

# Interchange Reactions Between Poly(ethylene terephthalate) and Its Copolyesters

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**ABSTRACT:** Poly(ethylene terephthalate) (PET) was blended with two kinds of *co*[poly(ethylene terephthalate-*p*-oxybenzoate)] (POB-PET) copolyester, designated P46 and P64. 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 times. The interchange reactions detected by proton nuclear magnetic resonance analysis occur during the processing at a greater level if the blending time increases. The interchange reactions are as a function of temperature, blending times, and composition of blends. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1591–1595, 1998

**Key words:** copolyester; interchange reaction; alcoholysis; transesterification; nuclear magnetic resonance

## INTRODUCTION

It has been reported by Kotliar<sup>1</sup> that blends of two different polycondensation polymers can react if their chain links are broken as a consequence of high-temperature treatments. He has reviewed interchange reaction involving the condensation polymers, polyesters, and polyamides. He discussed the statistics of three different interchange reactions in which the chains are terminated by hydroxyl or carboxyl groups. The reactions are alcoholysis, acidolysis, and transesterification. Recent papers about different aspects of the interchange reactions in different polyester blends have studied mixtures such as poly(ethylene terephthalate) (PET)/poly(butylene terephthalate) (PBT),<sup>2</sup> PET/polyacrylate,<sup>3–7</sup> bisphenol A polycarbonate (PC)/PBT,<sup>8–10</sup> and PC/PET,<sup>11–15</sup> and the blends with *co*[poly(ethylene terephthalate-*p*-oxybenzoate)] (POB-PET) copolyester, such as PBT/POB-PET<sup>16</sup> and PC/POB-PET.<sup>17,18</sup> It is well known that the interchange reaction in the poly-

mer blends depends strongly on their initial compatibility and blending conditions, including temperature, duration of mixing, preparation method, viscosity match, and presence of catalysts,<sup>11,14</sup> as well as inhibitors.<sup>19–21</sup> As shown in preceding papers, no other important reaction has been detected in PC/PBT<sup>8–10</sup> and PC/PET<sup>11–15</sup> blends under the experimental conditions used. The major conclusion of these studies was 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 the previous investigations of the PET blends with the POB-PET copolyester,<sup>22–25</sup> several conclusions exist concerning the miscibility in these blends, and no specific interchange reaction between the components has been shown; whereas in our previous research,<sup>26,27</sup> the level of transesterification is increased as the duration of melt-blending is prolonged. These interchange reactions hinder the crystallization processes of PET and improve the miscibility or interfacial adhesion between PET-rich and POB-PET copolyester-rich phases. This article reports the results that the interchange reac-

tions between PET and POB-PET copolyester are functions of temperature, blending times, and composition of blends. The most likely interchange reactions that may take place are also proposed and investigated.

## EXPERIMENTAL

### Materials

POB-PET copolyesters of P46 and P64 were synthesized according to the procedure reported in the previous paper.<sup>28</sup> These two copolyesters contain different POB/PET mole ratios: 40/60 in P46 and 60/40 in P64. The PET resin was kindly supplied by Far East Textile Co. (Taoyuan, Taiwan) having an intrinsic viscosity of 0.62 (dL/g) in 60/40 (w/w) phenol/tetrachloroethane at 30°C.

### Blending Method

PET and copolyesters were dried *in vacuo* at 105°C for 48 h before blending to avoid degradation reaction caused by moisture. The blends were prepared by melt-mixing in a Brabender Plasticorder at 275, 285, and 293°C and at a mixing blade speed of 30 rpm. Samples were taken at various times from the mixing bowl and immediately quenched in liquid nitrogen.

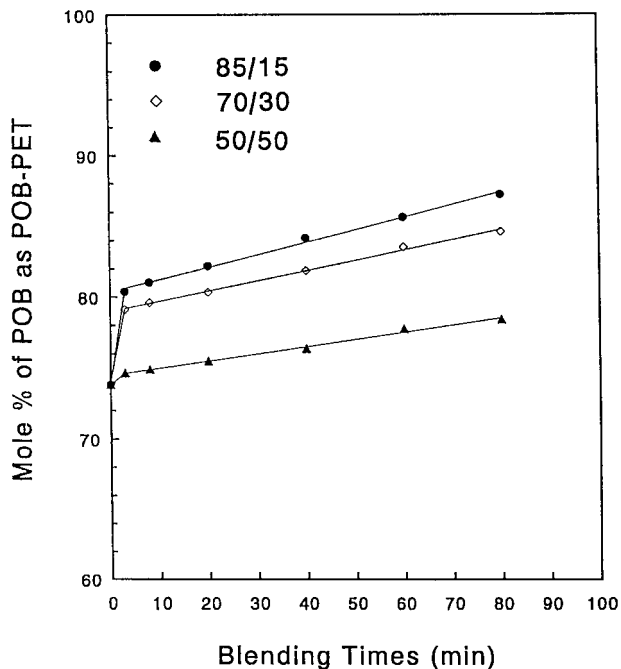
### NMR Spectra

For the nuclear magnetic resonance (NMR) spectra, 5 to 10 wt % solution of blend in deuteriated trifluoroacetic acid was prepared. The spectra were then taken within several hours of the sample dissolution and with tetramethylsilane as the internal standard. The spectra were obtained by a Varian Model Unity-300 NMR spectrometer operating at 300 MHz for observing protons. The identification of interchange reaction and the determination of the mol % of POB bonded to the PET unit by NMR analysis was according to Lenz and associates,<sup>29</sup> Nicely and colleagues,<sup>30</sup> and our previous paper.<sup>27</sup>

## RESULTS AND DISCUSSION

### Composition Effect on the Interchange Reaction

The level of interchange reaction depends on the time-temperature history of the blend. The occurrence of increasing levels of interchange reac-



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

tion 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 was tested. Figure 1 shows the mol % of POB bonded to PET 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 PET (i.e., the POB-PET dyad) increases with blending time for these blends. These results reveal that the interchange reaction occurs within 3 min of blending and the level of interchange reaction increases with the blending time in these blends. The different slopes of the line at the periods between 0 and 3 min and between 3 and 80 min, representing the rates of interchange reaction, depend on the PET/P46 ratio. The slope of the line between 0 and 3 min can be regarded as the initial rate of interchange reaction. According to our previous paper,<sup>26</sup> the 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 uniformity. For this reason we will investigate the rate of interchange reaction only between 3 and 80 min. The values of the slope at the period between 3 and 80 min are given in Table I; they are  $9.00 \times 10^{-2}$ ,  $7.29 \times 10^{-2}$ , and  $5.21 \times 10^{-2}$  (%/min) for PET/P46 (85/15), PET/P46 (70/30), and PET/P46

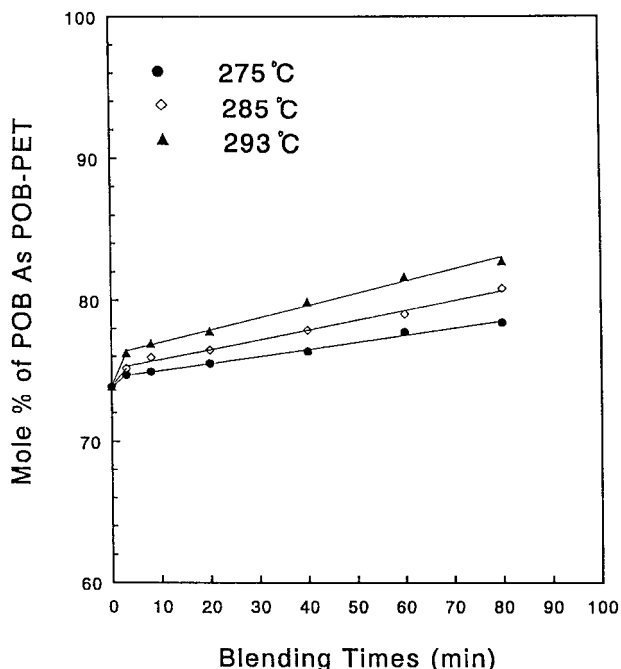
**Table I Values of Slope from Figure 1 for PET/P46 Blend as a Function of Composition at 275°C**

Composition (w/w) PET/P46	Values of Slope (%/min)
85/15	$9.00 \times 10^{-2}$
70/30	$7.29 \times 10^{-2}$
50/50	$5.21 \times 10^{-2}$

(50/50) compositions, respectively. The rate of interchange reaction seems to decrease with increasing the content of P46 in the blend. In other words, the lower the content of POB in the blend, the larger the interchange reaction rate. These results indicate that the level of interchange reaction depends strongly on both composition of blend and duration of mixing. The rate of interchange reaction depends on the composition of blend.

**Temperature Effect on the Interchange Reaction**

Figure 2 shows the mol % of POB bonded to PET in the PET/P46 (50/50) blend as a function of blending time and temperature at 275, 285, and 293°C. It is seen that the level of interchange reac-

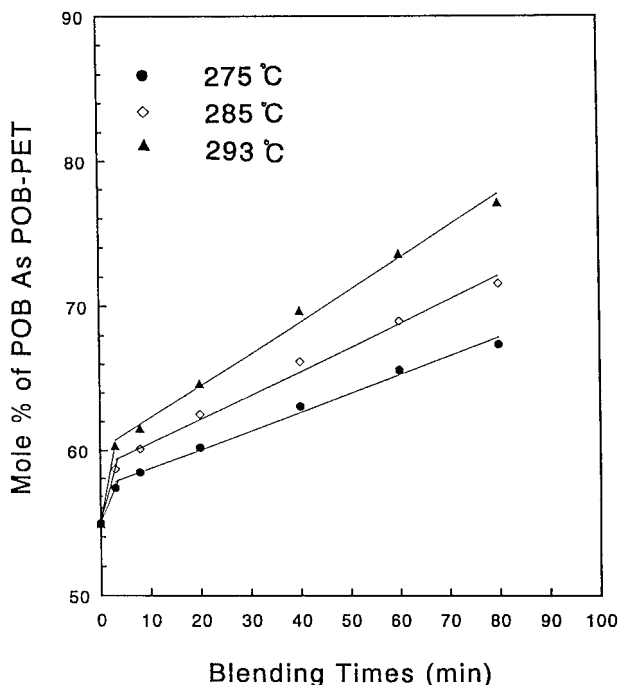


**Figure 2** Mol % of POB connected to PET (i.e., the POB-PET dyad) of the PET/P46 (50/50) blend as a function of blending time and temperature.

**Table II Values of Slope from Figures 2 and 3 for PET/P46 (50/50) and PET/P64 (50/50) Blends as a Function of Temperature**

Temperature (°C)	Values of Slope (%/min)	
	PET/P46	PET/P64
275	$5.21 \times 10^{-2}$	$1.27 \times 10^{-1}$
285	$7.86 \times 10^{-2}$	$1.71 \times 10^{-1}$
293	$8.71 \times 10^{-2}$	$2.21 \times 10^{-1}$

tion increases with the blending time at these temperatures. These lines exhibit different values of slope at the period of 3–80 min, indicating that the rate of interchange reaction depends on the reaction temperature. The values of the slope, as shown in Table II, are  $5.21 \times 10^{-2}$ ,  $7.86 \times 10^{-2}$ , and  $8.71 \times 10^{-2}$  (%/min) for 275, 285, and 293°C, respectively. The rate of interchange reaction increases with increasing the blending temperature. The result seems to agree with the kinetics of chemical reaction that the reaction rate will be increased by increasing reaction temperature. Figure 3 shows the mol % of POB bonded to PET in the PET/P64 (50/50) blend as a function of blending time and temperature at 275, 285, and



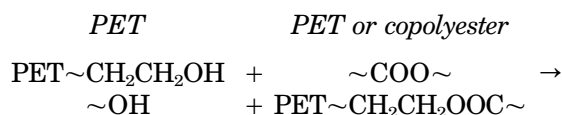
**Figure 3** Mol % of POB connected to PET (i.e., the POB-PET dyad) of the PET/P64 (50/50) blend as a function of blending time and temperature.

293°C. The level of interchange reaction increases with the blending time, and the rate of interchange reaction increases with increasing the blending temperature, as shown in Table II. The results are similar to those of the PET/P46 blend. On the other hand, the value of the slope for the PET/P64 blend is larger than that of the PET/P46 blend at the same blending temperature, indicating that the rate of interchange 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 level of interchange reaction depends strongly on both composition of blend and duration of mixing. The rate of interchange reaction depends on the composition of blend and blending temperature.

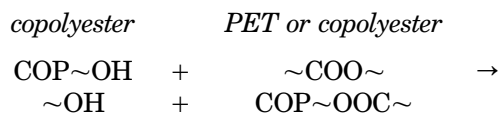
### Model Reaction Occurring in the Melt

The main interchange reactions that may take place between PET and PC, according to the three types of reactions proposed by Pilati and coworkers,<sup>11</sup> are assumed to be alcoholysis, acidolysis, and direct transesterification, if these reactions can be assumed to be valid in PET and PET copolyester blend systems also. The interchange reactions between PET and POB-PET copolyester are the following:

1. Reactions between hydroxyl end groups of PET with ester groups of PET or POB-PET copolyester (alcoholysis):

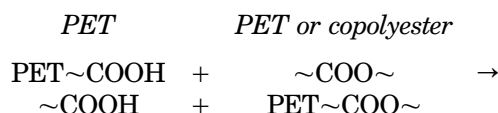


and between hydroxyl end groups of copolyester with ester groups of PET or POB-PET copolyester:

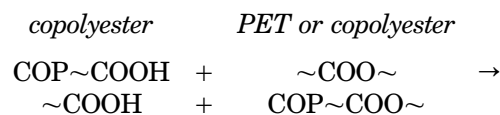


where COP represents a POB-PET copolyester.

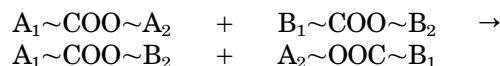
2. Reaction between carboxyl end groups of PET with ester groups of PET or POB-PET copolyester (acidolysis):



and between carboxyl end groups of POB-PET copolyester with ester groups of PET or POB-PET copolyester:

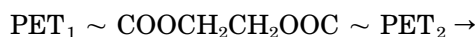


3. Reaction between PET or POB-PET copolyester ester groups with ester groups of PET or POB-PET copolyester (direct transesterification):

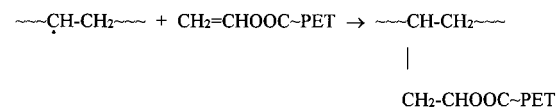


PET exhibits one kind of PET-PET ester group. POB-PET copolyester exhibits three kinds of ester groups: PET-PET, POB-POB, and POB-PET.

4. The pyrolysis reaction can be written as follows<sup>31</sup>:



This reaction leads to a molecular weight decrease. Due to the instability of the vinyl linkages at high temperatures, the mechanism of gel formation during PET pyrolysis proposed by Spaninger<sup>32</sup> as follows:



with the radicals being thermally initiated. Very little information is available about these reactions. From the experimental results of other investigators of the PC/PBT<sup>8-10</sup> and PC/PET<sup>11-15</sup> blend systems, there are three likely mechanisms taking place: alcoholysis and acidolysis of PC by, respectively, OH- and COOH-terminated PET or PBT; and direct transesterification. By comparing the values of rate constants, these researchers concluded that the main reaction occurring in the molten state is a direct ester-ester interchange reaction. From the <sup>1</sup>H-NMR analysis for PET/POB-PET blends, the ratio of POB-PET to POB-POB dyads increases progressively with blending time, meaning that a di-

rect ester-ester interchange reaction takes place during blending.

## CONCLUSIONS

From NMR analysis, the interchange reactions would take place in the PET/P46 and PET/P64 blend systems. The level of interchange reaction depends on composition of blend, blending times, and blending temperature. The rate of interchange reaction depends on the composition of blend and blending temperature. The model reactions in mixtures of molten PET and POB-PET copolyester were proposed. From the study of PC/PBT<sup>8-10</sup> and PC/PET<sup>11-15</sup> blend systems, we are led to the conclusion that the main reaction for the PET/POB-PET blend must be the direct ester-ester interchange reaction.

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