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Crystallization kinetics of poly(ε-caprolactone) in miscible thermosetting polymer blends of epoxy resin and poly(ε-caprolactone)

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Abstract

The results of a study on the isothermal crystallization kinetics and melting behavior of poly(ε-caprolactone) (PCL) in miscible thermosetting polymer blends of epoxy resin (ER) and PCL are reported. Blends of PCL and bisphenol-A-type ER were cured with 4,4′-methylenebis(3-chloro-2,6-diethylaniline) (MCDEA) and compared with blends of PCL with uncured bisphenol-A-type ER, i.e. diglycidylether of bisphenol-A (DGEBA). The crystallization behavior of PCL in blends is strongly influenced by factors such as composition, crystallization temperature and curing. The time dependence of the relative degree of crystallinity at high conversion deviates from the Avrami equation. The addition of a non-crystallizable component into PCL causes a depression of both the overall crystallization rate and the melting temperature. The influence of curing on the crystallization and melting behavior of PCL is rather complicated. In general, curing leads to an increase of the overall crystallization rate of the blends and enhances the nucleation rate of PCL. Experimental data on the overall kinetic rate constant K_n are analyzed according to the nucleation and growth theory. For the uncured blends, the surface free energy of folding, σ_e, increases with increasing DGEBA content, whereas for the cured blends, σ_e remains almost unchanged with the variation of composition.

Keywords: Crystallization kinetics; Thermosetting polymer blends; Poly(ε-caprolactone)

1. Introduction

Crystallization kinetics in miscible blends of non-crystalline/crystalline polymers have been extensively studied [1–14]. Generally, a depression of the growth kinetics of the crystallizable component is observed upon addition of the non-crystallizable component. The depression in growth kinetics has been attributed to a reduction of chain mobility due to an increase of the glass transition temperature (T_g) of the blends, as well as to dilution of the crystallizable component at the growth front, to changes in free energy of nucleation as a result of specific interactions, and to competition between the advancing spherulitic front and diffusion of the non-crystallizable component into interlamellar and interfibrillar regions. However, the study of the crystallization kinetics in miscible polymer blends where one of the components is crystallizable and the second is highly crosslinkable has received relatively little attention [15]. In such system, curing results in chain extension, branching, crosslinking and significant changes in chemical and physical properties of the non-crystallizable component, which may influence the chain mobility and the free energy of nucleation, and hence may have dramatic influence on the crystallization of the crystallizable component. Indeed, we have found that the crystallization kinetics of crystallizable component in thermosetting polymer blends [15–18] changed significantly after curing.

Poly(ε-caprolactone) (PCL) is a semi-crystallizable polymer and it has been found to be miscible with many other polymers [19–25]. Crystallization kinetics of PCL in miscible blends with other linear polymers has been well studied [5–7]. However, to our knowledge, there is not a detailed study on thermosetting system. Accordingly, we selected the system of PCL with a thermosetting polymer, i.e. epoxy resin (ER).

In a previous paper [26], we reported on the miscibility of PCL with an ER, showing that PCL is miscible not only with uncured bisphenol-A-type ER, i.e. diglycidyl ether of bisphenol-A (DGEBA), but also with 4,4′-methylenebis(3-chloro-2,6-diethylaniline) (MCDEA)-cured ER over the entire composition range. After curing, no phase-separated structures were detected in the molten state and in the glassy

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amorphous state of the blends. However, crystallization in such a system is very complicated and needs to be carefully studied. In this paper, we report the results of our study on isothermal crystallization kinetics of the uncured DGEBA/PCL blends as well as of the MCDEA-cured ER/PCL blends. Special attention will be focused on the influence of curing on the crystallization of PCL in the blends.

2. Experimental

2.1. Materials and preparation of samples

The PCL was obtained from Janssen Chemica, Belgium; it had a weight-average molecular weight M_w of 94,000 with $M_w/M_n = 2.79$ when measured by GPC in tetrahydrofuran at room temperature using polystyrene standards. The uncured ER is DGEBA (Epikote 828EL, Shell, Netherlands) and has an epoxide equivalent weight of 190. Prior to use, it was degassed under vacuum at 120°C for at least 24 h to remove any volatile impurities. MCDEA (Aldrich, USA) was used as curing agent. Uncured DGEBA/PCL blends were prepared by mixing DGEBA and PCL at 90°C for a sufficiently long time and then slowly cooled and kept at room temperature.

To prepare the MCDEA-cured ER/PCL blends, PCL was first dissolved in DGEBA with continuous stirring at 90°C. Then MCDEA was added to the mixture as the curing agent with continuous stirring until a homogeneous ternary mixture was obtained. MCDEA was used in stoichiometric epoxide/amine ratios. The samples of ternary mixture were cured successively at 130°C for 2 h, 150°C for 2 h and 170°C for 2 h.

2.2. Differential scanning calorimetry (DSC)

The calorimetric measurements were made on a Perkin–Elmer DSC-7 differential scanning calorimeter in a dry nitrogen atmosphere. Indium and tin standards were used for calibration for low and high temperature regions, respectively. The sample weight used in the DSC pan was about 8 mg. 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 100°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 of evaluating the relative degree of crystallinity, X_t:

$$X_t = \frac{\int_{t_0}^{t} (dH/dt)\, dt}{\int_{t_0}^{\infty} (dH/dt)\, dt} \quad (1)$$

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

To study the melting behavior, the isothermally crystallized samples were subsequently reheated to 80°C at a rate of 20°C/min. The melting temperature, T'_m, was attributed to the maximum of the endothermic peak.

3. Results and discussion

3.1. Overall crystallization rate

Typical crystallization isotherms, obtained by plotting X_t against time t, are reported in Fig. 1 for various uncured DGEBA/PCL and MCDEA-cured ER/PCL blends. It can be seen that the crystallization isotherms display characteristic sigmoidal. Furthermore, the slope of all isotherms decreases with increasing T_c, indicating progressively slower crystallization rates. This means that, in the used experimental conditions, nucleation is the dominant factor, determining the overall crystallization rate. The half-time of crystallization, $t_{1/2}$, defined as the time required for the development of half of the final crystallinity was evaluated from these curves. In Fig. 2, the obtained $t_{1/2}$ values are plotted against T_c for pure PCL as well as for both uncured and cured blends. From Fig. 2, the following observations result. First, incorporation of non-crystallizable component into PCL depresses the overall crystallization rate of PCL. Second, the overall crystallization rate decreases substantially with increasing concentration of the non-crystallizable component for both the uncured and the cured blends. Finally, the overall crystallization rate of the uncured DGEBA/PCL blends is significantly lower than that of the corresponding cured blends.

It is well known that the overall crystallization rate is determined by both the nucleation rate and the growth rate. Under the conditions we used, the nucleation process is the rate-controlling step. On other hand, it is believed that in miscible crystallizable thermosetting polymer blends, the curing would greatly reduce the overall crystallization rate due to the enhancement of glass transition temperature (T_g). Therefore, the results presented above suggest that the curing of ER promotes the nucleation of PCL, and hence enhances the nucleation rate of PCL. Similarly, it has been observed that the crosslinking of novolac resin enhanced the nucleation rate of poly(ethylene oxide) (PEO) in novolac/PEO blends [18].

The kinetics of the isothermal crystallization from the melt of both the uncured and cured blends was analyzed on the basis of the Avrami equation [27]:

$$\log[-\ln(1 - X_t)] = \log K_n + n \log t \quad (2)$$

where K_n is the overall kinetic rate constant and n the Avrami index which depends on the nucleation and growth mechanism of the crystals [28].

Typical plots of $\log[-\ln(1 - X_t)]$ vs. $\log t$ for various uncured and cured blends are shown in Fig. 3. It can be seen from Fig. 3 that the experimental data are fitted by

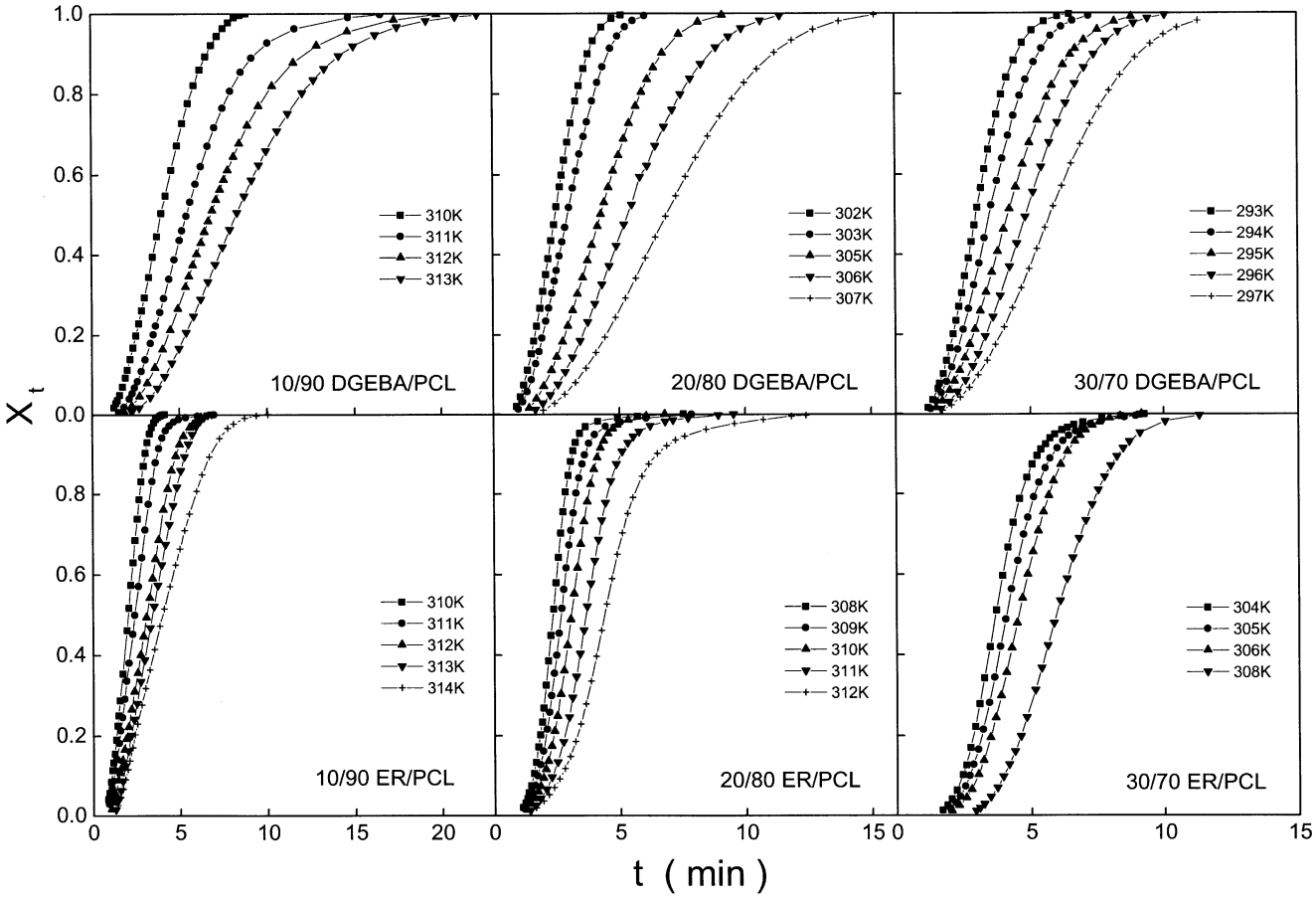

Fig. 1. Development of the relative degree of crystallinity with time for isothermal crystallization of uncured DGEBA/PCL and MCDEA-cured ER/PCL blends. The figures indicate the respective crystallization temperatures in K.

the Avrami equation only for the early part of transformation. However, the time dependence of the relative degree of crystallinity at high conversion deviates from the Avrami equation. A similar deviation from the Avrami equation has been reported by Ong and Price [5] for PCL/poly(vinyl chloride) blends. Wunderlich also showed that the Avrami equation is usually only valid at low conversion [29].

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

In almost all cases, the values of n are nonintegral, in contrast with the theoretical prediction. Nonintegral values are generally accounted for by mixed growth and/or surface nucleation and two-stage crystallization. Grenier and Prud'homme [30] have shown that experimental factors such as an erroneous determination of the 'zero' time or of the melting enthalpy of the polymer at a given time can cause n to be nonintegral.

It is noted that the values of n for the pure PCL are in the neighborhood of 6. As Morgan [31] illustrated, the relative larger value of n is expected for branching crystals. Macromolecular crystals are known frequently to have an inherent

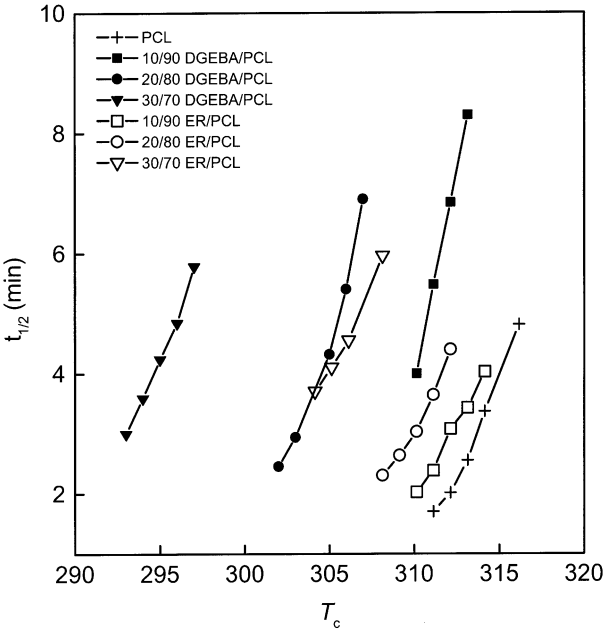

Fig. 2. Half-time of crystallization $t_{1/2}$ as a function of crystallization temperature T_c.

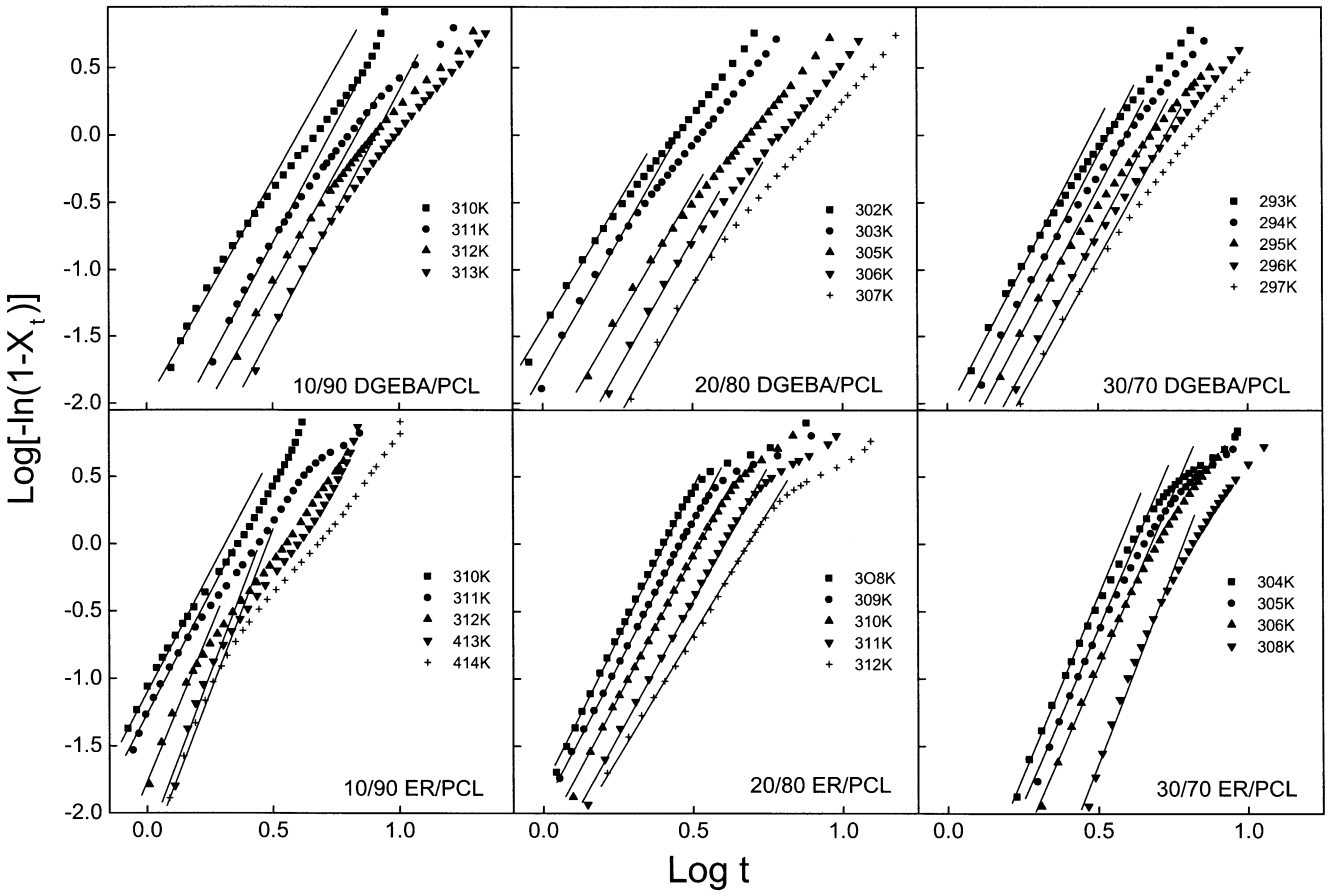

Fig. 3. Plots of $\log[-\ln(1 - X_t)]$ vs. $\log t$ for isothermal crystallization of uncured DGEBA/PCL and MCDEA-cured ER/PCL blends. The figures indicate the respective crystallization temperatures in K.

or a supercooling caused branching mechanism. From Table 1, it can be further seen that curing of the blends resulted in an increase of the *n*-value, suggesting that the nucleation mechanism has changed after curing. For the uncured DGEBA/PCL blends, the exponent of temperature, *n*, is between 3.3 and 4.2. For the MCDEA-cured ER/PCL blends, the *n* is between 4.0 and 5.7. 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 clear that the crystallization mechanism of PCL in the blends changes greatly after the curing.

3.2. Melting behavior and equilibrium melting points

The maximum of the re-melting DSC curve was considered to be the observed melting temperature, T'_m, corresponding to different crystallization temperatures, T_c. Table 1 also presents the observed melting temperature, T'_m, for the pure PCL as well as for both the uncured DGEBA/PCL blends and the MCDEA-cured ER/PCL blends. It is interesting to note that the 30/70 DGEBA/PCL blend show a double-melting temperatures at all the isothermal crystallization temperatures investigated. Fig. 4 shows the DSC thermograms of the 30/70 DGEBA/PCL blend after the isothermal crystallization at 293 K. It can be seen that there are two melting peaks at all the heating rates (Curves A–D). With increase of heating rates from 2.5 to 15°C/min, the higher melting temperature almost remains unchanged, whereas the lower melting temperature increases substantially. The magnitude of the higher temperature endotherm decreases relative to lower temperature endotherm with increasing heating rate. Fig. 4 also shows the DSC thermogram of the 30/70 DGEBA/PCL blend quenched from 85 to 20°C and reheating at 20°C/min (Curve E). No endotherm was observed, indicating that no crystallization happened during the quenching process. There are many papers concerned with the double-melting peaks of PCL and its polymer blends [23–25]. In an investigation by Defieuw et al. [24] on PCL/phenoxy blends, the isothermal crystallization process was interrupted after different time intervals and the DSC melting trace was immediately recorded. The highest melting endotherm reaches a constant area and position on the temperature scale after short time isothermal crystallization time (primary crystallization), whereas the lower melting peak only appears after much longer crystallization time (secondary crystallization). A similar phenomenon was

Table 1
Values of the overall kinetic rate constant K_n, the Avrami index n and the melting temperature T'_m at various crystallization temperature, T_c

	T_c (K)	T'_m (K)	K_n (min^{-n})	n
Pure PCL	311	333.2	5.49×10^{-2}	6.3
	312	333.2	2.05×10^{-2}	6.1
	313	333.9	5.72×10^{-3}	6.2
	314	333.9	2.76×10^{-3}	6.0
	316	334.6	7.05×10^{-4}	6.0
10/90 DGEBA/PCL	310	331.3	9.79×10^{-3}	3.3
	311	331.5	3.21×10^{-3}	3.5
	312	332.1	1.63×10^{-3}	3.3
	313	332.4	6.51×10^{-4}	3.5
20/80 DGEBA/PCL	302	327.2	3.40×10^{-2}	3.9
	303	327.6	1.56×10^{-2}	4.2
	305	328.2	4.79×10^{-3}	3.8
	306	328.5	1.77×10^{-3}	4.0
	307	329.1	8.57×10^{-4}	3.9
30/70 DGEBA/PCL	293	318.2/322.2	9.23×10^{-3}	4.2
	294	318.7/322.1	5.37×10^{-3}	4.2
	295	319.6/322.1	3.43×10^{-3}	4.0
	296	319.8/322.1	1.76×10^{-3}	4.0
	297	320.2/322.1	1.33×10^{-3}	3.8
10/90 ER/PCL	310	333.1	8.38×10^{-2}	4.2
	311	333.3	5.25×10^{-2}	4.3
	312	333.6	1.72×10^{-2}	4.4
	313	333.8	5.26×10^{-3}	5.3
	314	334.2	3.94×10^{-3}	5.2
20/80 ER/PCL	308	333.6	1.54×10^{-2}	4.5
	309	333.7	1.11×10^{-2}	4.3
	310	333.9	6.56×10^{-3}	4.2
	311	334.1	3.75×10^{-3}	4.1
	312	334.2	3.31×10^{-3}	4.0
30/70 ER/PCL	304	331.5	9.52×10^{-4}	5.3
	305	331.6	6.40×10^{-4}	5.1
	306	331.7	3.30×10^{-4}	5.1
	308	332.0	3.30×10^{-5}	5.7

also observed by Rim and Runt [25] in miscible PCL/poly-(styrene-*co*-acrylonitrile) blends. According to the mechanism proposed by Rim and Runt [25], the lower temperature endotherm was considered to be due to the melting of original crystals, whereas the higher temperature endotherm was due to the melting of the recrystallized materials. Therefore, in calculation of equilibrium melting point of the 30/70 DGEBA/PCL blend, the lower melting temperature corresponding to the melting of original crystals was used.

Plots of T'_m vs. T_c are shown in Fig. 5. It can be seen that, in the range of T_c examined, T'_m increases linearly with T_c. The experimental data can be fitted by the Hoffman–Weeks equation [32,33]:

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

where T_m^{eq} is the equilibrium melting point, $\phi = 1/\gamma$ the stability parameter which depends on the crystal thickness, whereas γ is the ratio of the lamellar thickness $\mathcal{L}$ to the lamellar thickness of the critical nucleus $\mathcal{L}^*$ at T_c. In Eq.

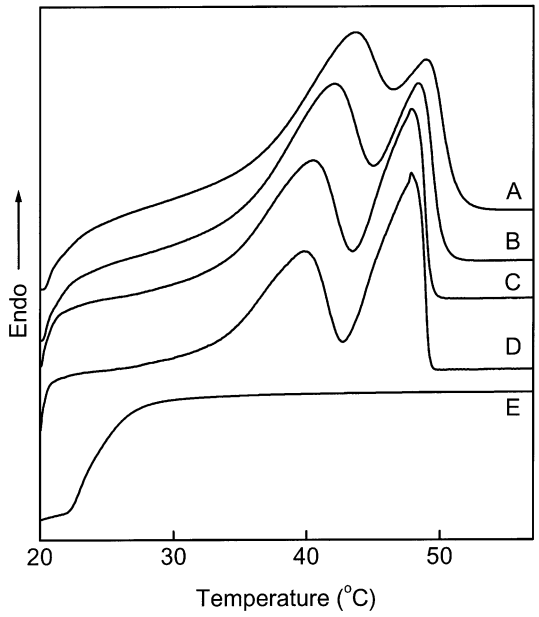

Fig. 4. DSC heating thermograms of 30/70 DGEBA/PCL blend after isothermally crystallized at 293 K. Heating rate: (A) 15°C/min; (B) 10°C/min; (C) 5°C/min; (D) 2.5°C/min; (E) for the sample quenched from 85°C and reheating at 20°C/min.

(3), ϕ may assume the values between 0 and 1. $\phi = 0$ implies $T'_m = T_m^0$, whereas $\phi = 1$ implies $T'_m = T_c$. Consequently, the crystals are most stable for $\phi = 0$ and are inherently unstable for $\phi = 1$.

As shown in Fig. 5, the values of T_m^{eq} can be evaluated by extrapolating the least-squares fit lines of the experimental data according to Eq. (3) to intersect the line of $T'_m = T_c$. The ϕ parameters can be determined from the slope of these fit lines. Both, the values of T_m^{eq} and of ϕ for all studied compositions are listed in Table 2. A depression of T_m^{eq} is evidently observed for both the uncured and the cured blends, and the magnitude of the depression increases with increasing amorphous component. The T_m depression is a common phenomenon for the miscible blends containing one crystallizable component [34]. It can also be seen that the T_m^{eq} is depressed more dramatically for the cured blends than that for the uncured ones. An increased T_m^{eq} depression in the cured blends implies that the interaction parameter for the cured blends is even more negative than that for the uncured blends. This can be accounted for by the existence of hydrogen bonding between the hydroxyl groups of MCDEA-cured ER and the carbonyl groups of PCL as revealed by FTIR studies in our previous work [26]. The curing reaction between epoxy groups and amine groups results in the formation of hydroxyl groups in the MCDEA-cured ER molecules which can form a large number of hydrogen bonds with the carbonyl groups of PCL.

In Table 2, the values of the stability parameter ϕ range from 0.123 to 0.459, suggesting that the crystals should be fairly stable. It is interesting to notice from Table 2 that the

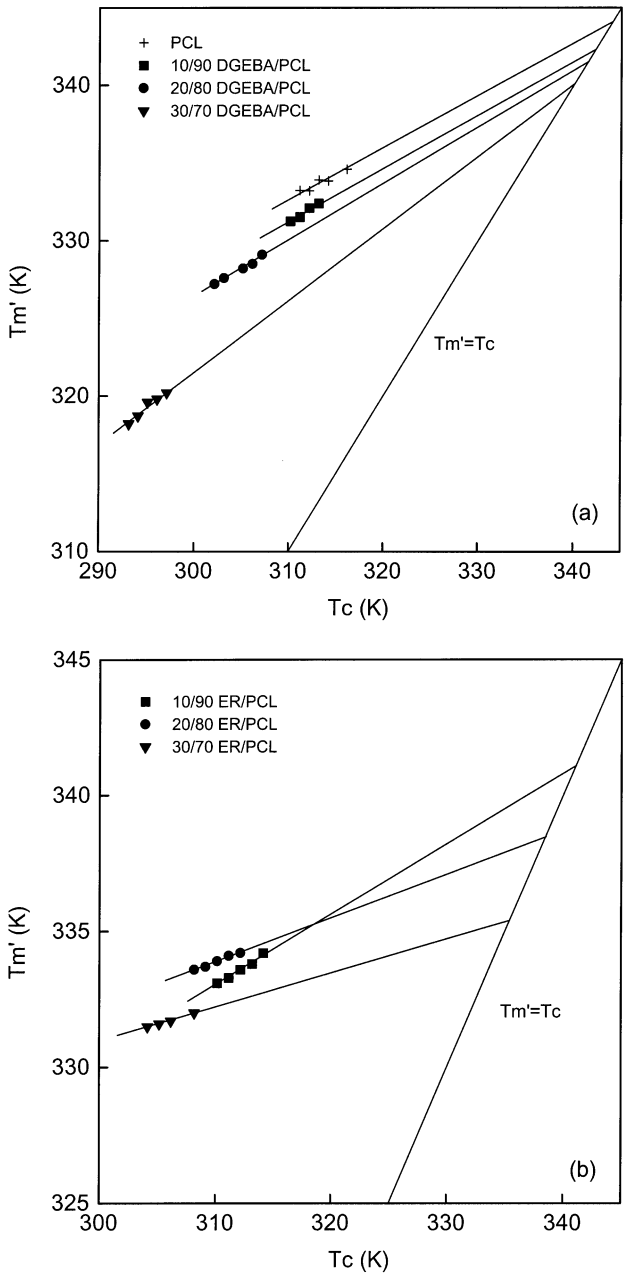

Fig. 5. Plots of the observed melting temperature T'_m vs. T_c for (a) uncured DGEBA/PCL blends and (b) MCDEA-cured ER/PCL blends.

ϕ values of the uncured blends are all larger than that of the pure PCL suggesting that the stability of the crystals in the uncured blends is lower than in the pure PCL. However, the ϕ values of the cured blends are all smaller than that of the pure PCL, which can be considered to be due to the relatively smaller $\mathcal{L}^*$ value of the uncured blends.

3.3. Temperature dependence of K_n

The kinetic theory of polymer crystallization developed by Hoffman et al. [35–37] has been generally used to analyze experimental crystallization data concerning the spherulite growth rate. According to this theory, the dependence of the growth rate G on the crystallization temperature, T_c, and the undercooling, $\Delta T = T_m^{eq} - T_c$, is described by the following equation:

$$G = v_2 G_0 \exp\left(\frac{-\Delta F^*}{RT_c}\right)\exp\left(\frac{-\Delta \Phi^*}{k_B T_c}\right) \quad (4)$$

where G_0 is a pre-exponential factor, generally assumed to be constant or proportional to T_c, ΔF^* the activation energy for the transport of the crystallizing units across the liquid–solid interface, $\Delta \Phi^*$ the free energy required to form a nucleus of critical size, R the gas constant and k_B the Boltzmann constant, whereas v_2 the PCL volume fraction.

According to Boon and Azcue [2], $\Delta \Phi^*$ in Eq. (4) can be expressed as

$$\frac{\Delta \Phi^*}{k_B T_c} = \frac{K_g}{f T_c \Delta T} + \frac{2\sigma T_m^{eq} \ln v_2}{b_0 \Delta H_f \Delta T} \quad (5)$$

$$K_g = \frac{Z b_0 \sigma \sigma_e T_m^{eq}}{k_B \Delta H_f} \quad (6)$$

$$f = \frac{2T_c}{T_m^{eq} + T_c} \quad (7)$$

where K_g is the nucleation factor, f the correction factor for the heat of fusion, σ and σ_e the interfacial free energies of the unit area parallel and perpendicular, respectively, to the molecular chain axis, b_0 the distance between two adjacent fold planes, $\Delta H_f = 136$ J/g [38] the enthalpy of fusion per unit volume of the crystalline component and Z a coefficient that depends on the growth regime: $Z = 4$ in Regimes I and III, and $Z = 2$ in Regime II [39].

The transport term ΔF^* in Eq. (4) may be estimated with a satisfactory precision using the WLF equation [40]:

$$\Delta F^* = \frac{C_1 T_c}{C_2 + T_c - T_g} \quad (8)$$

where C_1 and C_2 are constants (generally assumed as 4120 cal/mol and 51.6 K, respectively) and T_g the glass transition temperature whose values are listed in Table 2.

For the overall crystallization rate, we used $G = CK_n^{1/n}$,

Table 2
Values of the equilibrium melting temperature T_m^{eq}, the stability parameter ϕ and the glass transition temperature T_g

	T_m^{eq} (K)	ϕ	T_g (K)[a]
Pure PCL	344.0	0.334	210
10/90 DGEBA/PCL	342.4	0.343	225
20/80 DGEBA/PCL	341.5	0.354	231
30/70 DGEBA/PCL	340.1	0.459	237
10/90 ER/PCL	341.0	0.255	233
20/80 ER/PCL	338.5	0.162	249
30/70 ER/PCL	335.4	0.123	231

[a] These values are taken from previous work [26].

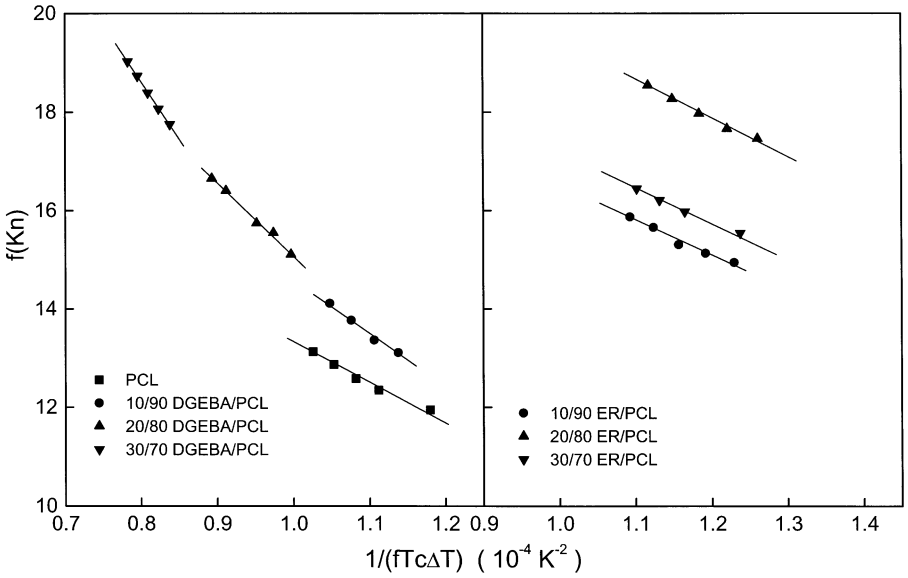

Fig. 6. Plots of the quantity $f(K_n)$ vs. $1/(fT_c\Delta T)$ for uncured DGEBA/PCL and MCDEA-cured ER/PCL blends.

where C is a constant. Assuming [41] that $\sigma = 0.1b_0\Delta H_f$ and taking into account relations (4), (5) and (8), the following expression is obtained:

$$f(K_n) = \frac{1}{n}\ln K_n - \ln v_2 + \frac{C_1}{R(C_2 + T_c - T_g)} - \frac{0.2T_m^{eq}\ln v_2}{\Delta T} = \ln A_0 - \frac{K_g}{fT_c\Delta T} \quad (9)$$

The plots of $f(K_n)$ vs. $1/(fT_c\Delta T)$ for both the uncured and the cured ER/PCL blends are shown in Fig. 6. The experimental data fit the straight lines quite well. From the slopes and the intercepts of these lines, values of K_g and A_0 can be obtained. They are listed in Table 3. By using Eq. (6), the K_g values can further be used to evaluate σ_e for all the studied compositions. These values are also summarized in Table 3. In calculation, we have employed the following parameters: $\sigma = 0.1b_0\Delta H_f$, $Z = 4$, $b_0 = 4.38\times10^{-8}$ cm, $R = 1.987$ cal/(mol K) and $k_B = 1.380\times10^{-23}$ J/K.

Table 3
Values of the nucleation factor K_g, the surface free energy of folding σ_e and the pre-exponential factor A_0

	K_g (K^2)	σ_e (J/m^2)	A_0
Pure PCL	8.26×10^4	4.32×10^{-2}	1.09×10^9
10/90 DGEBA/PCL	1.08×10^5	5.68×10^{-2}	1.22×10^{11}
20/80 DGEBA/PCL	1.48×10^5	7.81×10^{-2}	2.43×10^{12}
30/70 DGEBA/PCL	2.31×10^5	12.19×10^{-2}	1.12×10^{16}
10/90 ER/PCL	7.14×10^4	3.76×10^{-2}	3.99×10^{10}
20/80 ER/PCL	7.89×10^4	4.19×10^{-2}	7.45×10^{11}
30/70 ER/PCL	7.36×10^4	3.95×10^{-2}	2.67×10^{11}

In Figs. 7 and 8, the values of σ_e and A_0 are plotted vs. composition, respectively. For pure PCL, the value of σ_e is 4.32×10^{-2} J/m^2. As De Juana and Cortazer [7] indicated, σ_e is very sensitive to the equilibrium melting points used in the calculation. This is also evident from the literature where so many different values are given for σ_e of the pure PCL. These values range from 2.7×10^{-2} J/m^2 given by Ong and Price [5] to 11.2×10^{-2} J/m^2 obtained by Goulet and Prud'homme [6]. As shown in Fig. 7, σ_e of the uncured blends increases with increasing content of the non-crystallizable component. This is probably related

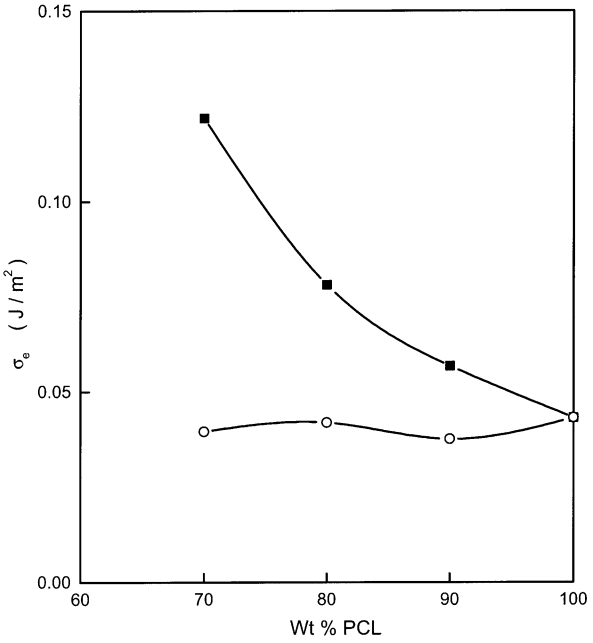

Fig. 7. Plots of σ_e vs. the weight fraction of PCL for uncured DGEBA/PCL blends (■) and MCDEA-cured ER/PCL blends (○).

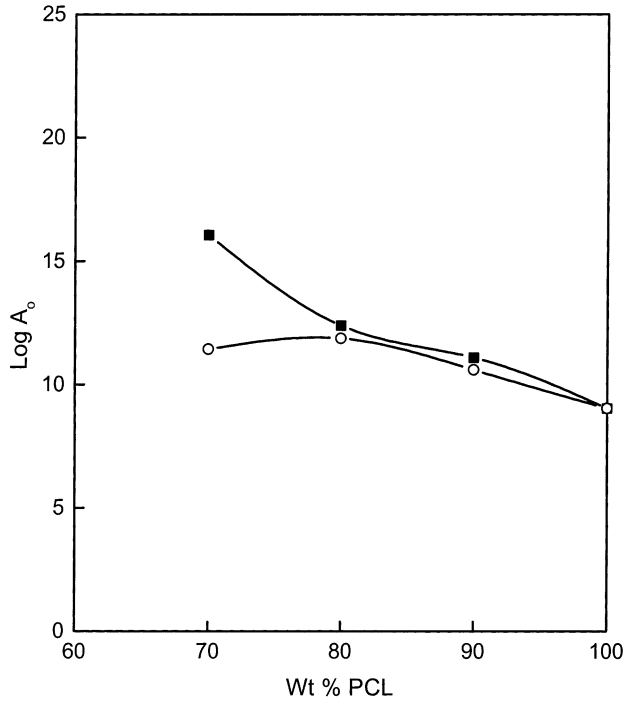

Fig. 8. Plots of log A_0 vs. the weight fraction of PCL for uncured DGEBA/PCL blends (■) and MCDEA-cured ER/PCL blends (○).

to the fact that during crystallization, non-crystallizable molecules may easily form entanglements with PCL molecules, favoring the formation of large loops on the surface of PCL lamellar crystals. This process will cause the increase of both terms that contribute to σ_e, i.e. the surface enthalpy and entropy of folding ($\sigma_e = H_e - TS_e$) [8]. The observation that σ_e increases with increasing DGEBA content should be ascribed to the fact that the variation of the enthalpic term overwhelms that of the entropic one. However, the surface free energy of folding σ_e remains almost unchanged with variation of composition, suggesting that neither the enthalpic term nor the entropic term is dominant in the cured blends. The pre-exponential factor A_0 also depends on the composition for both the uncured and the cured blends (Fig. 8). 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 cured blends is larger than that of the pure PCL.

4. Conclusions

It was found that the crystallization behavior of PCL from the melt is strongly influenced by the composition, the crystallization temperature, and the curing. At high conversion, the time dependence of the relative degree of crystallinity deviates from the Avrami equation. The addition of a non-crystallizable component into PCL causes a depression of both the overall crystallization rate and the melting temperature. The influence of curing on the crystallization of PCL is rather complicated. In general, curing results in an increase of the overall crystallization rate in the blends and a more profound depression of equilibrium melting point. The curing was also found to change the nucleation mechanism of PCL and enhance the nucleation rate. The surface free energy of folding σ_e shows an increase with increasing ER content for the uncured blends, whereas σ_e of the cured blends remains almost unchanged with variation of composition. The curing reduces the pre-exponential factor A_0.

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