# **Miscibilities and Rheological Properties of Poly(butylene succinate)–Poly(butylene terephthalate) Blends**

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**ABSTRACT:** An aliphatic/aromatic polyester blend has been dealt with in this study. As an aliphatic polyester, poly(butylene succinate) (PBS) was used, which is thought to possess biodegradability, but it is relatively expensive. It has been blended with poly(butylene terephthalate) (PBT) in order to obtain a biodegradable blend with better mechanical properties and lower cost. The miscibilities of PBS–PBT blends were examined not only from the changes of  $T_g$  but also from log  $G'-\log G''$  plots. Dynamic mechanical thermal analyzer (DMTA) was an appropriate, sensitive method to obtain the glass transitions properly. Thermal stabilities of PBS and PBT were also verified at the temperature of 240°C. A transesterification reaction between two polyesters at 240°C was hardly detectable so that it did not affect the miscibilities and properties of the blends. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 945–951, 1999

**Key words:** poly(butylene succinate); miscibility; rheological property; dynamic mechanical thermal analyzer; transesterification

## **INTRODUCTION**

Nowadays, synthetic polymers are indispensable in our daily living. Increasing volumes of synthetic polymers are produced for various applications. However, most synthetic polymers do not decompose naturally, which may cause the serious environmental problem by the waste polymers. Therefore, it is necessary to develop biodegradable polymers with a reasonable cost.

Blending and copolymerization techniques have been tried by many researchers to obtain biodegradable polymers with improved properties.1–3 Modified starch was blended with lowdensity polyethylene to substitute the nonbiodegradable packaging films.<sup>4-6</sup> Poly(hydroxybu-

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tyrate) (PHB) and poly(lactic acid) (PLA) were also blended with commercial polymers that may cover their mechanical weaknesses.7–9 For example, PHB suffers two limitations in its use, as follows: a narrow processability window and relatively low impact resistance.<sup>7,10</sup> In the case of polyester, the blend with two or more components may be changed into block or random copolyester by the transesterification reaction at the elevated temperature in the presence of an adequate catalyst.<sup>11,12</sup> Using this method, the segment of biodegradable polyester can be easily introduced into nonbiodegradable polyester, and the average sequence length of each unit in copolyester can be controlled. Hence, the biodegradability and physical properties of the blends can be modified for their specific usage. Aliphatic, linear polyesters usually have low transition temperatures, which make them useful as plasticizing agents to aromatic, fast-crystallized polyesters. They also endow the biodegradability to the blend. Aromatic polyester can induce the good mechanical proper-

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ties to the blend. Therefore, it may be very interesting to blend an aliphatic polyester with an aromatic polyester. In this study, poly(butylene succinate) (PBS), as an aliphatic polyester, and poly(butylene terephthalate) (PBT), as an aromatic polyester, were selected to develop a biodegradable polyester blend. We tried to determine the miscibility of PBS–PBT blends by various methods, including the use of a differential scanning calorimeter (DSC), a dielectric analyzer (DEA), a dynamic mechanical thermal analyzer (DMTA), and a rotational rheometer.

#### **EXPERIMENTAL**

PBS and PBT samples were obtained from Sae-Han Inc. in the pellet form. The weight-average molecular weights  $(M_w)$  of PBS and PBT were about 76,000 and 72,000, which were measured by gel permeation chromatography (GPC). The melting point of PBS is 114°C, and that of PBT is 225°C. The two samples were dried in a vacuum oven at 70°C for 24 h in order to minimize the thermal degradation during melt blending. PBS and PBT were blended by Mini-Max Extruder of Custom Scientific Instrument Inc. The processing temperature was chosen as 240°C under the nitrogen atmosphere. Mixing time was fixed within 2 min to minimize any possible reactions, such as the transesterification reaction or thermal degradation.

The  $T<sub>g</sub>$  of blends and homopolymers were measured by DEA 2970 (TA Instruments Inc.) and DMTA IV (Rheometric Scientific, Inc.). The  $T_g$  of a blend can be used to determine the miscibility of the blend system. Dielectric properties of the samples were obtained with increasing temperatures, 2°C/min under the nitrogen atmosphere. Mechanical properties of the samples were measured with the dual cantilever bending mode at 1 Hz and 2°C/min, under a nitrogen atmosphere. The samples were prepared using a Laboratory Carver press. After the samples were melted and pressed at 240°C for 3 min, they were quenched in the liquid nitrogen to preserve their morphologies at 240°C. The sample of DEA was a thin film,  $20 \times 20$  mm. That of DMTA was a bar,  $30 \times 10$  $\times$  2 mm.

Rheological properties of the blends in the dynamic flow field were measured using 50 mm cone and plate geometry of the rotational rheometer (Rheolab-MC120, Physica). From the preliminary experiments of the stress sweep, all measure-



**Figure 1** The changes of complex viscosity of PBS and PBT at the isothermal temperature, 240°C.

ments were performed at suitable stresses, depending on the temperature to maintain the linearity of viscoelastic response and the reliable torque level. The  $G'$ ,  $G''$ , and the complex viscosity were measured as a function of frequency at 240°C. Complex viscosity was measured as a function of time at the fixed frequency, 10 rad/sec to verify the thermal stabilities. The morphologies of the blends were observed by a Philips scanning electron microscopy (SEM). The samples were cut by the microtome knife after freezing. They were etched in chloroform to obtain the clear morphology.

<sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H-NMR) measurements were carried out using the Bruker AMX Fourier transform–NMR spectrometer operating at a resonance frequency of 500 MHz for protons. For the NMR spectra, 2–5 wt % solutions of the polymers were dissolved in *d*-TFA (deuteriated trifluoroacetic acid).

### **RESULTS AND DISCUSSION**

It is necessary to verify the thermal stability of blends since the blending temperature, 240°C, is apparently too high for PBS, of which the melting temperature is 114°C. Figure 1 shows the isothermal time sweep for PBS and PBT at the fixed frequency and deformation. It is surprising that PBS was not significantly degraded at 240°C so

that it is possible to blend PBS with PBT at this temperature. It is also expected that the transesterification reaction may occur in addition to the thermal degradation at this temperature.

Polymer blends, by definition, are physical mixtures of structurally different homopolymers and copolymers. At equilibrium, a mixture of two polymers in the amorphous phase may exist as a single phase of intimately mixed segments of the two components. Such a blend is homogeneous on a microscopic scale, which is considered to be miscible in the thermodynamic sense. When a mixture of two polymers separates into two distinct phases consisting primarily of the individual components, the blend is heterogeneous on the microscopic scale, which is considered to be immiscible in the thermodynamic sense. Most polymers are immiscible from the thermodynamic standpoint since the entropic contribution to the free energy of mixing is negligible.<sup>13</sup> The most commonly used method for establishing miscibility in polymer–polymer blends or partial phase mixing in such blends is through determination of the glass transition in the blend versus those of the unblended constituents. The glass transition is the temperature region where an amorphous material changes from a glassy phase to rubbery phase upon heating, or vice versa if cooling. A miscible polymer blend will exhibit a single glass transition between the  $T_g$  of the components with a sharpness of the transition similar to that of the components. In the case of the limited miscibility, there were two separate transitions between those of the constituents, depicting a component-1-rich phase and a component-2-rich phase.

Blends of crystalline polymers are more complex due to the potential crystallization of one or both components. The transitional behavior in such mixtures is generally very difficult to assess by traditional DSC due to the breadth and relatively low intensity of the glass transitions. In this study, we cannot get the glass transitions of the samples by DSC due to the poor sensitivity. DEA and DMTA were used to obtain the  $T_g$  of the samples because they are more sensitive than the traditional thermal analysis technique (DSC). DMTA is one of the most sensitive techniques available for characterizing and interpreting the mechanical behavior of materials. The concept of DMTA is based on observing the viscoelastic response of materials subjected to a small oscillatory strain. The viscoelastic response of a material is separated into the two components of modulus (*E*\*): a real part, which is the elastic



**Figure 2** Mechanical properties of PBS–PBT blends using DMTA IV (1 Hz, 2°C min).

modulus  $(E<sub>'</sub>)$ , and an imaginary part, which is the damping or viscous component  $(E<sup>n</sup>)$ . Figure 2 illustrates the mechanical properties, tan  $\delta$  (*E'*/ *E*<sup> $\prime$ </sup>) of the blends with increasing temperatures. There were two distinct  $T_{\rm g}$  values, as follows: the first at about  $-18.9^{\circ}$ C of PBS phase, and the second at about 66.1°C of the PBT phase. There were no significant changes in  $T_g$  values of the blends. If two  $T_g$  values are essentially apparent, then it suggests the presence of two separated phases. We can conclude that the PBS–PBT blends are immiscible in the whole compositions. DEA, which measures a material's response to an applied alternating voltage, provides an excellent means of characterizing thermoplastics. Since PBS and PBT have polar groups  $(C=0)$  in their structures, we may obtain the glass transitions by DEA instead. The electrical properties of polymers are analogous to mechanical properties. The dielectric constant  $\varepsilon'$  is similar to compliance, the dielectric loss factor  $\varepsilon$ " is similar to mechanical loss, and the dielectric strength is analogous to tensile strength. The dielectric loss factor and the dissipation factor, tan  $\delta$  ( $\varepsilon$ '/ $\varepsilon$ ''), are of primary interest as they are commonly used to ascertain polymeric transitions, such as the glass transition. The dielectric constant increases as molecular motions in the polymer increase; thus, large secondary relaxation and the glass transition will yield increasing dielectric constant. Figure 3 shows the dielectric dissipation factor, tan  $\delta$ , versus temperature at 1000 Hz for PBS–PBT blends. The blends can be characterized with two distinct *Tg* values similar to DMTA. PBS–PBT (3/7) blend has shown two distinctive  $T_g$  because of the im-



**Figure 3** Dielectric properties of PBS–PBT blends using DEA (1000 Hz, 2°C min).

miscibility. But PBS–PBT (7/3) and PBS–PBT (5/5) blends could not show the transition in PBT phase because of the rapid rise caused by the increasing ionic conductivity.14 The ionic conductivity increased significantly due to the premelting of the PBS phase. Hence, it is difficult to determine the miscibility of PBS–PBT blends by DEA.

Figure 4 gives the logarithmic plot of  $G<sup>1</sup>$  versus *G*<sup> $\sigma$ </sup> of PBS–PBT blends at 240°C. The curves of PBS and PBT homopolymers are superposed on a line. The storage modulus is increased before the terminal region in all compositions because of the immiscibility. It is consistent with DMTA results. It has been amply demonstrated in the litera $ture^{15-17}$  that when dealing with a heterogeneous polymer blend, the morphology of the blend (e.g., the state of dispersion, the domain size, and its distribution) controls its rheological properties. It is important to point out that the method of blend preparation (e.g., the method of mixing the polymers and the intensity of mixing) and the variables chosen for blend preparation (e.g., temperature, blend composition, and shear stress) strongly influence the morphology and the rheological properties of the blend. When a blend system is truly compatible on the molecular level, it gives rise to a composition-independent correlation. It should be remembered that  $G<sup>1</sup>$  may be interpreted as the energy stored and  $G<sup>′</sup>$  may be interpreted as the energy dissipated in the molecules during the shearing deformation. Therefore, as long as the molecular structure is kept the same, the ratio of the energy stored and the energy dissipated during the shearing deformation is expected to be independent of blend composition.<sup>18</sup> In the log *G*<sup> $\prime$ </sup> versus log *G*<sup> $\prime$ </sup> plot, the slope is about 2 in the terminal region for the most homophase polymer systems. The immiscible polymer blend systems, however, show that the slope is lower than 2 just before the terminal region due to the increase of storage modulus.

Figure 5 shows the scanning electron microscopy (SEM) photographs of PBS–PBT blends. We could not obtain the morphologies in PBS–PBT (7/3) and PBS–PBT (6/4) blends because the matrix phase was etched by the solution. PBS–PBT (5/5), PBS–PBT (4/6), and PBS–PBT (3/7) blends revealed the two-phase morphologies. It is consistent with previous results from DMTA and the rheometer.

In polymer processing, we need to know the rheological properties in order to control the process properly. Figure 6 shows the complex viscosity of PBS, PBT, and PBS–PBT blends as a function of frequency at 240°C. All blends show Newtonian behaviors. The complex viscosity of the blends is ordered sequentially as the composition changes.

It is widely recognized that almost all polycondensates have polymer links that are easily cleaved or exchanged at processing temperatures.



**Figure 4** Log  $G'$ -log  $G''$  plot of PBS–PBT blends at 240°C.



 $(a)$ 



 $(b)$ 



 $(c)$ 

**Figure 5** SEM photographs of the following PBS– PBT blends: (a) 5/5; (b) 4/6; and (c) 3/7 after etching in chloroform.



**Figure 6** Complex viscosity of PBS–PBT blends at 240°C.

The mechanisms of the interchange reactions that occur in polyester blends during melt processing involve acidolysis, alcoholysis, and direct transesterification. All these reactions result in the formation of new copolymers. Generally, transesterification reduces the interfacial tension in the melt state and leads to a finer dispersion of one phase in another. In addition, it results in large interfacial area in the reactive blend with finer morphology. Therefore, the finer morphology as a result of transesterification reaction is associated with the more miscible system. Figure 7 shows the  $\mathrm{^{1}H\text{-}NMR}$  spectra of PBS–PBT blends. In the NMR spectrum of PBS, three signals are shown at 4.40 ppm  $(-CH<sub>2</sub>),$  peak of 1,4-butanediol unit), 1.95  $ppm$  ( $-CH_2$ , peak of 1,4-butanediol unit), and 2.95 ppm  $(-CH_2-,$  peak of succinyl unit).<sup>19</sup> There are also three peaks in the PBT spectrum. They are also shown at 4.71 ppm  $(-CH<sub>2</sub>),$  peak of 1,4-butanediol unit), 2.23 ppm  $(-CH<sub>2</sub>),$  peak of 1,4-butanediol unit), and 8.30 ppm ( $\text{—CH}_2\text{—}$ , peak of terephthalic unit).<sup>20</sup> Park et al. reported the presence of the transesterification reaction between PBS and PBT using <sup>1</sup>H-NMR and other methods.<sup>21</sup> In our case, it was difficult to see any significant changes of the hetero unit peak (2.08 ppm) from <sup>1</sup>H-NMR when the blends were prepared at 240°C. Hence, it will be necessary to use a proper catalyst or to increase the blending temperature in order to induce the transesterification reaction. Then, the



Figure 7 <sup>1</sup>H-NMR spectra of the following PBS–PBT blends: (a) PBS; (b) PBT; (c) PBS–PBT (7/3); (d) PBS–PBT (7/3)<sup>h.t</sup>; (e) PBS–PBT (5/5); and (f) PBS–PBT (5/5)<sup>h.t</sup>. h.t: heat treatment at 240°C for 1 hr.

miscibility and mechanical properties of the blends can be altered.

## **CONCLUSIONS**

PBS (aliphatic polyester) and PBT (aromatic polyester) were considered as one of the candidates for biodegradable polyester blends. The blending temperature, 240°C, is suitable to mix them homogeneously, at which they are also thermally stable.

We cannot obtain the glass transitions of the blends by DSC and DEA due to the poor sensitivity and the rapid rise caused by the increasing The authors thank the Korea Science Foundation for financial support (95-0300-07-03-3). The partial support of Center for Advanced Functional Polymers is also appreciated. The authors also thank Sae-Han Inc. for supplying PBS and PBT samples.

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