

Crystallization Behavior of PHA/PEDEA Oligoester Blends

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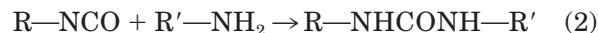
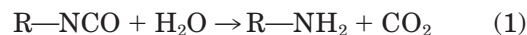
ABSTRACT: The crystallization behavior of oligoester blends prepared from crystalline poly(hexanediol adipate) (PHA) and amorphous poly(ethylene diethylene glycol adipate) (PEDEA) was studied using POM, WAXD, and DSC. The crystal form of both PHA and the blends are spherulites. The crystallinity, melting enthalpies, and crystallization rate increased with increased PHA content in the blends. Two sharp diffraction peaks of each blend were detected at the same position, where, respectively, $2\theta = 21.3^\circ$ and 24.1° . The research on the crystallization kinetics showed that the Avrami exponent of all the oligoester blends is approximately 4. It was demonstrated that the crystallization mechanism of PHA is not disturbed by amorphous PEDEA. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1363–1368, 2002; DOI 10.1002/app.10268

Key words: hot melt; oligoester blends; crystallization behavior; crystallinity; crystallization kinetics

INTRODUCTION

Polyurethane-based reactive hot-melt adhesives (RHMA)s are widely used in highly demanding applications, where superior green adhesion strength and ultimate setting properties are required. Because of their substantial adherence to a variety of substances and outstanding resistance to chemicals and heat, RHMA)s are drawing more and more attention in many fields.^{1–3} RHMA)s are low molecular weight methylene diphenylene isocyanate (MDI) end-capped polyurethane prepolymers, with an isocyanate content ranging from 2 to 4%, based on polyester and poly(ether polyol)s. Another key advantage of RHMA)s is their solvent-free application, which could meet both economic and environmental concerns. They are solid at room temperature. When heated, RHMA)s are melted to wetting adherends

and form joints by crystallization and hydrogen bonding quickly. While and after diffusion of air moisture into the adhesive bulk, the active isocyanate end group would react with moisture vapor. The overall curing reaction can be illustrated as follows:



Subsequently, chemical crosslink bonds are formed in such a way.⁴ It is noteworthy that crystalline units of prepolymers, if they exist, would serve as a barrier to air moisture and, therefore, defer a further curing reaction of the adhesive bulk. So, an urethane prepolymer exclusively derived from crystalline polyols, for a PHA (polyester based on adipic acid and hexanediol) oligodiols, for instance, would exhibit a superior initial ad-

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hesion strength but inferior ultimate setting properties. Contrarily, a prepolymer from absolutely amorphous polyols, for a PEDEA (polyester based on adipic acid and mixture of ethylene glycol and diethylene glycol), for instance, would take a long duration to cure. In general, the ratio between crystalline and amorphous polyols involved in RHMA systems and their crystallization performance would undoubtedly play a key part in the initial strength as well as in the ultimate properties of the RHMA system. The curing mechanism of RHMA systems was widely covered by Comyn in recent reports.^{5,6} The mechanism of the reaction between isocyanates and water is beyond our research. The goal for the present article focused on giving a deep insight into the crystallization behavior of oligoester diol blends. The crystallization performance of high molecular weight polyesters was comprehensively studied for the case of their utilization background. But seldom has research intensively touched on oligoester crystallization. Considering that crystalline units of oligoesters would remain undisturbed during the preparation and application of RHMA systems,⁷ we intended to study the crystallization of oligoester blends. For a practical case, PHA, a highly crystalline oligoester, and PEDEA, a perfectly amorphous oligoester, were applied to the crystallization study herein.

EXPERIMENTAL

Materials

PHA is a white solid with a number-average molecular weight (M_n) of 3405 and a hydroxyl number of 33; PEDEA is a light yellow viscous liquid at room temperature with an M_n of 2670 and a hydroxyl number of 42. Two oligodiols were supplied by the Dow Chemical Co. Both oligodiols were dehydrated for 1 h at 110°C under a pressure of 100–200 Pa with vigorous stirring.

Preparation of Blends

Blends were prepared with the PHA/PEDEA ratios of 100:0, 90:10, 75:25, 50:50, 25:75, and 10:90. PHA was dehydrated for 45 min at 100°C under a pressure of 100–200 Pa with vigorous stirring. After addition of stoichiometric PEDEA, the mixture was dehydrated for 1 h under the same conditions as mentioned above. Subsequently, a sample for a WAXD study was prepared by casting a

thin disc in a Teflon mold. The mold was kept in an oven conditioned at 42°C for 12 h.

Measurement Methods

A Leica DMLM/P polarizing optical microscope (POM) equipped with a heating and freezing stage was applied to observe the crystallization form of the blends. A minor sample was sandwiched between two glass plates. Prior to crystallization, the sample was heated to 80°C and kept for 2 min. Then, the sample was cooled to 42°C quickly. A camera was installed at the top of the POM apparatus to obtain photos of the crystallization form.

An X-ray diffractometer (Rigaku D/max-Rb) with Ni-filtered $\text{CuK}\alpha$ radiation working at 40 kV and 50 mA was used to obtain information on the crystallization of the blends. All the samples were tested at a scan speed of 4°/min at room temperature. The scanning range (2θ) was 3°–50°.

A Perkin–Elmer 2C differential scanning calorimeter (DSC) was used to detect the melting temperature (T_m) and the heat of crystallization (ΔH_m). The scanning circles were as follows: heating from room temperature to 100°C at 20°C/min, cooling from 100 to 0°C at 10°C/min, and then heating to 100°C again at a rate of 10°C/min. The second run was taken for the result data.

The crystallization kinetics of the blends was studied using an expanded polarizing optical microscope system based on the double-refraction properties of the crystal units. Sandwiched between two glass slides, the sample was heated in a melting vat at 80°C for 15 min. Then, it was transferred into a crystallization vat maintained at 44°C through an input rail. The intensity of the polarizing light that passed through the sample (I) was detected and recorded. The intensity increased while the crystal grew.

RESULTS AND DISCUSSION

Crystal Form

Oligodiols are known to be crystalline in the form of spherulites.^{8,9} Photos of four blends, with PHA/PEDEA ratios of 100:0, 75:25, 50:50, and 10:90, respectively, conducted by POM are shown in Figure 1. Clear Maltese-cross patterns appeared regardless of the crystalline oligoester content in the blends, which suggested that oligoester blends are crystalline in the form of spherulites.

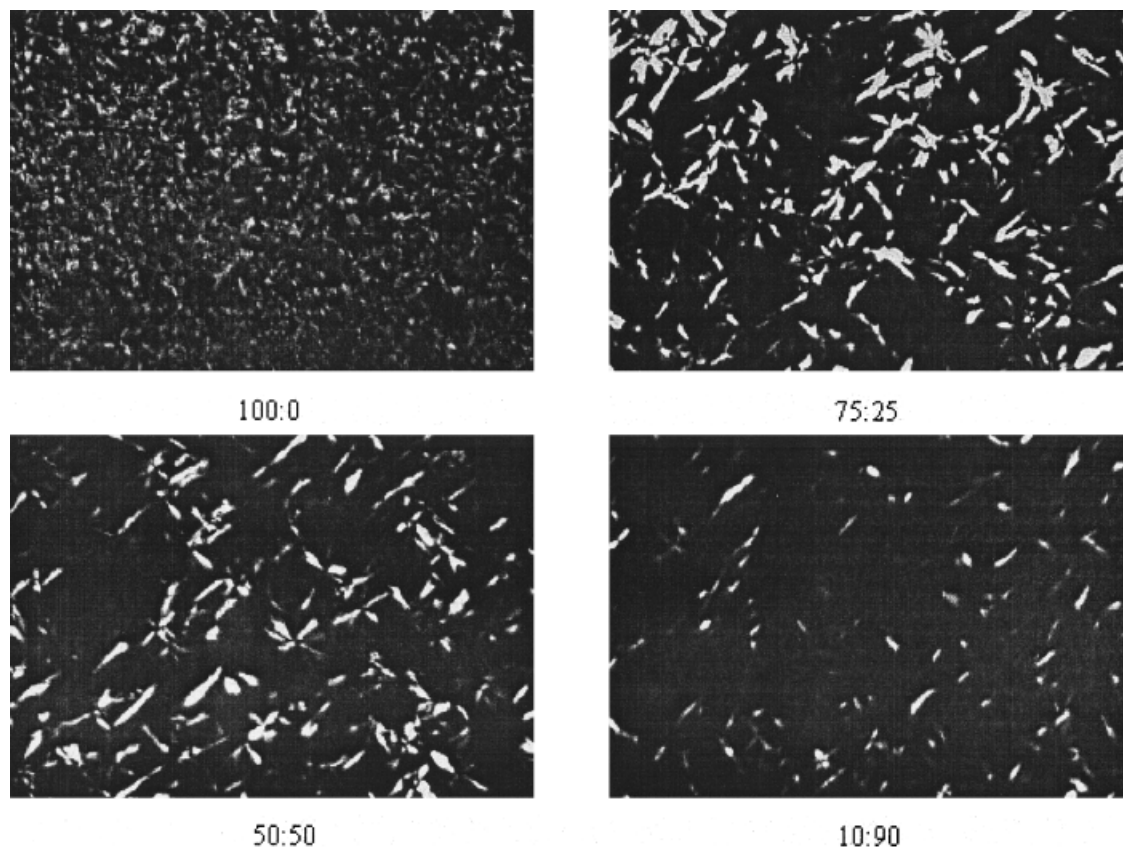


Figure 1 Crystal form of PHA/PEDEA blends.

Just as shown in Figure 1(a), the crystal radii of the pure crystalline oligoesters are too small to use to identify them from each other. But the crystal radii of the blends, as shown in Figure 1(b–d), become larger and larger with an increased PEDEA content. The reason for this outcome may be contributed to the strong tendency of PHA to crystallize. In the pure PHA system, many crystal seeds come into being almost at the same time. Every crystal nuclear may quickly become a spherulite. No time is available for further growth for a single crystal unit. Subsequently, the crystal structures are embodied in the form of a muster of many tiny spherulites. Contrarily, Figure 1(d) shows a clearer and larger appearance of spherulites. It seems that PHA segments are dissolved in the PEDEA. A more perfect crystal structure was formed under the dilution of PEDEA in this polymer blend.

Crystallinity

As an effective tool for crystal research, a wide-angle X-ray diffractometer (WAXD) is usually en-

gaged to study polymer crystals. Individual crystal morphology is often characterized in crystal-form parameters, which distinguishes one from another. Various crystals exhibit different curves in the WAXD patterns. The relation between the crystal morphology and the diffraction angle is quantitatively described as the well-known Bragg's equation: $2d \sin \theta = \lambda$, where d is a characteristic parameter corresponding to the crystal form; θ , the diffraction angle; and λ , the wavelength of the X-ray used. Here, only primary diffraction was considered. The diffraction intensity, corresponding to the crystallinity, is also presented by WAXD patterns.

Figure 2 shows X-ray profiles of oligoester blends containing various crystalline portions, which suggest that the main crystalline diffraction peaks of both pure PHA and blends appear at the same position, where $2\theta = 21.3^\circ$ and 24.1° , respectively. Moreover, the diffraction intensity of the two peaks increased without exception with an increase in the PHA content in the blends. The result of the WAXD analysis demonstrates that

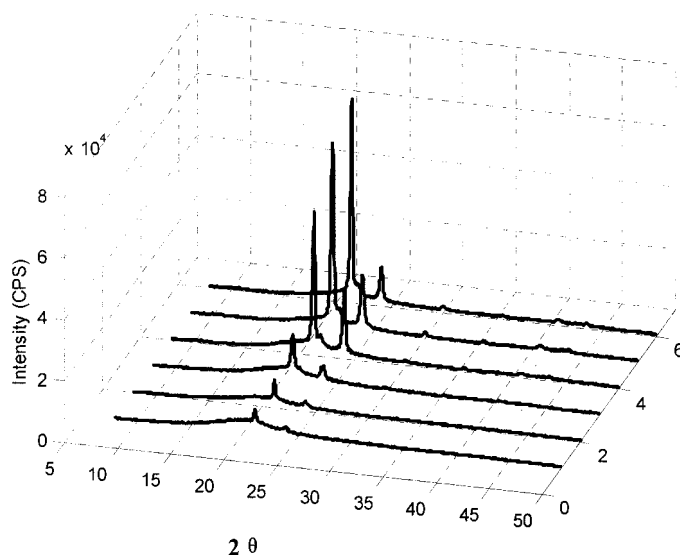


Figure 2 WAXD patterns of PHA/PEDEA oligodiol blends.

the introduction of amorphous PEDEA into crystalline PHA does not affect the formation of the crystal structure. On the other hand, the crystalline arrangement of PHA could not induce PEDEA segments to rearrange themselves to form a crystalline structure. This result is in accordance with the results of the POM measurements. Further information can be obtained by resolving the diffraction peaks. The results are listed in Table I, which suggest that the crystallinity decreased with increasing PEDEA content in the blends. It is noteworthy that even in the PHA/PEDEA 10/90 ratio blend the crystallinity is still 7.2%. This result confirms that the crystallization tendency of PHA is hardly affected by the amorphous PEDEA phase.

Compared with WAXD, DSC reveals dynamic information on the crystal structure. As shown in Table I, all the blends are melted at approximately 51–52°C. With increasing PEDEA con-

tent, the melting enthalpy of the blends decreases while the melting peak broadens correspondingly, which suggests that the blend under investigation is a relatively compatible system (Fig. 3).

Crystallization Kinetics

The crystallization kinetics of polymer melts is usually analyzed in terms of the well-known Avrami equation: $1 - X_t = \exp(-kt^n)$, where X_t is the fraction of material crystallized after time t ; k , a rate constant, which depends on the rates of nucleation and growth; and n , the Avrami exponent, which is in relation to the mechanism of the nucleation and growth geometry.^{10–12} In practical research, X_t can be expressed by the crystal enthalpies (ΔH), volume (V), and intensity of the polarizing light passing through the crystal (I). In this case, $1 - X_t$ can be replaced by $(I_\infty - I_t)/(I_\infty - I_0)$, where I_0 , I_t , and I_∞ are the intensities of the polarizing light at the beginning, t , and the end of the crystallization process. So, the Avrami equation can be rewritten as

$$\log\{-\ln[(I_\infty - I_t)/(I_\infty - I_0)]\} = \log k + n \log t \quad (4)$$

A plot of $\log\{-\ln[(I_\infty - I_t)/(I_\infty - I_0)]\}$ versus $\log t$ should yield a straight line, from which the Avrami exponent can be readily obtained.

The isothermal crystallization kinetics of the PHA/PEDEA blends was studied by an expanded POM system. As shown in Figure 4, all the plots are almost parallel to each other. The isotherms

Table I Crystallinity, ΔH , and T_m of PHA/PEDEA Blends

Blends	Crystallinity	ΔH (J/g)	T_m (°C)
100 : 0	0.621	19.33	50.9
90 : 10	0.609	19.17	51.5
75 : 25	0.528	13.51	51.2
50 : 50	0.235	8.88	51.1
25 : 75	0.103	4.15	52.0
10 : 90	0.072	1.92	52.7

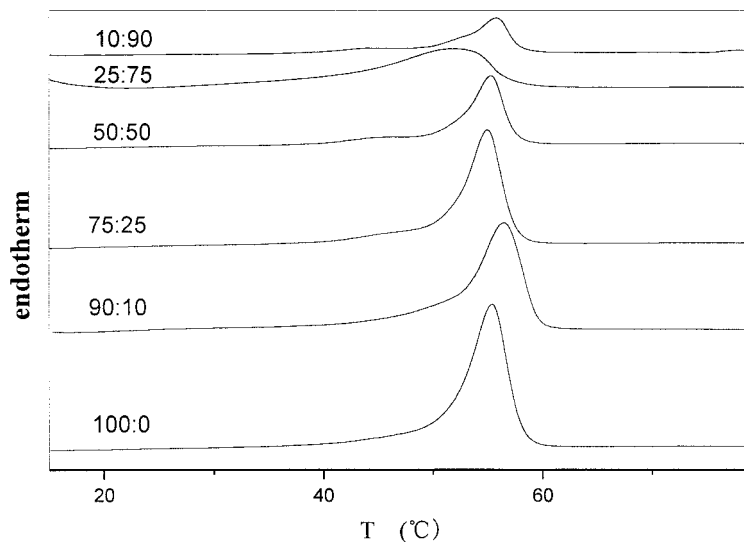


Figure 3 DSC patterns of PHA/PEDEA oligodiol blends.

show a progressive shift toward a longer crystallization time with the amount of PEDEA in the blends increasing, indicating that the overall crystallization kinetics of PHA is slowed as a result of blending. Further analysis of the Avrami plots gave quantitative data of the Avrami exponent (n), crystallization rate constant (k), and crystallization half-life ($t_{1/2}$). As shown in Table II, with the amount of PEDEA increased, the crystallization half-life increased while the Avrami exponent remained approximately equal to 4.

The research on crystallization kinetics showed that the nucleation mechanism and morphology of the crystal growth are not disturbed in the presence of PEDEA, which is well in agreement with previous results. In addition, the decrease of the crystallization rate can be attributed to the dilution effect of PEDEA. Just as was assessed by the POM study, the blends are homogeneous, like a polymeric solution at the melting state, in which PEDEA is a solvent and PHA is a solute. When cooled to the crystalline temperature, PHA is arranged into a crystal structure and

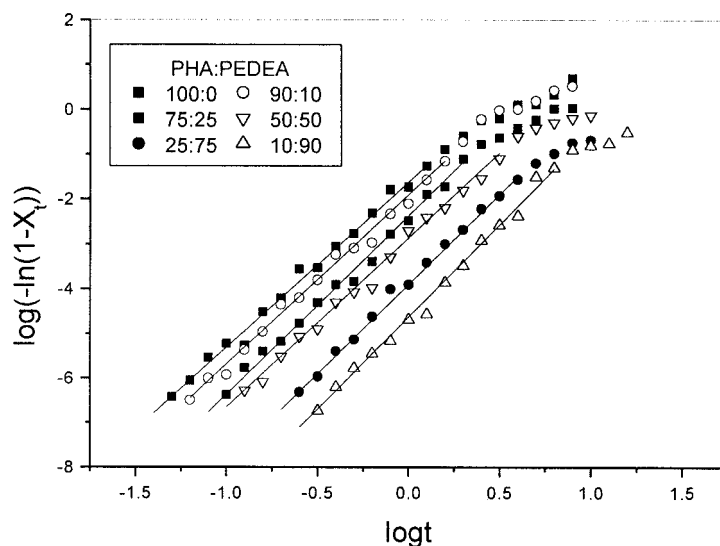


Figure 4 Avrami plots of isothermic crystallization of PHA/PEDEA blends at 42°C.

Table II Characteristic Data from Isothermal Crystallization of PHA/PEDEA Blends

Blends	$\log k$	n	$t_{1/2}$ (min)
100 : 0	-1.63	3.693	2.5
90 : 10	-1.916	3.783	2.9
75 : 25	-2.386	3.997	3.6
50 : 50	-2.871	3.790	5.2
25 : 75	-3.912	4.014	8.6
10 : 90	-4.645	4.127	12.2

PEDEA, meanwhile, is rejected from the crystal formation. When serving as a solvent, PEDEA does not enter into the crystal lattice, but hampers the arrangement of the crystal units and delays the formation of the crystal.

CONCLUSIONS

The crystallization behavior and kinetics of PHA/PEDEA oligoester blends was studied using POM, WAXD, and DSC. The photos obtained by POM demonstrated the presence of spherulites in these blend systems. The WAXD results showed that the positions of the diffraction peaks remain unchanged, while the intensities of the diffraction peaks decreased with increasing PEDEA content.

Study of the crystallization kinetics indicated that, although the crystallization rate decreased, the mechanism of nucleation and the crystal growth process are not disturbed by the introduction of amorphous PEDEA.

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