

Surface-induced crystallization of syndiotactic polystyrene on high modulus carbon fibers

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Summary

Measurements have been made using a polarized optical microscope equipped with hot stages to investigate the surface-induced crystallization of syndiotactic polystyrene(s-PS) on high modulus(HM) carbon fibers. Both the induction times and crystal growth rates at various crystallization temperatures were measured. Based on the theory of heterogeneous nucleation, the interfacial free energy difference function $\Delta\sigma$ of s-PS on HM carbon fibers was determined to be 0.61 ± 0.02 erg/cm². No difference in the crystal growth rate of s-PS has been found in either spherulites in the bulk or transcrystalline layers at the interface. From the morphology studies, it has been found that the thickness of the transcrystalline layer increases with crystallization temperatures, from 5 to 13 μm in the temperature range of 247-269°C. The efficiency of HM carbon fibers to induce the transcrystalline layer is found better in s-PS matrix than that in i-PP matrix based on the surface energies of the constituents.

(Keywords: transcrystalline layer • syndiotactic polystyrene • high modulus carbon fibers)

Introduction

Syndiotactic polystyrene(s-PS) is a new generation of polystyrenes that is rapidly gaining importance as an engineering thermoplastic due to its low dielectric constants, good chemical resistance, rapid crystallization rate and high melting temperatures. However, the brittleness in the mechanical properties is the main drawback for s-PS with a T_g (~100°C) higher than the ambient temperature. In practice, high performance fibers are used to develop s-PS composites to enhance the toughness. This gives rise to the need for studying the structure and properties of fiber-reinforced s-PS composites.

It is well known that when fibers are incorporated in semicrystalline polymers, under appropriate conditions, a highly oriented layer is developed at the fiber/matrix interface. This distinct morphology is called transcrystalline layer(TCL) and is a consequence of high nucleating ability of the fibers, compared to that of the bulk matrix. In contrast, isotropic spherulites are normally found in the bulk. Owing to its better mechanical properties, compared to the bulk matrix[1], TCL has draw much attention recently in

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studying fiber reinforced semicrystalline polymer composites [2-5]. There have been many theories proposed to account for the formation of the TCL[6-8]. However, the mechanism for the origin of TCL is still uncertain. In our previous articles[8-10], the formation and morphology of the transcrystalline layers in i-PP composites have been extensively discussed. Moreover, good agreements have been found between induction time approach and nucleation rate approach[6,11], based on a heterogeneous nucleation theory, in determining the interfacial free energy difference function $\Delta\sigma$. The tendency for TCL to develop is dependent on the relative magnitudes of $\Delta\sigma$ in the bulk and that on the fiber, respectively. In the present paper, we report on a series of further experiments on carbon fiber/s-PS composites. The aim of this study is to assess the application of induction time approach to deduce $\Delta\sigma$ value to characterize the nucleating ability of fibers in composites.

Experimental

s-PS pellets with weight average molecular weights, $M_w = 200$ kg/mol, was obtained from Dow Chemicals. High modulus(HM) carbon fibers(M40B) were supplied by Toray Industries, Inc. The fiber diameter is 8 μm . To clean fiber surface, the fibers were rinsed with acetone for 20 min and dried at the atmosphere. A single fiber was sandwiched between two s-PS films. Prior to crystallization, the specimens were held at 300°C for 10 min to erase the previous thermal effect. Then, the sample was quickly shifted to a well-controlled hot stage(Mettler, FP-82) where a pre-set crystallization temperature, T_c , was maintained. Dry nitrogen was introduced to eliminate any possible degradation in all cases. Crystallization of s-PS on fibers was observed with a polarized optical microscope(POM, Nikon MICROPHOT-FXA). Crystallization time was recorded after the samples were switched to the Mettler hot stage. Due to the highly dense nuclei occurring at the interface, it is not possible to count the nuclei number at the fiber surface directly in the temperature range studied, 257-273°C. Thus, the induction time approach was used to study the heterogeneous nucleation[6,11], i.e. the time when a fine bright line of crystals appeared next to the fiber to represent the induction time. The temperature dependence of growth rate of TCL and the crystal growth in the bulk were also measured using POM.

Results and discussion

Nucleation Study

In the bulk matrix, distinct s-PS morphologies of spherulites and axialites are observed simultaneously in the temperature range, 240-276°C, investigated in this study. As shown in Figure 1, it seems that spherulitic morphology is the dominant feature at low temperatures; whereas high crystallization temperatures result in crystals with axialitic morphology. On the other hand, a well-developed TCL was observed due to the highly dense nuclei of s-PS to nucleate on the carbon fiber surface. Figure 2 shows the population of spherulitic and axialitic crystals in the bulk as a function of crystallization temperatures. It is evident that number of axialitic crystals increases but the population of spherulites decreases when s-PS is crystallized isothermally at high T_c . At T_c higher than 272°C, growth of stacked lamellae with large lateral surface is observed. In addition, TCL crystals nucleating at the surface of HM carbon fibers resemble with those of stacked lamellae in the bulk. Under POM observation, the boundary of impingement of TCL and the bulk crystals is by no means smooth and a morphology with single-crystalline-like structure which is associated with the edge-on lamellae is detected[7].

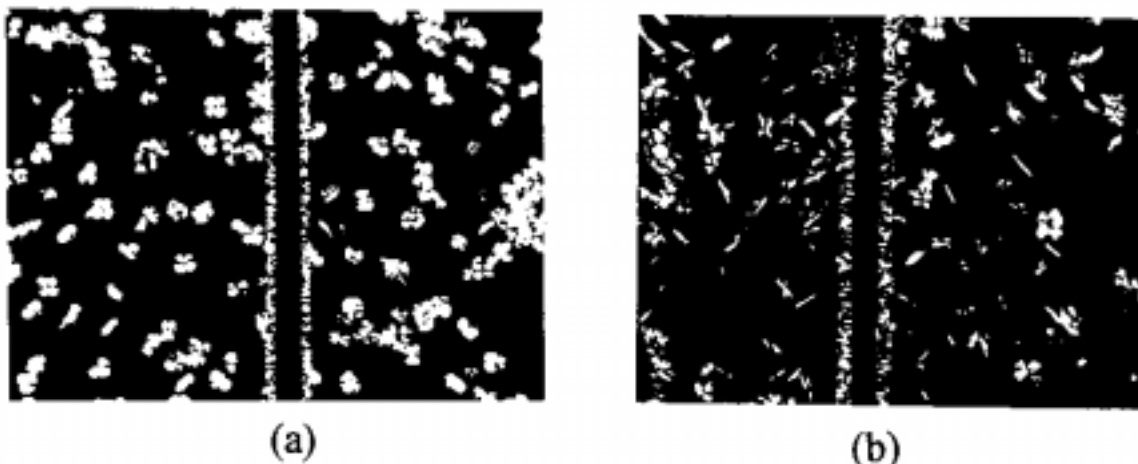


Figure 1: POM micrographs of s-PS crystallized at the surface of HM carbon fibers (a) $T_c=240^\circ\text{C}$ and (b) $T_c=260^\circ\text{C}$. (Note: the crack lines induced by thermal stresses after samples are rapidly quenched with liquid nitrogen are evident in (b))

The general trend for the development of i-PP TCL at the surface of various fibers has been systematically investigated and discussed[8]. It has been reported that at low crystallization temperatures the nucleation density is too high to count the number of nuclei directly. On the other hand, high crystallization temperatures result in the reduction of the nucleation density and the sporadic appearance of the nuclei which make the measurements of nucleation rate feasible. Moreover, there exists a maximum crystallization temperature, T_{\max} , for TCL to develop. For T_c higher than T_{\max} , no TCL can be observed, i.e. there is no preferential nucleation of the crystallizable molecules at the surface of fibers, compared to the nucleation in the bulk.

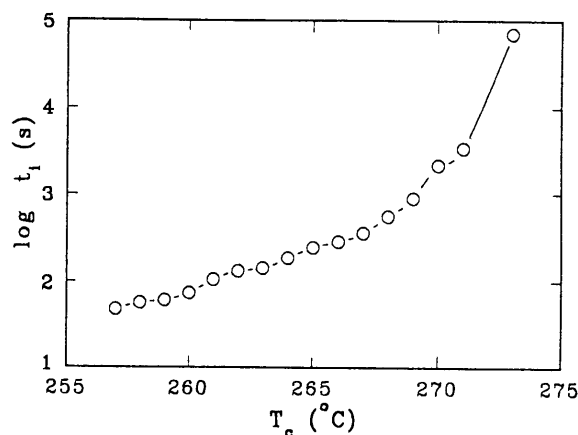
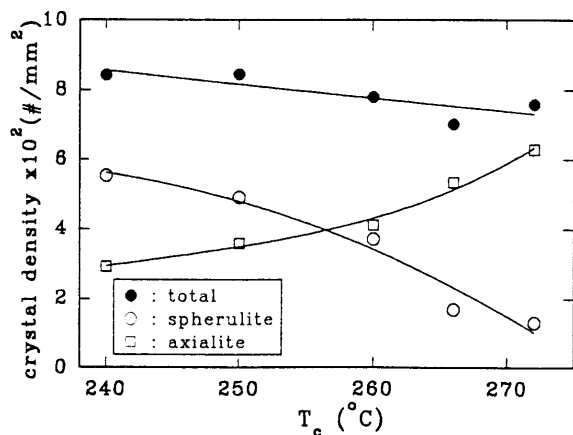


Figure 2: Variation of crystal density with T_c (Total crystal number of 850 was counted). Figure 3: Variation of induction time t_i of TCL with crystallization temperature.

In contrast to i-PP composites, no sporadic occurrence of nuclei but instantaneous appearance of s-PS TCL was observed at crystallization temperatures studied up to 273°C . It is attributed to a more efficient and better nucleation ability of s-PS, compared to that of i-PP. Indeed, a larger nucleation density in the bulk is found for the s-PS composites

which results in a smaller spherulites at the corresponding supercooling. The elapsed time for the first fine bright crystals next to the fiber to appear, termed induction time, increases significantly with increasing T_c , as shown in Figure 3, ca. 50 s at 257°C and 7000 s at 273°C. According to the theory of nucleation, the rate of heterogeneous nucleation, I , is given by[12]

$$\log I = \log I_0 - \frac{U^*}{2.303R(T_c - T)} - \frac{16\sigma\sigma_c\Delta\sigma T_m^0}{2.303kT_c(\Delta T\Delta h_f)^2} \quad (1)$$

where T_m^0 is the equilibrium melting temperature, σ and σ_c are the lateral and fold surface energies, respectively, ΔT is the supercooling ($=T_m^0 - T_c$) and the definitions of others are described elsewhere[8]. To take account of the energy change caused by the creation of a new surface on the top of foreign substrates, a quantity termed interfacial free energy difference, $\Delta\sigma$, is incorporated. Moreover, a simple relation[11] between I and the induction time, t_i , is found valid for the composites reinforced with high modulus carbon fibers, i.e. $I \sim 1/t_i$. Thus, a plot of $\log(1/t_i) + U^*/2.303R(T_c - T_\infty)$ against $1/T_c(\Delta T)^2$ would give a straight line whose slope is used to determine the surface energy parameter, $\sigma\sigma_c\Delta\sigma$. Figure 4 shows the variation of induction time with crystallization temperatures according to Equation 1. Values of U^* , T_∞ and Δh_f are taken as 1500 cal/mol, 343K and 8.79×10^8 erg/cm³ respectively[13,14]. The supercooling ΔT was calculated using the equilibrium melting temperature ($T_m^0 = 312^\circ\text{C}$) determined from the Lauritzen-Hoffman theory and an optimal technique developed recently[14,15]. The linear slope in Figure 4 is -3.91×10^6 K³ and the deduced value of $\sigma\sigma_c\Delta\sigma$ is 175.5 ± 0.5 erg³/cm⁶.

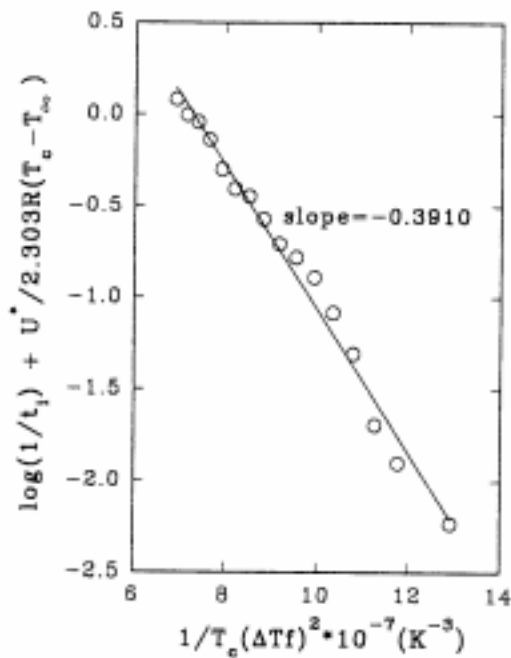


Figure 4: Variation of $1/t_i$ with $1/T_c(\Delta T)^2$ for s-PS TCL from the nucleation measurements.

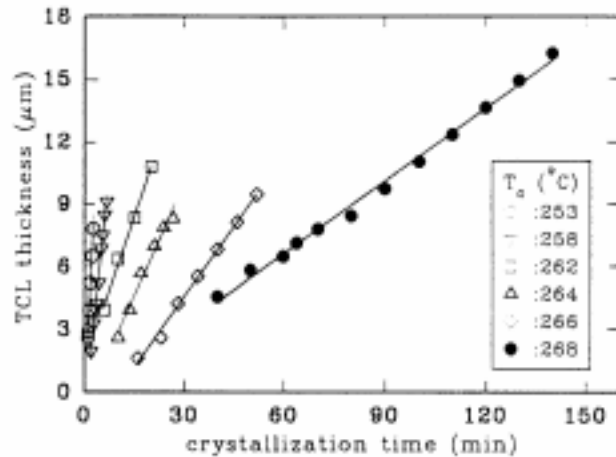


Figure 5: Variation of s-PS TCL thickness with crystallization time at various temperatures.

Crystal Growth Study

Figure 5 shows the variation of TCL thickness versus crystallization time at various T_c . The growth rates of TCL were determined from the linear slopes. In the bulk, the spherulitic radius and the length of major-axis of the axialitic crystals at different crystallization time were measured simultaneously and the determination of growth rates for each feature was carried out as well. Figure 6 shows the measured growth rates of s-PS crystals with different morphologies at various crystallization temperatures. It is evident that the crystals in the bulk (spherulites or axialites) have the same growth rate as that of TCL at a given temperature. The presence of fibers does not affect the rate of s-PS crystal growth. Similar results were also obtained in the composites of i-PP reinforced with different fibers[9,11]. Moreover, the growth rate decreases with the crystallization temperature, from 0.25 $\mu\text{m/s}$ at 240°C to 0.06 nm/s at 276°C. From the Lauritzen-Hoffman's kinetic theory, the growth rate, G , can be expressed as follows[16],

$$\log G = \log G_0 - \frac{U^*}{2.303R(T_c - T)} - \frac{nb_0\sigma\sigma_e T_m^0}{2.303kT_c\Delta T\Delta h_f f} \quad (2)$$

where b_0 is the layer thickness of growing plane and n is 2 for regime II and 4 for regime I or III. Therefore, the surface energy parameter $\sigma\sigma_e$ can be determined from the slope by a plot of $\log G + U^*/2.303R(T_c - T_\infty)$ versus $1/T_c(\Delta T f)$. Figure 7 shows the LH plot for the growth rate data. No transition in growth regime is detected and the slope is calculated to be $-1.7266 \times 10^5 \text{ K}^2$. Assuming crystals with orthorhombic unit cell and (040) growing front[14] and using the classical Z test[17], the substrate length L for regime II growth to take place is greater than 95 μm when s-PS is crystallized at 260°C which is unrealistic. On the other hand, the substrate length is about 73Å at $T_c=260^\circ\text{C}$ if crystal

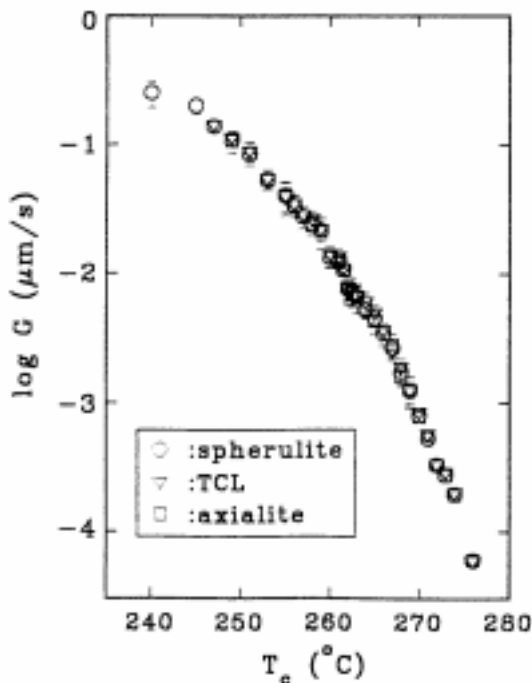


Figure 6: Growth rates of s-PS crystals with different morphologies at different crystallization temperatures.

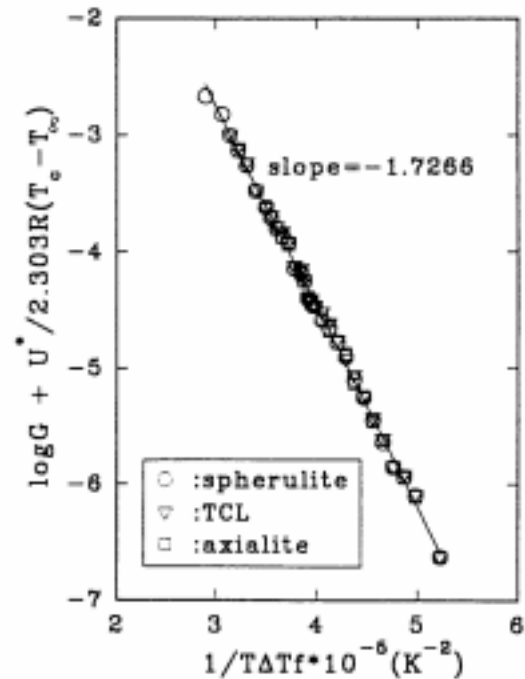


Figure 7: Variation of G with $1/T_c(\Delta T f)$ for s-PS crystals; G is in the unit of cm/s .

growth of regime I is applied. At higher T_c , the substrate length is increased whose magnitude is more consistent with previously reported values for PE. Based on the above derivation, it is concluded that the s-PS crystals (spherulites, axialites and TCL) all grow in the mode of regime I and the value of $\sigma\sigma_c$ is calculated to be $286.1 \pm 1.4 \text{ erg}^2/\text{cm}^4$, according to Equation 2 with $n=4$. It is interesting to note that $\sigma\sigma_c$ value for s-PS are the same in spite of crystals with different morphologies (spherulites, axialites and TCL).

Ability of matrix to develop TCL on HM carbon fibers

The value of $\Delta\sigma$ in the TCL was determined by dividing $\sigma\sigma_c\Delta\sigma$ with $\sigma\sigma_c$ which were obtained from the nucleation and growth rate experiments, respectively. The magnitude of $\Delta\sigma$ is used to characterize the nucleating ability of HM carbon fibers. The deduced value for s-PS to transcrystallize on the surface of HM carbon fiber is about $0.61 \pm 0.02 \text{ erg}/\text{cm}^2$. Since the energy barrier to deposit the first layer of s-PS crystals is rather low, nucleation of s-PS crystals is likely to take place on the HM carbon fibers which is consistent with experimental findings, as shown in Figure 1. Moreover, the calculated $\Delta\sigma$ value is merely one-half of that for i-PP to develop TCL at the same fiber[11]. It suggests that HM carbon fibers should demonstrate better nucleating ability toward s-PS rather than i-PP matrix at the same supercooling, ΔT .

A comparison of the TCL development of s-PS and i-PP on HM carbon fibers is shown in Figure 8 where the supercooling is about 50°C . The growth of isolated stable i-PP nuclei was observed until the impingement of the neighboring crystals. In contrast, a fine layer of s-PS nuclei quickly appears next to the fiber as soon as the TCL forms. As mentioned previously, it is attributed to the highly dense s-PS nuclei. It should be noted that the presence of the fiber is to provide a higher surface energy of substrate, γ_s , compared to that of the melt phase, γ_m , which results in a pronounced reduction of $\Delta\sigma$ according to

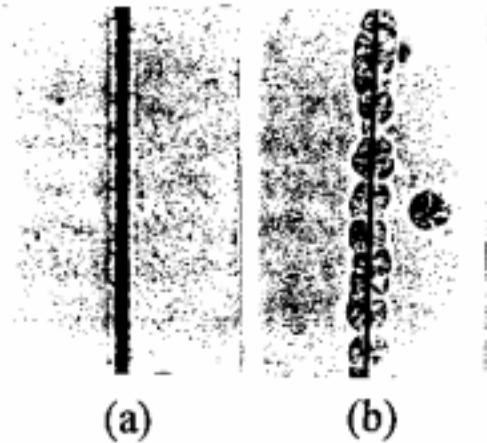


Figure 8: POM micrographs of TCL
(a) carbon fiber/s-PS at $T_c=265^\circ\text{C}$,
(b) carbon fiber/i-PP at $T_c=135^\circ\text{C}$.
(note: the supercooling ΔT is similar in both systems, ca. 50°C)

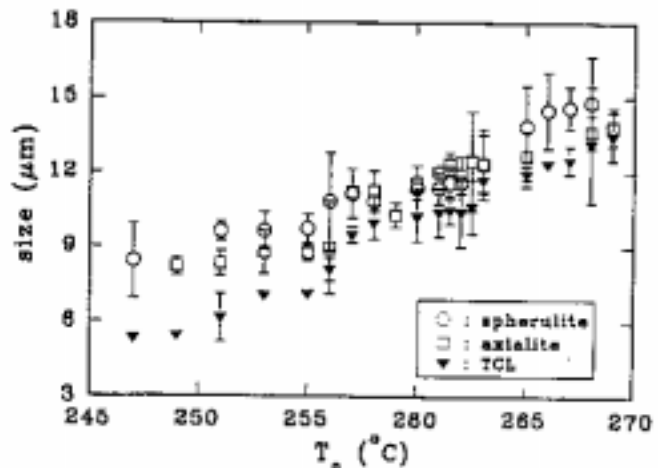


Figure 9: Variation of TCL thickness, spherulitic radius and half length of the major-axis of axialites with crystallization temperatures.

the relation given as follows[12]; $\Delta\sigma = 2(\gamma_c^{1/2} - \gamma_s^{1/2})(\gamma_c^{1/2} - \gamma_m^{1/2})$ where γ_c is the surface energy of s-PS crystals. The above relation is under the assumption that no specific interaction but the contribution from the dispersion forces between the constituents. It consists of two terms; one is the surface energy difference between crystals and melt of the crystallizable polymer itself and the other is the surface energy difference between the crystals and the substrate. Generally speaking, heterogeneous nucleation is more likely to take place on a substrate with higher surface energy for a given matrix. For a given fiber with γ_s , on the other hand, the crystallizable polymer with a γ_c magnitude similar to γ_s has a greater probability to develop TCL since the energy barrier to form a critical nucleus is reduced more. In other words, the magnitude $\gamma_c^{1/2} - \gamma_s^{1/2}$ can be used to estimate the relative ability of crystallizable polymer chains to develop TCL on the surface of a specific fiber. Moreover, the lateral surface energy of crystals, σ , is equal to $(\gamma_c^{1/2} - \gamma_m^{1/2})^2$ by definitions. Thus, a quantity $\Delta\sigma / \sqrt{\sigma}$ is suggested to compare the ability of matrix to develop TCL at a given fiber where the surface morphology and roughness is not necessarily taken into account[8,10]. For HM carbon fibers, the calculated $\Delta\sigma / \sqrt{\sigma}$ value for s-PS matrix is 0.23 erg^{1/2}/cm which is smaller than that for i-PP matrix, 0.34 erg^{1/2}/cm. It is consistent with the experimental finding, as shown in Figure 8.

A larger TCL thickness is obtained when isothermal crystallization is carried out at higher temperatures as shown in Figure 9. Similar trends were found in the i-PP composites as well[9]. However, the thickness of s-PS TCL is significantly smaller than that obtained in the i-PP composites, ca. 100 μm . In the bulk, a limited increase in the crystal sizes of spherulites and axialites is also found as the crystallization temperature is increased. It indicates that the nucleation sites remain so effective at high temperatures which renders an insignificant reduction of nucleation (or crystal) density, as shown in Figure 2.

Surface topography of HM carbon fibers has been investigated using atomic force microscopy and presence of many small-scale grooves parallel to the fiber axis is observed[8]. The depth of the grooves and the average width between two ridges are about 5 and 100 nm, respectively. Compared to the relative size of the critical nuclei, the groove region is the most probable location for the initial nucleus to deposit. We conclude that the grooves provide suitable nucleation sites and nucleation process is greatly enhanced to form dense nuclei at the fiber surface which develop TCL thereafter.

Ability of fibers to develop TCL of s-PS

In addition of HM carbon fibers, several other fibers are used for a preliminary study of the development of s-PS TCL. The fibers which can induce preferential nucleation of s-PS on their surfaces and form TCL are: PTFE, Kevlar 49, acid-treated copper wire, and PBO (p-phenylene-2,6-benzobisoxazole) fibers[15]. On the other hand, no preference of s-PS nucleation is found at the surfaces of glass fibers and high strength carbon(AS-4) fibers. Detailed studies of the nucleating ability for each fiber are carried out in this laboratory currently.

Acknowledgments

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