

Nucleation and Crystal Growth of PEEK on Carbon Fiber

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SYNOPSIS

The nucleation and crystal growth of poly(ether ether ketone) (PEEK) on carbon fiber during isothermal crystallization were studied using optical microscopy. It was shown that the nucleation rate on the fiber is affected by the crystallization and melting temperatures. Transcrystallinity of PEEK was found to appear in the range 280–315°C after PEEK was melted at rather high temperature. Its linear growth rates at various temperatures were found to be similar to those of the spherulite in the bulk. Also, its thickness depends on the crystallization and melting temperatures. Variation of the molecular weight of PEEK within a small range has no obvious influence on its nucleation rate on the fiber, but affects the transcrystalline growth rate. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ether ether ketone) (PEEK) is one of the leading thermoplastic polymers that have become particularly attractive for high-performance composite application. It has satisfactory mechanical properties, good processability, and excellent chemical and radiation resistance.¹ Composites based on PEEK show interesting advantages in comparison with thermoset composites and may be used in many specific areas like aircraft.^{2–6}

Since the fiber–matrix interface that transmits stress on the matrix to the fibers plays a vital role in influencing composite properties, concentrated studies have been given to the interface of fiber-reinforced PEEK. A transcrystalline layer may form around carbon, glass, SiC, or Kevlar-49 fiber when PEEK is nucleated on the fiber surfaces, depending on the nature of the fiber.^{7–11} Hartness found that PEEK transcrystallinity was the predominate growth only if the carbon fiber was a high-modulus type made up of much larger graphite planes oriented along the fiber axis.⁷ However, transcrystallinity was also obtained on the surface of high-strength carbon fiber that has a small graphite structure with a low orientation degree.^{8,11} Also, when the graphite size in the high-modulus carbon

fiber is reduced by oxidation, the ability of the fiber to induce the nucleation of PEEK remains unchanged.¹¹ Despite the dispute about the effect of the graphite structure, the graphite edge plane has been considered to be the possible reason why polymer can be nucleated onto carbon fiber.^{12,13} Besides fiber structure, the nucleation of PEEK onto fiber is affected by thermal treatment. Long-holding time in the melt, slow cooling from the melt, or high crystallization temperature were all found to favor the formation of transcrystallinity.^{8,9,11,14}

As a crystalline interlayer, PEEK transcrystallinity around carbon fiber is characterized by its lamellar organization. Lamellae in the transcrystallinity were revealed to be similar to those in the nearby spherulites, but oriented in the direction perpendicular to the fiber axis.^{15,16} The formation of transcrystallinity will strengthen the interfacial adhesion between matrix and the fibers. Some studies showed that carbon fiber-reinforced PEEK had higher interfacial bond strength and high transverse tensile strength when transcrystallinity formed.^{7,8,17}

Further information about the interfacial crystallization effect was obtained by studying overall crystallization rate of PEEK reinforced with carbon fiber. It was found that PEEK in the composites can crystallize at a lower supercooling.⁸ However, details about the nature of the nucleation and crystal growth are still unknown. In this work, an investigation has been made into the nucleation kinetics, the transcrystalline growth process, and their de-

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pendence on thermal treatment. The effects of molecular weight on them have also been investigated.

EXPERIMENTAL

Three PEEK powders, grades 150P, 380P, and 450P with \bar{M}_n of 11,000, 14,000, and 16,000, respectively, which were commercially available products of Imperial Chemical Industries (ICI), U.K., were used in this work. High-modulus carbon fiber M40 was obtained from Torica Co., Japan. Before use, the fibers were refluxed in acetone for 2 weeks to remove possible coatings.

PEEK was first dissolved in α -chloronaphthalene at 250°C and casted on glass plates. The carbon fibers were then embedded in the solution followed by the removal of solvent. After being melted and pressed, the films were placed in the heat stage of a Leitz optical microscope for observation. First, the temperature was raised to a certain temperature over the melting point of PEEK and held for 10 min, then lowered very quickly to the crystallization temperature, T_c , for isothermal crystallization. The number of nucleating sites on the fiber surface and that in the bulk PEEK were counted directly under the microscope equipped with a micrometer eyepiece during crystallization. The nucleation densities were calculated in terms of the number of nuclei per unit length for the nuclei on the fiber and number of nuclei per unit area for those in the bulk. The average thickness of transcrystalline layers and the average radius of the spherulites were measured with photographs taken at different time intervals. Nucleation rates were obtained from the maximum slopes of the nucleation density vs. time plots, and growth rates of the transcrystallinity and the spherulite obtained from the slopes of the thickness and the radius vs. time plots, respectively, as suggested by Chatterjee et al.¹⁸ The indicated temperature of the heat stage was calibrated with potassium bichromate before use.

RESULTS AND DISCUSSION

Nucleation

Under direct observation, it was found that nuclei of PEEK appear on the surface of carbon fiber sporadically. The typical variation of the nucleation density vs. time and its temperature dependence at the early stage of transcrystalline development are shown in Figure 1. After a specific time, it became

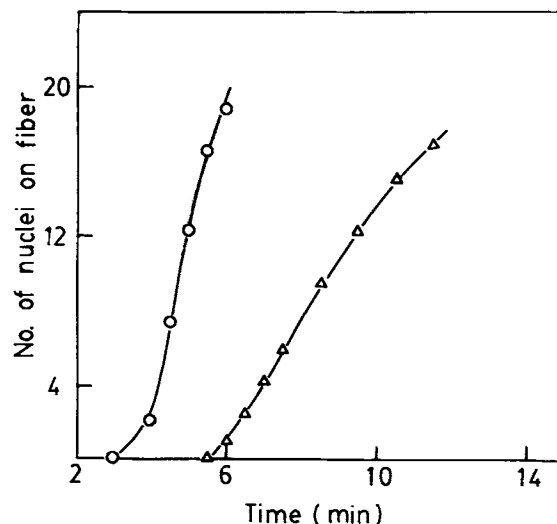


Figure 1 Nucleation density on carbon fiber as a function of time in the isothermal crystallization of PEEK 150P at (O) 305 and (Δ) 315°C.

difficult to count the nucleating sites directly with accuracy because there would be too many nuclei on the fiber. But it was found that the number of nuclei tended to be fixed finally with the help of amplified photographs taken at various time intervals. This is similar to the phenomenon observed for polypropylene in contact with various substrates and is considered to be the nature of heterogeneous nucleation.¹⁹ Also, like in other systems,^{18,19} the increase of nucleation density became weaker at higher crystallization temperatures.

The nucleation density in bulk PEEK is shown in Figure 2. The number of growing centers increased at the beginning and then tended to be constant before the total area was filled with spherulites. This is a characteristic of heterogeneous nucleation and indicates that heterogeneous nucleation is also involved in the bulk. The active heterogeneities that act as nucleating seeds in PEEK may be the impure particles, such as catalyst residues and dust particles. In this system, the bulk nucleation density is not affected by the fibers. The same values were obtained in the regions adjacent to the fibers and in the regions far away from the fibers. This is different from the result reported by Campbell and Qayyum.¹⁹ In their work on polypropylene, the nucleation density decreased with increasing the distance from fibers, and the diffusion of heterogeneities caused by the fiber-heterogeneity attraction was considered to be the reason.

Table I summarizes the nucleation rates of PEEK on the surface of carbon fiber (R_f) and in the bulk

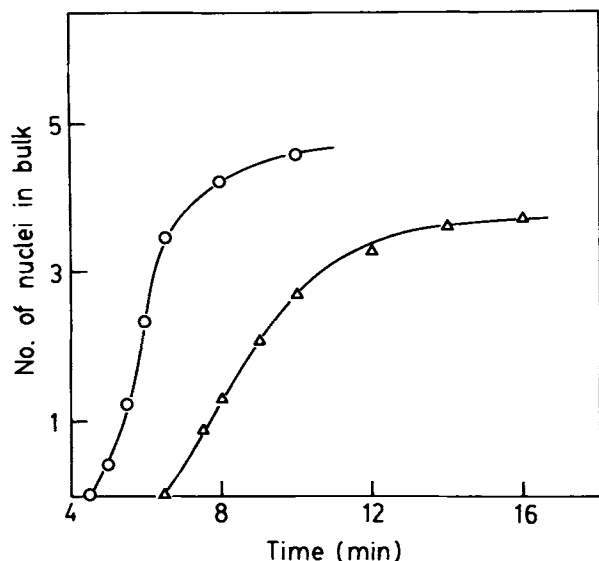


Figure 2 Nucleation density in the bulk as a function of time in the isothermal crystallization of PEEK 150P at (○) 305 and (△) 315°C.

(R_b) in the range 297–315°C. Both R_f and R_b increase with reducing crystallization temperature, in agreement with nucleation theory generally accepted.²⁰ Chatterjee et al.^{18,21} once proposed use of the ratio of the nucleation density on the substrate to that in the bulk, or the ratio R_f/R_b , as a measure of the nucleating ability of the substrate. When the ratio exceeded a certain value, transcrystalline formation occurred. The values of R_f/R_b in this system are also listed in Table I. A larger R_f/R_b value appears at higher temperature. This indicates that carbon fiber has better nucleating ability at higher temperature. However, the lower limit of the ratio R_f/R_b of PEEK transcrystalline formation is very difficult to determine. Since transcrystallinities were

finally obtained in the above cases, we can at least know that it should be smaller than the values listed in the table.

The crystalline morphology of PEEK in contact with carbon fiber is temperature-dependent. When the crystallization temperature is lowered to 280°C from 297–315°C, transcrystallinity can still develop as shown in Figure 3(a). But spherulite is the main interfacial morphology at 260°C [seen in Fig. 3(b)]. Although the nucleation rates were too fast to permit accurate counting in a short observation period in these cases, the nucleation on the fiber was observed to be unaffected at 280°C, but influenced by the bulk nucleation at 260°C. When the sample was held at 260°C, the space around the fibers was occupied soon by many small spherulites nucleated in the bulk. It is believed that the nucleation in the bulk might meddle with that on the fiber and that transcrystallinity can develop only when the nucleation on the fiber is unhindered. Also, on the basis of the above results, high crystallization temperature is concluded to be in favor of the transcrystalline formation.

If the crystallization temperature is too high, transcrystallinity cannot develop either. As shown in Figure 3(c), a radiating fanlike structure on the fiber is the morphology at 323°C. Although the nucleation in the bulk does not affect that on the fiber and the ratio R_f/R_b of 3.57×10^{-5} m is larger than those listed in Table I at this time, fewer nucleating sites on the surface can lead only to such morphology. Therefore, a large value of the ratio R_f/R_b does not certainly mean the formation of transcrystallinity. In other words, that the ratio R_f/R_b exceeds a certain value is only a necessary condition for transcrystalline formation. Because PEEK transcrystallinity on carbon fiber can be obtained in a wide crystallization temperature range of at least 280–315°C,

Table I Nucleation Rates of PEEK on Carbon Fiber and In Bulk^a

PEEK	Crystallization Temperature (°C)	Nucleation Rate on Carbon Fiber (No. Nuclei/min/m) ($R_f \times 10^{-5}$)	Nucleation Rate in Bulk (No. Nuclei/min/m ²) ($R_b \times 10^{-9}$)	$R_f/R_b \times 10^5$ (m)
150P	297	1.96	6.21	3.16
	305	0.91	2.64	3.45
	315	0.39	1.10	3.54
380P	305	0.88	2.84	3.09
450P	305	0.85	2.64	3.17

^a Melted at 420°C for 10 min.

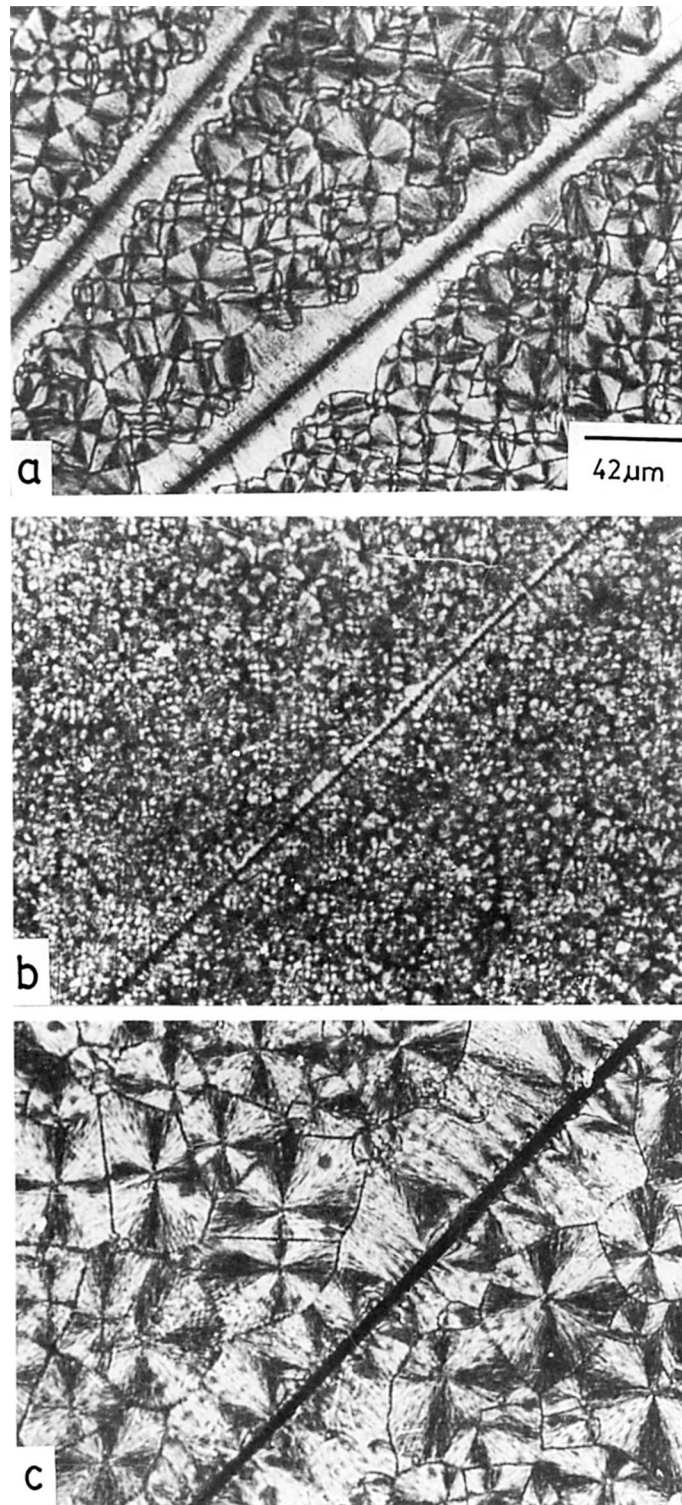


Figure 3 Crystalline morphology of PEEK 150P in contact with carbon fiber melted at 420°C for 10 min and then crystallized at (a) 280, (b) 260, and (c) 323°C.

Table II Nucleation Rates of PEEK^a on Carbon Fiber and in Bulk

Melting Temperature (°C)	Crystallization Temperature (°C)	Nucleation Rate on Carbon Fiber (No. Nuclei/min/m) ($R_f \times 10^{-5}$)	Nucleation Rate in Bulk (No. Nuclei/min/m ²) ($R_b \times 10^{-9}$)	$R_f/R_b \times 10^5$ (m)
390	305	0.68	5.43	1.25
400	305	0.84	3.87	2.17
410	305	0.94	2.96	3.18

^a 150P.

it will be easy to control the interface in the composite processing.

The molecular weight of PEEK within the range of this study has no significant influence on the nucleation rate on the fiber. As seen in Table I, R_f values of different PEEK powders are very similar when crystallized at the same temperature. However, the effects on the bulk nucleation rate is not clear. 380P, whose molecular weight is higher than that of 150P and lower than that of 450P, shows a slightly larger R_b value. This implies that 380P might have a higher heterogeneity content than that of the others. Since transcrystallinity was also obtained in 380P and 450P in contact with carbon fiber, little effect of molecular weight on the interfacial morphology is suggested.

Besides crystallization temperature, the melting temperature used to melt the samples is another factor that may affect the nucleation behavior and the morphology of PEEK. In Table II are listed the nucleation rates and the R_f/R_b values at 305°C after PEEK was melted at different temperatures for the same time as at 420°C (found in Table I). When the melting temperature is eliminated from 420 to 400°C, the nucleation rate on the fiber has no significant variation. But a smaller value was obtained after the sample was melted at 390°C. The rate reduction is thought to be related to the wettability of PEEK melt on the surface of carbon fiber on this condition because nucleation of a polymer on fiber is dependent on the contact of its melt with the fiber surface.^{22,23} The bulk nucleation rate was found to increase with decreasing melting temperature as seen in Tables I and II. This is associated with the unmelted crystals that can act as nucleating seeds. Kumar and his co-workers reported the dependence of spherulitic density of PEEK on the melting temperature from 380 to 420°C and considered that the density increase as a result of the melting temperature reduction was due to the larger amount of such crystal residues.²⁴

When the melting temperature is 390°C, the morphology around the fiber is not transcrystalline, as illustrated in Figure 4(a). This corresponds to the very small value of R_f/R_b and is also due to the interference from the nucleation in the bulk with that on the fiber. The morphology, after being melted at 400°C and then crystallized at 305°C, is close to transcrystallinity, as seen in Figure 4(b). Also, transcrystallinity is obtained when the temperature is 410°C. Thus, from the obtained R_f/R_b values and the corresponding morphologies, it is believed that the R_f/R_b value, over which transcrystalline formation of PEEK on the fiber might occur, should fall between 2.17×10^{-5} and 3.09×10^{-5} m.

Crystal Growth

Figure 5 shows the crystal growth of PEEK from the nuclei on the surface of carbon fiber and in the bulk. The transcrystalline thickness, which is the size in the direction normal to the fiber axis, varies linearly vs. time (Fig. 6), similar to the isothermal radial growth of PEEK spherulites.

The growth rates of transcrystallinity and spherulites of PEEK at different crystallization temperatures are listed in Table III. It can be seen that the rate of transcrystallinity decreases with increasing the temperature and is approximately the same as that of spherulite. Therefore, the perpendicular growth from any nucleus on the fiber is similar to spherulitic radial growth, which means that transcrystallinity that originates from crowded nuclei on fiber is essentially spherulitic. Based on this, the temperature dependence of the transcrystalline thickness is expected to be explained by the theories that have been successfully used to describe spherulitic growth of a large number of polymers over a wide range of temperature.

Another factor that will influence the growth rate is the molecular weight of PEEK. 380P and 450P, the higher molecular weight PEEK, have a lower

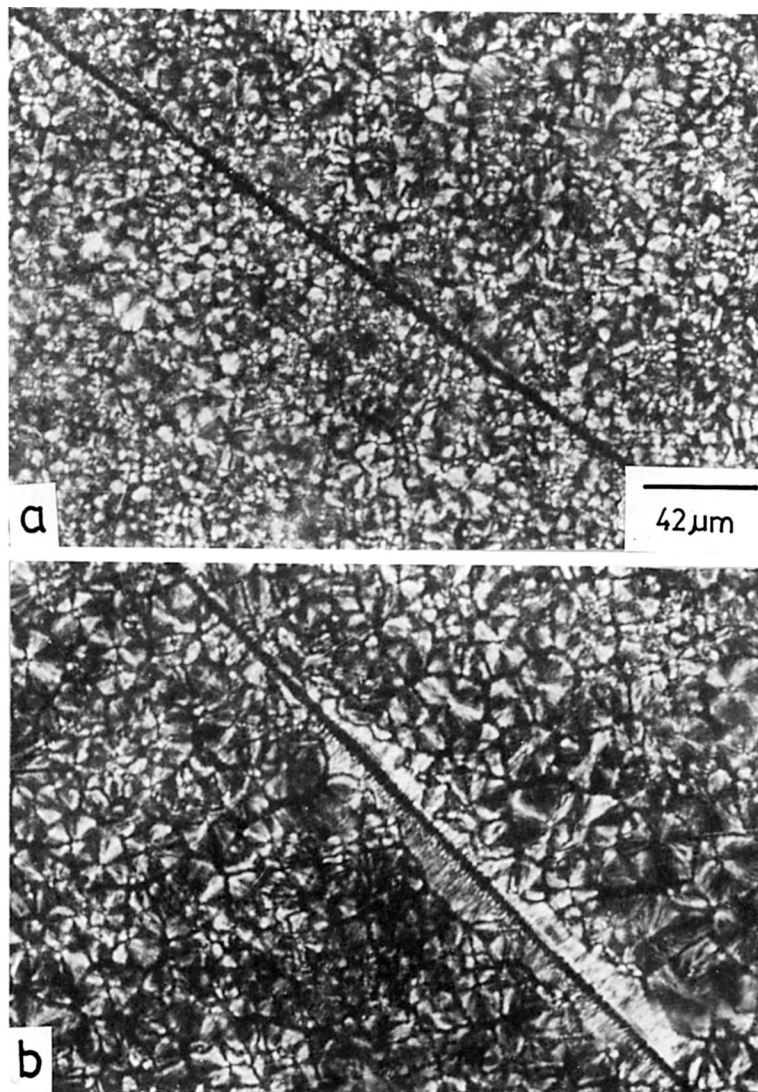


Figure 4 Crystalline morphology of PEEK 150P in contact with carbon fiber melted for 10 min at (a) 390 and (b) 400°C and then crystallized at 305°C.

transcrystalline growth rate and spherulitic growth rate than does 150P, as seen in Table III. This significant molecular weight effect is in contrast to the result of the nucleation rate discussed above. The reason is that the growth rate of polymer crystal has a strong molecular weight dependence.²⁵⁻²⁷

The final transcrystalline thickness was observed to be dependent on the nucleation density in the bulk. As seen in Figure 6, transcrystallinity stops growing in the regions where it impinges on its neighbor spherulites and continues growing in other regions. From this result, it is obvious that when the bulk nucleation density is higher the probability of transcrystallinity impinging on spherulites is

higher, resulting in the smaller transcrystalline thickness. Furthermore, it was also found that the value of the average thickness is close to that of the average spherulitic radius. Since the spherulitic radius of PEEK increases with decreasing the nucleation density,²⁴ it is known that the factors that may affect the bulk nucleation density should influence the thickness. In this work, we have studied the temperature effects and obtained some meaningful results. As listed in Table IV, PEEK transcrystalline thickness decreases with reducing crystallization temperature or melting temperature. This is helpful for us to design the composites, because it has been demonstrated that the transcrystalline

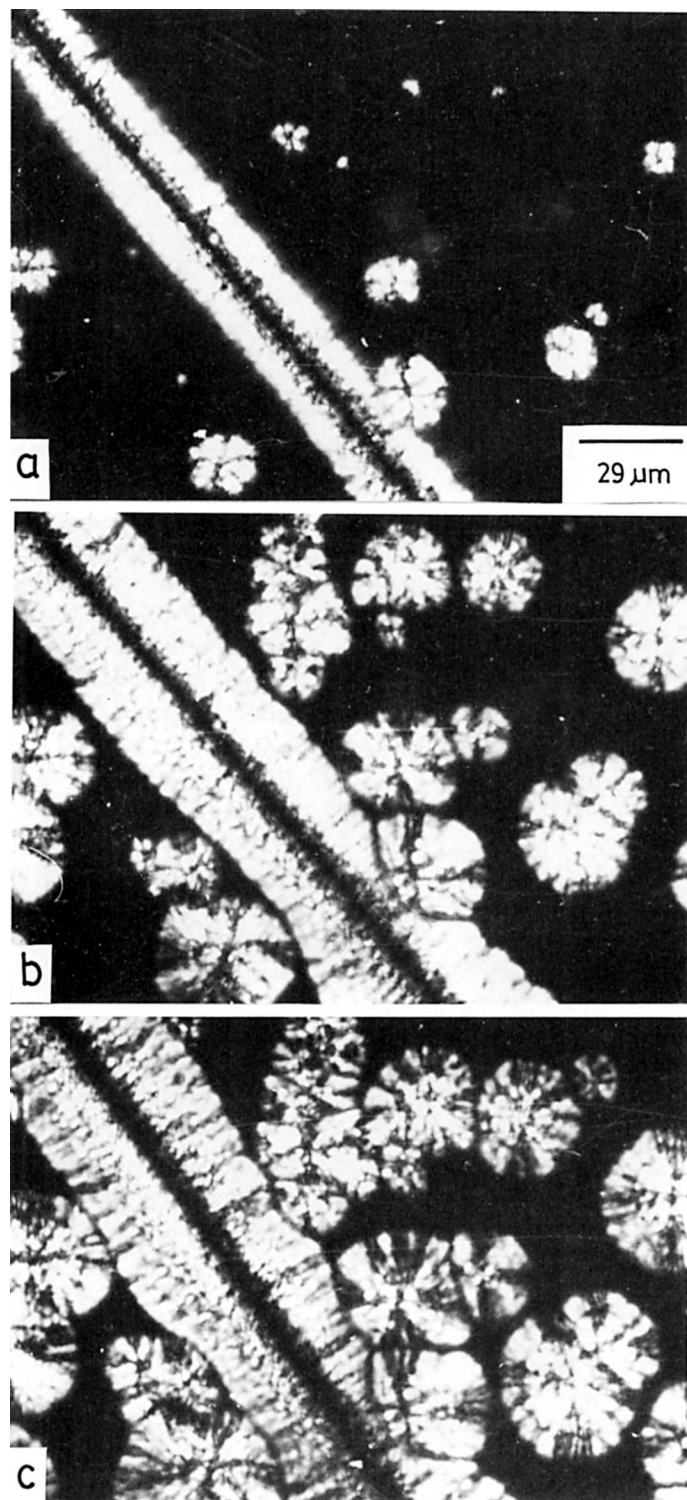


Figure 5 Transcrystallinity grown at 305°C for different time periods. PEEK 150P at (a) 8.5, (b) 11.4, and (c) 12.8 min.

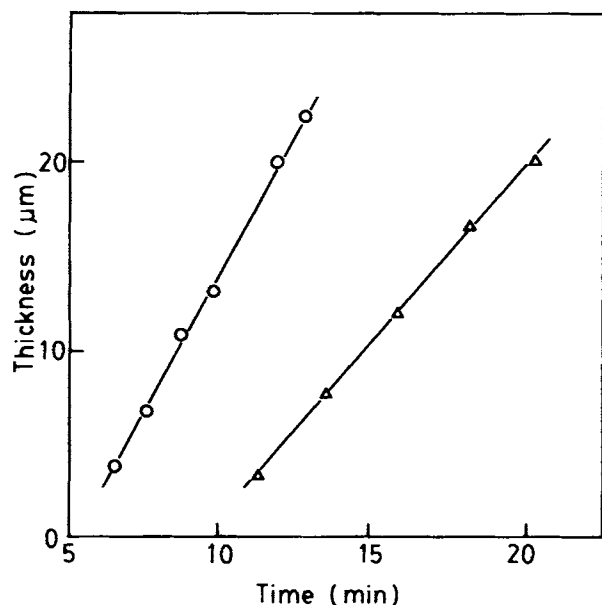


Figure 6 Transcrystalline thickness as a function of time. PEEK 150P crystallized at (○) 305 and (△) 315°C.

mechanical property of PEEK reinforced with carbon fiber depends on the thickness and greatly contributes to the composite property.²⁸

CONCLUSION

In this work, nucleation and crystal growth of PEEK on carbon fiber were studied. The nucleation rate on the fiber decreases greatly with increasing crystallization temperature and falls slightly when melting temperature is rather low. And the rate in the bulk decreases with rising crystallization temperature or melting temperature. Transcrystallinity

Table III Linear Growth of Transcrystalline Thickness Compared with the Radial Growth Rate of Spherulites in the Bulk^a

PEEK	Crystallization Temperature (°C)	Growth Rates of Trans-crystallinity (μ/min)	Growth Rates of Spherulite (μ/min)
150P	297	5.12	5.21
	305	2.96	3.04
	315	1.87	1.83
380P	305	1.67	1.57
450P	305	1.19	1.24

^a Melted at 420°C for 10 min.

Table IV Effects of Temperature on the Transcrystalline Thickness^a

Melting Temperature (°C)	Crystallization Temperature (°C)	Transcrystalline Thickness (μm)
420	280	14.9
	297	23.4
	305	26.6
	315	30.5
410	305	20.4

^a 150P.

appeared in a wide crystallization temperature range of 280–315°C. The reason is that the nucleation on the fiber is affected by that in the bulk at lower crystallization temperature and there are not enough nucleating sites on the fiber at higher temperature. Transcrystalline formation occurs only when the nucleation on the fiber is unaffected and a sufficient number of nuclei appear on the fiber. Also, the value of R_f/R_b can only be used to judge whether transcrystallinity can appear.

Linear growth is a characteristic of PEEK transcrystallinity on carbon fiber. The rate, which decreases with increasing crystallization temperature, is almost the same as that of bulk spherulite growth. It is affected by the molecular weight of PEEK within the range that we studied, although little effect of molecular weight on the nucleation rate on the fiber was found. Meanwhile, the final transcrystalline thickness depends on the melting temperature and crystallization temperature.

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