

Investigation on the Crystallization Behavior of Poly(ether ether ketone)/Poly(phenylene sulfide) Blends

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ABSTRACT: The morphology of nonisothermally crystallized poly(phenylene sulfide) (PPS) and its blend with poly(ether ether ketone) (PEEK) have been observed by polarized optical microscope (POM) equipped with a hot stage. The nonisothermal crystallization behavior of PPS and PEEK/PPS blend has also been investigated by differential scanning calorimetry (DSC). The maximum crystallization temperature for PEEK/PPS blend is about 15°C higher than that of neat PPS, and the crystallization rate, characterized by half crystallization time, of the PEEK/PPS blend is also higher than that of the neat PPS. These results indicate that the

PEEK acts as an effective nucleation agent and greatly accelerates the crystallization rate of PPS. The Ozawa model was used to analyze the nonisothermal crystallization kinetics of PPS and its blends. The Avrami exponent values of neat PPS are higher than that of its blend, which shows that the presence of PEEK changed the nucleation type of PPS from homogeneous nucleation to heterogeneous nucleation. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1829–1836, 2008

Key words: poly(phenylene sulfide); poly(ether ether ketone); crystallization; nucleation

INTRODUCTION

Blend alloy has long been one of the most interesting subjects with respect to the polymer modification, because large improvement was achieved in the physical properties, such as toughness, impact strength, ductility, etc., processability, and cost effectiveness by blending appropriate polymer materials.^{1,2} These properties of component polymer are mainly depended on the phase morphology, dispersion, and interfacial interaction. In a polymer blend system, the crystallization behavior of the matrix will be greatly influenced by the characteristics of disperse phase, such as miscibility, crystallizability, and dispersion parameters, etc. In addition, the melt temperature and crystallization temperature range of the dispersed phase should also be considered. Thus, it is important to understand the influence of the dispersed phase on the crystallization behavior of the matrix.

Poly(phenylene sulfide) (PPS) is an important high temperature engineering thermoplastic with good thermal stability, chemical resistance, flame resistance, and precision moldability. These superior properties of PPS are mainly dependent on its crys-

tallinity and superstructure. However, the crystalline PPS is rather brittle, and its glass transition temperature is low (about 85°C). And there is ~ 40% amorphous fraction for PPS, which greatly decreases its mechanical property when the service temperature is over 90°C.³ Hence, some approaches are always adopted to improve physical properties, such as improving the crystallinity and/or the glass transition temperature of PPS by blending with other polymers with higher melt temperature and/or higher glass transition temperature.

Recently, some literature reported the influence of the some thermoplastics on the properties of PPS.^{4–13} It was found that the toughness and impact strength of PPS were greatly improved by blending with other polymers, such as by blending with Polyamide 66 (PA66) the tensile strength and the impact strength of PPS was greatly improved.^{14,15} In addition, numerous investigations were focused on the phase morphology, crystalline degree, and crystallization behavior of PPS blends.^{16–26} For example, Shibata et al.¹⁸ found that the crystallization and melting behaviors of PPS was accelerated by blending with 10 wt % poly(ether sulfone) (PES) and further addition resulted in the retardation. Jog et al.²³ reported the isothermal crystallization kinetics of PPS in blends with high density polyethylene (HDPE) and poly(ethylene terephthalate) (PET), and found

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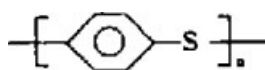
that the crystallization of PPS was accelerated in PPS/PET blends whereas retarded in PPS/HDPE blends. Despite these authors' efforts to study the influence of second component on the properties and crystallization behavior of PPS, little attention was paid to the crystalline morphologies of PPS, especially the crystallization mechanism of PPS in spatially limited regions inside the spherulites of the other component.

In this article, we briefly study the crystalline morphologies and nonisothermal crystallization kinetics of PPS and its blend with PEEK by the use of polarized optical microscope (POM) and differential scanning calorimetry (DSC). As is well known, poly(ether ether ketone) (PEEK) is a high performance thermoplastic resin with good resistance to attack by organic solvents.²⁷ Its glass transition temperature is about 145°C and melting point 340°C, being ~ 60°C higher than those of PPS.²⁸ This is one of the most important reasons considered to be blended with PPS for enhancing the properties of PPS. So far, some efforts have been done to improve the properties, such as thermal stability and rheology, toughness, friction, and wear characteristics, etc, of PPS by blending with PEEK.^{29–36} However, very few investigations are focused on the crystallization of PEEK/PPS blend. And it is well known that the crystallization behavior affects the crystalline morphologies and crystallinity, which further influence the properties of PPS blends. Thus, it is important to investigate the influence of PEEK on the crystallization behavior of PPS. Hereinto, we will introduce the nonisothermal crystallization process of PPS in the presence of crystalline PEEK.

EXPERIMENTAL

Materials and compounding

The PPS resin powder with molecular-mass ($\bar{M}_w=40,000$) obtained from the Honghe Limited Corporation (Zigong, China) was employed in this study. The samples were treated at 140°C for 4 h to remove the low molecular weight species. The crystallizable thermoplastic resin PEEK was obtained from Jida Gaoxin Limited Corporation (China). The chemical structure of PPS is



PEEK is an aromatic thermoplastic with a repeat unit of

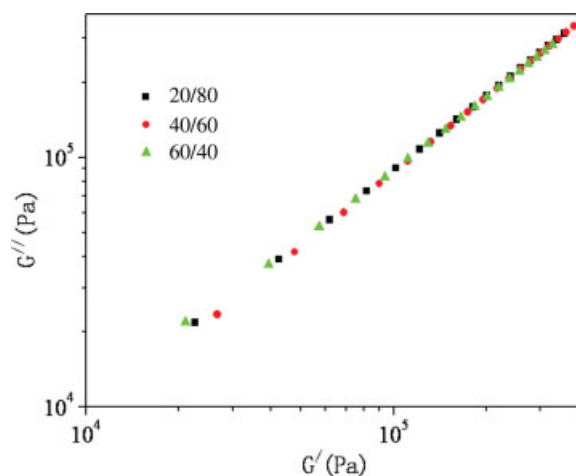
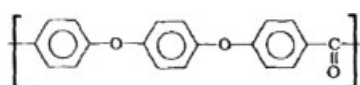


Figure 1 Storage modulus G' versus loss modulus G'' for PEEK/PPS blend at different contents: ■ 20/80, ○ 40/60, and ▲ 60/40. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Blending of PPS and PEEK was performed under a nitrogen atmosphere in a twin-screw compounding machine. The melt mixing was carried out at 350°C for 6 min to allow the complete blend.

After blended with PEEK, a circular film with 1 mm thickness and 25 mm diameter was prepared by a self-made oil pressure pump for rheological testing.

Rheological testing

The rheological testing of PEEK/PPS blend was performed by using a Stress PolyLab610 rheometer (RS600) equipped with a parallel plates (diameter 25 mm), scanning frequency was ranged from 0.01 to 100. The measurement temperature was carried out at 350°C. The data obtained are presented in Figure 1.

Morphology observation

The nonisothermal crystallization morphology of PPS and its blend with PEEK was observed by a polarized optical microscopy (POM) equipped with a CSS450 hot-stage. The samples were heated from 20 to 350°C at 20°C/min and kept at that temperature for 3 min to allow complete melting, then cooled down to the room temperature at a rate of 10, 15, 20°C/min, respectively.

Differential scanning calorimeter measurement

The nonisothermal crystallization of PPS and its blend with PEEK were performed in a nitrogen atmosphere using a Perkin-Elmer Diamond differential scanning calorimeter (DSC). The crystallization exotherm was recorded when the samples (ca. 8 mg)

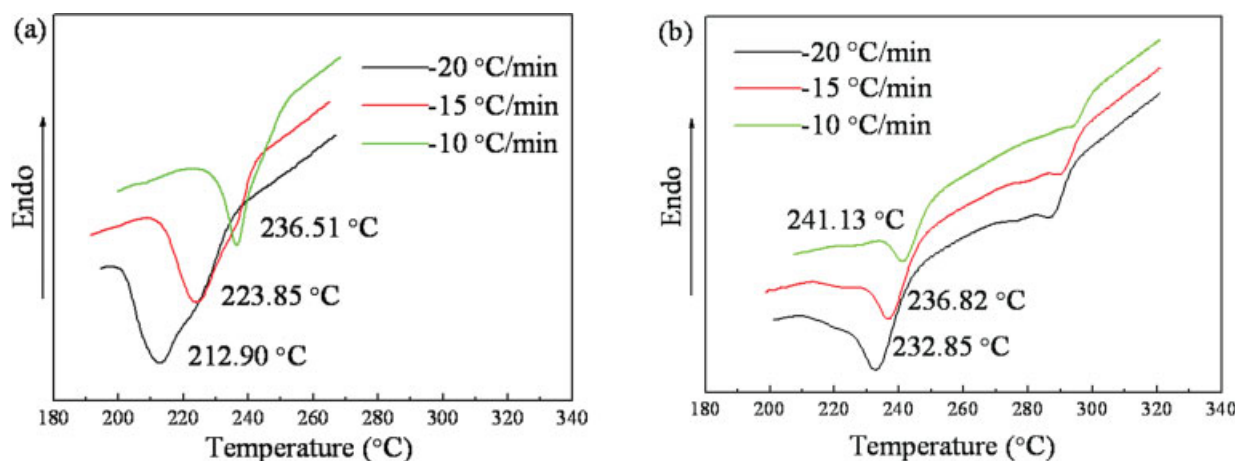


Figure 2 DSC cooling traces at predetermined cooling rates for (a) the neat PPS and (b) the PEEK/PPS blend (30 : 70 by weight). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

were heated to 350°C and held at that temperature for 3 min to ensure complete melting of the polymer, and then cooled down to the room temperature at a rate of 10, 15, 20°C/min, respectively,

RESULTS AND DISCUSSION

Compatibility of PEEK/PPS blends

The dependence of storage modulus G' upon loss modulus G'' for PEEK/PPS blends is shown in Figure 1. According to the criteria for rheological compatibility of polymer blends established by Han and Chuang,³⁷ the plots of storage modulus G' versus loss modulus G'' gives composition-independent correlations for compatible blends and composition-dependent correlations for incompatible blends. It can be seen that the plots of storage modulus G' versus loss modulus G'' is independent on the composition for the PEEK/PPS blends system. This phenomenon is consistent with what Han has observed in compatible blend systems such as PPO/PS system, SAN/SMA system, and Nylon 6/EVA system, etc. Also, Landry and Teecarden³⁸ found that miscibility between aromatic polyethers (PEK) or sulfides (PPS) and polyketones may increase as the aliphatic character of the ketone is increased. On the basis of these results, we can conclude that PPS is well compatible with crystallizable PEEK in the melt state.

Nonisothermal crystallization behavior of PEEK/PPS

Figure 2 represents the DSC curves obtained at predetermined cooling rates of 10, 15, and 20°C/min for PPS and its blend with PEEK. It can be seen that exothermic peaks of PPS are monomodel at different cooling rates. In the PEEK/PPS blend [Fig. 2(b)], two

crystallization peaks can be observed, the higher crystallization peak corresponds to the PEEK, the lower crystallization peak is due to PPS, which indicates that the crystallization of PPS occurred under the presence of crystalline PEEK. From these curves, some available crystallization parameters of PPS, such as maximum crystallization peak temperature (T_p), half crystallization time ($t_{1/2}$), initial crystallization temperature (T_0), maximum crystallization time (t_{max}), and degree of crystallinity (α), etc. are obtained, as shown in Table I. As can be seen, the crystallization peak shifts to the lower temperature when the constant cooling rate is increased, while T_0 , T_p , t_{max} , and $t_{1/2}$ reduce, indicating that the retarded effect of cooling rate on the nonisothermal crystallization of PPS. And in the case of PEEK/PPS blend system, the T_p and T_0 of PPS phase are higher than that of neat PPS at the same constant cooling rate. And the increment rises with the increasing cooling rate. For example, the increment of T_p between the neat PPS and PEEK/PPS blend is 4.58°C, 12.97°C, and 19.95°C, respectively, at 10, 15, 20°C/min. While the half crystallization time, $t_{1/2}$, is lower than that of neat PPS. On the basis of these results, it seems that the PEEK acted as an effective nucleating agent for nonisothermal crystallization of PPS phase. And the overall nonisothermal crystallization rate of PPS phase is greatly accelerated by the presence of crystalline PEEK. These results can be attributed to good compatibility of the two polymers in the melt state. And the occurrence of crystalline PEEK during the cooling process decreased the nucleating free energy, which promoted the formation of stable crystal nucleation. Also, the degree of crystallinity (α) calculated from the enthalpy of crystallization increases as the cooling rate increases, which shows that the cooling rate have an important role in the crystallization nucleation of PPS. As it is

TABLE I
Parameters for Neat PPS and PEEK/PPS Blend (30 : 70 by Weight) from DSC

Samples	Cooling rate (°C/min)	T_0 (°C)	T_p (°C)	α	t_{\max} (min)	$t_{1/2}$ (min)
Neat PPS	-10	253.86	236.51	0.1838	3.09	1.45
	-15	245.6	223.85	0.2790	2.45	1.17
	-20	242.22	212.90	0.3965	2.23	1.20
PEEK/PPS	-10	256.31	241.13	0.1569	2.24	1.22
	-15	250.83	236.82	0.2269	1.83	0.75
	-20	251.86	232.85	0.3643	2.08	0.83

well known, the crystallization of polymer is determined by the supercooling. The higher the supercooling is, the faster the crystallization nucleation rate is. The faster cooling rate means the higher supercooling, indicating that the nucleation rate of PPS is faster at higher cooling rate than that at lower one, which results the higher degree of crystallinity. As for the PEEK/PPS blend, the degree of crystallinity (α) of PPS phase in blend is a little lower than that of neat PPS. This result can ascribe to the faster crystallization rate, which leads to formation of the imperfect crystal of PPS phase in the blend.

Nonisothermal crystallization kinetics of PEEK/PPS blend

The overall nonisothermal crystallization kinetics of PPS and its blend with PEEK was analyzed according to the Ozawa formalism.³⁹ The Ozawa equation is one of the most popular means on studying the nonisothermal crystallization kinetics of polymer. This is based on the equation:

$$\ln[-\ln(1 - X_T)] = \chi - n \ln(\Phi) \quad (1)$$

where X_T is the volume fraction of material crystallized at temperature T , ϕ is the constant cooling rate, n is the Avrami exponent, and χ is the cooling crystallization function. This χ depends on the nucleation density and on the spherulitic radial growth rate, for both instantaneous and sporadic nucleation.

The dependence of amorphous fraction of PPS phase on the temperature at three predetermined cooling rates is presented in Figure 3. The effect of cooling rate on the nonisothermal crystallization of PPS phase is observed in these plots. With the decrease of cooling rate the crystallization of PPS shifts to the higher temperature, that is, the crystallization of PPS is retarded by the constant cooling rate. The double logarithm of amorphous fractions of the PPS phase for neat PPS and its blend with PEEK can also be plotted against the constant cooling rate, for different temperatures, as shown in Figure 4. It can be seen that these plots studied represent straight lines, thus showing that the Ozawa equation describes well the nonisothermal crystallization kinetics of the neat PPS and its PEEK/PPS blend.

From the slop of plots in Figure 4 the Avrami exponents n are obtained for neat PPS and its blend

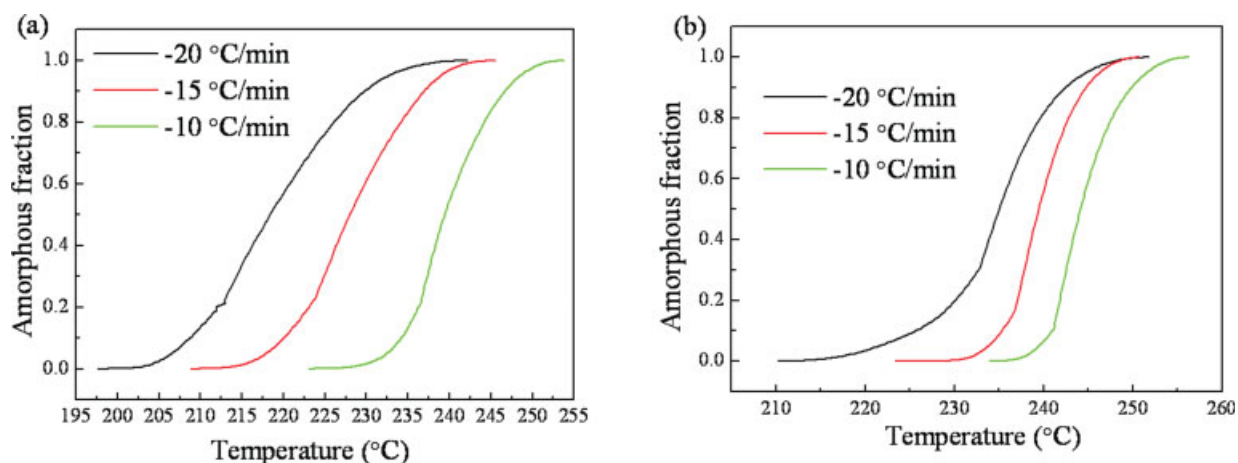


Figure 3 Plots of amorphous fraction of PPS as a function of temperature for (a) the neat PPS and (b) the PEEK/PPS blend (30 : 70 by weight) at different cooling rates. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

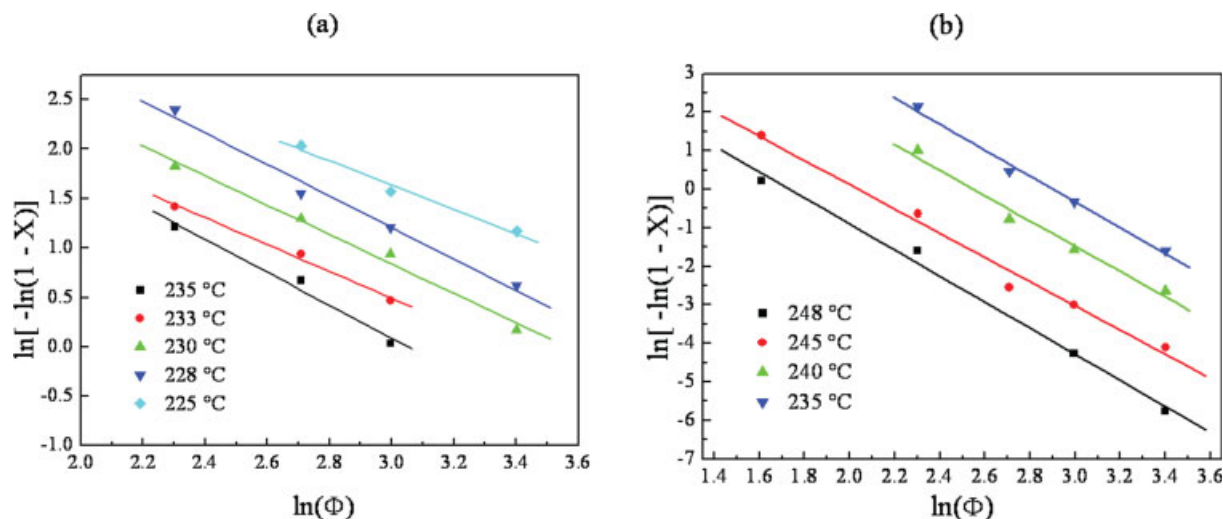


Figure 4 Plot of $\ln[-\ln(1-x(t))]$ as a function of $\ln|\Phi|$ for (a) neat PPS and (b) PEEK/PPS blend (30 : 70 by weight). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

with PEEK, as shown in Table II. As can be seen, the Avrami exponent of neat PPS is higher than that of PEEK/PPS blend at the experimental crystallization temperature range. This phenomenon shows that the presence of PEEK changes the nucleation type and crystal growth model of PPS. This process seems to involve the heterogeneous nucleation and three dimension growth of PPS, which means that crystallization of PPS changes from the homogeneous nucleation to heterogeneous nucleation and crystallized in spatially limited regions inside the spherulites of PEEK. Also, one can see that the Avrami exponent n varies with crystallization temperature, which shows that there exists a relationship between Avrami exponent n and temperature that can reflect the crystallization behavior of PPS. According to Regime Transition theory,⁴⁰ the nucleation rate and crystal growth of polymer are different at different crystallization temperature. And the overall rate of bulk crystallization varies rapidly when the Regime Transition occurs such as from Regime II to Regime III. While the Avrami exponent n depends on the nucleation rate and crystal growth rate, which shows that the values of Avrami exponent vary when the

crystallization of polymer is nonisothermal. Thus, we believe that the variation of n during nonisothermal crystallization process is relevant with the Regime Transition. Further studies are being carried out and will be reported.

As it is well known, the nonisothermal crystallization process of miscible crystalline/crystalline polymer blends from the homogeneous melt experienced phase transition. When the transition from liquid-liquid phase to crystalline-liquid phase occurs, the molecular chain motion of liquid phase polymer is greatly affected, which changed the nucleation type and crystal growth mechanism of liquid phased polymer, here PPS, when the temperature decreased. The presence of crystalline PEEK markedly accelerated the nucleation rate of PPS and changed the crystal growth mechanism of PPS. That means PEEK acted as nucleating agent during the melting crystallization course of PPS. The great influence of PEEK on the crystallization process of PPS can ascribe to the strong interface interaction between two polymers, which arises from the well compatibility of the two polymers in the melt state after PEEK crystallized during annealing from the melt.

The cooling crystallization function χ obtained from the intercept of plots in Figure 4 is presented in Figure 5 as a function of temperature. One can see that χ decreases with increasing temperature, and the values of χ of PEEK/PPS blend are higher than that of neat PPS. Although the mechanism of χ remains unclear, Ozawa³⁹ and Lopez and Wilkes^{41,42} suggest that the cooling crystallization function, χ , is related to the overall rate of bulk nonisothermal crystallization. Thus, the higher values of χ of PPS phase in blend system shows faster crystallization rate caused by the presence of crystalline PEEK.

TABLE II
The Kinetics Parameters from the Ozawa Analysis

T_c (°C)	n (Neat PPS)	n (PEEK/PPS)
255		2.86
250	3.381	1.825
245	2.53	1.5593
240	2.43	1.584
235	5.72	2.44
230	5.27	3.918

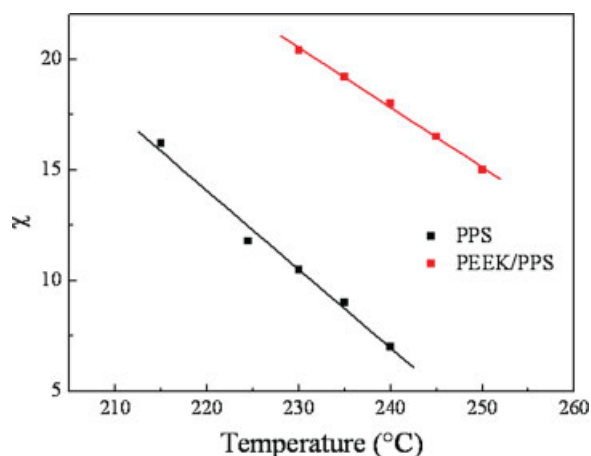


Figure 5 Plot of the cooling crystallization function, χ , as a function of temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Nonisothermal crystallization morphology of PEEK/PPS blend

The morphology of nonisothermally crystallized neat PPS and its blend with PEEK at predetermined cool-

ing rates of 10, 15, and 20°C/min are presented in Figures 6 and 7. It can be seen from Figure 6 that the neat PPS can form large nucleation density at a given cooling rate. The faster the cooling rate is, the more the nuclei are and the smaller the crystal is. In addition, the temperature at which nuclei can be observed under POM decreases with the cooling rate increasing. This phenomenon is consistent with DSC results. In the case of PEEK/PPS blend system, as is found by DSC, the PEEK start to crystallize at about 300°C, and the PPS crystallize in spatially limited regions inside the crystal of PEEK. These phenomena verify the results obtained from DSC.

On the basis of nonisothermal data of PPS and its blend with PEEK, the nonisothermal crystallization of PPS is greatly influenced by the PEEK. The presence of crystalline PEEK markedly accelerates the nonisothermal crystallization rate of PPS and confines the crystal growth of PPS in three dimensions. The interface interplay between the PEEK crystallite and the PPS melt because of miscibility of two polymers leads to occurrence of heterogeneous nucleation of PPS. This result is consistent with that reported by Mai et al.,^{19,20} who found that PEEK

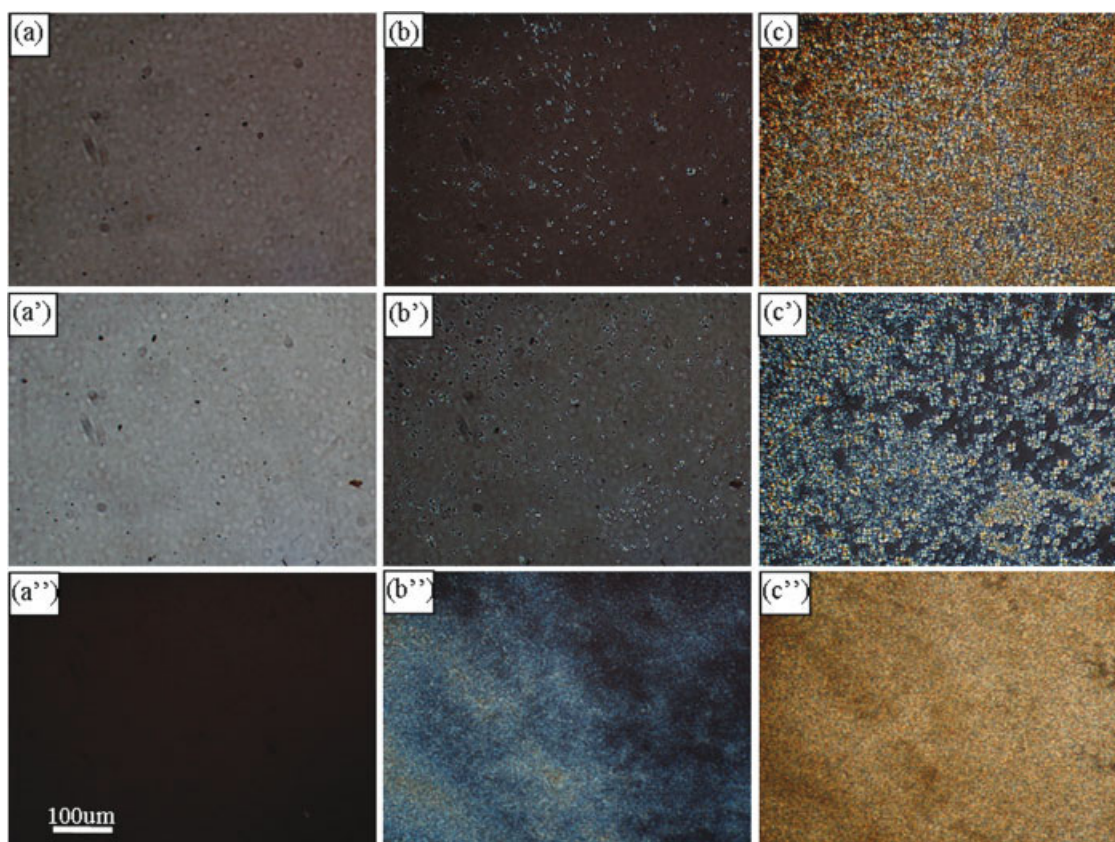


Figure 6 Optical micrographs of PPS non-isothermally crystallized for (a) 330°C, (b) 248°C (occurrence of crystal), and (c) 200°C at the rate of $-10^{\circ}\text{C}/\text{min}$; (a') 330°C, (b') 245°C (occurrence of crystal), and (c') 200°C at the rate of $-15^{\circ}\text{C}/\text{min}$; (a'') 330°C, (b'') 243°C (occurrence of crystal), and (c'') 200°C at the rate of $-20^{\circ}\text{C}/\text{min}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

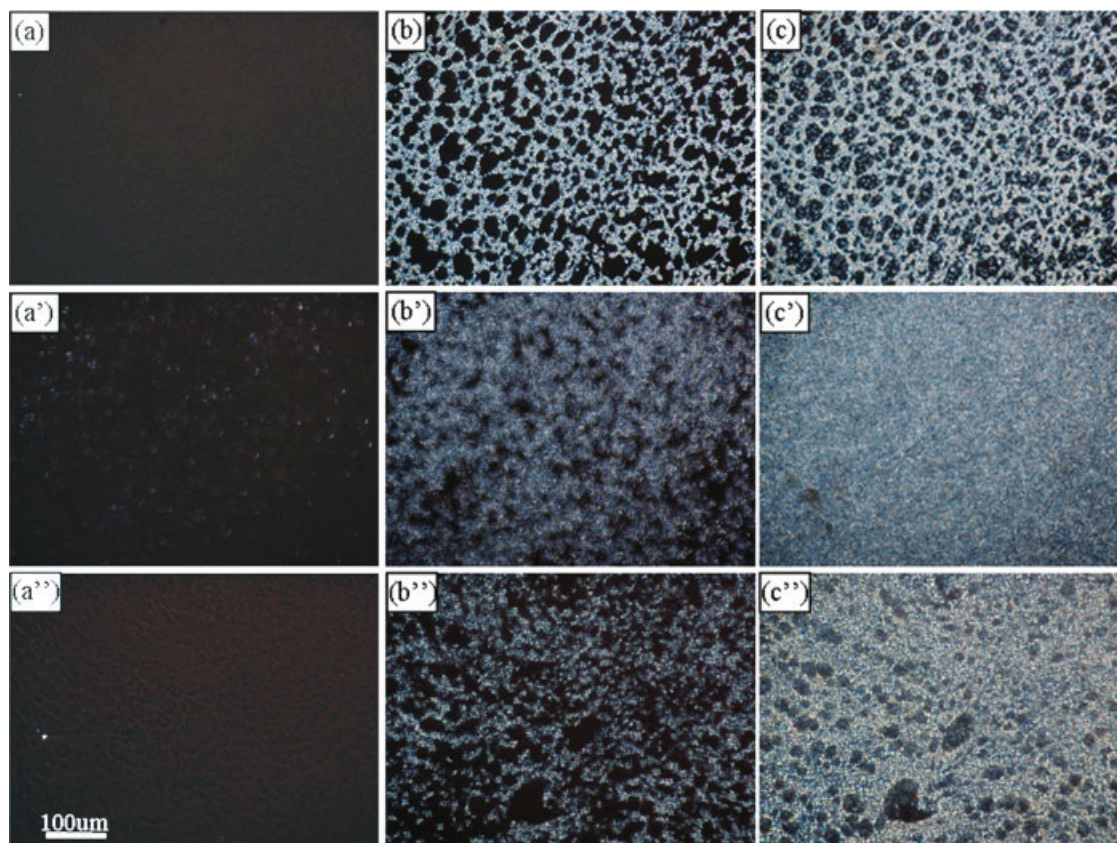


Figure 7 Optical micrographs of PEEK/PPS blend (30 : 70 by weight) nonisothermally crystallized for (a) 330°C, (b) 290°C (occurrence of crystal), and (c) 250°C at the rate of $-10^{\circ}\text{C}/\text{min}$; 330°C, (b') 285°C (occurrence of crystal), and (c') 245°C at the rate of $-15^{\circ}\text{C}/\text{min}$; (a'') 330°C, (b'') 280°C (occurrence of crystal), and (c'') 250°C at the rate of $-20^{\circ}\text{C}/\text{min}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

had an accelerating effect on PPS crystallization because of the heterogeneous nucleation arising from the interfacial interaction between two components in the blends. As it is well known, the presence of a foreign surface can reduce the critical nucleus size because the formation of an interface between the two components generally requires less surface free energy. Thus, the presence of PEEK crystallite decreases the surface free energy of critical nucleus of PPS and induces crystallization nucleation of PPS.

CONCLUSIONS

The nonisothermal crystallization morphologies and kinetics of PPS and its blend with PEEK have been investigated. The presence of PEEK has greatly influenced on the crystallization process of PPS. The crystallization rate of PPS is markedly accelerated by the PEEK. The crystalline PEEK acted as a nucleating agent and changed the crystallization mechanism of PPS from homogeneous nucleation to heterogeneous nucleation.

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