

# Efficient Method for Recycling Poly(ethylene terephthalate) to Poly(butylene terephthalate) Using Transesterification Reaction

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**ABSTRACT:** A method of recycling postconsumer poly(ethylene terephthalate (PET) using transesterification was studied. Shredded flakes of postconsumer PET waste were transesterified with higher diols, such as 1,4-butanediol, 1,4-cyclohexane dimethanol, and 1,6-hexanediol, to yield copolyesters in the presence of  $\text{Ti}(\text{iPrO})_4$  and  $\text{Sb}_2\text{O}_3$  as catalysts. The extent of the formation of undesirable tetrahydrofuran side products was dependent on the molar ratio of PET to 1,4-butanediol and the time of reflux during transesterification.

Quantitative insertion of the butylene moiety into PET could be achieved under appropriate reaction conditions. The mechanical properties of PBT obtained by a transesterification reaction of PET with 1,4-butanediol were comparable to those of virgin PBT (obtained by direct reaction of dimethyl terephthalate with 1,4-butanediol). © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3720–3729, 2004

**Key words:** recycling; polyesters; mechanical properties

## INTRODUCTION

Industrialization and urbanization has resulted in a large-scale generation of waste that is disposed off by landfill, incineration, composting, and recycling. Poly(ethylene terephthalate) (PET) is one of the most widely used consumer packaging material that is currently being recycled. PET waste is available in the form of fibers, films, bottles, and off-specification chips. The disposal of large volumes of waste PET by an economically viable recycling process has elicited considerable interest in the literature.

There are three main approaches to plastics recycling<sup>1</sup>: (i) primary recycling: It is a process regrind where the polymers are reprocessed singly or in combination with other materials; (ii) secondary recycling: recycling by physical and thermal reprocessing of waste plastics into secondary products; and (iii) tertiary recycling: regeneration of monomers either by (a) chemical recycling which involves depolymerization of off-spec products and in-plant scrap (useful for condensation polymers) or (b) thermal (also called quaternary) recycling where pyrolysis of plastic-rich waste is converted to an oil-type fraction (useful for addition polymers). The two main methods of recycling waste PET are (1) reacting the polyester wastes with polyols or poly(carboxylic acid)s to give new polyester oligomers<sup>2,3</sup> or (2) depolymerization of PET

waste to the starting raw materials and their reuse for the production of polyester.<sup>4–15</sup>

In all the methods reported so far, the objective is to convert waste PET to polyester raw materials or to PET for reuse. From the point of view of waste load on the environment, it would be desirable to convert waste PET into another product which has a longer life cycle in applications. This way, a short life-cycle product such as PET would become converted to a long life-cycle product, thus minimizing the environmental impact of waste generation.

Polyesters derived from 1,4-butanediol (BD) and 1,4-cyclohexane dimethanol (CHDM) are materials used in such long life-cycle applications. Thus, it would be advantageous to convert waste PET to poly(butylene terephthalate)s (PBTs) and poly(1,4-cyclohexane dimethylene terephthalate)s (PCHDMTs) or poly(1,6-hexamethylene terephthalate)s by direct transesterification of PET with BD, CHDM, and 1,6-hexanediol.

An examination of the prior literature shows that examples of such approaches to waste recycling are rare. We found only two patents describing the direct transesterification of PET to PBT using BD.<sup>16,17</sup> This article reports our results of an extensive study to delineate the scope of such transesterification reactions for the valorization of PET waste.

## EXPERIMENTAL

### Materials

Shredded flakes of postconsumer PET bottles supplied by Futura Polymers (Chennai, India) were used as received. The analysis of the PET flakes is shown in

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TABLE I  
Analysis of PET Waste

Form	Flakes
Color	Blue-, green-, and yellow-colored flakes
$\eta_{inh}$ (dL/g)	0.7
Acid no. (equiv/10 <sup>6</sup> g)	32
Sb content (ppm)	50

Table I. Phenol, 1,1,2,2-tetrachloroethane (S.D. Fine Chem., Bombay, India), and antimony trioxide (Sb<sub>2</sub>O<sub>3</sub>; Aldrich) were used as received. BD, 1,4-cyclohexanedimethanol, 1,6-hexanediol, and titanium(IV) isopropoxide [Ti(iPrO)<sub>4</sub>] were obtained from Aldrich and distilled prior to use.

### Polymerization

In a typical reaction, shredded flakes of postconsumer PET bottles (0.026 mol) were placed in a two-necked round-bottom flask fitted with a reflux condenser. Excess diol (0.065, 0.13, and 0.26 mol corresponding to a mol ratio of PET : diol of 1 : 2.5, 1 : 5, and 1 : 10, respectively) was added and heated between 230 and 250°C for 4 h in the presence of 0.05–0.5 wt % Sb<sub>2</sub>O<sub>3</sub> or Ti(iPrO)<sub>4</sub>, based on the weight of the PET flakes placed. After refluxing for 4 h, the reflux condenser was replaced with a Leibig condenser and the distillate was collected. The pressure inside the reactor was reduced to 100 mbar and the temperature was simultaneously increased to 250°C. The pressure was reduced from 100 to 1 mbar over a period of 40–50 min at 250°C. The reaction mixture was held at this temperature for 1 h. When no more distillate was col-

lected, the reactor was cooled under a vacuum and the resulting polyester was isolated.

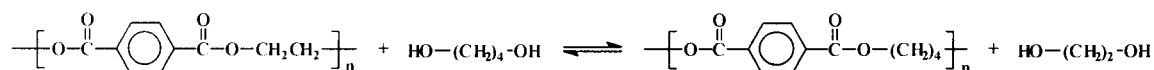
In the case of 1,4-cyclohexanedimethanol and 1,6-hexanediol, a PET : diol feed ratio of 1 : 4 was used. Owing to the higher melting nature of these diols, higher reaction temperatures (280–300°C) and longer reaction times were employed for the conversions.

### CHARACTERIZATION

The inherent viscosities ( $[\eta]_{inh}$ ) of 0.5% (wt/vol) solutions of the polymer in phenol : tetrachloroethane (60 : 40 wt/wt) were determined using a Schott Gerate AVS viscometer using an Ubbelohde viscometer at 25 ± 0.1°C. <sup>1</sup>H-NMR spectra were recorded on a Bruker 200-MHz spectrometer in a mixture of CDCl<sub>3</sub> : CF<sub>3</sub>COOH (4 : 1 vol/vol).  $T_g$  and  $T_m$  were measured on a Perkin-Elmer DSC-7 in aluminum pans at a heating rate of 10°C/min in a draught of nitrogen. GC analysis was performed using the following conditions—temperature program: 50°C (5 min), 45°C/min (ramp rate); carrier gas pressure: 7 psi (0.3 mL/min); injector: 250°C; FID: 280°C. Response factors for THF and ethylene glycol (EG) were determined from their respective calibration curves using phenol as the internal standard and were used in the calculations for determining the moles of THF and EG. Acid values were determined by Pohl's method.<sup>18</sup>

### RESULTS AND DISCUSSION

Transesterification is a process where one ester is transformed into another through the interchange of the alkoxy moiety. This reaction is an equilibrium reaction catalyzed by acids, bases, amines, or alkoxides and occurs, essentially, by mixing the two components<sup>19</sup>:



The transesterification reaction as an effective method of recycling postconsumer PET flakes was studied in detail using BD. The effect of the reaction time, feed ratio, catalyst concentration, and catalyst type were examined.

The composition of the resulting polyesters was determined from an integration of  $-(\text{CH}_2)_4-$  protons at 4.4  $\delta$  and  $-(\text{CH}_2)_2-$  protons at 4.8  $\delta$ . The conversion of PET to PBT was inferred by the absence of the  $-(\text{CH}_2)_2-$  protons and the appearance of the  $-(\text{CH}_2)_4-$  protons in the NMR spectra. Figure 1 is a typical spectrum of waste PET, virgin PBT, and a sample of PBT obtained after transesterification.

The use of excess diols in these transesterification reactions leads to glycolysis of PET. Further polycon-

densation leads to polyesters. It is recognized that during the transesterification reaction with BD in the presence of catalysts tetrahydrofuran (THF) is formed.<sup>20–23</sup> It was shown that an increase in temperature, BD-to-DMT feed ratio, or catalyst concentration leads to higher production of methanol, that is, higher transesterification. An increase in the temperature and the BD-to-DMT ratio also increased the THF formation. A higher catalyst concentration caused the amount of THF to decrease.<sup>21</sup>

#### Effect of reflux time on the conversion profile/transesterification reaction

PET flakes (5 g, 0.026 mol), BD (5.0 g, 0.065 mol), and the Sb<sub>2</sub>O<sub>3</sub> catalyst (0.0025 g, 0.05 wt % based on PET)

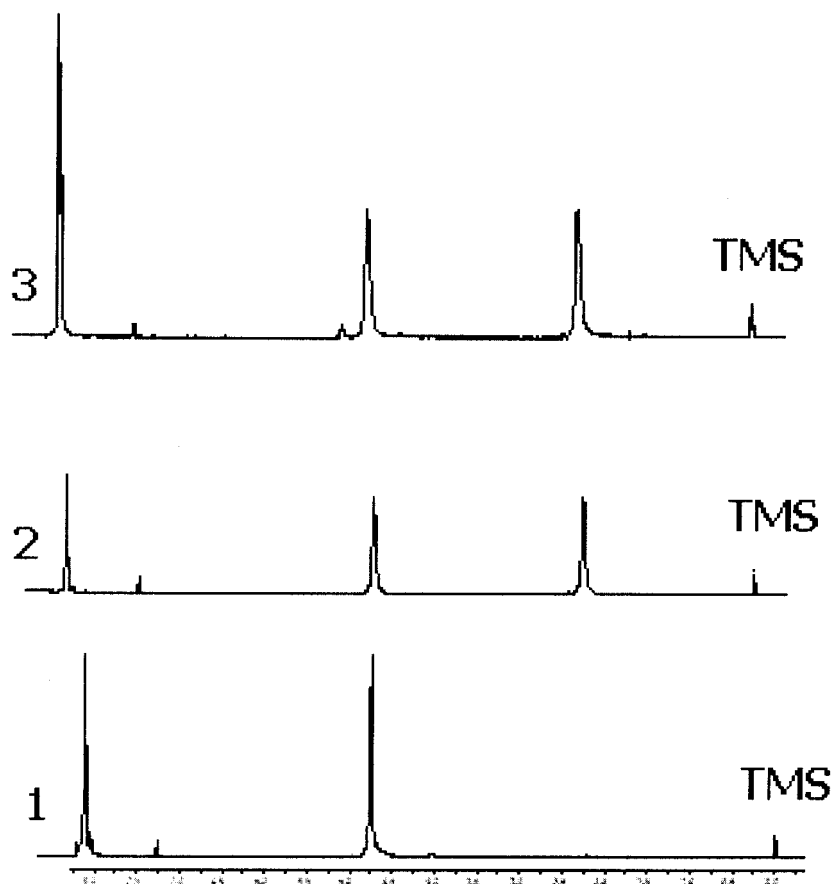


Figure 1  $^1\text{H-NMR}$  spectra of (1) PET, (2) PBT, and (3) transesterified product (97%) (Table III, entry no. 7).

were taken in a round-bottom flask and refluxed for varying lengths of time. A limiting conversion of 95% was reached in a reflux time of 4 h. Conversion as well as the extent of THF formation increased as a function of the reflux time (Table II). The conversion profile of transesterification reactions in the presence and absence of a catalyst is shown in Figure 2.

#### Effect of PET:BD ratio on THF formation on the presence and absence of externally added catalyst

During the degradation of PET with BD, a large number of hydroxybutyl end groups are formed which can either

undergo transesterification or cyclization to form THF. The greater the amount of BD, the greater will be the degradation of PET and the higher will be the concentration of the hydroxybutyl end groups. Intramolecular cyclization of the butyl end groups is unaffected by dilution, but this reaction may be reduced indirectly by use of a good transesterification catalyst and/or a higher catalyst concentration. THF can also be formed by dehydration of BD catalyzed by the acid groups generated as a result of intramolecular cyclization of the hydroxybutyl end groups or from the acid groups already present in PET (Scheme 1). The total amount of THF formed is a

TABLE II  
Conversion Profile in the PET-BD Transesterification Reaction

Sample no.	Reflux time (h)	THF (mol)	Mol % THF based on BD	Mol % butylene in PET	Inherent viscosity <sup>a</sup> $[\eta]_{\text{inlv}}$ dL/g	$T_m$ (°C)	Acid value <sup>b</sup> (equiv $10^6$ g)
1	1	0.004	6.5	44	0.31	184	49
2	2	0.013	20	63	0.33	184	63
3	3	0.026	40	75	0.32	191	77
4	4	0.026	40	82	0.35	194	75

Reaction conditions: 230°C/no  $\text{N}_2$  flow; 250°C/40 min/100–1 mbar; 250°C/1 h/0.05–0.03 mbar; PET : BD ratio 1 : 2.5; no catalyst; mol of BD = 0.065.

<sup>a</sup> Determined in 60 : 40 mixture of phenol + TCE at 25°C.

<sup>b</sup> Determined by Pohl's method.

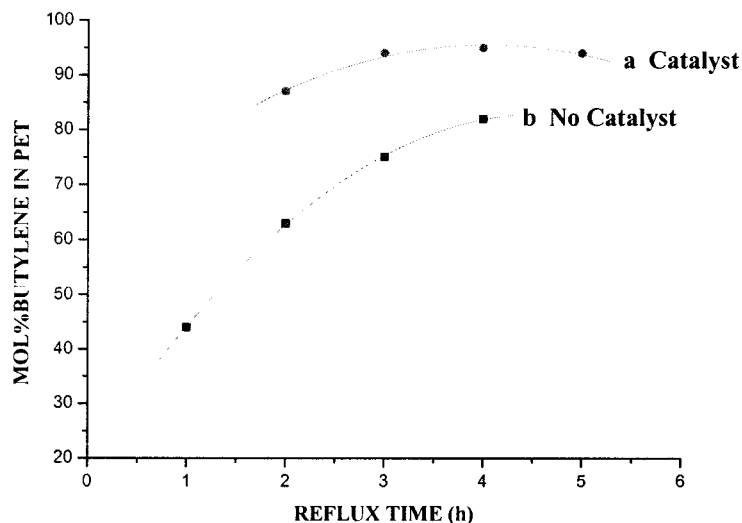
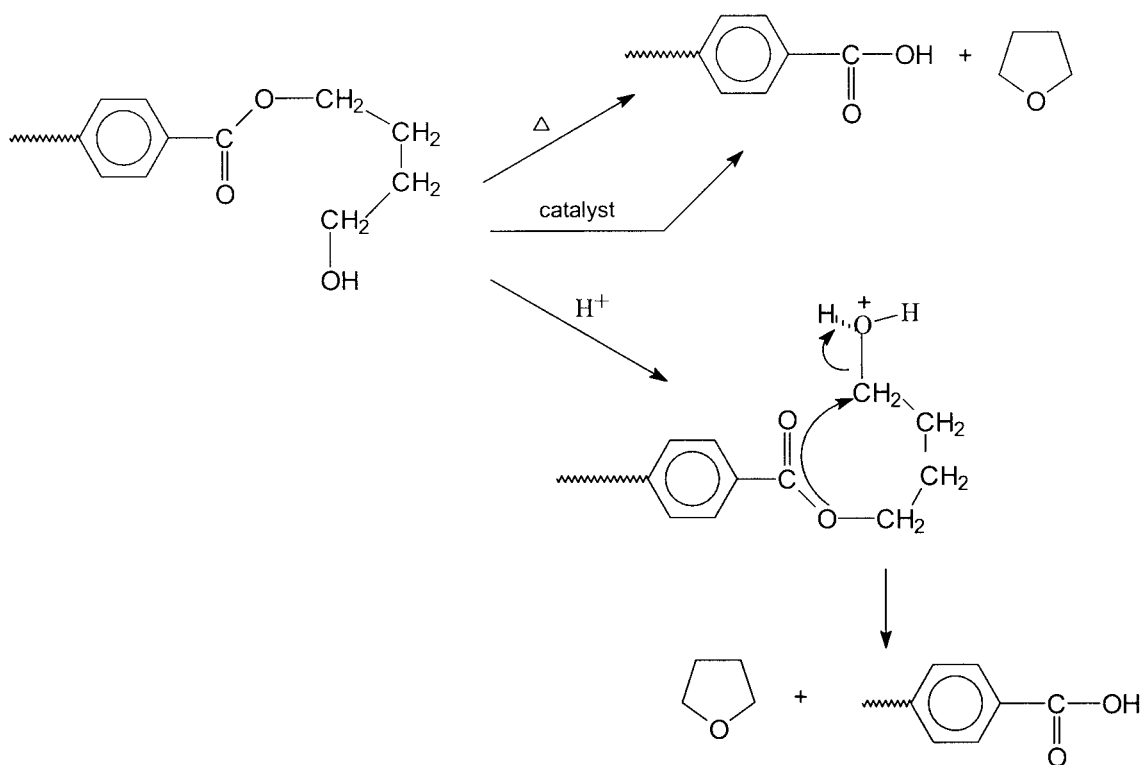


Figure 2 Effect of reflux time on transesterification.

net result of these two reactions, that is, intramolecular cyclization and acid-catalyzed dehydration. Catalysis by acid groups is often affected by dilution. The increase in THF from the cyclization reaction is compensated by the decrease in the THF formation by acid catalysis as the dilution increases. To verify this hypothesis, the following studies were undertaken:

PET and BD in different feed ratios were placed in a round-bottom flask and refluxed (i) without an addi-

tional catalyst, (ii) with an additional  $\text{Sb}_2\text{O}_3$  catalyst, and (iii) with an additional  $\text{Ti}(\text{iPrO})_4$  catalyst, as shown in Table III. It can be seen that in the absence of any catalyst the mol percent THF based on the BD added decreases inversely as the feed ratio of BD : PET increases. The mol percent butylenes in PET remains constant. The acid value of the transesterified polymer is higher than that of the starting material (PET flakes), indicating the occurrence of intramolecular cycliza-



Scheme 1 Formation of THF and carboxylic acid group during PET : BD transesterification reaction.

TABLE III  
Effect of PET : BD Ratio on Conversion and THF Formation

Sample no.	PET : BD ratio	BD (mol)	THF (mol)	Mol % THF based on BD	Mol % butylene in PET	Inherent viscosity <sup>a</sup> [ $\eta$ ] <sub>inh</sub> dL/g)	T <sub>m</sub> (°C)	Acid value <sup>b</sup> (equiv/10 <sup>6</sup> g)
1	1 : 2.5	0.065	0.028	42.0	83	0.35	197	98
2	1 : 5	0.130	0.041	31.5	82	0.33	197	—
3	1 : 10	0.260	0.048	18.5	76	0.33	189	102
Externally added catalyst = Sb <sub>2</sub> O <sub>3</sub> (0.0025 g)								
4	1 : 2.5	0.065	0.028	43.0	89	0.43	208	48
5	1 : 5	0.130	0.052	40.0	91	0.55	212	45
6	1 : 10	0.260	0.052	20.0	83	0.48	204	49
Externally added catalyst = Ti(iPrO) <sub>4</sub> (0.0025 g)								
7	1 : 2.5	0.065	0.022	34.0	97	0.55	220	24
8	1 : 5	0.130	0.060	46.0	99	0.52	225	24
9	1 : 10	0.260	0.096	37.0	100	0.48	223	22

Reaction conditions: 230°C/4 h/no N<sub>2</sub> flow; 250°C/40 min/100–1 mbar; 250°C/1 h/0.05–0.03 mbar.

<sup>a</sup> Determined in 60 : 40 mixture of phenol + TCE mixture at 25°C.

<sup>b</sup> Determined by Pohl's method.

tion. At the BD : PET feed ratio of 1 : 10, a large effect of dilution with BD on THF formation is seen. Therefore, although the amount of THF formed increases with an increase in the amount of BD, the overall mol percent THF formed based on moles of BD decreases with an increase in the BD amount, indicating a dilution effect.

In the presence of the Sb<sub>2</sub>O<sub>3</sub> catalyst, the mol percent of THF formed based on BD decreases as the feed ratio of BD : PET increases. Under these conditions, only a slight increase in the carboxyl group formation is observed in comparison with the PET flakes. Thus, Sb<sub>2</sub>O<sub>3</sub> promotes transesterification (as seen by the higher mol percent butylene in PET) over the dehydration of THF to form acid groups.

In the case of Ti(iPrO)<sub>4</sub>, as the PET : BD feed ratio increases, the mol percent THF formed increases from

34 to 46 mol %. With a feed ratio of 1 : 10, there is a decrease in the mol percent THF formed. There is a substantial increase in the mol percent butylene content in PET. The acid value also is lower when Ti(iPrO)<sub>4</sub> is used as compared to Sb<sub>2</sub>O<sub>3</sub>. These reaction conditions, thus, do not favor carboxyl group formation. Ti(iPrO)<sub>4</sub> promotes transesterification (as seen by the near complete substitution of the butylene moiety in PET) over the dehydration of THF to form acid groups (Figs. 3 and 4).

#### Effect of dilution of carboxyl groups with BD on THF formation

To study the effect of the dilution of the carboxyl groups with BD on THF formation, the following

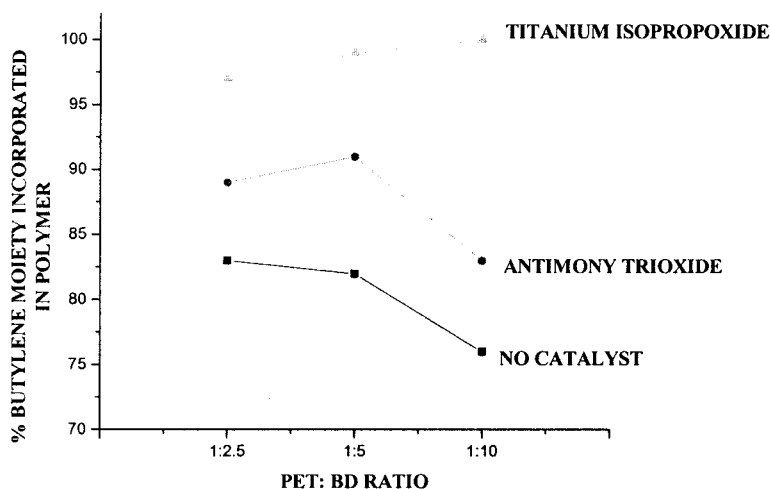


Figure 3 Effect of PET : BD feed ratio on conversion.

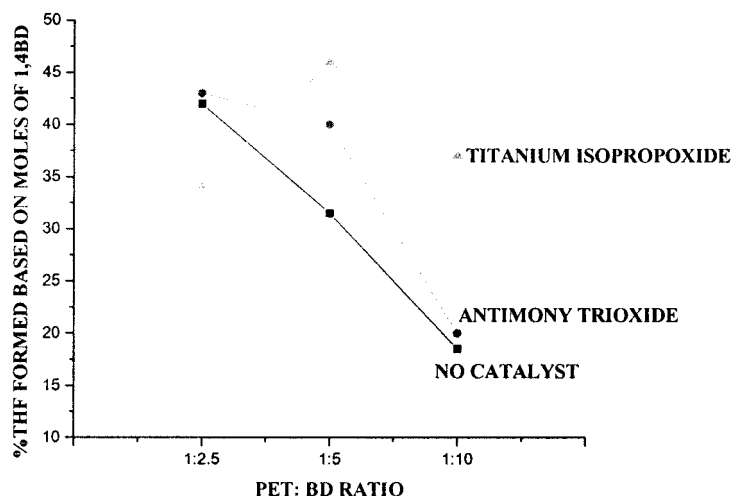


Figure 4 Effect of PET : BD feed ratio on THF formation.

model reactions were carried out, both in the presence and the absence of the  $\text{Sb}_2\text{O}_3$  catalyst: Benzoic acid (1 g) was heated with different amounts of BD at  $230^\circ\text{C}$  for 2 h without a nitrogen flow. It was observed that both in the presence and the absence of the  $\text{Sb}_2\text{O}_3$  catalyst the mol percent THF formed decreases slightly with an increase in the BD amount. This shows that there is a slight effect of the dilution of the carboxyl end groups with BD in the formation of THF catalyzed by carboxyl groups (Table IV and Fig. 5).

#### Effect of 4-HBB concentration on THF formation

Degradation of PET with BD leads to the formation of hydroxybutyl end groups that can either undergo transesterification or intramolecular cyclization to form THF, which is unaffected by dilution. To verify this hypothesis, 4-hydroxybutyl benzoate (4-HBB) and BD were heated at  $230^\circ\text{C}$  for 2 h in the presence of the  $\text{Sb}_2\text{O}_3$  catalyst. It was observed that in the presence of  $\text{Sb}_2\text{O}_3$  there is a marginal increase in THF formation. Thus, it is inferred that an increase in the 4-HBB concentration will lead to higher THF formation (Table V).

#### Effect of dilution on THF formation in the presence of 4-HBB

To explore whether dilution has any effect on the THF formation in the presence of 4-HBB, 4-HBB (1.5713 g, 0.0081 mol) was refluxed with varying amounts of BD. It can be seen that in the absence of a transesterification catalyst the mol percent THF increases with the amount of BD taken. An increase in THF is due to intramolecular cyclization. No effect of dilution is noticed. In the presence of the catalyst ( $\text{Sb}_2\text{O}_3$ ), there is also no effect of dilution.

Intramolecular cyclization is not affected by dilution. However, in the presence of the transesterification catalyst, an increase in BD increases THF marginally, which may be due the preponderance of the transesterification reaction over cyclization, leading to THF formation (Table VI).

#### Effect of $\text{Sb}_2\text{O}_3$ concentration on the exchange reaction

PET (5.0 g, 0.026 mol) and BD (5.0 g, 0.065 mol) were refluxed with 0.05, 0.1, and 0.5 wt %  $\text{Sb}_2\text{O}_3$  based on PET to study the effect of a varying concentration of the catalyst on the transesterification reaction. It was observed that with an increase in the catalyst concentration the conversion, as reflected by the mol percent insertion of butylene in PET, increases. The best re-

TABLE IV  
Effect of Dilution of Carboxyl Groups with BD on THF Formation

Sample no.	Amount of BD taken, g (mol)	THF (mol)	Mol % THF based on BD
Without catalyst			
1	5.9161 (0.066)	0.00474	7.3
2	11.7523 (0.13)	0.00636	4.9
3	23.4260 (0.26)	0.00800	3.1
Catalyst $\text{Sb}_2\text{O}_3$ : 0.0025 g			
4	5.8667 (0.065)	0.00442	6.8
5	11.7679 (0.13)	0.00573	4.4
6	23.4312 (0.26)	0.00738	2.8

Reaction conditions :  $230^\circ\text{C}/2$  h, no  $\text{N}_2$  flow; benzoic acid (1 g).



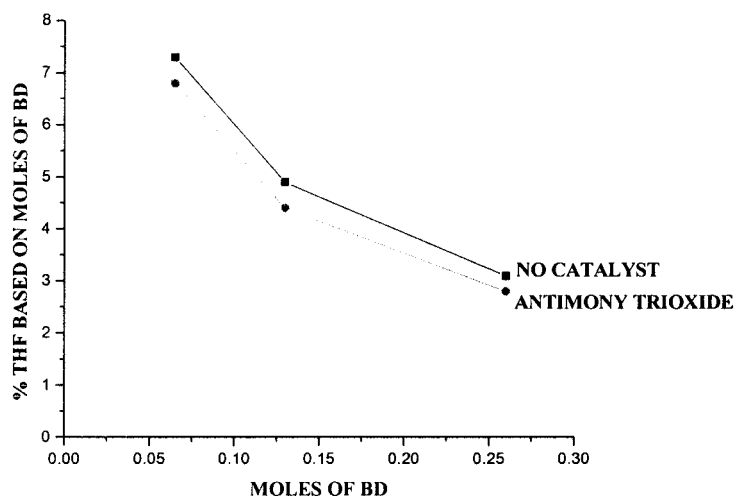


Figure 5 Effect of dilution of carboxyl groups with BD on THF formation.

TABLE V  
Effect of 4-HBB Concentration on THF Formation

Sample no.	Amount of 4-HBB g (mol)	Amount of BD, g (mol)	THF (mol)	Mol % THF based on BD
1	1.5882 (0.0081)	5.9323 (0.066)	0.021	33
2	3.1428 (0.0162)	5.8860 (0.065)	0.026	41

Reaction conditions : 230°C/2 h, no N<sub>2</sub> flow; Sb<sub>2</sub>O<sub>3</sub> : 0.0025 g.

sults (100%) were obtained at a concentration of 0.5 wt % catalyst (Table VII).

#### Effect of catalyst and its concentration on THF formation in the PET transesterification reaction

To study the effect of the catalyst type on THF formation, PET (5.0 g, 0.026 mol) and BD (5.0 g, 0.065 mol) were refluxed with 0.025 g Sb<sub>2</sub>O<sub>3</sub> and Ti(iPrO)<sub>4</sub> as shown in Table VIII. It can be seen that the Ti(iPrO)<sub>4</sub> catalyst results in a lower mol percent of THF formation as compared to Sb<sub>2</sub>O<sub>3</sub>. The Ti(iPrO)<sub>4</sub> catalyst gave a slightly higher acid value as compared to Sb<sub>2</sub>O<sub>3</sub>. This

indicates the higher efficiency of Ti(iPrO)<sub>4</sub> as a transesterification catalyst as compared to Sb<sub>2</sub>O<sub>3</sub>.

#### Effect of diphenyl ether (DPE) as a diluent on the transesterification reaction

To study the effect of a diluent on the transesterification reaction, PET : BD (feed ratio 1 : 2.5) in the presence of DPE as a diluent was carried out (Table IX). In the absence of the Ti(iPrO)<sub>4</sub> catalyst and a diluent, a higher mol percent THF formation is seen, indicating a higher intramolecular cyclization, while in the presence of a diluent, the mol percent THF

TABLE VI  
Effect of Dilution on THF Formation in the Presence of 4-HBB

Sample no.	Amount of 4-HBB (g)	Amount of BD (g)	THF (mol)	Mol % THF based on BD
Without catalyst				
1	1.5713 (0.0081)	5.9250 (0.066)	0.039	61
2	1.5868 (0.0081)	11.7337 (0.130)	0.110	85
With catalyst Sb <sub>2</sub> O <sub>3</sub> : 0.0025 g				
3	1.5882 (0.0081)	5.9323 (0.066)	0.021	33
4	1.5836 (0.0081)	11.8393 (0.130)	0.050	38

Reaction conditions : 230°C/2 h, no N<sub>2</sub> flow.

TABLE VII  
Effect of Antimony Trioxide Concentration on the Transesterification Reaction

Sample no.	Catalyst (Sb <sub>2</sub> O <sub>3</sub> ) concentration (wt % based on PET)	Mol % butylene in PET	Inherent viscosity <sup>a</sup> ( $[\eta]_{inh}$ , dL/g)	T <sub>m</sub> (°C)
1	No catalyst	86	0.10	186
2	0.05	94	0.35	212
3	0.10	98	0.23	214
4	0.50	99	0.14	213

Reaction conditions : 230°/4 h/N<sub>2</sub> flow, 250°/1/100–1, 250°/1/6–0.02; PET : BD : 1 : 2.5.

<sup>a</sup> Determined in 60 : 40 mixture of phenol + TCE at 25°C.

formation and the acid values are lower, indicating a favorable effect of the dilution. In the presence of the Ti(iPrO)<sub>4</sub> catalyst and in the absence of a diluent, a higher mol percent THF formation and a low acid value is seen in the resulting polyester. However, in the presence of a diluent, a low percent THF formation was observed, indicating high intramolecular cyclization.

#### Transesterification of PET with other diols

A transesterification reaction on PET was also carried out using 1,4-cyclohexanedimethanol and 1,6-hexanediol. These reactions resulted in complete transesterification (Table X). The <sup>1</sup>H-NMR spectrum of the polymer based on 1,4-cyclohexanedimethanol was characterized by the absence of —(CH<sub>2</sub>)<sub>2</sub>— protons of

PET (4.8 δ, s, 2 H) and the appearance of —(CH<sub>2</sub>)— protons (4.3–4.4 δ, m 4 H) and the cycloaliphatic protons (1.0–2.0 δ, m 11 H) from 1,4-cyclohexanedimethanol. Similarly, in the <sup>1</sup>H-NMR spectrum of the polymer based on 1,6-hexanediol, the —(CH<sub>2</sub>)<sub>2</sub>— protons of PET (4.8 δ, s, 2 H) were replaced by —(CH<sub>2</sub>)<sub>6</sub>— protons (4.4 δ, t, 4 H; 1.9 δ, m, 4 H; and 1.6 δ, m, 4 H) from 1,6-hexanediol.

#### Mechanical properties

The mechanical properties, namely, the tensile strength and the unnotched Izod impact strength of PBT obtained upon transesterification of scrap PET, were determined. These results are shown in Table XI. These values compare well with virgin PBT.

TABLE VIII  
Effect of Catalyst and Its Concentration on THF Formation in the Transesterification Reaction<sup>a</sup>

Sample no.	PET : BD ratio/ catalyst	BD (mol)	THF (mol)	Mol % THF based on BD	Mol % butylene in PET	T <sub>m</sub> (°C)	Inherent viscosity <sup>a</sup> ( $[\eta]_{inh}$ , dL/g)	Acid value <sup>b</sup> (equiv 10 <sup>6</sup> g)
1	1 : 2.5/Sb <sub>2</sub> O <sub>3</sub>	0.065	0.028	44	96	220	0.51	23
2	1 : 2.5/Ti(iPrO) <sub>4</sub>	0.065	0.016	25	98	226	0.54	39

Reaction conditions : 230°C/4 h/no N<sub>2</sub> flow; 250°C/40 min/100–1 mbar; 250°C/1 h/0.05–0.03 mbar; catalyst concentration : 0.5 wt % of PET = 0.025 g.

<sup>a</sup> Determined in 60 : 40 mixture of phenol + TCE at 25°C.

<sup>b</sup> Determined by Pohl's method.

TABLE IX  
Effect of Diphenyl Ether as a Diluent on the Transesterification Reaction

Sample no.	BD (mol)	Amount of DPE (g)	THF (mol)	Mol % THF based on BD	Mol % butylene in PET	Inherent viscosity <sup>a</sup> ( $[\eta]_{inh}$ , dL/g)	T <sub>m</sub> (°C)	Acid value <sup>b</sup> (equiv 10 <sup>6</sup> g)
1	0.065 <sup>c</sup>	Absent	0.028	42	83	0.35	197	98
2	0.065 <sup>c</sup>	17.55	0.003	5	42	0.27	185	63
3	0.065 <sup>d</sup>	Absent	0.016	25	98	0.54	226	39
4	0.065 <sup>d</sup>	17.57	0.012	18	99	0.68	222	86

Reaction conditions : PET : BD = 1 : 2.5, 230°C/4 h/no N<sub>2</sub> flow; 250°C/40 min/100–1 mbar; 250°C/1 h/0.05–0.03 mbar.

<sup>a</sup> Determined in 60 : 40 mixture of phenol + TCE at 25°C.

<sup>b</sup> Determined by Pohl's method.

<sup>c</sup> No catalyst was added.

<sup>d</sup> 0.025 g Ti(iPrO)<sub>4</sub> was added as a catalyst.



TABLE X  
Transesterification of PET with 1,4-Cyclohexane Dimethanol and 1,6-Hexanediol

Sample no.	Diol	PET : diol	Reaction conditions	% conversion	Inherent viscosity <sup>a</sup> ( $[\eta]_{inh}$ , dL/g)	$T_m$ (°C)
1	1,4-Cyclohexane dimethanol	1 : 4.03	283°C/5 h/N <sub>2</sub> flow + 283°C/2.5 h/100–1 mm of Hg + 283°C/2 h/1 mm of Hg + 300°C/1 h/1 mm of Hg	100	0.20	285
2	1,6-Hexanediol	1 : 4.07	280°C/5 h/N <sub>2</sub> flow + 280°C/1 h 40 min/100–1 mm of Hg + 280°C/2 h/1 mm of Hg	100	0.40	137

Catalyst : Sb<sub>2</sub>O<sub>3</sub> (0.5 wt % of PET, 0.025 g).

<sup>a</sup> Determined in 60 : 40 mixture of phenol + TCE at 25°C.

### CONCLUSIONS

Shredded flakes of postconsumer PET bottles as well as other forms of PET waste could be recycled to PBT by transesterification with BD. In the recycling of PET by transesterification, an optimum reflux time was found to be 4 h for achieving a limiting conversion of 95%.

In the absence of additional catalyst excess, BD results in a higher THF formation resulting from intramolecular cyclization. However, in the presence of transesterification catalysts, the percent THF formed is less and there is a preponderance of transesterification over dehydration to form THF. A higher 4-HBB concentration leads to higher THF formation by intramolecular cyclization, which is unaffected by dilution. An increase in the catalyst concentration leads to better conversion and the best results are obtained with a catalyst concentration of 0.5 wt %. Ti(iPrO)<sub>4</sub> is a better catalyst than is Sb<sub>2</sub>O<sub>3</sub>. In the absence of a catalyst and a diluent, THF formation is high compared to the

situation when a diluent is present. On the other hand, in the presence of a catalyst and in the absence of a diluent, higher THF formation is observed and a lower acid value when compared to the situation when a diluent is present. The conversion and extent of THF formation increased with an increase in the reflux time.

The composition of the resulting copolyester could be varied by a judicious choice of the diol/PET feed ratio, time, temperature, and catalyst used for transesterification. PET could also be converted to other poly(alkylene terephthalate)s, for example, poly(1,4-cyclohexane dimethylene terephthalate) and poly(1,6-hexamethylene terephthalate). The mechanical properties of PBT obtained from scrap PET are comparable to those of virgin PBT.

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TABLE XI  
Mechanical Properties of PBT Generated from Postconsumer PET Flakes

Properties	PBT virgin <sup>a</sup>	PBT generated from PET scrap
Tensile strength <sup>b</sup>		
At yield (MPa)	42.5	46.6
At break (MPa)	24.5	30.5
Elongation <sup>c</sup> (%) at yield	20	20
Izod impact strength <sup>b</sup> (unnotched) (J/m)	735	620
Color		Cement gray
Physical form		Powder
$\eta_{inh}$ <sup>d</sup> (dL/g)		0.90–1.00
Acid no. (equiv/10 <sup>6</sup> )		72–75
$T_m$ (DSC) (°C)		221–225
Ethylene glycol content (mol %)		<3

<sup>a</sup> Arnite-T 200 (AKZO).

<sup>b</sup> Instron tensile strength tester (Model 1122).

<sup>c</sup> CEAST impact strength tester (Model 6545).

<sup>d</sup> Phenol : tetrachloroethane (60 : 40 w/w).

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