Consecutive Steps of PET Recycling by Injection: Evaluation of the Procedure and of the Mechanical Properties

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ABSTRACT: The procedure of five consecutive recycling steps by injection moulding of postconsumer PET was evaluated on the basis of processing and drying parameters. The equations that govern the increase in sample mass of the polymer while in contact with the atmosphere were obtained on the basis of weight variation measurements before and after drying. Two series of consecutive recycling steps were also carried out, starting from virgin material (with and without sieving), which showed that, for the sieved material, the decrease in productivity was always in the same order of magnitude as the decrease in viscosity. Thus, the remaining differences, which exceeded 400%, can be attributed to the presence of powder. The crystallinity, transition temperatures, concentration of carboxyl end-groups, tensile properties, and impact resistance of the samples obtained in each step were determined. The number of carboxyl end groups increased by about three times after the five recycling steps and the crystallinity was enhanced, going from 23% to 37%, which explains the alterations in the modulus of elasticity, elongation at break, and impact resistance. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 266–275, 2000

Key words: PET recycling, drying, injection, mechanical properties and degradation

INTRODUCTION

In a study of the municipal solid waste of a Brazilian city of 200,000 inhabitants in 1995, the daily consumption of polyethylene terephthalate (PET) was found to be over 7000 2-L soft-drink bottles. Among rigid plastics (excluding films), PET represented the second most frequent type of plastic in terms of mass in the municipal solid waste of the town under study (the first was HDPE) and the first in volume.[1] However, studies conducted at the end of 1997 and in 1998 in the same town indicated that PET is the first also in mass.[2] Based on these figures, PET recycling is an important ecological alternative for the minimization of municipal solid wastes and, with appropriate studies, it can become more attractive economically and even aid in predicting the behavior and properties of the recycling process and of the final product. Because of the large quantity of bottles in urban waste, there are few studies on PET recycling from other sources, such as films.[3]

Mechanical recycling of PET from soft-drink bottles is the most common way of recycling polymers and usually involves collection-grinding-washing-drying-processing. During its life cycle (synthesis-processing-use-discarding-recycling), PET enters into contact with degrading agents

such as oxygen, light, mechanical stresses, temperature, and water (not only as a residue of the washing process, but also due to short periods of storage). Separately or in combinations, these degrading agents break the macromolecules, creating mainly carboxyl end groups and reducing molecular weight, thus altering the final properties and productivity during processing.[4–10]

Several important papers report on the development and analysis of new products made of recycled PET from bottles, as carried out by La Mantia et al.[11] with blends of PET and HDPE and Rebeiz et al.[12] with an unsaturated polyester resin deriving from chemically recycled soft-drink bottles.

Other papers discuss the execution of consecutive recycling steps and the subsequent evaluation of their effects on the structure and properties of the materials, as reported by La Mantia and Vinci[13] and by Giannotta et al.,[14] using PET from postconsumer soft-drink bottles. This type of study usually involves extruders as processing machines, and normally keep constant washing, drying, and processing parameters. The recycling procedures are not commonly evaluated or altered in order to study (and/or measure) how to improve the quality and productivity of the overall process.

Drying is an important factor in PET recycling that may have effects contrary to those expected, e.g., by increasing the temperature to remove water from the flakes of the ground material, one may enhance the oxidation effects and promote mainly hydrolysis, which occur more easily at temperatures higher than the polymer's glass transition temperature (about 70°C).[4–10,15] Thus, efficient drying (the acceptable residual humidity in the soft-drink bottles industry varies from 0.004 to 0.005%) should be performed at the lowest possible temperature and within the shortest possible time using vacuum, nitrogen or dry air.[4,16]

Processing is another important factor that can be maximized. The flakes are usually processed in extruders for later cutting, resulting in recycled pellets of a more suitable shape and density than the flakes for further processing and/or for mixing with virgin material. In the case of injected products made only of recycled material, this intermediary extrusion could be avoided, eliminating a processing cycle and contact with degrading agents.

The purpose of this study was to evaluate the recyclability of postconsumer soft-drink bottles through multiple injections of PET without intermediary extrusion for pellet production. The procedure adopted was evaluated by obtaining the equation of variation in mass as a function of the time of exposure of the recycled product to the atmosphere, which may provide information about the efficiency of drying. Using a similar procedure with virgin resin, the effects of the presence of powder in productivity by injection were also evaluated quantitatively. Changes in structure (chain break and crystallinity) and the consequences of those changes on some of the mechanical properties were determined.

EXPERIMENTAL

Preparation Of Test Specimens And Consecutive Recyclings

Five kilos of PET virgin resin supplied by Fibra Nordeste S.A. were vacuum-dried (10^{-1} atm, 3 h, 110°C) and injected into a mould cooled with running water in order to produce test specimens similar to type I of American Society for Testing and Materials (ASTM) 638.[17] The specimens were then ground, dried, and injected again until five injections were completed. These preliminary recycling steps served to evaluate the productivity and the suitability of the equipment for the procedure adopted. Following this, about 5 k of 2-L PET bottles were collected from the Selective Collection Deposit of the Federal University of São Carlos and ground, washed with water, and exposed to the air (48 h at room temperature) and then vacuum-dried. The ground material (flakes) was injected, ground once more, vacuum-dried and injected, until five recycling steps were completed, using the same equipment and under the same conditions as the consecutive recycling steps used for the virgin PET. At the end of each injection and each grinding step, samples were taken to test mass variations, tensile properties, impact resistance (test specimens), differential scanning calorimetry (DSC), variations of mass, and counts of carboxyl end-groups (flakes). The recycling steps were then labelled as follows, according to the number of injections: B1, B2, B3, B4, and B5. The ground bottle, washed, and dried, was called B0.

The hypothesis that powder generated in grinding could cause a decrease in productivity was tested with a new series of recycling steps, including a sieving stage before each injection
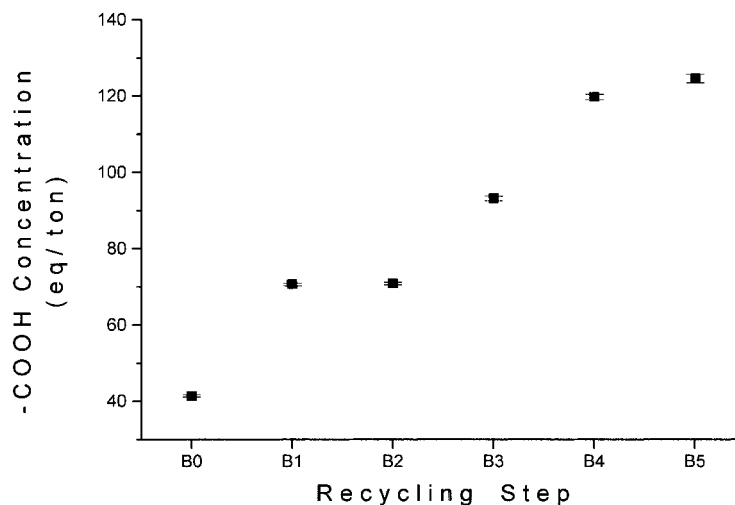
Figure 1 Carboxylic End-Group concentration versus recycling steps of postconsumer PET.

(sieve opening of about 1.5 mm) and measuring of the viscosity. In this specific study, the material chosen was the virgin resin, in order to avoid collection, the initial grinding, washing, and air drying.

Tests and Experimental Measurements

The productivity of the PET injection was measured by the time required for the injection moulding machine to melt a sufficient amount of material for the injection of a complete test specimen. In this study, this time was denoted processing time or dosing time.

The number of carboxyl end-groups was counted by the titration of ground PET diluted in hot benzyl alcohol, followed by reaction with a standard solution of sodium hydroxide in benzyl alcohol.[18]

The variations in the glass transition temperature (Tg), crystallization temperature (Tc), and melting temperature (Tm), and the heat of crystallization and/or Fusion (ΔHc and/or ΔHf) were determined with a DSC V2.2A Dupont 9900 apparatus according to the procedures suggested by ASTM D417 and D418.[19–20] Crystallinity was determined by dividing the ΔHf obtained by the heat of fusion of a 100% crystalline PET, tabulated as 140.1 J/g.[21]

After each injection step, three test specimens were immediately weighed on a Mettler 51 analytical scale (maximum160 g and minimum 0.01 mg). The mass determinations were periodically repeated over a period of three months, and a

curve of the variation of mass versus time, as well as the maximum variation and the time of occurrence of this variation, were obtained at the end of the experiment. The adjustment equation for the results was determined using the Microcal Origin 4.1 software. After three months (more than the time of maximum variation), the test specimens were ground and vacuum-dried in order to obtain a negative variation of mass of the flakes after drying. This measurement was labelled $M_{drying\ after\ three\ months}$.

The notches in the test specimens and the impact resistance tests were performed using Custom Scientific Instruments, according to ASTM D 256.[22]

The Tensile Modulus of Elasticity and the Tensile Elongation at Break were determined by tests using an Instron Machine, model 1172, according to ASTM D 638.[17]

The intrinsic viscosity was determined using an Ubbelohde Viscometer after the dissolution of PET in o-chlorophenol.

RESULTS AND DISCUSSION

Effects of the Recycling Steps on Structure

The titration results shown in Figure 1 indicate an increasing number of carboxyl end groups with an increased number of recycling steps. This behavior, which was expected, is related to successive passages through the mill, vacuum-oven, and injection moulding machine, involving mechanical stresses and/or temperatures associated with
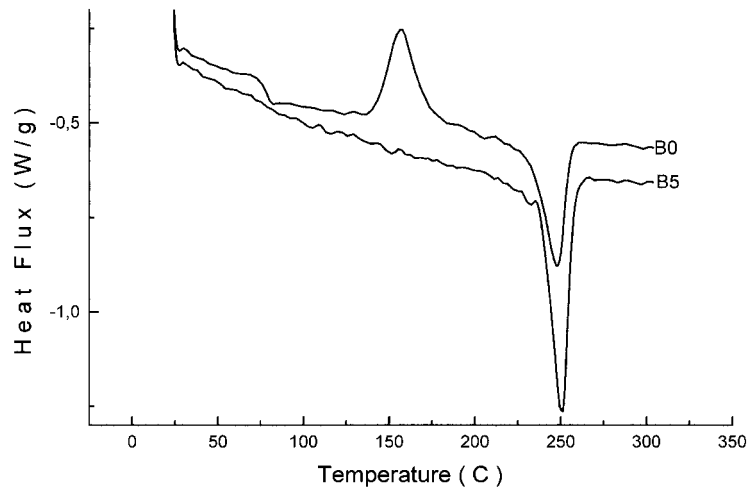
Figure 2   DSC Curves for the ground bottle, washed and dried (B0) and for the fifth recycling step (B5).

degrading agents (such as light, oxygen, and water) that degrade the material and generate mainly carboxyl end groups. This result indicates a decrease of the molecular weight of the polymer because of the chain breaks, causing a probable decrease in polymer viscosity. In addition to indicating the degradation the material has already undergone, the presence of carboxyl end groups can also be indicative of further degradation, because they can catalyse hydrolysis.[4–10] It was also noted that the most significant increase, about 70%, occurred from the ground bottle (B0) to the recycled bottle (B1), whereas the five consecutive processing steps under the experimental conditions caused an increase of about 300% in the number of carboxyl end groups.

Figure 2 presents the DSC curves for the ground bottle, washed, and dried (B0) and for the last recycling step (B5). The temperatures (Tg and Tm), heat of fusion, and crystallinity of the tested samples are given in Table I.

Table I shows that crystallinity increased with the number of recycling steps, probably due to the chain breaks, which is confirmed by the results of the titrations in Figure 1, and to their improved packing. This packing was facilitated by the presence of smaller chains that tended to fit among the larger ones, thus increasing the crystallinity. Crystallinity confers greater mechanical resistance to the material, although it decreases its deformation capacity, making it more fragile and easily pulverized during the grinding process.

The glass transition temperature tended to augment because the increase in crystallinity caused the amorphous areas, which were present in ever smaller numbers and were surrounded by more crystalline areas, to require more energy to vibrate. Temperatures between 247°C (for B0) and 251°C appear to be sufficient to melt most of the formed crystalline area.

These explanations lead to a better understanding of the shape of the DSC curves presented in Figure 2, which changed along the recycling steps. The difference of the baseline used to determine Tg became less and less clear, the heat of fusion (ΔHf) increased, and the heat of crystallization (ΔHc), present for B0 (26.0 J/g, at 156.6°C), disappeared in the remaining samples, indicating that the cooling applied to the sample after melting was sufficient to crystallize the polymer.

Table I   Values of Glass Transition Temperature (Tg), Melting Temperature (Tm), Heat of Fusion (ΔHf), and Crystallinity ($\%C$) of the Studied Samples Obtained from DSC Curves

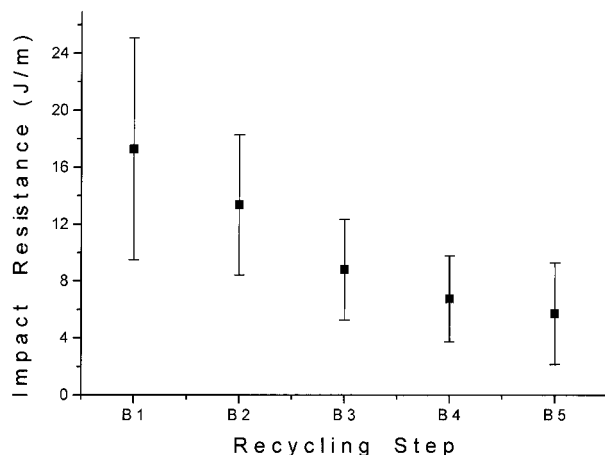| Sample	Tg (°C)	Tm (°C)	ΔHf (J/g)	$\%C$
B0	76.5	247.5	32.8	23.4
B1	77.8	250.9	39.5	28.2
B2	79.5	250.0	44.5	31.8
B3	80.4	250.5	45.8	32.7
B4	81.4	250.4	50.4	36.0
B5	80.8	251.3	53.0	37.8

Figure 3   Results of impact resistance versus recycling steps of postconsumer PET.

Effect of the Recycling Steps on Mechanical Properties

Figure 3 shows the results of the impact resistance test, indicating a strong tendency toward a decrease of about 70% from the first to the fifth step in the value of this property with an increased number of recycling steps. This behavior is associated to the decrease in molecular weight caused by the chain breaks and/or the increase in crystallinity, leading to decreased ductility. The standard deviation (SD) also decreased, particularly up to the third step.

Figures 4 and 5 present the results of the tensile test, respectively of the modulus of elasticity and elongation at break. The results of the fifth recycling step should be analyzed carefully, even when they go along with the tendencies, because superficial defects were noticed in these test specimens exactly at the point where the samples broke up. Analysis of the mean values of these properties should be interpreted with reservations due to the SD which, in some cases, disturbed the tendencies.

The increase in the percentage of the crystalline phase with the recycling steps is assumed to be the cause for the higher modulus of elasticity value (Fig. 4). As regards the elongation at break (Fig. 5), the reduction may be explained by the decrease in molecular weight and by the increase in crystallinity, with the increased number of recycling steps.

The results obtained for elongation at break in the first step showed a much higher SD than that observed in the other steps due to the different behavior of plastic deformation within the same

lot of samples. Figures 6 and 7 (Load $\times$ Strain curves) illustrate these differences, using samples taken from recycled bottles (B1).

With respect to the behavior illustrated in Figure 7, specifically in the region of the strain values from 1.23 to 1.92 (123% and 192%), some test specimens presented a radically changed appearance during the test, as shown in the photograph in Figure 8. One reason for this behavior could be the formation of a new crystalline structure during the orientation by stretching. This formation would not have been fast enough to accompany the speed of the test (5 mm/min), which may have caused the stress instabilities observed.

Evaluation of the Recycling Procedure

Figure 9 shows the experimental points (+) obtained in the test of variation of mass of a sample. The continuous line represents the equation of the mass of the sample as a function of the time of contact with air and the items at the bottom of the graph (A_1, A_2, to, and dt) represent the parameters of the Sigmoidal Boltzmann equation, shown in Equation 1:

$$M = \frac{A_1 - A_2}{\left(1 + e^{\frac{t - t_0}{dt}}\right)} - A_2 \qquad (1)$$

Table II presents the results of the test of variation in mass. The results of time of maximum variation, as well as the maximum variation (M-M0/M0, where M0 is the mass of the test speci-
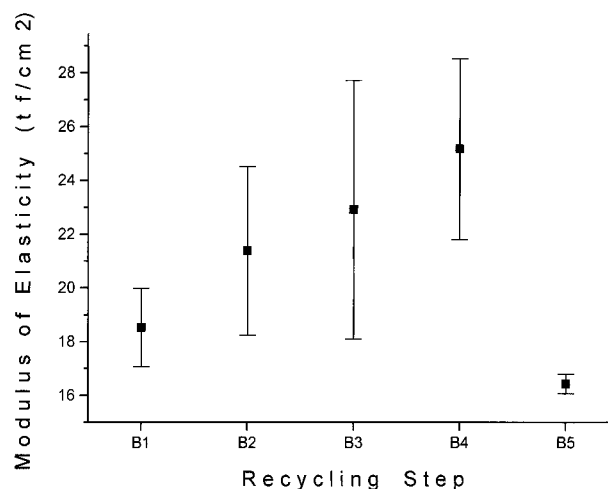

Figure 4   Results of modulus of elasticity versus recycling steps of postconsumer PET.
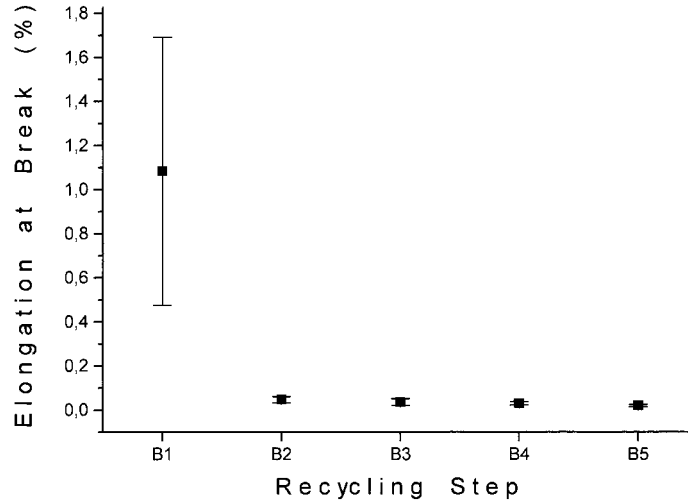
Figure 5 Results of elongation at break versus recycling steps of postconsumer PET.

men just after its injection) are the mean of the experimental results obtained for the three samples. Based on the equation for each recycling step, which was determined from the mean values of the parameters given by the software for the three samples, the values of the gain of mass in one day ($M_{t=1}$) and the theoretical variation of mass caused by contact with the air during the period between one injection and the next (M_{tinj}) were obtained. For example, after the injection, it took four days for the B1 test specimens to be ground, dried and injected again and, according to the obtained equation, this delay caused a gain of mass of approximately 0.18%. After one day, the mass of B1 test specimens increased by 0,048%. It

was discovered experimentally that, after 71 days or more, the increase in the B1 mass was 0.665% and that the drying of the B1 specimen flakes after three months caused a 0.670% reduction in mass.

Most of the test results for B0 are not presented here because the test was carried out using mainly test specimens and not flakes. Another reason is that it is practically impossible to determine the period of time that elapsed between production of the preform (which originated the bottle and later the B0 flakes) to its collection for the study.

By comparing the results in Tables I and II, it can be seen that the larger the number of recy-
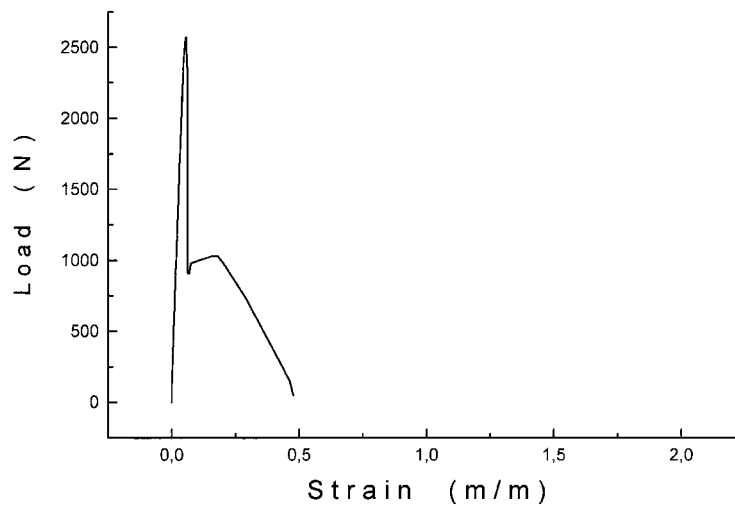

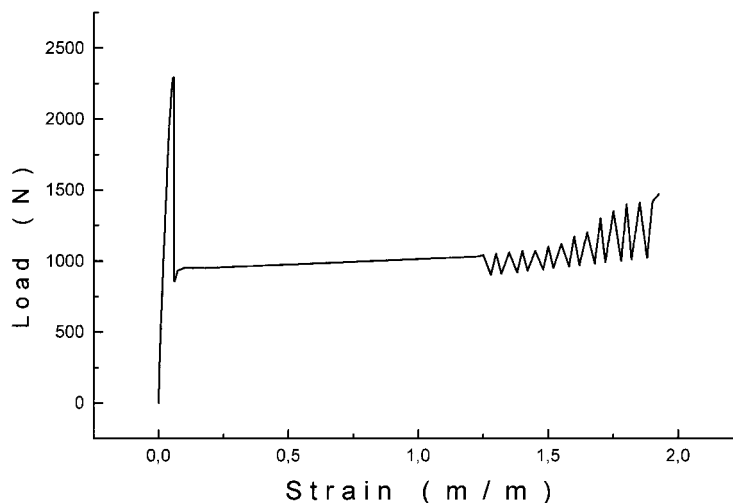
Figure 6 Load $\times$ strain curve of B1-sample 4.

Figure 7 Load × strain curve of B1-sample 1.

cling steps, the higher the crystallinity of the polymer, resulting in a more compact structure that makes it difficult for elements present in the air, such as water, to enter. After one day in contact with the air, the increase in mass was significant considering that the admissible level of humidity for PET bottle processing (0.004–0.005%) is about 10 times lower than the values obtained for $M_{t=1}$, although material other than water could also enter the structure. Thus, an attempt to inject B2 one day after the previous injection (of B1) without prior drying was unsuccessful, i.e., there was smoke, which was probably due to water vapor. There was also noise due to bubble bursting and low viscosity of the molten polymer, resulting in incomplete, porous, and brittle test specimens.

The last two columns of Table II show that the longer the period between one injection and the next, the larger the increase in mass and the greater the need to dry the material. Comparing these results with $M_{\text{drying after three months}}$, it can be seen that the drying conditions adopted were highly efficient (under a vacuum of 10^{-1} atm, for 3 h at 110°C) for all cases, because this drying process extracted a larger mass than the test specimens were able to gain. This caused unnecessary and expensive heating of the material, which can be optimized by reducing the time elapsed between recycling steps. For times closer to or longer than the time of maximum variation, this drying seems to be inefficient, because the maximum variation of test specimen mass was close to or even higher than the negative variation imposed by drying. Thus, it may be assumed that the drying of B0 flakes may have been inefficient due to the fact that the flakes have a more open structure and lower crystallinity than the B1 test specimens and because of the probably long time elapsed between the production of the bottles and the time when the study was carried out. During its lifespan, a bottle can absorb water both from the air and more directly, because it is a container for liquids, as well as after its disposal (e.g., rainwater) and during recycling (washing). The water that was not eliminated may have
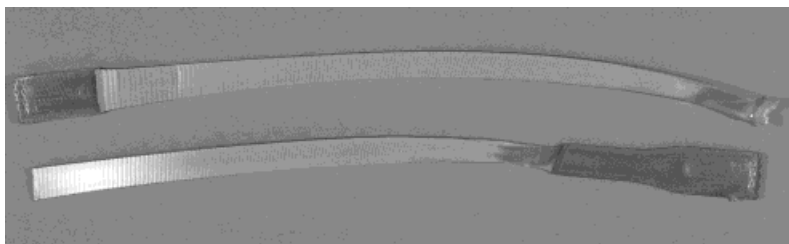

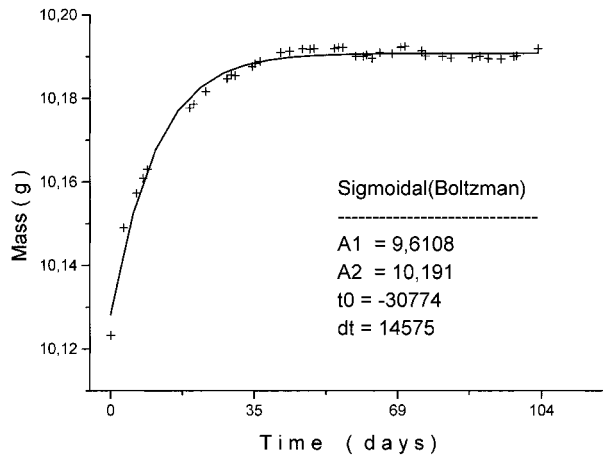**Figure 8** Photograph of B1 samples after the tensile properties test.

Figure 9 Variation of mass versus time of contact with air of B1-sample 1, experimental (+) and theoretical (continuous).

caused the negative variation of mass to be higher than the mass gained between two consecutive injections, as shown in the last three columns.

Studies like this may be useful to optimize recycling but they require data relating to the time elapsed between production and drying. For example, a manufacturer wishing to recycle a given by-product of his own could dry the flakes in the shortest possible time and at the lowest possible temperature. This can be done by carrying out some studies similar to those presented in Table II, in which drying time and temperature would be altered, and by controlling some important parameters such as the moment of production of the by-product.

A relationship between the processing time of each step divided by the processing time of the first recycling step was determined and is presented in Figure 10 for the three series of consecutive recycling steps performed, i.e., starting from

bottles (+), from virgin material after sieving (■), and from virgin PET without sieving (X). Figure 10 shows that the processing of PET based on ground bottles was reasonably productive up to the fourth step. This result suggests that it is possible to eliminate the intermediate extrusion for the production of pellets that is normally used by the recycling industry in the case of injected products made with 100% recycled PET.

The processing time was found to be 12 s for the first recycling step of the virgin material, with and without sieving, and 14.5 s for the ground bottle.

The tendency of the processing time to increase with an increased number of recyclings was observed even when the flakes were sieved, although it is difficult to see this on the scale used in Figure 10. The decrease in viscosity with an increased number of recycling steps is shown in Table III and was determined from the intrinsic viscosity of the flakes of the sieved material. The last column shows the increase in processing time for the consecutive recycling steps, starting from virgin PET without sieving.

Viscosity was found to be 0.75 g/dl for the virgin material (common viscosity of PET bottle grade) and 0.54 g/dl after the first injection (common viscosity of PET fiber grade).

The decrease in productivity of the sieved material was always of the same order of magnitude as the decrease in viscosity, showing that the remaining differences, which reached almost 500% when compared with the material without sieving, can be attributed to the presence of powder. The results shown in the last column compared with the preceding one show that the presence of powder already creates problems during the first injections without previous sieving. Contrary to what may be suggested by Figure 10,

Table II   Results of the Test of Variation of Mass

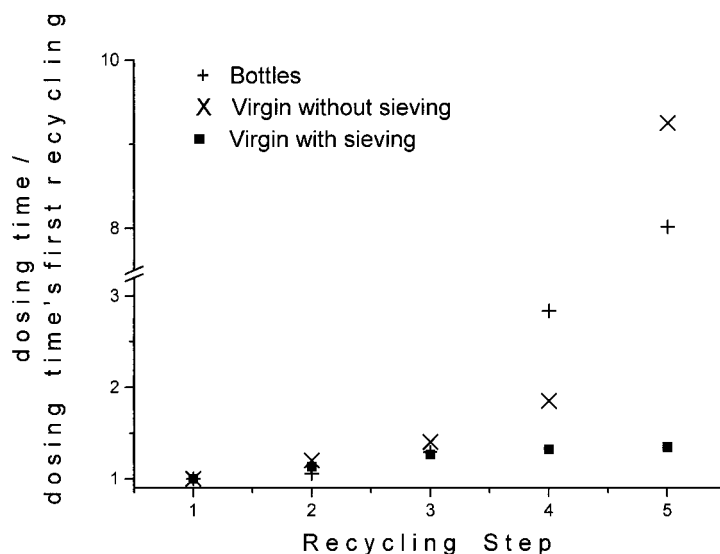| Sample	Time for Maximum Variation (days)	Maximum Variation (%)	$M_{t=1}$ (%)	$M_{\text{drying after three months}}$ (%)	Time of Injection (tinj) (days)	M_{tinj} (%)
B0	—	—	—	−0.780	—	—
B1	71	0.665	0.048	−0.670	4	0.180
B2	67	0.656	0.045	−0.580	2	0.090
B3	55	0.500	0.040	−0.510	2	0.080
B4	52	0.516	0.037	−0.550	1	0.037
B5	48	0.507	0.035	—	—	—

Figure 10 Measurements of the injection processing time versus recycling step of three series of consecutive recycling steps: starting from bottles (+), from virgin PET without sieving (X) and from virgin PET after sieving (■).

sieving is necessary at the very beginning so that longer processing times would probably be due to decreased viscosity. Figure 10 and Table III indicate that the effect of the presence of powder was much stronger after the third step, whereas the decrease in viscosity is more marked in the initial steps, corroborating the results of carboxylic end-group counts (Fig. 1) and, therefore, indicates more chain breaks at the beginning of the recyclings.

The decrease in viscosity might represent the benefit of a possible decrease in processing temperatures. However, all the operating characteristics were kept constant, including the temperature profile. Thus, it is probable that the polymer melted before the expected time, resulting in conveying difficulties that may have hindered the continuity of the process. However, the table shows that the principal effect was the presence of powder, because the increase in processing time was clearly lower when the powder was eliminated.

CONCLUSIONS

With respect to the effect of the number of recycling steps on the structure of postconsumer PET, it was observed that the number of carboxyl end groups increased by about three times from the first to the fifth recycling step, indicating structural changes in the macromolecules (chain breaks). This degradation and the increased crystallinity (from 23% for the ground bottle to 37% for the fifth recycling) explained the behavior of the mechanical properties, i.e., the increase in the modulus of elasticity and the loss of ductility and impact resistance.

When exposed to the atmosphere, recycled PET absorbs humidity and presents an exponential mass gain over time. It was also shown that the adjustment equation presented for the variation of mass can aid in the evaluation of the drying

Table III   Results of Consecutive Recycling Steps Starting From Virgin PET: Decrease in Viscosity (With Sieving) and Increase in Processing Time (With and Without Sieving)

	Initial Material: Virgin PET		
	With Sieving		Without Sieving
Recycling Steps	Decrease in Viscosity (%)	Increase in Processing Time (%)	Increase in Processing Time (%)
1° to 2°	10.5	14.5	34.2
2° to 3°	9.7	10.5	24.8
3° to 4°	3.5	3.8	52.2
4° to 5°	2.4	2.3	479.1

processes, so that drying in the shortest possible time and at the lowest possible temperature can be achieved.

The injection of ground bottles was found to be productive, suggesting that for injected products made exclusively of recycled PET, the intermediate extrusion for pellet production normally carried out by the recycling industry can be eliminated. Finally, sieving greatly improved the productivity of recycled PET along the various recycling steps, because the differences between the processing time of the two kinds of material (sieved and unsieved) reached almost 500%.

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