

# Chemical Recycling of PET Flakes into Yarn

Prasad S. Upasani, Ashwin K. Jain, Ninad Save, Uday S. Agarwal, Anil K. Kelkar

Reliance Technology Group, Reliance Industries Limited, B-4 MIDC Industrial Area, Patalganga, Dist. Raigad, Maharashtra, India

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**ABSTRACT:** Polyesters such as polyethylene terephthalate are widely used in textile fibers, films, and packaging of food and beverages. Originally driven by environmental reasons, recycling of postconsumer polyester bottles into textile fibers is now becoming commercially attractive. We studied the chemical recycling wherein part of the virgin raw-materials during preparation of polyester was replaced by washed post consumer polyester. During the process, the postconsumer polyester undergoes partial de-

polymerization before repolymerization. Role of reactor-agitator configuration in achieving the solid-slurry and solid-melt mixing, and in depolymerization, was studied. Finally, suitability of the polymer for melt spinning and drawing of polymer into yarn was examined. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 520–525, 2012

**Key words:** recycling; step-growth polymerization; polyesters; fibers

## INTRODUCTION

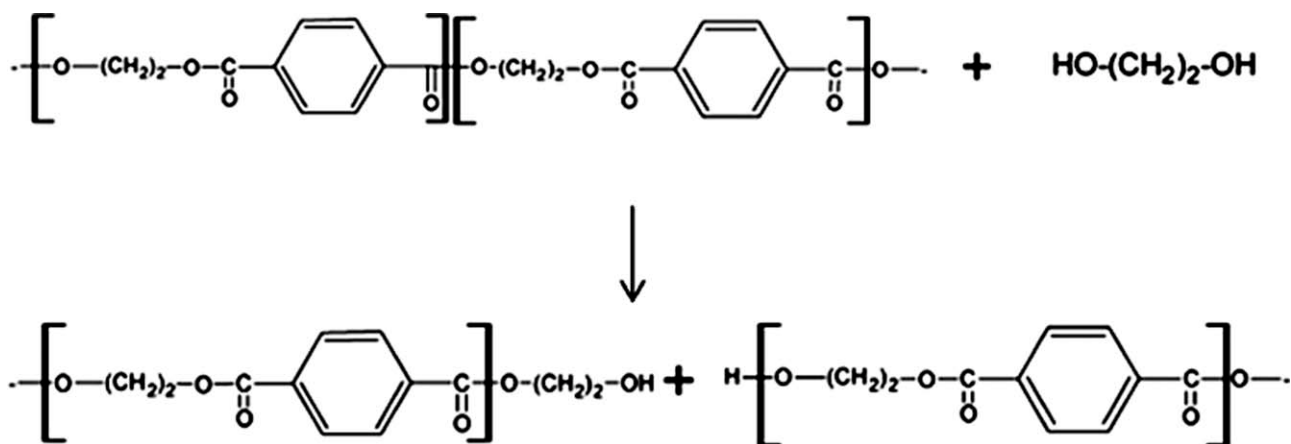
Poly(ethylene terephthalate) (PET) is a commodity polymer used as a high-molecular weight polymer (intrinsic viscosity,  $[\eta] \sim 0.82$  dL/g) in bottles for packaging fluids such as mineral water and soft drinks<sup>1,2</sup> and also used as a moderate molecular weight polymer ( $[\eta] \sim 0.6$  dL/g) in textile fibers. Recycling of the polymer is desired to reduce the environmental impact of plastics but suffers from the following factors. During the life cycle of PET polymer, the material characteristics change due to thermal and environmental influences. For example, the  $[\eta]$  of the PET bottle reduces from 0.82 dL/g to less than 0.76 dL/g. In addition, diffusion of filled product into the PET bottle polymer also causes contamination and degradation of the polymer. Finally, a simple recycling process that involves crushing the used bottles to obtain flakes from the bottle walls, washing and cleaning the flakes to remove external contaminants, drying, and then melt extrusion into desired product leads to the additional loss of molecular weight to  $[\eta] \sim 0.6$  dL/g. The melt extrusion step can optionally be carried out after blending with virgin PET so as to reduce the negative impact on the quality of the end product. In an alternative approach, the washed, recycled PET flakes can be completely or partially depolymerized by glycolysis with monethylene glycol (MEG; Scheme 1).

The depolymerization product can be filtered and then further repolymerized to give desired product  $[\eta]$ . This depolymerization-polymerization process can be carried out using the washed flakes as partial feeds in a polymerization plant operating with purified terephthalic acid (PTA) and MEG as feeds. As shown in the schematic representation of a typical polyester polymerization process (Fig. 1), PTA powder and MEG are mixed to obtain a high-solid content slurry, which is pumped to the esterification vessel operating under elevated pressure for obtaining molten oligomer of intermediate molecular weight. The molten oligomer is then subjected to polycondensation under high vacuum to obtain the polymer of  $[\eta] \sim 0.6$  dL/g. Glycolysis of recycled PET with MEG, especially with regards to kinetics, has been a subject of several prior studies.<sup>3–6</sup> However, these have most often addressed complete depolymerization of PET with MEG to bishydroxyethyl terephthalate, while in a commercial process, it is often more economical to only partially depolymerize the recycled PET with oligomer. In addition, we are not aware of any consideration being given to the role of mixing of the recycle flakes, as well as the role of contaminants on the subsequent processing of the PET into yarn.

As shown in Figure 1, we can use one of the two approaches to add the washed and cleaned recycled flakes to the polymerization system:

1. Addition to PTA-MEG feed slurry in the polymerization plant or
2. Addition to virgin oligomer obtained from partial polymerization of PTA-MEG

Correspondence to: U. S. Agarwal (uday.agarwal@ril.com).



Scheme 1 PET depolymerization with MEG.

Possibility of these two approaches was studied in this work. In the first approach, the flakes are needed to ground into powder (size 1–3 mm) before adding to the PTA-MEG slurry with high solid content, to enable convenient pumping into the esterification vessel. In the second approach, larger recycle flakes ( $\sim 10$  mm) could be added to esterification vessel without further grinding as the flakes could undergo rapid dissolution in the oligomer melt (and thus did not need to be pumped into polycondensation vessel as flakes). We further investigated the first approach by following the polymerization process given in Figure 1, to prepare the polyester containing 20 wt % recycle PET, and used this polyester to carry out melt spinning into yarn. The recycled PET flakes used here were from a commercial wash line where postconsumer plastic bottles were manually sorted, crushed into flakes, and further segregated from other plastics by using density-based separation. One of the contaminants in PET flakes is polyvinyl chlorides (PVC). Density of PVC being comparable to density of PET, the removal of PVC is incomplete.<sup>7</sup>

## EXPERIMENTAL

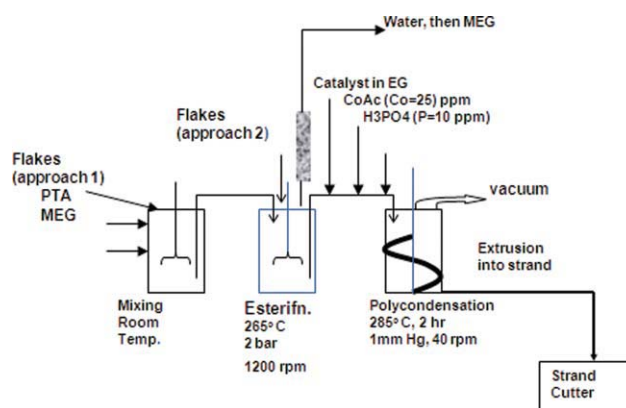
### Study of dispersion of PET flakes in MEG-PTA slurry

A beaker (diameter = 10 cm) equipped with an agitator (diameter = 5 cm) was used for studying the dispersion of flakes with MEG-PTA slurry. The MEG-PTA slurry at the desired mole ratio (MEG:PTA = 2 or 1.125, called high and low respectively, with the corresponding PTA solid concentration being 57 and 70 wt %, respectively) was first prepared in a cylindrical glass beaker. The mixture level in the beaker was adjusted as desired by taking the required amount of the slurry, and the agitator level in the beaker could be adjusted as desired by

lifting or lowering the beaker using a jack. Washed recycled PET flakes (1–3 mm) were gradually added to the agitated slurry at 40 °C when desired, to make up to 10 wt % of PTA. The dispersion behavior of the flakes into the MEG-PTA slurry was visually observed.

### Study of the dissolution and reaction in the molten oligomer

One hundred grams of oligomer was melted in a beaker placed in an oil bath at 255°C. The molten oligomer was stirred with a stirrer attached to a motor. Recycled PET flakes (10 wt%, size 10 mm) were added to the molten oligomer. Time taken for complete melting/dissolution of flakes was noted. Samples were taken at various intervals 30 s, 2 min, 5 min, and 10 min and were analyzed by gel permeation chromatography (GPC) and compared with physical mixture of oligomer and flakes in same proportion. For GPC, the mobile phase used was a mixture of hexafluoroisopropanol and chloroform



**Figure 1** A typical polyester polymerization process. Two approaches for adding recycle flakes are shown. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE I**  
**Effect of Agitator Speed and Solid Content of Slurry on Dispersion of Flakes (10 wt %) in PTA-MEG Slurry, with Height of the Agitator from Bottom Being 1 cm, and Total Height of Slurry in the Beaker Being 6 cm**

Expt. No.	Agitator speed (RPM)	MEG:PTA mole ratio	Solid content of slurry (wt %)	Observations
1	250	2	57	Flakes could be dispersed easily in slurry
2a	250	1.125	70	Flakes could not be dispersed easily in slurry as the slurry movement at the top surface was very slow
2b	1000	1.125	70	As compared to 2a, high RPM (1000) was required to ensure top surface liquid being drawn towards agitator. The slurry was very thick. (approx. 1000 cP)

(ratio 2 : 98), flowing at the rate of 0.6 mL/min. The column used was a high-resolution, mixed-bed low-molecular weight range (Waters HSPgel HR MB-L) column suitable for molecular weights 500–700,000.

### Pilot plant scale trial

PET polymerization with 20% recycled PET flakes

Recycled PET flakes were crushed by using a grinder to size of 1–3 mm.  $[\eta]$  of flakes was 0.712 dL/g. MEG (27 kg) was taken in a 60-kg capacity agitated batch autoclave. ZnAc (85 ppm) was added to the reactor for catalyzing the glycolysis reaction. PTA (36 kg) was added to the reactor, followed by addition of recycle PET flakes (20 wt %, 10.4 kg). The reaction mixture was pressurized to 2 bar under nitrogen. Temperature was gradually raised to 260°C over 3.5 h to allow esterification. Following depressurization, antimony trioxide catalyst (300 ppm Sb in PET) dissolved in ethylene glycol was added. The molten oligomer was transferred to polycondensation vessel. The mixture temperature was increased to about 285°C, while gradually reducing the pressure over 45 min to 1 mm of Hg to obtain the polymeric product. After 103 min of polycondensation when the required polymer viscosity was achieved (as indicated by the agitator torque), the vacuum was released and polymer was extruded under nitrogen pressure

into molten strands that were chilled in water bath and then cut into chips. The polyester chips were analyzed for usual properties such as the  $[\eta]$ , color, diethylene glycol (DEG) content, acid end-groups, and so on.

Melt spinning of the PET chips containing recycled PET

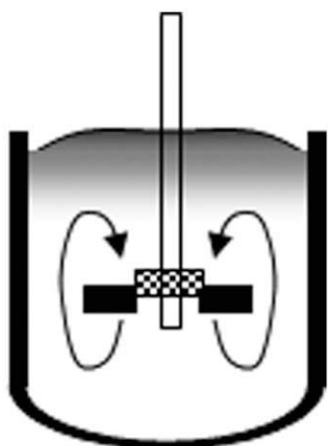
The polyester chips were crystallized and air dried at 140°C, melted in an extruder, and molten polymer was pumped at the rate of 1.75 kg/h through a spin-pack fitted with 36-hole spinneret (area 38 cm<sup>2</sup>) at 280°C. The extruded filaments were quenched using cold air at 18°C and taken up at a spinning speed of 1228 m/min on first godet maintained at 80°C and further drawn 2.85 times to second godet running at 3500 m/min maintained at 145°C, and then wound on paper tube to produce a fully drawn yarn (FDY). Spinnability and back pressure developed due to flow through spin pack were monitored. The yarn properties such as mechanical and linear mass variations (Uster) were measured as usual. The color measurements were done in the device-independent CIE  $L^* a^* b^*$  color space, where the  $L^*$  axis represents the lightness or brightness of the image, the  $a^*$  axis runs from red to green, and the  $b^*$  axis runs from yellow to blue.

**TABLE II**  
**Effect of Slurry Height Above the Agitator and Solid Content of Slurry on Dispersion of Flakes (10 wt %) in PTA-MEG Slurry with Total Height of Slurry in the Beaker Being 12.5 cm**

Expt. No.	Agitator Speed (RPM)	Agitator height from bottom (cm)	Slurry Height above agitator (cm)	MEG : PTA mole ratio	Solids in slurry (%)	Observations
3	500	2.5	10	2	57	Flakes could be dispersed easily in the slurry
4a	500–1500	2.5	10	1.125	70	Flakes were forming a stagnant layer at the top, and were not getting drawn into the slurry unless dipped manually with a rod. The slurry had high viscosity.
4b	500–1500	7.5	5	1.125	70	When compared with 4a the dispersion of flakes was possible when the agitator was moved up to bring closer to slurry top surface.



(a)



(b)

**Figure 2** Status of the flakes added to the slow agitated slurry with high solids content (a) top view and (b) flow pattern (downward fading represents flakes density reducing from surface downwards). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

## RESULTS AND DISCUSSION

### Dispersion of PET flakes in MEG-PTA slurry

To simulate the dispersion of flake into MEG-PTA slurry in the following approach of recycling, the flakes were added on surface of the MEG-PTA slurry under agitation in a beaker. Tables I and II show the observation of the dispersion behavior in response to various parameters of the process, such as the MEG-PTA mole ratio (or, solid content, and

hence viscosity of the slurry), the agitator speed, and the height of the slurry above the agitator.

Experiment 1 (Expt. 1) given in Table I shows that when the solid content in the slurry is low, even the low agitator speed and the corresponding flow at the slurry surface is sufficient for good dispersion. However, at the high solid contents, if the agitator speed is not high (Expt. 2a), the added powder accumulates at the slurry surface [Fig. 2(a)]. Thus, the powder does not get drawn into the bulk of slurry, and the dispersion does not take place. Only when the stirrer speed is increased (Expt. 2b), the circulatory flow generated by the agitator is sufficient for proper dispersion of the flakes into the PTA-MEG slurry.

Table II shows that when the solid content in the slurry is high (Expt. 4a) when compared with Expt. 3, even the higher agitator speed (500–1500 rpm) and the corresponding flow at the slurry surface are not sufficient to draw the powder into the vortex, as the slurry height above the agitator is large (10 cm). This is because the circulatory flow due to the agitator is not felt at the slurry surface due to its large vertical distance from the agitator [Fig. 2(b)]. When the agitator level is raised to bring it closer to the slurry surface (Expt. 4b), the flakes are pulled radially inward the slurry surface and then drawn into the shear zone near the agitator to enable the desired dispersion.

Thus, concentration of solid in slurry, agitator rpm, and slurry height above agitator are the critical parameters in determining the dispersion of the flakes added onto the slurry surface.

### Reaction-dissolution of PET flakes in molten oligomer

To simulate the second approach, recycle flakes (10 wt %) were added to molten oligomer under stirring.

At low agitator speed, the flakes float on the surface of the molten oligomer. At high agitator speed, the flakes get drawn toward the shaft into the molten oligomer due to the circulatory flow generated by agitator. When mixed with the molten oligomer, the flakes dissolve within 30 s. Within this short

**TABLE III**  
Change in Molecular Weight of Recycle Flakes (10 wt %) by Melt Mixing into Molten Oligomer at 250°C

Sr. No.	Sample Identity	Peak 1 Mp (% Area)	Peak 2 Mp (% Area)	Peak 3 Mp (% Area)	Peak 4 Mp (% Area)	Peak 5 Mp (% Area)
1	Flakes	50329 (98.5%)	–	–	512 (1.5%)	–
2	Oligomer	–	–	1816 (81.8%)	308 (10.9%)	93 (7.3%)
3	30 s	–	4559 (97.7%)	–	–	105 (2.3%)
4	2 min	–	4822 (97.9%)	–	–	105 (2.1%)
5	5 min	–	4822 (97.9%)	–	–	105 (2.1%)
6	10 min	–	4822 (97.9%)	–	–	105 (2.1%)

**TABLE IV**  
**Properties of the Polymer Prepared by Polymerization**  
**with 20% Recycled PET Flakes**

$[\eta]$	$L^*$	$a^*$	$b^*$	COOH	DEG	Melting point
0.654 dL/g	49.3	0.5	9.1	19 meq/Kg	2.30%	255°C

period, the peak molecular weight (as seen in GPC results in Table III) shifts to 4822, intermediate between that of the original flakes ( $M_{\text{peak}} = 50,329$ ) and oligomer ( $M_{\text{peak}} = 1816$ ). This leads us to conclude that exchange reactions lead to depolymerization of the flakes, nearly coinciding with the dissolution for flakes.

It was observed at low agitator RPM that the flakes float on the oligomer surface and stick to each other forming lump of flakes. These floating lumps, depending on their size, can take excess of 1 min to dissolve.

#### Pilot plant scale trial

PET polymerization with 20% recycled PET flakes

Recycled PET flakes were introduced into PTA-MEG slurry, and polymerization was carried out as described in Experimental section. Based on the above reaction-dissolution study (Study of the dissolution and reaction of PET flakes in molten oligomer Section), it can be presumed that esterification of PTA-MEG was accompanied by glycolysis of the flakes, following which the polycondensation at reduced pressure lead to PET of properties as shown in Table IV. Except the inferior color (compared for the yarn in "Melt spinning of the PET chips containing recycled PET" section below) of the polymer with 20 wt % recycled flakes, the properties such as  $[\eta]$ , acid end-groups, DEG, and melting point are in the range of fiber grade virgin PET free from recycled material.



**Figure 3** Chips with black specks. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 4** Black particle in HFIP-Chloroform solution of chips. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3 shows standard photograph of some of the chips using 20% recycled flakes. As seen, some of the chips (40 chips/50 g) contain black specks. These black specks are not seen in virgin PET batches made before and after this batch in the same reactor, which indicates that the black specks are caused due to contamination from recycle flakes. When the flakes were dissolved in HFIP-chloroform mixture, substantial contamination from dark insoluble material was visible (Fig. 4). An origin of these black particles could perhaps be found in the contamination of PVC with PET flakes, due to the similar use (packaging bottles), appearance (transparency), and density, making it difficult to manually separate PVC either prior or subsequent to grinding the bottles.<sup>7</sup> On exposure to heat, PVC first turns black as it also undergoes dehydrochlorination, chain scission, and crosslinking.<sup>8</sup> Thus, filtering of the polymer melt before melt spinning is clearly an important aspect of recycling PC PET.

Melt spinning of the PET chips containing recycled PET

Multifilament (36-filament) melt spinning of the polyester containing 20 wt % recycled flakes was

**TABLE V**  
**Spinning Parameters and Mechanical Properties of the Yarn from PET Containing Recycled Flakes**

Process Parameters	
Denier/Filament	75/36—FDY
Polymer	20 wt % recycled PET
Melt temperature (°C)	280
Pack pressure rise rate	3000 $\psi$ /h
Winding speed (m/m)	3500
Physical Properties	
Elongation (%)	35
Tenacity (g/d)	3.9
Uster (%)	1.9

**TABLE VI**  
**Comparison of Color of Yarns from Virgin PET and from PET Containing Recycled Flakes**

Sample identity	$L^*$	$a^*$	$b^*$
Virgin PET yarn	94.1	-0.46	1.9
PET yarn with 20% flakes	91.8	-0.11	2.5

done on pilot spinning machine to produce FDY of 75 denier (g per 9000 m). Spinnability was monitored, and in the beginning, it was found to be comparable with yarn making from virgin PET with regards to performance such as threadline breaks, spin-outs, dog-legging. The linear mass variation measured as Uster (%), as well as tenacity and breaking elongation were also comparable with that for similar yarn made from virgin PET (Table V). However, some deterioration of the yarn color reflected as decrease in  $L^*$  and a small increase in  $b^*$  in the yarn from PET with 20 wt % recycle flakes, when compared with the yarn from virgin PET (Table VI). Clearly, this can be expected to be related to degradation and contamination of the recycled flakes during their prior use as containers.<sup>9</sup> Small deterioration in color is considered acceptable in the trade, so long as color is consistent. In principle, degradation can be reduced by the addition of stabilizing chemicals.<sup>9</sup> Alternatively, optical whiteners can be added to mask the coloration.

As the spinning was continued, we began to see spin-outs/breaks in filaments, and the spin pack back-pressure was found to increase from 1750 psi to 3250 psi in 30 min of spinning (3000 psi/h), indicating increasing restriction in the spin-pack filtration medium, possibly due to the entrained particles in the polymer made by using 20% recycled flake, as seen in Figures 3 and 4. In comparison, back pressure rise with virgin PET is very slow (10 psi/h).

## CONCLUSIONS

We studied the addition of recycled flakes during PET polymerization, either to PTA-MEG slurry or directly to molten oligomer. Besides the system viscosity (as influenced by solids content) and agitator rpm, the location of agitator was also found to strongly influence the radially inward flow at surface of mixture. Certain minimum intensity of flow at the upper surface of the mixture was necessary for good mixing of the flakes into the slurry or the molten oligomer. Dissolution and depolymerization of the recycle flakes in the molten oligomer under good stirring were found to be very rapid, reaching equilibrium within 30 s. Contaminants in the PC PET flakes result in black specks in the polymer produced that need to be removed by filtering before extrusion into fiber, else increase in spinouts and spinning breaks, reduction in spin-pack life make the production unviable. Alternatively, contamination in recycled PET should be reduced during bottle sorting stage before feeding to polymerization.

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