Desorption studies of model contaminants from recycled PET in dry air and nitrogen atmosphere by thermogravimetric analysis

A. S. F. Santos[*], J. A. M. Agnelli[**]; Eliton S. Medeiros[***], Elisângela Corradini[***]; Sati Manrich[**]

[*]Laboratory of Chemical Processes and Particle Technology, Institute for Technological Research, São Paulo, SP, Brazil, ameliafs@ipt.br
[**]Department of Materials Engineer, Federal University of São Carlos, São Carlos, SP, Brazil, agnelli@power.ufscar.br, sati@power.ufscar.br
[***]Embrapa Instrumentação Agropecuária, São Carlos, SP, Brazil, eliton@cnpdia.embrapa.br

ABSTRACT

The closed-loop recycling of PET bottles has to prove its ability to decontaminate recycled plastics into a level that offers a negligible risk to public health and does not compromise the organoleptic properties of packed foods. Our previous work [1] resulted in a new bottle-to-bottle process that employs dry air atmosphere under ideal mass and heat transfer conditions to remove contaminants from polymer matrix. The experimental results showed that dry air was able to increase the productivity of PET super-clean technologies, based on solid-state polymerization processes (SSP). In this work we have evaluated the difference in desorption rate of model contaminants from recycled PET in dry air and nitrogen atmosphere by thermogravimetric analysis. Furthermore, it was investigated if sample exposed to synthetic air and nitrogen atmosphere during the thermogravimetric analysis presented any difference in their thermal properties. According to the results obtained in this work, the thermogravimetric analysis was not sensitive to detect difference in the rate of contaminant desorption from PET in synthetic air and in nitrogen atmosphere and any evidence of interaction between PET matrix and exposed atmosphere has not been observed by DSC analysis.

Keywords: desorption, surrogates, PET, atmosphere, thermogravimetry.

1 INTRODUCTION

The PET bottle-to-bottle recycling is a good example of a successful technology that allowed an increase of recycled plastic market as well as a reduced environmental risk through minimization of plastic waste volume. These technologies, also known as super-clean technologies, generally consist of conventional mechanical recycling followed by further steps that employ heat, vacuum, inert atmosphere, solid-state polymerization, solvent extraction, chemical surface treatments, vacuum degassing, supercritical fluid extraction (SFE) and steam distillation [2].

Among the super-clean technologies mentioned above, solid-state polymerization processes are the most disseminated ones [3-9]. These super-clean technologies are a kind of thermal extraction process, which main variables consist of type and composition of atmosphere, temperature, particle size, type/nature of equipment ad agitation system.

At the Residue Recycling Center in Federal University of São Carlos (UFSCar), comparative tests of the extraction rates of benzophenone from PET in dry air, vacuum or inert gas have demonstrated that the diffusion of this contaminant from plastic surface was the fastest in dry air [10]. Based on this result, a new super-clean process was proposed [1], which differs from others, once it uses only the conventional drying and crystallization recycling steps, at the upper temperature and dry-air flux limit. This process was developed to decontaminate the recycled plastic to the appropriate purity imposed by FDA and by the International Life Sciences Institute (ILSI) for recycled PET to be used in direct food contact applications. The new technology could be added to other ones with the possibility of increasing productivity rates and reducing both energy consumption and raw material costs, all advantages that go in hand with demands for clean technologies.

Aiming to confirm the previous results by a characterizing technique other than gas chromatography, this work evaluated the difference in desorption rate of model contaminants from recycled PET in dry air and nitrogen atmosphere by thermogravimetric analysis. Furthermore, any difference associated with the physical aging process of the sample treated in each atmosphere was also investigated through differential scanning calorimetry (DSC) analysis.

2 EXPERIMENTAL

2.1 Materials

All surrogates (toluene, trichloroethane, eicosan and benzophenone) and solvent (hexane) were analytical grade (purity higher than 99 %), and used without further purification.

Two-liter PET bottles donated by Plastipak Packaging do Brasil Ltda. (Campinas, Brazil) with intrinsic viscosity of 0.80 $dL.g^{-1}$were used. The bottles were cut, and the central parts of these bottles, due to their uniformity in

thickness, crystallinity, stretch ratio and carboxyl content, were used. These parts were subsequently cut into symmetric squares of 8x8 mm to standardize the physical, morphological and structural properties of PET flakes and reduce the variation of surrogates' content in PET matrix [11].

2.2 Contamination Condition

Virgin square PET flakes were soaked in spiked solution containing 15 % (w/v) of toluene and trichloroethane, 10 % (w/v) of d-limonene, 5 % (w/v) of benzophenone and 3 % (w/v) of eicosan dissolved in hexane. The mixture was placed in a special cell with flakes completely immersed in the surrogate solution. Then the cell was placed in an incubator and maintained at 40º C for two weeks. Afterwards, the flakes were removed from the spiked solution, rinsed with hexane and dried with a paper towel.

2.3 Thermogravimetric Analysis (TGA)

The contaminated PET squares were heated to 60ºC using heating rate of 50 ºC/min and maintained isothermally at this temperature in a thermogravimetric analyzer (Shimadzu 50) to follow the mass loss for two hours under synthetic air and nitrogen atmosphere. The purge gas flow rate was set at 20 mL/min for both cases. All tests were carried out in duplicate.

2.4 Differential Scanning Calorimetry (DSC)

In order to verify any change in the thermal characteristics of PET squares exposed to synthetic air and nitrogen atmosphere during the thermogravimetric analysis, they were analyzed by differential scanning calorimetry (DSC).

The DSC curves were recorded on a DSC Shimadzu 50 apparatus, with purge inert gas (N_2) flow rate of 50 mL/min. The samples were heated from 30 to 280 ºC using heating rate of 10 ºC/min. The crystallinity degree was determined by the ratio between melt enthalpy of sample and melt enthalpy of a sample 100% crystalline (119.8 J/g) [12].

3 RESULTS

In order to model the desorption rate from thermogravimetric analysis, it was assumed that the extraction process is diffusion-controlled and, consequently, the solvation or dissolution/dispersion stages were negligible [13, 14]. The kinetic of desorption obeys Fick's law and thus presents a linear behavior with the square of time at the first stages of desorption [15]. Figure 1 shows the thermogravimetric results calculated according to these hypotheses.

As could be observed, the desorption rate of contaminants in synthetic air atmosphere was slightly higher than in nitrogen. Nevertheless, considering the mean deviation of these results, they seemed similar. Probably, the sensitivity of this analysis for the range of mass loss evaluated was not enough to detect any difference between the rate of desorption of contaminants from PET in these two atmospheres. Therefore, those results could not confirm our previous study, which was carried out using chromatographic analysis and observed an increase of about 60% in diffusion coefficient of benzophenone in dry air atmosphere when compared with that one in nitrogen atmosphere [9].

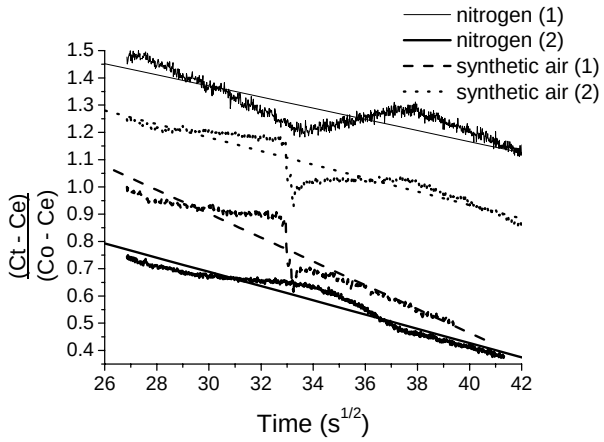

Figure 1: Thermogravimetric curves of PET squares at different atmospheres. Nitrogen (2) f=0.75, synthetic air (1), f=1, synthetic air (2), f = 1.25, nitrogen (1), f = 1.5. f, multiplying factor. 1 e 2, duplicates.

The DSC curves are depicted in Figure 2. These results did not show any significant difference in thermal properties of PET exposed to synthetic air or nitrogen atmosphere (Table 1).

Atmosphere	No.	Tg (ºC)	Tm (ºC)	Crystallinity (%)
synthetic air	1	95.9	250.3	28.4
	2	95.6	249.5	27.3
nitrogen	1	94.2	248.8	27.0
	2	93.3	249.3	26.1

Table 1: Tg, Tm and crystallinity values of PET samples exposed to different atmospheres at 60ºC.

Once has not been observed any increase in Tg of PET samples exposed to dry air atmosphere in relation to that one observed in nitrogen atmosphere, no specific interaction between that atmosphere and PET matrix or change in PET matrix process of enthalpic relaxation due to the type of atmosphere employed could be identified. Furthermore, a slightly higher Tg has just been observed for higher crystalline samples, as expected due to the greater restrained amorphous phase.

Once thermal treatment has been carried out below the Tg temperature of this polymer, the differences in crystallinity degree of PET samples could be inherent to PET sample variability. Nevertheless, the DSC analysis was not the most sensitive technique to measure Tg, mainly for semi-crystalline samples.

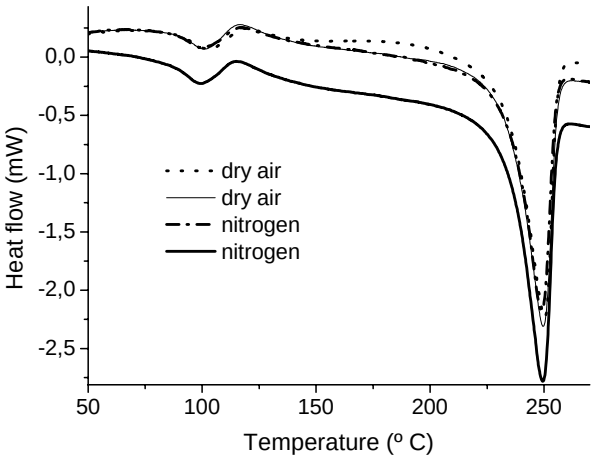

Figure 2: DSC curves of PET samples isothermally treated at 60º C in different atmospheres.

Other possible factors that probably contributed to improve the desorption rate of benzophenone from PET in dry air atmosphere were the reduced water content of dry air; the co-diffusion mechanism between contaminants and oxygen from dry air atmosphere through the polymer matrix, since nitrogen atmosphere is an inert gas of lower molar mass; and others. Nevertheless, none of them have been investigated in this article.

4 CONCLUSIONS

The results achieved in this work indicated that thermogravimetric analysis was not sensitive to detect difference in the rate of contaminant desorption from PET in synthetic air and in nitrogen atmosphere, considering the level of contaminant evaluated. In the same way, no difference in thermal properties, i.e. of interaction between PET matrix and exposed atmosphere, has been observed by DSC analysis.

5 ACKNOWLEDGMENTS

The authors are grateful to FAPESP for the financial support of this study.

REFERENCES

[1] FAPESP; UFSCar. S. Manrich, A. S. F. Santos; J. A. M. Agnelli. “Processo de descontaminação de poliéster reciclado”. 14 jun 2004. Nº. 002993. INPI-SP (in portuguese).

[2] S. Manrich, A. S. F. Santos. “An overview of recent advances and trends in plastic recycling”. In: Conservation and Recycling of Resources. Ed. Nova Science Publishers, 2006.

[3] BÜHLER AG. A. Christel; C. Borer; T. Hersperger. “Method and device for decontaminating polycondensates”. WO 01/34688, 17 Maio 2001.

[4] THE COCA-COLA COMPANY. M. Rule. “Process for removing contaminats from polyesters and controlling polymer molecular weight”. U.S.P. 6.103.774, 15 Ago. 2000.

[5] OHL APPARATEBAU&VERFAHRENSTECHNIK GmbH. F. Rudiger. “Method for recycling PET flakes”. U.S.P. 6.436.322, 20 Ago. 2002.

[6] VISY PLASTICS PTY LTD. E. Kosior. “Processo para preparar um poli(etileno tereftatalato) para contato com alimentos e poli(etileno terftalato) reciclado”. PI 0.014.094-5, 21 Maio 2002.

[7] WELLMAN, Inc. C. S. Nichols; C. Moore. “Food quality polyester recycling”. U.S.P. 5.876.644, 02 mar. 1999.

[8] KRONES AG. “Krones implements first bottle-to-bottle recycling facility”. PETticker, Maio 2002. Access at: www.petnology.com

[9] “PET bottle to bottle”. Recycling News, Linz, 1-2, 2000.

[10] A. S. F. Santos, Phd Thesis, Universidade Federal de São Carlos, 2004 (in portuguese).

[11] A. S. F. Santos, J. A. M. Agnelli, S. Manrich. In Proceedings of Brazilian Polymer Congress, 6., Gramado, 2001, CD-ROM.

[12] T. Toda, H. Yoshida, K. Fukunishi. “Structure and molecular motion changes in poly(ethylene terephthalate) induced by annealing under dry and wet conditions“. Polymer, 36 (4), 699-706, 1995.

[13] X. Lou; H. G. Janssen; C. A. Cramers. Anal. Chem. 69, 1598, 1997.

[14] R. W. Limm, H. C. Hollifield. Food Addit. Contam. 12, 609, 1995.

[15] J. Comyn. “Polymer permeability”. London: Elsevier Applied Science Publishers Ltd, 1988.