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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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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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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.

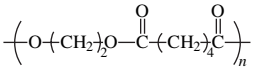
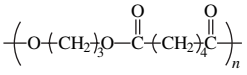
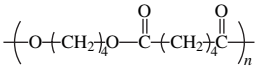
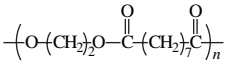
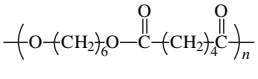
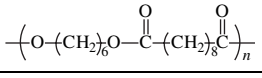
The above cited examples clearly indicate that a change in the structures of either polyethers or polyesters can lead to corresponding change in the phase behavior of the blends comprising the polyethers and polyesters. But the list of possible miscible blends involving polyethers and polyesters might 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, $T_g = -60$ °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		3.0
Poly(1,3-propylene adipate), PPA	−69	38	3800		3.5
Poly(1,4-butylene adipate), PBA	−62.2	56	12,000		4.0
Poly(ethylene azelate), PEAz	−57.7	33.1	50,000		4.5
Poly(1,6-hexamethylene adipate), PHA	−65	60	13,800		5.0
Poly(1,6-hexamethylene sebacate), PHS	−70	74	60,000		7.0