### Chain Extension of Poly(butylene terephthalate) by Reactive Extrusion

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ABSTRACT: The chain extension reaction in poly(butylene terephthalate) (PBT) melt was studied in detail. A high-reactivity diepoxy, diglycidyl tetrahydrophthalate, was used as a chain extender that can react with the hydroxyl and carboxyl end groups of PBT at a very fast reaction rate and a relatively high temperature. A Haake mixer 600 was used to record the torque during the chain extension reaction. The data show that this chain extension reaction could be completed within 2 to 3 min at temperatures above 250°C, and the reaction time decreased very fast with an increase in the temperature. Shear rate also had some effects on the reaction rate. The effect of the diepoxy chain extender on the flowability, thermal stability, and mechanical properties of PBT were investigated. The melt flow index (MFI) of the chain-extended PBT dramatically decreased as the diepoxy was added to PBT. In addition, the notched Izod impact strength and elongation-at-break of the chain-extended PBT also increased. The chainextended PBT is more stable thermally. Compared with the conventional solid postpolycondensation method, this approach is simpler and cheaper to obtain high-molecular-weight PBT resins. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1827–1834, 1999

Key words: poly(butylene terephthalate); diepoxy; chain extender; reactive extrusion

### INTRODUCTION

Poly(butylene terephthalate) (PBT) is well known as a commercial polymeric material with numerous applications, such as fiber, automobile parts, and engineering components. It has been produced by transesterifying and then polycondensing a mixture of dimethyl terephthalate and 1,4butanediol in the presence of catalysts at a high temperature and in a vacuum.<sup>1-2</sup> However, the general grades of PBT with a relatively low molecular weight have inferior mechanical properties and do not meet the requirements of some of the applications. The standard industrial poly-

Contract grant sponsor: Hong Kong Government Research Grant Council; contract grant number: HKUST 582/95P Journal of Applied Polymer Science, Vol. 71, 1827–1834 (1999) merization processes are efficient only in producing PBTs with a MFI higher than 20 g/10 min because the high viscosity makes it very difficult for small molecules, such as water or methanol, to escape. In addition, the degradation reaction rates and side reaction rates are faster than the polymerization reaction rate at high molecular weights. The carboxyl content could increase with an increase in the reaction time, leading to less thermal and hydrolytic stability.<sup>1</sup>

To overcome the limitation of the above-mentioned reaction, a post-polycondensation method in solid phase has been developed.<sup>3</sup> A highermolecular-weight PBT can be obtained by this method. The main disadvantages of this approach are a very slow reaction rate and the necessity of large special equipment, such as pumps and vessels, capable of operating at high temperatures and in high vacuum. Alternately, the reaction

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must be performed in a fluidized bed reactor filled with high-purity nitrogen. The chain-extended PBT with a relatively high molecular weight and a low carboxyl content have improved mechanical and chemical properties, such as toughness and hydrolytic stability. For this reason, using the so-called chain extender is a very attractive option. The chain extenders for PBT are generally bifunctional compounds that react easily with the end groups of PBT, for example, —COOH and —OH, and link two or more polymer chains together, producing relatively high-molecularweight PBT.<sup>2-17</sup>

Chemicals that can be used as chain extenders for PBT are diphenyl carbonate, diphenyl terephthalate, and diphenyl oxalate; but some byproducts, such as phenol, are generated by these chain extension reactions. These by-products having a high boiling point are difficult to be removed from the resultant PBT and may cause problems in some of the commercial applications. An example is shown in Scheme  $1.^2$ 

Therefore, an addition-type chain extender generating no by-products is much more desirable. Bifunctional compounds, such as diepoxy, diisocyanates, and bis(cyclic carboxylic anhydride), are this kind of chain extender. However, some of these bifunctional chain extenders, such as diisocyanates and bis(cyclic carboxylic anhydride), may cause undesirable branching or crosslinking and/or introduce less thermally stable linkages in the PBT molecular chains<sup>4</sup> (see Schemes 2 and 3).

Inata and Matsumara<sup>2,4–8</sup> used many types of oxazine, such as biscyclic-imino-ethers and biscyclic-imino-esters, as chain extenders for both PBT and PET. Some of the oxazines can react with the



The reaction with the carboxyl group is shown in Scheme 4.

The reaction with the hydroxyl group is shown in Scheme 5.

They studied the reaction rate, the carboxyl end group, and the intrinsic viscosity of the resultant products and pointed out that the reaction between this type of chain extender and the end groups of PBT produces no by-products and form linear molecular chains in approximately 5 min. Bikaris and Karayannidis<sup>9–13</sup> synthesized three

Bikaris and Karayannidis<sup>9–13</sup> synthesized three types of diepoxide and used them as chain extenders for PBT and PET. An increase in the intrinstic viscosity and a decrease in the carboxyl content of PBT and PET were obtained. However, the reactivity of these diepoxys toward the hydroxyl group and the carbonxyl group was a little too low; the chain extension reaction could take more than 1 h. These long reaction times make this type of reaction difficult to be carried in an extruder. They also pointed out that the crosslinking occurred after 30 min of reaction time, and that the amount of crosslinked PBT depended on the reaction time and the amount of chain extender added.

In this article, a new diepoxy, which can easily react with both the carboxyl group and the hydroxyl group, was selected as the chain extender for PBT. The chain extension reaction can be finished in approximately 3 min at 260°C. Hence, this reaction can be easily carried out in an ex-



Scheme 2



Scheme 4



truder. The resultant products have improved mechanical and thermal properties.

### **EXPERIMENTAL**

Poly(butylene terephthalate) (MFI = 35.4 g/10min) was supplied by Shanghai Polyester Factory, China. Diglycidyl tetrahydrophthalate was supplied by Qishi Chemical Co., China. 50 g of well-dried PBT was added into the mixing chamber of a Haake Rheomix 600 mixer. The rotor speed varied from 30 to 120 rpm, and the temperature ranged from 230 to 280°C. After complete melting of the pallets, the diepoxy was added to the PBT melt. The torque during mixing, which can be used to measure the extend of the reaction. was recorded. A reactive extrusion was performed on a 30-mm diameter corotating twin-screw-extruder with an L/D ratio of 25, and the extrusion was conducted at 30 rpm at temperatures ranging from 240 to 270°C. A mixture of well-dried PBT and the diepoxy was fed to the extruder. The residence time of the PBT was kept to be about 2.5 min by adjusting the extrusion rate. The extrudate was cooled by water and pelletized.

The chain-extended PBT pellets, which were dried at 80°C for 12 h, were injection-molded by using a Zhende XS-Z-80 injection molding machine to prepare impact and tensile bars. The injection molding temperature was between 220 and 250°C. Mechanical properties and melt flow index (MFI) were measured following the ASTM D638, D790, D265, and M1238 methods. Tensile tests were performed with an Instron with a crosshead speed of 10 mm/min. The MFI was measured by using a Jida XRZ-400 MFI testing instrument with a 2.16 kg load at 250°C. Differential scanning calorimetry (DSC) measurements were performed by a TA 2100 system. Sample weights ranged from 10 to 11 mg. The sample was heated to 260°C at 10°C/min, held at that temperature for 2 min, then cooled to  $-20^{\circ}$ C at  $10^{\circ}$ C/ min, and finally heated to 260°C again at 10°C/ min. The gel content was determined by dissolving 100 mg of the chain-extended PBT in 25 mL of a mixture of phenol and terechloroethane with a

volume ratio of phenol to terechloroethane of 6 to 4 for 4 h at 120°C. The PBT gel was separated from the solution with a filter, washed with terechloroethane, and then dried at 140°C for 2 h. The gel content was determined by measuring the weight increase of the filter paper containing the gel.

The apparent viscosity of the PBTs was measured as a function of shear rate, ranging from 20 to  $3000 \text{ s}^{-1}$  at 250°C using a Göettfert Rheograph 2003 with a die diameter of 1 mm and a die length of 30 mm.

### **RESULTS AND DISCUSSION**

The reaction of the diepoxy with the PBT end groups can be summarized into the three steps shown in Scheme 6.

The epoxy group can react with both the carboxyl group and the hydroxyl group of PBT at a relatively high temperature. The epoxy group reacts more preferentially to the carboxylic group than to the hydroxyl group. Therefore, the chainextended PBT has a relatively low carboxyl group concentration and higher hydrolysis stability. However, in addition to the reactions between the epoxy group and the hydroxyl or carboxyl end groups of PBT, a side hydroxyl group can be formed on the chain-extended PBT molecules, which can further react with the epoxy or carboxyl group to form a branched chain or crosslink. However, the rate of the branching reaction and the crosslinking reaction should be much lower than that of the linear chain-extension reaction because of stereo hindrance.

## Effect of Temperature and Shear Rate on Chain Reaction Time

An Arrhenius type plot showing the relationship between reaction time and temperature is presented in Figure 1. The time needed for the completion of the reaction was determined by measuring the torque. The time when the torque reached the maximum value was regarded as the time for the completion of the reaction. The time required for the completion of the reaction decreased dramatically with increasing reaction temperature. The chain-extension reaction was completed in 3 min at a rotor speed of 30 rpm when the reaction temperature was above 260°C. In addition to temperature, the shear rate also has some effects on the chain-extension rate, as



shown in Figure 2. An increase in the shear rate increases the diffusion rate of diepoxy in the PBT melt; hence, the chain-extension reaction rate increases. Since the diepoxy can completely react with the end groups of PBT in approximately 3 min at 260°C, the extension reaction can be carried out in an extruder (single- or twin-screw extruder). A very small amount of residual diepoxy, which does not produce any side effects on the finished product, can act as a stabilizer to prevent PBT from degradation during further processing.

The chain-extended PBT has good thermal stability, as shown in Figure 3. A torque rheometer was used to measure the thermal stability of the chain-extended PBT. After the addition of the diepoxy to the PBT melt, the torque immediately increased very fast. The increase in the torque



**Figure 1** Plot of  $\ln t$  versus 1/T.



**Figure 2** Relationship between the time for the reaction to complete and rotor speed.



**Figure 3** Torque as a function of reaction time with 1 wt % diepoxy at 250°C and 30 rpm.

was caused by the chain-extension reaction. After the chain-extension reaction was completed, the torque was maintained at a stable value for a very long time (300 s) and then gradually went down. The data shown in Figure 3 indicate that the chain-extended PBT has good thermal stability.

# Mechanical Properties and Melt Flow Index of Chain-Extended PBT

Table I summarizes the results of tensile strength, elongation-at-break, flexural strength, notched Izod impact strength, and MFI of the



Figure 4 MFI as a function of diepoxy content.

chain-extended PBT. The MFI of the chain-extended PBT decreases as a function of the concentration of the diepoxy, as shown in Figure 4. The decrease in the MFI is attributed mainly to the increase in the molecular weight of PBT. An increase in the molecular weight results in an increase in the notched Izod impact strength, as shown in Figure 5 and Table I. The increase in the molecular weight also causes a dramatic increase in the elongation-at-break but only small changes in the tensile and flexural strengths.

Figure 6 shows the stress-strain curves of the chain-extended PBTs. The stress-strain curves change with an increase in the diepoxy content.

Amount of Diepoxy Added (Wt %)	Tensile Strength (MPa)	Elongation at Break (%)	Flexural Strength (MPa)	Izod Impact Strength (J M)	Melt Flow Index (g/10 min)
0	53.7	50.2	88.6	19.9	35.4
0.4	54.4	62.3	91.2	20.2	29.8
0.5	53.9	76.9	91.7	22.9	23.5
0.7	52.3	101.8	93.2	23.2	17.8
0.8	52.6	130.4	89.3	24.1	15.4
0.9	52.3	267.7	93.3	25.7	13.1
1	53.5	262.5	92.1	26.3	10.3
1.2	53.0	278.5	92.5	34.4	8.4
1.3	53.0	329.2	93	39.2	5
1.4	52.9	360.1	92.4	51.9	3.6
1.6	52.1	360	92.2	49.5	2.6

Table I The Effects of the Diepoxy Content on Mechanical Properties



**Figure 5** Relationship between notched Izod impact strength and diepoxy content.

The unmodified PBT is a quasi-brittle polymer, and the elongation-at-break is about 40%. After the chain-extension reaction with 1 wt % diepoxy, the elongation-at-break reaches 260%. The neck propagated almost through the entire gauge length of the specimen. For all chain-extended PBT samples with a diepoxy content above 0.8 wt %, first, the neck propagated to one direction, and



**Figure 6** Plot of tensile stress versus strain for a neat PBT and six chain-extended PBTs (for clarity, each successive curve was shifted up by 5 MPa).

Table IIThe Effect of the diepoxy Content onMelting Point and Crystallization Temperature

Amount of Diepoxy Added (%)	$T_m$ (°C)	$T_c$ (°C)	
0	224.4	178.9	
0.4	223.7	186.5	
0.8	223.5	188.9	
1.0	223.4	189.3	
1.2	222.9	189.4	
1.4	222.1	189.4	

the tensile strength increased by about 30% when that side of gauge length was entirely extended. Then the propagation direction changed to the other side of the PBT sample. This phenomenon can be seen in the stress–strain curves. The change in the direction of the neck propagation occurred at the peaks of the curves. Furthermore, secondary neck propagation was observed in some highly chain-extended PBT (1.4 wt % diepoxy).

### **Thermal Properties**

Table II shows that the chain-extended PBT has a slightly lower melting temperature. The melting temperature decreases as the diepoxy concentration increases. This can be explained by the fact that, in addition to the linear extension of the



**Figure 7** Torque curves for solid-polymerization and chain-extended PBTs as a function of shear mixing time at 250°C and 30 rpm.



**Figure 8** Plots of tensile strength and flexural strength as a function of MFI.

PBT chains, branches that attach to the PBT polymer chains could be formed during the chainextension reaction. The side branches are defects in the crystal lamellae<sup>11</sup>; hence, the heavily chain-extended PBTs have lower melting points. This is also consistent with the fact that the heavily chain-extended PBTs have higher values of  $T_c$ , as shown in Table II.

To test the thermal stability of the chain-extended-PBT, PBT pellets were put in a Haake mixer at 250°C. The torque as a function of mixing time at a constant rotor speed of 30 rpm is shown in Figure 7. The comparison of the torque curves of a commercial PBT produced by solid polymerization and the chain-extended PBT can be used to determine the thermal stability of these materials. Initially, the torque value for the solid-polymerization PBT is higher than that of the chain-extended PBT. However, after 1000 s of



**Figure 9** Plots of elongation-at-break and notched Izod impact strength as a function of MFI.

shear mixing, the torque value of the chain-extended PBT is higher. These results indicate that the chain-extended PBT has better thermal stability, possibly due to the presence of a small amount of residual diepoxy in the chain-extended PBT acting as a stabilizer, and a lower concentration of carboxyl end groups on the PBT chains.

#### **Crosslink of the PBT**

A disadvantage of using the diepoxy as a chain extender for PBT is that crosslinking may be accompanied with the chain-extension reaction. The degree of crosslinking increases with the level of chain extension. This can introduce some problems during the processing of this material. Table III shows the effects of the concentration of the diepoxy on the gel content of chain-extended PBTs. The gel content in PBTs increases as the

Amount of Diepoxy Added (Wt %)	Weight of Chain-Extended PBT Sample (mg)	Filter Paper Weight Increased (mg)	Gel Content (Wt %)
0.4	100.9	0.2	_
0.8	100.7	0.1	_
1.0	100.6	-0.1	_
1.2	100.3	0.3	_
1.4	100.4	8.0	7.97
1.6	100.4	15.1	15.04

Table III The Gel Content of the Chain-Extended PBTs

diepoxy concentration increases, agreeing with the results of Bikiaris and Karayannidis.<sup>9</sup> When the amount of diepoxy was less than 1.2 wt %, there were almost no crosslinks in the PBTs. However, when the amount of the diepoxy was more than 1.2 wt %, the crosslinks started to appear. Some small gel particles could even be seen in the solution of the chain-extended PBT (1.6 wt % diepoxy). Hence, the amount of the diepoxy used should be less than 1.2 wt %. Above that level, crosslinking during the chain-extension reaction becomes significant.

### CONCLUSION

From the above results, the following conclusions can be drawn.

- 1. The diepoxy used in this study is an effective chain extender for PBT.
- 2. The time needed for this chain-extension reaction is less than 3 min; hence, it can be performed in a corotating twin-screw-extruder.
- 3. The chain-extended PBTs have significantly higher mechanical properties and better thermal stability.

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