Study on the Kinetics of Transesterification Reaction between Poly(ethylene terephthalate) and its Copolyesters

CHENG FANG OU, MIN SHIUN CHAO, SHIH LIANG HUANG

National Chin-Yi Institute of Technology, Department of Chemical Engineering, Taichung, Taiwan, Republic of China

Received 4 December 1998; accepted 6 March 1999

ABSTRACT: Polyethylene terephthalate (PET) was blended with two kinds of co[poly-(ethylene terephthalate-*p*-oxybenzoate)] (POB-PET) copolyester, designated as P46 and P64, respectively. The PET and POB-PET copolyester were combined in the ratios of 85/15, 70/30, and 50/50. The blends were melt mixed in a Brabender Plasticorder at 275, 285, and 293°C for different amounts of time. The transesterification reactions during the melt mixing processes of PET with POB-PET copolyester blends were detected by proton nuclear magnetic resonance analysis. The values of the rate constants are a function of temperature and the composition of blends. The transesterification reactions that may occur during the melt mixing processes have been discussed also. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2727-2732, 1999

Key words: copolyester; transesterification reaction; nuclear magnetic resonance; blend; kinetics

INTRODUCTION

Recent articles about different aspects of the interchange reactions in different polyester blends have studied mixtures like PET/PBT,¹ PET/polyacrylate-(PAr),^{2–6} bisphenol A polycarbonate (PC)/poly(butylene terephthalate) (PBT),^{7–9} PC/PET^{10–14} and in the blends with POB–PET copolyester such as PBT/POB–PET¹⁵ and PC/POB–PET.^{16–17} As shown in preceding articles, no other important reaction has been detected in PC/PBT^{7–9} and PC/ PET^{10–14} blends in the experimental conditions used. The major conclusions of these studies were that the most likely mechanism of the interchange reaction was a reversible direct transesterification catalyzed by catalyst residues present in commercial PBT and PET polymers.

In our previous research,^{18–20} the transesterification level in the PET and POB–PET blend is a function of temperature, blending times and the

Correspondence to: C. H. Ou.

Journal of Applied Polymer Science, Vol. 73, 2727-2732 (1999)

composition of blends. The most likely interchange reactions that may take place have been proposed and discussed in our research.²⁰ In the present article, we base our kinetic approach on the direct transesterification mechanism and study the kinetic parameters.

THEORETICAL

In terms of a direct ester–ester interchange, the overall reaction mechanism in the PET and POB– PET copolyester blends can be written as

$$\begin{array}{lll} \mbox{PET or copolyester} & \mbox{PET or copolyester} \\ A_1 \sim COO \sim A_2 & + & B_1 \sim COO \sim B_2 & \leftrightarrow \\ A_1 \sim COO \sim B_2 & + & A_2 \sim OOC \sim B_1 \end{array} \tag{1}$$

 A_1 , A_2 , B_1 , and B_2 represent the molecular fragments of PET or POB-PET copolyester. The mol % of POB bonded to the PET unit increases with the level of transesterification reaction. Assuming

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/132727-06

a first order with respect to the reagents for the transesterification reaction, the rate equation for a second-order reaction can be written as

$$\frac{dx}{dt} = k(a - x)(b - x) - k'x^2$$
(2)

In this equation, k and k' represent the rate constants for the forward reaction and reverse reaction, respectively; a and b are the initial mol fraction of the POB-POB dyad and PET-PET dyad in the blend, a + b = 1; x is the mol fraction of POB-PET dyad at time t. Because the concentration of product is much lower than that of reactant at the initial state of reaction, and the $k(a-x)(b-x) >> k'x^2$. With this assumption, eq. (2) is written as

$$\frac{dx}{dt} = k(a-x)(b-x) \tag{3}$$

The rate law may be integrated after arranging it in the form

$$\int_{x_0}^{x} \frac{dx}{(a-x)(b-x)} = \int_{0}^{t} k \, dt \tag{4}$$

If the mol fraction of POB–PET dyad is x_0 at time t = 0, and x at time t, integration yields

$$\frac{1}{(b-a)}\ln\frac{(a-x_0)(b-x)}{(a-x)(b-x_0)} = kt$$
(5)

Defining the transesterification ratio r = x/a, then x = ar, $x_0 = ar_0$. r_0 and r represent the mol fraction of POB as POB–PET in the POB–PET copolyester before blending and in the blends at time t, respectively. On substituting from eq. (5), we obtain a kinetic expression:

$$\frac{1}{(b-a)}\ln\frac{(1-r_0)(b-ar)}{(1-r)(b-ar_0)} = kt$$
(6)

Equation (6) represents the relation between the transesterification ratio and blending time t. The plot of

$$rac{1}{(b-a)} \ln rac{(1-r_0)(b-ar)}{(1-r)(b-ar_0)}$$

vs. t is linear for such a second-order reaction, and the slope is equal to the second-order rate constant k.

EXPERIMENTAL

Materials

POB–PET copolyesters of P46 and P64 were synthesized according to the procedure reported in the previous article.²¹ These two copolyesters contain different POB/PET mol ratios: 40/60 in P46 and 60/40 in P64. The PET resin was generously supplied by Far East Texile Co. (Taoyuan, Taiwan) having an intrinsic viscosity of 0.62 (dL/g) in 60/40 by weight phenol/tetrachloroethane solvent at 30°C.

Blending Method

The blending procedure for PET and copolyesters was described in our previous article.^{18,19} The transesterification kinetic experiments were carried out in the molten state in the barrel of a Brabender Plasticorder at 275, 285, and 293°C.

Determination of the Dyads Fraction

The dyads fractions or the mol % of POB bonded to PET unit were determined from a Varian Model Unity-300 NMR spectrometer as described in Lenz²² and Nicely²³ et al. and our previous article.¹⁹

RESULTS AND DISCUSSION

Cmposition Effect

The occurrence of increasing levels of transesterification reaction in the PET/P46 blends at 275°C after blending times of 3, 8, 20, 40, and 80 min in each PET/P46 weight ratio has been tested. Figure 1 shows the mol % of POB bonded to PET unit as a function of blending time for PET/P46 (85/ 15), PET/P46 (70/30), and PET/P46 (50/50) compositions. It is clearly seen that the mol % of POB bonded to the PET unit (i.e., POB–PET dyad) increases with increasing blending time for these blends. According to our preceding article,¹⁷ the



Figure 1 Mol % of POB connected to PET (i.e., POB– PET Dyad) as a function of the PET/P46 ratio and blending times at 275°C.

uniformity of copolyester dispersed in the PET matrix is increased by increasing the blending time, and at least 3 min is needed to obtain the lower limit of uniformity. For this reason, we will investigate the rate of transesterification reaction



Figure 2 The figure according to eq. (6) as a function of the PET/P46 ratio at 275°C.

Table IThe Values of a and b for Blends withDifferent Composition

	Composition (by Weight)	a	b
PET/P46	85/15	0.0637	0.9363
PET/P46	70/30	0.1078	0.8922
PET/P46	50/50	0.2010	0.7990
PET/P64	50/50	0.3020	0.6980

only between 3 and 80 min. The figure according to eq. (6) as a function of the PET/P46 ratio is shown in Figure 2. The values of a and b in eq. (6) are given in Table I determined by NMR according to Lenz²² and Nicely²³ et al. The values of the rate constants as shown in Table II decrease with increasing the content of P46 in the blend. In other words, the less the content of POB in the blend is, the larger the transesterification reaction rate is. These results indicate that the level of transesterification reaction strongly depends on both the composition of blend and the duration of mixing. The rate of transesterification reaction is a function of the composition of the blend.

Temperature Effect

Figures 3 and 4 show the mol % of POB bonded to PET unit of the PET/P46 (50/50) and PET/P64 (50/50) blends as a function of blending time and temperature at 275, 285, and 293°C. It is seen that the level of transesterification reaction in these two blending systems increases with the blending time at these experimental temperatures. The figures according to eq. (6) as a function of the blending temperature are shown in Figures 5 and 6. The values of the rate constants are given in Table III. The rate constant of THE transesterification reaction increases with increasing the blending temperature in the PET/ P46 (50/50) and PET/P64 (50/50) blends. The result seems to be in accord with the kinetics of the

Table IIRate Constants k as a Function of thePET/P46 Ratio at 275°C

Composition (w/w) PET/P46	$k imes 10^3~({ m min}^{-1})$
85/15	7.89
70/30	3.73
50/50	3.24



Figure 3 Mol % of POB connected to PET (i.e., POB–PET Dyad) of the PET/P46 (50/50) blend as a function of blending times and temperature.

chemical reaction in that the reaction rate will be increased by increasing the reaction temperature. On the other hand, the value of rate constant for the PET/P64 blend is larger than that of the PET/



Figure 5 The figure according to eq. (6) of the PET/ P46 (50/50) blend as a function of temperature.

P46 blend at the same corresponding blending temperature, indicating that the rate of transesterification reaction for the PET/P64 blend is always larger than that of the PET/P46 blend at the same temperature. These results reveal that the rate of transesterification reaction depends on the



Figure 4 Mol % of POB connected to PET (i.e., POB–PET Dyad) of the PET/P64 (50/50) blend as a function of blending times and temperature.



Figure 6 The figure according to eq. 6) of the PET/ P64 (50/50) blend as a function of temperature.

Temperature (°C)	$k imes 10^3 \; (\mathrm{min}^{-1})$		
	PET/P46	PET/P64	
275	3.24	6.65	
285	4.92	9.43	
293	6.33	14.80	

Table III Rate Constants *k* of the PET/P46 (50/50) and PET/P64 (50/50) Blends as a Function of Temperature

composition of the blend and the blending temperature.

Model Transesterification Reaction Occurring in the Melt

The chemical structure of the POB-PET copolyester consists of the following two moieties:



The overall transesterification reaction between PET and the POB–PET copolyester can be written as in eq. (1). According to the results by Viney²⁴ et al., three kinds of ester groups, which were designated as PET-CO-O-PET, POB-CO-O-POB, and POB-CO-O-PET are shown as follows:



All of the three kinds of ester groups are found in POB–PET copolyesters, but the PET polymer only possesses a PET-CO-O-PET ester group. The possible transesterification reactions in the PET and POB–PET copolyester blends are suggested as the following:

Reaction 1: between two PET-CO-O-PET ester groups of PET and copolyester

~PET ₁ -CO-O-PET ₂ ~	+	~PET ₃ -CO-O-PET ₄ ~	\rightarrow
(PET or copolyester) \sim PET ₁ -CO-O-PET ₄ \sim	+	(PET or copolyester) \sim PET ₃ -CO-O-PET ₂ \sim	
Reaction 2: between tw	o PO	DB-CO-O-POB ester	

groups in copolyester

$\sim POB_1$ -CO-O-POB ₂	+	\sim POB ₃ -CO-O-POB ₄ \sim	\rightarrow
(copolyester)		(copolyester)	
~POB ₁ -CO-O-POB ₄ ~	+	~POB ₂ -CO-O-POB ₂ ~	

Reaction 3: between two POB-CO-O-PET ester groups in copolyester

$\sim POB_1$ -CO-O-PET ₁ \sim	+	\sim POB ₂ -CO-O-PET ₂ \sim	\rightarrow
(copolyester)		(copolyester)	
\sim POB ₁ -CO-O-PET ₂ \sim	+	$\sim POB_{o}-CO-O-PET_{1} \sim$	

Reaction 4: between PET-CO-O-PET ester group of PET or copolyester with POB-CO-O-PET ester group of copolyester

Reaction 5: between POB-CO-O-POB ester group of copolyester with POB-CO-O-PET ester group of copolyester

$\sim POB_1$ -CO-O-POB $_2 \sim$	+	$\sim POB_3$ -CO-O-PET ₁ \sim	\rightarrow
(copolyester)		(copolyester)	
$\sim POB_1$ -CO-O-PET ₁ \sim	+	\sim POB ₃ -CO-O-POB ₂ \sim	

Reaction 6: between PET-CO-O-PET ester group of PET or copolyester with POB-CO-O-POB ester group of copolyester

\sim PET ₁ -CO-O-PET ₂ \sim	+	$\sim POB_1$ -CO-O-POB $_2 \sim$	\rightarrow
(PET or copolyester)		(copolyester)	
${\sim}\text{PET}_1\text{-}\text{CO-O-POB}_2$	+	${\sim}\text{POB}_1\text{-}\text{CO-O-PET}_2{\sim}$	

Our study on the kinetics of transesterification reaction in the PET and POB–PET copolyester blend systems is based on the increase of the number of POB-CO-O-PET ester groups or the mol % of POB bonded to the PET unit. In other words, the level of transesterification reaction increases with the increase of the number of the POB-CO-O-PET ester groups or the mol % of POB bonded to the PET unit. Reactions 1 to 6 are the possible transesterification reactions in the blend systems. As to which one exhibits an effect on the increase or decrease of the mol % of POB unit bonded to PET unit, we will discuss as follows.

Reactions 1 and 2 do not exhibit any POB-CO-O-PET ester group in the reactants and products, indicating that these two reaction have no effect on the increase or decrease of the mol % of POB bonded to PET unit. The number of POB-CO-O-PET ester groups in the products is the same as that of the reactants in reactions 3, 4, and 5, indicating that the mol % of POB bonded to the PET unit cannot be increased or decreased by these three reactions such as reactions 1 and 2.

Reaction 6 can increase the mol % of POB bonded to the PET unit, because it produces two new POB-CO-O-PET ester groups by consuming one PET-CO-O-PET ester group and one POB-CO-O-POB ester group. From the results of reactions 1 to 6, the only reaction that can increase the number of POB-CO-O-PET ester groups or the mol % of POB bonded to the PET unit in the PET and POB-PET copolyester blend systems is reaction 6.

CONCLUSIONS

From NMR analysis, the transesterification reactions would take place in the PET/P46 and PET/ P64 blend systems. From the results of transesterification kinetic study, we observed that the reaction can be described by a second-order kinetic model. These kinetic results reveal that the rate of transesterification reaction depends on the composition of blend and temperature.

REFERENCES

- 1. Porter, R. S.; Wang, L. H. Polymer 1992, 33, 2019.
- Kimura, M.; Salee, G.; Porter, R. S. J Appl Polym Sci 1984, 29, 1629.
- Eguiazabal, J. I.; Calahorra, M. E.; Cortazar, M. M.; Iruin, J. J. J Polym Eng Sci 1984, 24, 608.

- Eguiazabal, J. I.; Ucar, G.; Cortazar, M.; Iruin, J. J. Polymer 1986, 27, 2013.
- Eguiazabal, J. I.; Cortazar, M.; Iruin, J. J. J Appl Polym Sci 1991, 42, 489.
- Martinez, J. M.; Nazabal, J.; Eguiazabal, J. I. J Appl Polym Sci 1994, 51, 223.
- Devaux, J.; Godard, P.; Mercier, J. P. J Polym Sci Polym Phys Ed 1982, 20, 1875, 1881, 1895, 1901.
- Devaux, J.; Godard, P.; Mercier, J. P. Polym Eng Sci 1982, 22, 229.
- 9. Birley, A. W.; Chen, X. Y. Br Polym J 1984, 16, 77.
- Pilati, F.; Marianucci, E.; Berti, C. J Appl Polym Sci 1985, 30, 1267.
- Godard, P.; Dekoninck, J. M.; Dolcesaver, V.; Devaux, J. J Polym Sc Part A 1986, 24, 3301.
- Godard, P.; Dekoninck, J. M.; Dolcesaver, V.; Devaux, J. J Polym Sci Part A 1986, 24, 3315.
- Wang, L. H.; Lu, M.; Yang, X.; Porter, R. S. J Macromol Sci Phys 1990, B29, 155.
- Wang, L. H.; Lu, M.; Yang, X.; Porter, R. S. J Macromol Sci Phys 1990, B29, 171.
- Kimura, M.; Porter, R. S. J Polym Sci Polym Phys Ed. 1984, 22, 1697.
- 16. Blizard, K. G.; Baird, D. G. Polym Eng Sci 1987, 27, 653.
- Nobile, M. K.; Amenderla, E.; Nicolais, L. Polym Eng Sci 1988, 29, 244.
- Ou, C. F.; Lin, C. C. J Appl Polym Sci 1996, 59, 1379.
- Ou, C. F.; Lin, C. C. J Appl Polym Sci 1996, 61, 1455.
- 20. Ou, C. F. J Appl Polym Sci 1998, 68, 1591.
- Shinn, T. H.; Chen, J. Y.; Lin, C. C. J Appl Polym Sci 1993, 47, 1233.
- Lenz, R. W.; Jin, J. I.; Feichtinger, K. A. Polymer 1983, 24, 327.
- Nicely, V. A.; Dougherty, J. T.; Renfro, L. W. Macromolecules 1987, 20, 573.
- 24. Viney, C.; Windle, A. H. J Mater Sci 1982, 17, 2661.