니트로기 치환 폴리벤즈이미다졸과 폴리에테르이미드와의 블렌드

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Miscible Blend of Nitro-Substituted Polybenzimidazole and Polyetherimide

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1. Introduction

Miscible binary blends of high performance polymers have drawn much attention for several decades. As a new blend pair, poly[(2,2,-*m*-phenylene)-5,5′-bibenzimidazole] (polybenzimidazole, PBI) has been a notable candidate to reveal excellent thermal stability and chemical resistance. For example, up to now, miscible polymer blends based on PBI and aromatic polyimides (PI) [1-10] or the other polymers such as polyarylate [11], polyaramide [12, 13], polyamic acid [14], and polysulfone [15] has been reported. Miscibility in these blends is related to a specific interaction between phthalimide carboxyl groups of PI and imidazolic amine groups of PBI. However, PBI has a disadvantage to be blended in solution owing to its insolubility in most organic solvents. Selective solvents for PBI are only dimethylacetamide (DMAc) and concentrated sulfuric acid. However, PBI does not dissolve completely in these solvents and separates into bulk fractions by decreasing solution temperature. Moreover, PBI solution cannot be stored for long periods of time without phase separation into polymer rich phase and polymer poor phase. Actually, in solution blending procedure, PBI solution was prepared in a pressure vessel at 225 ℃ with subsequent filtration of insoluble residue.

For this reason, challenging attempts to improve solubility of PBI have been made. Recently, we synthesized organo-soluble PBI by introducing nitro group in the phenylene ring through reaction of PBI with nitric acid [16]. This nitro-substituted PBI (NO_2-PBI) had an extensive solubility in general polar aprotic solvents like DMAc and acidic solvents.

In this study, novel organo-soluble NO_2-PBI/polyetherimide (PEI) blend was successfully prepared through a simple solution blending in DMAc at 80 ℃. Miscibility and thermal property of the blend were investigated by dynamic mechanical and spectroscopic analyses.

2. Experimental

2.1 Preparation of NO_2-PBI

1.84 g of PBI powder (Aldrich) was dissolved completely in 200 ml of sulfuric acid at room temperature. After 1.03 g of nitric acid was added at 0 ℃, the solution was well stirred at the same temperature for 1 h. The solution was poured into an ice water to produce a yellowish precipitate. The pH of the solution from which the precipitate was formed was adjusted to 5.0 using a concentrated sodium hydroxide solution. The final product was obtained after complete washing and drying in a vacuum oven for 12 h. Degree of substitution of NO_2-PBI prepared was 1.94. NO_2-PBI was perfectly soluble in DMAc at room temperature.

2.2 Preparation and characterization of NO_2-PBI/PEI blend film

NO_2-PBI/PEI blend films were prepared by casting 3 g/dl solutions of the polymer mixtures on stainless steel plates at 80 ℃ for 24 h. The films were washed in water at 60 ℃ for 24 h and dried under vacuum at 80 ℃ for 2 days.

Dynamic mechanical thermal analysis (DMTA) was carried out at a scanning rate of 5 ℃/min to measure glass transition temperature (T_g) and dynamic storage modulus (E') of the blend film. Infrared (IR) spectra were obtained at a resolution of 4 cm^{-1}. Solid state ^{13}C nuclear magnetic resonance (NMR) spectra were obtained with a contact time of 2.5 ms. Tensile strength and modulus of the blend film were measured by Instron at an extension speed of 10 mm/min.

3. Results and Discussion

Miscibility of NO_2-PBI/PEI blend was confirmed evidently by the presence of single T_g lying between those of the constituent polymers and by the formation of

an absolutely transparent film.

In binary blend systems, miscibility is often attributed to the existence of specific interactions between blend components. IR spectroscopy has been widely used in characterizing miscible polymer blend systems. Composition-dependent frequency shifts and band broadenings for many blends have been ascribed to specific intermolecular interactions. In the present study, two regions (N-H and carbonyl stretchings) in IR spectrum were investigated.

Figure 1 shows the IR spectra in the N-H stretching region of NO_2-PBI and NO_2-PBI/PEI blends. In case of NO_2-PBI, a peak assigned to isolated, nonhydrogen-bonded N-H groups was found at lower frequency than that of PBI (3357 cm^{-1}). By blending with PEI, the absorption at 3357 cm^{-1} shifted to lower levels as increasing PEI content. In Figure 2, the shifts of symmetric and asymmetric carbonyl stretchings around 1780 cm^{-1} and 1725 cm^{-1} toward lower levels were clearly observed with increasing NO_2-PBI content in the blend. Such a spectral change is related to the hydrogen-bonding interaction between N-H groups in NO_2-PBI and carbonyl groups in PEI, which was an origin of the miscibility between the two polymers.

Thermal and chemical properties of PEI are expected to be enhanced by blending with NO_2-PBI. A steep increase of E' of the blend film at high temperature in comparison with that of PEI is well presented in Figure 3. The thermomechanical properties of PEI film could be improved by blending with NO_2-PBI.

4. References

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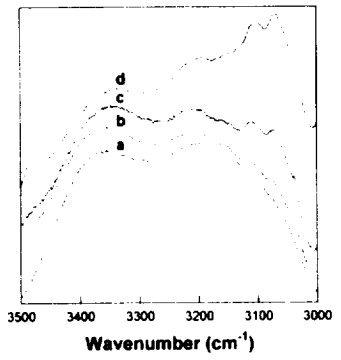

Figure 1. IR spectra in the N-H stretching region of NO_2-PBI and NO_2-PBI/PEI blends: a, NO_2-PBI; b, 70/30 wt% blend; c, 50/50 wt% blend; d, 30/70 wt% blend.

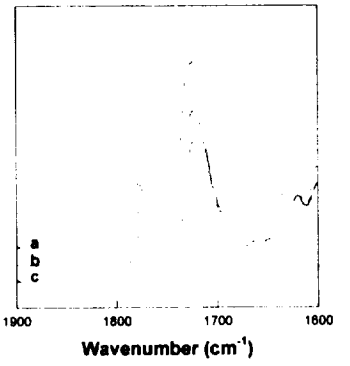

Figure 2. IR spectra in the carbonyl stretching region of PEI and NO_2-PBI/PEI blends: a, PEI; b, 30/70 wt% blend; c, 70/30 wt% blend.

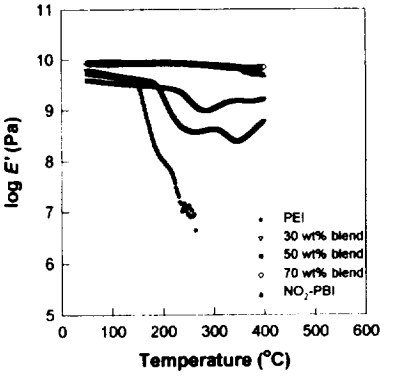

Figure 3. Dynamic storage moduli of PEI, NO_2-PBI, and NO_2-PBI/PEI blend films.