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ScienceDirect

Polymer 47 (2006) 6826−6835

polymer

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Correlation between interactions, miscibility, and spherulite growth in crystalline/crystalline blends of poly(ethylene oxide) and polyesters

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Received 22 May 2006; received in revised form 18 July 2006; accepted 20 July 2006
Available online 8 August 2006

Abstract

Crystalline/crystalline blend systems of poly(ethylene oxide) (PEO) and a homologous series of polyesters, from poly(ethylene adipate) to poly(hexamethylene sebacate), of different CH_2/CO ratios (from 3.0 to 7.0) were examined. Correlation between interactions, miscibility, and spherulite growth rate was discussed. Owing to proximity of blend constituents' T_g's, the miscibility in the crystalline/crystalline blends was mainly justified by thermodynamic and kinetic evidence extracted from characterization of the PEO crystals grown from mixtures of PEO and polyesters at melt state. By overcoming experimental difficulty in assessing the phase behavior of two crystalline polymers with closely spaced T_g's, this work has further extended the range of polyesters that can be miscible with PEO. The interaction parameters (χ_{12}) for miscible blends of PEO with polyesters [poly(ethylene adipate), poly(propylene adipate), poly(butylene adipate), and poly(ethylene azelate) with CH_2/CO = 3.0−4.5] are all negative but the values vary with the polyester structures, with a maximum for the blend of PEO/poly(propylene adipate) (CH_2/CO = 3.5). The values of interactions are apparently dependent on the structures of the polyester constituent in the blends; interaction strength for the miscible PEO/polyester systems correlate in the same trend with the PEO crystal growth rates in the blends.

Keywords: Crystalline/crystalline blend; Miscibility; Interactions

1. Introduction

Statistically, the number of binary miscible blends comprising two crystallizable polymers is far fewer in comparison to the binary amorphous/crystalline or amorphous/amorphous blend systems documented in the literature. It has been experimentally difficult to investigate subjects of blend miscibility (in the amorphous phase), in which both constituents in blends are semicrystalline polymers. Miscibility refers to the amorphous phase in blends; thus, if both constituents are highly crystalline, the fraction of the amorphous phase in the blends becomes relatively less. Unless the crystalline/crystalline blends can be melt-quenched and frozen in amorphous glasses, the conventional criteria for judging blend miscibility based on T_g behavior may become vague. Poly(L-lactide) (PLLA) is a widely studied biodegradable polyester with CH/CO ratio = 1.0 (in the main-chain segment, if not counting the pendant methyl); naturally, blend systems of PLLA with PEO have attracted a lot of interest. A couple of earlier examples of crystalline/crystalline blend systems can be given by poly(ethy lene oxide) and poly(L-lactide) (PLLA) [1−3]. However, conflicting opinions regarding phase behavior of the PEO/PLLA blend system are being debated, which has been determined to be a partially miscible blend system of polyether/polyester by some investigators [1,2], but a miscible one by others [3]. Nishi et al. [4,5] have reported in the literature that the PEO/PESu (CH_2/CO = 2) and PEO/PBSu blends are miscible. Although poly(ethylene oxide) and poly(L-lactide) (PLLA) were assessed to be miscible by Pennings et al. [3], however, a note must be commented here on the reported phase behavior of the PEO/PLLA blend. By judging from the blend morphology with heterogeneity and some missing T_g data for

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doi:10.1016/j.polymer.2006.07.039

intermediate blend compositions, a more plausible conclusion for the PEO/PLLA blend might be partially miscible, which would then be in agreement with the results reported by Nakafuku [1,2]. These examples illustrate points of characterization difficulty or confusion in determining phase behavior in crystalline/crystalline blends.

Later on, more blend systems of two semicrystalline polymers, miscible and immiscible, have been investigated and reported. Examples in the literature are a few miscible blend system such as PEO/poly(ethylene succinate) (PESu) [4] and PEO/poly(butylene succinate) (PBSu) [5], or immiscible (or termed as ‘‘partially miscible’’) PEO/poly(ε-caprolactone) (PCL) [6], etc. Runt et al. [7] have done comparisons of crystallization kinetics between neat PEO and melt-miscible PEO blends. Amorphous poly(propylene oxide) (PPO), alternatively named poly(propylene glycol) (PPG), is a homologous ether to PEO. Although the blends of PPG cannot be classified as crystalline/crystalline blends, they are worthy of studying to evaluate effect of structural change in polyethers on blend phase behavior. Hashida et al. [8] have concluded that blends of PPG with poly(hexamethylene adipate) (PHMA) are miscible, but blends of PPG/poly(hexamethylene sebacate) (PHMS) are not. The fact also suggests that the structures of either the polyether or the polyester influence the phase behavior of the blend of polyether/polyester.

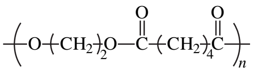
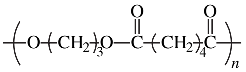
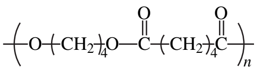
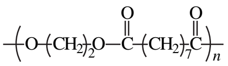
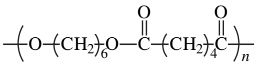
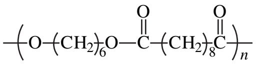
The above cited examples clearly indicate that a change in the structures of either polyethers or polyesters can lead to corresponding change in the phase behavior of the blends comprising the polyethers and polyesters. But the list of possible miscible blends involving polyethers and polyesters might not have been exhausted; the objectives of this study thus were to search further miscible blends composing two semicrystalline polymers. Factors leading to miscibility in blends of two crystalline polymers were further explored. Methodology was refined in dealing with blends of two polymers whose constituents' crystallinity, crystalline domains, and closely spaced T_g's might add up complexity. In this study, analyses of phase behavior and miscibility in the amorphous domains of blends of two semicrystalline polymers were based on characterization either on quenched amorphous glass or at above the melt state.

2. Experimental

2.1. Materials and preparation

Poly(ethylene oxide) (PEO), semicrystalline with $M_w = 2 \times 10^5$ g/mol, $T_g = -60\ ^\circ C$, was obtained from Aldrich Co. (USA). A series of homologous polyesters were used, whose names, basic properties, and sources are listed in Table 1. The molecular weights for most polyesters in this study, with one exception, are high enough to be between 10,000 and 60,000 g/mol. Note that polyesters with an odd number of methylene [such as poly(propylene adipate), PPA, used in this study] were difficult to synthesize with high molecular weights. $M_w = 3800$ g/mol was near the highest possible. However, at this M_w, it has at least 20 repeat units (average) in chain length; and thus, possesses the basic properties of a polymer. The structures of the polyesters, represented by the average ratio of methylene per carbonyl (CH_2/CO) in main chains, range from poly(ethylene adipate) (PEA) to poly(hexamethylene sebacate)

Table 1
Structures, molecular weights, and physical properties of polyesters used in this study

Aliphatic polyesters	T_g (°C)	T_m (°C)	M_w (g/mol)	Structures	(CH_2/CO) ratio
Poly(ethylene adipate), PEA	−52.7	45.4	10,000	 $\left(O-(CH_2)_2-O-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C} \right)_n$	3.0
Poly(1,3-propylene adipate), PPA	−69	38	3800	 $\left(O-(CH_2)_3-O-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C} \right)_n$	3.5
Poly(1,4-butylene adipate), PBA	−62.2	56	12,000	 $\left(O-(CH_2)_4-O-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C} \right)_n$	4.0
Poly(ethylene azelate), PEAz	−57.7	33.1	50,000	 $\left(O-(CH_2)_2-O-\overset{\overset{O}{\|}}{C}-(CH_2)_7-\overset{\overset{O}{\|}}{C} \right)_n$	4.5
Poly(1,6-hexamethylene adipate), PHA	−65	60	13,800	 $\left(O-(CH_2)_6-O-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C} \right)_n$	5.0
Poly(1,6-hexamethylene sebacate), PHS	−70	74	60,000	 $\left(O-(CH_2)_6-O-\overset{\overset{O}{\|}}{C}-(CH_2)_8-\overset{\overset{O}{\|}}{C} \right)_n$	7.0

(PHS). Note that T_g's of these polyesters are between −53 and −70 °C, which are quite close to that of PEO (−60 °C).

Blend samples of PEO/polyester were prepared using solvent mixing, followed by film casting. Several solvents (all HPLC grades) were tested for goodness in blending of the systems in this study, and chloroform ($CHCl_3$) was chosen. Total polymers of 4 wt% (PEO, polyester) in the solvent was dissolved and well stirred in flasks kept just below 40 °C. Solvent in polymer mixtures during film casting was first allowed to evaporate by convection under hood. Two film-casting temperatures were used: ambient (∼25 °C) and 45 °C. The two temperatures yielded similar results, but the latter temperature of film casting was found to be slightly better. The resulting films were further dried in vacuum at 40–45 °C for 72 h to drive off residual solvent.

2.2. Apparatus and procedures

2.2.1. Optical microscopy (OM)

Polarized-light microscope (Nikon Optiphot-2, POL) equipped with a charge-coupled device (CCD) digital camera, was used for observing the phase structure of as-cast blends and for monitoring phase transition of blends upon heating. Blend samples were cast as thin films (solvent cast at controlled temperatures and vacuum drying) and placed on a microscope heating stage (Linkam THMS-600 with TP-92 temperature programmer) for OM examination. Growth of spherulites in neat PEO as well as PEO/polyester blends was observed on CCD digital camera/video. The growth was directly recorded and analyzed via a CCD software package, which allowed the size of the spherulites in samples be conveniently and automatically measured/recorded at set intervals. The cast-films with the free surface (i.e., uncovered) upward were first melted on one hot stage at 90 °C for 5 min, and then were rapidly transported to the microscopic heating stage (Linkam THMS-600 with TP-92 temperature programmer) controlled at desired T_c. The purpose was to quickly bring the samples to a designated isothermal temperature.

2.2.2. Differential scanning calorimetry (DSC)

Thermal transitions of blends were characterized with a differential scanning calorimeter (DSC-7, Perkin–Elmer Corp., USA) equipped with an intracooler for quenching and cooling. Before each T_g measurements, samples were first uniformized in DSC cells (furnace and sample holders) by heating to about 80 °C and quenched to sub-ambient (−50 °C) before initiating second scans at 20 °C/min. Prior to DSC runs, the temperature and heat of transition of the instrument were calibrated with indium and zinc standards. A continuous nitrogen flow in the DSC sample cell was maintained.

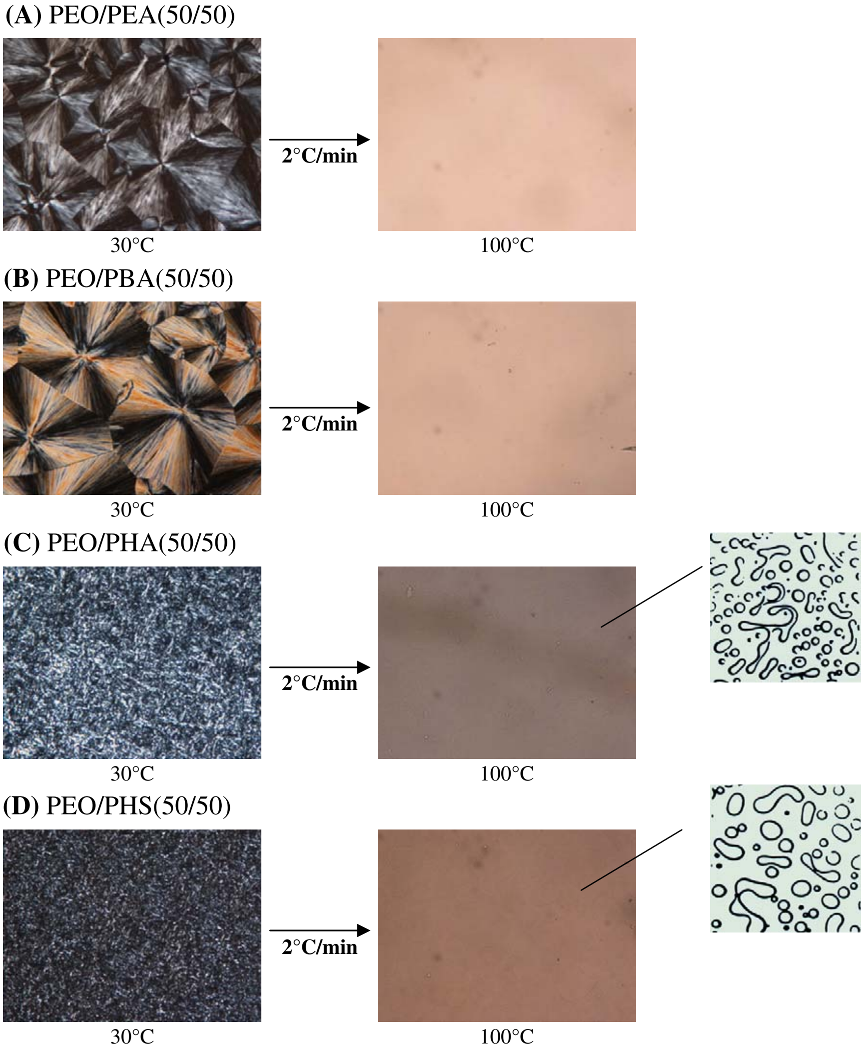
3. Results and discussion

3.1. Morphology of blends below and above melt

OM characterization was performed on all blend systems of various compositions, which were heated from ambient to above melt on a microscope heating stage (temperature programmed). Preliminary OM result revealed that some blends were visually transparent, homogeneous, and free of any heterogeneity or domains (ca. 800×), while others appeared cloudy and apparently phase separated, depending on the structures of polyesters that were blended with PEO. For brevity, only a representative blend composition of four different blend systems is shown here and discussed. Fig. 1 shows OM micrographs (at 800×) for four different blend systems: (A) PEO/PEA, (B) PEO/PBA, (C) PEO/PHA, and (D) PEO/PHS, all of the same 50/50 composition, at the crystalline and liquid states. All four blends are compared at the same (50/50) composition at two different temperatures (30 and 100 °C). The morphologies for the blends are shown at 30 °C (crystals in blends) and 100 °C (liquid above melting). The OM graphs for (A) PEO/PEA and (B) PEO/PBA at above melt clearly exhibit no discernible heterogeneity or domains in the OM resolution limit. In addition, the PEO/PPA ($CH_2/CO = 3.5$) and PEO/PEAz ($CH_2/CO = 4.5$) blends were found to be also clear and free of heterogeneous domains when held at above the melt; for brevity, their OM micrographs are not shown here. In all, blends of PEO/PEA, PEO/PPA, PEO/PBA, and PEO/PEAz appeared as clear and homogeneous liquids when held above melting. Further details of phase behavior and miscibility for these blend systems will be addressed by evidence yet to be shown and discussed in the following sections. By distinct contrast, the morphologies of some PEO/polyester blends were easily confirmed to be phase separated and immiscible when they were heated to above the crystals' melting. The OM graphs for (C) PEO/PHA ($CH_2/CO = 5$) and (D) PEO/PHS ($CH_2/CO = 7$) blends at above melting exhibit discernible heterogeneity with mix patterns of spinodal and bimodal phase separation. The result shows that blends of PEO/PHA ($CH_2/CO = 5$) and PEO/PHS ($CH_2/CO = 7$) are immiscible, which is to say that PEO is immiscible with polyesters of CH_2/CO ratios equal to or greater than 5.0.

The fact of immiscible PEO/PHA ($CH_2/CO = 5.0$) is in a reasonable comparison with the literature report [6] that PEO is immiscible with PCL ($CH_2/CO = 5.0$). Note that the chemical structure of PHA is different from PCL; however, if the CH_2/CO ratio is taken as a valid parameter representing the average of chain segment polarity of the polyesters, then there is good agreement between the results of immiscibility for the PEO/PHA blend in this study and the immiscible (or partially miscible) PEO/PCL blend as reported by Nishi et al. [6]. In all, PEO/PEA, PEO/PPA, and PEO/PBA were deemed to be miscible according to the blend T_g criteria, crystalline morphology and phase homogeneity above melt.

Reversely, the PEO/polyester blends were monitored as they were being cooled from above the melt to form crystalline domains. Blend systems of various compositions were first held at liquid state and then slowly cooled down to temperatures below the melt at 45 and 30 °C, respectively. For brevity, only a representative blend composition (50/50) of miscible PEO/PEA and immiscible PEO/PHA blend systems is shown here and discussed. Fig. 2 shows an originally homogeneous (miscible) liquid of PEO/PEA (50/50) blend at 70 °C being cooled (5 °C/min) to 30 °C. Note that for PEO/PEA



(A) PEO/PEA(50/50)

(B) PEO/PBA(50/50)

(C) PEO/PHA(50/50)

(D) PEO/PHS(50/50)

Fig. 1. OM micrographs (at 800×) for four blend systems: (A) PEO/PEA, (B) PEO/PBA, (C) PEO/PHA, and (D) PEO/PHS, all of 50/50 composition.

(50/50) blend at 30 °C, only the PEO constituent in the blend is crystallizable while PEA remains liquid. The PEO spherulites are fewer but round and larger, reflecting a homogeneous nucleation and growth. Finally, when fully crystallized, the PEO/PEA blends (50/50) below melting point are characterized with distinctly large PEO spherulites in initial stage, prior to subsequent or eventual appearance of polyester's smaller crystals occluded among the PEO lamella. The crystal–crystal phase boundary, however, is not visible in the entire crystalline morphology.

Fig. 3 shows an originally heterogeneous (immiscible) liquid of PEO/PHA (50/50) blend at 70 °C being cooled (5 °C/min) to two temperatures at 45 and 30 °C. Note that for PEO/PHA (50/50) blend at 45 °C, only the PEO constituent is crystallizable and PEO spherulites are clearly visible while the PHA constituent remains liquid. However, the crystalline domain at 45 and 30 °C for the immiscible PEO/PHA blend is completely different from that of the miscible PEO/PEA miscible blend. There are at least two major differences. Firstly, the PEO spherulites, crystallized from the phase-separated PEO/PHA blend, are more numerous but smaller; secondly, the PEO spherulites are interspersed with tiny domains of phase-separated polyester-rich phase. These polyester-rich domains and interfaces may act as extra nuclei for PEO crystallization. Both features indicate a more heterogeneous nucleation for PEO crystallization from a phase-separated liquid of PEO/PHA blend. In addition, the heterogeneous phase boundary and immiscible domains are quite apparent in the entire crystalline morphology.

More evidence for homogeneity in phase behavior and miscibility in the PEO/polyester blends would be discussed from the thermal analysis data to be discussed as following. A small glass transition difference of only ∼10 °C between PEO and most of the polyesters may make it inconclusive regarding criteria for a single T_g. Note that prior to scanning in DSC up to the temperature where T_g was identified, the quenched blends remained essentially amorphous with virtually no crystallinity. DSC traces show a single T_g in blends, although the closely spaced T_g's of these two constituent polymers might render it uncertain as evidence of phase homogeneity.

Other thermal evidence in addition to blend T_g is discussed. Fig. 4 shows T_m of (A) neat PEO and (B) PEO/PEA blend

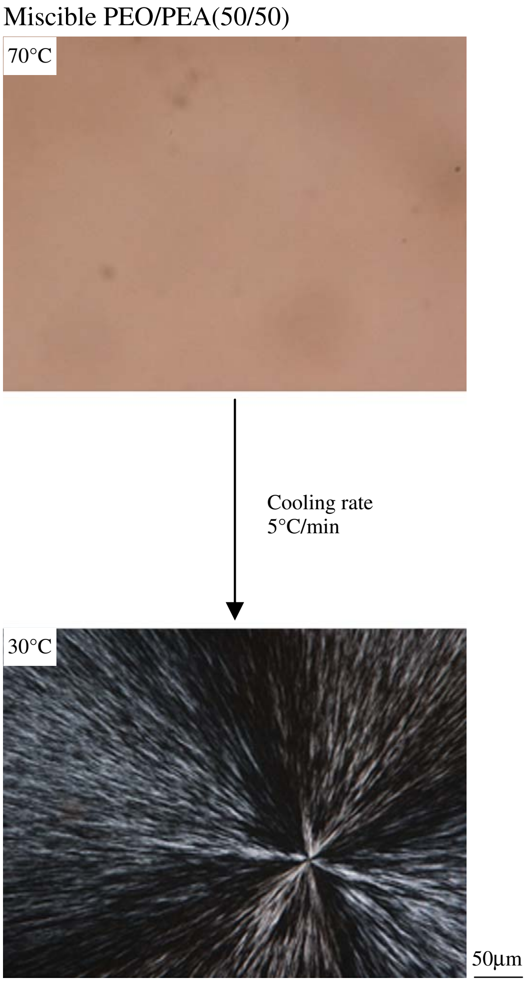


Fig. 2. Homogeneous (miscible) liquid of PEO/PEA (50/50) blend originally at 70 °C being cooled (5 °C/min) to 30 °C.

(80/20) crystallized at $T_c = 40$, 45, or 50 °C. Note two features in the figure. Firstly, PEA remains liquid at these T_c's, thus only one melting peak (PEO) is seen in the blend of two crystalline polymers; secondly, the values of T_m of either neat PEO or PEO/polyester blends change with T_c at which the polymer or blends are isothermally crystallized. When held at these T_c temperatures, PEO crystallized rather rapidly, while the polyester constituent, with lower T_m, remained as liquid. Thus, the polyester constituent could be regarded as an amorphous species in the blend that acted as a diluent in lowering the melting of the PEO crystallizing species. Thus, interactions between PEO and polyester, if any, could be estimated by depression of the equilibrium melting points of PEO in the PEO/polyester blends.

For high-molecular weight polymers with folded-chain packing, equilibrium melting points for fully extended chain conformation are usually estimated by an extrapolation approach. Equilibrium melting points for PEO in the blend could be estimated by the following relationship proposed by Hoffman and Weeks [9]:

$$T_m = \left(1 - \frac{1}{\beta}\right) T_m^0 + \frac{1}{\beta} T_c \tag{1}$$

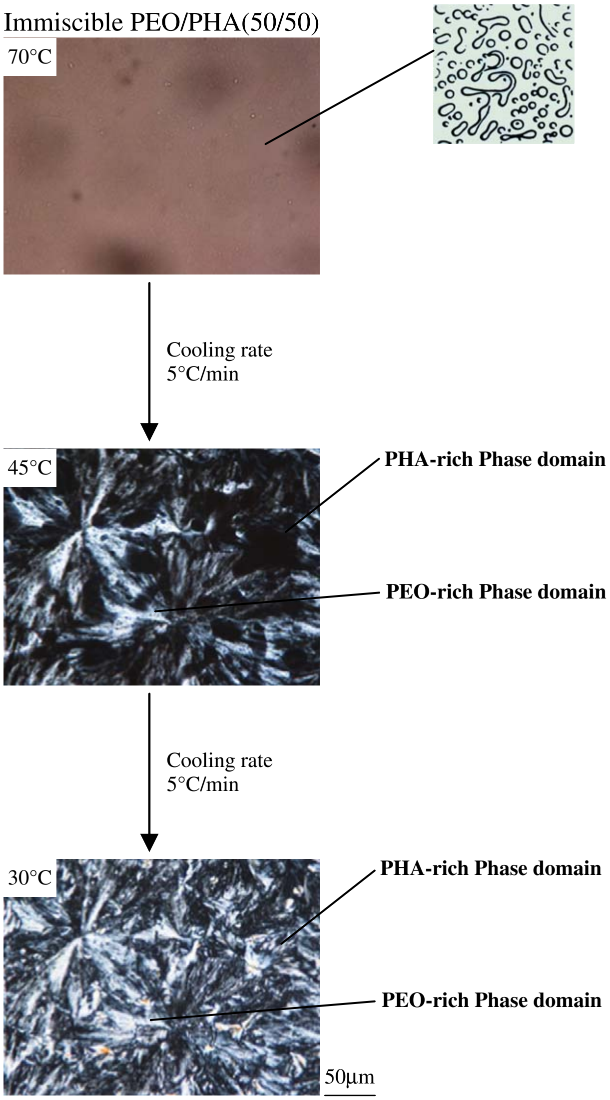


Fig. 3. Heterogeneous (immiscible) liquid of PEO/PHA (50/50) blend originally at 70 °C being cooled (5 °C/min) to 45 °C and 30 °C.

Fig. 5 shows such representative plots according to the Hoffman and Weeks relationship for (A) PEO/PEA and (B) PEO/PPA blends (three compositions) along with neat PEO. The extrapolation lines are reasonably linear for all blend compositions. The intercepts with the $T_m = T_c$ line yield the values of T_m^0 for blends. Owing to quite lengthy time needed for each data point, it was not feasible to generate a large number of points for extrapolation; however, the limited data points do fall into a reasonable straight line with negligible scattering. Similar plots were also generated and analyzed for other blend systems: PEO/PBA and PEO/PEAz, which were judged to be miscible with negative values of interaction parameters. Owing to similarity of plots, they all are not shown here. To summarize the results, Table 2 lists the numerical values of the measured equilibrium melting points for PEO and its miscible blends with PEA, PPA, PBA, and PEAz.

The intercepts at the $T_m = T_c$ lines give the equilibrium melting temperature (T_m^*) for each of the blend compositions.

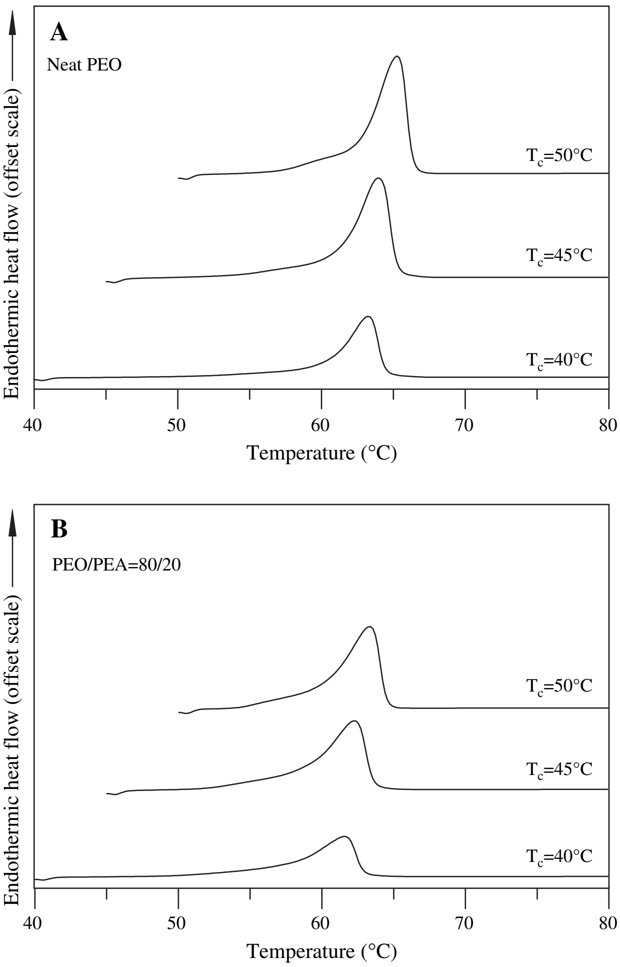


Fig. 4. T_m of (A) neat PEO and (B) PEO/PEA blend (80/20), crystallized at $T_c = 40$, 45, or 50 °C.

Table 2
List of measured equilibrium melting points of PEO and its miscible blends

Blend compositions	PEO/PEA T_m^0 (°C)	PEO/PPA T_m^0 (°C)	PEO/PBA T_m^0 (°C)	PEO/PEAz T_m^0 (°C)
100/0 (neat PEO)	68.8	68.8	68.8	68.8
95/05	67.3	67.0	68.1	67.5
90/10	66.8	66.5	67.8	67.2
80/20	66.3	65.8	67.2	66.4

Then, from the T_m^* of each blend composition, the interaction parameter (χ) between PEO and polyester was estimated from the Flory–Huggins relationship (by ignoring the entropic term contribution) [10,11]:

$$\left(\frac{1}{T_m^*} - \frac{1}{T_m^0}\right) = -\left(\frac{RV_2}{\Delta H_f V_1}\right)\left[\frac{\ln \phi_2}{n_2} + \left(\frac{1}{n_2} - \frac{1}{n_1}\right)\phi_1 + \chi\phi_1^2\right] \tag{2}$$

where χ is the Flory–Huggins interaction parameter. At the chosen T_c, only one constituent polymer (PEO), and not both was capable of crystallizing while the polyester remained liquid and amorphous. Symbols of T_m^* and T_m^0 are the equilibrium melting points of PEO in the polymer blend and neat crystallizable polymer (PEO), respectively. The subscript "1" indicates the non-crystallizing polyester, at the chosen T_c, and "2" the crystallizing polymer (PEO). V_1 and V_2 are the molar volumes of the repeat units of the non-crystallizing and crystallizing polymers, and n_1 and n_2 are degrees of polymerization of these two polymer components, respectively. The parameter of $V_1 = 132.6$, 148.7, 164.8, and 180.9 cm^3/mol for the homologous polyesters of PEA, PPA, PBA, and PEAz, respectively [12]. The value of V_2 (for PEO) is 38.9 cm^3/mol [12]. ΔH_f is the heat of fusion (melting) of the fully crystalline polymer (PEO) per mole repeat unit. The enthalpy of fusion for PEO has been reported to be $\Delta H_f = 2100$ cal/mol [13]. ϕ_1 is the volume fraction of the non-crystallizing polyester, which can be converted from the weight fractions in blends.

Fig. 6 shows a summary plot for determination of interaction parameters for four PEO/polyester blend systems, which are PEO/PEA, PEO/PPA, PEO/PBA, and PEO/PEAz, respectively. For examples, from the plot of $((1/T_m^*) - (1/T_m^0))$ vs. ϕ_1^2,

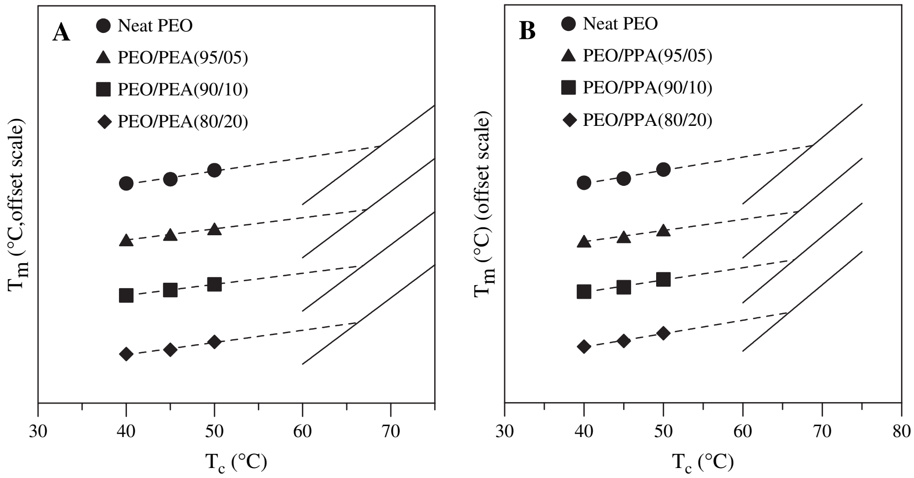


Fig. 5. Representative plots according to the Hoffman–Weeks relationship for (A) PEO/PEA blends (three compositions and neat PEO), (B) PEO/PPA blends (three compositions and neat PEO).

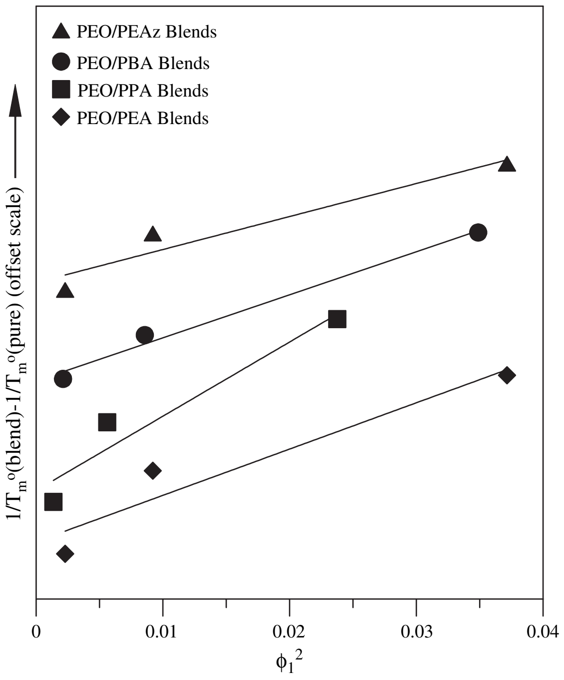


Fig. 6. Plots for determination of interaction parameters for four PEO/polyester blend systems.

a negative value of χ_{12} was obtained as -0.788 for the PEO/PEA blend, which confirmed the miscibility and favorable interactions between the constituents. One wonders quantitatively how the interactions in blends may vary with the structure of polyester that forms blends with PEO. Similar analyses were performed on PEO/PPA and PEO/PBA blends. Different, but similarly negative values were obtained for them. The interaction parameters (χ) for the PEO/PPA, PEO/PBA, and PEO/PEAz blends, respectively, were found to be -1.65, -1.06, and -0.89, by the same extrapolation and/or plotting procedures already demonstrated to the PEO/PEA blend system. The negative values of interaction parameters confirmed the miscibility and favorable interactions between the constituents in these blend systems. The values are all negative but different, which are dependent on the polyester constituent in the PEO/polyester blends.

Prior to this study, PEO was known to be miscible mainly with polyesters of greater polarity (lower average CH_2/CO ratios in repeat units), such as poly(ethylene succinate) [4]. For other polyesters with less polarity and thus lower T_g's, there was experimental difficulty that had deterred attempts for evaluating miscibility of blend of PEO with the polyesters of lesser polarity, owing to proximity or overlap of T_g's of the PEO and polyesters. But this study has taken novel approaches to overcome the difficulty, leading to discovery of yet more miscible PEO/polyester blends and further widening up the range of polyesters of intermediate polarity that may become miscible with PEO. Furthermore, by summarizing the results from this study and those from the literature, PEO is miscible with aliphatic polyesters whose main-chain segment has CH_2/CO ratio between 2.0 and 4.5. By comparison, polyesters of low polarity (with CH_2/CO ratio equal or larger than 5.0) apparently are immiscible with PEO; partially miscible or immiscible PEO/polyester blend systems are demonstrated by the apparent phase-separated morphology seen in PEO/PHA ($CH_2/CO = 5.0$) and PEO/PHS ($CH_2/CO = 7.0$) blends.

It is clear that there is a trend of variation, depending on the polyester's structure, in the values of interaction strengths for these blends. Fig. 7 shows interaction parameters (χ) or energy densities (B) plotted as a function of CH_2/CO ratio (in polyester's repeat unit) for blends of PEO with the homologous polyesters (PEA, PPA, PBA, PEAz). The plot shows that a maximum (i.e., the greatest negative value) of interaction strength in blends is located at blend of PEO/PPA ($CH_2/CO = 3.5$). One may wonder about the effect of the relative low molecular weight of PPA on the estimated value of interaction strength, especially for the PEO/PPA blend. From Eq. (2), it is apparent that the slope of the straight line yields the value of χ parameter by plotting the left-hand term vs. ϕ_1^2. The two other terms in the bracket (related to entropic contribution) only contribute to slight non-linearity of the line and a non-origin intercept on y-axis. Thus, the values of the interaction parameter so estimated were little influenced by the entropic contribution. However, in Fig. 7, to show possible uncertainty of the contribution of low-molecular weight effect, an error bound is shown on the data point of the PEO/PPA ($CH_2/CO = 3.5$) blend. The upper bound of the respective curves shows the possible error range of the interaction strength caused by the low molecular weight of PPA, in comparison to those of other polyesters, used in this study.

With either increase or decrease of CH_2/CO ratio away from 3.5 in the polyester's structure, the interaction strength between the PEO and polyester in the blends decreases. Note in the plot, the interaction parameters (filled triangle) for the PEO/PBSu ($CH_2/CO = 3.0$) blend were estimated

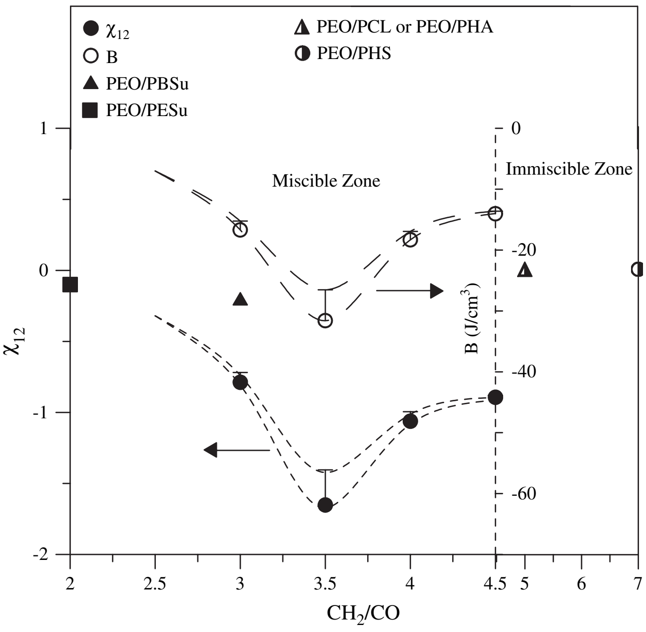


Fig. 7. Interaction parameters (χ) or energy densities (B) plotted as a function of CH_2/CO ratio (in polyester's repeat unit) for blends of PEO with the homologous polyesters (PEA, PPA, PBA, PEAz).

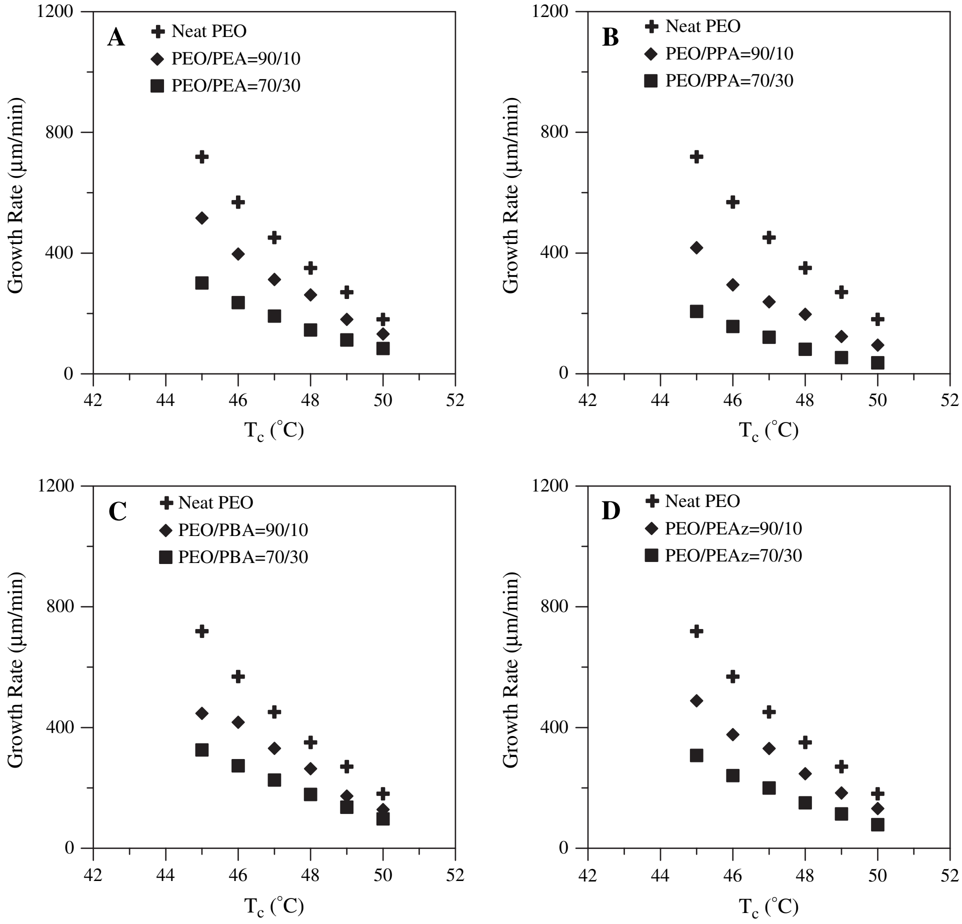


Fig. 8. Spherulite growth rates (i.e., slopes taken from plots of radius as functions of time) as functions of T_c between 46 and 50 °C for four miscible PEO/polyester blend systems: (A) PEO/PEA, (B) PEO/PPA, (C) PEO/PBA, and (D) PEO/PEAz.

and calculated from the melting point data of PBSu (which is the higher-melting crystal species) in the blends that Nishi et al. have reported in the literature [5]. In this study, however, the melting point data of PEO (higher-melting crystal species) in the PEO/PEA blend were used for the estimation of the interaction strength. Nevertheless, both PEO/PBSu and PEO/PEA blends yielded negative values of interaction parameter, indicating a state of blend miscibility in both blends. Ultimately, the polyesters with $CH_2/CO = 1.0$ or equal to 5.0 become either partially miscible or fully immiscible with PEO. By varying the CH_2/CO ratio in polyester's structure, the overall polarity of the polymer chains changes accordingly. The literature contains abundant reports that document similar trend of variation of interaction strength in a series of miscible blends comprising an amorphous polymer [such as poly(vinyl chloride), phenoxy, or poly(vinyl *p*-phenol)] and a polyester whose structure is varied systematically by the average CH_2/CO ratio [14–17].

3.2. Spherulite growth in miscible crystalline/crystalline blends

Growth kinetics of PEO spherulites in blends were expected to be influenced by the interaction strength between PEO and polyesters. Fig. 8 shows spherulite growth rates (i.e., slopes taken from plots of radius as functions of time) as functions of T_c between 46 and 50 °C for four miscible PEO/polyester blend systems: (A) PEO/PEA, (B) PEO/PPA, (C) PEO/PBA, and (D) PEO/PEAz. In each diagram, data for three blend compositions (neat PEO, blends of PEO/polyester = 90/10 and 70/30) are plotted as three individual curves. The comparison in this figure clearly shows that the growth rates are functions of not only T_c but also types of miscible blends, whose two constituents may interact with different strengths.

The growth rates of these miscible PEO/polyester blends apparently are influenced by the type (or structure) of polyester that forms a blend with PEO. The growth rates at three T_c's were compared with respect to the structure of polymers. The objective was to clearly identify the trend of variation of spherulite growth rates that might be influenced by the intermolecular interaction strengths between PEO and polyesters. Fig. 9A and B shows spherulite growth rates of PEO/polyester blends as a function of CH_2/CO ratio (in polyester repeat unit) at $T_c = 45$, 47, or 50 °C, respectively. Fig. 9A shows plots for the PEO/polyester blends of a fixed 90/10 composition. A minimum of the spherulite growth rates is clearly seen at $CH_2/CO = 3.5$, regardless of $T_c = 45$, 47, or 50 °C. Similarly, Fig. 9B shows plots of spherulite growth rates of the

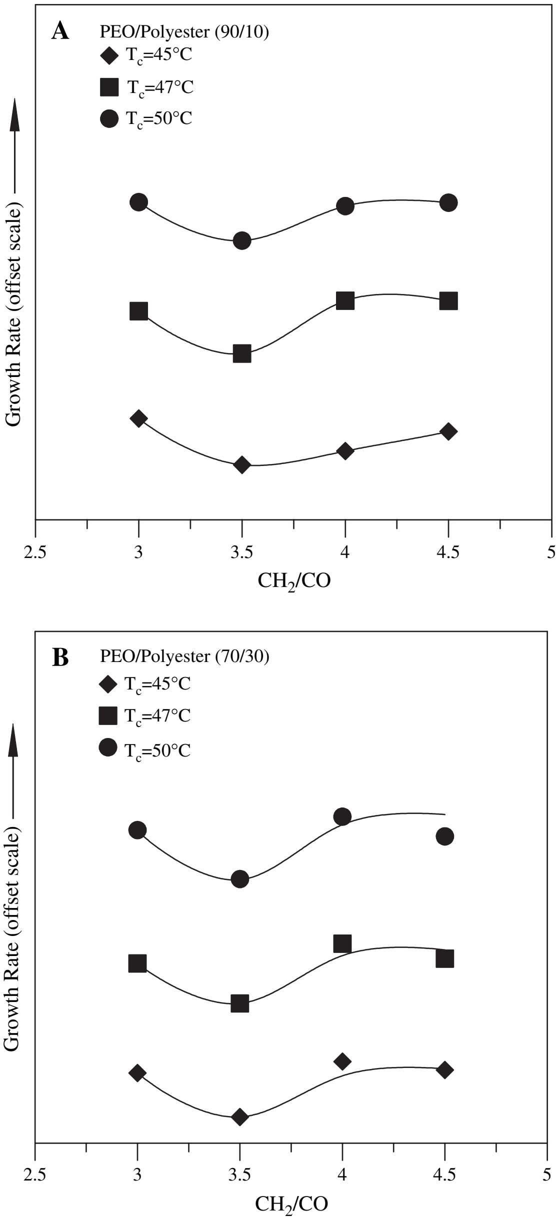


Fig. 9. Spherulite growth rates of PEO/polyester blends of two compositions: (A) 90/10 and (B) 70/30, as a function of CH_2/CO ratio at $T_c = 45$, 47, or 50 °C.

PEO/polyester blends of another fixed composition of 70/30 (weight ratio). Again, for this blend composition, a minimum of the spherulite growth rates is clearly seen at $CH_2/CO = 3.5$, regardless of $T_c = 45$, 47, or 50 °C. That is, regardless of the PEO/polyester blend compositions, the minimum in the growth rates occurs at or near polyester structural parameter of $CH_2/CO = 3.5$. The polyester structural parameter at which the minimum of spherulite growth rate is located coincides with the greatest negative values of χ shown in Fig. 7 obtained from thermal analyses data and Flory–Huggins analysis.

Di Lorenzo [18], in a review article, has discussed various main factors of miscibility that contribute to increase or decrease the growth rate of spherulites in blends comprising at least one crystalline constituent. It is reasoned that the interactions that are often established between two constituents in miscible blends can also contribute to slowing down of the rate of crystallizing species being drawn into (or diffusing to) the crystals. PEO is known to be miscible with amorphous poly(methyl methacrylate) and poly(vinyl acetate), via weak interactions between the two constituent polymers [19,20]. By comparing the spherulite growth rate (*G*), at the same T_c and composition, of PEO in blends with PMMA or PVAc (with similarly weak interactions), *G* is lower in the blend containing the amorphous polymer of higher T_g (i.e., PMMA), suggesting that chain mobility is a factor [18]. However, when the amorphous polymer diluent forms strong or specific interactions with PEO, the spherulite growth rate is more significantly reduced; and such a phenomenon is demonstrated in blends of PEO with a random copolymer of ethylene (45%) and methacrylic acid (55%) or in blends of PEO with a random copolymer of styrene (50%) and *p*-hydroxystyrene (50%) [21–24]. When the interactions are equally strong, then the polymer's higher T_g produces a greater reduction in *G*. Effect of chain mobility on crystallization kinetics of polymers has also been discussed by Inoue et al. [25].

To summarize the discussion, the spherulite growth result was based on the analysis of the crystalline spherulite domains which were being packed from liquid mixtures of PEO and polyester. By comparison, the values of intermolecular interactions (χ) were obtained from crystal's equilibrium melting between PEO crystal and polyester in liquid mixtures of PEO and polyester. The coincidence and agreement between the results of spherulite growth rates and the results of intermolecular interactions (χ) suggest that the structural factors governing the interactions between PEO and polyester are likely applicable to influence the growth rates in the blends. Note that all polyesters of CH_2/CO between 3.0 and 4.5 possess similar values of T_g differing only slightly. Thus, influence of blend's T_g and chain mobility/rigidity on the spherulite growth rate (*G*) in the PEO/polyester blends can be regarded as negligible; rather, it is the interaction strength between PEO and polyester that determines the relative magnitudes of the spherulite growth rate. Apparently, the interaction strengths estimated from the blend melting points correlate quite well with the spherulite growth rates of the corresponding blend systems.

4. Conclusion

By overcoming the experimental difficulty in assessing the phase behavior of two crystalline polymers with closely spaced T_g's, this work has further extended the range of polyesters that can be miscible with PEO. The interaction parameters (χ_{12}) for miscible blends of PEO with polyesters [poly(ethylene adipate), poly(propylene adipate), poly(butylene adipate), and poly(ethylene azelate) with $CH_2/CO = 3.0–4.5$] are all negative but the values vary with the polyester structures, with a maximum for the blend of PEO/poly(propylene adipate) ($CH_2/CO = 3.5$). Furthermore, the values of interaction strength are apparently dependent on the structures of the polyester constituent in the blends; and miscibility and interaction strength for the miscible PEO/polyester systems correlate in the same trend with the PEO crystal growth rates in the blends. Apparently, the interactions' strength estimated from the blend melting points correlates quite well with the spherulite growth rate of the corresponding PEO/polyester blend systems. Coincidence and agreement between the results of the spherulite growth rates and intermolecular interaction strength (χ) suggest that the structural factors governing the interactions between PEO and polyester are likely applicable to influence the growth rates in the blends. All polyesters of CH_2/CO between 3.0 and 4.5 possess similar values of T_g that differ only slightly. Thus, influence of blend's T_g and chain mobility/rigidity on the spherulite growth rate (G) in the PEO/polyester blends can be regarded as negligible; rather, it is the interaction strength between PEO and polyester that determines the relative magnitude of spherulite growth rate.

Acknowledgment

This work was financially supported by a basic research grant (NSC-94 2216 E006 003) in three consecutive years from *National Science Council* (NSC) of Taiwan.

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