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A completely miscible ternary blend system of poly(3-hydroxybutyrate), poly(ethylene oxide) and polyepichlorohydrin

S.H. Goh*, X. Ni

Department of Chemistry, National University of Singapore, Singapore 119260, Singapore

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Abstract

The miscibility of a ternary system of poly(3-hydroxybutyrate), poly(ethylene oxide) and polyepichlorohydrin was studied by differential scanning calorimetry. The three binary blend systems are individually miscible. All the ternary blends were found to be miscible as shown by the existence of a single glass transition temperature in each blend. The interaction parameters of the three binary pairs are of similar magnitude and do not lead to a "$\Delta\chi$" effect. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The addition of a suitable polymer to an immiscible binary polymer blend provides a simple means of compatibilization. A classic example is the ternary poly(methyl methacrylate) (PMMA)/poly(ethyl methacrylate) (PEMA)/poly(vinylidene fluoride) (PVDF) blend system [1]. While PMMA and PEMA are immiscible with each other, the addition of a suitable amount of PVDF leads to a miscible ternary blend since PVDF is miscible with both PMMA and PEMA.

The miscibility of ternary polymer blends comprising three miscible binary pairs has also been studied. Depending on the interaction parameters of the three binary pairs, the ternary blend system may be completely miscible [2–10] or may show the existence of an immiscibility loop [8,11–14].

Poly(3-hydroxybutyrate) (PHB) is a biodegradable polymer. However, the commercial exploitation of PHB has been hampered by its high cost, brittleness and narrow processability window [15,16]. To overcome these disadvantages, PHB has been blended with other polymers. PHB is miscible with poly(ethylene oxide) (PEO) [17], poly(vinyl acetate) [18], polyepichlorohydrin (PECH) [19,20], poly(vinylidene fluoride-co-acrylonitrile) [21] and poly(*p*-vinylphenol) [22,23]. However, ternary blend systems involving PHB have received scant attention. The miscibility of PHB/PEO/PMMA ternary blends has been studied [24]. PEO is miscible with both PHB and PMMA, but PHB is immiscible with PMMA. The four ternary PHB/PMMA/PEO blends studied by Yoon et al. [24] were all found to be immiscible. Since PECH is miscible with PEO [2], the ternary blend system PHB/PECH/PEO consists of three miscible binary pairs. It is of interest to study if this system is completely miscible or it shows the existence of an immiscibility loop.

2. Experimental

PHB of bacterial origin was obtained from Aldrich Chemical Company, Milwaukee, USA.; it was dissolved in chloroform, filtered to remove cell wall residues and then precipitated into methanol. The number- and weight-average molecular weights of purified PHB are 87 and 230 kg mol^{-1}, respectively, as determined by gel permeation chromatography. PECH with a reported weight-average molecular weight (M_w) of 700 kg mol^{-1} and PEO with a reported M_w of 100 kg mol^{-1} were also obtained from Aldrich, and they were used as received.

Ternary blends of varying compositions were prepared by solution casting from chloroform. After the solvent was evaporated slowly at room temperature, the blends were dried in vacuo at 50°C for 1 week.

Differential scanning calorimetric measurements were conducted on a TA Instruments 2920 differential scanning calorimeter. The instrument was calibrated with an indium sample and a nitrogen atmosphere was used. Each sample was first heated to 200°C and was kept at that temperature

* Corresponding author. Fax: + 65-7791691.
E-mail address: chmgohsh@nus.edu.sg (S.H. Goh)

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Table 1
Characteristics of ternary polymer blends

Weight ratio of PHB/PECH/PEO	Experimental T_g (°C)	Calculated T_g (°C)	T_m of PEO (°C)	T_m of PHB (°C)
10/20/70	− 45	− 53	63	171
10/45/45	− 34	− 42	60	171
10/70/20	− 32	− 31	57	170
20/20/60	− 38	− 45	61	171
20/40/40	− 34	− 36	60	171
20/60/20	− 31	− 27	59	170
30/20/50	− 37	− 37	61	172
30/35/35	− 34	− 30	61	172
30/50/20	− 28	− 24	59	172
40/15/45	− 30	− 31	61	172
40/30/30	− 21	− 25	59	171
40/45/15	− 25	− 18	59	171
50/10/40	− 28	− 26	61	172
50/25/25	− 15	− 19	58	170
50/40/10	− 11	− 12	59	171
60/20/20	− 11	− 13	59	172
70/15/15	− 8	− 7	57	172
80/10/10	− 4	− 2	58	172

for one minute. The sample was then rapidly quenched to −100°C. The quenched sample was scanned to 200°C with a heating rate of 20°C min^{-1}. The initial onset of the change of slope of the D.S.C. curve was taken as the glass transition temperature (T_g) and the temperature of the melting peak was taken as the melting point (T_m).

3. Results and discussion

Eighteen ternary blends of varying compositions were prepared and examined. D.S.C. measurements showed the existence of a melting point near 60°C for PEO, a melting point near 170°C for PHB and a composition-dependent T_g for each blend (Table 1). The T_g values of the blends agree quite well the those weight-average values calculated from the equation

$$T_g = \sum (w_i T_{gi})$$

where w_i and T_{gi} are the weight fraction and T_g of polymer i in the blend, respectively. The T_g values of PHB, PEO and PECH are 10, −75 and −25°C, respectively. Moreover, all the blends became transparent when heated above the melting point of PHB. Transparency of a polymer blend can be taken as an indication of miscibility if the difference in refractive indices of the polymers is more than 0.01 [25]. The refractive indices of PHB, PEO and PECH are estimated to be 1.464, 1.463 and 1.498, respectively, using the Vogel method [26]. The estimated refractive index of PEO agrees well with the literature value of 1.4648 [27]. Since the refractive index of PECH is substantially larger than those of PEO and PHB, the transparency of the ternary blends is a good indication of miscibility. Based on the transparency of the melt and the single-T_g criterion, all the ternary blends are miscible. Thus, the PHB/PEO/PECH system is a completely miscible ternary blend system.

It is well known that for a ternary polymer 1/polymer 2/solvent system in which the two polymers are soluble in the solvent, an immiscibility loop may exist if the two binary polymer/solvent interaction parameters are sufficiently different, the so-called "$\Delta\chi$" effect [28,29]. Similarly, a ternary polymer system consisting of three miscible binary pairs may not be completely miscible especially when there is an asymmetry in the binary interaction parameters. For example, the three binary interaction parameters for the ternary PMMA/PEO/phenoxy system are −0.35, −0.61 and −1.90 for $\chi_{PMMA/PEO}$, $\chi_{PMMA/phenoxy}$ and $\chi_{PEO/phenoxy}$, respectively [14]. One of the interaction parameters is much more negative than the other two. Such an asymmetry leads to the development of an immiscibility loop in the PMMA/PEO/phenoxy system [14].

For the ternary PHB/PEO/PECH system, $\chi_{PHB/PECH}$ and $\chi_{PHB/PEO}$ are −0.068 [19] and −0.096 [17], respectively. The interaction energy density (B) for PECH/PEO blends is −3.93 J cm^{-3} [2]. Since $\chi = BV_1/RT_m^\circ$, $\chi_{PECH/PEO}$ is calculated to be −0.092 using the equilibrium melting point (T_m°) of 76°C for PEO [2] and the molar volume (V_1) of 68.03 cm^3 mol^{-1} for PECH [30]. All the three binary interaction parameters are negative as expected for miscible blend systems. Moreover, the three interaction parameters are of similar magnitude and thereby the $\Delta\chi$ effect does not arise. As a result, an immiscibility loop is not expected for the PHB/PEO/PECH system. It is worthwhile to note that for a ternary blend system involving a self-associable polymer that are capable of interacting with the other two polymers via hydrogen-bonding interactions, the difference between the inter-association equilibrium constants plays an important role on the phase behavior of the system [8,31].

In summary, the ternary PHB/PEO/PECH blend system is a completely miscible system as shown by the existence of a single T_g in each of the blend.

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