

Article

## Recyclability of Pet from Virgin Resin

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Bottle grade virgin PET (polyethylene terephthalate) resin was investigated through five consecutive injection molding steps to simulate recycling cycles. Tests were carried out after each recycling to evaluate degradation, crystallinity (by density and Differential Scanning Calorimetry-DSC measurements), hardness, and tensile and flexural properties. Consecutive recycling resulted in cumulative chain breaks caused by the material's contact with degrading agents such as temperature, oxygen, mechanical stresses, light, and water. In the fifth recycling step, for example, the number of carboxylic end groups, an indicator of the extent of chain-break, tripled in comparison to the initial molecule. The smaller chains that were formed fit more easily among the larger ones, thus increasing the percentage of crystalline phase in the structure. These two changes in the polymer's structure explained the recycled products' final properties, *i.e.*, the injected samples became progressively harder and more fragile in each recycling step.

**Keywords:** *recycling, PET, crystallinity, degradation, mechanical properties*

### 1. Introduction

The production of PET, which was first introduced as a synthetic fiber, grew rapidly after the development of solid state post-polymerization, a technique that increases the viscosity of PET, rendering it more suitable for blow molding of disposable soft-drink bottles<sup>1-2</sup>.

The bottle manufacturing industry commonly uses three types of PET. The first, PET homopolymer, is polymerized in a proportion of 1:1 terephthalic acid - TPA, or dimethyl terephthalate - DMT, and ethylene glycol - EG. The second type, known as PET copolymer, is polymerized with an excess of TPA (no more than 3% mol) or 1,4-cyclo-hexanedimethanol (up to 5% mol) and appears to be the most adequate material in high-speed blow-molding. The third type, PETG (polyethylene terephthalate glycol), is a copolyester obtained from the polymerization of DMT with 15-34% mol of 1,4-cyclo-hexanedimethanol, mainly used for credit cards, blisters and displays<sup>3</sup>.

The PET homopolymer and its copolymer have similar characteristics, such as semi-crystallinity, their glass transition temperature (T<sub>g</sub>) is about 76 °C, their melting temperature (T<sub>m</sub>) approximately 250 °C, density between 1.3

and 1.4 g/cm<sup>3</sup>, minimum viscosity is 0.7 dL/g, and they have similar infrared spectra. PETG, however, presents an infrared spectrum that differs from the other two types, with a density of approximately 1.27 g/cm<sup>3</sup>, minimum viscosity of 0.65 dL/g, and T<sub>g</sub> around 86 °C. Moreover, because it is essentially amorphous, it does not have a melting peak<sup>3</sup>.

PET can be recycled by three different methods, using throwaways: 1) Energy recycling, which burns the plastic to use its calorific content. 2) Chemical recycling, as shown in Fig. 1, in which PET is subjected to reactions that are the opposite of those of polymerization (such as hydrolysis - Fig. 1) to obtain intermediary products such as polyglycols, or even monomers or initial materials (TPA or DMT and EG) from which plastic is made. 3) Mechanical recycling, the most commonly used method to recycle PET, consisting of a series of simple, well known and relatively cheap processes to grind, dry, wash and reprocess throwaways. This sequence of processes generally results in a degraded recycled structure when compared to the initial molecule, since the chains have been subjected to mechanical stresses, heat, light, oxygen and, in the case of PET, also water.

Thermodynamic estimates have shown that the weakest chemical connection in the PET chain is the ester link<sup>4</sup>, indicated in Fig. 1 by an arrow. Most of these degrading agents' attack mechanisms concentrate here because less energy is required to break this link<sup>1,4-9</sup>. The lower molecular weight of degraded chains facilitates their arrangement in the melted state, resulting in increased crystallinity after cooling and affecting the product's final properties.

A recent study<sup>10</sup> evaluated the properties of PET recycled from throwaways. However, the bottles were collected regardless of factors such as manufacturer, the time elapsed from production to collection, and exposure to degrading agents.

The purpose of this study was to evaluate the properties of PET recycled from virgin resin, such as the number of carboxylic end-groups, density, and thermal and mechanical properties as a function of consecutive recycling steps. An injection molding machine equipped with a water-cooled mold was used to simulate conditions to which virgin resin is first subjected when injected for later blow-molding of the bottle. The use of virgin resin permits one to control variables such as the resin's origin, and the length of time it has been used and exposed to degrading agents, to improve the usability of materials recycled from PET.

## 2. Experimental

The resin that was studied was a bottle grade virgin PET, with 0.76 dL/g intrinsic viscosity, supplied by Fibra Nordeste S.A. The granules were vacuum oven dried at 110 °C for 3 h and injected into a PIC injection molding machine in the form of tensile<sup>11</sup> and flexural<sup>12</sup> specimens. Some specimens were subjected to mechanical testing and the remainder were ground. Flakes taken from the ground material were then subjected to differential scanning calorimetry (DSC), density and titration tests. The procedure was repeated until five injections had been completed. The virgin resin was labeled R0, while the injected samples were labeled R1, R2, R3, R4 and R5, according to their recycling step.

Carboxyl end-chains were counted by the Pohl method, based on the dissolution of the polymer in hot benzyl alcohol, followed by titration with a solution of sodium hydroxide in benzyl alcohol<sup>13</sup>.

Variations of T<sub>g</sub>, T<sub>m</sub>, and crystallization and fusion enthalpies were determined by DSC analyses (DuPont 9900), based on the ASTM D3417 and D3418<sup>14-15</sup> codes. The crystallinity was obtained in relation to a hypotheti-

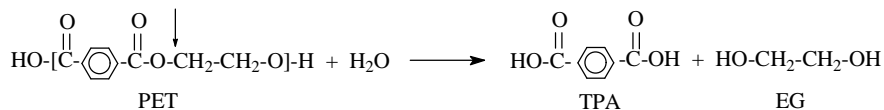


Figure 1. Equation of PET depolymerization by hydrolysis.

cally 100% crystalline polymer, with a fusion enthalpy of 140.1 J/g<sup>16</sup>.

Sample density was determined by immersing the flakes in ethyl alcohol and carbon tetrachloride solutions, the former being less dense and the latter more dense than the polymer. Small amounts of one and/or the other solvent were added until the flakes became stabilized in the solution. The density of the liquid was then measured with a pycnometer and the resulting value adopted as flake density. Crystallinity was determined as relation to 100% amorphous and 100% crystalline polymer densities, 1.331 g/cm<sup>3</sup> and 1.455 g/cm<sup>3</sup>, respectively<sup>17</sup>.

Test specimen hardness was measured with a Shore D type durometer<sup>18</sup>, while flexural and tensile tests were carried out with an Instron machine, model 1122<sup>11-12</sup>.

## 3. Results and Discussion

Figure 2 shows the number of carboxylic end-groups measured by titration after each injection step. As expected, increasing the number of recycling steps resulted in an higher number of carboxylic end-chains, with a final value almost triple that of virgin resin. In other words, successive grinding, drying and processing steps, associated or not with degrading agents such as oxygen, light and water, caused chain-breaks and a consequent drop in molecular weight with each new recycling step.

Figure 3 shows the R0 and R5 specimen thermograms obtained by DSC. Table 1 presents DSC and density data, as well as the crystallinity for each recycling step, according to each method.

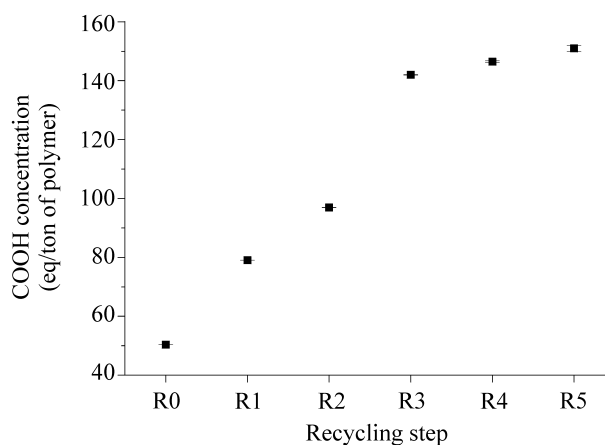
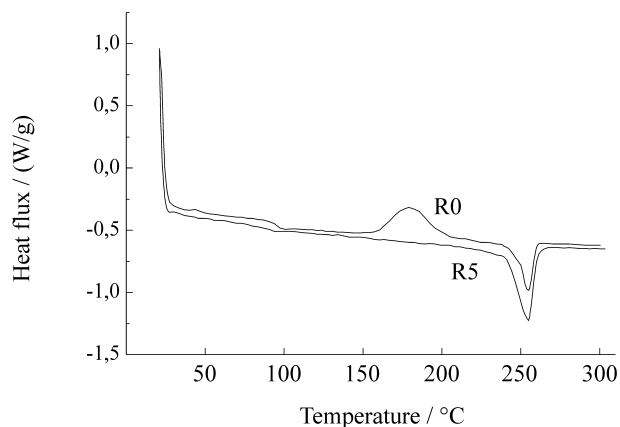


Figure 2. Carboxylic end group concentrations of PET samples starting from virgin resin as a function of the recycling step.



**Figure 3.** DSC curves for the R0 (virgin PET) and R5 samples (virgin PET subjected to five injection steps).

The area of the melting peak grew with each successive recycling step, reaching a maximum in the R5 specimen, thus indicating a higher percentage of crystalline structure, which is only destroyed at temperatures in the range of 250 °C. This probably means that the cumulative chain breaks to which the polymer was subjected caused the smaller macromolecular units formed to fit more easily among the larger ones during cooling (quenching).

Significant differences were also observed in the other DSC results. At about 75 °C, there was a small deviation in the baseline of R0, which is characteristic of T<sub>g</sub>. For R5, however, the difference was imperceptible on this scale since the amorphous chains, which begin to vibrate in this temperature range, were fewer and more immobilized by the growing number of crystalline units. The exothermic crystallization peak at around 160 °C only occurred with R0 and R1, indicating that, for the remaining samples, quenching was sufficient for the polymer to achieve maximum crystallization.

Table 1 also presents the results of two R1 and two R2 samples, labeled R1t, R1o, R2t and R2o. The letters “t” (transparent) and “o” (opaque) indicate the presence of two

types of basic flakes of ground material. There was probably a temperature gradient throughout the thickness of the injected test specimens due to uneven mold cooling. Abrupt cooling on the surface of the test specimen closest to the heat exchange source caused the amorphous phase to freeze, producing flakes that were transparent after grinding. The greater the distance from the heat exchange is, the lower the cooling rate is. This allows molecules to exist at high temperatures for longer periods of time, giving them mobility to become organized and, later, producing opaque flakes. A crystallinity gradient was formed throughout the samples’ thickness, which could, for example, affect the reproducibility of mechanical tests.

Visual differences between test specimens were only observed in tensile test specimens. The R1 specimens were highly transparent, while the R2 specimens were translucent and the remainder (R3, R4 and R5) were opaque.

Table 1 also shows the highly significant drop in crystallinity and density from the virgin sample (R0) to the first injection sample (R1). Virgin PET crystallinity is designed to be high to improve its processibility and future properties such as barrier to gases. However, this crystallinity is partially lost during cold mold injection, as was observed in the experiment. Similar and successive processing causes the melted resin to crystallize more and more easily owing to chain-breaks. Crystallinity has a tendency to increase, even under adverse conditions such as a cold mold, reaching the initial value.

Figure 4 shows the hardness test results, where one can see a clear tendency for increasing hardness at each successive recycling step. This was expected since crystallinity, the percentage of rigid phase in the structure, also increased.

Figures 5 and 6, respectively, show the results of Flexural Modulus of Elasticity and the Maximum Strain. The results shown in Fig. 6 indicate high standard-deviation values, except in the last two recycling steps. One of the explanations for the low reproducibility of the test is the

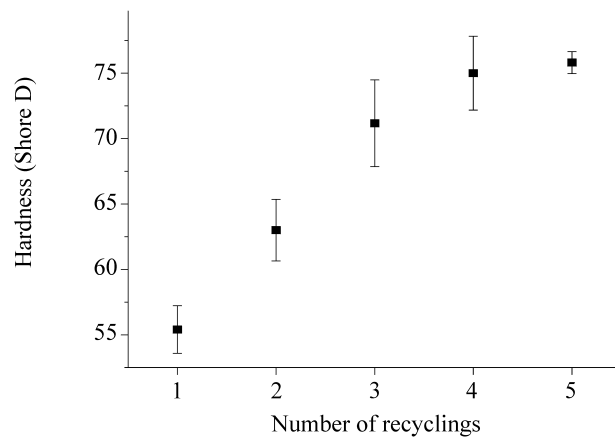
**Table 1.** DSC and Density tests results and the respective crystallinity of PET samples starting from virgin resin as a function of recycling step

Sample	T <sub>g</sub> (°C)	T <sub>c</sub> (°C)	T <sub>m</sub> (°C)	ΔH <sub>c</sub> (J/g)	ΔH <sub>f</sub> (J/g)	%C (DSC)	Density (g/cm <sup>3</sup> )	%C (Density)
R0	76.4	164.5	249.4	32.0	35.5	25.3	1.378	38.0
R1t	83.1	132.6	253.1	5.5	29.4	21.0	1.334	4.3
R1o	84.8	-	253.2	-	37.6	26.8	1.339	6.3
R2t	76.7	-	252.4	-	37.9	27.1	1.337	4.9
R2o	82.9	-	253.0	-	44.8	32.0	1.364	18.8
R3	87.3	-	252.3	-	46.5	33.2	1.362	25.1
R4	85.7	-	253.1	-	48.9	34.9	1.373	34.2
R5	83.9	-	254.9	-	51.7	36.9	1.377	36.9

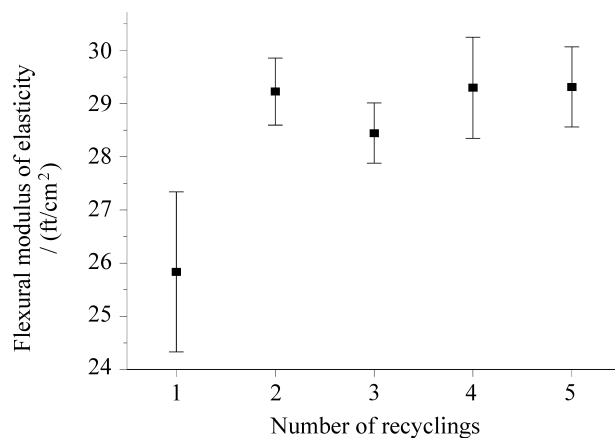
shrinkage that occurred in almost all the flexural test specimens due to the decreased volume caused by the transformation of the molten resin (essentially amorphous) into solid (semi-crystalline). Since shrinkage did not occur uniformly throughout the specimens' three dimensions, the specimens had to be put through a filing plane to obtain the flat surface required for the test, varying the thickness from one specimen to the other. This variation was added, for example, to the variation in the crystallinity in each sample, resulting in high standard-deviations.

The average results, however, particularly those relating to Maximum Strain, were in agreement the results of crystallinity obtained by DSC and Density measurements, since the higher the specimens' crystallinity, the lower the structure's ductile phase. Moreover, the drop in molecular weight from one injection step to the next, indicated by the results in Fig. 2, also contributed to decreased deformation by reducing the average size of deformation resistant chains.

Figures 7 and 8 present the results of Modulus of Elasticity -also known as Young's Modulus- and Elonga-

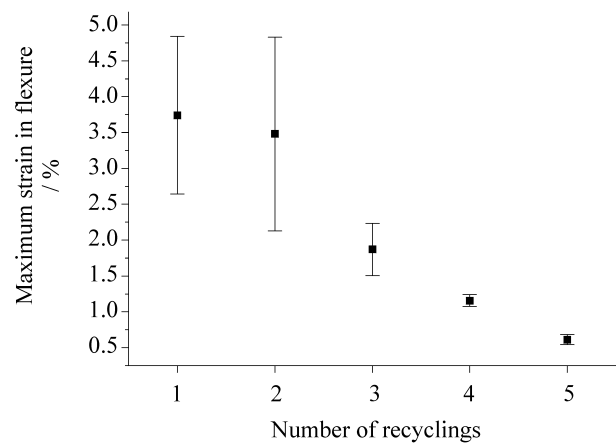


**Figure 4.** Hardness of PET samples produced from virgin resin as a function of the number of recycling steps.

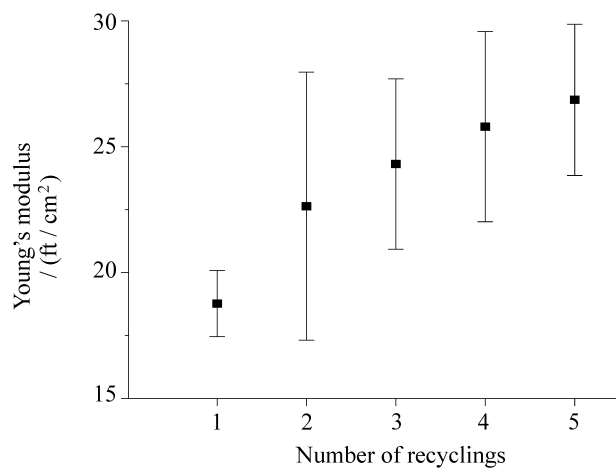


**Figure 5.** Results of flexural modulus of elasticity of PET samples starting from virgin resin as a function of the number of recycling steps.

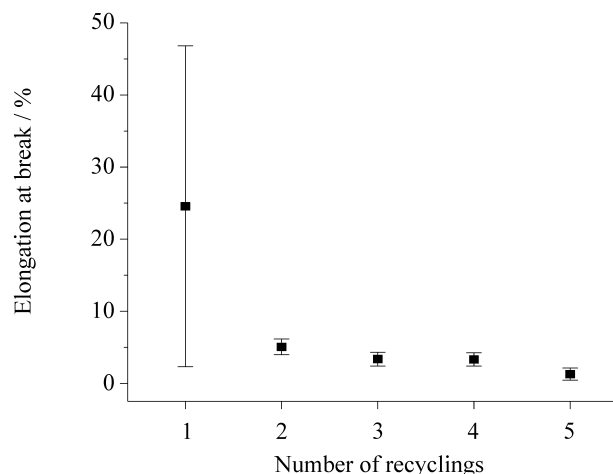
tion at Break obtained by tensile testing. Again, the standard-deviation was high, particularly in the Modulus of Elasticity. The problems relating to the test specimens' surface uniformity that occurred in the flexural test specimens were not present in the tensile ones, which were thinner and, therefore, less influenced by dissimilar contractions between the center and surface of the sample. Thus, we can state that these results are related to different mechanical behaviors, with variations in crystallinity in the same sample lot for each step, or even in a single specimen. This statement also applies to the flexural results, and therefore reduces the effects of the problems that occurred with these specimens on the final results. The upward trend of the average results depicted in Fig. 7, however, is obvious and is in agreement with the increased crystalline phase. The explanation for the Elongation at Break is similar to the one pertaining to Fig. 6: there was a reduction in molecular weight and an increase in the crystalline phase.



**Figure 6.** Results of maximum strain in flexure of PET samples starting from virgin resin as a function of the number of recycling steps.



**Figure 7.** Results of Young's Modulus for virgin PET samples as a function of the number of recycling steps.



**Figure 8.** Results of elongation at break starting from virgin PET as a function of the number of recycling steps.

A comparison of the results presented here with a recent study<sup>10</sup> on recycling of post-consumer resin shows only very slight differences in the properties' behavior through five recycling steps. Therefore, it is not possible to establish any of the proposed correlation for most of the properties studied, except in regard to standard-deviations.

The standard-deviations of samples recycled from virgin resin were usually lower than those of samples recycled from throwaways. This was more evident in the results of Elongation at Break in the tensile tests, with injected ground throwaways showing standard-deviations approximately three times higher than the deviation found in the R1 sample.

The uniformity of the virgin material, of a well-known single origin, unlike the possibly diffuse origin of collected bottles, was probably the factor that contributed the most to the improved reproducibility of the results for samples recycled from virgin material.

The above indicates that the procedures for recovery of resin from throwaways -collection, grinding, washing and air-drying-, do not adversely affect the technical quality of recycled throwaways. On the contrary, recycling of resin from throwaways produces materials whose mechanical properties are similar to those produced from recycling virgin resin, where several parameters can be controlled.

The results presented herein lead us to make some comments on the possible applications of recycled PET products. If R2 were a bottle, its volume would probably be smaller than that of the original (R1, assuming that the virgin resin is transformed into a bottle) and would not be applicable in the food industry. The recycled material could, however, be used as plastic wrapping material or sheets for later thermoforming. The R3 product probably does not have sufficient molecular weight for blow-molding, but is probably suitable for the manufacture of weaving fibers (for carpets, clothes, etc.) or other applications

(brooms, geotextiles, etc). The R4 product presents a high degree of degradation and its molecular weight is probably suitable for use as fiber-fill material (pillows, shoulder-pads, sleeping-bags, etc.). The R5 product is the most suitable for chemical recycling for the recovery of initial materials, monomers or useful intermediary products such polyglycols.

## 4. Conclusions

The successive recycling steps caused cumulative degradation of the polymer's macromolecular structure. The number of carboxylic end groups increased from 50 eq/ton to 148 eq/ton of polymer from the virgin resin to the material injected five times, indicating broken chains and a reduction of the structure's molecular weight. The presence of small chains mixed with large ones resulted in a better fit, which increased crystallinity, as shown by the density and DSC values. Cooling of the test specimens differed according to their distance from the cold mold, causing the appearance of transparent and opaque regions that became clearly visible when the material was ground into flakes.

The crystallinity of the test specimens' strongly influenced the results of the material's mechanical properties. Crystallinity increased at each successive recycling step, increasing the values of the Modulus of Elasticity in both the flexure and tensile tests and decreasing the values of Maximum Strain in the flexure test and of Elongation at Break in the tensile test.

Comparing these results with a recent study on similar experiments using throwaway resin<sup>10</sup>, one can conclude that the successive recycling steps beginning with virgin resin provided better reproducibility of the results, probably due to the uniformity of the virgin resin. Other factors such as crystallinity of the initial samples, time elapsed between production and research, or procedures for the recovery of resin from throwaways, did not result in significant alterations in the behavior of the properties. This is a good argument in favor of disposable plastic bottle recycling, since the material thus obtained is similar to the material obtained from virgin resin.

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