

# Morphology Investigation of Transcrystallinity at Polyamide 66/Aramid Fiber Interface

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**ABSTRACT:** The morphology of PA66/Kevlar-129 fiber specimens was investigated by means of polarized optical microscopy and scanning electron microscopy. The results indicated that, at crystallization temperatures ranging from 100 to 220°C, the transcrystallinity (TC) interphase always occurs. Both the TC interphase and spherulite morphology

were present under various crystallization conditions. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2980–2983, 2004

**Key words:** polyamide 66; fibers; transcrystallinity; thermoplastic; morphology

## INTRODUCTION

Thermoplastic composites reinforced with fibers or textiles have preferred mechanical properties compared to those of pure materials, and are drawing increasing attention. The occurrence of transcrystallinity (TC) on the fiber surface has been observed in various kinds of resin/fiber systems.<sup>1–6</sup> In general, TC results from crystallization on a highly nucleating foreign surface.

The process of transcrystallization seems to be generally understood, and the conditions under which the fiber surface tends to induce nucleation of matrix have been summarized<sup>6</sup>; however, the essential mechanism for TC (i.e., why the fiber surface can induce the nucleation of the resin matrix) is still unclear. The occurrence of TC in various polymer/fiber systems may be interpreted based on different principles. For example, the TC interphase in poly(ether ether ketone) (PEEK)/aramid fiber system is attributed to the epitaxial effect, whereas a thermal conductivity mismatch is considered to be the major cause of TC in PEEK-based composites reinforced with carbon and E-glass fibers.<sup>6</sup>

TC probably has an effect on the performance of thermoplastic composites, which can be ascribed to two aspects. First, the interface strongly influences the mechanical performance of the composite materials because the stress applied to the matrix must be transmitted to the fiber across the interface. In the case of a composite with TC, the TC interphase between the fiber and the matrix can be seen as a so-called inter-

face; hence, the structure, morphology, and the dimension of TC may influence the process of stress transmission and the mechanical properties of the composite. Second, because it is often sufficiently thick, TC can be considered as a separate phase, and its direct influence on the performance of composite materials may be considerable.<sup>7</sup> For some systems, TC may improve the mechanical properties, but for others, it does not improve the stress transfer ability of the interface<sup>8</sup> or it may even play an inverse role. So, in the design of the polymer-based composite, the effect of TC on the performance should be treated as an important problem and investigated in detail for different polymer/fiber systems.

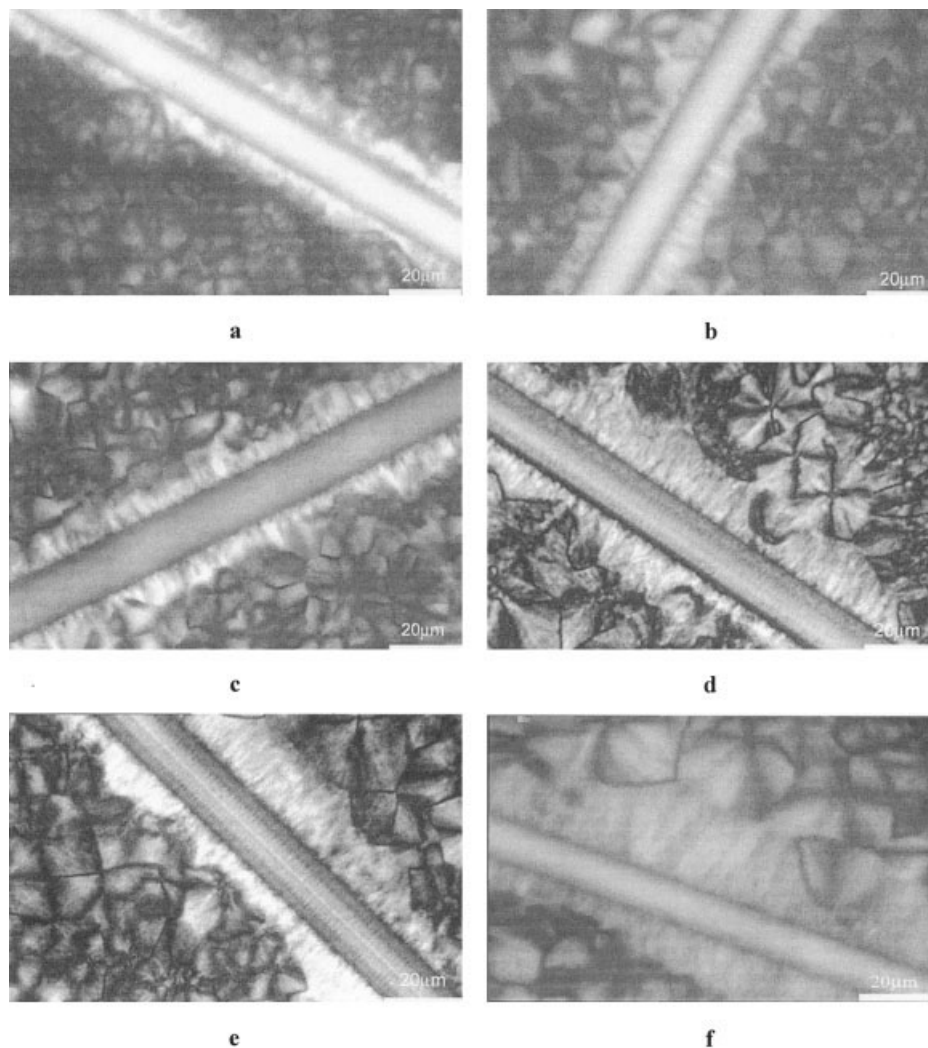
It is well known that the performance is mainly dependent on the structure and the morphology of the materials. Morphology is of essential importance, and materials with same chemical structure but different morphology usually present significantly different performance. For fiber-reinforced thermoplastic composites, the morphology usually involves two aspects: one is of TC and the other is of the bulk matrix. Undoubtedly, both exert an important influence on the mechanical performance. Simultaneously, the interface performance is associated closely with changes of the morphology of the matrix.<sup>1,9</sup> Thus, the morphology of TC and the matrix is the key problem in determining the mechanical performance of the composite and both aspects must be taken into account simultaneously in design of the composite.

Polarized optical microscopy (POM) is a convenient method to investigate the morphology of crystallites. The process of crystal growth, the shape, and the size of crystallites can be traced or determined from POM microphotographs.

Preferential crystallization has been addressed in many earlier works, although most of the works are

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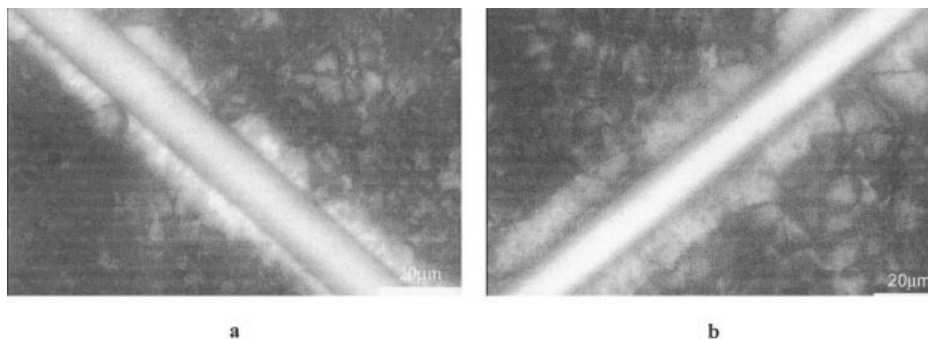
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**Figure 1** POM micrographs of isothermal crystallization samples. Crystallization time: 10 min; crystallization temperature: (a) 100°C; (b) 140°C; (c) 170°C; (d) 180°C; (e) 200°C; (f) 220°C.

based on polyolefin resins. Compared to others, polyolefin resins possess relatively simple molecular structure and therefore good crystallization ability. Polyamide-related research has not been widely reported.

Aramid fibers have high strength, high modulus, and high temperature resistance. Such good mechanical performances make it an excellent candidate to enhance polymer-based composites. Systems of iPP/aramid fiber,<sup>4,5,9-12</sup> PA66/aramid fiber,<sup>7,13</sup> and other



**Figure 2** POM micrographs of (a) sample quenched in air and (b) sample cooled in a stove.

TABLE I  
Mean Thickness of Transcrystallinity Layer of Isothermal Crystallization Samples

Crystallization temperature (°C)	100	110	120	130	140	150	160	170	180	200	220
TC thickness ( $\mu\text{m}$ )	5.1	5.1	6.8	6.8	7.9	7.2	7.5	7.8	12.3	10.4	18.7

kinds of polymer/aramid fibers<sup>6</sup> have been investigated by various methods.

For this article, we investigated the system of PA66/aramid fiber, in which the morphology of both TC and spherulites under various crystallization conditions were observed with POM.

## EXPERIMENTAL

### Materials

Pellets of nylon 66 (Yingshan Petroleum Chemical Factory of Baling Petroleum Chemical Co., China) were used as a matrix. Single filaments of Kevlar-129 aramid fiber (DuPont, Wilmington, DE) were used as the reinforcing component.

### Preparation of specimens

PA66 (16 wt %)/formic acid solution was dropped on a cover slide on which the Kevlar-129 fiber was previously placed. After the solvent volatilized, the specimen in which a single aramid fiber was embedded was obtained.

### Crystallization procedure

Isothermal crystallization was performed using a homemade DPL-II crystallization rate meter. The sample was first molten at 270°C for 30 s, then crystallized at certain selected temperatures for 10 min. The crystallized sample was finally taken out and cooled naturally to room temperature.

Another two sets of samples were obtained through different routes. The sample was first molten at 270°C for 30 s, followed by either quenching in air or cooling in a stove at 2.5°C/min to room temperature.

### Morphological observation

The morphology of the spherulites and TC layer was investigated with a polarized optical microscope (Olympus BH-2, Tokyo, Japan) equipped with a CCD probe (Panasonic WV-cp 230) for collection of images. A pulling-out test with one isothermal crystallization sample was performed. The morphology of the pulled-out fiber surface was observed with a scanning electron microscope (S-4300F; Hitachi, Ibaraki, Japan).

## RESULTS AND DISCUSSION

### Morphology investigation of PA66/aramid fiber system

Figure 1 shows POM microphotographs of isothermal crystallization samples, from which transcrystallinity and spherulites can be identified clearly. TC occurs around the fiber surface when the isothermal crystallization temperature ranges between 100 and 220°C, indicating that Kevlar-129 fiber is an effective nucleation agent for PA66 crystallization and the initiation of TC on its surface is easily achieved.

The morphology of spherulites can also be observed from the micrographs in Figure 1. We can see that, when the crystallization temperature is low, there are some integral spherulites with smaller size dispersing in the PA66 bulk phase, whereas when the crystallization temperature is elevated, more and more spherulites, with greater size, form in bulk and crowd around the TC. In our opinion, for both TC and spherulites, the size changes with temperature are attributed to the decrease of nucleation density in the bulk when the crystallization temperature increases.<sup>14</sup> Figure 1 shows the apparent size and location relations between TC interphase and spherulites in the bulk phase: at various crystallization temperatures investigated in this study the thickness of the TC layer was almost equal to the radii of the spherulites, and there was an apparent boundary line between the TC layer and the spherulites.

Figure 2 shows the POM micrographs of samples quenched in air and cooled in a stove. In both cases, TC occurs around the fibers and there are few spherulites formed in the matrix of PA66. Transcrystallization is generated even in conditions that do not favor crystallization, like quenching in air and cooling in a stove, which confirms the nucleating ability of the fibers.

### Thickness of TC layer

The influence of crystallization temperature on the mean thickness of the TC layer is shown in Table I. It is obvious that the thickness of the TC layer is temperature dependent and increases with increased crystallization temperature. Table II lists the TC thickness values of samples quenched in air and cooled in a stove.

In general, there is a critical volume fraction of the fibers, and if the actual fraction is greater than the critical

**TABLE II**  
**Mean Thickness of Transcrystallinity Layer for Samples Quenched in Air and Cooled in Stove**

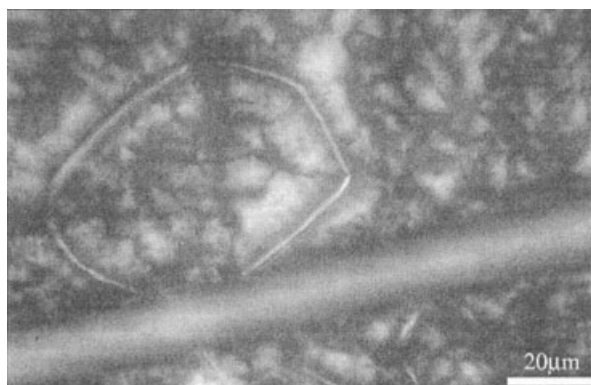
	Sample	
	Quenched in air	Cooled in stove
TC thickness ( $\mu\text{m}$ )	6.8	11.1

value, there will be no spherulites and only TC formed in the composite system. The value of the critical volume fraction is determined by the TC thickness. The fiber-reinforced composites with full TC are expected to possess entirely different mechanical performance, compared with that of both spherulites and TC.

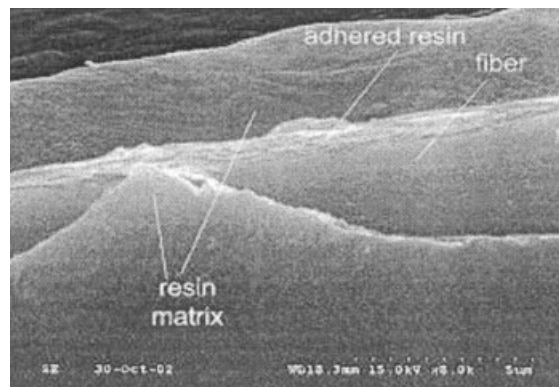
It was also found that the TC thickness is independent of the diameter of the fiber. It is well known that Kevlar fiber has poor abrasion resistance because of its weak lateral bond force.<sup>9</sup> Thus, it is easily fibrillated when rubbed against another rigid material. We obtained the morphology of TC that occurred on a fibril of Kevlar fiber (see Fig. 3). It can be seen that the TC thickness is small in proportion relative to the diameter of the fiber. TC thickness is suspected to be a function of the fiber surface condition and the crystallization temperature.

#### SEM investigation of sample with pulled-out fibers

Figure 4 shows the morphology of an isothermally crystallized sample with the embedded fiber partially pulled out. It may be seen clearly that some resin adhered to the surface of the pulled-out fiber, suggesting good bonding strength in fiber–matrix interfaces. A good interface bond between the fiber and matrix makes it easier for stress transmission from matrix to fiber; thus, the mechanical performance may be improved.



**Figure 3** POM micrographs of TC occurring along the fibril of Kevlar fiber.



**Figure 4** SEM micrographs of isothermal crystallization (220°C) sample with the fiber pulled out.

## CONCLUSIONS

Based on the above discussion, the following conclusions were obtained:

1. The transcrystallinity interphase can easily occur in PA66/Kevlar-129 systems.
2. The morphology of both transcrystallinity and spherulites is determined by the crystallization conditions.
3. The thickness of the transcrystallinity layer is temperature dependent, but independent of the geometry characteristics of the reinforcement.

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