

Characterization of Poly(ethylene terephthalate) after Multiple Processing Cycles

M. A. SILVA SPINACÉ, M. A. DE PAOLI

Laboratório de Polímeros Condutores e Reciclagem, Instituto de Química/UNICAMP, C.P. 6154, 13083-970, Campinas, S.P., Brazil

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ABSTRACT: Poly(ethylene terephthalate) (PET) pellets used for production of soft drink bottles were reprocessed in a single-screw extruder and cut into pellets in five processing cycles. The reprocessed pellets were characterized by its rheological, mechanical, and thermal properties. Carboxylic end groups number concentration and melt flow index were also determined. After three reprocessing cycles the mechanical properties and crystallinity degree changed drastically. Moreover, after five cycles we did not observe changes in the onset temperature of mass loss; therefore, the samples were thermally stable. However, an increase in melt flow index and carboxylic end groups concentration indicated a certain degree of mechanochemical degradation. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 20–25, 2001

Key words: PET; recycling; processing

INTRODUCTION

Poly(ethylene terephthalate) (PET) was first prepared in 1946, and was commercially introduced in 1953 as a textile fiber. Due to the good barrier properties of blow-molded containers made with PET, it became a very important commercial plastic used in food packaging, films and carbonated soft drink bottles. Semicrystalline PET also presents good thermal and mechanical properties, such as high melting temperature (ca. 250°C), and is also used in reinforced plastics.^{1–4} Recently, recycling of plastic wastes, particularly postconsumed PET, has received considerable attention from the media, and the chemical and mechanical recycling of PET has been extensively studied.^{5–8} It is known that PET undergoes hydrolysis when heated in the presence of moisture

above its glass transition temperature (T_g) and near the melting temperature (T_m) resulting in formation of oligomers with unsaturated olefinic and carboxylic end groups.^{9,10} Therefore, the presence of acidic compounds at the processing temperatures, catalyses the hydrolysis of ester bonds leading to the formation of low molar mass fragments with a higher amount of carboxylic end groups.^{9, 10} There is also a decrease in the molar mass due to the thermomechanical degradation, with a consequent increase in the crystallinity degree.⁶ Changes in the coloration of PET also occur.¹¹ PET with a high molar mass is necessary for bottles production; thus, the degradation occurring during reprocessing might turn it useless for this specific purpose. The reprocessed material, however, can be used for many other applications through extrusion or injection molding.

In this work reprocessed PET was characterized by its thermal and mechanical properties. Melt flow index and the concentration of carboxylic end groups were correlated with the number of extrusion cycles. This was done to give an eval-

Correspondence to: M. A. De Paoli.
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uation of the properties of PET as a function of the number of processing cycles to which it was submitted.

EXPERIMENTAL

PET pellets used for production of soft drink bottles (RHOPET® S78, $[\eta] = 0.78 \text{ dL g}^{-1}$) were supplied by Rhodia Ster S.A. These pellets of virgin PET were dried at 160°C for 6 h prior to processing. All the extrusion runs were performed using a Wortex single-screw extruder (D/L = 30, D = 32 mm) with five heating zones. The profile type of the single-screw used is Maddock Mixing Screw.¹² The thermal profile used was 220, 260, 285, 290, and 295°C from the feeding zone to the head and the rotational speed was 102 rpm for all runs. The extruded strand was quenched into cold water and chopped into pellets. Here, one processing cycle is constituted by: extrusion, quenching, and pelletization. The processing conditions, profiles of temperature, and rotational speed were optimized to produce the lowest change in the melt flow index and the lower content of carboxylic end group. These conditions were used for all processing cycles.

The melt flow indexes were measured in an Extrusion Plastometer (DSM Instrumentação Científica Ltd) according to ASTM D1238, using procedure B (automatically timed flow rate measurement). The carboxyl end group (CEG) determination was done following the method described by Pohl.⁹ The samples were dissolved in hot benzyl alcohol, diluted with chloroform, and titrated with a sodium hydroxide solution in benzyl alcohol. A differential scanning calorimetric apparatus (DSC TA instruments, model 2100 coupled to a TA 2100 data analysis system) was used to evaluate glass transition temperature (T_g , mid point), crystallinity degree (X_c), and melting temperature (T_m). The temperature corresponding to the maximum of the exothermic peak in the cooling curve was taken as a measure of the crystallization rate (T_{cc}). The investigated temperature range was between 30 and 290°C . The samples were heated at $10^\circ\text{C min}^{-1}$ up to 290°C (under nitrogen), held at that temperature for 3 min, and cooled at $10^\circ\text{C min}^{-1}$ until 30°C . The thermograms of the polymers were obtained from the second heating cycle. Crystallinity degree (X_c) was calculated using eq. (1).¹³ ΔH_{melt} is the apparent melting enthalpy per gram of PET, and $\Delta H_{\text{literature}}$ is the heat of melting per gram of

100% crystalline PET (140 Jg^{-1}).¹⁴ In the thermogravimetric measurements the sample cell was heated at an uniform rate of $10^\circ\text{C min}^{-1}$, from 20 to 600°C under nitrogen flow (thermal degradation) and in air flow (thermal-oxidative degradation). The thermal stability was studied using these data.

$$X_c = (\Delta H_{\text{melt}} - \Delta H_{\text{cryst}}) / \Delta H_{\text{literature}} \times 100\% \quad (1)$$

For all the stress/strain measurements the samples were injection molded (ASTM D638 Type I) in a PIC BOY 15 Petersen machine. The injection molding condition were: feeding temperature 270°C , nozzle temperature 280°C , and cooling time 20 s. Tensile strengths of the injected specimens were measured using an EMIC model DL2000 equipment, according to ASTM D638. A Macbeth 1500 plus color measurement system was used to measure the color of injected samples according to ASTM D 1925. A illuminant C and 2-degree viewing angle were used. The 3 mm-thick injection-molded round samples were measured.

RESULTS AND DISCUSSION

Rotation Speed and Temperature Profile Selection

The range of values used to select the optimum parameters were (a) 24, 51, and 102 rpm as rotation speed, and (b) two temperature profiles A (220 , 260 , 270 , 275 , and 280°C) and B (220 , 260 , 285 , 290 , and 295°C). Measurements of melt flow index variation and carboxylic end-group concentration as a function of rotational speed indicated little changes of these parameters for both temperature profiles when the highest rotation speed was used [Fig. 1(a) and (b)]. The effect of the changes of the temperature profile is more drastic using a low rotation rate (increase in the melt flow index and carboxylic end-group concentration), indicating that residence time has a direct influence on polymer degradation. From the above considerations we have chosen to work with the temperature profile B and with the higher rotation speed of 102 rpm, because the productivity is higher.

Melt Flow Index (MFI)

Changes in MFI are used to study the extent of thermal and shear degradation of polymeric ma-

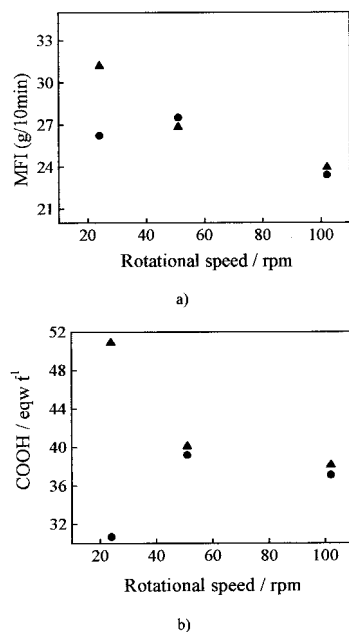


Figure 1 Variation of (a) MFI and (b) carboxylic end group concentration as a function of rotational speed in a different temperature profile (● profile A, and ▲ profile B).

materials. This measure might be a good indicator of the processing effects through the history of a polymer.^{15,16} The results obtained by this method can, however, be used only in a comparative manner. Normally, PET industries use intrinsic viscosity measurements instead of the flow parameters. The intrinsic viscosity measurement method has been avoided in this work because it uses carcinogenic solvents (phenol/tetrachloroethane or *ortho*-chlorophenol). On the other hand, MFI measurements uses no solvent and shows low deviations, making it suitable for PET characterization. The only drawback is the need of costly equipment.

The MFI values showed an exponential variation as a function of number of extrusion cycles, it varied from 23 to 80 g 10 min⁻¹ for virgin PET and for the material after five processing cycles, respectively [Fig. 2(a)]. The increase of MFI is probably caused by the thermal-mechanical degradation of the material.

Carboxylic End Groups Determination (CEG)

Thermal-oxidative degradation and hydrolysis occur during the extrusion process, both producing carboxylic end groups.¹⁷ End group analysis is one of the most important absolute methods for

obtaining the number average molar mass of condensation polymers of known structure. Various physical methods have been employed to determine the end-group concentration; these include FTIR,^{18,19} ¹³C nuclear magnetic resonance,^{20–22} dielectric methods,²³ and chemical analysis.²⁴ Recent works²⁰ show that, when CF₃COOH mixtures are used as solvent for NMR measurements, esterefication occurs with formation of hydroxyl end groups. Therefore, for ¹³C-NMR quantitative identification of end groups, a mixture of hexafluoro *iso*-propanol (HFIP) and deuterated chloroform (CDCl₃) is recommended as solvent. These methods normally show disadvantages because the solvent, HFIP, is very expensive and the quantitative measurement by FTIR is difficult to obtain.

In this work the carboxylic end groups were determined by titration. As observed in Figure 2(b), the carboxylic end groups concentration increases almost linearly with the number of processing cycles, changing from 36 for virgin PET to 100 eqw/10⁶g after five cycles. This behavior shows the same trend as the MFI measurements, and confirms the occurrence of thermal mechanical chain scission leading to hydrolysis of the ester bonds.

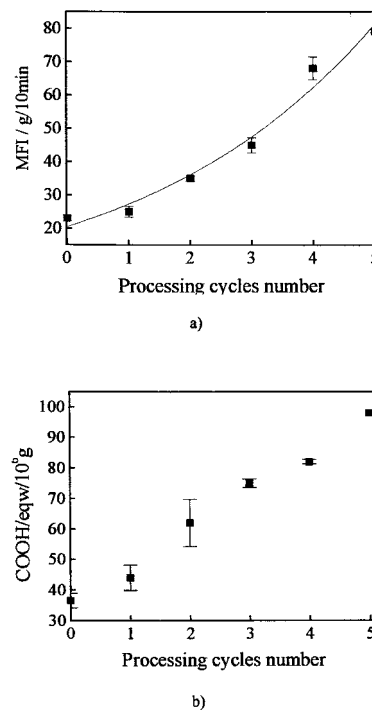


Figure 2 Variation of (a) MFI and (b) carboxylic end group concentration as a function of the number of processing cycles.

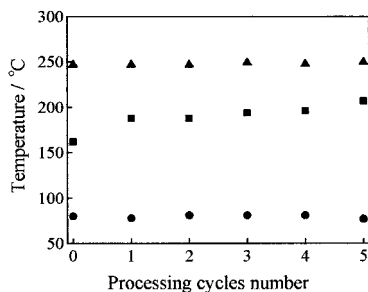


Figure 3 Variation of T_{cc} (■), T_g (●), and T_m (▲) as a function of the number of processing cycles.

Thermal Properties

The variations of the values of T_g , T_{cc} , and T_m for virgin PET and reprocessed PET as a function of the number of processing cycles are shown in Figure 3. Virgin PET shows T_g , T_{cc} , and T_m of 80, 160, and 250°C, respectively. After five cycles, no changes in T_g and T_m were observed; however, T_{cc} increases by 40°C from 160 to 200°. The constant T_g value indicates that the degradation produced by the processing cycles do not affect the viscosity of the polymer. The maximum T_m value taken from the peak in the DSC curves show no change; however, a second less intense peak at lower temperatures is observed, indicating that variations in the distribution of crystallite sizes have occurred (Fig. 4). Chain scission improves chain packing, increasing crystallite size, and, consequently, shifting T_{cc} to higher temperatures.

Thermal stability was evaluated by thermogravimetric curves, analyzing shifts in the onset temperature of mass loss. Thermogravimetric curves for virgin and for reprocessed PET are coincident, showing only one mass loss process starting at ca. 350°C, either under argon or air. This indicates that five processing cycles caused no changes in the thermal degradation behavior of PET.

Mechanical Properties of Virgin and Reprocessed PET

The mechanical properties (elongation at break, tensile strength and tensile strength at break) for virgin and reprocessed PET are reported in Table I. The elongation at break and tensile strength at break are strongly affected by the number of processing cycles, while the tensile strength is less affected. The tensile strength at break value is 25 MPa for virgin PET, and shows no change until the second processing cycle, after this it increases

asymptotically to 55 MPa. After three extrusions the reduction of elongation at break is drastic, varying from 112 (± 23)% for virgin PET to 6.0 (± 0.3)% for PET reprocessed for three cycles (Table I). These changes are probably due to variations in the molar mass distribution and changes in the crystallization behavior. The crystallinity degree increases with the number of processing cycles, varying asymptotically from 24 for virgin PET to 38% for reprocessed PET after three cycles (Table I). This is caused by the hydrolytic chain scission that reduces the molar mass, mainly after the third extrusion. This is also indicated by the concentration of carboxylic end groups and Melt Flow Index measurements. Both results indicate that chain scission or a drastic change of the polydispersity occurs.

The results obtained for the variation of elongation at break and crystallinity degree are similar to those reported in the literature. For semi-crystalline polymers, most mechanical properties depend critically on crystallinity.¹⁵ After three processing cycles, the material is less ductile than virgin PET, probably due to the increase in the crystallinity degree. Elongation at break and tensile strength show the same value, indicating that PET has lost its plastic properties.

Color

The color change in the production of PET is a serious drawback. As PET degrades, its color changes, first to yellow then to brown, and finally to black. Virgin PET is transparent and the reprocessed material shows an increasing colouring after each processing cycle (Table I). The yellowing index increasing six times after five processing cycles. The colorimetric data were consistent

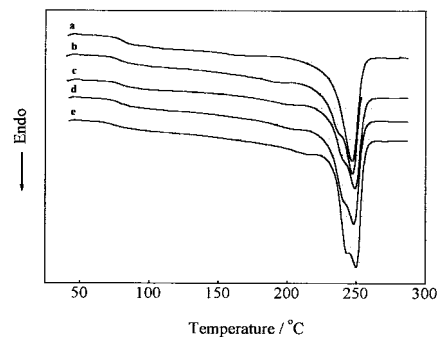


Figure 4 DSC curves of PET ($10^\circ\text{C min}^{-1}$): a, b, c, d, and e corresponds to the first, second, third, fourth, and fifth processing cycle, respectively.

Table I Mechanical Properties of Virgin and Reprocessed PET

Processing Cycle	Crystallinity Degree (%)	Tensile Strength at Break (MPa)	Elongation at Break (%)	Tensile Strength (MPa)	Yellowing Index (a.u.)
0	24	25.0 (\pm 0.7)	112 (\pm 23)	63.0 (\pm 2.9)	9
1	27	26.0 (\pm 0.6)	167 (\pm 42)	60.0 (\pm 1.6)	14
2	35	27.0 (\pm 1.9)	140 (\pm 45)	60.0 (\pm 1.7)	17
3	38	52.0 (\pm 3.1)	6.0 (\pm 0,7)	52.0 (\pm 2.9)	27
4	38	54.0 (\pm 2.1)	6.0 (\pm 0,2)	54.0 (\pm 2.0)	48
5	38	55.0 (\pm 2.3)	6.0 (\pm 0,3)	55.0 (\pm 2.2)	52

with visual examination. Chain scission leads to the formation of chromophoric substances, which are difficult to isolate and are responsible for light absorption in the near UV and visible range. We also observed that the material became opaque, probably because the decrease in chain length improves chain packing, increasing the crystallinity degree and crystal size.

CONCLUSIONS

After three processing cycles the mechanical properties and crystallinity degree of PET changes drastically. After two cycles the material can be used again for applications where virgin PET is usually employed. Carboxylic end-group content, melt flow index, and color properties change after the first processing cycle. Thermal properties, such as onset temperature of mass loss, glass transition, and melting temperature do not change, showing that this material is thermally stable until the fifth processing cycle. Variations are observed in the crystallization temperature, indicating changes in the crystallization kinetics due to chain scissions. The same tendency in the mechanical behavior was observed by La Mantia⁶ and Mancini,²⁵ however, our value of elongation at break is higher, probably because they used different processing equipments and PET with different molar mass. The increase in the number of processing cycles causes a stepwise increase in the degree of degradation, which was indicated by the increase in the concentration of carboxyl end groups and melt flow index. After a certain degree of degradation the mechanical properties of the reprocessed material deteriorate drastically, turning useless for several applications. To preserve the mechanical properties it is necessary to use (because the first processing) hydrolysis stabilizing agents and nucleation ad-

ditives for minimizing opacity, or to dilute the processed material with virgin PET. Care should be exercised when working with postconsumed PET, because some contaminants can also accelerate degradation.

Based on these results it is possible to make reasonable predictions concerning the use of postconsumed PET for specific applications. We are presently developing an FTIR-based method to obtain quantitative information of carboxylic end group concentration.

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