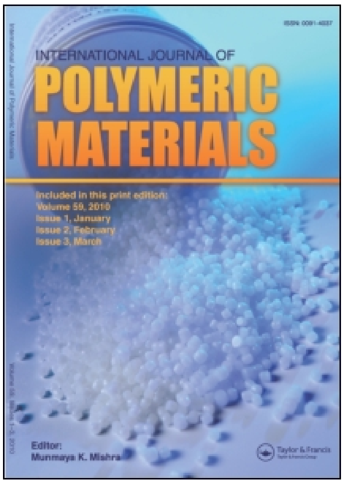


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Characterization of Post-Consumer PET after Removal of the Original Surface: Influence of Raw Material

Sandro Donnini Mancini[a]; Alex Rodrigues Nogueira[a]; Jonas Age Saide Schwartzman[a]; Dennis Akira Kagohara[a]
[a] UNESP - Universidade Estadual Paulista, Campus Experimental de Sorocaba, Environmental Engineering Department, Sorocaba-SP, Brazil

To cite this Article Mancini, Sandro Donnini , Nogueira, Alex Rodrigues , Schwartzman, Jonas Age Saide and Kagohara, Dennis Akira(2010) 'Characterization of Post-Consumer PET after Removal of the Original Surface: Influence of Raw Material', International Journal of Polymeric Materials, 59: 6, 407 — 423

To link to this Article: DOI: 10.1080/00914030903538538

URL: http://dx.doi.org/10.1080/00914030903538538

International Journal of Polymeric Materials, 59:407–423, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030903538538

Characterization of Post-Consumer PET after Removal of the Original Surface: Influence of Raw Material

Sandro Donnini Mancini, Alex Rodrigues Nogueira, Jonas Age Saide Schwartzman, and Dennis Akira Kagohara

UNESP – Universidade Estadual Paulista, Campus Experimental de Sorocaba, Environmental Engineering Department, Sorocaba-SP, Brazil

Post-consumer cooking oil and soft drink PET bottles (PET_{oil} and $PET_{soft\ drink}$) were ground and washed only with water (conventional washing). The polymer was then chemically washed (10 min in an aqueous solution of sodium hydroxide $5\,mol \cdot L^{-1}$ at 90°C) and rinsed. The materials before and after chemical washing were characterized by intrinsic viscosity, differential scanning calorimetry, thermogravimetry, elemental analysis, scanning electron microscopy with X-ray spectrum microanalysis, and gas chromatography coupled to mass spectrometry. The results indicated that conventionally washed PET_{oil} is the material that most differs among the four tested ones, and that the other three are more similar to each other and to what is expected for pure PET. For example, the composition of PET_{oil} washed only in water contained 30 volatile organic compounds, 5 nonvolatile compounds, and 7 metals, while $PET_{soft\ drink}$ washed conventionally and chemically contained 5 volatile organic compounds and no metal or nonvolatile organic compounds.

Received 6 November 2009; in final form 15 November 2009.

The authors wish to thank FAPESP (processes 04/08718-9 and 06/55213-5) and PIBIC-UNESP/CNPq for the financial support. They are also grateful to Dr. Amélia Severino Ferreira e Santos and the environmental engineering students Camila Bernadete Benassi Parra, Camila Silva Franco, Raquel Carramilo Keiroglo and Vansessa Alves Mantovani.

Address correspondence to Sandro Donnini Mancini, Environmental Engineering Department, Universidade Estadual Paulista (UNESP), Campus Experimental de Sorocaba, Av. 3 de Março, 511 – Altos de Boa Vista, Sorocaba-SP, CEP 18087-180, Brazil. E-mail: mancini@sorocaba.unesp.br

Keywords impurities, oil bottles, PET, soft drink bottles, washing

INTRODUCTION

Approximately 231 thousand tons of poly(ethylene terephthalate) were recycled in Brazil in 2007, which corresponds to 53% of all the resin consumed in the country in the form of soft drink, oil, isotonic and other bottles. The most common way to recover the PET contained in bottles is through mechanical recycling, which represented about 94% of recycling in Brazil in this period [1].

With regard to this form of recycling, it is known that the quality of the recycled end product is directly associated with both the technological characteristics of the processes involved and the quality of the raw material to be recycled [2,3]. According to the Brazilian PET Industry Association, only 10% of the PET recycled in Brazil in 2007 came from industrial waste, which usually contains a lower level of aggregated impurities than that found in post-consumer waste, corresponding to the remaining 90% [1]. The fact that selective waste collection is restricted to only about 14% of the population means that post-consumer raw material sent for recycling in the country is usually of low quality since it is mixed with other types of waste, notably food waste [4]. A study conducted at a sanitary landfill of a city with a population of 175 thousand revealed that, in terms of mass, 40% of the waste consisted of food waste and 1% of PET, confirming the possibility that they may be mixed. About 70% of the PET discarded in the municipality is colorless bottles, and three out of every four discarded colorless bottles held soft drinks and one held cooking oil [5].

In this context, albeit in wide use, the sequence of processes traditionally adopted in mechanical recycling, i.e., grinding, washing, drying and reprocessing of the polymer, may not suffice to obtain packaging with adequate molar mass, color and/or transparency, among other properties [2,3]. This is due to the fact that the traditional recycling processes may not be able to remove remnants of the previously packaged product and impurities impregnated during the product's life cycle, thus impairing the quality of recycled resin. It is therefore interesting to develop techniques that ensure a more efficient removal of impurities than the conventional processes, aiming to improve the properties of the end product.

One way of obtaining PET with a higher level of impurity removal than that afforded by the conventional route can be based on the removal of the original surface and the impurities associated with it, as though the polymer were peeled, revealing a new and, in theory, impurity-free surface. The surface of PET can be removed by means of a superficial chemical reaction, as has been demonstrated in the chemical recycling of solid-state PET using alkalis in aqueous solutions or ethylene glycol solutions [6–9]. The removed surface can be subjected to another industrial process to obtain terephthalic acid (TPA), starting from the acidification of salt produced in the superficial chemical reaction (water-soluble disodium terephthalate) [10].

The objective of this paper is to present our findings about the properties of post-consumer PET from soft drink and oil bottles without its original surface, which was removed by reaction in a concentrated solution of sodium hydroxide followed by rinsing. Because this is a superficial reaction, it presumably does not ensure that a polymer suitable for direct contact with food will be obtained, since any contaminants the polymer may contain inside it will not be removed. However, a much cleaner polymer than material washed only with water is expected, since the material's contact with impurities begins at the surface, where it is normal to find the highest concentrations of impurities [11]. Removal of the original surface and the impurities associated with it tends to improve the final properties of recyclates, allowing for a wider range of final applications.

MATERIALS AND METHODS

Obtaining the Samples

The samples, i.e., the post-consumer cooking oil and soft drink bottles, were supplied by the company Soma Plásticos (Sorocaba, SP, Brazil). They were ground into flakes and sifted through an 8 mm mesh sieve, after which they were washed only in water at room temperature for 3 min with stirring. The flakes were then allowed to dry naturally for 48 h, followed by 12 h at 50°C.

After drying, they were subjected to optimized reaction for 10 min at 90°C with an aqueous solution of sodium hydroxide, $5\,\mathrm{mol}\cdot\mathrm{L}^{-1}$ (2.94 g of PET in 25 mL of solution) [12]. After this reaction, hereafter called chemical washing, a filtration step separates the solid and liquid phases. The solid phase was then rinsed, also in an optimized condition, in two batches of 2 min with 50 mL of distilled water in each batch [13]. After drying again, the samples chemically washed and rinsed, as well as the samples only submitted to conventional washing (only with water), were characterized by thermogravimetry, differential scanning calorimetry, intrinsic viscosity, elemental analysis, gas chromatography coupled to mass spectrometry and scanning electron microscopy coupled to microanalysis by X-ray.

The sodium hydroxide wash was optimized based on tests of 24 different conditions: 2.94 g polymer in 25 mL of $5\,\mathrm{mol}\cdot\mathrm{L}^{-1}$, $7.5\,\mathrm{mol}\cdot\mathrm{L}^{-1}$ and $10\,\mathrm{mol}\cdot\mathrm{L}^{-1}$ solution reacted at 80°C and 90°C for 0 (time for the solution to reach the temperature), 10, 20 and 30 min. Surface mass loss was determined gravimetrically after filtration, rinsing with 250 ml of distilled water and drying. The lowest weight loss was 1.74% ($5\,\mathrm{mol}\cdot\mathrm{L}^{-1}$, 80°C and 0 min) and the highest was 14.2% ($10\,\mathrm{mol}\cdot\mathrm{L}^{-1}$, 90°C and 30 min) [12].

A removal of about 5% was established as sufficient for a new surface to appear, and this was achieved under nine conditions. After a visual comparison of the flakes, analysis of the histograms of the images of membrane filters, as well as turbidity and solids content of the filtrate, it was determined that the reaction with $5\,\mathrm{mol}\cdot\mathrm{L}^{1}$ solution for 10 min at 90°C was the best condition [12]. During the chemical wash, the polymer surface was removed by a saponification reaction, which caused its depolymerization, generating ethylene glycol (which remained in the liquid phase) and a salt of terephthalic acid soluble in water (i.e., in the rinse). The acid can subsequently be recovered in a high purity through acidification, precipitation, filtration and drying, as reported previously. Ethylene glycol can also be recovered from the liquid phase [10].

The 250 ml of water used for rinsing after the chemical wash optimization assays was assumed to be excessive, since this amount was established for chemical recycling systems with more than 90% of depolymerization [14]. Therefore, PET samples were subjected to the optimized reaction conditions and then rinsed in 5 beakers containing 50 mL of distilled water at room temperature for preestablished times (1, 2 and 4 min) by shaking. After going through each beaker, the solids were filtered and immediately placed in the next beaker. Aliquots of the filtered liquid were subjected to colorimetric titrimetry assays with phenolphthalein as indicator and a standard oxalic acid solution for the detection of sodium hydroxide. Thus, the use of 100 mL of water (in two batches of 50) for 2 min each was found to be the best rinsing method [13].

The surface removal and rinsing optimizations tests were carried out using PET from soft drink bottles ($\mathrm{PET}_{\mathrm{soft\ drink}}$). The repetition of the optimized conditions for samples of PET from cooking oil bottles ($\mathrm{PET}_{\mathrm{oil}}$) yielded similar results to those obtained with $\mathrm{PET}_{\mathrm{soft\ drink}}$ samples.

Characterization of the Samples

The viscosity test was performed with a viscometer (Ubbelohde type 1B) and was based on the determination of the relative viscosity, at 30°C, at a sole concentration (0.5%, i.e., 0.5 g of polymer per dL of a 60/40 phenol/tetrachloroethane solution), which was then related to the intrinsic viscosity by Billmeyer's equation [15].

The DSC tests were conducted in a TA Instruments MDSC 2920 differential scanning calorimeter at Materials Characterization and Development Center of Federal University of São Carlos (CCDM-UFSCar), after heating the sample and the reference at 10°C/min in an inert atmosphere (super dry nitrogen). The thermogravimetric analyses were carried out with a TA Instruments Hi-Res TGA 2950 thermogravimeter at CCDM-UFSCar, in which the samples were also heated at 10°C/min. The test was conducted in an argon atmosphere until total loss of the sample's mass or 400°C was reached.

The elemental analysis used equipment from Fisons Instruments EA 1108 CHNS-O, at Chemical Department of UFSCar. By means of redox reactions and gas chromatography, this technique indicates the percentage quantity of carbon, hydrogen, nitrogen, sulfur and oxygen (by difference) in the samples.

After coating the samples with gold, the scanning electron microscope (Philips XL30 FEG SEM) from the Department of Materials Engineering at UFSCar was used to obtain micrographs of the samples' surfaces. Microanalysis assays by energy dispersive spectroscopy (EDS) based on the reflected X-rays were also carried out.

The analyses by gas chromatography coupled to mass spectrometry were performed in a Shimadzu GC MS QP 5050A spectrometer and a Shimadzu HeadSpace AOC 5000 Autosampler at the São Paulo State Institute for Technological Research. The purpose of this procedure was to make a qualitative analysis of the organic compounds in the samples. The initial analysis, which aimed to identify the most volatile compounds, consisted of heating about 1 g of sample in a flask at 120°C for 20 min. The compounds volatilized under these conditions were injected into a chromatograph (injector temperature of 200°C) equipped with an HP-FFAP column ($50\,\mathrm{m} \times 0.2\,\mathrm{mm} \times 0.33\,\mu\mathrm{m}$) and the different compounds were separated and identified. The second analysis, which served to identify the less volatile compounds, involved the immersion of 1 g of sample in 4 mL of dichloromethane for 24 h at room temperature. The extract was concentrated by bubbling nitrogen for 6 h, after which 1 μL of this extract was injected into the chromatograph (injector temperature of 280°C) equipped with a CP-Sil 5CB-MS ($30\,\mathrm{m} \times 0.25\,\mathrm{mm} \times 0.25$) column, and the separate compounds were identified.

RESULTS AND DISCUSSION

Table 1 lists the results of intrinsic viscosity, differential scanning calorimetry, thermogravimetry and elemental analysis of the $\mathrm{PET_{oil}}$ and $\mathrm{PET_{soft\ drink}}$ flakes obtained after the optimized chemical washing and rinsing, as well as of the flakes subjected only to conventional washing.

Table 1 indicates that the viscosity of the flakes of cooking oil and soft drink bottles washed only with water (conventional washing) appears to be affected by the presence of impurities with higher or lower viscosity, respectively, than the polymeric solution. In contrast, the viscosity of chemically washed and rinsed flakes is very similar to the values reported for PET flakes produced from thoroughly cleaned 2-liter soft drink bottles (0.75 dL/g) and 900-mL cooking oil bottles (0.71 dL/g) [16]. The fact that the viscosity of the polymers subjected to the reaction with sodium hydroxide followed by rinsing was similar to that normally obtained for clean flakes suggests that the

Table 1: Intrinsic viscosity, differential scanning calorimetry (DSC), thermogravimetry (TGA) and elemental analysis of conventionally washed polymers and polymers subjected to optimized chemical washing and rinsing.

			DSC		TGA		
Sample	**Processes carried out**	**Intrinsic viscosity (dL/g)**	**Tg (°C)**	**Tm (°C)**	**Residue at 250°C (%)**	**Residue at 400°C (%)**	**Elemental analysis %C**
$PET_{soft\ drink}$	Conventional Washing	0.72	80.4	247.3	99.97	95.53	62.41
	Conventional Washing, Chemical Washing and Rinsing	0.77	80.5	245.3	99.97	95.58	62.60
PET_{oil}	Conventional Washing	0.79	75.7	248.1	98.03	88.71	60.46
	Conventional Washing, Chemical Washing and Rinsing	0.73	80.7	246.5	99.78	95.26	62.50

sodium hydroxide reaction occurred only superficially, leaving the internal portion of the particle intact [6–9].

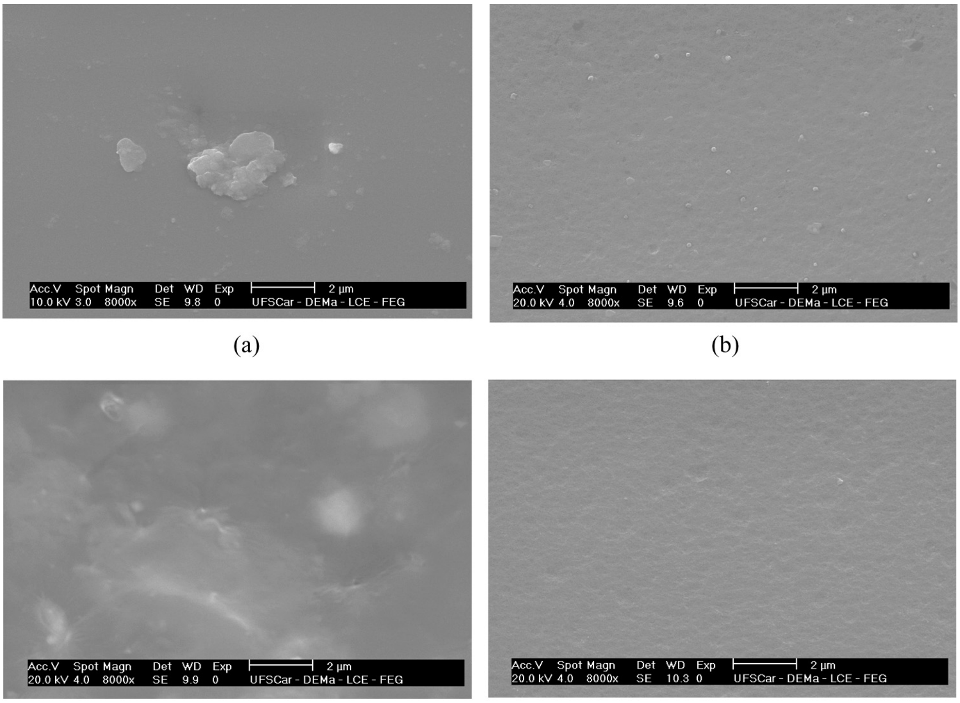
Table 1 also shows relatively similar Tm results for the four samples. However, the Tg results indicate that the material differing the most among the four tested ones is PET_{oil} washed only with water, which showed a Tg of 75.7°C, while the Tg of the other three exceeded 80°C, which is usually reported as the glass transition temperature of bottle-grade PET. The DSC curves followed the general shape of similar curves of other PET samples [17].

This table also shows that, consistent with the values of the glass transition temperature, the results of the thermogravimetric and elemental analysis also allow us to state that the most different material of the four is PET_{oil} washed only conventionally. The thermogravimetric curves for $PET_{soft\ drink}$ washed only with water and $PET_{soft\ drink}$ and PET_{oil} washed conventionally and chemically are very similar and also followed the general shape of similar curves of other PET samples [18]. They showed a thermal stability that can be considered good (practically without mass loss) up to 320°C, which is more than 70°C above the melt temperature reported in the DSC assay. This is an excellent indicator of the reprocessability of these materials, provided proper care is taken with the atmosphere in a new melt during recycling. In contrast, the thermogravimetric curve of PET_{oil} washed only with water is quite different, since it indicates mass loss starting at 120°C. Similarly, the carbon content determined by elemental analysis of PET_{oil} washed only conventionally is the most different of the materials and farthest from the theoretical, which is 62.5%.

In general, Table 1 indicates that the chemical wash appears to have brought both $PET_{soft\ drink}$ and PET_{oil} to the expected values. The removal of the original surface, which undoubtedly contains impurities that have physical and chemical properties that differ from those of the polymer, contributed to bring the values much closer to the expected ones. In other words, the removal of the surface cleaned the material, transferring the impurities together with a layer of polymer to the reagent solution.

Figure 1 shows SEM micrographs with 8,000X magnification of $PET_{soft\ drink}$ and PET_{oil} samples washed conventionally (a and c, respectively), and of $PET_{soft\ drink}$ and PET_{oil} washed conventionally and chemically, followed by rinsing (b and d, respectively). At 1,000X magnification, the images were quite similar in all the regions of the sample, which appeared to be composed of a background matrix and apparent incrustations. The image with 8,000X magnification was taken close to an incrustation. This image was subjected to at least two microanalyses of X-ray spectra: one of the matrix and the other of the incrustation.

Figure 1a reveals a smooth matrix with a few points in high relief, whose shape suggests depositions (incrustations), given their stacking appearance. Figure 1b shows smaller incrustations and a rougher matrix with a series of cavities. While the images in Figures 1d and 1b are very similar, there is a



(a) (b)

(c) (d)

Figure 1: SEM micrographs with 8,000X magnification of $PET_{soft\ drink}$ flakes after (a) only conventional washing and (b) after conventional and chemical washing and rinsing, (c) as well as PET_{oil} after conventional washing, and (d) after conventional and chemical washing and rinsing.

clear difference between the micrographs in 1a and 1c, the latter corresponding to PET_{oil} washed only in water. In fact, it was quite difficult to obtain relatively clear images of this sample, since it was not possible to clearly distinguish between the matrix and the incrustation visible in the other three photomicrographs. Apparently, a good part of the image presented in 1c (particularly from the center downward) is composed of stacked incrustations, which are observed more discretely in the $PET_{soft\ drink}$ in Figure 1a.

A comparison of the images suggests that chemical washing removed the depositions, attacking the original surface and revealing a new surface resulting from the removal of impurities as well as part of the polymer. The removal of polymer is evidenced by the presence of cavities resulting from the attack by sodium hydroxide on the previously smooth matrix. Ng et al. (2009) [9] and Collins and Zeroninan (1992) [19] reported the formation of cavities after attack by an alkaline solution on PET fibers.

Micrographs 1b and 1d suggest that the chemical attack eliminated the large incrustations, but tiny dots are visible, which are more numerous in $PET_{soft\ drink}$ than in PET_{oil}. If these dots can be considered small incrustations, the larger ones visible in 1a and 1c may not necessarily be composed only of impurities, but may also be regions of the polymeric matrix with a higher relief.

Table 2 presents the percentage results of the analysis of each X-ray spectrum obtained for the different regions of each of the materials analyzed by scanning electron microscopy, associating them with each image (Figure 1) where the microanalysis was made. According to molar mass calculations based on the structural formula of PET, which is used in the discussion of the elemental analysis results presented in Table 1, pure polymer should contain 62.5% of carbon, 4.17% of hydrogen and 33.33% of oxygen. Because energy dispersive spectroscopy (EDS) does not detect hydrogen, the percentages for pure PET change to 65.22% of carbon and 34.78% of oxygen. However, the discussion and analysis of the percentage results should take into account the fact that EDS applied to this work is considered a semi-quantitative analysis.

Corroborating the results of Table 1 and Figure 1, Table 2 also indicates that the most different sample of the four analyzed samples, in terms of both matrix and incrustation, is PET_{oil} washed only with water (sample III). This sample presented the only matrix with other elements (in this case, aluminum and silicon), in addition to the expected carbon and oxygen. Even for carbon and oxygen, the values are quite different from the percentages calculated for pure PET. In contrast, all the other matrices presented only carbon and oxygen and in percentages close to the expected ones (in sample IV,

Table 2: Percentage results of the analyses of each spectrum obtained for the different regions of each of the materials analyzed by SEM, as well as the region in the figure which was microanalyzed.

			Chemical element									
Sample	**Place**	**Figure**	**C**	**O**	**Al**	**Si**	**Fe**	**Ti**	**K**	**Ca**	**Na**	**Total**
I	Matrix	1a	64.33	35.67	–	–	–	–	–	–	–	100.00
	Incrustation	1a	52.78	42.73	1.81	1.75	0.92	–	–	–	–	100.00
II	Matrix	1b	66.06	33.94	–	–	–	–	–	–	–	100.00
	Incrustation	1b	65.51	34.49	–	–	–	–	–	–	–	100.00
III	Matrix	1c	70.58	28.92	0.28	0.22	–	–	–	–	–	100.00
	Incrustation	1c	54.87	39.34	0.77	0.78	3.72	0.16	0.06	0.14	0.16	100.00
IV	Matrix	1d	67.20	32.80	–	–	–	–	–	–	–	100.00
	Incrustaion	1d	65.90	33.65	–	–	–	–	–	–	0.45	100.00

Where:

I – $PET_{soft\ drink}$ flakes after only conventional washing;

II – $PET_{soft\ drink}$ flakes after conventional and chemical washing and rinsing;

III – PET_{oil} flakes after conventional washing;

IV – PET_{oil} flakes after conventional and chemical washing and rinsing.

conventionally and chemically washed PET_{oil}, these percentages diverge a little more from the expected ones).

The analysis of the composition of what we identified as incrustations indicates that they can be considered sites of concentrations of impurities, in the case of samples washed only in water (I and III). The most critical case was that of PET_{oil} washed only with water, in which seven other elements were detected besides carbon and oxygen. In the conventionally and chemically washed samples, whose carbon and oxygen percentages were very close to the expected values, the incrustations are probably high relief dots in the polymer matrix, as suggested by the analysis of Figure 1. The sodium found in sample IV (PET_{oil} washed in water and with alkali) may have been left behind by incomplete rinsing.

As can be seen in Table 2, chemical washing was efficient in cleaning the material, since samples II and IV showed much fewer superficial impurities than samples I and III, respectively. The results also seem to confirm the assumption proposed in the discussion about Figure 1, i.e., that the impurities appear to be deposited on the surface, and that chemical washing apparently removes them. For example, the chemical wash that generated sample II seems to have removed the aluminum, silicon and iron from sample I and aluminum, silicon, iron, titanium, potassium and calcium from III to obtain sample IV.

The identification of metals on the surface of PET particles is relatively problematic for recycling, since it suggests the presence of inorganics adhering to the surface even after washing in water, although they were removed by chemical washing. These inorganic compounds may originate from several sources, but they probably come from the polymerization catalysts, the packaged product, the label and other residues that were in contact with the polymer. In view of the results presented here, it can be stated that the cooking oil packaging has a greater tendency to aggregate impurities.

Figure 2a, b, c and d shows the chromatograms obtained by gas chromatography and the identification by mass spectrometry of the volatile compounds present in samples of, respectively, $PET_{soft\ drink}$ subjected only to conventional washing, $PET_{soft\ drink}$ subjected to conventional washing and to chemical washing and rinsing, PET_{oil} subjected only to conventional washing, and PET_{oil} subjected to conventional washing and to chemical washing and rinsing.

As can be seen in this figure, the chemical wash reduced the number of organic compounds (number of different peaks) in PET_{oil} (Figure 2d in relation to 2c), but not in $PET_{soft\ drink}$ (Figure 2b in relation to 2a). Although it cannot be stated unequivocally because quantitative assays were not performed, the concentration of each organic compound detected appears to have been reduced by chemical washing, since chromatogram “b” shows narrower and smaller peaks than those in “a”, and especially those of chromatogram “d” in relation to “c”. Again, note that PET_{oil} washed only conventionally is the sample that differed the most among the four under study.

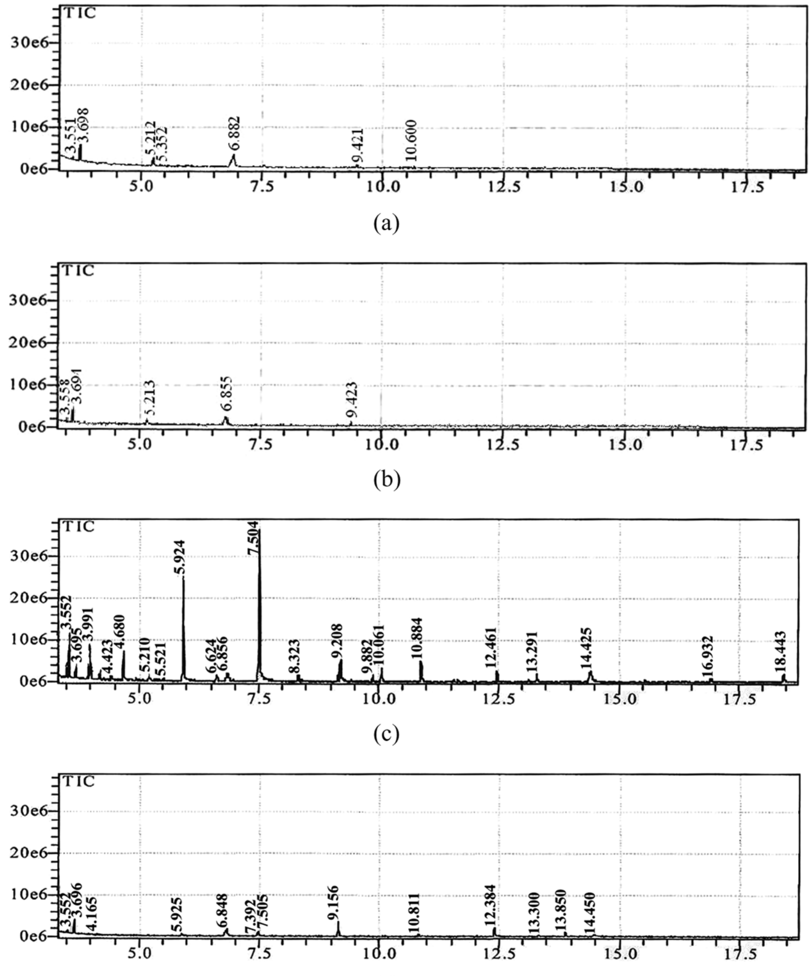


Figure 2: GC/MS chromatograms of the volatile compounds in (a) conventionally washed $PET_{soft\ drink}$, (b) conventionally washed and chemically washed and rinsed $PET_{soft\ drink}$, (c) conventionally washed PET_{oil}, and (d) conventionally washed and chemically washed and rinsed PET_{oil}.

Table 3 describes the locations of the peaks and their respective identification for the chromatograms of Figure 2. The results listed in this table follow the same nomenclature as that used in Table 2.

As can be seen in Table 3 and Figure 2, the starting raw material may be even more important that the washing method employed. This finding reinforces the importance of the efficient separation of wastes at the waste producer source, and of the subsequent selective collection, since the composition of the samples of PET_{oil} washed only in water presented 30 volatile compounds compared to 5 in the PET from soft drink bottles.

Table 3: Compounds identified in the chromatograms of the samples under study and the samples in which each peak was recorded.

Retention time (min)	Compound	Sample			
		I	II	III	IV
3.20	Hexane			x	
3.40	Heptane			x	
3.50	Acetaldehyde	x	x	x	x
3.60	Carbon Difulfide	x	x	x	x
3.94	Octane			x	
3.99	Propionaldehyde			x	
4.10	Acetone			x	x
4.40	Acrolein			x	
4.60	Butyraldehyde			x	
4.90	Methyl Ethyl Ketone			x	
5.21	Ethanol	x	x	x	x
5.25	2-Nonene			x	
5.50	Ethyl Furane			x	
5.90	Pentanal			x	x
6.60	n-Propanol + non identified compound			x	x
6.80	Water + Toluene	x	x	x	x
7.50	Hexanal			x	x
8.30	Butanol			x	
9.10	2-Heptanone			x	x
9.20	Heptanal			x	
9.40	Limonene	x	x		
9.80	2-pentyl-furane			x	
10.00	Pentanol			x	
1080	Octanal			x	x
12.30	2-Nonanone				x
1240	Nonanal			x	
13.20	Acetic Acid			x	x
13.80	2-decanone				x
14.30	Formic Acid			x	x
14.40	Propanoic Acid			x	
15.50	Butanoic Acid			x	
16.90	Pentanoic Acid			x	
18.40	Hexanoic Acid			x	

Where:

I – $\text{PET}_{\text{soft drink}}$ flakes after only conventional washing;

II – $\text{PET}_{\text{soft drink}}$ flakes after conventional and chemical washing and rinsing;

III – PET_{oil} flakes after conventional washing;

IV – PET_{oil} flakes after conventional and chemical washing and rinsing.

Four of the five compounds identified in $\text{PET}_{\text{soft drink}}$ (carbon disulfide, acetaldehyde, ethanol and toluene) appeared in all the samples – including those of oil – and were expected in very small concentrations in the composition of post-consumer PET. This is because acetaldehyde is a characteristic product of the degradation of PET, while the other three compounds identified probably resulted from migration to the polymer of fuels improperly stored in PET bottles after their original use [20]. The organic compound identified only in the $PET_{soft\ drink}$ samples is limonene, which may be attributed to the essences used in soft drink formulations [21].

Nineteen of the 30 compounds identified in the cooking oil sample before chemical washing (sample III) appear to have been removed, since only 11 remained after the chemical wash (sample IV). However, 2 "new" compounds were identified in sample IV (2-nonanone and 2-decanone), which may have been products of the eventual degradation, that occurred during chemical washing and/or drying, of some of the compounds detected in sample III.

The compounds identified both in the samples washed only in water and in those washed conventionally and chemically, indicate that chemical washing, which is considered sufficient to remove metals (Figure 1 and Table 2), was not as efficient for organic compounds. These compounds were probably on the surface and inside the post-consumer polymer and were not removed by chemical washing, which, as mentioned earlier, is restricted to the surface of the material. It is therefore necessary to quantify the remaining compounds and to devise other methods for their removal if the recyclate is to be used for direct contact with food.

Table 4 describes the locations of the peaks and their respective identification in the chromatograms of the concentrated extract of the four samples, aiming at a qualitative characterization of the less volatile compounds they contain. These chromatograms do not show significant differences in the height and width of the peaks of the samples subjected to chemical washing in relation to those washed only with water, so they are not presented here. Twelve different compounds were identified, 5 of which (2-heptanone, 2-nonanone, 2-decanone, octanal and decanal) were also identified as volatile (Table 3).

As can be seen in Table 4, sample II ($PET_{soft\ drink}$ after chemical washing) did not present any compound considered less volatile extracted with dichloromethane. The sample prior to chemical washing (I) presented only one compound, dibutyl phthalate, probably from packaging or impregnation of ink, insecticide or solvent. The PET_{oil} sample prior to chemical washing (III) presented seven organic compounds (aldehydes and carboxylic acids), none of which was identified in the sample subjected to chemical washing (IV). In contrast, sample IV presented seven other elements, of which all the identified ones (4) were ketones. All these "new" compounds were probably products of degradation of some of the compounds detected in PET_{oil} flakes only conventionally washed (sample III).

An important conclusion may be drawn by analyzing the results in Table 3 from the standpoint of the assay procedure for obtaining the more volatile compounds. These compounds (which numbered 30 in the case of PET_{oil} prior to chemical washing) can leach out of the polymer during recycling, if not entirely then at least a good part of them, since this occurred at a furnace time of 20 min at 120°C. These conditions are usually milder than those to which

Table 4: Compounds identified in the chromatograms of the concentrated extracts of the samples under study and of the samples in which each peak was recorded.

		Sample			
Retention time (minutes)	**Compound**	**I**	**II**	**III**	**IV**
2.75	Diacetone alcohol				x
3.15	2-Heptanone				x
3.98	Hexanoic Acid			x	
4.16; 5.54 and 6.65	Non-identified compounds				x
4.30	Octanal			x	
5.12	Heptanoic Acid			x	
5.38	2-Nonanone				x
5.55	Nonanal			x	
6.39	Octanoic Acid			x	
6.71	2-Decanone				x
7.70	Nonanoic Acid			x	
15.45	Dibutylphthalate	x			
15.59	Hexadecanoic Acid			x	

Where:

I – $\mathrm{PET}_{\mathrm{soft\ drink}}$ flakes after only conventional washing;

II – $\mathrm{PET}_{\mathrm{soft\ drink}}$ flakes after conventional and chemical washing and rinsing;

III – $\mathrm{PET}_{\mathrm{oil}}$ flakes after conventional washing;

IV – $\mathrm{PET}_{\mathrm{oil}}$ flakes after conventional and chemical washing and rinsing.

PET is subjected prior to reprocessing by mechanical recycling. Due to the polymer's high susceptibility to hydrolysis, it is common for PET drying systems to apply 150°C for up to 8 h of drying in atmospheres of dry air, nitrogen or even vacuum.

The sample used in the gas chromatography assay was in the form of ground and washed flakes (washed conventionally and/or chemically), which were subsequently allowed to dry naturally for 48 h and then at 50°C for another 12 h. The material normally sent to reprocessing units is PET washed only with water and subjected to simple drying (usually in a centrifuge).

This paper suggests sending to the reprocessing unit conventionally washed PET, subjected to simple drying and subsequently to chemical washing, followed by rinsing and another simple drying. Independently of the processes to which the material is subjected at the reprocessing unit, the flakes should be subjected to extensive drying (for example 150°C, 8 h in dry air) prior to those processes. This drying can remove the major part of the contaminants, mainly the more volatile ones.

However, drying PET prior to reprocessing would probably not remove the less volatile compounds (or would only remove them partially) and, in this case, samples originating from soft drink bottles contain fewer contaminants. The only organic compound that was identified in the samples from soft drink bottles was probably restricted to the surface and appeared to have been removed by the chemical wash. A similar case occurred in these samples with respect to metals (and/or their oxides, Table 2): the existing ones were apparently removed by chemical washing.

Thus, although chemical washing yielded a polymer with fewer impurities, especially volatiles, it cannot be considered sufficient to ensure the complete purification of the sample, even with extensive subsequent drying. However, the preference for using post-consumer soft drink bottles rather than cooking oil bottles is important, since the former yield less impure polymer, even when simply washed only in water.

It should be emphasized that if the recyclate is intended for direct contact with foods, it would be necessary to quantify all the impurities present before and after the proposed procedures (conventional washing, chemical washing and drying). It is also a common practice to deliberately incorporate compounds that are volatile or not, polar or not, to test the efficiency of methods aimed at supplying recycled PET authorized for use in direct contact with foods. If these compounds are present in concentrations exceeding the allowed levels, they must be removed by other methods. Longer washing times, both conventional and chemical, can also be tested.

CONCLUSIONS

The results indicate that control of the raw material, by means of efficient separation at the waste producer source and subsequent selective waste collection, may be as important as the method employed to improve the properties of the final recyclate. The characterization performed in this study indicated that even washed in water, post-consumer $\mathrm{PET}_{\mathrm{soft\ drink}}$ and $\mathrm{PET}_{\mathrm{oil}}$ are materials with impurities, but that $\mathrm{PET}_{\mathrm{oil}}$ contains more impurities, both organic (30 different volatile compounds compared to 5 in $\mathrm{PET}_{\mathrm{soft\ drink}}$) and in the form of metals (7 different metals compared to 1 in $\mathrm{PET}_{\mathrm{soft\ drink}}$).

The chemical wash effectively improved the material as a whole, notably its surface, by revealing a new and much cleaner surface than the original one washed only with water. The results of intrinsic viscosity indicated that the reaction was superficial, leaving the inside of the particles intact. Thus, it can be concluded that the use of chemical washing tends to improve the quality of the final recyclate and its possible applications.

The results of DSC, thermogravimetry and elemental analysis confirmed the X-ray and chromatography results, i.e., $\mathrm{PET}_{\mathrm{oil}}$ washed only in water is the material that differs the most among the four tested materials, and the other three (chemically washed $\mathrm{PET}_{\mathrm{oil}}$, conventionally washed $\mathrm{PET}_{\mathrm{soft\ drink}}$, and chemically washed $PET_{soft\ drink}$) are more similar to each other and close to what is expected for pure PET.

However, because the chemical wash is a superficial reaction, it is expected that impurities located inside the polymer are not removed by the process. This was evident particularly from the results of the GC/MS of volatile elements. Therefore, chemical washing cannot be considered sufficient to obtain resins for direct contact with food.

REFERENCES

[1] ABIPET – Associação Brasileira da Indústria de PET (Brazilian PET Industry Association) 2008. http://www.abipet.org.br [accessed 30.08.09].

[2] Ehrig, R. J. (1992). *Plastics Recycling: Products and Processes*, Hanser Publishers, New York.

[3] La Mantia, F. P. (2002). *Handbook of Plastics Recycling*, Rapra Technology, Shawbury.

[4] CEMPRE – Compromisso Empresarial para a Reciclagem (Business Commitment to Recycling). Technical Files 2008. http://www.cempre.org.br. [accessed 30.08.09].

[5] Mancini, S. D., Nogueira, A. R., Kagohara, D. A., Schwartzman, J. A. S., and Mattos, T. *Waste Manag. Res.* **25**, 517 (2007).

[6] Kumar, S., and Guria, C. J. *Macromol. Sci, Pure Appl. Chem.* **42**, 237 (2005).

[7] Ruvolo Filho, A. C., and Curti, P. S. *Ind. Eng. Chem. Res.* **45**, 7895 (2006).

[8] López-Fonseca, R., González-Velasco, J. R., and Gutiérrez-Ortiz, J. I. *Chem. Eng. J.* **146**, 287 (2009).

[9] Ng, R., Zhang, X., Liu, N., and Yang, S. T. *Process. Biochem.* **44**, 992 (2009).

[10] Mancini, S. D., Schwartzman, J. A. S., Nogueira, A. R., Kagohara, D. A., and Zanin, M. *J. Clean. Prod.* **18**, 92 (2010).

[11] Durham, K. (1961). *Surface Activity and Detergency*, Macmillan, London.

[12] Nogueira, A. R., Mancini, S. D., Martins, A. C. G., Kagohara, D. A., Schwartzman, J. A. S., and Franco, C. S. (2007). In *Proceedings of the 9° Congresso Brasileiro de Polímeros*, Campina Grande, Brazil.

[13] Kagohara, D. A., Mancini, S. D., Nogueira, A. R., Schwartzman, J. A. S., Darbello, S. M., and Keiroglo, R. C. (2007). In *Proceedings of the XIX Congresso de Iniciação Científica da UNESP*, Presidente Prudente, Brazil.

[14] Mancini, S. D. (2001). Ph.D. thesis, Federal University of São Carlos, Brazil.

[15] ASTM – American Society for Testing and Materials, D4603 – Standard test method for determining inherent viscosity of poly(ethylene terephthalate) (PET) by glass capillary viscometer, (2003) 1–3.

[16] Matos, I. G., Mancini, S. D., and Almeida, R. F. *Polim: Ciência e Tecnol.* **14**, 69 (2004).

[17] Torres, N., Robin, J. J., and Boutevin, B. *Eur. Polym. J.* **36**, 2075 (2000).

[18] Nascimento, C. R., and Dias, M. L. *J. Therm. Anal. Calorim.* **69**, 551 (2002).

[19] Collins, M. J., and Zeronian, S. H. *J. Appl. Polym. Sci.* **45**, 797 (1992).

[20] Pierce, D. E., King, D. B., and Sadler, G. D. (1995). In C. P. Rader, S. L. Baldwin, G. D. Sadler, and R. F. Stockel, Eds., American Chemical Sociey, Washington, pp. 458–471.

[21] Santos, A. S. F., Baraldi, P. T., Agnelli, J. A. M., Correa, A. G., and Manrich, S. (2004). In *Proceedings of 3rd International Symposium on Food Packaging*, Barcelona, Spain.