

Miscibility of Biodegradable Aliphatic Polyester and Poly(vinyl acetate) Blends

TAE K. SHIN,¹ JINHO KIM,¹ HYOUNG J. CHOI,¹ MYUNG S. JHON²

¹ Department of Polymer Science and Engineering, Inha University, Incheon, 402-751, Korea

² Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, USA

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ABSTRACT: We report miscibility behavior for synthetic biodegradable aliphatic polyester (BDP) and poly(vinyl acetate) (PVAc) blends by investigating their thermal, rheological, and mechanical properties. Two separate glass transition temperature peaks for the BDP/PVAc blends proved that these blend systems are immiscible. From the rheological measurement, the shear viscosity as a function of shear rate is observed to increase with increasing PVAc content in BDP/PVAc blends, since PVAc has a relatively high molecular weight compared to BDP. Moreover, BDP blends with 10 wt % PVAc have excellent mechanical properties. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1348–1352, 2000

Key words: biodegradable aliphatic polyester; miscibility; poly(vinyl acetate); mechanical property; rheological property; biodegradable polymer

INTRODUCTION

Synthetic polymers generally possess many advantages, including well-balanced supply, low cost, manufacturing easiness, and good processability, and these properties have led to useful applications of polymers from cheap daily necessities to expensive industrial composites and advanced medical materials. However, these polymers, generally obtained from the petrochemical industry, have a low recovery rate and low reproduction, and are nonbiodegradable. Most plastics cause pollution and even cause direct damage to the human body. These problems can be reduced by increased incineration and recycling, and by using biodegradable polymers.

Various biodegradable polymers have been extensively investigated,¹ including poly(hydroxybutyrate) (PHB), pullulan, chitosan derivatives, polyglycolide, and polylactide, as potential candidates to reduce pollution caused by plastic wastes. Among these, much attention has been placed on a bacterial aliphatic PHB^{1,2} and its copolymer³ produced by various types of microorganisms. PHB also has been found to be miscible with various polymers, including poly(ethylene oxide),^{4–8} poly(epichlorohydrin),^{9,10} poly(vinyl acetate) (PVAc),^{11,12} and poly(ϵ -caprolactone).¹³

In contrast, synthetic biodegradable aliphatic polyesters (BDP), which are usually synthesized from a diol and dicarboxylic acid through condensation polymerization,^{1,14,15} are also known to be completely biodegradable. However, they possess some difficulties in practical applications because of their low melting temperature (T_m), weak thermal stability, and low molecular weight. Commercially available, BDP, trademarked Bionolle,

Correspondence to: H. J. Choi (hjchoi@inha.ac.kr).
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showed potential applications through different processing methods.¹⁴

Recently, synthetic BDP with high T_m and excellent mechanical strength has 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, and also degraded biologically in soil, freshwater, and seawater while stable in air. The BDP in our study is known to have similar physical properties to those of polyethylene and polypropylene. Even though it is comparable with PHB in cost, applications of this polymer are still limited due to its higher cost compared to conventional polymers. Therefore, various blend studies are needed. However, very few investigations have been reported on miscible blend systems with synthetic BDP. Choi et al.⁸ measured the miscibility behavior and rheological properties for blends of BDP and linear low density polyethylene, and found that the blend system was immiscible, showing two separate glass transition temperature (T_g) values in all compositions. In addition, Kim et al.¹⁶ recently studied the miscibility and thermal behavior of blends of BDP with poly(epichlorohydrin) using both differential scanning calorimetry (DSC) and a dynamic mechanical thermal analyzer. They observed a single glass transition temperature in agreement with the Fox equation, indicating that these blend mixtures are miscible.

In this article, we investigate the miscibility behavior for BDP/PVAc blends by investigating their thermal, rheological, and mechanical properties.

EXPERIMENTAL

Materials and Specimen Preparation

BDP (Skygreen 2109) samples, synthesized from diols (1,4-butanediol, ethylene glycol) and dicarboxylic acids (succinic acid, adipic acid) through condensation polymerization, were obtained from Sunkyong Industry (SKI, Korea). The weight-average molecular weight of the BDP measured from gel permeation chromatography (GPC) was 6.0×10^4 g/mole. PVAc sample was purchased from Aldrich Chemical Co. (USA) in pellet form. The weight-average molecular weight of the PVAc measured from GPC was 1.67×10^5 g/mol. The

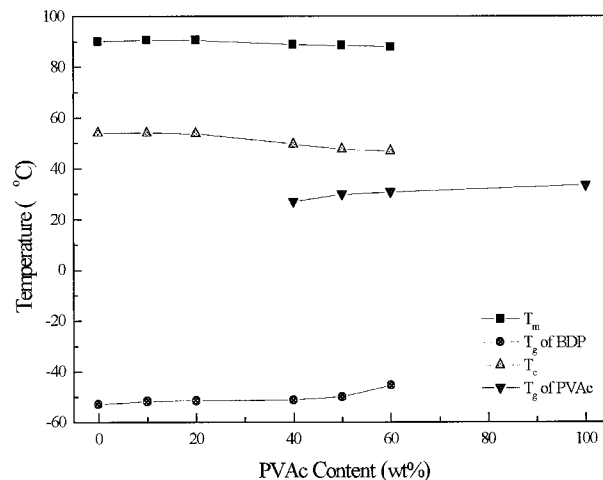


Figure 1 T_g , T_m , and T_c of the BDP and PVAc blends.

BDP/PVAc blend samples were then prepared from the solution blending method, using chloroform (CHCl_3) as a cosolvent. BDP/PVAc blending ratios were 100/0, 90/10, 80/20, 60/40, 50/50, 40/60, and 0/100 by weight; their code names were BDP100 (or BPVAc100), BPVAc90, BPVAc80, BPVAc60, BPVAc50, BPVAc40, and PVAc100 (or BPVAc0), respectively. The BDP/PVAc solutions were mixed by stirring for about 3 days at room temperature and dried to constant weight in a vacuum oven at 30°C. Finally, both film and disk types of BDP/PVAc samples were prepared using a hot press for the universal testing machine (UTM; Hounsfield Co., UK) and rheological measurements.

Analysis

DSC (Perkin-Elmer DSC-7) was used to measure the T_g s of the blends and the homopolymers. In order to measure the T_g , T_m , and crystallization temperature (T_c) of the molten mixtures, blend samples were heated from -100 to 120°C with a heating rate of $10^\circ\text{C}/\text{min}$ and annealed from 120 to -100°C with a cooling rate of $-10^\circ\text{C}/\text{min}$ using liquid nitrogen (to measure the T_c). Then, they were reheated from -100 to 120°C at $10^\circ\text{C}/\text{min}$ to measure the T_m . In addition, the degree of dispersion and phase separation between domains were investigated using scanning electron microscopy (SEM) at a magnification of 1000 at 10 kV. After being dried, the sample was fractured in liquid nitrogen so that its surface was not affected by an external stress. The BDP/PVAc blend samples were immersed in ethanol for 3 h in order to

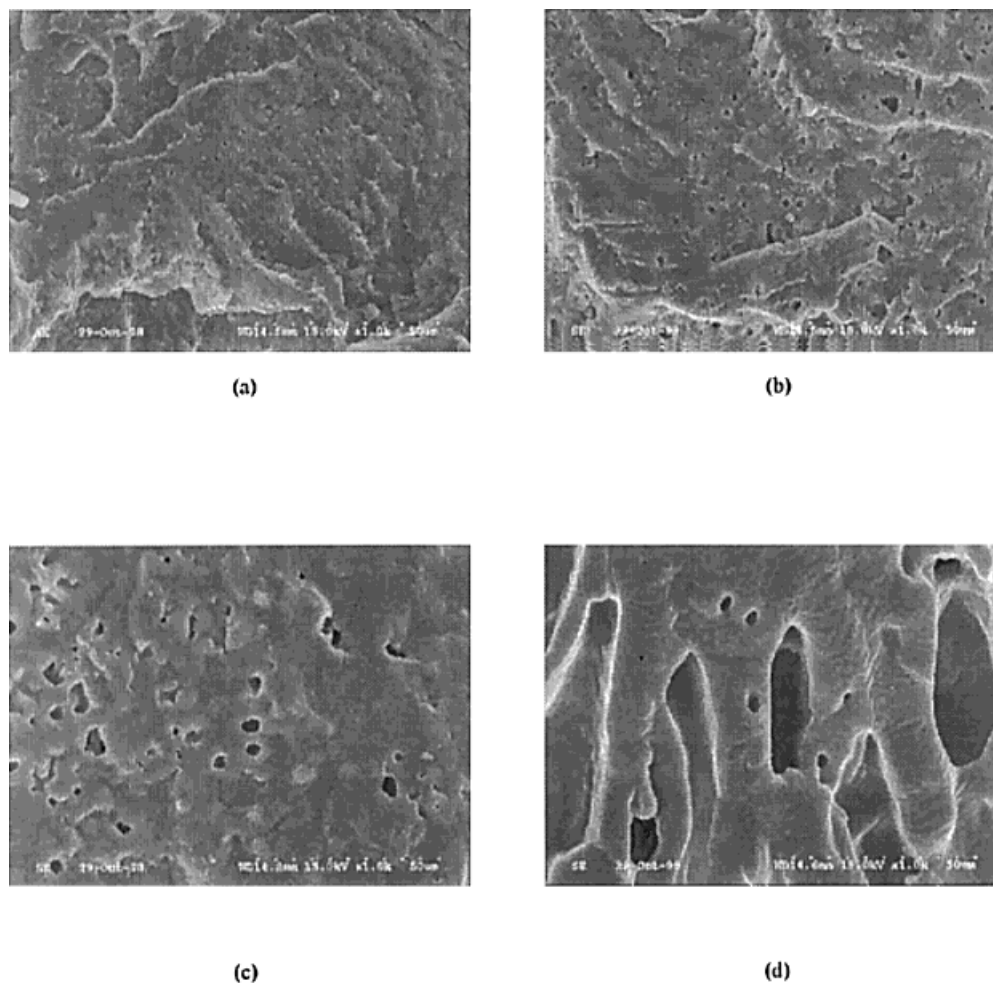


Figure 2 SEM micrographs of the fracture surface of BDP/PVAc blends: (a) BPVAc90, (b) BPVAc80, (c) BPVAc60, and (d) BPVAc50.

observe the PVAc domains easily, since only the PVAc fraction is soluble in ethanol. For the morphological measurement, the sample was coated with gold to allow an electric current on its surface.

Rheological properties of the blend systems were also investigated using a rotational rheometer (Physica, Inc., MC-120, Germany). Samples having 1 mm thickness and 6 mm radius were analyzed using a parallel plate geometry. Shear viscosity (or shear stress) was measured in the melt state as a function of shear rate at a fixed temperature of 110°C.

The premixed material was compression molded to produce sheets at 120°C and 9000 psi in a heated press. The sheets were cut into rectangles with dimensions of 0.15 mm thickness and 5.0 mm width. A UTM was used to measure both

tensile strength and elongation at break with a speed of 30.0 mm/min and 30.0 mm of sample length at room temperature.

RESULTS AND DISCUSSION

The DSC experimentation was used to determine the miscibility behavior of BDP/PVAc blends. As shown in Figure 1, the BDP/PVAc blends display only a slight shift of the melting endotherm of the BDP with variation in the blend composition. All the experimental temperatures from the DSC were measured with an accuracy of 0.1°C. Moreover, two T_g s were observed over the entire composition ranges studied. The position of T_g was found to be almost independent of composition at -53 and 33°C, respectively, very close to the val-

ues observed for pure components. Therefore, BDP/PVAc blend systems are immiscible. However, slight shifts of T_m , T_c , and T_g show the possibility of partial miscibility. Note that PVAc was found to be miscible with PHB in a melt, showing a single glass transition and a drastic depression of equilibrium melting temperature of PHB.¹²

Figure 2 shows SEM micrographs of the impact fractured surface of the BDP/PVAc blends. The SEM studies were performed on ethanol-extracted samples to discern the macrostructure of BDP in the blends. Being a good solvent to PVAc, but a relatively poor solvent to BDP, ethanol can selectively remove the PVAc component from BDP/PVAc blends. Thus, the SEM micrographs in Figure 2 may clearly represent the phase behavior of BDP/PVAc blends. The blend compositions affect the morphological structure of the blends. As shown in Figure 2, in the blend films with various blend ratios extracted with ethanol at a constant time, the PVAc phase domains are uniformly distributed in the BDP phase and the distributive size of the PVAc component becomes larger with increased content in the blends. These morphological observations also show the incompatibility between BDP and PVAc, as we found from the miscibility test.

Figure 3 shows the steady shear viscosity as a function of shear rate for the BDP/PVAc blends measured via a rotational rheometer. The shear viscosity of the blend system decreases with increasing shear rate, exhibiting shear thinning be-

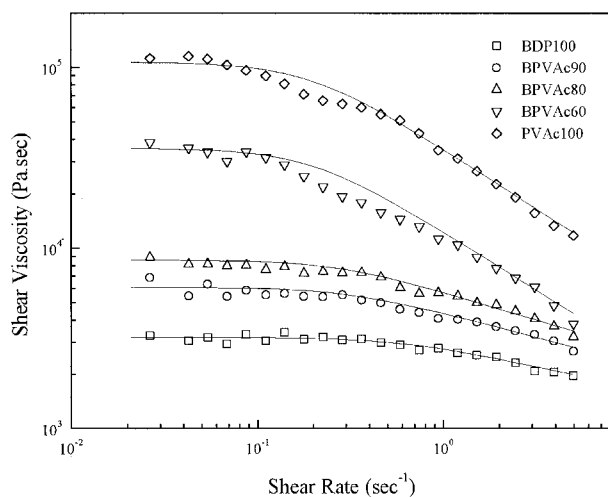


Figure 3 Shear viscosity as a function of shear rate of BDP/PVAc blends.

Table I Carreau Model [Eq. (1)] Parameters Obtained from BDP/PVAc Blend Systems

	η_0 (Pa · s) $\times 10^{-4}$	λ (s)	n
BDP100	0.319	1.70	0.78
BPVAc90	0.607	3.21	0.72
BPVAc80	0.859	3.64	0.69
BPVAc60	3.57	5.07	0.35
PVAc100	10.7	5.23	0.33

havior similar to not only many other polymeric systems but also biodegradable polymers.^{3,7,17} It also decreases with increasing BDP content. In the case of the BDP homopolymer, not much shear dependence is observed. The shear-thinning behavior seems to increase with increasing PVAc content, because PVAc has a relatively high molecular weight compared to BDP. Furthermore, in order to investigate the dependence of the shear viscosity (η) on shear rate ($\dot{\gamma}$), we fitted the measured viscosity to the Carreau model¹⁸ given in Eq. (1):

$$\eta = \frac{\eta_0}{[1 + (\dot{\gamma}\lambda)^2]^{(1-n)/2}} \quad (1)$$

Here, η_0 is the zero shear rate viscosity, λ is the characteristic time, and the parameter n is dimensionless. The slope in the power-law region is given by $n - 1$. Note that in the special case of $n = 1$ or $\dot{\gamma}\lambda \rightarrow 0$, this model reduces to the Newtonian fluid model possessing constant viscosity, and if $n < 1$, the model predicts shear-thinning behavior. From the calculated values for η_0 , n , and λ shown in Table I, we can predict that zero shear viscosity, shear-thinning behavior, and characteristic time increase with increasing PVAc content. Furthermore, shear-thinning and zero shear viscosity drastically increase with the amount of 40% PVAc content.

The mechanical properties of BDP/PVAc blends containing up to 50 wt % of PVAc were studied. From the tensile tests shown in Figure 4, it can be thought that BDP/PVAc blends are nearly immiscible because tensile strength and elongation at break of BDP/PVAc blends are not predictable. Nonetheless, BPVAc90 exhibits excellent mechanical properties. Therefore, it can be considered that blending of 10 wt % of PVAc increases mechanical properties of BDP from solvent cast.

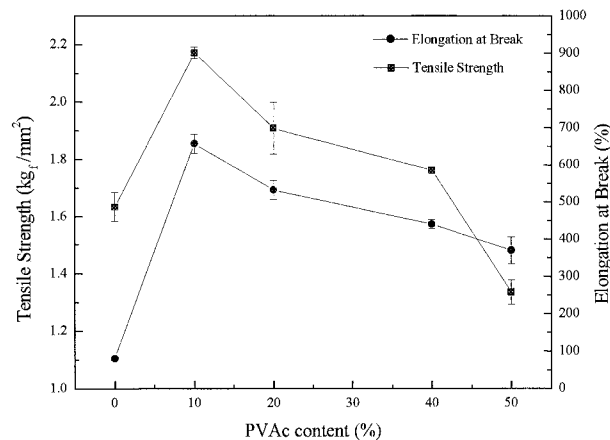


Figure 4 Tensile strength and elongation at break for BDP/PVAc blends.

In conclusion, we examined the compatibility, mechanical properties, and morphological and rheological properties for BDP/PVAc blends in this article. DSC showed two separate glass transition temperatures for BDP and PVAc, indicating that BDP/PVAc blends are immiscible in amorphous regions. Nonetheless, slight shifts in the T_m , T_c , and T_g for BDP indicate the possibility of partial miscibility. From SEM micrographs, even though PVAc shows a dispersed phase, BDP blends with 10 wt % of PVAc have good mechanical properties as derived from the UTM test. Furthermore, we found that the Carreau model fits the shear viscosity of BDP/PVAc blend systems quite well.

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