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Interface layers of fiber reinforced composites with transcrystalline morphology

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Summary

In fiber reinforced polymer composites with transcrystalline structure, an interface layer can exist between the fiber and the transcrystalline area. Polymer chains orient along the fiber when the matrix consists of liquid crystalline polymers and form row structures on the fiber surface. The interface layer is not oriented and consists of crystalline aggregates, when the matrix is a flexible polymer. The interface layer can be easily etched by a chemical etchant or by ion etching, whereas the transcrystalline areas are revealed by controlling the degree of etching. As a result, the interface layer and the transcrystalline area can be well distinguished from each other by using scanning electron microscopy (SEM).

INTRODUCTION

The crystallization behavior of polymer matrices are influenced by the properties of fibers in fiber reinforced polymer composites[1]. The crystal growth changes from the radial direction of spherulites to the direction normal to the fiber surface when nucleation occurs with a sufficiently high density along the fiber surface, i.e. transcrystalline growth, and it is believed that the occurrence of the transcrystalline growth is one of the key factors for the improvement of some composite properties[2,3]. The transcrystalline phase has been found in many fiber reinforced polymer composites[4-7].

Morphological features in polymer composites greatly influence their ultimate properties, but remain poorly understood. Therefore, the morphology and structure of fiber reinforced polymer composites should be fully understood in order to improve their properties. In this study, the morphology and structure of fiber reinforced polymer composites with transcrystalline phases are studied by

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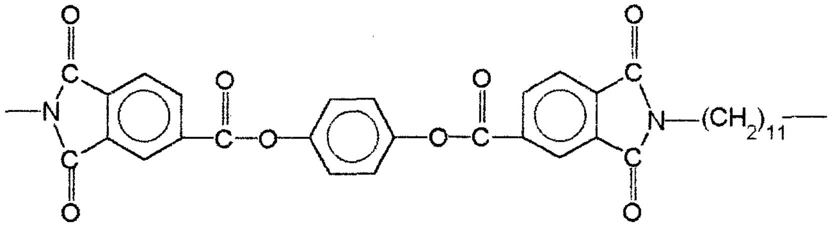
optical and electron microscopy and the interface layer between fibers and transcrystalline areas is discussed.

EXPERIMENTAL

Polybutene-1 (PB-1) used in this study was supplied by Chemische Werke Marl in Germany and its molecular weight Mn was about 8×10^5. Liquid crystalline poly (ester imide)(PEI) was supplied by professor Kricheldorf and its molecular formula was as follows[8]:



The melting temperature of PEI was about 216℃ and the transformation from anisotropic melt to isotropic one occurred at 230℃. The carbon fiber (T-300) and glass fiber were from BASF and only treated with acetone to clean the surface before using.

A small piece of the polymer film, previously pressed at 180℃ for PB-1 or at 220℃ for PEI between two glass slides, was placed on a microscope slide with a carbon fiber or glass fiber, single or more, and covered by a cover slip. The specimen was heated at 5-6℃/min to 180℃ for PB-1 or to 244℃ for PEI and held at these temperatures for 5 min to clear residual structure. Subsequently, it was cooled at about 5℃/min to the desired temperatures (210℃ for PEI and 115℃ for LB-1) and subsequently the fiber was gently drawn (at about 1mm/sec) to produce a strain in the polymer around the fiber surface. Isothermal crystallization was carried out using a hot stage at this temperature and the morphology was observed by a polarizing microscope(Leitz, ORTHOPLAN-POL)

The specimen was then etched using two methods. The first one was by using 0.7/1/1 (w/v/v) solution of potassium permanganate/orthophosphoric acid/ sulphuric acid. The specimen washed with distilled water after etching, successively with hydrogen peroxide to remove any manganese dioxide or permanganate present, and finally by distilled water again. The second method was ion etching, which was carried out by an ion coater (IB-5, Kiko Engineering Co., Ltd.). The specimen was etched in gas ion of air with the pressure of 13-26 Pa. The ionizing current was 6 mA and the ionization voltage was 2,000V in etching. The specimen was fixed to the SEM specimen stub and observed by a scanning electron microscope (SEM)(S-430, Hitachi) after being coated with a platinum film.

RESULTS AND DISCUSSION

The formation of oriented spherulites in a thermal gradient is attributed to the steric hindrance and the anisotropic growth rate parallel and normal to the thermal gradient[9]. The growth rate of lamellae, however, in isothermal crystallization is the same in all directions. Consequently, the formation of oriented spherulites is attributed to the steric hindrance in isothermal crystallization[10]. The density of nuclei on the fiber surface is very high when the nucleation is caused by strain, and the lamellae can only grow in the direction normal to the fiber surface to form the transcrystalline growth.

The transcrystalline phase grows in normal direction to the surface of fibers. The polymer matrix in the vicinity of the fiber surface, however, is not oriented, which we may call the interface between the fiber and the transcrystalline phases. This can be observed under a polarizing microscope (Figure 1). The dark straight line (indicated by an arrow) in Figure 1 is a carbon fiber, which is parallel to the polar direction of the analyzer. The lamellae are parallel to the polar direction of the polarizer in Figure 1. Therefore, the perfect transcrystalline phase, in which the brightness is strongest when the angle between the fiber and the polar direction of the polarizer is 45°, can be observed. Moreover, with the rotation of the specimen,

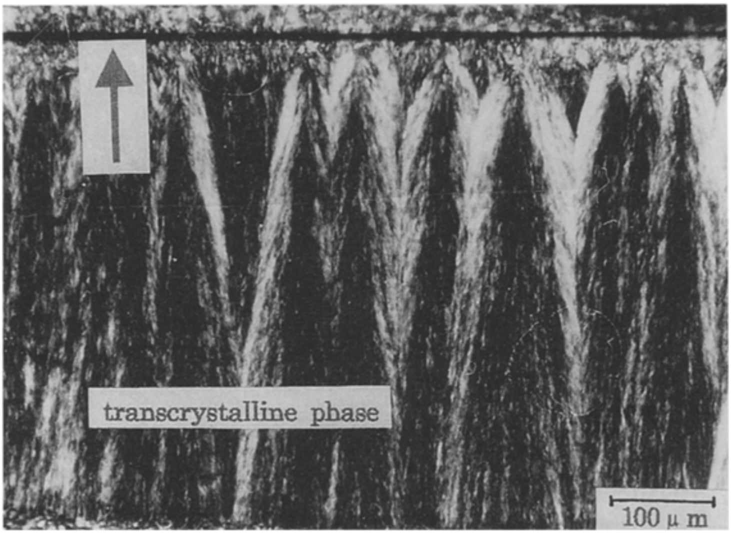


Figure 1. Polarizing optical micrograph of PB-1/carbon fiber composite. The dark line indicated by the arrow is a carbon fiber.

it is confirmed that the polymer matrix between the fiber and the transcrystalline phase is not oriented.

The transcrystallization of PB-1 can be induced by strain resulting in very high nucleation density at the fibers, and the steric hindrance of the growth of crystal lamellae. In the process of the nucleation induced by strain, the formation of the nuclei is very fast and the density of nuclei is very high on the surface of fibers. A vast amount of small crystalline aggregates with imperfect structure are formed on the surface of the fibers. The growth of lamellae is hindered by other lamellae and the lamellae stop growing except in the direction perpendicular to the fiber surface. At this stage, the lamellae can grow only in this direction and finally, the transcrystalline growth occurs. In the beginning of crystallization, therefore, only disordered and small crystal particles with imperfect structure can be formed in the very close vicinity of the fiber surface.

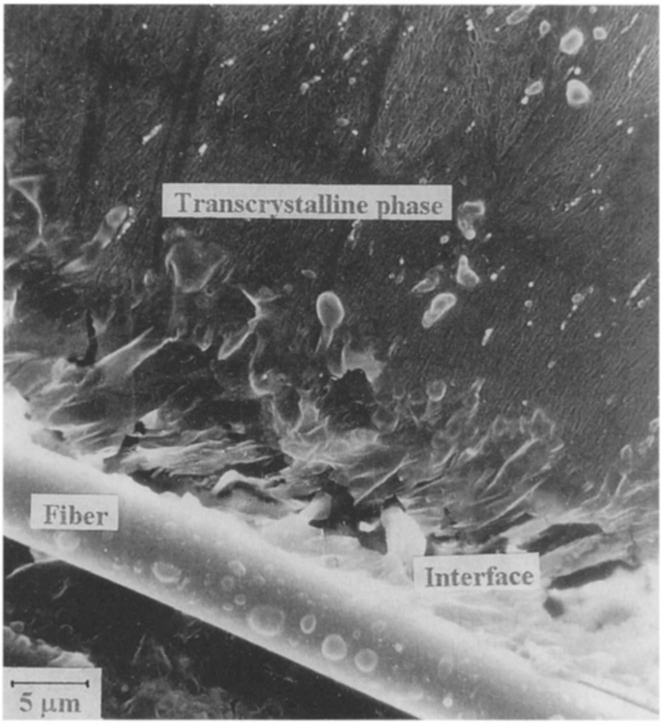


Figure 2. SEM micrograph of the PB-1/glass fiber composite with transcrystalline structure, slightly etched.

The small crystalline aggregates with imperfect structure on the surface of the fibers can be partly or totally destroyed by etching, and the interface can be distinguished from the transcrystalline phases by SEM. Figure 2 shows a SEM micrograph of a PB-1/glass fiber composite after slightly etching with potassium permanganate/orthophosphoric acid/sulphuric acid etchant. Because amorphous parts are etched, the transcrystalline structure of PB-1 is clearly revealed, which grows in the direction normal to the surface of fibers. Between the transcrystalline phase and the fiber surface, however, there is a partly destroyed region, which we call the interface layer between the fiber and the transcrystalline area. Some globular particles are still on the fiber surface. It is evident from that picture that the structure in the interface layer is not oriented. This result is in agreement with that observed by polarizing optical microscopy.

In the PEI/glass fiber system, similar to the PB-1/glass fiber, the transcrystallization can also occur after the glass fibers are slightly drawn at the crystallization temperature. The high nucleation density along the fibers is due to the orientation of PEI polymer chains near the fiber surface. Figure 3 is a SEM micrograph of a PEI/glass fiber composite etched by ions. The transcrystalline phase is clearly observed and the row structure, which are nearly normal to the fiber (indicated by arrows in Figure 3), is exposed by etching, as seen in the SEM micrograph. The fiber in Figure 3 is 1-2 μm thicker than that without polymers and this indicates that the interface layer, which covers the fiber with 2-3 μm in thickness, is partly destroyed by ion etching but a residual part of the interface layer still exists on the surface of the fiber.

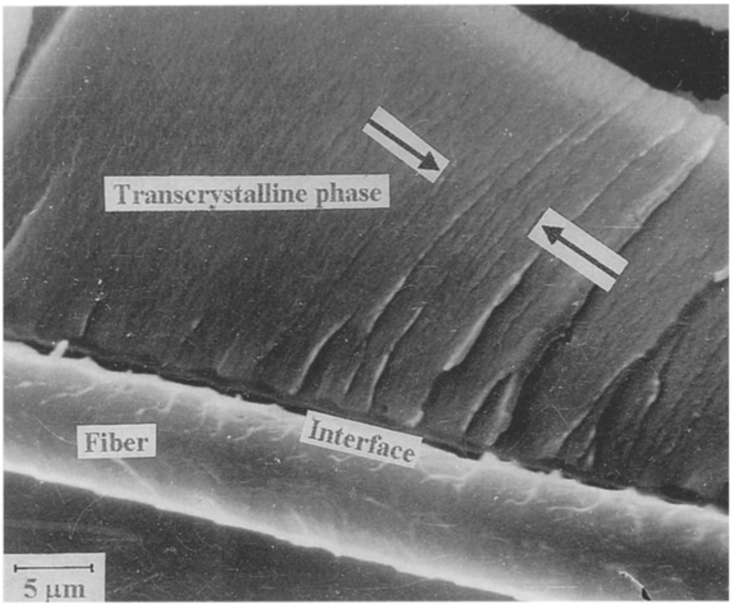


Figure 3. SEM micrograph of the PEI/glass fiber composite, etched by ions.

The morphological features of the composites with transcrystalline phases is schematically demonstrated in Figure 4. The interface layer, which is 2-5 μm in thickness, exists between the fiber and the transcrystalline area. In the interface layer, the morphology is different according to the pattern of nucleation and the nature of the polymer matrix. When the polymer matrix is PB-1, there are many globular particles or small spherulites with imperfect crystalline structure and when the matrix is a liquid crystalline PEI, polymer chains orient along the fiber and cover it. The reason may be because, on the one hand, that polymer chains of the liquid crystalline PEI are oriented more easily than those of the flexible PB-1, when the fiber is slightly drawn at the crystallization temperature. Polymer chains in the very close vicinity of the fiber surface orient in drawing the fiber, but relaxation of orientation occurs with time. The orientation of liquid crystalline PEI chains is stable and its relaxation is difficult compared to the PB-1 chains, which are flexible. Consequently, PEI polymer chains retain their orientation along the fiber in the beginning of crystallization and form a row structure on the fiber surface. The orientation of the PB-1 polymer chains relax before crystallization and many small spherulites form on the fiber surface. On the other hand, a few of elements, such as Si, N, Sn, etc. may exist on the carbon fiber surface[11] and the elements of Si and O can exist on the glass fiber surface. PB-1 is composed of carbon and hydrogen but there are many C=O groups on PEI chains. The fiber surface may be moistened by PEI chains but cannot by PB-1 chains, because the interactions between the fiber surface and PEI chains is stronger than PB-1. The interfacial free energy between the fiber surface and PEI will be lower than that between the fiber surface and PB-1. Consequently, PEI chains can lie on the fiber surface and PB-1 chains can only aggregate to globular particles.

Such an interface layer can be totally destroyed by deeply etching. Figure 5 is a SEM micrograph of a PB-1/glass fiber composite, which is deeply etched by potassium permanganate/orthophosphoric acid/sulphuric acid. The interface layer is totally destroyed but the oriented transcrystalline structure is still clearly observed. This result confirms that the small spherulites in the interface layer between the fiber and the transcrystalline area for PB-1/glass fiber composites are imperfect in their structure and, similar to amorphous parts, are easily destroyed by chemical etching. Also, the lamellae are also clearly revealed after the specimen is deeply etched. The thickness of lamellae is about 13 nm and some lamellae twist in their growth, which may be related with the features of their growth.

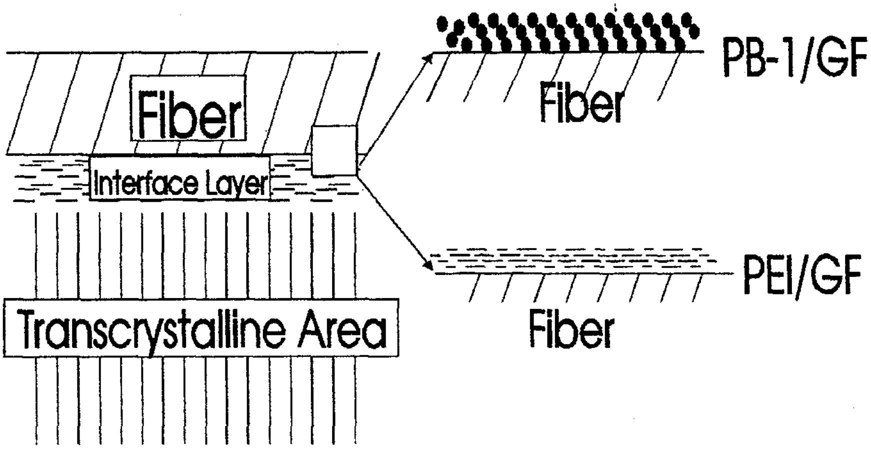


Figure 4. Scheme of the morphology of fiber reinforced composites with transcrystalline structure and the interfacial layer.

Amorphous material and small crystal particles with imperfect structure are destroyed in etching by an etchant or ions more easily. In transcrystalline areas, however, the crystalline structure is more ordered and consequently, the oriented transcrystalline structure is more difficult to be destroyed.

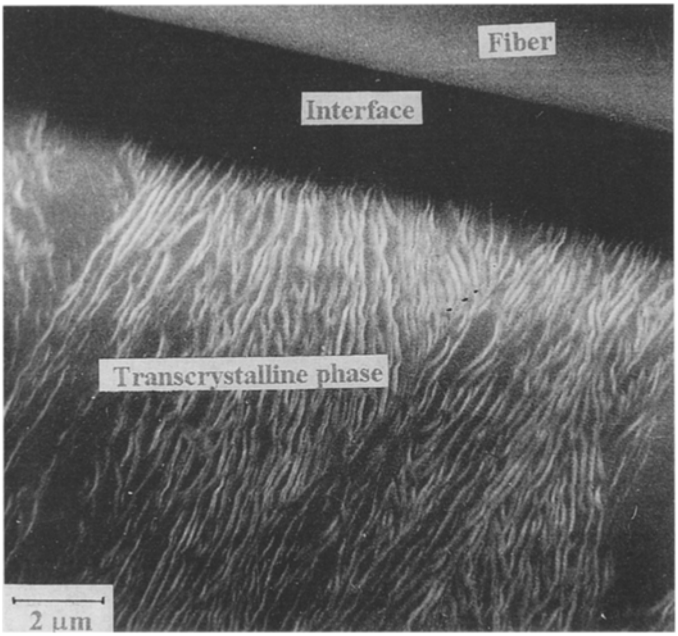


Figure 5. SEM micrograph of the PB-1/glass fiber composite, strongly etched

CONCLUSIONS

An interface layer between fibers and transcrystalline structures in fiber reinforced polymer composites exists, with the transcrystalline structure and the morphological features depending on the pattern of crystallization and the natures of the polymer chains. The interface layer is composed of small disordered crystal particles with imperfect structure when matrix is a flexible polymer such as PB-1. This interface layer is formed by the fast nucleation along the fiber surface by strain. Polymer chains orient along the fiber and form row structures in the interface layer for rigid or semirigid polymers such as liquid crystalline PEI. This interface layer is formed by the fast nucleation on the fiber, induced by strain on the surface of the fibers and before the relaxation of polymer chains occurs. The interface layer and the transcrystalline area can be distinguished by appropriate etching with a chemical etchant or ion.

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