

Poly(ethylene 2,6-naphthalene dicarboxylate) / Poly(ethylene isophthalate) Blends

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Introduction

Poly(ethylene 2,6-naphthalene dicarboxylate)(PEN) is quite useful for many packaging applications, due to good mechanical properties¹, low permeability of oxygen and carbon dioxide², and good thermal properties (high melting and high glass transition temperatures)³. However, PEN exhibits a high melt viscosity and is also expensive. In order to overcome these limitations, several studies have been focused on PEN/poly(ethylene terephthalate)(PET) blends^{4,6}.

By the way, poly(ethylene isophthalate)(PEI) is a fully amorphous polymer whose glass transition temperature(T_g) is lower than that of PET by about 10°C. Hence PEN/PEI blends can be the other candidate to compensate for the shortcomings of PEN. However, PEN is immiscible with PEI. In order to achieve compatibility in PEN/PEI blends, it is necessary to induce and control the transesterification between the two polymers⁵.

In this study, we have investigated the effect of the reaction temperature on the degree of transesterification and also the change of miscibility with the degree of transesterification for PEN/PEI blends.

Experimental

PEN was supplied by Kolon Ind., and PEI was synthesized in our laboratory. Solution/precipitation blend of PEN/PEI (55/45, mol/mol) was prepared by dissolving two polymers in a mixed solvent of phenol and 1,1,2,2-tetrachloroethane (6/4, w/w). This solution was added dropwise to a large excess of acetone causing rapid coprecipitation. The precipitate was filtered off and Soxhlet extracted for 24 h and dried in vacuo.

Heat treatment for transesterification was carried out on a DSC system (Perkin-Elmer DSC-7) under dry nitrogen atmosphere. Samples were heated rapidly from room temperature to the reaction temperature (270, 285, or 300°C), maintained at that temperature for various time intervals, and quenched with liquid nitrogen.

Thermal analysis was performed at a heating rate of 20°C/min from -30°C to 290°C. ¹H-NMR spectra were measured in a mixed solvent of trifluoroacetic acid/deuterated chloroform (1/5, v/v) and tetramethylsilane(TMS) was used as internal reference.

Results and Discussion

Fig. 1~3 show DSC thermograms of PEN/PEI blends transesterified at three different temperatures. For all the blends, two T_{g} s approach mutually closer with the increase of reaction time, until finally only one T_{g} is observed. These results indicate that two phases (PEN-rich and PEI-rich) become one phase gradually with the reaction time due to transesterification.

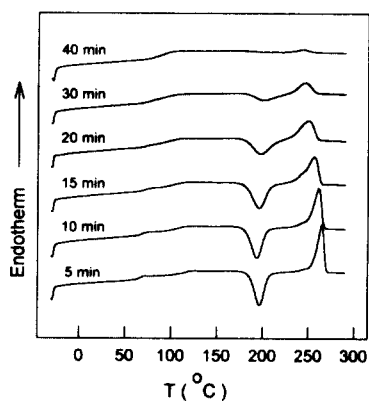


Fig. 1. DSC thermograms of PEN/PEI blends after transesterification at 270 °C.

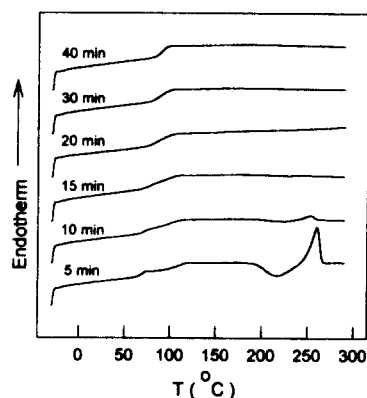


Fig. 2. DSC thermograms of PEN/PEI blends after transesterification at 285 °C.

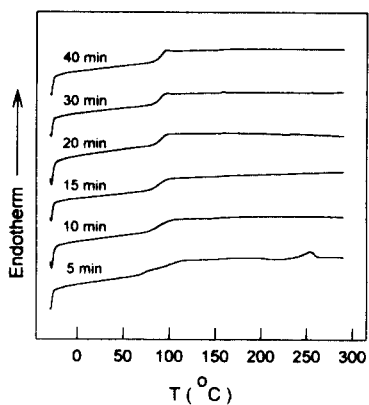


Fig. 3. DSC thermograms of PEN/PEI blends after transesterification at 300 °C.

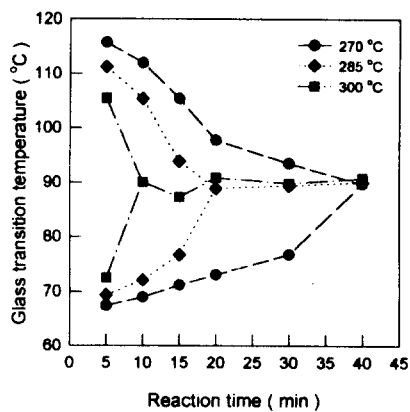


Fig. 4. Changes of glass transition temperature of PEN/PEI blends after transesterification.

Cold crystallization temperature(T_c) and melting temperature(T_m) shifts to higher and lower temperature with reaction time, respectively. Heat of fusion(ΔH_m) decreases with increasing reaction time. These thermal behaviors suggest that the crystallization is hindered due to the disruption of the chain periodicity as a consequence of transesterification. Fig. 4 shows that the higher the reaction temperature is, the shorter the required time to observe a single glass transition is.

Degree of randomness and average sequence length evaluated from NMR spectra⁷ is shown in Fig. 5 and Fig. 6, respectively. Degree of randomness increases and average sequence length decreases, as the reaction time increases. It can be seen that at 300°C the values of degree of randomness become almost 1, indicative of the formation of a random copolymer. For all the blends, this same trends exist, but the length of time needed for the formation of random copolymer is too long for 270 and 285°C. When the value of degree of randomness is greater than about 0.4, a single phase is observed for all the blends.

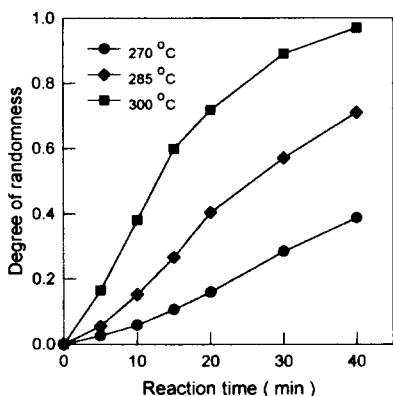


Fig. 5. Changes of degree of randomness during transesterification.

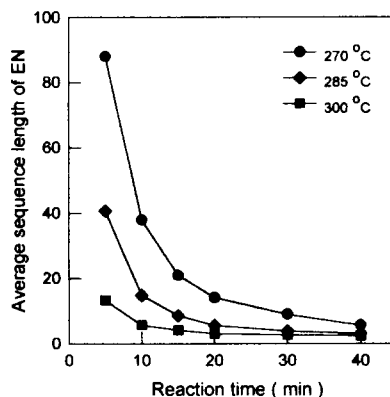


Fig. 6. Changes of the average sequence length of ethylene naphthalate during transesterification.

Reference

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