

# PET Recycling: Evaluation of the Solid State Polymerization Process

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**ABSTRACT:** Many studies have been carried out to make bottle-to-bottle recycling feasible. One of the difficulties found is the decrease in the polymer's molar mass, which damages the injection blow molding process. A method usually employed to increase the molar mass of virgin PET consists of solid-state polymerization (SSP). In this work, we studied the SSP process applied to post-consumer recycled PET by analyzing the inherent viscosity and amount of carboxylic end groups, and the results of dynamic flow rheometry. Although the results show that the recycling

process decreases polymer molar mass, and this indicates degradative processes, SSP was successful in increasing molar mass in post-consumer recycled PET. This made feasible bottle-to-bottle recycling. In addition, the parallel plate rheometry technique was powerful in assessing the degradative process and, therefore, that the SSP process was successful. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2117–2123, 2006

**Key words:** recycling; post-consumer; poly(ethylene terephthalate); degradation; solid-state polymerization

## INTRODUCTION

The growing applications of polyethylene terephthalate (PET) mainly in the soft drink market, associated with the lack of adequate management of municipal solid waste, has caused serious environmental problems in Brazil.<sup>1</sup>

Even with the current mechanical recycling functioning in various regions of Brazil, tons of plastic continue to be wasted. According to data of the Brazilian Association of PET Packaging (ABEPET),<sup>2</sup> the consumption of PET resin for packaging in 1994 was on the order of 80 kton. This number rose to 300 in 2002, which represented an increase of 375%, as shown in Table I. On the other hand, the recycling of this material, which had been 19% (13 kton), grew to 35% (105 kton). Although apparently these numbers are encouraging, in reality 195 kton of post-consumer PET resin were wasted in 2002, as compared with 67 kton in 1994.

As the principal PET application is in blow-molded packaging, it would be extremely useful if this material could be treated in such a way as to return it to a form suitable to its original purpose. However, during its life cycle PET comes in contact with degrading

agents such as oxygen, light, high temperatures, shearing, and water (not only as a residue of the washing process but also due to short storage periods). These factors cause degradation through chain scission, which results in molar mass polymer decrease and, consequently, in inherent viscosity, which prevents bottle-to-bottle recycling.<sup>3</sup> However, molar mass increase of recycled polymer can be obtained by postcondensation in the solid state through the reactions of esterification and transesterification, as shown in Figure 1. This is done by heating the polymer to below its melting temperature while remaining above its glass transition temperature. At this temperature, a slowing of the thermal degradation process occurs, the polymer is further condensed, and the molar mass increases while subproducts are being removed by vacuum application or flushing with inert gas.<sup>4,5</sup>

Many studies have been done<sup>6–8</sup> to analyze the variables influencing the solid-state polymerization (SSP) process on virgin PET. Kim et al.<sup>6</sup> researched the kinetics of the SSP reaction on PET varying the inherent viscosity of the precursor with temperature variation. According to these authors, precursors with higher initial molar mass exhibited higher rates of SSP than those with lower initial values. Furthermore, activation energies decreased at temperatures above 200°C, indicating a change in the SSP reaction mechanism. At temperatures between 200 and 300°C, similar activation energies were required for the polymerization of all samples, i.e., with three different values

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TABLE I  
PET Resin Consumed in Packaging and Quantity  
of Post-Consumer Recycled PET

	PET used for packaging (kton)	Post-consumer recycled PET (kton)
1994	80	13 (19%)
2002	300	105 (35%)

in the molar mass. On the other hand, Agarwal and coworkers,<sup>7</sup> after examining the influence of environmental reaction on SSP, concluded that when nitrogen is used as a carrier gas, the reaction rate and the extent of molar mass build-up are somewhat lower compared with that of SSP under vacuum. A sublimate was collected during SSP under vacuum, which these researchers found to be made up of terephthalic acid, monohydroxyethyl terephthalate, bishydroxyethyl terephthalate, and cyclic oligomers. This indicates the presence of a new condensation mechanism during SSP under vacuum. Duh<sup>8</sup> studied the effect of the catalyst antimony (Sb) on the SSP of PET. He concluded that while the activation energy decreases, there is an increase in the rate constant linear with increasing catalyst concentration within the range of 0–100 ppm Sb.

Despite these studies, little research has been done on increasing the molar mass in recycled PET. However, Karayannidis et al.<sup>9,10</sup> have studied SSP in PET recycled from postconsumer soft drinks bottles by dissolution in various solvents and precipitation in methanol. The effect of reaction temperature and time was related with inherent viscosity and carboxylic and hydroxyl end groups. As a result, and demonstrating the efficiency of the process, PET with a molar mass of about 60,000 g/mol was obtained from PET bottles with 20,000 g/mol after dissolution in solvents like *o*-chlorophenol or nitrobenzene and heating at 230°C under vacuum for 8 h. For its part, the present work aimed ultimately at increasing the applicability of recycled plastics by preserving the properties of the

TABLE II  
Terminology Used for the Materials During the Work

Terminology	Description <sup>a</sup>
PETv	PET virgin resin (S-80)
PETr	PET post-consumer resin (already reprocessed)
PETr-pos	PETr resin after pass the SSP
PETbv	Material from virgin bottles
PETbr	Material from recycled bottles

<sup>a</sup> All materials were pulverized on a Mikro-Bantam Cryogenic Mill.

materials of which plastic residues are composed. To that end, the degradative processes by which reprocessing can occur were identified, and the increase of the molar mass of postconsumer recycled PET through SSP was studied. The end product was bottles produced through the blow-molding process. The SSP process was evaluated by carboxylic acid end group determination, yellowness index, parallel plates rheometry, inherent viscosity, and differential scanning calorimetry (DSC). In addition, the parallel plate rheometry technique was powerful in assessing the degradative process and, therefore, that the SSP process was successful.

## EXPERIMENTAL

### Materials

The used virgin PET (S-80), supplied by Mossi and Ghisolfi S.A. (M & G), Brazil, has an inherent viscosity of 0.8 dL/g (norm ASTM D 2857) and a density of about 1.39 g/cm<sup>3</sup> (norm ASTM D 1505). It comes in pellet form and is used for soft-drink bottle manufacture.

The recycled material was PET from colorless soft-drink bottles, supplied by Recipet S.A., Brazil.

To facilitate interpretation and identification throughout this work, the samples were named as shown in Table II.

### Esterification



### Transesterification

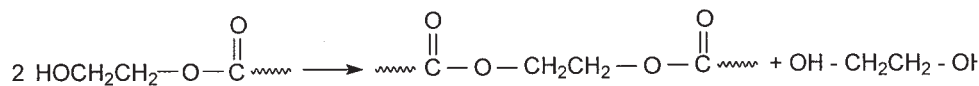
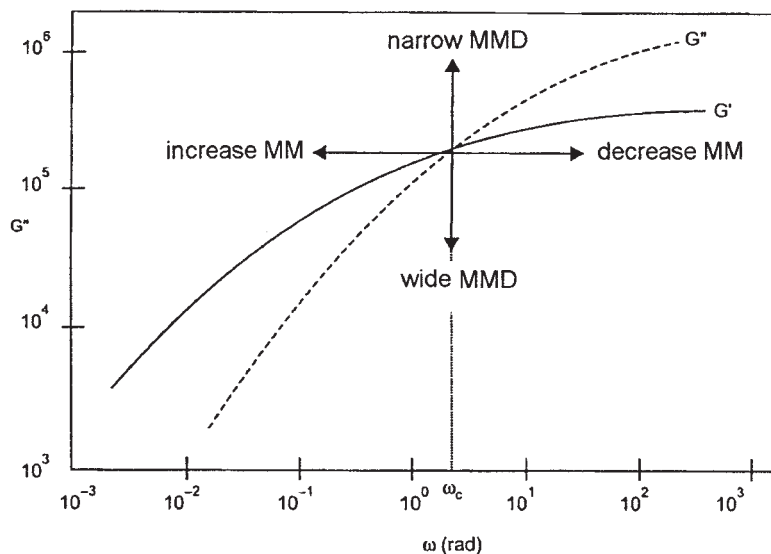


Figure 1 Esterification and transesterification reaction on PET.



**Figure 2**  $G'$  and  $G''$  curves of a hypothetical polymer, indicating how the frequency shifts with molar mass and molar mass distribution.<sup>13</sup>

### SSP process

The SSP was done for a total of 11.5 h in a postcompensator at the PET Development Center (M & G). In the first 6 h, nitrogen flux at 140°C was used to promote complete crystallization of the material. In the last 5.5 h, the temperature was increased to ~220°C, and the inert atmosphere changed to a vacuum.

### Injection molding process

The virgin PET (S-80) and the recycled PET resulting from the SSP process then went through the injection-blow process (Nissei ABS-50). This was carried out in three steps. First, the postcondensed PET was dried for 6 h at 170°C in a silo with air flux. After that, the dry resin was processed by preform injection followed by blowing to obtain a bottle. In the injection process, the barrel temperature used was 260°C, with injection velocity range 20–14 cm/s and injection pressure range 14–0.5 bar. In the blow process, preblow pressure and blow pressure used were 11 and 25 bar, and the mold temperature used was 10°C.

### Carboxylic acid end group determination

Carboxylic acid end group determination was done by titration of ground PET diluted in hot benzyl alcohol, followed by reaction with standard solution of sodium hydroxide in benzyl alcohol.<sup>11</sup>

### Inherent viscosity measurement

Inherent viscosity measurements were done at (30.0 ± 0.1)°C in an Ubbelohde type viscometer on solu-

tions in (60/40)% w/w, phenol/1,1,2,2-tetrachloroethane at a polymer concentration of 0.25% w/v. The average molar mass was determined by the Berkowitz equation.<sup>9</sup>

### Yellowness index determination

The yellowness index was determined using a diffuse reflectance spectrophotometer (Macbeth Coloreye 2180UV) according to ASTM D 1925.

### Differential scanning calorimetry

The melting point and heat of fusion were determined using a Perkin-Elmer DSC-7, according to ASTM D 417. The heating rate employed was 10°C/min. Crystallinity was determined by dividing the  $\Delta H_m$  obtained by the heat of fusion of 100% crystalline PET (135 J/g).<sup>12</sup>

### Parallel plates rheometry

A Rheometrics Scientific SR 200 instrument was used at 180°C, between 0.1 and 500 rad/s in a nitrogen atmosphere. The geometry used was parallel plate, with a 25-mm diameter. The results were analyzed by displacement of the point where  $G'$  coincides with  $G''$ , which allows prediction of whether the molar mass is increasing or decreasing, as well as whether the molar mass distribution is narrowing or widening, as shown in Figure 2.

## RESULTS AND DISCUSSION

The SSP process was employed to make possible bottle-to-bottle recycling by increasing the molar mass

**TABLE III**  
Parameters Used in the SSP and Measured  
Inherent Viscosity (IV)

Time (h)	Temperature (°C)	Environmental atmosphere	IV (dL/g)
0	25	N <sub>2</sub>	—
2.0	170	N <sub>2</sub>	—
4.0	170	N <sub>2</sub> /vacuum	—
5.5	220	vacuum	0.68
7.5	220	vacuum	0.71
9.5	220	vacuum	0.75
11.5	220	vacuum	0.80

and then the inherent viscosity. Table III presents the time, temperature, and environmental atmosphere that occurred in the SSP process and shows the inherent viscosity values registered during the process.

Table III shows that the SSP occurred in ~11.5 h. In the first 4 h, the material was maintained in an inert atmosphere using nitrogen at 170°C. These conditions promoted an increase in the crystallinity of PET, since SSP requires 40% crystallinity to reduce pellets adhesion. Adhesion can occur if some oligomers have a lower molar mass and melting point.

After crystallization, the temperature was increased to 220°C, for 4 h. At this temperature, the carboxylic or hydroxyl end groups content or ester bonds to near the end of chain are activated and bond with each other. This promotes an increase in the polymer molar mass by esterification and transesterification reactions as shown previously.

After the SSP process, the recycled material, now post condensed, has adequate inherent viscosity to injection-blow molding process. The first reprocessing step, drying, is very important in determining the bottle quality. This is because, when PET is submitted to high temperature in the presence of water, it will undergo hydrolysis decreasing its molar mass.

#### Carboxylic acid end group determination and inherent viscosity

Table IV presents the results obtained by carboxylic acid end groups concentration [COOH], inherent vis-

**TABLE IV**  
Carboxylic End Groups Concentration (mmol/g)  
to PETv, PETr, and PETr-pos

Samples	[COOH] (mmol/g)	[ $\eta$ ] (dL/g)	$M_n$
PETv	$35 \times 10^{-3}$	0.78	22400
PETr	$43 \times 10^{-3}$	0.68	18200
PETr-pos	$37 \times 10^{-3}$	0.78	22400
PETbv	—	0.70	19000
PETbr	—	0.72	19000

**TABLE V**  
Yellowness for PETv, PETr, PETr-pos, PETbv, and PETbr

PET	$\Delta b^*$ (Yellowness)
PETv	—
PETr	3362
PETr-pos	5717
PETbv	—
PETbr	5398

cosity, and to the average molar mass calculated by the Berkowitz equation.

The titration results showed an increase of ~20% in the [COOH] with recycling. Similar results have been described in the literature.<sup>9,10</sup> Mancini and Zanin<sup>3</sup> studied the variation in carboxylic end groups concentrations as a function of the consecutive steps of PET recycling with injection molding. They concluded that, after the third recycling step, these groups increased by 57%. Following the SSP process, the carboxylic end group concentrations decreased since this process promotes esterification and transesterification reactions.

With recycling, a decrease in inherent viscosity and molar mass is observed. This behavior is due to degradative processes triggered by a chain scission that occurs with reprocessing, as confirmed by the end group carboxylic results. With the SSP process, the material presents the same inherent viscosity as virgin resin (0.78 dL/g), demonstrating the efficiency of this process and making feasible the blow-molding process. In addition, the PETbv fell by about 10% in the value of inherent viscosity as compared with virgin resin. This proves that during the bottle manufacturing process, in spite of taking the necessary precautions, principally in drying, the material suffers degradation. Surprisingly, in spite of post-PETr presenting the same inherent viscosity as virgin resin, after reprocessing, there was a less pronounced fall in the value of inherent viscosity (0.72 dL/g) when compared with PETbv (0.70 dL/g). The samples were done in duplicate, and all of them yielded the same value, indicating the reliability of this technique.

#### Yellowness index

Table V presents the results of spectrophotometry in the visible range for the samples of PETv, PETr, PETr-pos, PETbv, and PETbr after the incidence of illuminants D65. Samples of PETv and PET were used as standards.

Table V shows a tendency with reprocessing to yellowing in the material, a behavior associated with the presence of chromophores resulting from degradative processes. Edge et al.<sup>14</sup> studied, through fluorescent spectra, the chromophore groups appearing in degraded PET. In general, these groups can be poly-

**TABLE VI**  
Melting Temperature ( $T_m$ ), Heat of Fusion ( $\Delta H_m$ ),  
and Crystallinity (%C) of PETv, PETr, PETr-pos,  
PETbv, and PETbr

	PETv	PETr	PETr-pos	PETbv	PETbr
1st heating					
$T_m$ (°C)	239	242	235	242	242
$\Delta H_m$ (J/g)	53.5	40.2	54.9	48.0	48.7
%C	39	30	40	35	36
2nd heating					
$T_m$ (°C)	238	235	233	240	233
$\Delta H_m$ (J/g)	37.4	44.5	46.3	46.8	47.1
%C	28	33	34	34	35

aldehydes, unsaturated polyvinyl ester molecules, cyclic oligomers, polyenic segments, and a bisphenol structure.<sup>14,15</sup>

When comparing PETr with postPETr, this tendency practically doubles, a behavior also observed by Teixeira<sup>16</sup> in a study of PET recycling by SSP. According to this author, the high temperatures employed in the SSP process produce an increase in yellowing as a result of the SSP time. This result indicates that in spite of SSP being widely used to increase through esterification and transesterification reactions, it can cause the formation of other forms such as chromophores and still others of less molar mass. This behavior was also clearly shown in comparing PETbv with PETbr.

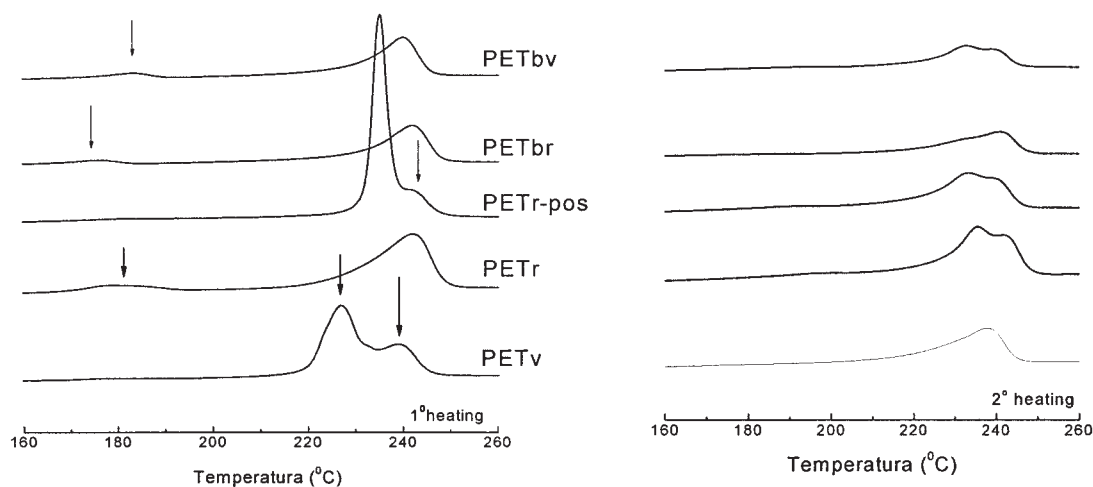
### Differential scanning calorimetry

Table VI presents the melting temperature ( $T_m$ ), heat of fusion ( $\Delta H_m$ ), and crystallinity (%C) of the studied samples obtained from DSC curves. These results show that all samples present high crystallinity due to their previous thermal history. The PETv and PETr-pos show the highest crystallinity values (39 and 40%,

respectively). This fact was already expected since both the PETv and the PETr-pos went through the SSP process, in which the resin is subjected to a temperature intermediate between the glass transition temperature ( $T_g$ ) and  $T_m$ . At this temperature, amorphous chains are mobile, which results in an increase in crystallinity values. This process is still more effective in PETr-pos as the material is maintained longer at this temperature than PETv.

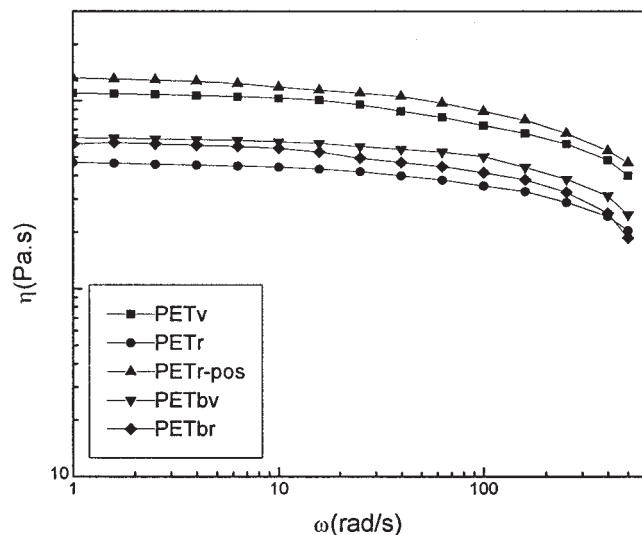
Figure 3 presents the thermogram obtained for the samples. The very narrow endothermic peak for PETr-pos when compared with the results of the other samples is due to the homogeneity of crystals obtained during the SSP.

An endothermic peak of  $\sim 180^\circ\text{C}$  is also observed for PETv and PETr for the first heating, and PETr and PETr-pos for the second heating. Many studies<sup>17,18</sup> have described PET thermal behavior and its crystallinity. Medellin-Rodriguez et al.<sup>17</sup> reported triple melting peaks occurring in PET. According to these authors, the first peak is related to secondary crystallization ( $10\text{--}15^\circ\text{C}$ ) following crystallization temperature ( $T_c$ ); the second endothermic peak was related with perfect crystal fusion in the sample; and the third was related with crystal reorganization during heating. Similar results are described in Zhou and Clough [cited in ref. 19]. For Al Raheil [cited in ref. 19], the first peak was related to imperfect lamellas presenting temperatures less than that of PET fusion, while the second peak refers to perfect crystals whose fusion occurs at greater temperatures. The appearance of the first peak, principally in the case of PETr, PETr-pos, and PETbr, at a temperature  $10\text{--}15^\circ\text{C}$  above that of crystallization, can be caused by impurities in the material, which impair crystallization by forming imperfect crystals that fuse at lower temperatures.



**Figure 3** DSC thermograms obtained for PETv, PETr, PETr-pos, PETbv, and PETbr for the first and second heating.





**Figure 4** Rheological properties in an oscillatory regime as a function of the frequency for PETv, PETr, PETr-post, PETbv, and PETbr at 270°C.

### Parallel plates rheometry

In parallel plate rheometry, rheological properties are measured by imposing a drag flow, in this case by rotating an upper parallel-shaped plate at a given angular velocity. Although this type of rheometer may be used to measure low shearing rates ( $<100 \text{ s}^{-1}$ ), it can also provide important rheological information correlated with polymer molecular structure.

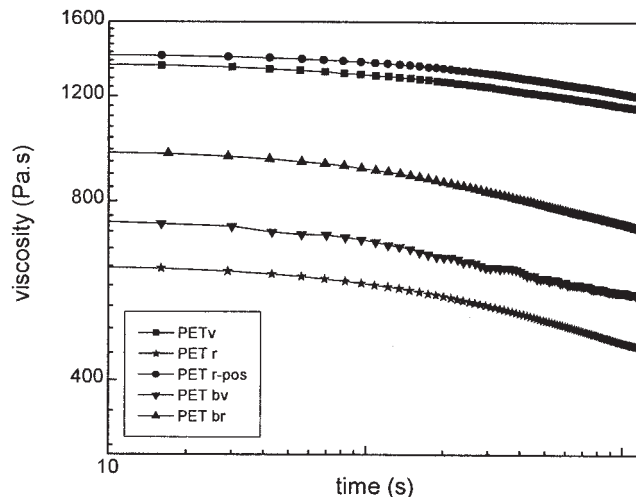
Melted PET presents viscoelastic behavior, i.e., it has a component composed of an elastic part and a viscous part. Deformations in viscoelastic polymers present a narrow amplitude, and the resulting tensions oscillate at the same frequency but not in the same phase as the strain.

Figure 4 shows viscosity results, obtained by parallel plates rheometry, as a function of the frequency for PETv, PETr, PETr-pos, PETbv, and PETbr at 270°C.

An analysis of the results in Figure 4 reveals that PETr-pos presents a viscosity slightly superior to that of virgin resin. As viscosity indicates molar mass, according to inherent viscosity results, PETr-pos presents a molar mass similar to that of PETv. These results are comparable to those obtained for inherent viscosity.

Degradation analyses were also done to samples in this study by complex viscosity ( $\eta^*$ ) as a function of time, as shown in Figure 5.

PETr-pos presents the highest viscosity, followed PETv and PETr, results according to both inherent viscosity and complex viscosity as a function of frequency. In addition, in spite of all samples presenting a very similar viscosity profile, the decrease in the plateau is slightly faster for the PETr, PETbv, and PETbr samples. These results indicate that these sam-



**Figure 5** Complex viscosity as a function of time at 270°C for PETv, PETr, PETr-pos, PETbv, and PETbr.

ples are more sensitive to degrading processes as compared with PETv and PETr-pos. The recycled material presented this behavior because they had already been through the recycling process, which as previously mentioned entails degrading processes. The PETbv sample, which had already been processed, was obviously less stable than was resin S-80. It is important to note that the PETbr sample, probably because its prime material is PETr-pos, presented a higher viscosity than the material used to make recycled bottles.

We also determined the  $G'$  and  $G''$  values as a function of frequency. As for viscoelastic properties in the molten state,  $G'$  and  $G''$  can range with the molar mass and molar mass distribution (MMD) of the polymer.

A dislocation of the point at which  $G'$  coincides with  $G''$  allows us to predict if an increase or decrease, as well as if narrowing or widening, will occur in the molar mass, as shown in Figure 2.

Table VII indicates the values of axis  $x$  and  $y$  at the point where  $G'$  coincides with  $G''$  in the PETv, PETr, PETr-pos, PETbv, and PETbr samples. It should be mentioned that for all samples, point  $G'(\omega) = G''(\omega)$  was determined by extrapolation from the  $G'$  and  $G''$  curves because, as bottle-grade PET is a polymer presenting a short relaxation time as a consequence of its

**TABLE VII**  
Crossing Point Where  $G' = G''$  for PETv, PETr, PETr-pos, PETbv, and PETbr

Samples	$x$	$y$
PETv	572	176600
PETr	788	81300
PETr-pos	522	189900
PETbv	355	36700
PETbr	588	93000

relatively low molar mass, the crossing point occurs at frequencies of more than 500 rad/s, which is the upper limit of the equipment used in this work.

Table VII shows a decrease of molar mass as well as a MMD widens from PETv to PETr and PETbv to PETbr. Besides, and corroborating the results for complex viscosity (Fig. 5), the PETr-pos molar mass is demonstrated to be slightly superior to that of PETv, indicating the effectiveness of the SSP process. In addition, a MMD narrowing is revealed for SSP.

### CONCLUSIONS

The SSP done in this work, for the purpose of rendering molar mass of recycled material suitable for use in making new bottles, was successful as evidenced by inherent viscosity increase and, consequently, molar mass increase. The occurrence of degradative processes resulting from polymer recycling was shown by the increase in carboxylic end group concentration, the decrease in inherent viscosity and molar mass values, and by the presence of chromophores groups that alter the colorimetry parameters, as well as the alterations in the crystallinity parameters and the fusion temperature. All of these alterations are related to degradation by chain scission that may have occurred either in preparing the material for reprocessing, e.g., in grinding or in reprocessing owing to the high temperatures used, in addition to catalytic agents like humidity and oxygen involved in these processes.

Furthermore, the parallel plate rheometry results yielded valuable information about polymer molecular structure. This technique has proven extremely sensitive to molar mass variation, as demonstrated by its ability to detect the slightly superior molar mass of

PETr-pos compared with that of virgin resin, which could not be determined by inherent viscosity results.

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