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Miscibility of poly (etherimide) and poly (butylene naphthalate) blends

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Summary

Differential scanning calorimeter (DSC), optical microscopy (OM) and scanning electron microscopy (SEM) were performed to characterize the miscibility of a blend system comprising poly (butylene naphthalate) (PBN) and poly (ether imide) (PEI). DSC scans showed there was only one single Tg for each blend and the glass transitions increase monotonously with the increase of PEI content. The glass transition temperatures of the blends fitted the Fox equation well implying that the blends exhibited fine segmental scale of mixing. No lower critical solution temperature (LCST) was observed by OM for the blends. SEM micrographs showed the fracture surface of quenched sample exhibited a homogeneous structure. No obvious IR peak shift of C=O absorption at 1780 cm^{-1} was observed suggesting a relatively low level of specific interaction between two molecules. It was concluded that these blends were miscible with non-specific intermolecular interactions.

Introduction

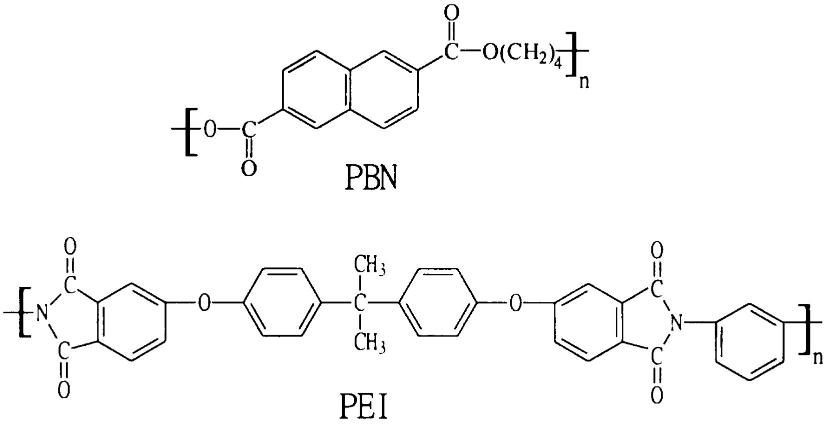
Blending of polymers of different properties is usually an attractive route for the development of new polymer materials that offer a special combination of performance characteristics. Poly (ether imide), an amorphous polymer with a glass transition temperature of 220 °C, has good physical properties such as tensile, flexural and compressive strength and electrical insulation. However, due to its high glass transition, it is difficult to process (processing temperature is about 380 °C). Furthermore, the blending of PEI with a crystalline polymer can enhance its solvent resistance. Thus, the blending of PEI with a crystalline polymer having melting point much lower than the processing temperature of PEI becomes an interesting and important topic. PEI has been found to form a miscible blend with poly (ethylene terephthalate) (1-2), poly (butylene terephthalate) (3-4), poly (ethylene naphthalate) (5) in the melt. Poly (butylene naphthalate), a semicrystalline polymer with a similar structure with poly (butylene terephthalate) and poly (ethylene naphthalate), may be miscible with PEI. Although miscibility is not a prerequisite for blends applications, it is an easy way to design new polymer materials. The objective of this study is to explore the phase behavior of blends comprising amorphous PEI with semicrystalline PBN by DSC, OM, SEM and FTIR.

Experimental

PEI with Mw of 30000g/mol and without additives was purchased from Polyscience, Inc. PBN with inherent viscosity of 0.68 g/dl was kindly supplied by CCP Taiwan. The structures of PEI and PBN were shown in Scheme 1. DSC scans were obtained from 3~5 mg samples in a nitrogen atmosphere at a heating rate of 20 °C/min using a Perkin-Elmer DSC 7. Temperature calibration was carried out using pure samples of In and Zn. The apparent enthalpies were determined using the conventional method, comparing the areas under the DSC curve with the corresponding areas of a standard sample of Indium, taking ΔH_f=28.45 Jg^{-1}. Tg was determined by the analytic software of Perkin Elmer DSC 7. Thermal gravimetric analysis (TGA) was performed with a Perkin-Elmer TGA 7 at a heating rate of 20 °C/min under air from 40 °C to 800 °C. Cloud point measurement of the blend was performed with Nikon Optiphot 2-POL by placing the samples on a microscope heating stage (THMS600 with TP 92 controller) with a programmed heating rate of 2 °C/min from 180 °C to 360 °C. The morphology (fracture surface) of the blends was examined using a scanning electron microscope (Model JEOL JXA-840). The fractured blend samples were coated with gold. IR spectra were performed by Jasco FTIR-410. Spectra were obtained at 4 cm^{-1} resolution and average spectra were obtained at 64 scans in the wave number range of 600-4000 cm^{-1}.

Blending Method

The blending was performed in solution. Blends of PEI/PBN in various weight ratios (100/0, 80/20, 60/40, 50/50, 40/60, 20/80, 0/100 w/w) were prepared by dissolving the component polymers in dichloroacetic acid to form a homogeneous solution and then poured into a large excess of water. The precipitated blends were filtered and washed with excess water for 4 times to ensure no residual dichloroacetic acid in the blends. After that, they are dried in a vacuum oven at 120 °C for 2 day. TGA was used to ensure there is no any solvent exhibited in the blends after they are dried.



Scheme 1. Structures of PBN and PEI.

Results and discussion

TGA results

Figure 1 showed TGA heating scans of solution PBN/PEI blends after dried in a vacuum oven at 120 °C for 2 day. There was no any obvious weight loss before 300 °C implying no dichloroacetic acid exhibited in the blends after the precipitated blends were filtered and washed with excess water. Thus, we could make sure the miscibility of PBN and PEI was not influenced by the effect of dichloroacetic acid.

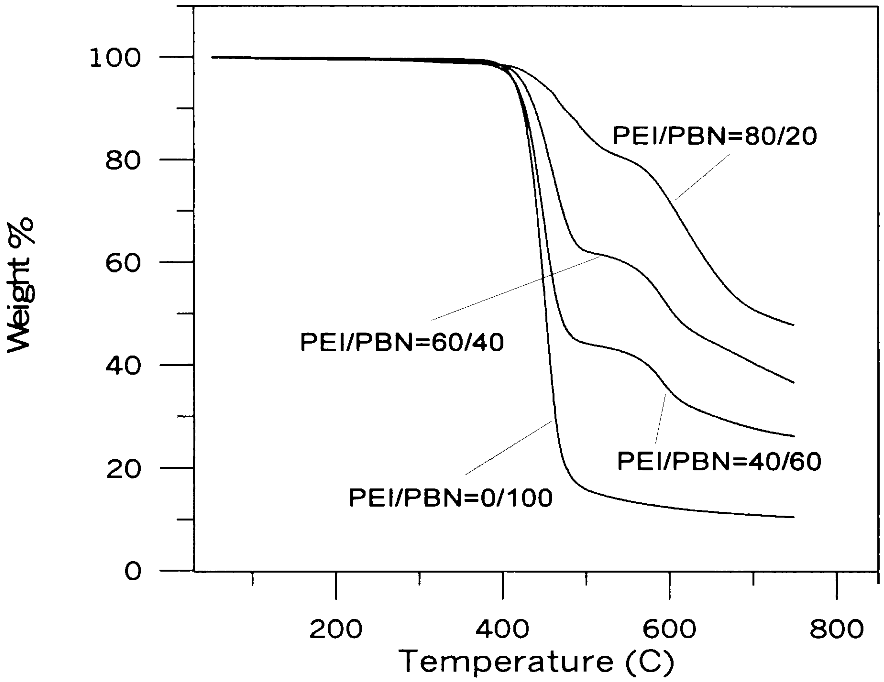


Figure 1. TGA heating scans of solution PBN/PEI blends after dried in a vacuum oven at 120 °C for 2 day..

DSC scans

Figure 2 showed DSC heating scans (20 °C/min) of PBN/PEI blends after melting at 280 °C for 3min and then cooling (-20 °C/min) to room temperature. There was only one single Tg in each blend composition and the crystallization tendency of PBN is quickly suppressed by blending with PEI. From the presence of a single glass transition temperature, it is clear that the blends are miscible over the complete range of compositions. The glass transition temperature increased monotonously with the increases in the content of PEI. Figure 3 showed composition dependence of the experimental Tg data of the blends. The composition dependence relationship for this system was well predicted by the Fox equation (6). Generally speaking, polymer blends with fine segmental scale of mixing may also be expected to follow this rule. Thus, the glass transition temperatures of these blends fitted the Fox equation well implying that the blends exhibited fine segmental scale of mixing.

OM and SEM micrographs

The blend samples were inspected microscopically on a heating stage with a slow heating rate (2 °C/min) up to 360 °C to monitor whether or not a cloud-point transition could be observed. Just as the blend of Poly(butylenes terephthalate) (PBT) and PEI, a transparent melting liquid without LCST was observed for this system (the pictures of OM were not shown for brief). SEM micrographs were also taken on the fracture surfaces of quenched PBN/PEI samples at various compositions. Figure 4 show the SEM micrographs of the fracture surface of four blend compositions: 80/20, 60/40, 40/60 and 20/80, at 3000X and 5000X magnifications respectively. As shown in Figure 4, the samples exhibited a homogeneous structure, further indicating that a homogeneous state was achieved in this blend system.

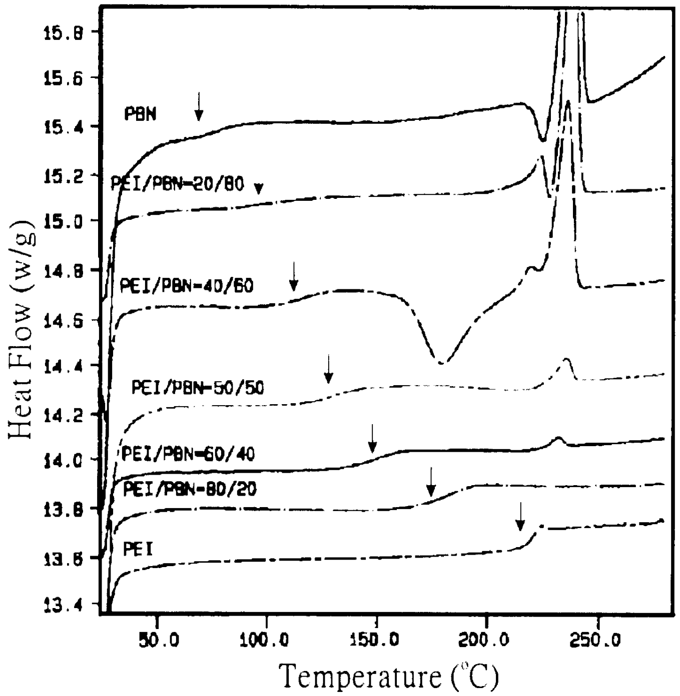


Figure 2. DSC heating scans (20 °C/min) of PBN/PEI blends after melting at 280 °C for 3min and then cooling (-20 °C/min) to room temperature.

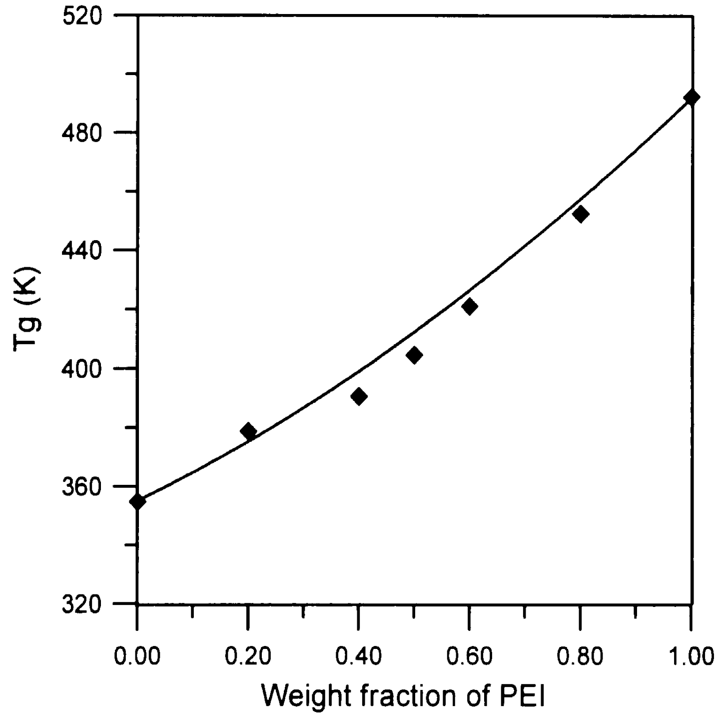
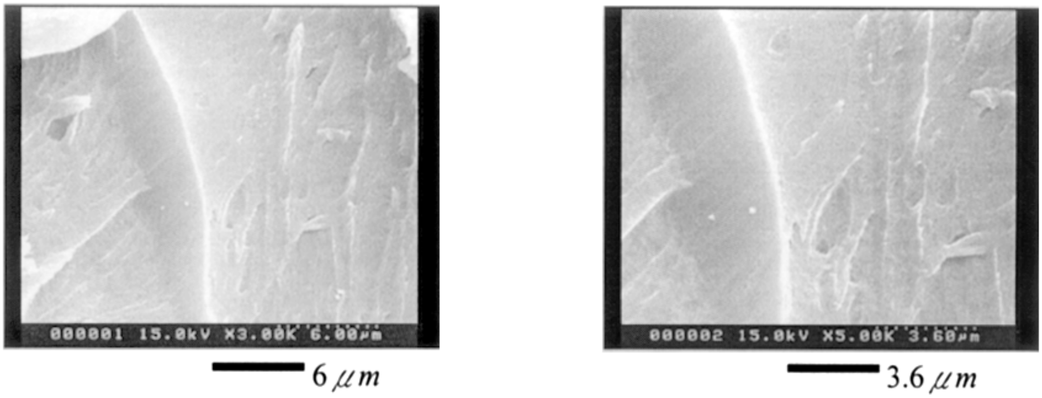
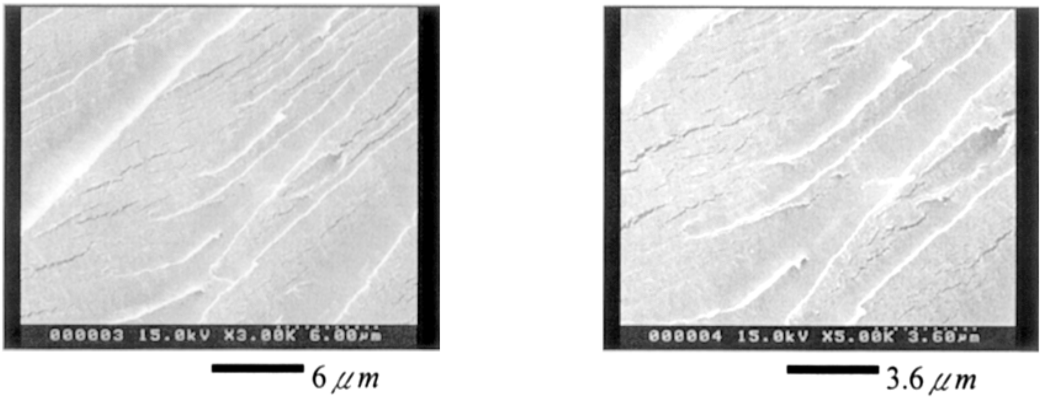


Figure 3. The plot of Tg versus composition for PEI/PBN blends. The solid line is plotted according to the Fox equation.

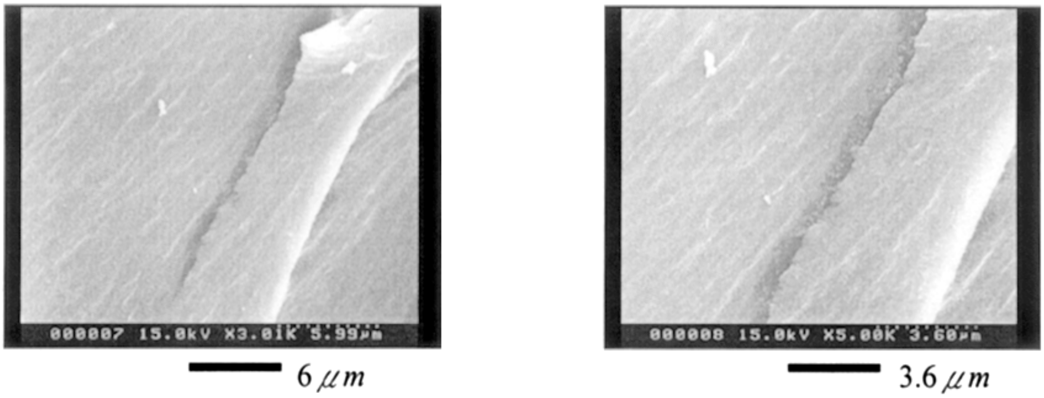
PEI/PBN=20/80



PEI/PBN=40/60



PEI/PBN=60/40



PEI/PBN=80/20

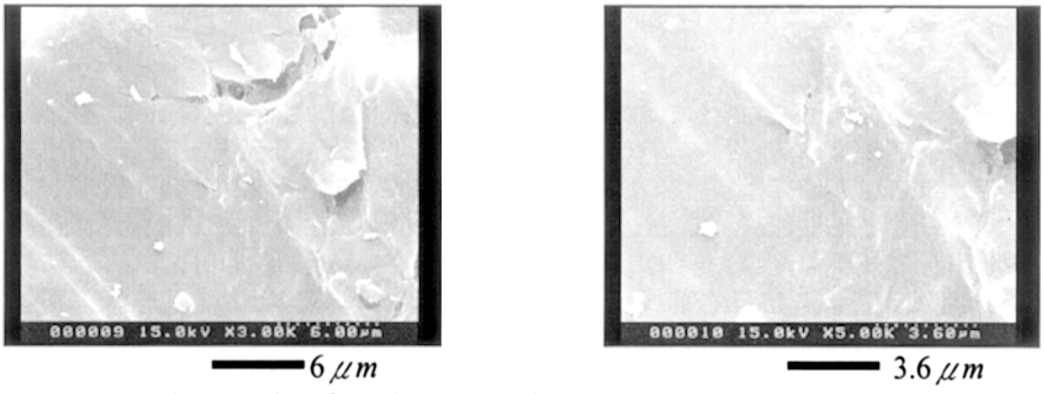


Figure 4. SEM micrographs of the fracture surface for PEI/PBN 20/80, 40/60, 60/40 and 20/80, at 3000X (left) and 5000X (right)

IR spectra

The IR spectra of the carbonyl (C=O) absorption for PEI/PBN blends were examined. According to our experimental data, PEI exhibited two C=O absorption located at 1778 cm^{-1} and 1726 cm^{-1}. For PBN, the C=O absorption is located at 1715 cm^{-1}. The overlap of two C=O absorptions at around 1715-1726 cm^{-1} makes it difficult to calculate shift of wavenumber due to molecular interaction. If we examine another C=O absorption at 1780 cm^{-1} as shown in Figure 5, no significant shifting was observed. This suggests that a relatively low level of specific interaction, if any, may be present between the two molecules.

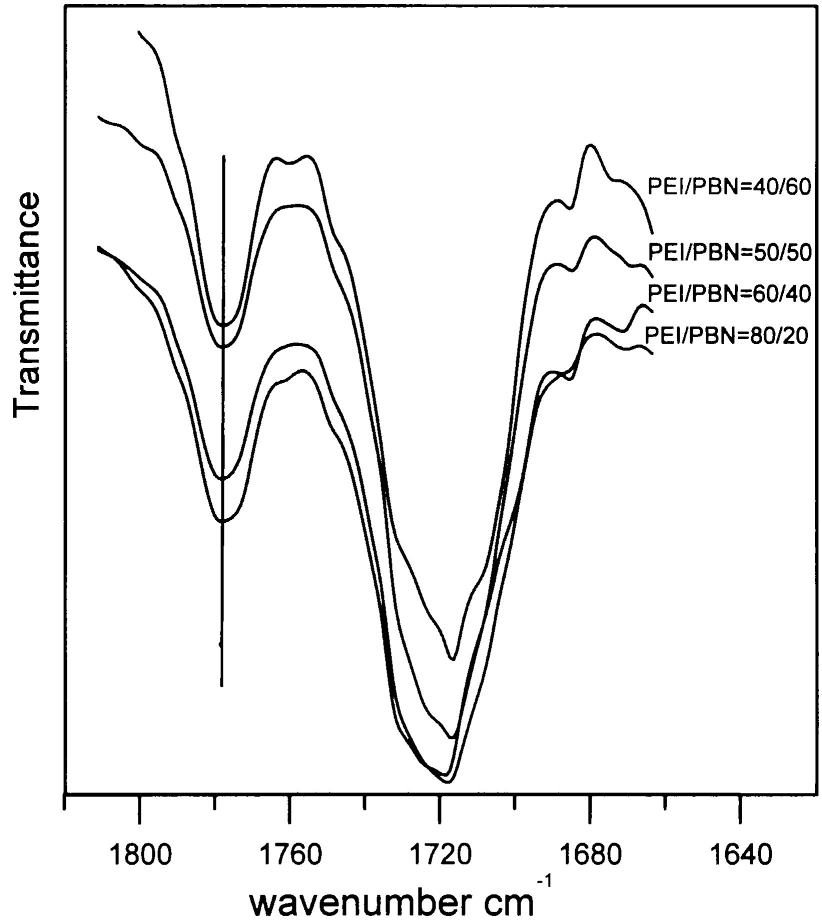


Figure 5. IR spectra of the carbonyl (C=O) absorption for PEI/PBN blends (40/60, 50/50, 60/40, 80/20).

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