polymer

Crystallization kinetics of miscible thermosetting polymer blends of novolac resin and poly(ethylene oxide)

Z. Zhong, Q. Guo*

Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, People's Republic of China

Abstract

Results of an investigation of isothermal crystallization and melting behavior of both uncured and hexamine-cured novolac/poly(ethylene oxide) (PEO) blends were reported. The crystallization behavior of PEO in blends is strongly influenced by factors such as composition, crystallization temperature, and cross-linking. The time dependence of the relative degree of crystallinity deviated from the Avrami equation at high conversion. The addition of non-crystalline component into PEO caused a depression in both the overall crystallization rate and the melting temperature. The influence of curing on the crystallization and melting behavior of PEO is rather complicated. In general, curing led to increase of the overall crystallization rate of the blends, and enhanced the nucleation rate of PEO. The crystallization mechanism of PEO changed after curing. Curing also resulted in relatively slow depression of equilibrium melting point, and reduced the stability of PEO crystals in the blends. Experimental data on the overall kinetic rate constant Kn were analyzed according to the nucleation and growth theory. The surface free energy of folding σ_e showed an increase with increase of novolac content for the uncured blends, whereas σ_e displayed a maximum at 90/10 PEO/novolac composition for the cured blends. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Crystallization kinetics; Thermosetting polymer blend; Poly(ethylene oxide)

1. Introduction

In past decades, crystallization kinetics in miscible blends of non-crystalline/crystalline polymers have been extensively studied [1–16]. In general, there shows a depression in growth kinetics of the crystalline component upon the addition of the non-crystalline component. Such a depression in growth kinetics has been attributed to several factors—(1) reduction in chain mobility due to an increase of the glass transition temperature (T_g) of the blends; (2) dilution of the crystallizable component at the growth front; (3) changes in free energy of nucleation due to specific interactions; and (4) competition between the advancing spherulitic front and diffusion of the non-crystalline component into interlamellar and interfibrillar regions. However, the study of the crystallization kinetics for thermosetting polymer blends where one component is crystalline and another is highly cross-linked has received relatively little attention [17]. In such a system, curing results in chain extension, branching, cross-linking and significant changes in chemical and physical properties of the non-crystalline component, which may change the chain mobility and the free energy of nucleation, and hence have dramatic influence on the crystallization of the crystallizable component. Therefore, crystallization in such a system becomes very complicated and has to be carefully studied.

Poly(ethylene oxide) (PEO) is a semi-crystallizable polymer and it has been found to be miscible with many other polymers [18–20]. Some authors [6,8,14,21] have also studied crystallization kinetics in miscible blends of PEO with other linear polymers. However, to our knowledge, there is no such a study on thermosetting system. Here, we select a thermosetting polymer blend system of PEO and cross-linkable novolac resin. The miscibility of PEO with other thermosetting resins such as epoxy resin [22–25], unsaturated polyester [26–29] and novolac resin [30,31] have been reported by other authors and us. In previous work [31], we established the miscibility of PEO with novolac resin and found that PEO is miscible not only with uncured novolac resin but also with highly hexamine-cured novolac resin over the entire composition range. In this work, we will further study the crystallization kinetics of the uncured novolac/PEO blends as well as the highly hexamine-cured blends. Special attention will be focused on the role of cross-linking in influencing crystallization of PEO in the blends.

* Corresponding author. Fax: +86-551-3631760.
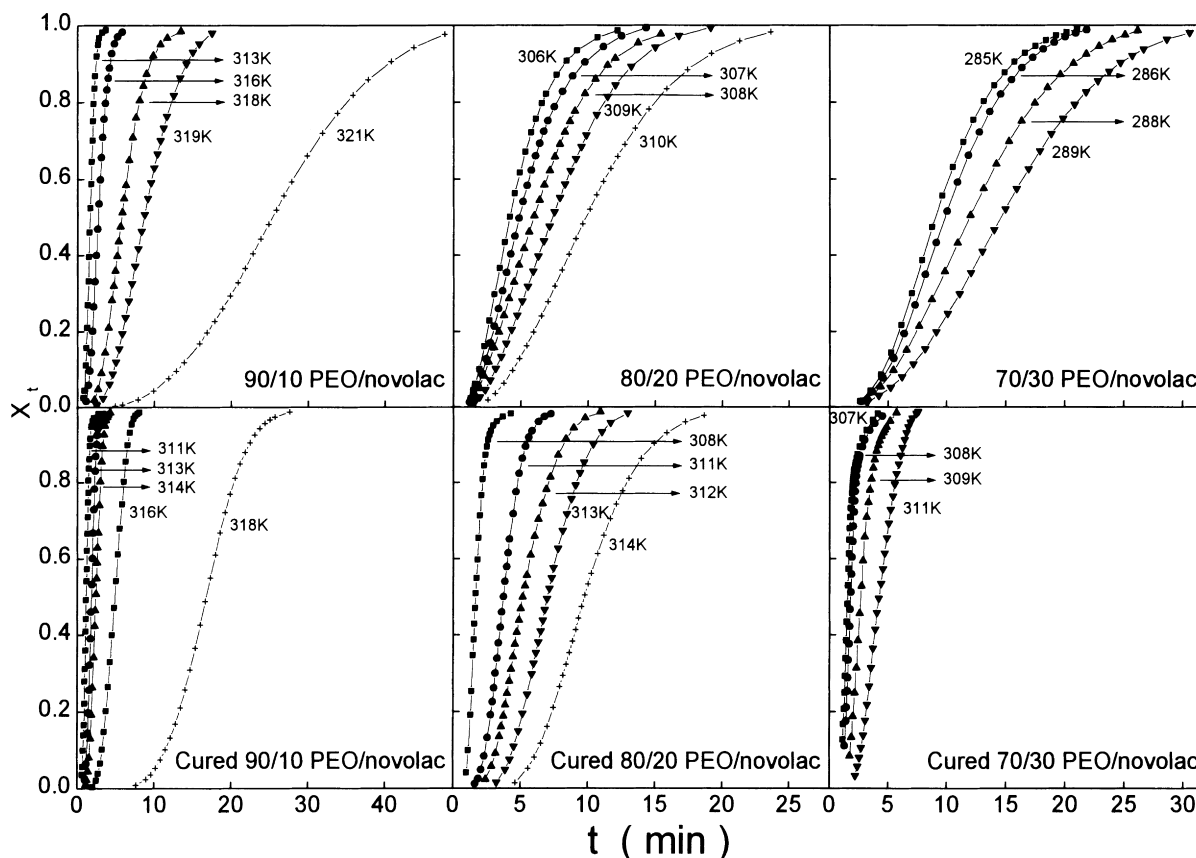 *E-mail address:* guolab@mail.ustc.edu.cn (Q. Guo)

Fig. 1. Development of relative degree of crystallinity with time for isothermal crystallization of the uncured PEO/novolac blends and the HMTA-cured PEO/ novolac blends.

2. Experimental

2.1. Materials and preparation of samples

The PEO had a quoted number-average molecular weight $M_n = 18\,000–20\,000$ was obtained from Shanghai Reagent Inc., Shanghai, China. The novolac resin with a number-average molecular weight $M_n = 565$ determined by vapor phase osmometry was obtained from Hefei Perfumery Factory, Hefei, China. The novolac was used without further purification. Hexamine (hexamethylene-tetramine, HMTA) was chemically pure and was used as cross-linking agent.

Films of uncured novolac/PEO blends were prepared by solution casting from *N,N*-dimethylformamide (DMF) at 50°C. To remove the residual solvent, the blends were further dried in a vacuum oven at 50°C for at least two weeks.

Novolac/PEO blends formed in DMF were cured with 15 wt.% HMTA relative to the content of novolac in the mixtures, i.e. with HMTA/novolac $= 0.15$. The curing was performed successively at 100°C for 2 h, at 160°C for 2 h and finally at 190°C for 2 h.

2.2. Differential scanning calorimetry

A Perkin–Elmer DSC-7 differential scanning calorimeter

(DSC) was employed to detect thermal transitions and to monitor the rate of heat flow from the sample during isothermal crystallization from the melt. The measurements were conducted under a nitrogen atmosphere and calibrated with an Indium standard. The samples were first heated to 100°C and maintained at this temperature for 5 min in order to remove prior thermal histories. They were then cooled to the appropriate crystallization temperature, T_c, at a rate of 80°C/min. The heat generated during the development of the crystalline phase was recorded up to a vanishing thermal effect and analyzed according to the usual procedure to obtain the relative degree of crystallinity, Xt:

$$Xt = \frac{\int_{t_0}^{t} \left(\frac{dH}{dt}\right) dt}{\int_{t_0}^{\infty} \left(\frac{dH}{dt}\right) dt} \tag{1}$$

where t_0 is the time at which the sample attains isothermal conditions, as indicated by a flat base line after the initial spike in the thermal curve.

To observe the melting behavior, the isothermally crystallized samples were reheated to 100°C at a rate of 20°C/min. The observed melting temperature, T'_m was taken as the maximum of the endothermic transition.
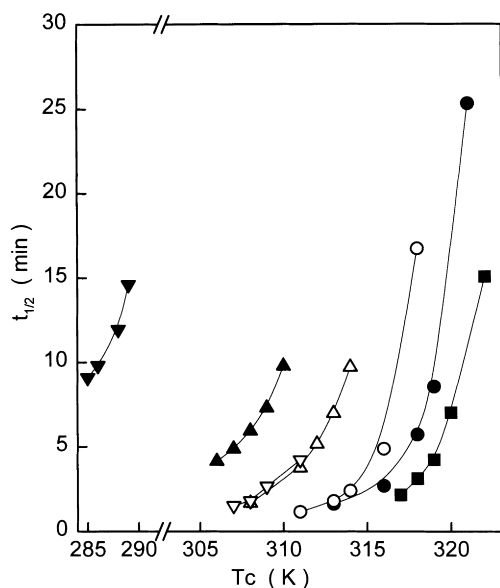
Fig. 2. Half time of crystallization $t_{1/2}$ as a function of crystallization temperature T_c. The pure PEO (■), the uncured 90/10 (●), 80/20 (▲), and 70/30 (▼) PEO/novolac blends, and the HMTA-cured 90/10 (○), 80/20 (△), and 70/30 (▽) PEO/novolac blends.

3. Results and discussion

3.1. Overall crystallization rate

Typical crystallization isotherms, obtained by plotting Xt against time t, are shown in Fig. 1 for various uncured and HMTA-cured PEO/novolac blends. It can be seen that the crystallization isotherms display characteristic sigmoidal. Furthermore, the isotherm curves shift to right along the time axis with increasing T_c, indicating progressively slower crystallization rate. This means that, in the present experimental conditions, supercooling is relatively lower and nucleation is dominant factor determining the overall crystallization rate. From these curves, the half time of crystallization $t_{1/2}$, defined as the time required for half of the final crystallinity to be develop, was obtained. The $t_{1/2}$ are plotted against T_c for pure PEO and for various blend compositions in Fig. 2. From Fig. 2, we found that the overall crystallization rate of PEO decreases after incorporating of the non-crystalline component. At constant T_c, the overall crystallization rate decreases with increasing concentration of the non-crystalline component, and it is more significant for the uncured blends.

It is believed that in miscible crystallizable/cross-linkable polymer blends, the cross-linking would greatly reduce the overall crystallization rate due to the improvement of T_g. However, form Fig. 2, it can be seen that the overall crystallization rate of the PEO/novolac blends increases
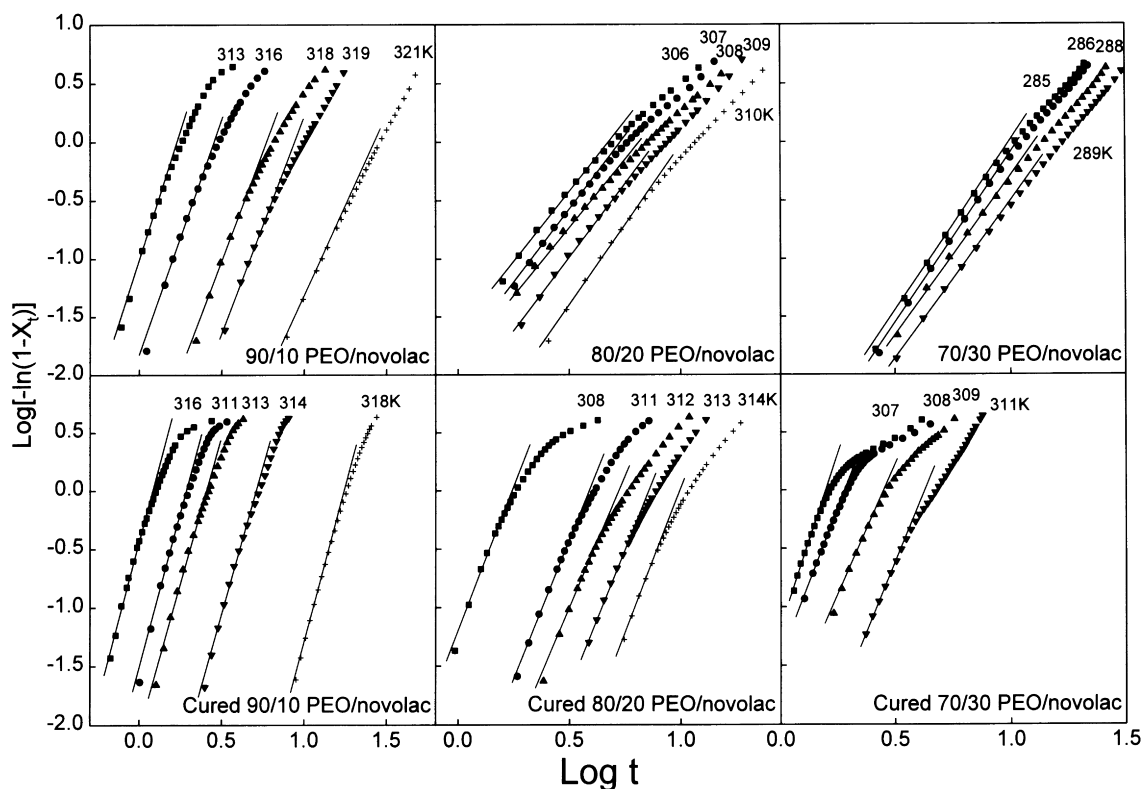

Fig. 3. Plots of $\log\{-\ln[1 - X_t)]\}$ vs. log t for isothermal crystallization of the uncured PEO/novolac blends and the HMTA-cured PEO/novolac blends.

Table 1
Values of the glass transition temperature T_g, the equilibrium melting temperature T_m^{eq}, the stability parameter ϕ, and the overall kinetic rate constant Kn and the Avrami index n at various crystallization temperatures T_c

	T_g (K)[a]	T_m^{eq} (K)	ϕ	T_c (K)	Kn (min^{-n})	n
Pure PEO	211	349.2	0.192	317	6.8×10^{-2}	3.0
				318	1.6×10^{-2}	3.4
				319	5.2×10^{-3}	3.4
				320	3.6×10^{-4}	3.9
				322	7.3×10^{-5}	3.4
90/10 PEO/novolac blend	261	346.2	0.191	313	9.0×10^{-2}	4.3
				316	1.4×10^{-2}	4.0
				318	1.4×10^{-3}	3.6
				319	4.7×10^{-4}	3.4
				321	6.7×10^{-5}	2.9
80/20 PEO/novolac blend	255	344.2	0.225	306	1.9×10^{-2}	2.5
				307	1.2×10^{-2}	2.6
				308	1.2×10^{-2}	2.3
				309	5.1×10^{-3}	2.5
				310	2.1×10^{-3}	2.6
70/30 PEO/novolac blend	234	334.3	0.120	285	1.5×10^{-3}	2.7
				286	1.2×10^{-3}	2.7
				288	1.5×10^{-3}	2.5
				289	8.0×10^{-4}	2.5
90/10 Cured PEO/novolac blend	237	348.2	0.281	311	3.8×10^{-1}	5.5
				313	2.6×10^{-2}	5.5
				314	7.1×10^{-3}	5.4
				316	1.8×10^{-4}	5.4
				318	1.5×10^{-7}	5.5
80/20 Cured PEO/novolac blend	238	345.2	0.280	308	5.8×10^{-2}	5.0
				311	1.2×10^{-3}	5.0
				312	3.5×10^{-4}	4.9
				313	5.2×10^{-5}	5.0
				314	5.2×10^{-6}	5.3
70/30 Cured PEO/novolac blend	237	341.3	0.309	307	7.6×10^{-2}	5.4
				308	3.8×10^{-2}	5.0
				309	1.2×10^{-2}	4.2
				311	1.1×10^{-3}	4.6

[a] These values were taken from previous works [31].

dramatically after curing with HMTA except for the 90/10 PEO/novolac blend. As we have mentioned that the nucleation process is the rate-controlling step under the conditions we used, therefore, the cross-linking of novolac enhances the nucleation rate of PEO.

The kinetics of the isothermal crystallization from the melt of all the uncured and cured blends was analyzed on the basis of Avrami equation [32–34]:

$$\log[-\ln(1 - Xt)] = \log Kn + n \log t, \qquad (2)$$

where Kn is the overall kinetic rate constant, and n is the Avrami index depend on the nucleation and growth mechanism of the crystals [35].

Plots of $\log[-\ln(1 - Xt)]$ vs. $\log t$ are shown in Fig. 3. It can be seen from Fig. 3 that the experimental data fit the Avrami equation only for the early part of the transformation. The deviation from the Avrami equation at high conversion ratio is more significant for the cured PEO/novolac blends. Similar phenomenon of deviation from the Avrami equation has been reported by Ong and Price in poly(ϵ-caprolactone)/poly(vinyl chloride) blends [3].

Wunderlich also showed that the Avrami equation is usually only valid at low conversion as larger as the impingement is not serious [36].

In order to obtain Kn and n, only the experimental data at low conversion are used. The values of Kn and n determined by the intercepts and slopes, respectively, of these straight lines shown in Fig. 3 are listed in Table 1.

In almost all cases, the values of n are non-integer, different from the theoretical prediction [32]. These non-integer values are generally accounted for by mixed growth and/or surface nucleation modes. Grenier and Prud'homme [37] found that experimental factors such as erroneous determination of the "zero" time and of the enthalpy of melting of the polymer at a given time can cause n to be non-integer. From Table 1, it can also be seen that the value of n for the cured PEO/novolac blends is larger than that of the corresponding uncured blends. The n value of the cured blends is around 5.0, which is essentially invariant with the blend composition. The relative large value of n for the cured blends is probably due to the branching mechanism of macromolecular crystals. From the discussion above, it is
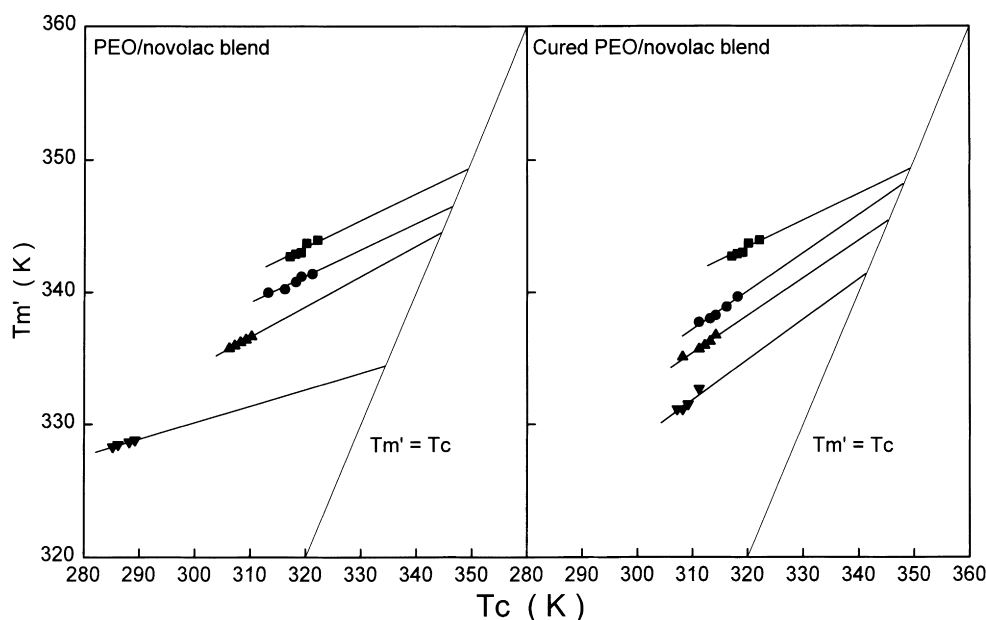
Fig. 4. Plots of the observed melting temperature T'_m vs. T_c for the uncured PEO/novolac blends and the HMTA-cured PEO/novolac blends. PEO/novolac: 100/0 (■), 90/10 (●), 80/20 (▲), and 70/30 (▼).

clear that the crystallization mechanism of PEO in the PEO/novolac blends changes greatly after the curing of novolac with HMTA.

3.2. Equilibrium melting points

The maximum of the re-melting DSC-curve was taken as the observed melting temperature T'_m, corresponding to different crystallization temperature T_c. Plots of T'_m against T_c for both the uncured and the cured PEO/novolac blends were shown in Fig. 4. It can be seen that T'_m increases linearly with T_c in the range of T_c examined. The experimental data can be fitted by [38–40]:

$$T'_m = \phi T_c + (1 - \phi)T_m^{eq}, \qquad (3)$$

where T_m^{eq} is the equilibrium melting point, $\phi = 1/\gamma$ is the stability parameter which depends on the crystal thickness, and γ is the ratio of the lamellar thickness ℓ to the lamellar thickness of the critical nucleus ℓ^* at T_c. In Eq. (3), ϕ assumes the values between 0 and 1, and $\phi = 0$ implies $T'_m = T_m^{eq}$ where $\phi = 1$ implies $T'_m = T_c$. Therefore, the crystals are most stable at $\phi = 0$ and are inherently unstable at $\phi = 1$.

As shown in Fig. 4, the values of T_m^{eq} can be obtained through extrapolating the least-squares fit line of the experimental data by Eq. (3) to intersect the line of $T'_m = T_c$. The parameter ϕ can be determined from the slope of the fit line. Both the values of T_m^{eq} and the values of ϕ for all the compositions studied are listed in Table 1. A depression in T_m^{eq} is evidently observed for all the uncured and cured blends, and the magnitude of the depression increases with increasing amorphous component. It can also be found that the T_m^{eq}

depresses more dramatically for the uncured blends than that for the cured blends. In Table 1, the stability parameter ϕ ranges from 0.12 to 0.31, suggesting that the crystals should be fairly stable. It is interesting to note that, for the uncured blends, blending with non-crystalline novolac decreases the ϕ value of PEO crystals except for the 80/20 PEO/novolac composition, while the HMTA-cured PEO/novolac blends have larger ϕ value than that of the pure PEO and those of the uncured blends. Therefore, the PEO crystals in the uncured blends are more stable than in pure PEO and cross-linking of novolac reduces the stability of PEO crystals in the blends.

3.3. Temperature dependence of Kn

The kinetic theory of polymer crystallization developed by Hoffman and co-workers [41–43] has been generally used to analyze experimental data concerning spherulite growth rate. In this theory, the dependence of the growth rate G on the crystallization temperature T_c and on the undercooling $\Delta T = T_m^{eq} - T_c$ is described by the following equation:

$$G = G_0 \exp\left(\frac{-\Delta F^*}{RT_c}\right) \exp\left(\frac{-\Delta \Phi^*}{k_B T_c}\right), \qquad (4)$$

where G_0 is a pre-exponential factor that is generally assumed to be constant or proportional to T_c; ΔF^* is the activation energy for the transport of crystallizing units across the liquid–solid interface; $\Delta \Phi^*$ is the free energy required to form a nucleus of critical size; R is the gas constant and k_B is the Boltzman constant. For a polymer-diluent
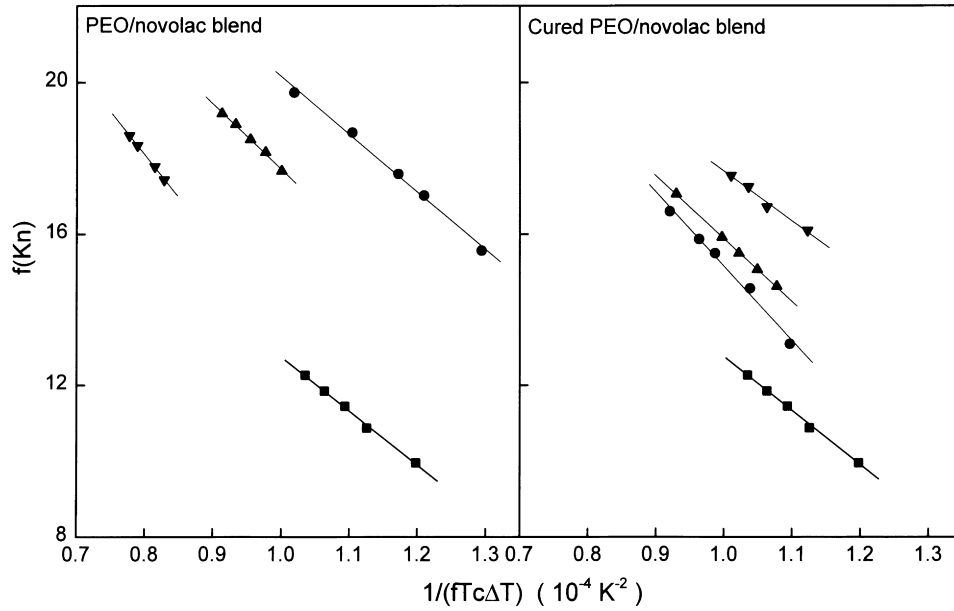
Fig. 5. Plots of the quantity f(Kn) vs. $1/(fT_c\Delta T)$ for the uncured PEO/novolac blends and the HMTA-cured PEO/novolac blends. PEO/novolac. PEO/novolac: 100/0 (■), 90/10 (●), 80/20 (▲), and 70/30 (▼).

system, the Eq. (4) was modified by Boon and Azcue [2]:

$$G = v_2 G_0 \exp\left(\frac{-\Delta F^*}{RT_c}\right)\exp\left(\frac{-\Delta \Phi^*}{k_B T_c}\right). \tag{5}$$

In Eq. (5), the pre-exponential factor is multiplied by the PEO volume fraction v_2, because the rate of nucleation is proportional to the concentration of crystallizable units.

Fig. 6. Plots of σ_e vs. the weight fraction of PEO for the uncured PEO/novolac blends (■) and the HMTA-cured PEO/novolac blends (○).

According to Boon and Azcue [2], $\Delta \Phi^*$ in Eq. (5) can be expressed as:

$$\frac{\Delta \Phi^*}{k_B T_c} = \frac{Kg}{fT_c\Delta T} + \frac{2\sigma T_m^{eq} \ln v_2}{b_0 \Delta H_f \Delta T}, \tag{6}$$

$$Kg = \frac{Zb_0 \sigma \sigma_e T_m^{eq}}{k_B \Delta H_f}, \tag{7}$$

$$f = \frac{2T_c}{T_m^{eq} + T_c}, \tag{8}$$

where Kg is the nucleation factor; f is the correction factor for the heat of fusion; σ and σ_e are the interfacial free energies for unit area parallel and perpendicular respectively to the molecular chain axis; b_0 is the distance between two adjacent fold planes; ΔH_f is the enthalpy of fusion per unit volume of the crystalline component; and Z is a coefficient that depends on the growth regime: $Z = 4$ in Regimes I and III, and $Z = 2$ in Regime II [44–46].

The transport term ΔF^* in Eq. (5) may be calculated by means of the Williams, Landel and Ferry relation [47]:

$$\Delta F^* = \frac{C_1 T_c}{C_2 + T_c - T_g}, \tag{9}$$

where C_1 and C_2 are constants (generally assumed as 4120 cal/mol and 51.6 K, respectively) and T_g is the glass transition temperature whose value are listed in Table 1.

If we assume [48,49] that $\sigma = 0.1b_0\Delta H_f$, taking into account relations (5), (6) and (9), the following expression
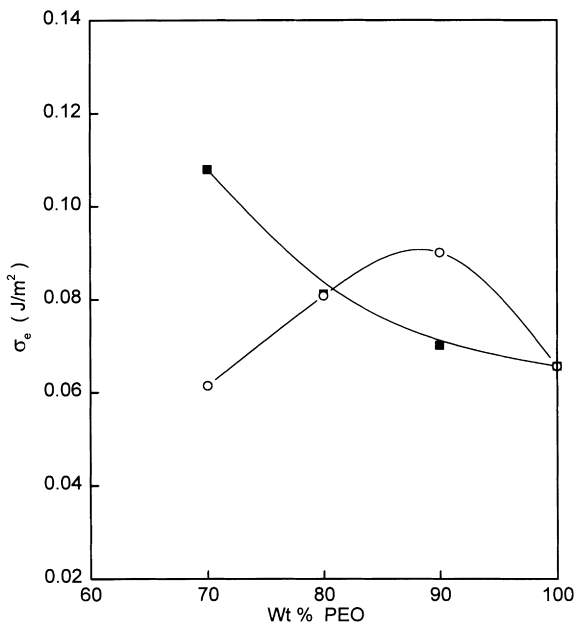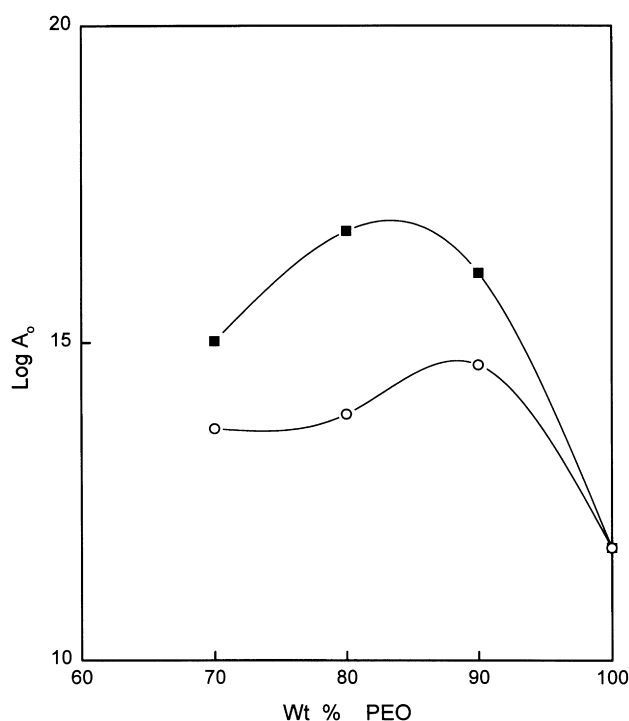
Fig. 7. Plots of A_0 vs. the weight fraction of PEO for the uncured PEO/novolac blends (■) and the HMTA-cured PEO/novolac blends (○).

may be written:

$$f(G) = \ln G - \ln v_2 + \frac{C_1}{R(C_2 + T_c - T_g)} - \frac{0.2T_m^{eq} \ln v_2}{\Delta T}$$

$$= \ln G_0 - \frac{Kg}{fT_c\Delta T}.$$

(10)

For the overall crystallization rate, we used $G = CKn^{1/n}$ where C is a constant. Therefore, we have:

$$f(Kn) = \frac{1}{n}\ln Kn - \ln v_2 + \frac{C_1}{R(C_2 + T_c - T_g)}$$

$$- \frac{0.2T_m^{eq} \ln v_2}{\Delta T}$$

$$= \ln A_0 - \frac{Kg}{fT_c\Delta T}.$$

(11)

The plots of $f(Kn)$ against $1/(fT_c\Delta T)$ for both the uncured and the cured PEO/novolac blends are shown in Fig. 5. The experimental data fit the straight lines quite well. From the slopes and the intercepts of these lines, values of Kg and A_0 can be obtained. By using Eq. (7), the Kg values can further give the value of σ_e for all the compositions. In these calculation, we have employed the following: $\sigma = 0.1b_0\Delta H_f$, $Z = 4$, $b_0 = 4.65 \times 10^{-8}$ cm, $R = 1.987$ cal/(mol K) and $k_B = 1.380 \times 10^{-23}$ J/K.

In Figs. 6 and 7, the values of σ_e and A_0 are plotted against composition, respectively. It was be found that the

value of σ_e is 6.56×10^{-2} J/m^2 for the pure PEO, and this value is comparable with that obtained by Martuscelli et al. [14] $(6.0 \times 10^{-2}$ J/m$^2)$ and by Cimmino et al. [6] $(7.5 \times 10^{-2}$ J/m$^2)$. As shown in Fig. 6, σ_e increases with increasing content of the non-crystalline component for the uncured blends. These findings are probably related to the fact that during crystallization, non-crystalline molecules may easily form entanglements with PEO molecules favoring the formation of large loops on the surface of PEO lamellar crystals. This process will probably cause the increase of both terms that contribute to σ_e, namely the surface enthalpy and entropy of folding ($\sigma_e = H_e - TS_e$). The observation that σ_e increases with increasing novolac content should be ascribed to the fact that the variation of the enthalpy term overwhelms that of the entropy one. However, the composition dependence of σ_e for the HMTA-cured PEO/novolac blends is complicated, and exhibit a maximum at the vicinity of 90/10 PEO/novolac, suggesting that the entropy term is dominant when PEO content is less than 90% in the cured blends. The pre-exponential factor A_0 also depends on the composition, showing a parabolic curvature for both the uncured and the cured PEO/novolac blends (Fig. 7). The value of A_0 of the cured blend is lower than that of the corresponding uncured blend, however, the value of both the uncured and the cured PEO/novolac blends is larger than that of the pure PEO.

4. Conclusions

From the results shown above, it can be found that the crystallization behavior of PEO from the melt is strongly influenced by the composition, the crystallization temperature, and the curing. The dependence of the relative degree of crystallinity on time deviated from the Avrami equation at high conversion. The addition of non-crystallizable component into PEO caused a depression in both the overall crystallization rate and the melting temperature. The influence of curing on the crystallization behavior of PEO is rather complicated. In general, curing resulted in increase of the overall crystallization rate in the blends, and relative slower depression of equilibrium melting point. The cross-linking of novolac with HMTA was also found to change the nucleation mechanism of PEO and enhanced the nucleation rate. The crystal of PEO in the uncured blends is stable than that in the pure PEO, while the crystal of PEO in the cured blends is unstable than that in the pure PEO. The surface free energy of folding σ_e showed an increase with increasing of novolac content for the uncured blends, whereas σ_e displayed a maximum at the 90/10 PEO/novolac composition for the cured blends. The curing reduced the pre-exponential factor A_0.

References

[1] Keith HD, Padden FJ. J Appl Phys 1964;35:1270–1286.

[2] Boon J, Azcue JM. J Polym Sci: Part A-2 1968;6:885.

[3] Ong CJ, Price FP. J Polym Sci: Polym Symp 1978;63:59.

[4] Wang TT, Nishi T. Macromolecules 1977;10:421.

[5] Yeh GS, Lambert SL. J Polym Sci: Part A-2 1972;10:1183.

[6] Cimmino S, Martuscelli E, Silvestre C, Canetti M, Delalla C, Seves A. J Polym Sci, Polym Phys Ed 1989;27:1781.

[7] Amelino L, Martuscelli E, Sellitti C, Silvestre C. Polymer 1990;31:1051.

[8] Alfonso GC, Russell TP. Macromolecules 1986;19:1143.

[9] Martuscelli E, Silvestre C. Makromol Chem 1989;190:2615.

[10] Runt J, Miley DM, Zhang X, Gallagher KP, McFeaters K, Fishburn J. Macromolecules 1992;25:1929.

[11] Martuscelli E, Silvestre C, Gismondi C. Makromol Chem 1985;186:2161.

[12] Martuscelli E, Pracella M, Yue WP. Polymer 1984;25:1097.

[13] Bonfatti AM, Canetti M, Sadocco P, Seves A, Martuscelli E. Polymer 1993;34:990.

[14] Dubini Paglia E, Beltrame PL, Canetti M, Seves A, Marcandalli B, Martuscelli E. Polymer 1993;34:996.

[15] De Juana R, Cortazat M. Macromolecules 1993;26:1170.

[16] Pearce R, Brown GR, Marchessault RH. Polymer 1994;35:3984.

[17] Guo Q. In: Shonaike GO, Simon G, editors. Polymer blends and alloys, New York: Marcel Dekker, 1999 Chap. 6.

[18] Olabisi O, Robeson LM, Show MT. Polymer-Polymer Miscibility, New York: Academic Press, 1979.

[19] Ultracki LA. Polymer alloys and blends, Munich: Hanser Publishers, 1989.

[20] Coleman MM, Graf JF, Painter PC. Specific interaction and miscibility of polymer blends, Lancaster, PA: Technomic Publishers, 1991.

[21] Katime IA, Anasagasti MS, Peleteiro MC, Valenciano R. Eur Polym J 1987;23:907.

[22] Guo Q, Peng X, Wang Z. Polym Bull 1989;21:593.

[23] Guo Q, Peng X, Wang Z. Polymer 1991;32:53.

[24] Luo X, Zheng S, Zhang N, Ma D. Polymer 1994;35:2619.

[25] Zheng S, Zhang N, Luo X, Ma D. Polymer 1995;36:3609.

[26] Mucha M. Colloid Polym Sci 1994;272:1090.

[27] Zheng H, Zheng S, Guo Q. J Polym Sci, Polym Chem Edn 1997;35:3161.

[28] Zheng H, Zheng S, Guo Q. J Polym Sci, Polym Chem Edn 1997;35:3169.

[29] Guo Q, Zheng H. Polymer 1999;40:63.

[30] Zhong Z, Guo Q. J Polym Sci, Polym Chem Edn 1998;35:401.

[31] Zhong Z, Guo Q. Polymer 1998;39:517.

[32] Avrami M. J Chem Phys 1939;7:1103.

[33] Avrami M. J Chem Phys 1940;8:212.

[34] Avrami M. J Chem Phys 1941;9:177.

[35] Schultz JM. Polymeric material science, New York: Prentice Hall, 1981.

[36] Wunderlich B. Macromolecular physics, 2. New York: Academic Press, 1976. p. 146.

[37] Grenier D, Prud'homme ER. J Polym Sci, Polym Phys Ed 1980;18:1655.

[38] Hoffman JD, Weeks JJ. J Chem Phys 1962;37:1723.

[39] Hoffman JD, Weeks JJ. J Res Natl Bur Stand, Section A 1962;66:13.

[40] Nishi T, Wang TT. Macromolecules 1975;8:909.

[41] Hoffman JD. Soc Plast Engng Trans 1960;4:315.

[42] Hoffman JD, Frolen LJ, Ross GS, Lauritzen JI. J Res Natl Stand, US 1975;79A:671.

[43] Hoffman JD. Polymer 1983;24:3.

[44] Clark EJ, Hoffman JD. Macromolecules 1984;17:878.

[45] Monasse B, Haudin JM. Collid Polym Sci 1985;263:822.

[46] James JJ, Stephen ZDC, Paul AG. Macromolecules 1991;24:2253.

[47] Williams ML, Landel RF, Ferry JD. J Am Chem Soc 1955;77:3701.

[48] Hoffman JD. SPE Trans 1964;4:315.

[49] Hoffman JD, Davis GT, Lauritzen JI. In: Hannay NB, editor. Treatise on solid state chemistry, III. New York: Plenum Press, 1976 Chap. 7.