

# Dissolution/Reprecipitation: A Model Process for PET Bottle Recycling

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**ABSTRACT:** A dissolution/reprecipitation route was followed for the recycling of poly(ethylene terephthalate) (PET). Model experiments on virgin material, either in the form of pellets or blow-molded bottles, are presented. The process proposed comprises dissolution of the plastic in an appropriate solvent, reprecipitation by using a nonsolvent, thorough washing of the material obtained, and drying. The solvent mixtures involved are separated by fractional distillation for further reuse. *N*-Methyl-2-pyrrolidone (NMP)/*n*-octane + *n*-hexane proved to be a particularly effective solvent/nonsolvent system. Further investigation was focused on the effect of the sample history through successive recycling cycles. The recycled material was evaluated in terms of molecular weight, crystallinity, and grain-size analysis, resulting in an excellent quality, competing with the virgin grade. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 91–95, 2001

**Key words:** recycling; poly(ethylene terephthalate) (PET); dissolution/reprecipitation; bottles

## INTRODUCTION

Based on the concept of “*selective dissolution*,” according to which one polymer could be dissolved at a time, dissolution-based processes can be used for the separation of mixed plastic wastes.<sup>1–3</sup> Especially for poly(ethylene terephthalate) (PET), relevant recycling efforts can be reviewed as follows:

An integrated chemical process for recycling commingled plastics was developed at the Rensselaer Polytechnic Institute in cooperation with the M. W. Kellogg Co. Two technologies, selective dissolution and flash devolatilization, are basic to this process. A mixture of the six main thermo-

plastics (PS, LDPE, HDPE, PP, PVC, and PET) are dissolved in xylene to form a homogeneous mixture of concentrations of 5–10 % by weight, followed by controlled temperature–solvent extractions that separate the individual polymers.<sup>1,4,5</sup> Alternatively, a process was described for separating a waste stream of 2-L bottles consisting of PET, an HDPE base cup, paper, or a PP label, and PP or an aluminum cap. The bottles are shredded, air-classified to remove the paper, washed with a detergent/water mixture, then sent to a sink–float tank containing water. Dried chips from the sink–float system are washed with the process solvent at a temperature sufficient to remove soluble impurities, but insufficient to dissolve the target polymer. For example, in the PET case, this washing will remove any adhesive, PS, or PVC which may be present from use in 2-L bottles or from sortation errors.<sup>6,7</sup> Finally, recycling of polyester/cotton blend fabrics can be ac-

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completed by separating the polyester from the cotton fabric. The polyester is dissolved into a sulfone solvent, while maintaining the integrity of the cotton. The dissolved polyester solution is then dispersed into a sulfone/water coagulation solution where the polyester is precipitated out of the solution. The solution is filtered while hot, and the filtrate is filtered repeatedly. The cotton samples are contained within the autoclave.<sup>8,9</sup>

In the present article, the possibility of recycling PET by the aforementioned dissolution/reprecipitation technique was investigated, while taking into account that this process can be safely applied in successive cycles, since it is carried out at mild temperatures, in contrast with melt recycling.<sup>10–15</sup> As a model experiment, two successive recycling cycles were applied to virgin PET to assess their influence on the structure of the recycled products. Moreover, blow-molded bottles for edible-oil packaging are recycled for use as a commercial end product, the collection of which, as a single-type plastic waste, is easy. *N*-Methyl-2-pyrrolidone (NMP)/*n*-octane + *n*-hexane proved to be a particularly suitable solvent/nonsolvent system, according to the following criteria<sup>3</sup>: (i) precipitation of the polymer in an acceptable form, (ii) total recovery of the polymer, and (iii) limited, as much as possible, quantities of the solvent and nonsolvent employed. The aforementioned solvent/nonsolvent system could be characterized as more effective than were others proposed in the past,<sup>5,8</sup> as it can be separated and almost fully recycled by a conventional distillation process, whereas PET is dissolved at relatively ambient temperatures, high polymer concentration, and using rather simple equipment. Characterization studies on the recycled grades were focused on the molecular weight, crystallinity, as well as grain-size distribution.

## EXPERIMENTAL

### Materials

1. Virgin PET pellets under the code name STA-22 (SKC Co., Korea) were used as the starting virgin material for the production of blow-molded bottles (0.5 and 1.5 L), for edible oil and water packaging.
2. All solvents used were general reagent-grade chemicals.

### Polymer Recovery by the Solvent Process

Pellets of virgin PET or PET bottles cut into pieces were dissolved into NMP up to the level of

0.20 kg L<sup>-1</sup> at 165°C. The upper concentration level was kept at this value, because with further increase of the concentration, the solutions became so viscous that they could not be processed under our experimental conditions. A 2-L reaction vessel, fitted with stirrer, reflux condenser, and thermometer, was employed. Stirring was applied for 90 min to assure quantitative dissolution of the polymer. The polymer solution was then filtered through a Seitz Merkur EF 6/03 device with volume capacity of 300 mL, using as filter paper 5500 Seitz-T-Filter sheets of an exclusion size in the range of 20–70 μm. V<sub>1</sub> L of *n*-octane was then properly added to the hot filtrate and the polymer contained was precipitated. The polymer grains were isolated by filtration under a vacuum. The phase-separated solvents were then replaced by V<sub>2</sub> L of *n*-hexane and stirring was again applied for 40 min. This washing procedure was repeated once more (V<sub>3</sub> L *n*-hexane employed). The reclaimed polymer was dried in a vacuum chamber at 90°C for 14 h. This once-recycled grade represented by the code name 1stREC was again subjected to the same procedure to produce the twice-recycled grade (2ndREC). Furthermore, the term “Recycled from Bottles” describes the product derived upon applying this recycling procedure once on the bottles. The ternary solvent/nonsolvent mixture was separated for reuse in a distillation column (0.85 m height) filled with Raching Rings and equipped at the top with a side condenser.

### Viscosity Measurements: Molecular Weight Determinations

The number-average molecular weight  $\bar{M}_n$  was calculated, applying the Mark–Houwink–Sakurada

**Table I Results on PET Recycling Using the Dissolution/Reprecipitation Technique (NMP/*n*-Octane + *n*-Hexane)**

Measurement	Concentration (kg/L) 0.20
Polymer mass dissolved (kg)	0.1
NMP volume (L)	0.5
<i>N</i> -Octane volume (L)	1.0
<i>N</i> -Hexane volume for washings, V <sub>2</sub> + V <sub>3</sub> (L)	2.0
Polymer recycled (%)	100
NMP recycled (%)	98
<i>N</i> -Octane recycled (%)	99
<i>N</i> -Hexane recycled (%)	98.5

**Table II Results of Number-Average Molecular Weight ( $\bar{M}_n$ ) Determinations**

Virgin Grade	1st REC from Virgin	2nd REC from Virgin	Recycled from Bottles
26,750	26,000	26,150	24,700

correlation with the intrinsic viscosity data. The solvent employed was a 40/60 w/w phenol/tetrachloroethane mixture, at 35°C, with  $K = 125 \times 10^{-3}$  mL/g and  $\alpha = 0.65$ .<sup>16</sup>

#### Differential Scanning Calorimetry (DSC)

A Perkin–Elmer DSC-4 calorimeter was used to obtain thermograms of the virgin material and the recycled grades. The measurements were carried out between 50 and 300°C in a nitrogen atmosphere and using an empty capsule as a reference. Sample weights varied from 5.0 to 11.0 mg and the heating rate was fixed at the level of 10°C/min. Melting points and heats of fusion were determined.

#### Grain-size Analysis

U.S. sieves were used for evaluating the particle-size distribution.

## RESULTS AND DISCUSSION

#### Yield in Polymer and Solvent/Nonsolvent System

Table I shows the operating conditions of a typical example of the recycling procedure. Recovery yields of the polymer, solvent, and nonsolvent represent the mean value of eight iterations for each recycling cycle. The applied solution/nonsolvent (*n*-octane) ratio was 1:2, while the additional quantity of *n*-hexane for each washing step was kept at a ratio of 1:2. Under our experimental conditions, the yield in the polymer nearly attains the theoretical value, while separation and recov-

ery of the solvent (NMP) and both of the nonsolvents (*n*-octane, *n*-hexane), obtained by fractional distillation, stand equally at excellent levels. Obviously, the effect of scaling up will lead to even better values, not deviating from the theoretical limits, that is, to closed-loop solvent recycling.

#### Number-average Molecular Weights

The results of the number-average molecular weight determinations are presented in Table II. The results indicate that no degradation occurs during the recovery process even when repeating the treatment cycle. The slight decrease of  $\bar{M}_n$  encountered in the bottle grade can be safely correlated with the completely different history of this material in terms of both the bottle processing and the additives employed.

#### Crystallinity and Melting Ranges

DSC runs were performed to study the fusion behavior and crystallinity of the PET samples. It is well known that the heat of fusion is the amount of energy necessary to transform a polymer from a crystalline or a partially crystalline state to a completely disordered amorphous state. Valid heat effects of a physicochemical process can be estimated by measuring the area under a well-defined thermogram peak. If the heat of fusion  $\Delta H_f$  of perfectly crystalline PET is known, the percentage crystallinity  $x$  can be derived as follows:

$$x = (\Delta H_{\text{exp}}/\Delta H_f) \times 100$$

where  $\Delta H_{\text{exp}}$  is the actual heat of fusion of the sample tested.  $\Delta H_{\text{exp}}$  is calculated by measuring the area under the thermogram peak, while  $\Delta H_f$  is taken here equal to 32.5 cal g<sup>-1</sup>, corresponding to the heat of fusion of the 100% crystalline polymer.<sup>17</sup>

The resulting crystallinity values, according to this approach, are listed in Table III. Virgin PET possesses a crystallinity content of 44.8%,

**Table III Thermal Analysis Data**

Measurement	Virgin Grade	1st REC from Virgin	2nd REC from Virgin	Recycled from Bottles
Crystallinity (%)	44.8	25.2	27.0	25.0
Melting point (°C)	249	248	248	247
Melting range (°C)	28.3	40.4	38.9	41.8

whereas the once-recycled polymer, the twice-recycled polymer, and the recycled bottles possess a crystallinity of 25.2, 27.0, and 25.0%, respectively. On the other hand, the melting point remains practically unchanged. Nevertheless, the melting range of the recycled grades is apparently broader than that of virgin PET since the lower is the degree of crystallinity, the broader is the melting range. The rather broad  $T_m$  observed for the recycled grades could also be attributed to plasticization of the polymer due to the presence of trace amounts of the solvent that would likely remain in the polymer structure.

In addition, the variation of the crystalline content could be correlated with the dissolving and precipitation procedure itself. The polymer is induced to reprecipitate from its hot solution by adding a cold nonsolvent. This sudden cooling apparently inhibits PET to develop crystallinity. The higher crystallinity seen with the virgin polymer is to be expected, as this polymer was presumably made via solid-phase polymerization, which amounts to a 12–24-h annealing at about 200°C. Without such annealing, or significant mechanical drawing, high crystallinities are not seen in PET.

Finally, the polymer concentration seems to be a critical factor affecting the crystallization ability of PET. Crystallinity measurements of recycled PET at different concentration levels (0.05, 0.10, 0.15, and 0.20 kg L<sup>-1</sup>) revealed that by increasing the concentration crystallinity decreases (Table IV). The levels of crystallinity seen in the solution-crystallized samples are likely due to solvent-induced crystallization of the polymer, again consistent with some level of plasticization by the solvent.

### Grain-size Analysis

According to the grain-size analysis (Table V), over 94% of the recycled polymer mass has a grain size smaller than 1 mm, suitable for feeding the PET processing units.

**Table IV Crystallinity Versus Polymer Concentration**

Measurement	Concentration (% w/w)			
	0.05	0.10	0.15	0.20
Crystallinity (%)	38.1	28.7	25.9	25.2
Melting point (°C)	248	247	248	248
Melting range (°C)	35.3	36.9	39.1	40.4

**Table V Results of Grain-size Distribution**

Grain-size Distribution (mm)	Concentration (kg/L) 0.20
$d < 0.5$	31.3%
$0.5 < d < 0.8$	37.2%
$0.8 < d < 1.0$	25.8%
$d > 1.0$	5.7%

### CONCLUSIONS

A model dissolution/precipitation process was investigated to recycle virgin PET and PET bottles. Concentrated solutions in NMP were employed (0.20 kg L<sup>-1</sup>) and the polymer was precipitated, in the form of small grains, through the addition of *n*-octane and subsequent washing with *n*-hexane. Excellent recoveries in the polymer and solvents are achieved. The evaluation of the effect of the previous history on the properties of the recycled product was accomplished by applying two successive recycling cycles on the PET pellets.

The dissolution/precipitation once or twice applied did not appear to affect the molecular weight characteristics of the final product. The recycled grade, free of any soluble or insoluble additives, can be used in many different applications, competing with the virgin material. Larger-scale experiments are expected to result in even higher concentration levels and also in “closed-loop” solvent recycling.

The results quoted do not aim to propose this dissolution-based process as a tool to recycle single-type PET waste, for obvious cost reasons. However, this effort could be very useful in separating PET from other polymers, in applications where different phases coexist.

### REFERENCES

1. Ehrig, R. J. *Plastics Recycling: Products, Processes*; Hanser: Munich, Vienna, New York, Barcelona, 1992.
2. Brandrup, J.; Bittner, M.; Michaeli, W.; Menges, G. *Recycling, Recovery of Plastics*; Hanser: Munich, Vienna, New York, Barcelona, 1996.
3. Papaspyrides, C. D.; Poulakis, J. G. In *The Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC: Boca Raton, FL, 1996; p 7403.
4. Nauman, E. B.; Lynch, J. C. Preprints, IUPAC International Symposium on Polymer Materials

- (Polymer 91), Melbourne, February 10–14, 1991; pp 291–292.
5. Nauman, E. B.; Lynch, J. C. U.S. Patent 5 278 282, 1994.
  6. Vane, L. M.; Rodriguez, F. ACS Symposium Series 513; American Chemical Society: Washington, DC, 1992; p 147.
  7. Rodriguez, F.; Vane, L. M.; Schlueter, J. L.; Clark, P. ACS Symposium Series 513; American Chemical Society: Washington, DC, 1992; p 99.
  8. Serad, S. L. U.S. Patent 5 342 854, 1994.
  9. Serad, S. L. Eur Patent, 063 664 6A1, 1994.
  10. Kampouris, E. M.; Diakoulaki, D. C.; Papaspyrides, C. D. *J. Vinyl Technol* 1986, 8, 79.
  11. Kampouris, E. M.; Papaspyrides, C. D.; Lekakou, C. N. *Polym Eng Sci* 1988, 28, 534.
  12. Papaspyrides, C. D.; Gouli, S.; Poulakis, J. G. *Adv Polym Technol* 1994, 13, 213.
  13. Poulakis, J. G.; Papaspyrides, C. D. *Polym Recycl* 1995, 1, 125.
  14. Poulakis, J. G.; Papaspyrides, C. D. *Adv Polym Technol* 1995, 14, 237.
  15. Poulakis, J. G.; Papaspyrides, C. D. *Resourc Conserv Recycl* 1997, 20, 31.
  16. Brandrup, J.; Immergut, E. M. *Polymer Handbook*, 2nd ed.; Wiley: New York, 1975.
  17. Muller, A. J.; Feijoo, J. L.; Alvarez, M. E.; Febles, A. C. *Polym Eng Sci* 1986, 27, 796.