Melting and Crystallization Behavior of PA1010/TPU Blends

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ABSTRACT: PA1010/TPU blends were prepared by melt blending. The melting, crystallization behavior, and isothermal crystallization kinetics were investigated using differential scanning calorimetry (DSC). The results showed that the DSC thermograms of blend samples exhibit double melting peaks. With increasing the TPU content, the position of the double melting peaks shifted to a lower temperature, and the total heat of fusion decreased. With increasing the heating rates, the position of the lower melting peak shifted to a higher temperature, while the position of the higher melting peak shifted to a lower temperature; however, the total heat of fusion remained almost constant. With prolong-ing the annealing time and increasing the crystallization temperature, the position of the lower melting peak shifted to a higher temperature, while the position of the higher melting peak almost did not change; however, the total heat of fusion increased. The addition of TPU could promote the crystallization of PA1010 but not affect the crystallization mechanism. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 839–844, 2004

Key words: melting point; crystallization; differential scanning calorimetry (DSC)

INTRODUCTION

Polyamide 1010 (PA1010) is a semicrystalline engineering plastic and has poor low-temperature impact resistance at temperatures below T_g, especially in a dry state. This drawback could be improved by incorporating a toughening agent. In this field some research work of toughening PA1010 has been done.[1–3]

As a semicrystalline polymer, the thermal behavior of PA1010 would be influenced somewhat when it was incorporated with a toughening agent. In the present article we will report the melting and crystallization behavior of toughening the PA1010 system with TPU.

EXPERIMENTAL

Materials

The polyamide 1010 (PA1010) was supplied by Jilin Nylon Chemical Engineering Limited Liability Company, China, and its relative viscosity is 2.1. Thermoplastic polyurethane elastomer (TPU) was JZ85 from Tianjin Plastics Group Limited Company (China). JZ85 (shore hardness A = 85; M_w = 188,773 g/mol, M_w/M_n = 4.38) is a kind of ester-based TPU, with soft segments based on poly(ethylene adipate) diol, and with a hard segment based on MDI (diphenylmethane diisocyanate) and 1,4-butanediol.

Preparation of blends

The pellets of PA1010 were dried at 100°C in a vacuum oven for 8 h, and the pellets of TPU were dried at 100°C in a vacuum oven for 2 h before melt blending. PA1010/TPU blends were prepared using a ZSK30 twin-screw extruder (WP) operating at a temperature range of 190–210°C and at 65 rpm. The weight ratio of the PA1010/TPU blends were 100/0, 98/2, 95/5, 90/10, and 80/20.

Melting and crystallization behavior investigation

The melting and crystallization behavior of the PA1010/TPU blends were investigated by means of a Mettler Toledo Differential Scanning Calorimeter (DSC821^e). Indium was used as the reference for the calibration of temperature and energy scales. To prevent thermal oxidative degradation of the materials, all experiments were performed under a nitrogen atmosphere.

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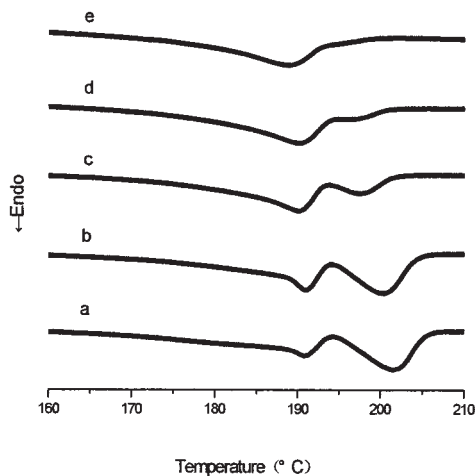
Figure 1 DSC thermograms of PA1010/TPU blends: (a) 100/0; (b) 98/2; (c) 95/5; (d) 90/10; (e) 80/20.

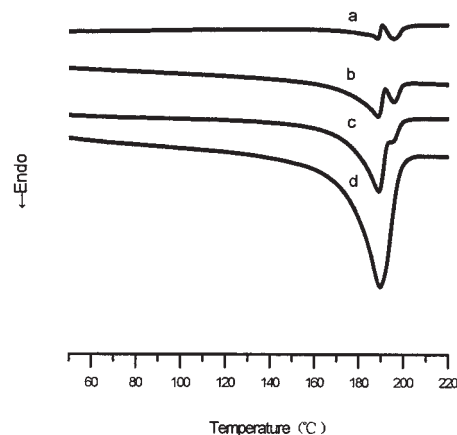**Figure 2** DSC thermograms of the PA1010/TPU (90/10) blend at different heating rate: (a) 2°C/min; (b) 5°C/min; (c) 10°C/min; (d) 20°C/min.

RESULTS AND DISCUSSION

Melting behavior of the blends

Effect of TPU content

Figure 1 shows DSC thermograms of the PA1010/TPU blends heated at 10°C/min, up to 250°C, held for 5 min to eliminate the residual nuclei, cooled at 10°C/min to 20°C so as to observe the crystallization behavior, and reheated at 10°C/min up to 250°C to further observe the melting behavior. From Figure 1 it can be seen that pure PA1010 shows double melting peaks, which overlap more or less, that is, a lower temperature peak (T'_m) at ca 190°C and the higher temperature peak (T_m) at ca 200°C. The melting peak appearing at the lower temperature results from the melt of the relatively unstable, imperfect, and thin crystal formed during the cooling process or during the thermal treatment, whereas the melting peak appearing at the higher temperature results from the melt of the relatively more stable, more perfect, and thicker crystal formed during the heating run in DSC.[4] For the pure PA1010, the area of the higher temperature peak was larger than that of the lower temperature peak. With increasing the TPU content, the position of the two peaks shifted to lower temperature (see Table I), the area of the lower temperature peak remained almost

TABLE I
Effect of TPU Content

PA1010/TPU (W/W)	T'_m °C	T_m °C	ΔH_f J/g
100/0	191	202	66.0
98/2	191	200	67.8
95/5	190	198	63.9
90/10	190	—	57.6
80/20	189	—	50.9

constant, whereas the area of the higher temperature peak decrease finally disappeared. When TPU content was up to 10 or 20%, only a broad low-temperature melting peak with a shoulder could be seen. The total heat of fusion (ΔH_f) for PA1010 in the blend was calculated from an area under the overlapping melting peaks and divided by the weight fraction. The values are listed in Table I. Similar to the melt temperature, the total heat of fusion also decreased with increasing the TPU content. These phenomena imply that TPU inhibits PA1010 to develop a thicker crystal and more perfect crystallite when it is crystallized from the melt. This effect of inhibition may result from the interaction of the two polymers.

Effect of heating rate

Figure 2 shows DSC thermograms of the PA1010/TPU(90/10) sample heated at 10°C/min, up to 250°C, held for 5 min to eliminate the residual nuclei, cooled at 10°C/min to 20°C, and reheated at different heating rates up to 250°C. The heating rates were 2, 5, 10, and 20°C/min, respectively. From Figure 2, it can be seen that at the heating rates of 20°C/min, that only one melting peak (T'_m) is observed; while at low heating rates, two melting peaks (T'_m and T_m) appear. With increasing the heating rates, the melting peak at T'_m shifted to a higher temperature and the relative peak area also increased, while the melting peak at T_m shifted to a lower temperature and the relative peak area also decreased. However, the total areas of the two peaks remained almost constant. The values of T'_m, T_m, and ΔH_f are seen in Table II. This phenomenon should be attributed to the fact that the higher heating rate inhibits recrystallization and the lower heating rate promotes recrystallization,[5] namely, at the higher heating rate, because the recrystallization is inhibited, the relative peak area at T_m will decrease, and the

TABLE II
Effect of Different Heating Rate

Heating rate (°C/min)	T'_m °C	T_m °C	ΔH_f J/g
2	188	196	54.4
5	189	196	56.3
10	190	—	57.6
20	190	—	60.2

TABLE III
Effect of Annealing Time

Annealing time	T'_m °C	T_m °C	ΔH_f J/g
2 h	181	201	63.8
8 h	185	200	73.1
24 h	192	199	73.7
48 h	193	199	75.9

perfect degree of the crystal will decrease so that T_m shows the tendency of decrease.

Effect of annealing treatment

Effect of annealing time. Figure 3 shows DSC thermograms of the PA1010/TPU (90/10) sample annealed. The sample was annealed at 175°C for 2, 8, 24, and 48 h, respectively, and were directly heated from 20 to 250°C at 10°C/min. To study the influence of annealing time on melting behavior, the DSC endotherms of these samples are shown in Figure 3. Just like the samples crystallized from the melt, the annealed samples also showed double melting peaks if the annealing time was not too long. With prolonging annealing time, the lower temperature peak (T'_m) shifted to a higher temperature and the relative peak area increased, while the higher temperature peak (T_m) seemed not to be affected by the annealing. With prolonging annealing time, the double melting peaks overlaped step by step; finally, the high temperature peak almost disappeared, and the range of the melting temperature was reduced (see Table III). This phenomenon may be attributed to the influence of the annealing time on the thickness of the lamella. The melting temperature (T_m) of the semicrystalline polymer depends on the crystal thickness (lamella thickness of the spherulite of the semicrystalline polymer)
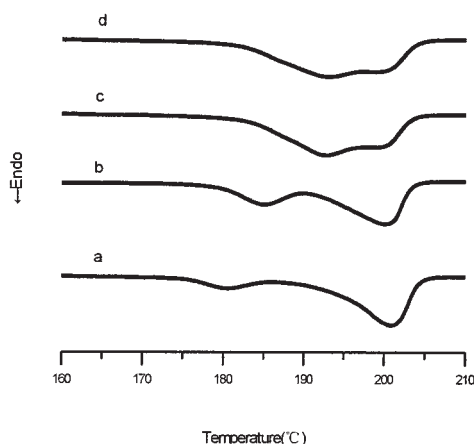
and the T_m is proportional to the thickness of the lamella.[6] When the semicrystalline polymer is annealed at a temperature not far from T_m, the thickness of the lamella will increase to reduce the surface free energy of crystallization and increase stability. With prolonging the annealing time, the thinner lamellae, corresponding with the low melting temperature (T'_m), will be thickened, and more stable crystallite with one higher T'_m will appear.

Effect of blend composition during annealing treatment. Figure 4 shows DSC thermograms of the PA1010/TPU blends that have been annealed. The samples were annealed at 150°C for 2 h, and were directly heated from 20 to 250°C at 10°C/min. To study the influence of blend compostion on melting behavior during annealing treatment, the DSC endotherms of these samples are shown in Figure 4. It is clear that the annealed samples showed double melting peaks. Furthermore, the lower temperature peak (T'_m) of the PA1010/TPU blends was lower than that of the pure PA1010; however, the higher temperature peak (T_m) of the PA1010/TPU blends was almost equal to that of the pure PA1010. The phenomenon further proved there was interaction between the two polymers mentioned earlier. Because the interaction may inhibit the crystalli-
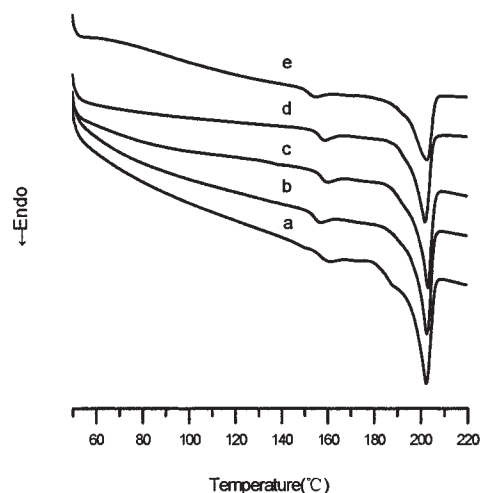

Figure 3 DSC thermograms of the PA1010/TPU (90/10) blend annealed at 175°C for (a) 2 h; (b) 8 h; (c) 24 h; (d) 48 h.

Figure 4 DSC thermograms of PA1010/TPU blends annealed at 150°C for 2 h: (a) 100/0; (b) 98/2; (c) 95/5; (d) 90/10; (e) 80/20.
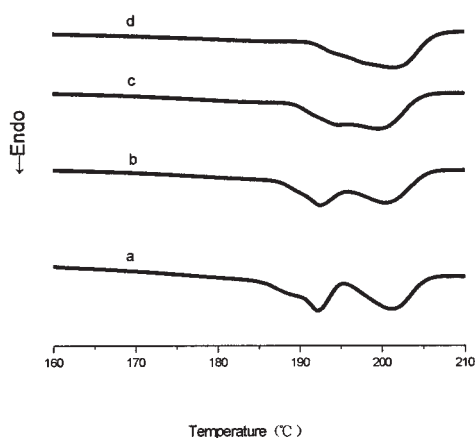
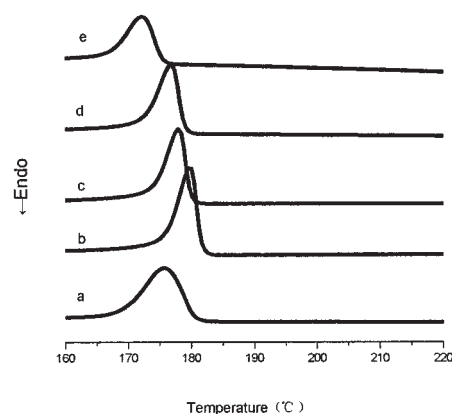**Figure 5** DSC thermograms of the PA1010/TPU (90/10) blend under different crystallization temperatures: (a) 182°C; (b) 184°C; (c) 186°C; (d) 188°C.

Figure 6 DSC crystallization exotherms of PA1010/TPU blends: (a) 100/0; (b) 98/2; (c) 95/5; (d) 90/10; (e) 80/20.

zation of the PA1010 molecular segments, the crystal formed in the annealing treatment of the PA1010/TPU blends was thinner or more imperfect than that of the pure PA1010.

Effect of crystallization temperature

Figure 5 shows DSC thermograms of the PA1010/TPU (90/10) sample heated at 10°C/min, up to 220°C, held for 5 min to eliminate the residual nuclei, cooled to a predetermined temperature T_c at 200°C/min, and held for 30 min to investigate the isothermal crystallization kinetics. To further observe the melting behavior after the isothermal crystallization, the sample was cooled to 20°C and reheated at 10°C/min up to 220°C. The predetermined crystallization temperatures of T_c were 182, 184, 186, and 188°C, respectively. The influence of the crystallization temperature T_c on the melting behavior of the PA1010 in the PA1010/TPU (90/10) blend is shown in Figure 5. The thermogram of the sample crystallized at 182°C showed two separated melting peaks at 192 and 201°C, respectively, while only one melting peak was seen for the sample crystallized at 188°C. At the intermediate crystallization temperatures such as 184 and 186°C, two overlapping melting peaks were observed. The lower temperature peak (T'_m) shifted to a higher temperature

with increasing the crystallization temperature, while the higher temperature peak (T_m) seemed not to be influenced by the crystallization temperature. With increasing the crystallization temperature the total heat of fusion (ΔH_f) increased (see Table IV). These phenomena indicate that the higher crystallization temperature facilitates PA1010 to develop a thicker crystal and more perfect crystallite when it crystallized from the melt.

Crystallization behavior of the blends

The influence of composition on the crystallization behavior was rather complicated. The detailed method is seen as shown earlier. DSC thermograms of the PA1010/TPU blends on the cooling run and the corresponding values of T_c (the temperature of the maximum crystallization rate) and ΔH_c are shown in Figure 6 and Table V, respectively. It is clear that the addition of a small amount TPU into PA1010 is favorable for crystallization of PA1010 from the melt so that the crystallization could take place at a higher temperature, namely the T_c of PA1010/TPU (98/2), (95/5), and (90/10) are higher than that of pure PA1010. As the amount of TPU is large enough, the crystallization will be rather difficult, namely T_c is depressed.

TABLE IV
Effect of Crystallization Temperature

Crystallization temperature	T'_m °C	T_m °C	ΔH_f J/g
182 °C	192	201	53.5
184 °C	193	200	66.4
186 °C	195	200	66.9
188 °C	—	201	69.7

TABLE V
The Values of T_c and ΔH_c during DSC Cooling Scans of PA1010/TPU Blends

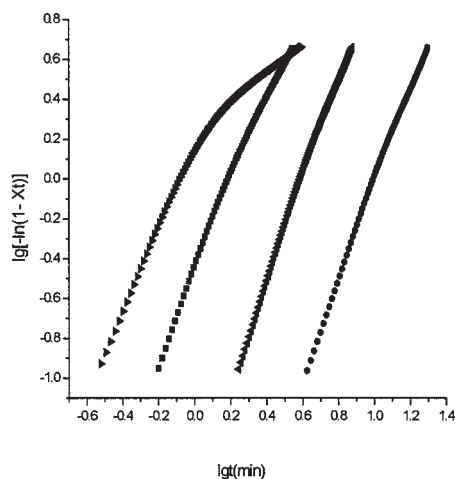| PA1010/TPU (W/W)	T_c °C	ΔH_c J/g
100/0	176	55.5
98/2	180	61.6
95/5	178	57.9
90/10	177	41.7
80/20	172	32.0

Figure 7 Avrami plot for pure PA1010 under different crystallization temperatures: (▼) 182°C; (■) 184°C; (▲) 186°C; (●) 188°C.

As a kind of impurity, TPU may accelerate or inhibit the crystallization of PA1010 in the blends depending on the function in crystallizing process and the content. In the case of the PA1010/TPU (98/2) blend, a small amount of TPU, as a nucleation agent, may be favorable for the formation of nucleus; therefore, PA1010 shows a higher T_c. With increasing the content of TPU, the interaction of the two polymers increase and the concentration of PA1010 decreases. In such a case, the crystallization of PA1010 would be rather difficult, and take place at a lower temperature.

Isothermal crystallization kinetics of the blends

The isothermal crystallization kinetics of PA1010 and its blend were studied in a temperature range from 182 to 188°C (see earlier). The result was analyzed by means of the Avrami equation:[7]

$$1 - X_t = \exp - kt^n \qquad (1)$$

Equation (1) is often written in the logarithmic form:

$$\ln(1 - X_t) = - kt^n \qquad (2)$$

where k is the rate constant of crystallization and n is the Avrami exponent, which can be related to the type of nucleation and the geometry of crystal growth. Plots of $\lg[-\ln (1-Xt)]$ vs $\lg t$ for pure PA1010 and PA1010/TPU (95/5) blend are shown in Figures 7 and 8, respectively. Each curve showed an initial liner portion, followed by a gradual roll-off. This fact indicates the existence of a secondary crystallization process of the pure PA1010 and the PA1010/TPU blends, namely the crystallization process, which contains two stages: a primary stage, and a secondary stage. From

the intercept and slop of the linear part, the values of k and n were calculated, respectively.

The t_i, the time to reach the maximum rate of heat flow, and $t_{1/2}$, the half time of crystallization, can be calculated using the follow equations:

$$t_1 = [(n - 1)/nk]^{1/n} \qquad (3)$$

$$t_{1/2} = (\ln2/k)^{1/n} \qquad (4)$$

The values of n and k, as well as t_i (t_{max}) and $t_{1/2cal}$ ($t_{1/2exp}$), are listed in Table VI. The Avrami exponent n, is in a range from 1.8 to 2.9, and almost independent on the blend composition and crystallization temperature. The values of the kinetic rate constant k are influenced by blend composition and crystallization temperature. For a given composition, k decreased with increasing crystallization temperature T_c, while the crystallization rate constant of PA1010 in the blends was always higher than that of pure PA1010 at a given crystallization temperature. This implies that as a nucleation agent, TPU may promote the crystallization process of PA1010, but not affect the crystallization mechanism. From Table V, it is clear that the time to reach the maximum rate of heat flow and the half time of the crystallization decreases with decreasing the crystallization temperature for a given composition, and the time to reach the maximum rate of heat flow and the half time of the crystallization in the blends are lower than those in pure PA1010 for a given crystallization temperature, as well as the fact that there is not much difference between the values calculated with eqs. (3) and (4) and those experimentally measured. The agreement in values t_i (t_{max}) and $t_{1/2cal}$ ($t_{1/2exp}$) suggests that the Avrami equation works well in describing the initial crystallization process of PA1010.
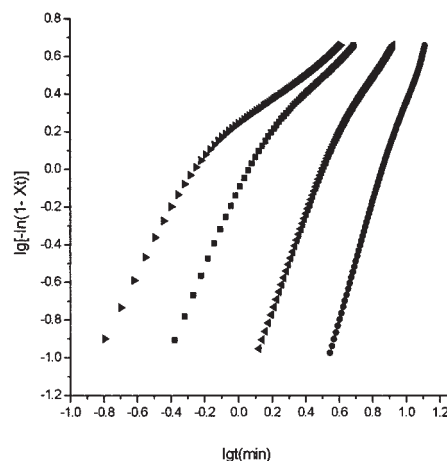

Figure 8 Avrami plot for the PA1010/TPU (95/5) blend under different crystallization temperatures: (▼) 182°C; (■) 184°C; (▲) 186°C; (●) 188°C.

TABLE VI
Avrami Parameter n, k, $t_{1/2exp}$, $t_{1/2cal}$, t_{max}, t_1

PA1010/TPU (w/w)	Crystallization temperature	n	k (l/min)	$t_{1/2exp}$ (min)	$t_{1/2cal}$ (min)	t_{max} (min)	t_1 (min)
100/0	182°C	2.2	1.58	0.68	0.68	0.54	0.61
	184°C	2.6	0.36	1.30	1.30	1.10	1.23
	186°C	2.9	0.02	3.38	3.46	3.08	3.37
	188°C	2.6	2.51E-3	8.60	8.58	7.72	8.18
98/2	182°C	2.0	4.51	0.39	0.39	0.30	0.33
	184°C	1.9	1.86	0.60	0.59	0.44	0.49
	186°C	2.4	0.14	1.92	1.97	1.78	1.82
	188°C	2.1	0.08	2.81	2.17	2.63	2.44
95/5	182°C	1.8	3.31	0.42	0.42	0.28	0.32
	184°C	2.2	0.85	0.93	0.91	0.70	0.82
	186°C	2.6	0.05	2.70	2.80	2.34	2.66
	188°C	2.9	2.82E-3	6.48	6.58	7.17	7.11
90/10	182°C	1.9	3.63	0.44	0.41	0.29	0.34
	184°C	2.3	0.69	1.02	1.00	0.80	0.92
	186°C	2.5	0.04	3.05	3.16	2.78	2.99
	188°C	2.1	0.06	3.18	3.13	3.00	2.77
80/20	182°C	1.9	2.95	0.58	0.41	0.38	0.38
	184°C	1.9	0.87	0.88	0.89	0.73	0.73
	186°C	1.9	0.11	2.66	2.69	2.41	2.17
	188°C	1.8	0.04	5.40	5.10	4.32	3.88

CONCLUSION

The position and the corresponding area of the double melting peaks of PA1010/TPU blends are varied with the blend composition, heating rate, thermal history, and crystallization temperature.

When PA1010/TPU blends are melted, usually two melting peaks appear. With increasing the TPU content, the area of the lower temperature peak remains almost constant, whereas the area of the high temperature peak decreases until it disappears, and the two peaks shift to a lower temperature and overlap each other. This phenomenon may be due to the interaction between the two polymers so as to inhibit the motion of the PA1010 molecular segments. At a higher heating rate only one melting peak is observed; when the heating rate is lower, two melting peaks appear as a consequence of reorganization of the original crystalline structure and melting at a higher temperature. With prolonging the annealing time, the area of the lower temperature peak increases, whereas the area of the high temperature peak decreases until it disappears. The lower temperature peak shifts to a higher temperature, whereas the higher temperature peak is not affected by annealing, and the melting range reduces. With increasing the crystallization temperature T_c, the higher temperature peak is not changed, whereas the lower peak shifts to a higher temperature and only one melting peak can be seen when T_c is enough high.

A small amount of TPU can promote the crystallization process of PA1010, but not change the nucleation and growing mechanisms.

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