI = 3.5

Fig. 2. Optical microphotographs showing the variation of the interfacial microstructure with MFI for PP with E-glass fibers, crystallized upon rapid cooling from the melt held at 220℃ for 30 min.

dition are intermediate between those for the water cooling and the air cooling. Hence, the rapid cooling has been taken as the standard cooling condition, unless otherwise noted. Meanwhile, the reason why the size of the spherulites is the largest for the air cooling is that the residence time near 130℃, corresponding to the maximum crystallization temperature of PP, is longer compared to other cooling conditions.

Fig. 2 represents the variation of the fiber-matrix interfacial morphology with the MFI (or MW) of the polymer in E-glass fiber/PP composites, each sample crystallized from the melt held at 220℃ for 30 min by rapid cooling (based on the use of steel plates) to room temperature. For the lowest MW (or highest MFI) polymer studied, it can be seen that the nucleation density along the fiber is high and the lateral extent of the transcrystalline layer is also remarkable.

On the other hand, as the MW of the polymer is increased, the transcrystalline layer becomes less uniform and less pronounced.

This behavior can be explained as follows. In case of the low MW polymer, there are a number of chain ends ; accordingly, the probability of an attachment of the polymer molecules onto the fiber surface is increased, thereby rendering the increased nucleation density and transcrystalline growth along the fiber.[8] However, this will be more difficult for longer chains because of the inhibiting effect caused by chain entanglements.[8] The same reasoning can be applied to the size of the spherulites in the matrix phase.

In Fig. 3, the optical microphotographs showing the variation of the interfacial microstructure with the fiber diameter in E-glass fiber/PP composites are given, each crystallized by rapid cooling from the melt similarly to the previous case. From this figure, we can see that as the fiber diameter decreases, the thickness of the transcrystalline layer is considerably increased relative to the fiber diameter.

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A qualitative, though speculative, explanation for this could be made in terms of the surface phenomenon, more specifically Laplace equation on the pressure difference between inside and outside the bubble. That is, if we plausibly assume the fiber embedded in the matrix fluid to act as "bubble", such as occurring during the melt fabrication for sample preparation, the pressure within the bubble will be inversely proportional to the fiber diameter, hence the large wetting (or shrinkage) force being exerted to the smaller-diameter-fiber by matrix fluid.

As a result, the tendency of fiber to nucleate the crystallization of matrix polymer will be promoted, thus leading to the increased transcrystalline region responsible for a strong interfacial bond. In addition, from the investigation made on the interfacial microstructure of E-glass fiber/PP composite samples obtained at different final cooling temperatures as described in the experimental section, though not given here for want of space, it has been found that as the final cooling temperature is lowered, both the thickness of transcrystalline region and the radius of the spherulites in matrix decrease, which is probably because there is no sufficient time for the polymer molecules to crystallize, in particular around 130℃ of the maximum crystallization rate, due to the rapid cooling rate.

As shown in Fig. 4, experiments on the interfacial microstructure of E-glass fiber/PP composite samples obtained using different holding times of 10, 60, and 120 min were also carried out, according to which as the holding time is increased, both the transcrystalline and the spherulitic growth become more pronounced, as may be expected from the previous results.

The optical microphotographs showing the interfacial microstructure of PP with untreated glass fibers of different drying condition are given in Fig. 5. From this figure, it can be seen that the transcrystallinity is less developed on glass fiber surface for the moistened fiber than for the dried
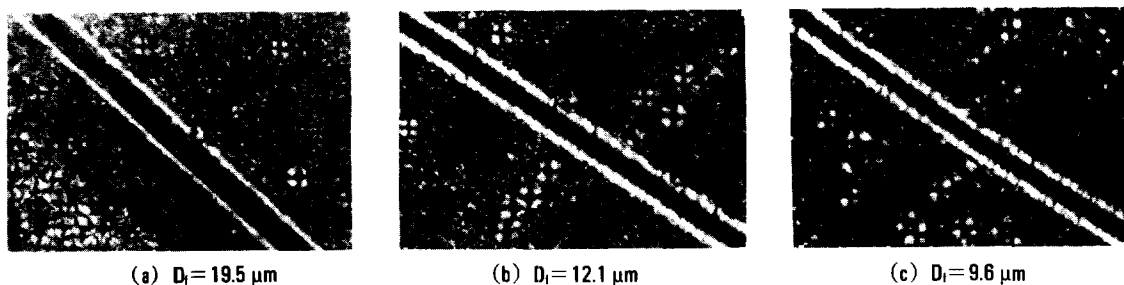

(a) $D_f = 19.5 \ \mu m$ (b) $D_f = 12.1 \ \mu m$ (c) $D_f = 9.6 \ \mu m$

Fig. 3. Optical microphotographs showing the variation of the interfacial microstructure with fiber diameter for PP with E-glass fibers, crystallized upon rapid cooling from the melt held at 220℃ for 30 min (MFI=15).
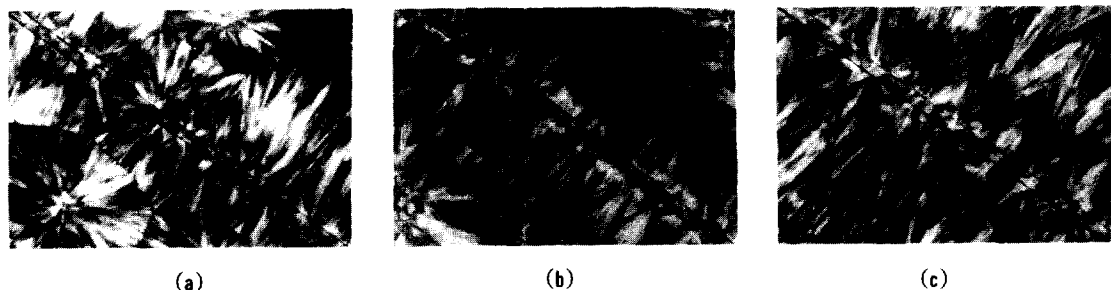

(a)   (b)   (c)

Fig. 4. Interfacial microstructure of PP with E-glass fibers : samples held at 220℃ for 30 min, rapid-cooled to 130℃, where held again for (a) 10 ; (b) 60 ; (c) 120 min followed by rapid cooling to room temperature.

one. This difference may be attributable to the fact that the critical surface tension of fiber is decreased due to the absorption of moisture, thus resulting in the decrease in wettability by the liquid, and hence the decrease in nucleating ability of fiber.

As follows from the comparison of the results between the treated and the untreated (dried) glass fibers, the lateral extent of the transcrystalline layer does not seem to differ so much in both cases. In addition, as evident from the previous results noted, the thickness of the transcrystalline layer is almost the same as the radius of the largest spherulites in matrix, implying that glass fiber surface and nuclei surviving in the bulk have almost the same activity.

Fig. 6 shows the interfacial microstructure of PP composite samples based on epoxy-treated and untreated carbon fibers, chosen for reference, revealing that any distinctive difference does not seem to exist between the two cases. When compared to the results for the glass fiber under about the same heat-treatment condition, the case for the carbon fiber has been found to have a more pronounced transcrystalline region owing to the effect of the lower fiber diameter, as stated before.

In order to investigate the interfacial morphology as found in actual E-glass fiber/PP composites, optical microphotographs of composite samples obtained by molding the matrix polymer with multi-fiber are given in Fig. 7. It can be easily seen that as the inter-fiber spacing becomes wider, the spherulites are seen to be formed between the transcrystalline layers developed on glass fiber surface, suggesting that nucleation on the fiber is dominant over the matrix nucleation, i. e., transcrystallinity along the fiber is predominantly formed over the spherulites in matrix.

Consequently, we may expect that the formation of transcrystallinity on fiber surface causes the
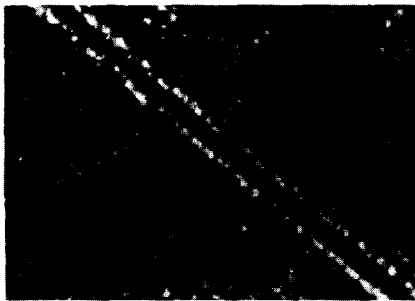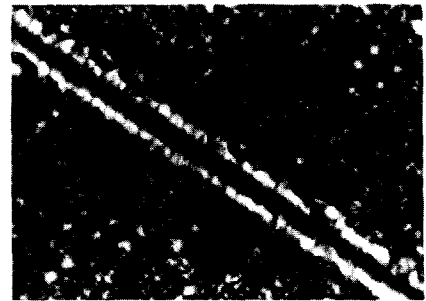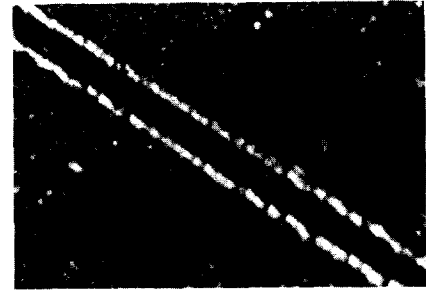

(a)
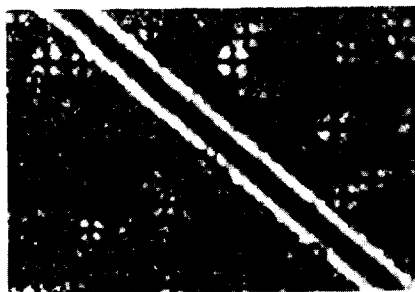
(b)

Fig. 5. Interfacial microstructure of PP composites based on untreated glass fibers : (a) moistened ; (b) dried ; GF, crystallized upon rapid cooling from 220℃.

(a)

(b)

Fig. 6. Interfacial microstructure of PP composites based on (a) untreated-, and (b) treated-carbon fibers, crystallized upon rapid cooling from 220℃.
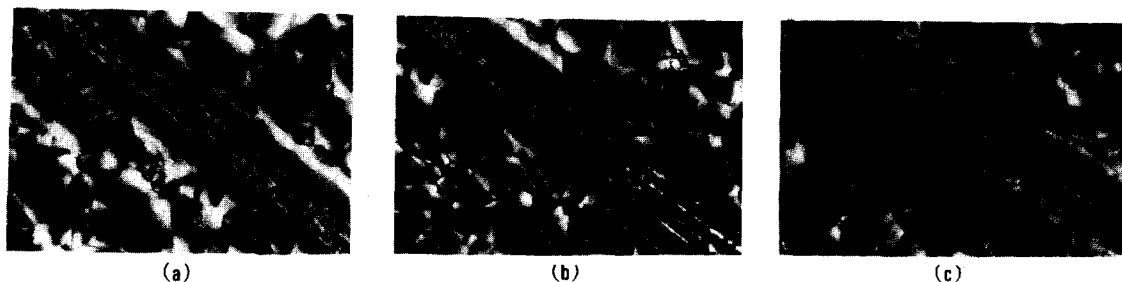
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(a)   (b)   (c)

Fig. 7. Cross-polar optical microphotographs of E-glass fiber reinforced PP composites, crystallized from the melt held at 220℃ for 30 min by air cooling to room temperature.

properties of the fiber surface and the matrix to become more similar, thus yielding the effective wetting of fibers by matrix, strong interfacial adhesion, good dispersion of fibers in the matrix, and hence strong mechanical properties of composites. Although this view has been already confirmed in case of carbon fiber reinforced polyethylene composites, the work along this line for the PP composite system is in progress.

CONCLUSION

The finding made from this study can be summarized as follows :

1. The interfacial transcrystalline structure is significantly affected by fiber diameter of GF and molecular weight of PP.

2. The thickness of transcrystalline region is almost the same as the radius of the largest spherulites in matrix.

3. The size of the spherulites in matrix depends largely on both the holding time at the crystallization temperature and the cooling condition (or rate) from the melt to room temperature.

4. The formation of the transcrystalline structure in fiber reinforced composites based on semicrystalline thermoplastic resins impedes the spherulitic formation and development within the matrix phase.

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