Effect of Blending on the Multiple Melting Behavior of Polyphenylene Sulfide

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ABSTRACT: The effects of melting time (t_{melt}) and annealing time (t_a) at a temperature closer to the melting point of polyphenylene sulfide (PPS) on the multiple melting behavior of neat PPS, and PPS component in their blends have been investigated by differential scanning calorimetry (DSC). It is found that double endotherm peak of PPS annealed at 275°C for less than three hours is different from that annealed for twelve hours. Double endotherm peak of PPS in PEEK/PPS blends shifts to lower temperature, and the intensity of the upper melting peak decreases significantly by addition of polyether ether ketone (PEEK). An additional third melting peak could be observed. The temperature of third melting peak is above 310°C and increases as the t_a and PEEK content are increased. For PEK-C/PPS blends, the lower and upper melting temperatures of the PPS component are higher than that of neat PPS annealed at 275°C for twenty-three hours. © 1996 John Wiley & Sons, Inc. J Appl Polym Sci **63**: 1001–1008, 1997

Key words: Polymer blends; polyphenylene sulfide; polyether ether ketone; melting behavior

INTRODUCTION

The multiple melting endotherms during normal differential scanning calorimetry (DSC) scans have been observed in many semicrystalline homopolymers crystallized either from the melt or the solid amorphous state. This behavior exhibits that a lower temperature endotherm often occurs about 10°C above the crystallization or annealing temperature and increases as the crystallization temperature increases, whereas the higher temperature endotherm (regarded as the normal melting endotherm) is relatively insensitive to the crystallization temperature. However, above certain crystallization temperature (generally closer to the melting point), the higher temperature endotherm also increases with an increase in crystallization or annealing temperature. Hypotheses have been

proposed in order to explain the multiple melting phenomenon. One of those is based on reorganization[1–3] and the other on the possible existence of different crystal structures and morphologies.[4–11] The multiple melting behavior of polyphenylene sulfide (PPS) has been investigated by a number of workers.[12–16] Chung and Cebe[14] found that the multiple melting behavior and the dependence of melting temperature on the crystallization temperature cannot be explained solely on the basis of either a reorganization or a morphology based model and presented a model in which the distribution of crystal perfection aerated during melt crystallization controls the multiple melting behavior of PPS. At low undercooling condition, a bimodal distribution of crystals could form, which eventually may become two morphologies. At high undercooling conditions, a broad distribution of crystals could form, a part of which may have melted and reorganized during the normal DSC scans. However, previous studies of PPS and other crystalline

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polymers focused on the effect of the experimental conditions on the multiple melting behavior of homopolymers. Up until now, the multiple melting behavior of PPS in its blends and the effect of blending on the multiple melting behavior of crystalline homopolymers have not been studied extensively.[17] In this work, the multiple melting behavior of PPS in its blends crystallized at a temperature close to its melting point from amorphous state and the influence of amorphous or crystalline thermoplastics on the multiple melting behavior of PPS were investigated. The effect of melting time and annealing crystallization time were also discussed.

EXPERIMENTAL

Amorphous thermoplastic poly(aryl ether ketone bearing phthalidylidene group) (PEK-C; systematic name, poly(phthalidydene-1,4-phenyleneoxy-1,4-phenylenecarboxyl-1,4-phenyleneoxy-1,4-phenylene) with reduced viscosity 1.1 produced by the Xuzhou Engineering Plastic, China, were dissolved in 1,2-dichloroethane to make 5 wt % solution. High-temperature, high-performance crystalline thermoplastic polyether ether ketone (PEEK) powder was supplied from Jilin University, China. Polyphenylene sulfide (PPS) powder (M_n = 2200 g/mol) produced by the Changshou Chemical Plant, China, was mixed in the PEK-C solution uniformly. Then the suspension was poured onto clean glass plates, allowing evaporation of the solvent at room temperature and drying in vacuum at 120°C for 3 h. PEEK/PPS blends were prepared in powder mixing. PPS and its blends were melted in the DSC cell at 360°C for various times and quenched in ice water. The quenched samples were annealed in DSC at 275°C for a certain period of time, followed by cooling to room temperature in air. The multiple melting behavior of annealing crystallized PPS and its blends was determined using a Perkin-Elmer DSC-7 at a heating rate of 20°C/min in static air. The melting peak temperatures and the heat of fusion of the DSC endotherm were calibrated using indium standard.

RESULTS AND DISCUSSION

The Influence of Melting Time and Annealing Time on the Multiple Melting Behavior of PPS

The crystallization and melting behavior of PPS depend upon the thermal history. Table I shows

DSC results of PPS, PEEK, and their blends after melted at 360°C for 10 min, followed by quenched in ice water. It can be seen from Table I that the addition of PEEK component with high T_g and T_m and the increase in the PEEK content leads to the decrease in the melt temperature (T_m) and heat of fusion (ΔH_m), the onset of crystallization temperature (T_{co}), crystallization temperature (T_c), and heat of crystallization (ΔH_c) of PPS component. The increase in glass transition temperature of PPS component in PEEK/PPS blends indicated that the amorphous regions are miscible. However, T_m, ΔH_m, T_{co}, T_c, and ΔH_c of the PEEK component increase with the addition of PPS component and by increasing the PPS content up to 50 wt %.[18–20] In a crystalline/crystalline multicomponent system, the thermal and chemical environment under which a polymer crystallizes is modified as a result of the presence of the second component. Due to the large difference in the melting points and crystallization temperatures of PPS and PEEK, the crystallization of PEEK with high T_m and T_c takes place in the presence of the melt of the PPS component, whereas the low melting second component (PPS) would crystallize in the presence of the solid phase of the PEEK component. The presence of the second component either in the molten and solid state would influence the crystallization and melting behavior of the blends.

Multiple melt peaks were observed as the quenched PEEK/PPS blends were annealed at temperature between T_g and T_m of PPS. Figure 1 shows the collective melting endotherms of PPS that had been melted at 360°C for various time and annealed at 275°C for 0.5 and 12 h, respectively. The dual endotherm peak has been observed on most of the melting thermograms. The lower melting peak temperature (T_{m1}), upper melting peak temperature (T_{m2}), and the heat of fusion (ΔH_m) of PPS related to melting time (t_{melt}) at 360°C and annealing time (t_a) at 275°C are shown in Table II. It can be seen from Figure 1 and Table II that the multiple melting behavior of PPS annealed at a temperature close to its melting point for a long time is different from that for a short time. The resulting melting endotherms of PPS annealed at 275°C for 0.5 h show a dual endotherm regardless of the melting time at 360°C. However, the lower and upper melting peak temperatures and the area of the upper melting peak decrease as the melting time increases. Longer melting time at 360°C might re-

Table I   DSC Results of Quenched PEEK/PPS Blends with No Annealing

PEEK/PPS (wt/wt)	PPS or PEEK	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_{co} (°C)	T_c (°C)	ΔH_c (J/g)
100 : 0	PPS	94.5	280.4	50.9	229.9	225.5	44.1
80 : 20	PPS	95.6	277.2	33.4	221.7	208.1	29.1
50 : 50	PPS	103.2	269.1	17.4	223.7	204.1	15.2
20 : 80	PPS	—	259.7	6.7	—	—	—
100 : 0	PEEK	152.2	332.6	31.8	293.5	284.0	38.4
80 : 20	PEEK	—	334.3	34.8	296.5	289.8	41.7
50 : 50	PEEK	—	337.1	42.1	302.0	294.5	46.4
20 : 80	PEEK	—	332.8	27.0	288.7	271.4	18.5

sult in higher degree of branching and cross-linking of PPS due to the thermal oxidation. The mechanism of the reaction has been reported.[21,22] Once a PPS sample has been melted, annealed, and rescanned, it is not possible to obtain an endotherm identical to the initial PPS, as evidenced by the drop in the T_m, T_c, ΔH_m, and ΔH_c.[18,23] The branching and cross-linking would retard the annealed crystallization of PPS, especially the formation of the upper melting crystal of PPS. It can also be seen from Figures 1 and 2 that the lower
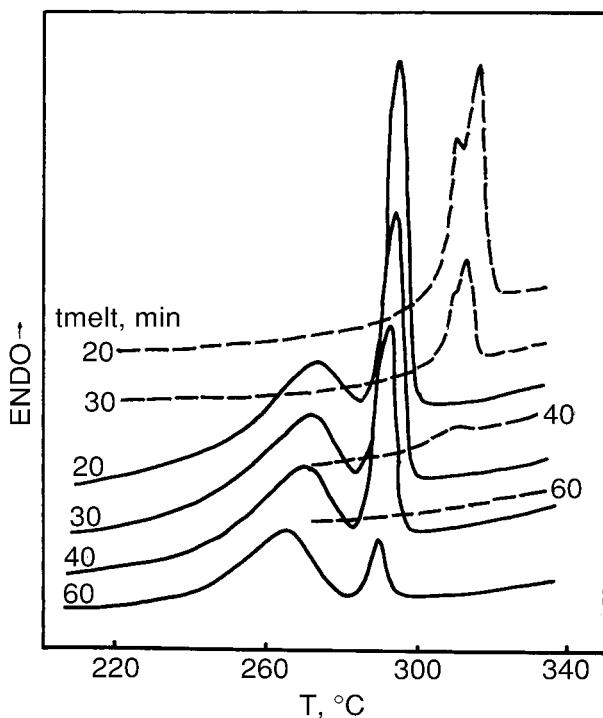
melting peak temperature is lower than the annealing crystallization temperature and shifts to lower temperature as annealing time is increased, suggesting that the lower melting peak temperature is due to melting of PPS crystal formed during cooling process from annealing temperature to room temperature and DSC scanning process. The heat of fusion and the height of dual melting peak decrease as annealing time is increased due to the occurrence of the branching and cross-linking of PPS annealed at 275°C for long time. When PPS is annealed at a temperature closer to its melting point, the segment mobility would be high enough to allow large-scale annealing to take place. The perfection of preexisting crystals increases so that the upper melting peak temperature shifts to higher temperature as the annealing crystallization time is increased. It is interesting to note that the lower and upper melting peak temperatures of PPS annealed 275°C for 12 h are higher than the annealing temperature and the normal melting point of PPS. It is not explained by reorganization. Chung and Cebe[14] have also found an additional third melting peak, whose temperature is higher than the normal melting point of PPS. The existence of the third melting peak suggests that more than one kind of distribution of crystals perfection may occur for PPS annealed at a temperature closer to the melting point for a long time.

The Effect of Crystalline PEEK with High Melting Point on the Multiple Melting Behavior of PPS

Figure 3 shows the collective melting endotherms of PPS in PEEK/PPS blends annealed at 275°C for 0.5 h. The melting temperatures and heats of fusion of PPS in its blends are also shown in Table

Figure 1   The collective melting endotherms of PPS melted at 360°C for various times and annealed at 275°C for 0.5 h (——) and 12 h (----).

Table II Melting Temperatures and Heat of Fusion of PPS in PEEK/PPS Blends[a]

PEEK/PPS	t_{melt} (min)	t_a (h)	T_{m1} (°C)	ΔH_{m1} (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)	T_{m3} (°C)
0 : 100	20	0.5	271.8		293.3	(35.39)	—
		1	269.9	16.61	294.4	18.73	—
		12	308.0	9.23	313.7	11.84	—
0 : 100	30	0.5	270.4	16.73	291.9	19.64	—
		1	268.3	15.82	293.7	19.33	—
		3	250.3	3.64	297.3	5.03	—
		12	307.9	—	311.2	(6.91)	—
0 : 100	40	0.5	269.1	11.46	290.6	18.22	—
		1	268.8	14.88	294.9	2.62	—
		3	256.3	4.34	—	—	—
		12	—	—	309.0	0.72	—
0 : 100	60	0.5	264.7	—	289.9	(17.74)	—
		1	266.6	17.14	293.0	3.50	—
		3	256.3	2.36	—	—	—
20 : 80	20	0.5	268.4	12.68	289.4	1.90	307.2
		1	265.0	15.90	291.1	1.28	310.3
		3	260.4	1.94	—	—	314.8
		12	—	—	310.2	1.44	324.2
20 : 80	30	0.5	263.1	13.65	288.0	0.54	—
		1	263.0	11.45	290.2	0.41	308.4
		12	—	—	308.1	0.48	324.6
20 : 80	40	0.5	257.5	10.26	—	—	—
		1	258.9	6.88	—	—	309.0
		3	252.9	6.56	—	—	316.7
20 : 80	60	0.5	254.7	6.56	—	—	—
		1	254.9	6.15	—	—	—
50 : 50	20	0.5	259.8	2.02	293.3	2.68	335.9
		1	258.6	4.80	301.8	12.70	331.4
		3	—	—	301.8	36.96	—
		12	—	—	317.6	40.44	—
50 : 50	30	0.5	—	—	292.1	—	331.4
		1	249.9	2.42	302.2	10.76	330.4
		3	—	—	311.8	30.08	—
		12	—	—	317.0	32.40	—
50 : 50	40	0.5	253.2	1.42	296.3	4.65	329.1
		1	251.1	1.08	302.3	9.92	330.3
		3	—	—	312.8	25.88	—
		12	—	—	316.7	24.80	—
50 : 50	60	0.5	251.2	0.76	293.3	—	327.4
		1	—	—	304.8	7.62	328.1
		3	—	—	313.2	18.92	—
		12	—	—	317.0	17.26	—

[a] T_{melt} = 360°C. T_a = 275°C. ( ): $\Delta H_{m1} + \Delta H_{m2}$.

II. It can be seen from Figure 3 and Table II that the addition of PEEK results in a significant drop in the height and area of the upper melting peak of PPS. The lower and upper peak temperatures shift to lower temperature. It is indicated that the crystalline PEEK with higher melting point (T_m of PEEK is higher than that of PPS) can retard the annealed crystallization of PPS in PEEK/PPS powder blends, especially the formation of the upper melting crystal of PPS. The effect of addition of PEEK is more significant than that of melting temperature on the multiple melting behavior. The collective melting endotherms of PPS in PEEK/PPS20/80 blends melted at 360°C and an-
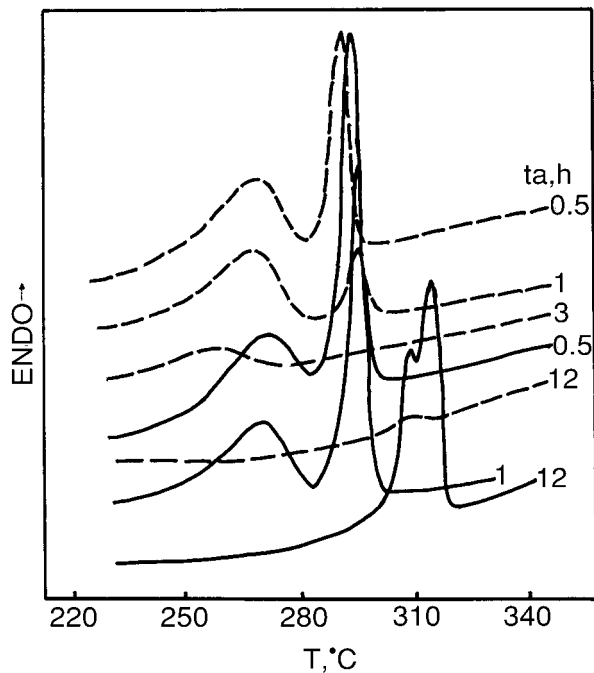
Figure 2 The collective melting endotherms of PPS melted at 360°C for 20 min (——) and 40 min (----) and annealed at 275°C for various times.
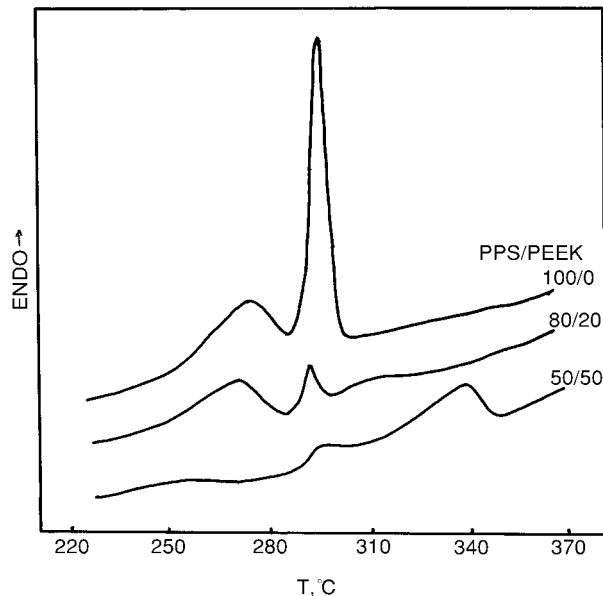

Figure 3 The collective melting endotherms of PPS in PEEK/PPS blends melted at 360°C for 20 min and annealed at 275°C for 0.5 h.

Figure 4 The collective melting endotherms of PPS in PEEK/PPS = 20 : 80 blend melted at 360°C and annealed at 275°C for various melt times (in min): (——) 20, (– – –) 30, (– · – · –) 40, and (– · · – · · –) 60.

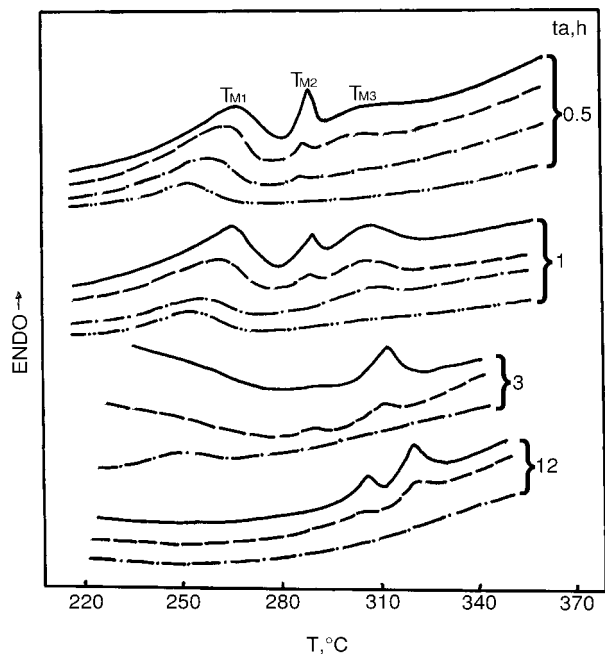nealed at 275°C for various times are shown in Figure 4. It is found that the lower melting peak temperatures of PPS in its blends decreases more significantly than that of neat PPS, and the lower, as well as upper, melting peak tends to disappear with increasing the melting time due to the increase in the degree of the branching and cross-linking of PPS during melting and annealing process, as well as the effect of PEEK component. It is interesting to note that a third melting peak (T_{m3}) at even higher temperature has been observed in PEEK/PPS blends. The temperature of T_{m3} is higher than T_{m2} and the normal melting point of PPS but lower than T_{m2} of PEEK. The intensity and temperature (above 310°C) of T_{m3} depends upon the annealing crystallization time and melting time. The temperatures of T_{m3} and T_{m2} also increase by increasing the annealing time and disappears by increasing the melting time. The T_{m2} peak may be attributed to the melting of more perfect PPS crystals formed during long annealing process. The T_{m3} peak may be due to the melting of imperfect PEEK crystals or co-crystals of PPS and PEEK formed during long crystallization process. The existence of T_{m3} peak suggests that more than one kind of distribution of crystal perfection may occur. It can be also seen from Figure 4 that the T_{m1} decreases significantly

and disappears by increasing the melting time and the annealing time due to the increase in the degree of the branching and crosslinking of PPS during melting and annealing process.

The Effect of Amorphous PEK-C with High Glass Transition Temperature on the Multiple Melting Behavior of PPS

In our laboratory, the crystallization and melting behavior, mechanical property, fracture morphology, etc., of PPS modified with polysulfone and PEK-C thermoplastics have been investigated.[21,24] In our previous article,[15] the double melting phenomena of PPS and its blends with high performance amorphous thermoplastics polysulfone (PSF) and PEK-C have been investigated. It was found that amorphous thermoplastic PSF and PEK-C with high glass transition temperature have no influence on the lower melting peak temperature but retard the crystallization of the upper melting crystals of PPS in its blends annealed at 240°C. The addition of PSF and PEK-C results in a drop in the height of the upper melting peak of PPS and disappears as the contents of PSF and PEK-C are increased. The thermoplastics with different glass transition temperature and viscosity exert different influences on the multiple melting behavior of PPS. In the blends, the multiple melting behavior of PPS is much more sensitive to the changes in melting and annealing conditions than that of neat PPS.

In this article, our purpose is to investigate the multiple melting behavior of PPS in its blends annealed at a temperature closer to the normal point of PPS and the effect of thermoplastic on the multiple melting behavior of PPS component. Figure 5 shows the collective melting endotherms of PPS and its blends with PEK-C that had been melted at 360°C for 10 min, followed by annealing at 275°C for 23 h. The DSC results is shown in Table III. Although the dual melting peak of neat PPS and PEK-C/PPS blends can be observed, the melting endotherms of PPS are different from that of its blends. As the annealing time at 275°C is increased to 23 h, the height of upper melting peak of neat PPS is higher than that of the lower melting one. However, the temperatures of T_{m1} and T_{m2} of PPS in PEK-C/PPS25/75 blend are higher than that of neat PPS, and the height of T_{m1} peak is higher than that of the upper melting one. Blending of PPS with PEK-C modifies the crystallization behavior of PPS and increases the
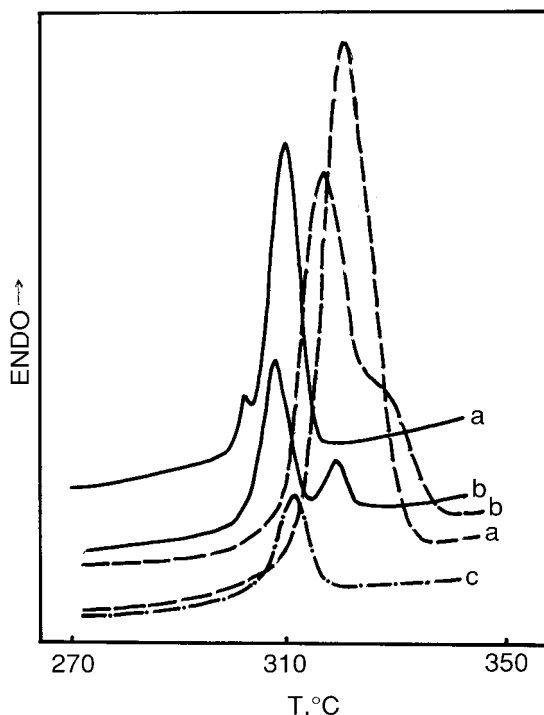

Figure 5 The collective melting endotherms of (a) PPS and PPS in (b) PEK-C/PPS = 25 : 75 blend and (c) PEEK/PPS = 20 : 80 blend melted at 360°C for 10 min and annealed at 275°C for 23 h. Heating rates: 20°C/min (——), and 80°C/min (----).

crystal perfection of PPS in blend annealed at 275°C. It is suggested that blending of PPS with PEK-C would enhance the crystal perfection of PPS when the blends were annealed at a temperature closer to the normal melting point of PPS. The incompatibility and intermolecular repulsion interaction between PPS and PEK-C at higher annealing temperature above the glass transition temperature (225°C) of PEK-C may enhance the nucleation and growth of lower melting crystals of PPS and increase the perfection of PPS crystallization. On the other hand, there would be a certain degree of interpenetration and entanglement of molecules in the interface between PPS and PEK-C, retarding the crystallization of the upper melting crystals of PPS and resulting in a decrease in the intensity and area of the upper temperature melting peak. The multiple melting behavior of PPS in PEEK/PPS blends is different from that of PPS in PEK-C/PPS blends annealed at 275°C for 23 h. Although dual melting peak can be seen for PEEK/PPS20/80 blends annealed for 12 h, as the annealing time is increased to 23 h, only one melting peak between the lower and up-

Table III   Melting Temperature and Heat of Fusion of PPS and Its Blends[a]

	Heating Rate (°C)	T_{m0} (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)
PPS	20	304.4	303.6	310.4	35.12
PPS	80	313.2	—	319.9	26.06
PEK-C/PPS	20	303.4	307.8	319.0	35.57
25/75	80	309.9	316.2	326.1	29.65
PEEK/PPS	20	306.8	—	311.9	16.53
20/80	80	314.8	—	321.6	19.09

[a] $T_{\text{melt}} = 350°C$. $t_{\text{melt}} = 10$ min. $T_a = 275°C$. $t_a = 23$ h.

per melting peak of PPS in PEK-C/PPS blends can be observed for PPS in PEEK/PPS blends. The peak temperature is about 310°C, the same as the upper melting peak temperature of neat PPS annealed at 275°C for 23 h.

CONCLUSIONS

The multiple melting behavior of PPS and its blends annealed at a temperature closer to the normal melting point of PPS from amorphous state depends on the melting and annealing condition and is different from that of PPS annealed at a temperature below the normal melting point of PPS. The resulting melting thermograms of PPS annealed at 275°C for 0.5 h shows a dual melting endotherm. As the annealing time increases, the lower melting peak temperature decreases, and the upper melting peak temperature increases. However, the heat of fusion and the height of the dual melting peak decrease significantly. Although two melting peaks have been also observed for PPS annealed at 275°C for 12 h, it is different from that of PPS annealed for 1 h. The lower and upper melting peak temperatures are higher than the annealing temperature and the normal melting point of PPS, suggesting that a bimodal distribution of crystals with better crystal perfection would be formed at higher annealing temperature for a long time. The addition of crystalline PEEK results in a significant drop in the height of the upper melting peak and heat of fusion. When the PEEK/PPS blends are annealed at 275°C for 1 h, a third melting peak ($T_{m3} > T_{m2}$) has been observed. The temperature of the T_{m3} is above 310°C and increases as the annealing time increases. Although amorphous PEK-C retards

the crystallization of the upper melting crystals of PPS annealed at a temperature below the normal point of PPS, the lower and upper melting peak temperatures of PPS in PEEK/PEK-C blends are higher than that of neat PPS annealed 275°C for 23 h.

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