Crystallization Kinetics of Thermosetting Polymer Blends of Poly(ε -caprolactone) and Unsaturated Polyester Resin

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ABSTRACT: A study has been made of the isothermal crystallization kinetics of poly(ε -caprolactone) (PCL) in partially miscible crosslinked polyester resin (PER)/PCL blends by using differential scanning calorimetry (DSC). For comparison, miscible blends of PCL with uncured polyester resin, i.e., oligoester resin (OER), were also investigated. The overall crystallization rate of PCL remarkably decreased with the addition of amorphous component, OER or PER. The kinetic rate constant K_n decreased sharply for both the OER/PCL blends and the crosslinked PER/PCL blends with decreasing PCL concentration. The mechanism of nucleation and geometry of the growing PCL crystals was not remarkably affected by the incorporation of OER, but changed considerably with the addition of PER. However, the overall crystallization rate of PCL in the crosslinked PER/PCL blends, which is attributable to the phase-separated structure and the reduced miscibility in the crosslinked blends. According to the nucleation and growth theories, the nucleation process was considered to be the rate controlling step in the crystallization. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 322–327, 1999

Key words: crystallization kinetics; $poly(\varepsilon$ -caprolactone); unsaturated polyester resin; thermosetting polymer blends

INTRODUCTION

Thermosetting polymers are among the most important materials in many industries, and are being used increasingly in engineering applications. They are generally amorphous, highly crosslinked polymers, possessing various excellent properties such as high tensile strength and modulus, easy processing, good thermal and chemical resistance, and dimensional stability. However, they have low toughness and poor crack resistance, and are, hence, normally brittle at room temperature. This is the basic reason for toughening thermosetting polymers for many end-use applications. One of the most successful methods of improving the toughness of a thermosetting polymer is to incorporate a second phase of dispersed rubbery particles or thermoplastic domains into the crosslinked polymer. The developments in the area of toughening thermosetting resins with elastomers or thermoplastics have been included in several excellent books.¹⁻⁴

However, relatively few systematic studies have been paid to the miscibility, phase behavior, and crystallization in blends of thermosetting resins with linear polymers. Because the resulting morphology and extent of phase separation is known to affect the optical and mechanical properties of the cured blends, the need for an understanding of the miscibility and phase behavior in thermosetting polymer blends is of great practical

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importance. Furthermore, it is also of much academic interest to examine these basic aspects of such thermosetting polymer blends. Particularly, in the thermosetting polymer blends where the linear component is crystallizable, crystallization will be greatly affected by the miscibility and phase behavior of the blends. The interrelationship between the miscibility, phase behavior, crystallization, and composition is very complicated in such thermosetting polymer blends.⁵ We have reported a series of study on poly(ethylene oxide) (PEO)/epoxy resin blends,⁶⁻⁹ PEO/novolac resin blends,^{10,11} poly(*e*-caprolactone) (PCL)/novolac resin blends,^{12,13} and PEO/unsaturated polyester resin blends.^{14,15} It was found that the miscibility, morphology, and crystallization of these thermosetting blends were remarkably affected by crosslinking.

In the previous work,¹⁶ we showed that PCL is completely miscible with uncured polyester resin, i.e., oligoester resin (OER), but only partially miscible with crosslinked polyester resin (PER); phase separation occurred in the crosslinked PER/PCL blends. In this article, we further present the results of our investigation on the isothermal crystallization kinetics of PCL in both the uncured OER/PCL blends and the crosslinked PER/PCL blends. To our knowledge, little work has been reported in the literature concerning crystallization kinetics of a linear crystalline polymer in its miscible or partially miscible thermosetting polymer blends. Therefore, this study is of great academic importance to understand the effect of crosslinking on the overall crystallization rate and, hence, on the mechanism of nucleation and growth of the PCL crystals in thermosetting blends.

EXPERIMENTAL

Materials and Preparation of Samples

The poly(ε -caprolactone) (PCL, Placcel H-7) was purchased from Daicel Chemical Ind., Ltd., Japan; it had a quoted number-average molecular weight M_n of 70,000–100,000. The unsaturated polyester resin (OERS) composed of 67 wt % oligoester resin (OER) ($M_n = 1000$) and 33 wt % styrene as a crosslinking monomer, was supplied by Shanghai Institute of Synthetic Resins, Shanghai, China. The OER was a precopolymer of isophthalic acid (PA), fumaric acid (FA), and propylene glycol (PG) with molar ratio PA/FA/PG = 1/1/2.2, it was terminated with α -propyleneglycol. The pure OER was obtained through coprecipitation of the OERS with an excess amount of petroleum ether. To remove the residual petroleum ether and styrene, the as-obtained sample was dried in a vacuum oven for at least 2 weeks. The OER/PCL blends were prepared by solution casting from chloroform at room temperature. To remove the residual solvent, the blends were dried in a vacuum oven at room temperature for approximately 2 weeks. Blend compositions studied were 20/80, 30/70, 40/60, and 50/50 OER/PCL in terms of weight ratio.

To prepare crosslinked PER/PCL blends, OERS and PCL were mixed at 70°C to form a homogenous clear liquid blend, then 1.5 wt % benzoyl peroxide (relative to OERS) was added to the blend with continuous stirring until a clear mixture was obtained (in approximately 3 min). The mixture was poured into a stainless steel mold and cured in an oven at 65°C for 14 h, followed by successive postcuring at 90°C for 3 h and 120°C for 3 h. Blend compositions studied were 0/100, 20/80, 30/70, 40/60, and 50/50 PER/ PCL in terms of weight ratio.

Differential Scanning Calorimetry (DSC)

The calorimetric measurements were carried out on a Perkin-Elmer DSC-7 differential scanning calorimeter in a dry nitrogen atmosphere. Indium and zinc standards were used for calibration for low- and high-temperature regions, respectively. For isothermal crystallization measurements, all the samples (about 8 mg in weight) were first heated to 140°C and maintained for 5 min to melt any crystallinity. Then they were cooled quickly to isothermal crystallization temperature and maintained at that temperature until the crystallization was complete. Exotherms of isothermal crystallization were obtained; the heat of crystallization was recorded as a function of performance time at the isothermal crystallization temperature.

RESULTS AND DISCUSSION

OER/PCL Blends

According to the thermograms obtained in isothermal crystallization, the conversion degree of crystallization at time t, Xt, was determined by using the following relation.



Figure 1 Development of relative degree of crystallization Xt with time t for isothermal crystallization of the OER/PCL blends at $T_c = 28^{\circ}$ C.

$$Xt = \int_{0}^{t} \left(\frac{dH}{dt}\right) dt / \int_{0}^{\infty} \left(\frac{dH}{dt}\right) dt \qquad (1)$$

where the first integral is the heat generated at time t and the second is the total heat of crystallization.

Figure 1 shows the Xt values obtained as functions of crytallization time (t) for the OER/PCL blends at 28°C. It can be seen from the figure that the characteristic sigmoidal isotherms are shifted to right along the time axis with OER content from 20 to 50 wt % in the blends, indicating progressively slower crystallization rate. From the curves in Figure 1, half-times of crystallization, $t_{1/2}$, defined as the time required for half of the crystallinity to develop, were obtained and presented in Table I.

The kinetics of the isothermal crystallization can be analyzed on the basis of the Avrami equation 17

Table IParameters of IsothermalCrystallization of OER/PCL Blends at $T_c = 28^{\circ}$ C

OER/PCL	$t_{1/2} \\ (\min)$	$\Delta H_c \ ({ m J/g})$	$K_n (\min^{-n})$	n
20/80 30/70 40/60 50/50	1.7 2.8 3.8 6.2	$61.3 \\ 53.1 \\ 45.1 \\ 36.2$	$egin{array}{l} 7.5 imes10^{-2}\ 1.6 imes10^{-2}\ 3.0 imes10^{-3}\ 1.7 imes10^{-4} \end{array}$	$4.0 \\ 3.7 \\ 4.0 \\ 4.4$



Figure 2 Plots of $\log[-\ln(1-Xt)]$ vs. logt for isothermal crystallization of the OER/PCL blends at $T_c = 28^{\circ}$ C.

$$Xt = 1 - \exp(-K_n t^n) \tag{2}$$

where K_n is the overall kinetic rate constant, and n is a parameter that depends on the type of nucleation and on the geometry of growing crystals. Values of K_n and n can be derived from the intercept and the slope of straight lines obtained by plotting $\log[-\ln(1-Xt)]$ vs. $\log t$, as shown in Figure 2. The results of these isothermal crystallization parameters of the OER/PCL blends are also summarized in Table I. The n values obtained are between 3.7 and 4.4, which can be considered to be almost unchanged, regardless of OER concentration in the OER/PCL blends. This fact indicates that the incorporation of OER does not remarkably influence the mechanism of nucleation and growth of the PCL crystals.

The observed linear trends from Figure 2 indicate the crystallization kinetics of these blends at 28°C follow the Avrami equation up to a high degree of conversion. With the increase of PCL content in the blends, the line is shifted along the logt-axis, which results in a more negative intercept. The more negative the intercept, the smaller the K_n . Figure 3 shows plots of crystallization rate constant (K_n) and time of half crystallization ($t_{1/2}$) vs. PCL content for the OER/PCL blends at T_c = 28°C. It can clearly be seen from Figure 3 that with increasing OER content, overall kinetic rate constant (K_n) decreases sharply while the time of half crystallization ($t_{1/2}$) increases rapidly, which



Figure 3 Plots of crystallization rate constant (K_n) and time of half crystallization $(t_{1/2})$ vs. the PCL content for the OER/PCL blends at $T_c = 28$ °C.

is an indication of progressive difficult crystallization. Table I also shows that the heat of crystallization (ΔH_c) of PCL decreases with a decrease of the PCL content in the OER/PCL blends. This is the result of the dilution and inhibitions of the amorphous OER component.

PER/PCL Blends

For the crosslinked PER/PCL blends, isothermal crystallization kinetics was also investigated here. It has been shown that the crosslinked PER/ PCL blends were only partially miscible and had a phase-separated structure.¹⁶ The overall crystallization rate of PCL in the crosslinked PER/ PCL blends was much higher compared with the corresponding uncured OER/PCL blends, which is attributable to the phase-separated structure and the reduced miscibility in the crosslinked blends. As a result, it is impossible to find a common crystallization temperature to obtain DSC exotherms of isothermal crystallization for both the OER/PCL blends and the crosslinked PER/PCL blends. Therefore, isothermal crystallization of both the PER/PCL blends and the pure PCL were investigated at a much higher crystallization temperature.

Figure 4 shows the isotherms of crystallization for the pure PCL and the PER/PCL blends stud-



Figure 4 Development of relative degree of crystallization Xt with time t for isothermal crystallization of the PER/PCL blends at $T_c = 37^{\circ}$ C.

ied at 37°C. It can clearly be seen that the isotherms are shifted along the time axis with increasing crosslinked PER content, clearly indicating progressively difficult crystallization. Figure 5 shows linear trends of $\log[-\ln(1-Xt)]$ vs. $\log t$,



Figure 5 Plots of $\log[-\ln(1-Xt)]$ vs. $\log t$ for isothermal crystallization of the PER/PCL blends at $T_c = 37^{\circ}$ C.

PER/PCL	$t_{1/2} \\ (\min)$	$\Delta H_c \ ({ m J/g})$	$K_n (\min^{-n})$	n
0/100 20/80 30/70 40/60 50/50	2.6 3.0 3.7 4.3 6.6	$79.4 \\ 59.0 \\ 50.0 \\ 39.4 \\ 29.6$	$\begin{array}{c} 11.2\times10^{-3}\\ 3.1\times10^{-3}\\ 2.0\times10^{-3}\\ 1.4\times10^{-3}\\ 4.2\times10^{-4} \end{array}$	$4.9 \\ 4.9 \\ 4.4 \\ 4.1 \\ 3.9$

Table II Parameters of Isothermal Crystallization of PER/PCL Blends at $T_c = 37^{\circ}$ C

suggesting that the crystallization kinetics of these blends follow the Avrami equation for all the compositions investigated. The related results are summarized in Table II. It can be seen that the n values decrease regularly with decreasing PCL content in the blends, from 4.9 for the pure PCL to 3.8 for the 50/50 PER/PCL blend. The changing tendency of *n* indicates that the mechanism of nucleation and geometry of the growing PCL crystals changed gradually with the addition of PER, implying that the crosslinking of OER had a great influence on the crystallization mechanism of PCL. Table II also clearly shows that the heat of crystallization (ΔH_c) of PCL decreases with a decrease of PCL content in the PER/PCL blends. It can be seen from Table II that with decreasing the PCL content, the heat of crystallization (ΔH_c) for the PER/PCL blends decreases more rapidly than that for the OER/PCL blends (Table I).

Figure 6 shows the K_n as a function of PCL content, which clearly shows that K_n increases markedly with increasing the PCL content within the composition ranging from 50 to 100 wt % PCL. It can also be found from Figure 6 that $t_{1/2}$ decreases greatly with increasing the PCL content. The overall crystallization rate of PCL in the crosslinked PER/PCL blends was greatly enhanced compared to that in the uncured OER/PCL blends. This is attributable to the phase-separated structure and the reduced miscibility in the PER/PCL blends.¹⁶

Although the isothermal crystallization for the OER/PCL blends and the PER/PCL blends was studied at different temperatures, to compare the variation tendency of K_n with the blend compositions for both systems is practicable. By comparing Figure 6 with Figure 3, it can be seen that with increasing the PCL content, the K_n for the OER/PCL blends increases more rapidly than that for the PER/PCL blends. The OER/PCL

blends were previously shown to be completely miscible; amorphous OER could be incorporated in interlamellar or interfibrillar regions of PCL spherulites,¹⁶ which should greatly hinder the crytallization of PCL. With increasing the OER content, this hindrance becomes stronger and stronger. On other hand, the PER/PCL blends are only partially miscible and with a phase-separated structure;¹⁶ a small concentration of PER in the PCL-rich phase should have relatively little influence on the crystallization of PCL.

From the mechanism of nucleation and growth, we can give a qualitative explanation of isothermal crystallization of the OER/PCL blends and the PER/PCL blends. In general, the overall crystallization rate includes nucleation and growth of crystallization. The general form of the spherulitic growth rate can be illustrated by the Turnbull-Fisher equation:¹⁸

$$G = G_0 \exp[-\Delta F^*/(RT)] \exp[-\Delta E/(RT)] \quad (3)$$

where ΔE is the activation energy of nucleation, ΔF^* represents the barrier restricting movement to the crystallizing surface, and has been suggested by Hoffman and Weeks¹⁹ to be satisfied by the Williams, Landel, and Ferry (WLF) equation.²⁰



Figure 6 Plot of crystallization rate constant (K_n) and time of half crystallization $(t_{1/2})$ vs. the PCL content for the PER/PCL blends at $T_c = 37^{\circ}$ C.

$$\Delta F^* = 4120T/(51.6 + T - T_g) \tag{4}$$

From the uncured OER/PCL blends to the cured PER/PCL blends, the T_g s of the corresponding polymer blends increase. It can be seen from eq. (4) that the ΔF^* for the PER/PCL blends is higher than that for the OER/PCL blends. If the growth process is the rate controlling step, according eq. (3), the overall crystallization rate should decrease quickly with the curing of the amorphous component. Because the experimental results revealed that the crystallization rate dramatically increases after the curing, the nucleation process should be the rate-controlling step in the crystallization of PCL in both the uncured and the cured blends.

CONCLUSIONS

From the results presented here, it can be concluded that the crosslinking had a great influence on the overall crystallization rate and the mechanism of nucleation and growth of the PCL crystals in the blends. The overall crystallization rate of PCL remarkably decreased with the addition of the amorphous component OER or PER. With decreasing the PCL concentration, the kinetic rate constant K_n decreases sharply for both the OER/PCL blends and the crosslinked PER/PCL blends. In the miscible OER/PCL blends, amorphous OER was incorporated in the interlamellar or interfibrillar regions of PCL spherulites, which greatly hindered the crytallization of PCL. However, in the crosslinked PER/PCL blends, which are partially miscible and phase separated, a small concentration of PER in the PCL-enriched phase had relatively little hindrance on the crystallization of PCL. The mechanism of nucleation and geometry of the growing PCL crystals was not remarkably affected by the incorporation of OER, but changed considerably with the addition of PER. The crystallization rate of PCL in the crosslinked PER/PCL blends was much higher compared with the corresponding uncured OER/ PCL blends, which is attributed to the phaseseparated structure and the reduced miscibility in the crosslinked blends. From the mechanism of nucleation and growth, the nucleation process was proposed to be the rate-controlling step in the crystallization.

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