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polymer communications

The change of the molecular weight of poly(ethylene 2,6-naphthalate) and poly(ethylene terephthalate) blend with reaction time

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The extent of transesterification reaction, intrinsic viscosity, weight-average molecular weight and hydrodynamic radius of poly(ethylene 2,6-naphthalate) (PEN)/poly(ethylene terephthalate) (PET) (50/50, w/w) blend were measured as a function of reaction time at 280°C. In PEN/PET blend, the reactions between end groups as well as the transesterification should be considered since the molecular weight of the blend increases with reaction time. © 1997 Elsevier Science Ltd.

(Keywords: PEN/PET blend; transesterification; end group reaction)

Introduction

In polyester blends, transesterification reactions commonly occur in the molten state, which produces first block copolymers and finally random copolymers. In the present paper, transesterification is used as a general term to describe all reactions, such as, alcoholysis, acidolysis and direct ester interchange reaction. Many studies[1–9] have been focused on miscibility and transesterification reactions in polyester blends. If only transesterification reactions occur, there is no net change in the number of molecules; hence, the number-average molecular weight (M_n) will be unaffected by reorganization process. On the other hand, the molecular weight distribution (MWD) initially bimodal, changes and produces corresponding changes in the weight-average molecular weight, resulting in the decrease of the weight-average molecular weight (M_w) and intrinsic viscosity (η) with reaction. However, there are few papers in which the increase of the molecular weight due to the end group reaction was quantitatively considered. Pilati *et al.*[10] reported that the end group reaction could be mentioned through solubility test of the melt blend of poly(ethylene terephthalate) (PET) and polycarbonate (PC) with reaction time.

In this communication, we report the increase of molecular weight due to the reaction of end groups in poly(ethylene 2,6-naphthalate) (PEN) and PET blend, which has been reported as a immiscible blend[11–13].

Experimental

Materials. PEN was prepared from dimethyl naphthalate and ethylene glycol by melt polymerization. PET was also prepared by the same method from dimethylene terephthalate and ethylene glycol. The polymerization was described in detail elsewhere[11,14]. The weight-average molecular weight of PEN and PET, measured by the laser light scattering method, were 20300 and 39300 g/mol, respectively.

Blend preparation. A blend of PEN/PET (50/50, w/w) was prepared by dissolving the component polymers in a mixed solvent of phenol/o-dichlorobenzene (60/40, v/v). The polymer solution was poured into a large excess of acetone. The precipitated blend was filtered and then dried in a vacuum oven at 60°C for 24 h. Heat treatment for transesterification was carried out on a differential scanning calorimeter (DSC) (du Pont 910) under a nitrogen atmosphere.

Measurements. In order to determine the extent of transesterification with reaction time in PEN/PET (50/50) blend, a 500 MHz FT-NMR spectrometer (Bruker AMX-500) was used. The mixed solvents used were deuterated trifluoroacetic acid/chloroform (70/30, v/v).

The solution properties (i.e. (η), M_w^{app}, R_H) of the reacted blend samples were measured in hexafluoroisopropanol (HFIP) at 35°C, and we diluted the concentration to measure several points.

In order to measure the apparent weight-average molecular weight (M_w^{app}) and the hydrodynamic radius (R_H), a commercial laser light scattering spectrometer (Brookhaven BI-20OSM detector system, BI-9000AT digital correlator) was used with a He–Ne laser (Spectra Physics model 127, operated at $\lambda_0 = 632.8$ nm and 35 mW). The scattered intensity was calibrated with benzene and the weight-average molecular weight was obtained by means of Zimm plot. In static light scattering from a mixture of homopolymers or the copolymer, the apparent molecular weight (M_w^{app}) is obtained instead of the true weight-average molecular weight (M_w)[15]:

$$M_w = M_w^{app} - 2P\left(\frac{v_1 - v_2}{v}\right) + Q\left(\frac{v_1 - v_2}{v}\right)^2 \qquad (1)$$

where $v_i[=(dn/dC)_i]$ and v are the specific refractive index increment of the ith pure component and the copolymer (or

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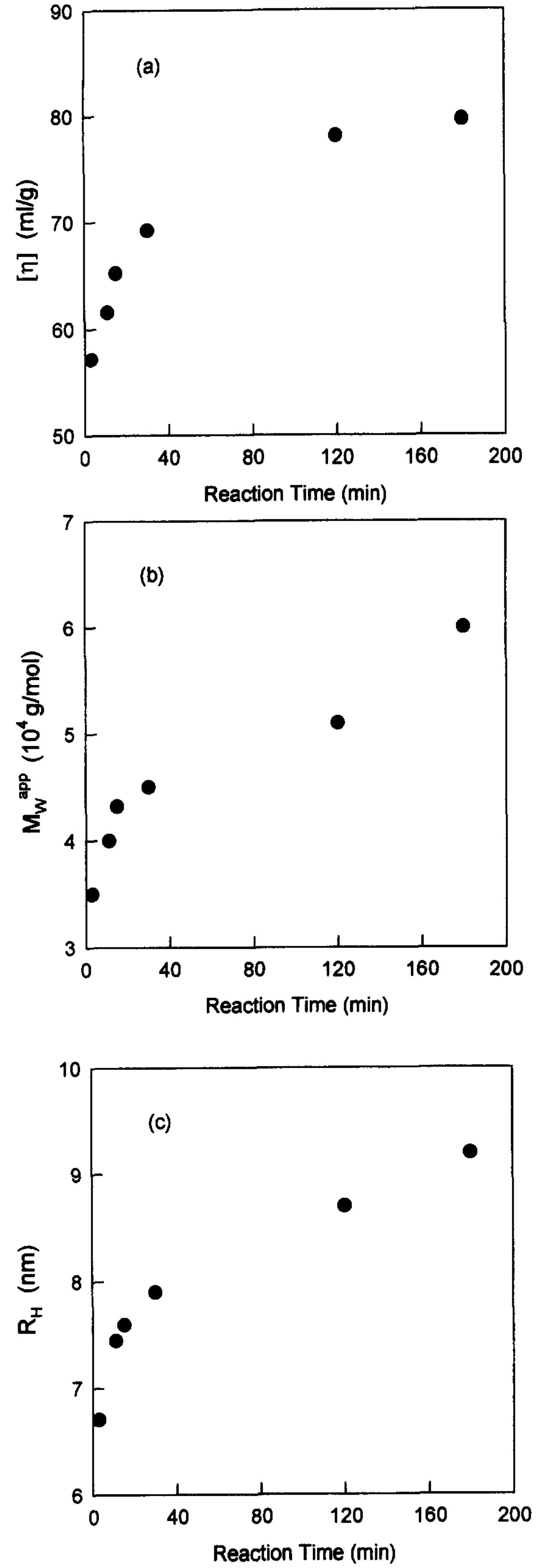

Figure 1 Changes of (a) intrinsic viscosity, (b) apparent weight-average molecular weight and (c) hydrodynamic radius as a function of reaction time at 280°C for PEN/PET (50/50) blend

mixture of homopolymers), respectively. The values of the specific refractive index increment for PEN, PET, and PEN/PET (50/50) blend with various reaction times were measured by a home made differential refractometer at $\lambda_0 =$ 632.8 nm and 35°C: PEN/HFIP, 0.368 mL/g; PET/HFIP, 0.257 mL/g, PEN/PET (50/50)/HFIP, 0.301 mL/g. The values of υ for PEN/PET blend appeared to be independent of reaction time, within experimental error of 2%. P and Q factors depend on both the polymer composition and structure as given:

(i) mixture of homopolymers

$$P = w_1 w_2 (M_{w1} - M_{w2}) \tag{2}$$

$$Q = w_1 w_2 (w_2 M_{w1} + w_1 M_{w2}) \tag{3}$$

(ii) diblock copolymer

$$P = w_1 w_2 [(M_{w1} - M_{n1}) - (M_{w2} - M_{n1})] \tag{4}$$

$$Q = w_1 w_2 [w_2 (m_{w1} - M_{n1}) + w_1 (M_{w2} - M_{n2})] \tag{5}$$

where wi, M_{wi} and M_{ni} represent the weight fraction, the weight-average molecular weight and the number-average molecular weight of component i, respectively.

In dynamic light scattering, z-average characteristic linewith ($<\Gamma>$) could be calcalated from the time autocorrelation function of the scattered intensity by the second-order cumulant method. The effective hydrodynamic radius (R_H) of the polymer chain was calculated from the z-average translational diffusion constant (D_0) using the Stoke–Einstein equation

$$D_0 = (<\Gamma>/q^2)_{c=0,q=0} = k_B T / 6\pi\eta_0 R_H \tag{6}$$

where q is the amplitude of the scattering vector, k_B is the Boltzmann constant, T is the absolute temperature, and η_0 is the solvent viscosity.

Results and discussion

The PEN/PET (50/50) blend was held on the DSC at 280°C for periods from 0 to 180 min. In order to determine the extent of transesterification, the ^{1}H-NMR spectrum of each sample was measured and the results are listed in *Table 1*. The mole fraction of ethylene 2,6-naphthalate–ethylene terephthalate (EN–ET) dyad which resulted from the transesterification reaction and the degree of randomness (B) increase continuously with reaction time.

First, we can estimate the molecular weight of the reacted blend sample at equilibrium state by simple kinetic theory. The weight-average molecular weight of the blend before reaction has the form:

$$(M_w)_0 = w_1 M_{w1} + w_2 M_{w2} \tag{7}$$

The weight-average degree of polymerization (X_{wi}) of each component is related to the degree of reaction (P_i) by

$$X_{wi} = \frac{1 + P_i}{1 - P_i} \tag{8}$$

The weight-average degree of polymerization ultimately obtained by transesterification is given by

$$(X_w)_{EQ} = \frac{1 + P'}{1 - P'} \tag{9}$$

where the subscript EQ represents the equilibrium state and $P' = w_1 P_1 + w_2 P_2$. The weight-average molecular weights of PEN and PET are 20 300 and 39 300 g/mol, respectively, and the calculated value of $(M_w)_0$ of the 50/50 blend is 29 800 g/mol. The values of P_1 and P_2 from equation (8) are 0.976 and 0.990, respectively. From these values, the weight-average molecular weight at equilibrium, $(M_w)_{EQ}$

Table 1 Dyad fractions for PEN/PET (50/50) blend with various reaction time at 280°C

Reaction time (min)	$X^{a}_{\mathrm{EN-EN}}$ (mol %)	$X^{b}_{\mathrm{ET-ET}}$ (mol %)	$X^{c}_{\mathrm{EN-ET}}$ (mol %)	B^{d}
0	44.2	55.8	0	0
3	43.2	54.3	2.5	0.05
7	43.0	51.6	5.4	0.11
11	43.0	48.0	9.0	0.18
13	41.1	48.5	10.4	0.21
15	42.0	47.9	10.1	0.20
20	39.0	48.0	13.0	0.26
30	36.7	44.6	18.7	0.38
40	34.1	42.7	23.2	0.47
60	32.1	37.9	30.0	0.61
120	26.9	33.3	39.8	0.81
180	25.4	30.1	44.5	0.90

[a] mole fraction of ethylene 2,6-naphthalate–ethylene 2,6-naphthalate (EN–EN) dyad
[b] mole fraction of ethylene terephthalate–ethylene terephthalate (ET–ET) dyad
[c] mole fraction of ethylene 2,6-naphthalate–ethylene terephthalate (EN–ET) dyad
[d] degree of randomness, $B = X_{\mathrm{EN-ET}}/2X_{\mathrm{EN}}X_{\mathrm{ET}}$

can be obtained and its value is 25 300 g/mol. The weight-average molecular weight after the transesterification should decrease from 29 800 g/mol initially to 25 300 g/mol at equilibrium.

Figure 1a, however, shows the increase of the intrinsic viscosity with reaction time at 280°C for PEN/PET (50/50) blend, which can be explained with two factors. One is the increase of the molecular weight. The other is the change of solvent quality. In order to confirm which factor is more dominant, the weight-average molecular weight and the hydrodynamic radius (R_H) were measured by means of laser light scattering, and these results are shown in *Figure 1b* and *c*, respectively. Again, we observed that the apparent molecular weight and the hydrodynamic radius also increase with reaction time. At this moment, it is necessary to estimate the magnitude of the difference between the true M_w and the apparent M_w^{app}. For the mixture of homopolymer, the values of the second and third terms of equation (1) become −4750 and 7450 g/mol, respectively. Thus, the true molecular weight (M_w) will be higher than M_w^{app} by 2500 g/mol. For diblock copolymers, such a correction becomes of the order of 1250 g/mol if $M_w/M_n \cong 2$. Finally, for random copolymer[15] M_w^{app} becomes M_w due to $P = 0$, $Q \cong 0$ at $M_w \geq 10^4$ g/mol. Hence, we are sure that the increase of the apparent molecular weight from 29 800 g/mol up to 61 000 g/mol after 180 min is beyond the range of this correction. As a result, it is thought that the molecular weight increases due to the end group reaction. In polyester blends, many studies have been focused mainly on transesterification, such as, alcoholysis, acidolysis and direct interchange reaction. In this PEN/PET blend system, the end group reaction as well as the transesterification should be considered to understand correctly the physical properties of this system.

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