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Fingerprinting of bottle-grade poly(ethylene terephthalate) via matrix-assisted laser desorption/ionization mass spectrometry

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ABSTRACT

Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) has been shown to provide a valuable technique to study the thermomechanical degradation of poly(ethylene terephthalate) (PET). MALDI-MS has been tested to monitor both the admixture of post-consumption bottle-grade PET (PET_{pc}-btg) with virgin bottle-grade PET (PET_{v}-btg) and the thermomechanical degradation effects on the chemical properties of PET_{v}-btg. Principal component analysis of MALDI-MS data classify the samples into groups with specific features: a) PET-btg with intrinsic viscosities of 0.80 or 0.65–0.60 dL g^{-1}); b) processed or virgin PET with the same intrinsic viscosity; c) PET_{v}-btg from PET containing PET_{pc}-btg; and d) PET_{v}-btg from different manufacturers. MALDI-MS data is therefore able to reveal the quality of PET-btg resins preventing frauds and illegal use of recycled PET-btg.

1. Introduction

A major fraction of the polymer market is related to the food packaging industry. In Brazil, for instance, nearly 1/3 of the polymer market is for food packing. Poly(ethylene terephthalate) (PET) is mainly used in soft-drink bottles and consequently the amount of post-consumption bottle-grade PET (PET_{pc}-btg) in urban solid waste (USW) is high. Polymers contribute to ca. 20 wt% of the USW collected in larger Brazilian cities, and PET_{pc}-btg is one of the major component of these polymers [1,2].

The mechanical recycling index (MRI) is used to report the percentage of recycled polymers in relation to manufactured polymers. The Brazilian MRI is currently ca. 20 wt%. For PET, however, the Brazilian MRI is much higher (53% in 2006), being second only to Japan (62%) [1,2].

In general, the main application of PET_{pc}-btg is in the textile industry (43 wt%) and its increasing demand has helped improving the growth of PET recycling [2]. Other applications for PET_{pc}-btg are in the manufacture of alkydic and unsaturated resins by paint and adhesives industries to make injection molded goods.

Beginning in 2010, recycling companies will be demanded to use new technologies known as superclean® or bottle-to-bottle®. With these new technologies, the use of PET_{pc}-btg will be allowed in manufacturing new soft-drink bottles [2]. These new recycling technologies are also approved by the Food and Drug Administration in the United States and the Fraunhofer Institute in Germany [3–10]. The main change is the addition of new steps to the recycling process, such as post-condensation, which are used to correct the molar mass and, consequently, the PET intrinsic viscosity [1,2]. To comply with the coloring standards, however, the bottles will be produced with a maximum of 10 wt% of PET_{pc}-btg [1,2]. This new policy wills therefore calls for analytical techniques able to measure the level of PET_{pc}-btg mixed in virgin PET used to produce new bottles.

For years, we have been engaged in a large effort to develop mass spectrometric techniques able to typify and detect adulteration or counterfeiting such as for drug tablets, oil, perfumes,

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gasoline, soybeans and biofuels [11,12]. Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) has been shown to be an invaluable technique to study thermal [13], thermo-oxidative [14], plasma-oxidative [15], hydrolytic [15,16] and, recently, thermomechanical degradation of PET [17] and other polyesters [18,19] at "real world" processing temperatures. However, until now, MALDI-MS has not been systematically tested for its ability to detect PET_{pc}-btg in PET-btg samples. In this work we have investigated the use of MALDI-MS coupled to principal component analysis (PCA) to perform this important analytical task in polymer analysis.

2. Experimental

Samples of virgin bottle-grade poly(ethylene terephthalate), PET_v-btg, were supplied by three different Brazilian producers and are designed as PET_v-btg I, PET_v-btg II and PET_v-btg III ([η] of ≈0.80 dL g^{-1}, melting temperature of 240–245 °C, density of 1.20–1.40 g cm^{-3} and diethylene glycol (DEG) content of 1.3–1.6 mol%). Discarded soft-drink PET bottles were subjected to the superclean® recycling process by Bahia PET Reciclagem Company (Salvador, BA, Brazil) and samples were supplied as pellets. Sample used in this work and called "PET clean I" was subjected to a single superclean® recycling process and were colorless. Sample designated "PET clean II" was subjected twice to the superclean® recycling process and displayed green color. According to the producers, these samples have [η] of 0.81 and 0.82 dL g^{-1}, respectively.

To obtain the PET_{pc}-btg, we used discarded 2 L soft-drink bottles, which were washed with tap water and milled in a three knife rotary mill (Rone®, NFA 1533). Flakes were dried in an oven at 160 °C. The measured [η] of these samples was 0.76 dL g^{-1}.

Trifluoracetic acid (TFA) and the MALDI-MS matrix 2,5-dihydroxybenzoic acid (DHB) were both purchased from Sigma–Aldrich Chemicals, USA. Chloroform, acetone, phenol and 1,1,2,2-tetracloroethane (analytical grade) were supplied by Labsynt Produtos para Laboratório Ltda. (Brazil).

3. 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 prior to 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 was 50 cm^3. The rotors were coupled to a Haake Rheocord 90 torque rheometer and the changes of torque and temperature were 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 50.0 g. After removal from the mixer and cooling to room temperature, the mixtures were milled in a three knife rotary mill.

4. Characterization

Intrinsic viscosity ([η]) was measured according to ASTM D 4603 [20] using a mixture of phenol and 1,1,2,2-tetracloroethane (60/40 wt%) at 30 °C. Measurements were done in duplicate and [η] was calculated using Eq. (1), where $[\eta_r]$ = relative viscosity and C = polymer solution concentration (g dL^{-1}). Phenol and 1,1,2,2-tetracloroethane (analytical grade) were supplied by Sigma–Aldrich Chemicals, USA, and used as received. The [η] values of samples are listed in Table 1 [2].

$$[\eta] = [0.25 \times ([\eta_r] - 1 + 3\ln[\eta_r])]/C \quad (1)$$

Table 1
PET Samples analyzed by MALDI-MS and PCA.

Samples	Classes	[η] dL g^{-1}
PET_v-btg I/PET_{pc}-btg blends		
1–4	100/0 wt%	0.658 ± 0.010
5–8	75/25 wt%	0.647 ± 0.001
9–12	50/50 wt%	0.639 ± 0.001
13–16	25/75 wt%	0.612 ± 0.006
17–20	0/100 wt%	0.598 ± 0.003
Manufactured Samples		
21–24	PET clean I	0.810[a] ± 0.010
25–28	PET clean II	0.820[a] ± 0.010
29–31	PET_v-btg I	0.800 ± 0.003
32, 33	PET_v-btg II	0.790[a] ± 0.010
34–37	PET_{pc}-btg	0.763 ± 0.016
38,39	PET_v-btg III	0.800[a] ± 0.010

[a] values supplied by the manufacturers.

MALDI-MS data was collected for the soluble parts after extraction with solvents [17]. About 0.1 g of the PET sample was dissolved in 1 mL of TFA. The solution was diluted with 8 mL of chloroform plus 2 mL of acetone with continuous stirring. The PET solution was separated from the precipitated polymer by vacuum filtration. The solution with the extracted oligomers was spotted (1 μL) directly onto a MALDI plate and dried. A freshly prepared matrix solution of DHB (154 g L^{-1}) in methanol was then added to the spots. MALDI-MS was performed in a MALDI-TOF Premier Mass Spectrometer (Waters – Micromass, Manchester, UK). The mass spectra were obtained in the positive ion mode with a nitrogen laser, using the following principal parameters: *m/z* range from 700 to 2500, scan time of 2 s, resolution of ca. 10,000 in the "V" mode, trigger threshold of 700 mV, signal sensitivity of 80 mV and microchannel-plate photomultiplier set to 2100 V. Each spectrum was collected over a 1 s scan, and spectra were accumulated over ca. 0.5 min. At least 15 spectra were collected and combined. The instrument was controlled by MassLynx 4.1v software (Waters – Micromass, Manchester, UK). All data obtained from MALDI-MS were treated using MassLynx 4.1v software.

5. Chemometric analysis

MALDI-MS data were processed to generate a final data matrix containing 36 variables (*m/z* values of the oligomers detected in the 700–2500 *m/z* range) for the 39 samples analyzed. For the classification of the PET samples, PCA was performed on the MALDI-MS data using the PLS-Toolbox 4.02 for Matlab v. 7.0.1 software. Table 1 summarizes the data from all samples analyzed.

6. Results and discussion

Fig. 1a–b show the MALDI-MS in the *m/z* 700–2500 range from the extracted oligomers of (1a) PET_v-btg I and (1b) processed PET_{pc}-btg (0/100 wt %), whereas Table 2 summarizes the main oligomeric species detected in these spectra. The predominant oligomeric species are cyclic oligomers: **[TG]**$_n$, where T = terephthalate and G = glycol units and underline is used for the cyclic species, detected as Na^+ adducts ($[M + Na]^+$: *m/z* 791, 983, 1175, 1367, 1559, 1751, 1943, 2135 and 2327 and protonated molecules ($[M + H]^+$: *m/z* 769, 961, 1153, 1345, 1537, 1729, 1921, 2113, 2305 and 2497); and cyclic oligomers with an extra glycol linkage in the backbone **[TG]$_n$-G** : $[M + Na]^+$ of *m/z* 835, 1027, 1219, 1411, 1603, 1795, 1987, 2179 and 2371, and $[M + H]^+$ of *m/z* 1005, 1197, 1389, 1581, 1773, 1965, 2157 and 2349. Linear oligomers **[TG]$_n$** having hydroxyl and carboxyl end groups were also detected as $[M + Na]^+$ ions of *m/z* 809, 1001, 1193, 1385, 1577, 1769, 1962, 2154 and 2346; as well as oligomer **G-[TG]$_n$**

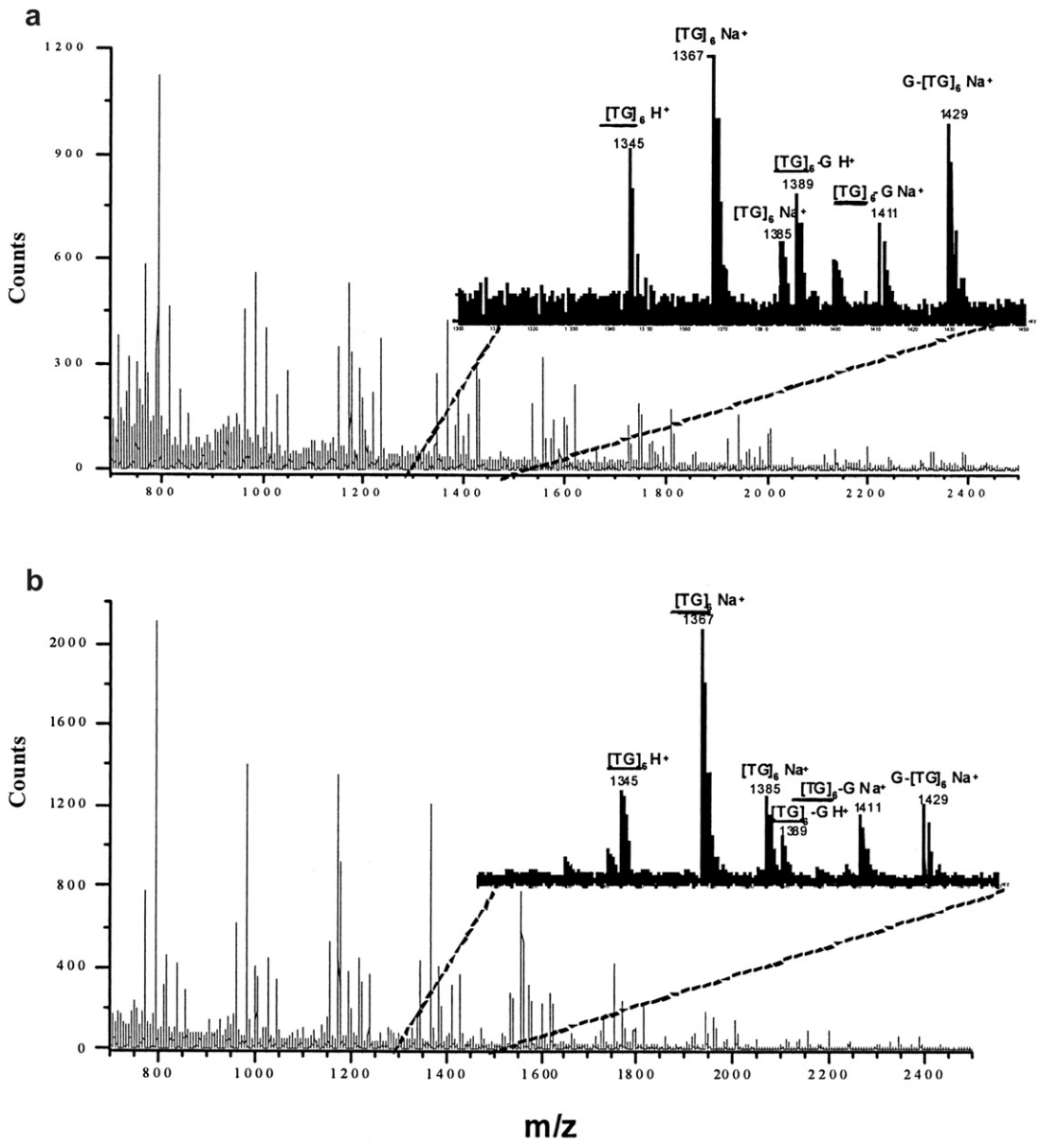


Fig. 1. MALDI-MS of oligomers extracted from (a) virgin bottle-grade PET resin (PET_v-btg I) and (b) PET from post-consumed soft-drink bottles (PET_{pc}-btg), processed using a counter-rotating twin-rotors mixer at 250 °C, 50 rpm for 5 min. The inserts show an expanded view of the spectra in the *m/z* range of 1300–1450.

having two glycol end groups: $[M + Na]^+$ of *m/z* 853, 1045, 1237, 1429, 1621, 1813, 2005, 2197 and 2389.

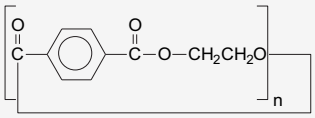
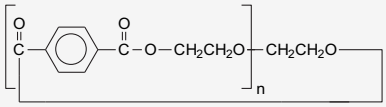
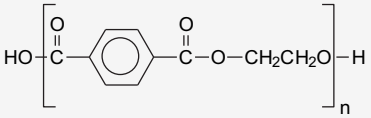
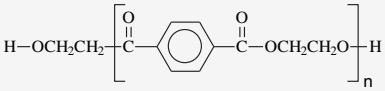
The thermomechanical degradation process changes the oligomeric composition of the PET sample, as clearly visualized in the MALDI-MS by the increase of the relative abundance of cyclic oligomers **[TG]$_n$**. Note in the insert of Fig. 1 (expanded view for *m/z* 1300–1450) the increase in the relative abundance of the **[TG]$_6$** ion of *m/z* 1367 as compared to those of *m/z* 1429 and 1389, corresponding to **G-[TG]$_6$** and **[TG]$_6$-G,** respectively. Similar results have been reported previously [14,17].

Fig. 2 summarizes the mechanism leading to the changes in the oligomeric composition during the thermomechanical degradation of PET-btg. Oligomers **G-[TG]$_n$** are the most reactive species, which produces cyclic oligomers **[TG]**$_n$ by eliminating G (ethylene glycol, route I). They can also produce linear oligomers **[TG]$_n$** by conversion of G to acetaldehyde (AA), which leaves COOH end groups (route II) [14,15,21]. The **[TG]$_m$** oligomers can also be formed from an alternative mechanism via chain-scission reactions of the ester groups from oligomers **G-[TG]$_n$** producing the oligomers **[TG]$_m$,** where $m = n-1$, by the loss of $CH_2=CHOCO$ ~~~ (route III) [15]. This type of reaction is facilitated by shear during the thermomechanical processing.

A decrease of the average M_W of **[TG]**$_n$ is also observed as a function of thermomechanical degradation, and this effect may be due to intramolecular cyclization reactions leading to two lighter **[TG]**$_n$ products, as reported by Goodman et al. [22] (route IV). The decrease of the relative ion concentrations **[TG]$_n$-G** is known and is due to thermo-oxidative degradation [23–25] and was previously observed by our group during bottle-grade PET reprocessing [17].

MALDI-MS data for oligomers **[TG]**$_n$, **[TG]$_n$**, **[TG]$_n$-G** and **G-[TG]$_n$** detected as $[M + Na]^+$ ions (Table 2) were subjected to chemometric treatment via PCA. This treatment was done to statistically evaluate the performance of MALDI-MS [26] in classifying PET-btg for quality control purposes. Fig. 3 shows the PCA plots of the different classes of PET-btg analyzed. High quality PET-btg samples display $[\eta] \approx 0.8$ dL g^{-1} [1,23,27,28]. The PC3 × PC2 plot is

Table 2
MALDI-MS data for PET-btg samples and oligomers detected as $[M + Na]^+$ and used for PCA.

Species	Structure	Variables $[M + Na]^+$
[TG]$_n$		791 (1), 983 (2), 1175 (3), 1367 (4), 1559 (5), 1751 (6), 1944 (7),
[TG]$_n$-G		835 (10), 1027 (11), 1219 (12), 1411 (13), 1603 (14), 1795 (14), 1987 (16), 2179 (17) and 2371 (18)
[TG]$_n$		809 (19), 1001 (20), 1193 (21), 1385 (22), 1577 (23), 1769 (24), 1962 (25), 2154 (26) and 2346 (27)
G-[TG]$_n$		853 (28), 1045 (29), 1237 (30), 1429 (31), 1621 (32), 1813 (33), 2005 (34), 2197 (35) and 2389 (36)

interesting because it separates, according to PC3, the PET-btg samples into two groups: good quality ($PC3 > 0$, $[\eta] \approx 0.8$ dL g^{-1}) and poor quality ($PC3 < 0$, $[\eta] < 0.65$ dL g^{-1}), see Table 1. Note that all samples submitted to thermomechanical degradation in our laboratory, that is, the blends, are located in the poor quality negative region ($PC3 < 0$).

For the good quality samples ($PC\ 3 > 0$), samples could also be separated into two large groups according now to PC2: (a) $PC2 > 0$ corresponding to PET_v-btg, where it was also grouped according to the manufacturers; (b) $PC2 < 0$ for PET_{pc}-btg from two industrial processes: injection-blow and superclean processing. Although the PC2 × PC3 plot failed to separate the PET clean and PET_{pc}-btg samples, this separation is achieved by the PC2 × PC1 plot (Fig. 3b). Also note that some samples, such as samples 2, 6, 15, 18 and 23, were not grouped into their respective classes on the PC3 × PC2 plot (Fig. 3a). Their grouping is however

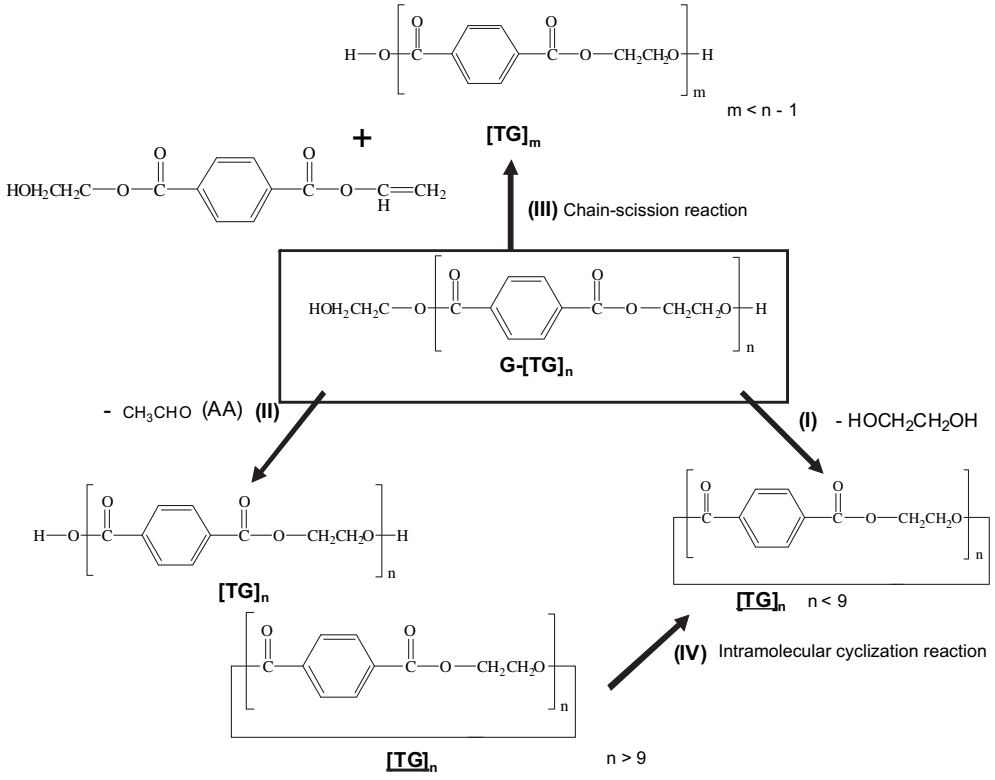


Fig. 2. Oligomers extracted from PET and detected by MALDI-MS and the mechanism for their formation via thermomechanical degradation.

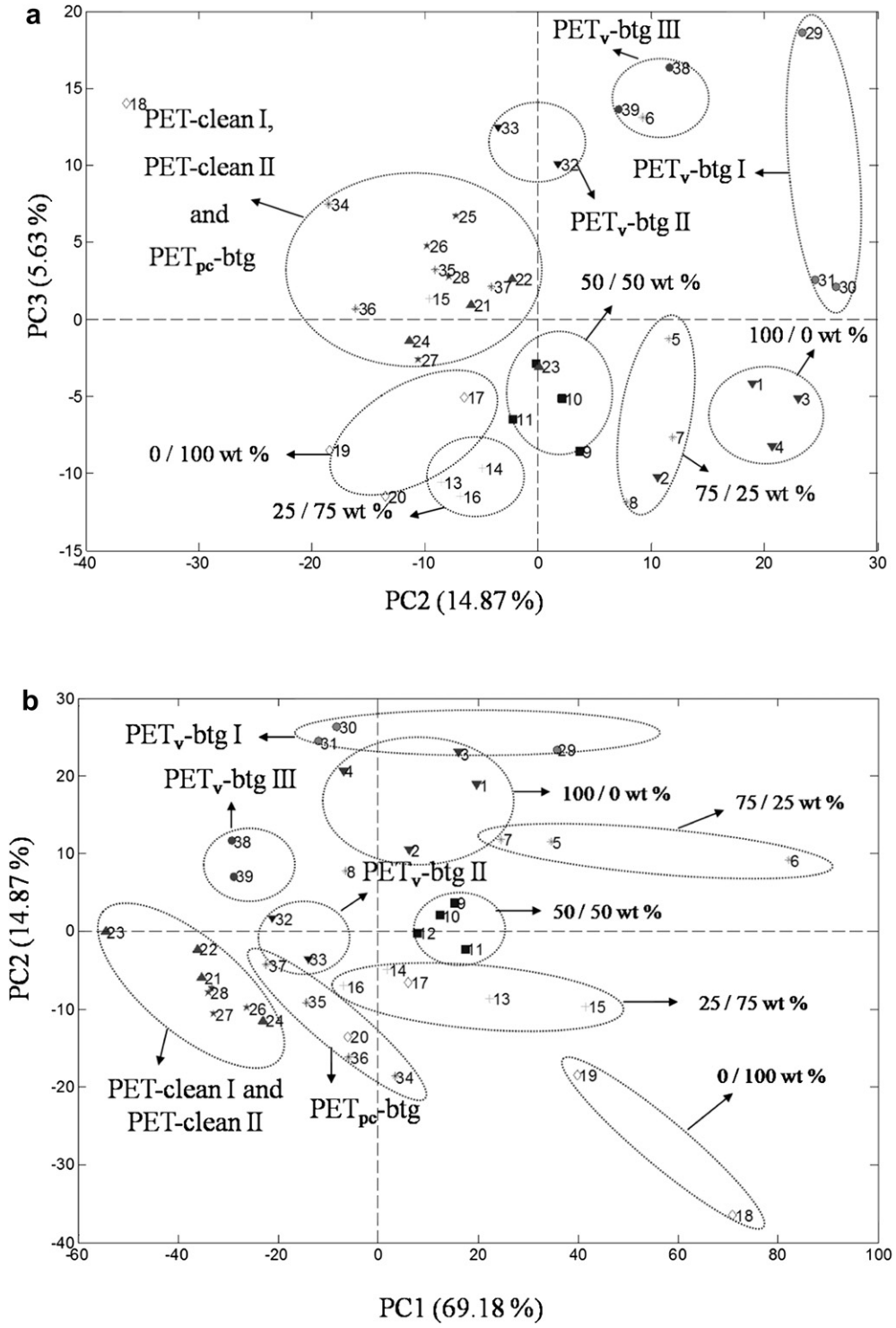


Fig. 3. PCA plots for MALDI-MS data: a) PC3 × PC2 and b) PC2 × PC1, where PET$_v$-btg I, II and III = virgin bottle-grade PET resins; PET$_{pc}$-btg = PET from milled post-consumed soft-drink bottles; PET-clean I and II = PET from post-consumed bottles subjected to single and twice superclean recycling process, respectively; and weight percent ratio of PET$_v$-btg I/PET$_{pc}$-btg corresponds to the mixture of virgin bottle-grade PET resins (PET$_v$-btg I) with milled post-consumed PET bottles (PET$_{pc}$-btg).

reached when analyzing the same samples via the PC2 × PC1 plot (Fig. 3b).

In relation to the bad quality samples in Fig. 3a, samples were also grouped as a function of the percentage of PET$_{pc}$-btg in the blend. An increase in the wt % of PET$_{pc}$-btg from 0% to 25%, 50%, 75% and 100% shifts the samples from the positive side into the negative side of the PC2 region; hence, MALDI-MS coupled to PCA seems to be a suitable technique to estimate the wt % of PET$_{pc}$-btg in PET$_v$-btg I/PET$_{pc}$ blends. PC2 seems to indicate the % of PET$_{pc}$-btg, whereas PC3 describes quality, as measured by [η]. For instance, samples 29–31 and 1–4 display the same % of PET$_{pc}$-btg (zero %) but different [η] values; hence, they are placed in the same PC2 region, but in different PC3 quadrants.

Fig. 4a–b show the plots for PC2 and PC3 loadings pointing to variables most significant to group the samples. For PC2 (Fig. 4a), the variables in the negative region (samples with higher wt % of

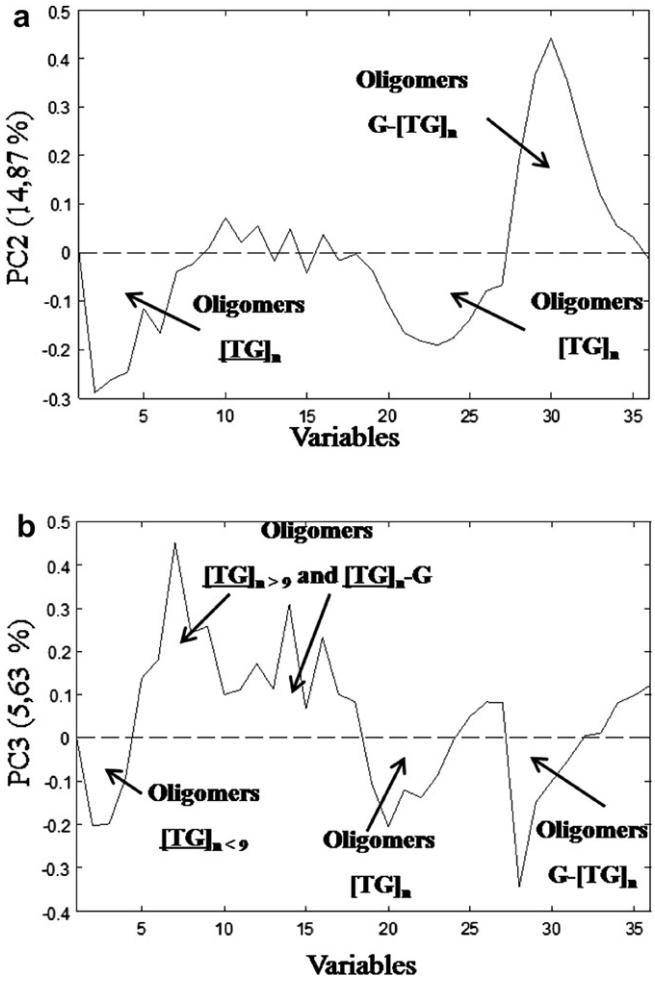


Fig. 4. (a) PC2 and (b) PC3 loadings of MALDI-MS data, where **[TG]**$_n$ = cyclic oligomers; **[TG]$_n$-G** = cyclic oligomers with an extra glycol linkage in the backbone; **[TG]$_n$** = linear oligomers; and **G-[TG]$_n$** = linear oligomers having two glycol end groups, being **T** = terephthalate, **G** = glycol units and underline is used for the cyclic species.

PET_{pc}-btg, see Fig. 3) were **[TG]$_n$** (variables 1–9) and **[TG]$_n$** (variables 19–27). Therefore, these oligomers increase as a function of the wt % of PET_{pc}-btg in the blends. On the positive side of PC2, the **G-[TG]$_n$** (variables 28–36) species, responsible for **[TG]$_n$** and **[TG]$_n$** formation (Fig. 2), are the most important. Therefore, the amount of **G-[TG]$_n$** decreases as a function of the thermomechanical processing and the presence of PET_{pc}-btg in the blends.

Similar to PC2 loadings, the PC3 loadings (Fig. 4b) show that in the negative region the oligomers **[TG]$_n$** (variables 1–5), **[TG]$_n$** (variables 19–27) and **G-[TG]$_n$** (variables 28–36) are the most important, whereas **[TG]$_n$** (variables 5–9) and **[TG]$_n$-G** (variables 10–18) are the most important for the positive region. Therefore, the loadings of the MALDI-MS data are in agreement with the mechanism of thermomechanical degradation, as Fig. 2 summarizes.

Recently, MS plus separation techniques have been applied to quality control of recycling process of PET_{pc}-btg. Franz et al. [4] showed, for instance, that the headspace gas chromatography coupled to mass spectrometry (GC–MS) can be used to establish average levels of contaminants such as acetaldehyde and limonene. These compounds are used as markers for degradation and recycling. Ohkado et al. [6] used high performance liquid chromatography mass spectrometry (HPLC–MS) to monitor PET quality analyzing levels of formaldehyde, acetaldehyde and several types of PET oligomers. As compared to the MALDI-MS approach herein reported, both GC–MS and HPLC–MS techniques provide less composition information and require more efforts for sample preparation and separation with lower analytical frequency. These features limit their application in routine quality control. In contrast, sample preparation for MALDI-MS is minimum, analysis is fast (in ca. 20 s a spectrum is acquired), sensibility is high (femtomoles), and structural information is rich, making MALDI-MS an attractive technique for quality control of PET for food packaging.

7. Conclusion

MALDI-MS data coupled to PCA analysis was capable to monitor the wt % of PET_{pc}-btg present in PET-btg blends and its overall quality as a function of intrinsic viscosity due to thermomechanical degradation. Moreover, subtle changes in oligomeric composition were also detected by MALDI-MS, allowing the separation of PET-btg samples from different manufacturers. MALDI-MS seems to provide therefore a fast and reliable technique for PET-btg characterization and quality control and to discriminate between PET_v-btg and PET_{pc}-btg.

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