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Miscibility of biodegradable synthetic aliphatic polyester and poly(epichlorohydrin) blends

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Abstract

Miscibility and thermal behavior of blends of synthetic biodegradable aliphatic polyester (BDP) with poly(epichlorohydrin) (PECH) were investigated by both differential scanning calorimetry and a dynamic mechanical thermal analyzer. Single glass transition temperatures in agreement with the Fox equation indicate that these blend mixtures are miscible. This was further clarified from the cryogenically fractured surface of BDP–PECH blends by scanning electron microscopy. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Biodegradable aliphatic polyester; Miscibility; Blend

1. Introduction

As possible candidates to reduce pollution problems caused by plastic wastes, various biodegradable polymers have been extensively investigated [1]. Much attention has been placed on a bacterial aliphatic polymer produced by various types of micro-organisms such as poly(hydroxybutylate) (PHB) [1,2], since PHB is known to be completely biodegradable and known to have good mechanical properties. Application of this polymer, however, is limited due to its high cost. Therefore, by blending this biodegradable material with conventional thermoplastics, low-cost materials with improved properties may possibly be produced. PHB has been found to be miscible with polymers such as poly (ethylene oxide) [3–7], poly(epichlorohydrin) (PECH) [8], poly(vinyl acetate) [9], poly(vinylidene fluoride) [10] and poly(ϵ-caprolactone) [11]. Yoon et al. [12] studied miscibility of PHB in both PEO and poly(methyl methacrylate) (PMMA) using a vapor sorption technique. Polymer–polymer interaction parameters obtained by this technique were found to be negative for PHB–PEO and positive for PHB–PMMA systems. Choi et al. [6] also investigated the rheological properties of PHB blended with PEO and found that an 80:20, by weight, PHB–PEO blending ratio exhibits higher values of rheological properties than those of pure PHB. In addition, the PHB–PECH blend was observed to have a single glass transition temperature (T_g) in agreement with the Fox equation and depression of the equilibrium melting temperature (T_m^0) [8,13].

On the other hand, synthetic biodegradable aliphatic polyesters (BDP), which are usually synthesized from diol and dicarboxylic acid through condensation polymerization [1,14,15] are also known to be completely biodegradable in the environment; and are thereby known to be some of the effective packing materials that can alleviate environmental pollution. However, they possess some difficulties for application because of their low melting temperature, weak thermal stability, and low molecular weight.

Recently, synthetic BDP with high melting points and excellent mechanical strength have been developed [15]. BDP made from a polycondensation reaction of aliphatic dicarboxylic acids with aliphatic diols is an aliphatic polyester that is degraded into water and carbon dioxide by microorganisms. It is degraded biologically in soil, fresh water, and seawater while being stable in the atmosphere. In addition, BDP in our study is known to have similar physical properties to those of polyethylene and polypropylene. Even though it can compete with PHB in cost, applications of this polymer are still limited due to its higher cost in comparison with conventional polymers. Therefore, various blend studies are needed. However, little work has been done on the miscible blend systems with synthetic aliphatic polyesters. Choi et al. [7] measured miscibility behavior and rheological properties with mechanical spectroscopy studies

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Table 1
Polymers used in our study

Polymer	Name	Manufacturer	Molecular weight
Poly(epichlorohydrin)	PECH	Scientific polymer products	$M_w = 700\,000$ $M_n = 15\,000^a$
Skygreen 2109	BDP	SKI	$M_w = 60\,000^a$

[a] GPC in chloroform at 44°C.

of blends of BDP and linear low density polyethylene and found that the blend system was immiscible, showing two separate T_g values in all compositions.

Here, we investigate the miscibility of BDP with an uncrystallizable, rubbery PECH, which is a homopolymer of epichlorohydrin. It is a useful rubber that has excellent resistance to ozone, oils, heat and weathering, and also has very low gas permeability. PECH was used for the PHB blend. A single T_g was observed intermediate to PHB and PECH, and decreased with the increase in PECH content [8].

2. Experimental

The synthetic BDP used in this study, supplied from SKI in Korea, was the copolymer obtained from the polycondensation reaction of aliphatic glycols (ethylene glycol and 1,4-butanediol) and aliphatic dicarboxylic acids (succinic acid and adipic acid). Poly(epichlorohydrin) (PECH) sample was provided by Scientific Polymer Products, Inc., USA. Information on both BDP and PECH is given in Table 1.

A solution blending technique was adopted using dichloromethane as a cosolvent. A BDP–PECH solution in dichloromethane was initially blended by stirring for 24 h at room temperature. It was then dried under vacuum at 50°C until it reached constant weight. Blends with weights ratios of 100:0, 90:10, 80:20, 70:30 and 60:40 BDP–PECH were prepared. Each sample was used to make a film using a hot press at 150°C.

The T_g of each blend was obtained from both differential scanning calorimetry (DSC) (Perkin–Elmer DSC 7) and a dynamic mechanical thermal analyzer (DMTA) (Rheometric Scientific). At first the blended films obtained by casting were heated from 30 to 100°C at a rate of 10°C/min and then held at 100°C for 2 min (run I). The samples were then quenched in liquid nitrogen, taken from melt state to −100°C. Finally, after about 2 min at −100°C, the temperature was raised to 150°C by using a scan rate of 10°C/min (run II). For non-isothermal crystallization behavior of BDP–PECH, we cooled the samples from 150 to 0°C at a decreasing rate of 10°C/min. For the DMTA test, a film of polymer samples (0.7 cm × 2 cm × 0.05 cm) was clamped in a frame and subjected to three-point bending. We applied a frequency of 1 Hz and a heating rate of 3°C/min from −100 to 50°C, using a tension mode. The variation of the storage moduli, loss moduli and tan δ was then recorded. In addition, the degree of dispersion and phase separation between domains were investigated using scanning electron microscopy (SEM) (GS130) with 1000 ×

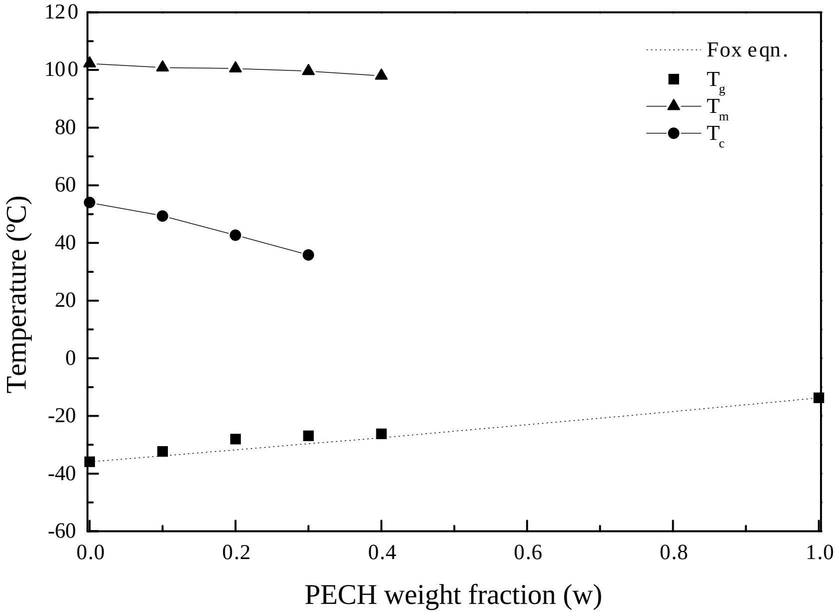


Fig. 1. T_g, T_m and T_c of BDP–PECH blends from DSC measurements.

Table 2
Thermal properties of BDP–PECH blends

BDP–PECH	T_g (°C)	T_g width (°C)	ΔC_p (kJ/kg °C)	T_m (°C)	ΔH_f (kJ/kg)	T_m (°C)	ΔH_c (kJ/kg)
100:0	− 35.9	7.94	0.264	102.2	37.06	54.0	44.52
90:10	− 32.3	7.22	0.263	100.8	36.52	49.4	42.82
80:20	− 28.0	6.98	0.345	100.5	33.64	42.7	33.22
70:30	− 26.9	9.02	0.395	99.6	29.63	35.9	24.10
60:40	− 26.2	2.58	0.310	98.0	22.00	–	–
0:100	− 13.7	3.85	0.439	–	–	–	–

magnification at 25 kV. SEM micrographs were taken in the liquid nitrogen fractured surface of the specimens. After drying, the sample was immersed in tetrahydrofuran (THF) for 3 h in order to observe PECH domains easily, since PECH is soluble in THF.

3. Results and discussion

A single T_g was observed for all BDP–PECH blend ratios from DSC. The dependence of T_g (on blend ratio) from DSC is illustrated in Fig. 1. The dotted line was calculated using the Fox equation [16], given in Eq. (1).

$$\frac{1}{T_g(w)} = \frac{1-w}{T_g(0)} + \frac{w}{T_g(1)} \tag{1}$$

where $T_g(w)$ is the glass transition temperature of the blend, $T_g(0)$ and $T_g(1)$ are those of pure BDP and PECH, respectively, and w is the weight fraction of PECH. Note that Fig. 1 shows excellent agreement between the experimental and theoretical (dotted line) values, indicating that BDP and PECH are miscible. Although these blend systems have a difference of only 22.2°C for T_g of each homopolymer as given in Table 2, they have a sharp slope (ΔC_p) of T_g and narrow T_g widths. This finding strongly suggests that BDP–PECH blend systems which we investigated are compatible in the melt and amorphous state. In the case of the PHB–PECH blend, single T_g decreases from 5 to −20°C with the increase in w [8].

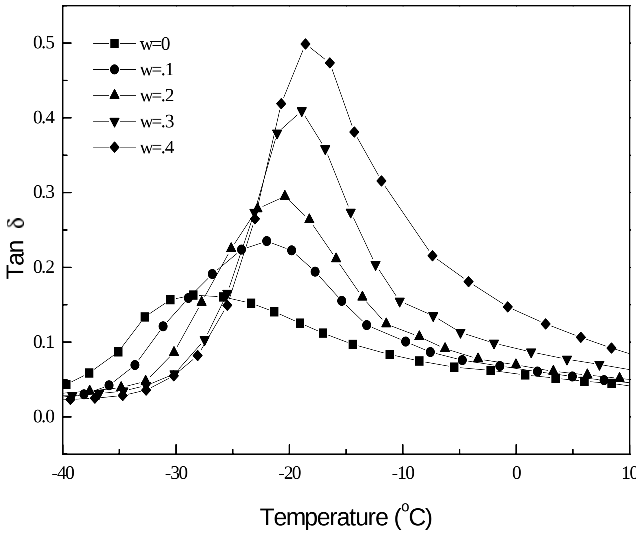


Fig. 2. Tan δ versus temperature for BDP–PECH blend from DMTA measurements.

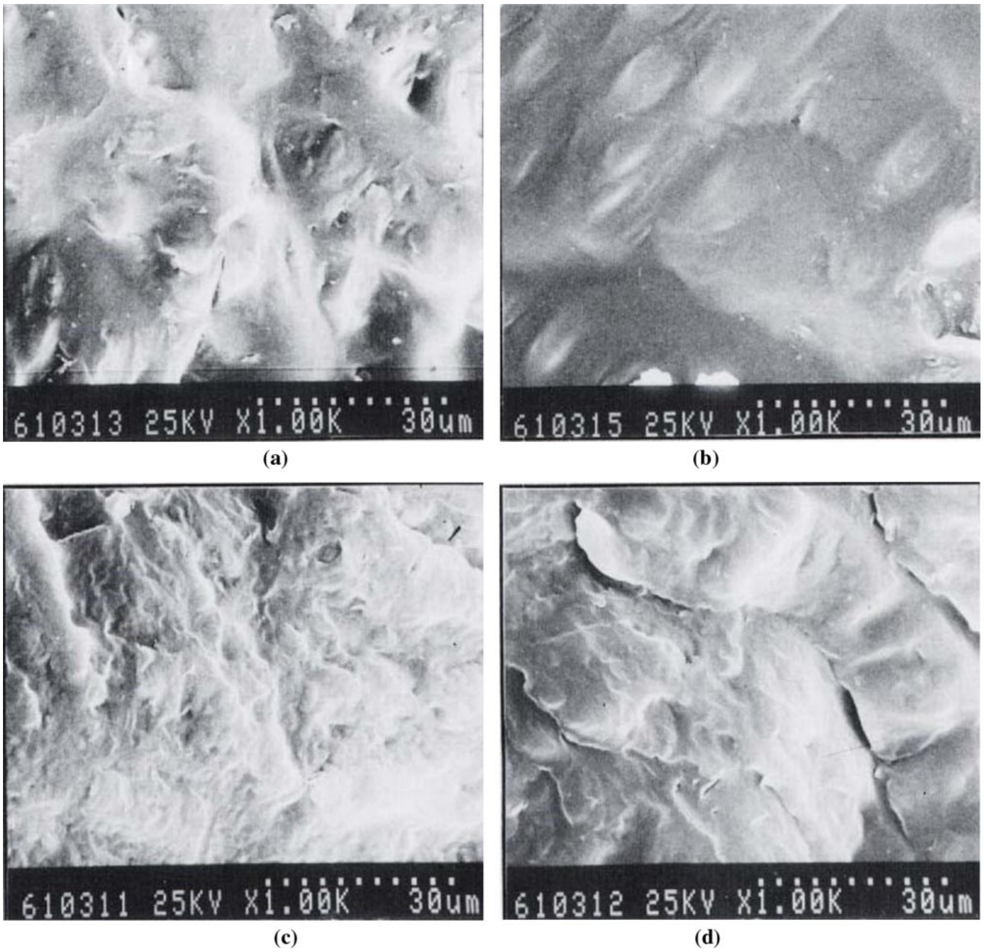
We also found that the non-isothermal crystallization peak temperature (T_c) and heat of crystallization (ΔH_c) of the two polymers is sharply depressed with increasing w in the blends. Furthermore, the BDP–PECH blend with $w \geq 0.4$ did not show a crystallization exotherm. Similar results were found by Avella et al. [3–5] in the PHB–PEO blends. This result implies that crystallization of BDP in the blend becomes progressively more difficult with increasing PECH content, supporting the idea that BDP is miscible with PECH in the melt. It is also related to the depression of the spherulite growth rate due to the mutual dilution effect of the two polymers. In addition, it was observed that the addition of PECH causes a slight depression in the T_m and ΔH_f of BDP in the blend. The T_m depression is a common phenomenon for the miscible blends containing one crystallizable component [8].

In addition, in order to examine the miscibility of each blend system using different test methods, we also measured T_g of the blends using DMTA. T_g was evaluated at the point where tan δ from the DMTA exhibits a maximum. As shown in Fig. 2, T_g of blends have single peaks, which are dependent on composition. These results strongly suggest that polymers of each blend are miscible.

SEM micrographs of the fractured surface of the BDP–PECH blends are shown in Fig. 3. If this system were phase-separated, the PECH phase could be preferentially etched with THF solvent, while the BDP phase remained unaffected. For all compositions of blends, this system appears as the homogeneous phase. It thereby clarifies the result of the single T_g, which means our blend systems are miscible.

In addition, even though the biodegradability of the BDP–PECH blends was not investigated in this study, the previous study on biodegradation of PHB–PECH blends by Sadocco et al. [9] might be useful to figure out how the addition of the PECH affects the biodegradability of our blend systems. They reported that the biodegradation rate decreased with increasing a PECH content in the blend [9], up to films containing 60% (w/w) PECH, at which biodegradation was completely inhibited.

In conclusion, we examined the miscibility of the blend of biodegradable synthetic BDP with PECH. From the DSC



(a) (b) (c) (d)

Fig. 3. SEM of fractured surfaces for BDP–PECH blends etched with THF: (a) 90:10; (b) 80:20; (c) 70:30; (d) 60:40.

experiments, we observed a single T_g with good agreement between the experimental and theoretical values (Eq. (1)) for both blend systems. The single T_g of the blends suggests that BDP and PECH form miscible blends in the whole composition range in the melt. In addition, T_c of BDP–PECH blends was found to be sharply depressed by the presence of the second component, even though T_m of those was slightly depressed.

Such a result indicates that PECH is able to act as a diluent for BDP and the two polymers are compatible in the melt phase. Furthermore, T_g with a single peak is found to be dependent on the composition from DMTA measurements. Corresponding to the T_g data, SEM observations reveal that each blend has no dispersed phase and is homogeneous. From the thermal analysis and morphological studies, we strongly suggest that polymers of each blend are miscible.

Acknowledgements

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