Analysing Metals in Bottle-Grade Poly(ethylene terephthalate) by X-ray Fluorescence Spectrometry

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ABSTRACT: After a rigorous cleaning process, recycled food-grade poly(ethylene terephthalate) (PET), can be mixed with virgin PET resin in different concentrations and used for packaging of soft drinks. Therefore, it is important to have an experimental method to distinguish the presence of recycled polymer in a batch and to check its "true quality." One of the issues to be verified is the presence of inorganic contaminants due to the recycling process. X-ray fluorescence technique is one alternative for this kind of analysis. The results obtained in this work show that bottle-grade PET samples (PET-btg) are made either via direct esterification or by a transesterification process. Samples that were subjected to thermo-mechanical processings (superclean® processing, PET-btg blends processed in our laboratory and soft drink PET packaging) present Fe Kα emission lines with higher intensities than those presented by virgin bottle-grade PET. After applying principal component analysis, it can be concluded that Fe is an intrinsic contaminant after the recycling process, furnishing a way to indicate class separations of PET-btg. A calibration and validation partial least squares model was constructed to predict the weight percent of post-consumption bottle-grade PET in commercial PET samples. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2993–3000, 2010

Key words: fluorescence; polyesters; processing; recycling; classification

INTRODUCTION

Soft drinks are commercial beverages whose industrial production was initiated in 1830. They are constituted mainly of water, carbon dioxide, and syrup, characterizing the beverage flavor. The use of poly(ethylene terephthalate) (PET), to replace glass bottles as containers has increased the consumption of soft drinks. In Brazil, PET production for soft drink containers correspond to 71 wt % of overall PET market.[1,2] Soft drinks are classified as food and their packaging inspection is an important procedure to maintain and verify the quality control of products intended for final consumers.

PET is made either via a direct esterification process (EP) from terephthalic acid (TPA) and ethylene glycol (EG) or by a transesterification process (TP) involving the dimethyl ester of TPA and EG. After this step, PET is subjected to a polycondensation process.[3,4] In EP, catalysts are not used, because the acid functional groups of TPA can catalyze the reaction.[4–10] TP is commonly catalyzed by manganese or zinc acetate, whereas the polycondensation process is catalyzed by an antimony-oxide-based compound.[3] Many researchers have studied the effects of other catalysts for the TP and polycondensation processes. In the polycondensation process, the activity of the catalysts increases in the order Ti > Sn > Sb > Mn > Pb.[11] Among them, Sb oxide historically emerged as the catalyst of choice, because it demonstrates a good balance of catalytic activity in the presence of the phosphorus-based stabilizer, color, and cost.[3] However, the use of this catalyst in plastics for packaging applications was demonstrated to be a potential hazard to health, as Sb is considered a toxic trace element with no known physiological function.[4,12] In some PET final products such as food packaging or soft drink bottles, the release of Sb compounds is observed, therefore having a potential impact on public health.[13]

Recently, our research group has developed methodologies to detect and to quantify the presence of the bottle-grade post-consumption PET (PET_{pc}-btg) in bottle-grade virgin PET (PET_v-btg), preventing frauds and illegal uses of recycled PET_{pc}-btg in the Brazilian food packaging industry, thus assuring the quality of the final product. However, the techniques developed monitor only the organic part of PET such as oligomer relative concentration changes using MALDI-MS (matrix-assisted laser desorption ionization mass spectrometry) measurements.[14,15]

Beginning in 2010, Brazilian recycling companies will use new technologies, like superclean® or bottle-to-bottle®, to manufacture soft drink bottles.[16] The main change is the addition of new steps to the recycling process like: an efficient sorting process, a hot water-washing of the ground bottles, and a further deep-cleaning of the flakes with high temperatures and vacuum. Additionally, the well-known post-condensation process is also performed.[17,18] The superclean® process is conventionally performed using a single-screw extruder, where PET-btg is subjected to shearing and inorganic contaminants can be extracted from the metallic components of the equipment (screw and barrel).

X-ray fluorescence (XRF) is a suitable technique for characterization of the presence of metals.[1] This technique has advantageous features like multielemental capability, good detectivity, high precision, short analysis times, and nondestructive, which makes it suitable to be extended to a great variety of samples, thus presenting an analytical methodology for metal determination in food packaging.[1,19–21] XRF allied to chemometrics has been applied to the study of complex samples.[1,20–22] In this article, PET_v-btg supplied by different producers, PET_{pc}-btg, and PET_{pc}-btg processed by the superclean® method were analyzed by XRF and principal component analysis (PCA) to detect catalyst residues and possible contaminants present in PET-btg samples. PET_v-btg I/PET_{pc}-btg blends were also prepared in our laboratory, where XRF measurements with partial least squares (PLS) were used to quantify the presence of PET_{pc}-btg in PET-btg blends.

THEORY

In PCA,[23–25] the data set (matrix X) composed by samples (rows) and variables (columns) is decomposed in two new sets, named scores and loadings. Scores and loadings have information about samples and variables, respectively, and analyzing both informations together, the matrix X is visualized in a smaller dimension (named principal components). The purpose of PCA is data reduction, facilitating an exploratory analysis.

In PLS,[26] two matrixes are needed: X (in this case, background signals) and Y (the total concentration of concomitants). These matrices are decomposed in scores and loadings according to the equations:

$$X = TP^T + E$$

where, T and P are the matrixes with the scores and loadings, respectively, for the matrix X. And

$$Y = UQ^T + E$$

where, U and Q are the matrices with the scores and loadings, respectively, for the matrix Y.

In PLS, the scores from both matrixes are combined in order to calculate regression coefficients (b):

$$U = b \times T$$

These coefficients are used to calculate the total concentration of the concomitants and a better precision can be obtained. In contrast to this, using signal area or signal height only one coefficient is calculated.[25]

As a validation method of PLS, cross validation (CV) is an internal validation method which seeks to validate the calibration model without independent test data and thus does not obtain data only for testing. In full cross validation, one repeats the calibration "I" times, each time treating one I-th of the whole calibration set as prediction objects. In the end, all the calibration objects have been treated as prediction objects. Finally, the predicted values are compared to the actual ones, calculating the mean-square error of cross validation (MSECV) and/or the root–mean-square error of cross validation (RMSECV), which measures the predictive power of the model.[27]

EXPERIMENTAL

Bottle-grade virgin PET samples, PET_v-btg, with intrinsic viscosity ([η]) of about 0.80 dL g^{-1} were supplied by three different Brazilian producers and are designed as PET_v-btg I, II, and III. Samples processed by the superclean® process (PET-recycled) were supplied by Bahia PET Reciclagem (Salvador, BA Brazil). The first sample (PET-recycled I) was colorless and was subjected to a single superclean® process. The second sample (PET-recycled II) was green and was subjected twice to the superclean® process. According to the producers, PET-recycled I and PET-recycled II show [η] of 0.81 and 0.82 dL g^{-1}, respectively. PET_{pc}-btg was obtained from commercial 2 L soft drink bottles. It was washed, dried,

and milled in a three knife rotary mill (Rone®, NFA 1533) and its measured [η] was 0.76 dL g^{-1}.[15]

Formulation of PET$_v$-btg I/PET$_{pc}$-btg blends

The materials were dried for 6 h in a Cole Parmer vacuum oven (27 kPa) at 160°C before mixing. The PET$_v$-btg I/PET$_{pc}$-btg mixtures were prepared in an internal mixer with counter-rotating twin-rotors (Haake Rheomix® 600) at 250°C, 50 rpm for 5 min. The volume of the mixing chamber is 50 cm^3. The rotors are coupled to a Haake Rheocord 90 torque rheometer and the changes of torque and temperature are recorded as a function of mixing time. The mixtures were processed in different proportions: 0, 25, 50, 75, and 100 wt % of PET$_{pc}$-btg. The total amount of processed material was always 50 g. After removal from the mixer and cooling to room temperature, the mixtures were milled in a three knife rotary mill.[15]

Before performing the XRS measurements, all samples were dried and milled in a three knife rotary mill (Rone®, NFA 1533) obtaining an average grain size of about 2 mm.

Characterization

The ED-XRF experiments were performed using a bench top X-ray fluorescence equipment, Shimadzu EDX 700 (Kyoto, Japan). This equipment is provided with a rhodium X-ray tube that can be operated at a maximum voltage of 50 kV. The measurements were performed in air, with a beam collimation of 3 mm, 25% of detector dead time, and the current was automatically adjusted during spectrum acquisition. The Shimadzu EDX 700 has also the following characterics: (1) X-ray generator, tube voltage from 5 to 50 kV, tube current from 1 to 100 μA, and exposure area from 1 to 10 mm diameter, and (2) detector, Si(Li), detection area of 10 mm^2, and resolution of <155 eV.

For spectral acquisition, ~ 4 g of sample were placed into Teflon cells and then covered with a Mylar^{TM} film (3 μm thickness). The measurement time was 500 s. In all cases, the spectra were recorded from 0 to 40 keV, with a resolution of 0.02 keV, resulting in 2048 points for each spectrum. All samples were prepared and irradiated in triplicate.

Chemometric analysis

To proceed with the chemometric analysis, X matrices of independent variables were constructed in such a way that the columns refer to the spectrum energies whereas the lines correspond to each sample. The spectral data were mean centered and treated by chemometrics though PCA analysis. The entire spectrum was used for PCA analysis (0–40 keV), resulting in 2048 points (variables). The PCA analysis was also performed only in the region corresponding to catalyst and impurities (0–10 keV). Table I summarizes data from all samples analyzed.

Calibration and validation method

In PLS model, X and Y matrixes are constructed. The X matrix is the same used in PCA analysis. The Y matrix is constructed with K columns with chemical or physical information (in this case, PET$_{pc}$-btg concentration in PET-btg blends) and n rows corresponding to samples.[28] PLS was used to correlate spectral information with PET$_{pc}$-btg concentration in the PET-btg blends. The best number of latent variable (LV) was determined by the minimum value of the predictive residual sum of squares (PRESS).

For the construction of the validation and calibration data set or cross validation, 21 samples were used. The matrix of samples consisted of processed blends and dilution (solid/solid mixture of blends) in another 16 proportions. The concentrations were: 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, and 100 wt % of PET$_{pc}$-btg. The samples chosen to calculate PET$_{pc}$-btg predicted values (external validation) are manufactured samples, Table I. For data treatment of PCA and PLS, the software The Unscrambler, version 9.2, from Camo® was used.

RESULTS AND DISCUSSION

Figure 1 shows an example of ED-XRF spectrum of a PET$_v$-btg I sample. The spectrum shows the presence of Kα characteristic lines for S (2.28 keV), Cl (2.62 keV), Mn (5.82 keV), Fe (6.32 keV), Cu (7.94 keV), and Sb (26.28 keV). The region of high intensity lines is related to the Compton [Kα (19.20 keV) and Kβ (21.56 keV) lines] and Rayleigh [Kα (20.16 keV) and Kβ (22.74 keV) lines] effects. The Compton (incoherent scatter) and Rayleigh (coherent scatter) effects contribute significantly to quantitative organic ED-XRF analysis. The scattering region from the X-ray spectrum is mainly associated with light elements (C, H, O, among others) from the matrix, and the characteristic lines for these elements are not visualized on ED-XRF spectra; however, this region can present powerful properties for qualitative or even quantitative determination of light elements when treated with chemometrics.[21,29,30]

Among the elements found in the X-ray spectra, Mn and Sb are classified as catalysts. Probably, the PET$_v$-btg I sample was produced from TP, as discussed previously.[3] Others metals and counters-ions (Fe, Cu, S, and Cl) are impurities originating from

TABLE I
PET Samples Analyzed for ED-XRF Plus PCA

Symbols	Description	Classes	$[\eta]$ dL g^{-1}	Mn (μg g^{-1})	Fe (μg g^{-1})
Manufactured samples					
■	Bottle-grade virgin PET resins	PET$_v$-btg I	0.800 ± 0.003	74 ± 2	17 ± 2
●		PET$_v$-btg II	0.790[a] ± 0.010	–	–
▲		PET$_v$-btg III	0.800[a] ± 0.010	–	–
▼	Milled soft drink PET bottles	PET$_{pc}$-btg	0.763 ± 0.016	–	29 ± 2
◄	Recycled soft drink PET bottles	PET-recycled I	0.810[a] ± 0.010	–	38 ± 2
►		PET-recycled II	0.820[a] ± 0.010	–	35 ± 2
PET$_v$-btg I/PET$_{pc}$-btg blends					
□	Mixture of bottle-grade	100/0 wt %	0.658 ± 0.010	71 ± 2	19 ± 2
○	virgin PET resins with	75/25 wt %	0.647 ± 0.001	54 ± 6	33 ± 3
△	milled soft drink PET bottles	50/50 wt %	0.639 ± 0.001	38 ± 1	32 ± 1
◁		25/75 wt %	0.612 ± 0.006	29 ± 2	38 ± 2
▽		0/100 wt %	0.598 ± 0.003	–	52 ± 2

[a] Values supplied by the manufacturers.

monomer synthesis or from the reactors used in the manufacture of PET-btg.

The ED-XRF spectra obtained for PET$_v$-btg I, PET$_v$-btg I/PET$_{pc}$-btg blends in different proportions (0, 25, 50, 75, and 100 wt % of PET$_{pc}$-btg) and PET$_{pc}$-btg is shown in Figure 2. The spectra are vertically shifted for easier comparison, nevertheless, they were remained in the same scale. Different from PET$_v$-btg I, the PET$_{pc}$-btg sample was produced using only Sb as catalyst; hence, its industrial production was performed using EP.[4–10] When comparing the ED-XRF spectra of PET$_v$-btg I/PET$_{pc}$-btg blends, it can be observed that Mn Kα lines decrease as the wt % PET$_{pc}$-btg increases in the blends. Another important observation is the increase of Fe Kα lines as a function of wt % PET$_{pc}$-btg in the blends after thermo-mechanical processing. Two hypotheses can be inferred for this kind of contamination: Fe is a contaminant appearing during the

cleaning process (steel and abrasion with mineral brushes) that was performed between each processing of blends or it originated via a migration process from the counter-rotating twin-rotor mixer to the polymeric blend matrix.

An explanation for the Fe contamination in blends is better discussed when a magnification is shown in the 5–7 keV regions of the ED-XRF spectra, Figure 3, corresponding to Mn and Fe Kα lines. This Figure shows ED-XRF spectra of samples of manufactured PET$_v$-btg (PET$_v$-btg I, II, and III), samples processed by the superclean® process (PET-recycled I and II), PET$_{pc}$-btg and processed PET$_{pc}$-btg (0/100 wt %) mixed in our laboratory. All samples that were subjected to thermo-mechanical processing (PET$_{pc}$-btg, PET-recycled I, PET-recycled II, and processed PET$_{pc}$-btg (0/100 wt %)) present Fe Kα lines stronger
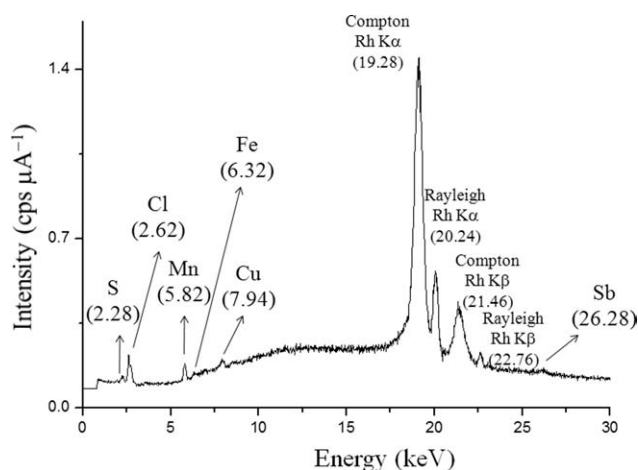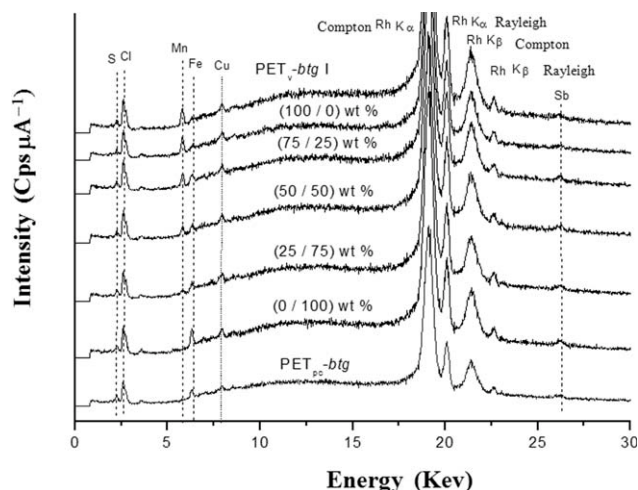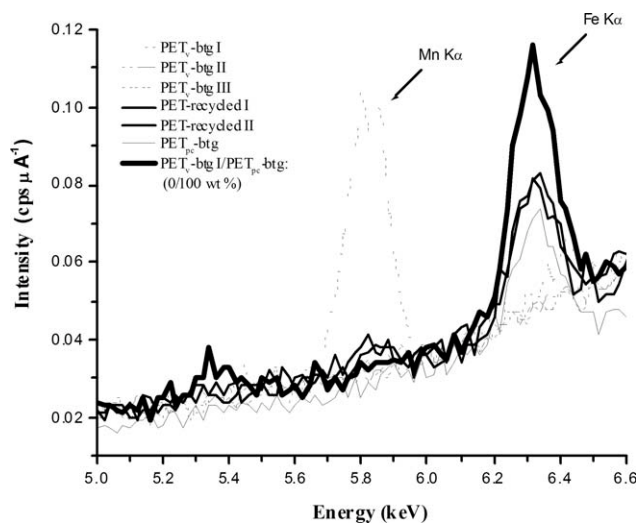

Figure 1 ED-XRF spectrum of PET$_v$-btg I.

Figure 2 ED-XRF spectra for PET$_v$-btg I, PET$_v$-btg I/PET$_{pc}$-btg blends in different proportions (0, 25, 50, 75, and 100 wt % of PET$_{pc}$-btg) and PET$_{pc}$-btg samples.

Figure 3 An expanded view of the ED-XRF spectra in the 5–7 keV region, for manufactured samples and processed PET$_v$-btg /PET$_{pc}$-btg blend (0/100 wt %).

than manufactured PET$_v$-btg (PET$_v$-btg I, II, and III). Therefore, Fe is an intrinsic contaminant in the PET recycling process. The values are shown in Table I, and range from 19 to 52 ± 2 μg g^{-1}, corresponding to processed PET$_v$-btg I (100/0 wt %) and processed PET$_{pc}$-btg samples (0/100 wt %), respectively. Intermediary values were obtained for blends (75/25, 50/50, and 25/75 wt %, respectively), PET-recycled I, PET-recycled II, and PET$_{pc}$-btg. In all cases, a significant increase is observed. Thus, more attention should be taken in Brazilian and other countries legislation due to the real possibility of inorganic impurities being present in the PET matrix after recycling; as in the future, this polymeric material will be used by the food packaging industry to produce soft drink bottles.

For quantitative analysis of Fe and Mn elements, the fundamental parameter method (FP method) has been used. Because the sample composition is known, the results allow theoretical calculation of the intensities of generated fluorescent X-rays using the measuring conditions and physical constants from FP. The FP method utilizes these characteristics in a reverse manner, that is, it tries to obtain the composition from the actually measured intensities.[31–34]

ED-XRF data were subjected to chemometric treatment via PCA. PCA was used to statistically evaluate the performance of ED-XRF spectra in classifying PET-btg for quality control purposes. Figure 4(a,b) shows the PC1 × PC2 scores and loadings plots.

In PC1 × PC2 scores plot, Figure 4(a), a separation into two groups is observed for manufactured samples according to the PC2 region. In first group, PET$_v$-btg I is separated due to presence of Mn catalyst (PC2 > 0), where this variable has a significant

influence for PC2 loading, as shown in Figure 4(b). Another group is PET$_v$-btg II, PET$_v$-btg III, PET-recycled I, PET-recycled II, and PET$_{pc}$-btg (PC2 < 0). All samples use only Sb as catalyst; therefore, we can also say that the recycled PET samples such as PET-recycled I and PET-recycled II samples originated from PET$_v$-btg II or PET$_v$-btg III.

Now analyzing the PC1 region, three classes groupings are observed as a function of [η] changes: 0.80 dL g^{-1} (manufactured samples), 0.76 dL g^{-1} (PET$_{pc}$-btg) and <0.65 dL g^{-1} (blends), Figure 4(a).

Figure 4(b) shows PC1 × PC2 loading plot. For PC1 loadings, most information is located in the Rh scattering region (17–20 keV), ≈ 91%, is responsible for indicating some chemical change in the PET structure, that is, the weight-average molar mass, M_w. For PC2 loadings, the information is concentrated both in
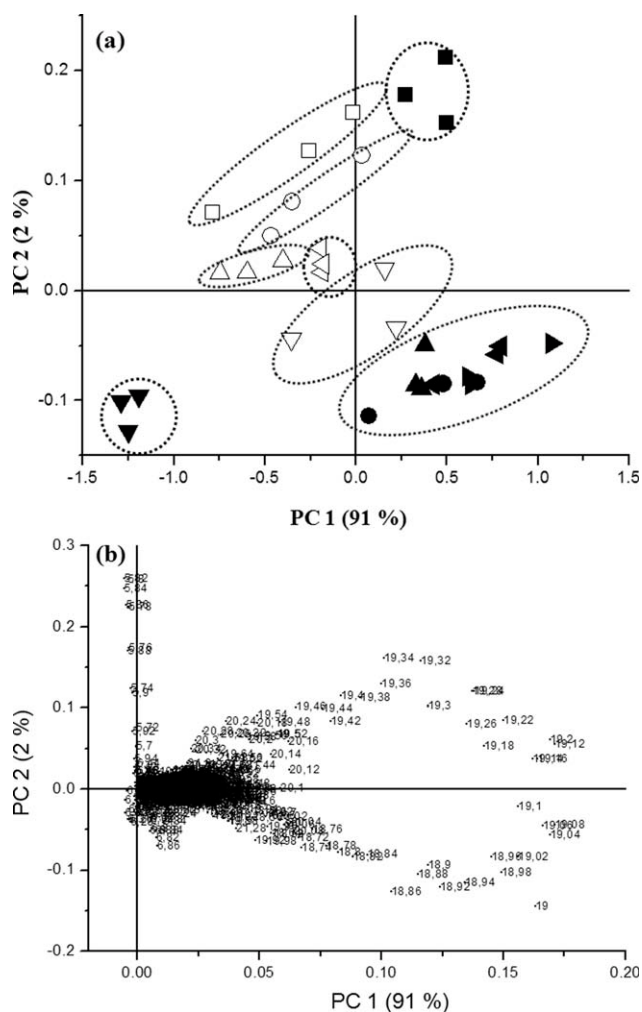
Figure 4 PC1 × PC2 scores (a) and (b) loadings plots for all ED-XRF data (manufactured samples: (■) PET$_v$-btg I, (●) PET$_v$-btg II, (▲) PET$_v$-btg III, (▼) PET$_{pc}$-btg, (◄) PET-clean I, and (►) PET-clean II; and PET$_v$-btg I/PET$_{pc}$-btg blends: (□) 100/0 wt %, (○) 75/25 wt %, (△) 50/50 wt %, (◁) 25/75 wt %, and (▽) 0/100 wt %).
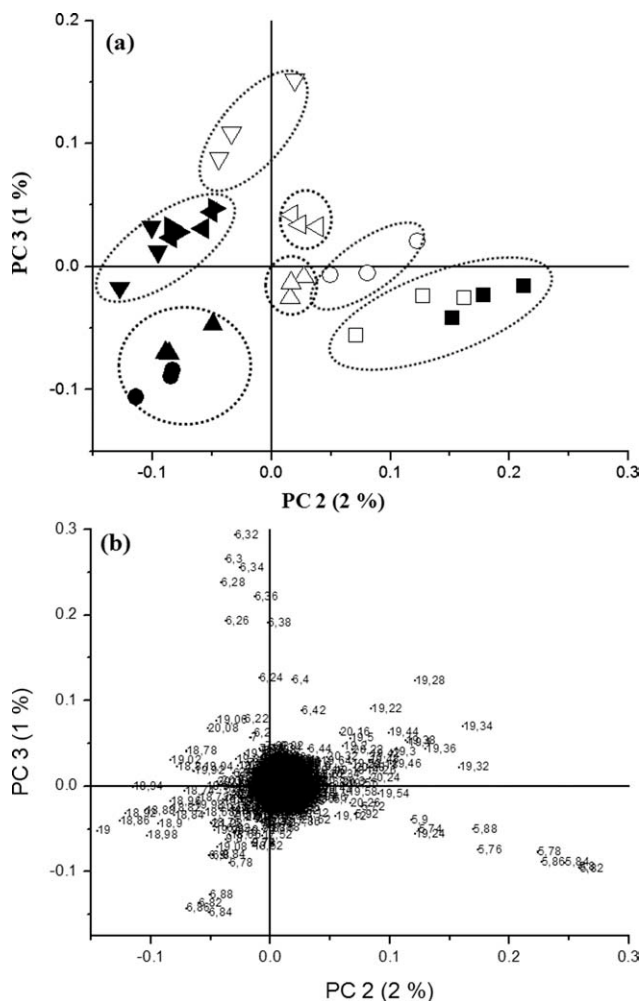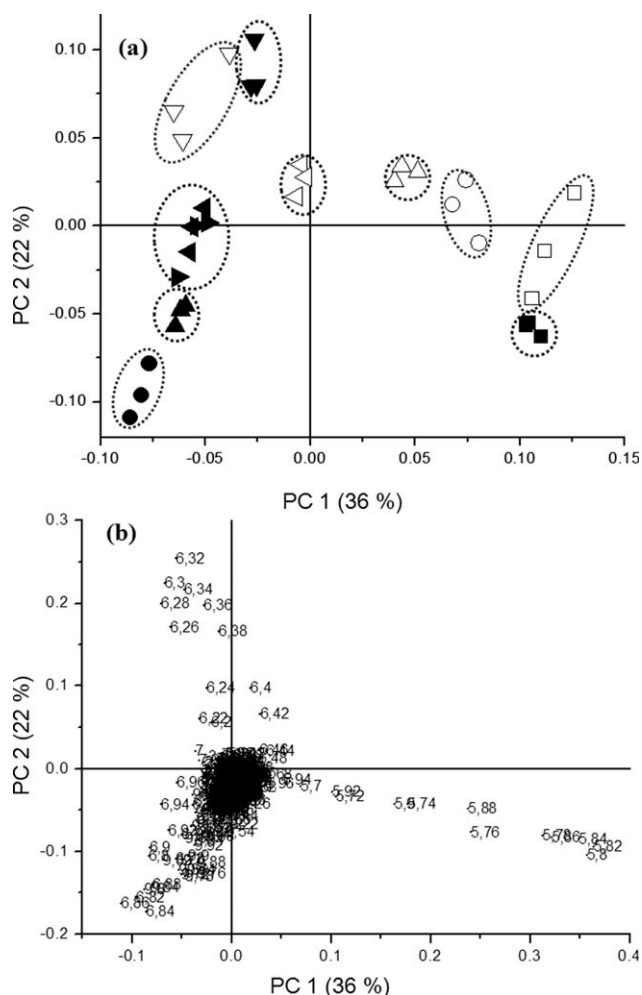
Figure 5 PC2 × PC3 scores (a) and (b) loadings plots for all ED-XRF data (manufactured samples: (■) PET$_v$-btg I, (●) PET$_v$-btg II, (▲) PET$_v$-btg III, (▼) PET$_{pc}$-btg, (◄) PET-clean I, (►)PET-clean II; and PET$_v$-btg I/PET$_{pc}$-btg blends: (□) 100/0 wt %, (○) 75/25 wt %, (△) 50/50 wt %, (◁) 25/75 wt %, (▽) 0/100 wt %).

the Rh scattering region and in the Mn Kα lines (5.6–6.0 keV), being this last one corresponding to about 2% of total variance.

Figure 5(a,b) shows the PC2 × PC3 scores and loadings plots of different classes of analyzed PET-btg.

A better separation among classes is observed between virgin samples (PET$_v$-btg II and PET$_v$-btg III) and samples subjected to thermo-mechanical processing (PET-recycled I, PET-recycled II, and PET$_{pc}$-btg) when analyzing the PC2 × PC3 scores plot, Figure 5(a). Samples with higher Fe contents are shifted from PC3 < 0 to PC3 > 0 regions, as processed and reprocessed samples. For PET$_v$-btg I/PET$_{pc}$-btg blends, the Fe content increase when the wt % PET$_{pc}$-btg increases in blends. For PC3 loadings, most information is from the Fe Kα lines (6.2–6.6 keV), Figure 5(b), correspond to about 1% of total variance.

With the objective of obtaining a better separation of the classes, the PCA analysis was performed only in the region corresponding to catalyst and impurities (0–10 keV). Figure 6 shows scores and loading plots for PC1 × PC2. The samples were separated into two large groups: PET$_v$-btg samples (PET$_v$-btg I, PET$_v$-btg II, and PET$_v$-btg III) that are in PC2 < 0; and processed PET-btg samples (PET$_{pc}$-btg, PET-recycled I, PET-recycled II, and blends) that, generally, are in PC2 > 0 where, a separation clearly is observed among them. Therefore, the samples with a better quality are located in the negative PC2 region. A decrease in variance values is observed for PC1 × PC2 (≈ 58%), Figure 6, when compare with PC1 × PC2 of Figure 4(a) (≈ 93%). It is due to the variance attributed to the organic composition is higher than the inorganic composition alone (0–10 keV).

Figure 6 (a) Scores and (b) loadings plots for PC1 × PC2 of ED-XRF data in 0–10 keV region where manufactured samples: (■) PET$_v$-btg I, (●) PET$_v$-btg II, (▲) PET$_v$-btg III, (▼) PET$_{pc}$-btg, (◄) PET-clean I, (►) PET-clean II; and PET$_v$-btg I/PET$_{pc}$-btg blends: (□) 100/0 wt %, (○) 75/25 wt %, (△) 50/50 wt %, (◁) 25/75 wt %, (▽) 0/100 wt %.
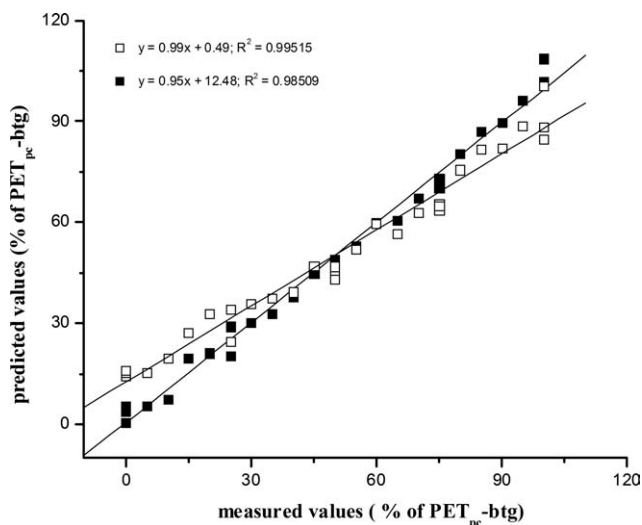
Figure 7 (■) Calibration and (□) validation curves obtained from PLS for PET_v-btg I/PET_{pc}-btg blends in different proportions: 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, and 100 wt % of PET_{pc}-btg.

All spectral regions were used to construct the validation and calibration PLS model. The model obtained presented LV equal to 3. The internal calibration and validation values were practically coincident, Figure 7, indicating good accuracy of the model (0.98 and 0.99, respectively). To predict percent PET_{pc}-btg values in manufactured PET-btg samples (external validation), the constructed PLS model was used. A good correlation was observed for PET_v-btg I and PET_{pc}-btg samples, where the model predicts 0 and 100 ± 3 wt % of PET_{pc}-btg, respectively. This is results is agreement with true concentration of PET_{pc}-btg present in the samples. For other samples (PET_v-btg II, PET_v-btg III, PET-recycled I, and PET-recycled II), percent PET_{pc}-btg predicted values are about 90 wt %, not being with agreement with true concentration of PET_{pc}-btg. It is due to the model being constructed from PET-btg blends containing mainly Mn as catalyst, as this variable influences the PC2 loading plot, Figure 4(b). Therefore, as the other samples do not have Mn in their compositions, the predictive model calculates a similar value to percent PET_{pc}-btg present in the processed PET_{pc}-btg (0/100 wt %), that makes no use of Mn as catalyst. Better validation and calibration models can be constructed if all samples used the same catalysts, or more sophisticated models, such as PARAFAC (Parallel Factor Analysis), were used, where the presence of inorganic contaminants does not interfere in their construction.[35,36]

CONCLUSIONS

ED-XRF results were used to demonstrate that bottle-grade PET samples are made either via a direct

EP (PET_v-btg II, PET_v-btg III, PET-recycled I, PET-recycled II, and PET_{pc}-btg) or by the TP (PET_v-btg I), as the first uses only Sb, whereas the last uses both Mn and Sb as catalysts, simultaneously.

We can also observe that samples subjected to thermo-mechanical processing (injection-blow molding process, superclean® process and the blends prepared in an internal mixer with counter-rotating twin-rotors) present Fe Kα lines stronger than virgin bottle-grade PET. Therefore, Fe is a contaminant intrinsic to the PET recycling process, improving a better classification of classes analyzed via PCA.

Calibration and validation PLS models had good correlations to calculate the predicted PET_{pc}-btg values in PET-btg blends. However, because it was constructed from blends containing both Mn and Sb, the PET_{pc}-btg predicted values for samples that present only Sb will be always about 100 wt %.

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