LEACHING BEHAVIOR OF POLYETHYLENE TEREPHTHALATE CONTAINERS USED FOR WATER BOTTLING

Adriana C. MÂRŞOLEA[1], Cristina ORBECI[2]*, Liliana BOBIRICĂ[3], Constantin BOBIRICĂ[4]

The objective of this study was to investigate the leaching behavior of PET containers used for water bottling by Toxicity Characteristic Leaching Procedure (TCLP) test. It was highlighted that the leachability of organic contaminants increases with storage time extension and temperature. An increase in the mobility of organic contaminants was found with the decrease in the thickness of the walls of the PET containers. This result could indicate a predominantly diffusional leaching mechanism. The investigation of the mobility of contaminants in PET containers based on tests and leaching models indicated a significant potential for their long-term leaching and demonstrated the influence of storage conditions on it.

Keywords: polyethylene terephthalate, water bottles, leaching behavior, organic contaminants

1. Introduction

It is well known at present that polyethylene terephthalate (PET) containers are very often used for bottling several types of alcoholic and non-alcoholic beverages [1]. In the drinking water industry, PET containers occupy a leading place, as there are currently different types with different characteristics on the market [2]. Although one of the strengths of these PET containers is stability over time and under different storage conditions, certain organic compounds added as additives in the manufacturing process, or contaminants that appear during the PET

[1] PhD student, Faculty of Chemical Engineering and Biotechnologies, National University of Science and Technology POLITEHNICA Bucharest, Romania, marsolea22@yahoo.com
[2] Department of Analytical Chemistry and Environmental Engineering, Faculty of Chemical Engineering and Biotechnologies, National University of Science and Technology POLITEHNICA Bucharest, Romania, cristina.orbeci@upb.ro *Corresponding author (Cristina. ORBECI).
[3] Department of Analytical Chemistry and Environmental Engineering, Faculty of Chemical Engineering and Biotechnologies, National University of Science and Technology POLITEHNICA Bucharest, Romania, l_bobirica_ro@yahoo.com
[4] Department of Analytical Chemistry and Environmental Engineering, Faculty of Chemical Engineering and Biotechnologies, National University of Science and Technology POLITEHNICA Bucharest, Romania, c_bobirica@yahoo.com

recycling process pose a series of problems regarding the contamination of the products bottled in them as well as the contamination of the environment in which they can end up [3,4]. After single-use packaging, many of the PET containers still end up into domestic landfills, and part of the organic constituents can pass into the leachate [5]. The leaching potential of PET containers can be tested with the help of the TCLP (Toxicity Characteristic Leaching Procedure) test, which is designed to simulate the harshest leaching conditions that can occur in various situations, especially in domestic landfills [6]. In fact, the leaching solution used in such a test (the acetic acid solution) simulates the domestic landfill leachate [7]. Although numerous deficiencies have been highlighted in this test over time, it still remains the main compliance leaching test in this field [8,9]. However, there is very little information about the long-term leaching potential of PET containers that have arrived in different environmental conditions [10]. Evaluating the mobility of various organic compounds present in PET containers could help to better understand their leaching mechanisms [11-12].

Therefore, the objective of this work is to investigate, for the first time in this field, through compliance leaching tests and leaching models, the leaching behaviour of PET containers depending on their storage conditions and physical characteristics. Thus, the calculation of observable diffusion coefficients is considered, which quantifies the mobility of organic compounds susceptible to leaching from PET containers under conditions like those in domestic landfills.

2. Material and Methods

2.1 Materials

Three types of polyethylene terephthalate (PET) containers used by three different Romanian brands of non-carbonated mineral water were subjected to leaching tests. Because it was not desired to divulge the brands, the PETs were coded. Their codes and characteristics, as well as the experimental conditions are presented in Table 1.

Table 1

Codification and experimental conditions

Brand	Walls thickness, mm	Storage time, h	Storage temperature, °C
A	0.25	24, 48, 168	20, 40, 60, 80
B	0.5		
C	0.8		

2.2 Leaching tests

After the PET containers were cut into pieces with a size below 9.5 mm, as specified in the TCLP (Toxicity Characteristic Leaching Procedure) test, they were kept in airtight containers for different times and at different temperatures in the oven. Each experimental variety was subsequently subjected to the TCLP test. In short, the TCLP test involves cutting or crushing the samples to be tested into pieces to a particle size of less than 9.5 mm, and continuously mixing them with acetic acid solution of pH 3 (leaching solution) at a solid-to-liquid ratio of 1/21 (m/V), for 18 hours. In order to make an estimate of the initial content of leachable organic material in PET, each assortment of PET was kept at 150 °C for 2 weeks in acetic acid solution at pH 3 under continuous stirring. The conditions were chosen so as not to start the depolymerization of PET in acetic acid (i.e., 180°C, in the presence of a catalyst) [13]. It should be noted that, to keep the thickness of the walls constant, the neck and bottom of the PET containers were removed, and therefore only their cylindrical part was used in the leaching tests. Next, the samples were filtered and prepared for measuring the concentration of organic contaminants by COD (Chemical Oxygen Demand) analysis according to the colorimetric method, and by using a LT 200 digestion unit and DR 3800 spectrophotometer (Hach Lange GmbH).

3. Results and discussion

The results of the leaching tests are presented in Fig. 1 and Fig 2. As it can be seen, the concentration of organic contaminants in the leachate increases with the increase of both the temperature and the storage time. Thus, the concentration of organic contaminants in the leachate is approximately 1.6 times higher in the case of PET (0.25 mm) stored for 168 hours at a temperature of 80 °C compared to that stored for the same period at a temperature of 20 °C. Similarly, in the case of PET (0.25 mm) stored at a temperature of 80 °C for 168 hours, the concentration of organic contaminants in the leachate is approximately 1.8 times higher than that corresponding to the leachate obtained for PET (0.25 mm) stored at the same temperature but for 24 hours. This trend is also maintained for the other two categories of PET (0.5 mm and 0.8 mm), but with a slight decreasing trend of the concentration of organic contaminants in the leachate in the sense of increasing the thickness of the PET containers. For the PET with 0.25 mm thickness stored at 20 °C for 168 hours, the concentration of contaminants in the leachate is 1.2 times higher than that recorded for the PET with 0.8 mm thickness kept under the same conditions. Although the difference is not very high, the results highlight the fact that the thickness of the PET containers plays an important role in terms of the stability of their manufacturing additives. It should be noted that between PET with a wall thickness of 0.25 mm and that of 0.5 mm, the difference in terms of the concentration of organic contaminants in the leachate is the same as the difference recorded between PET with a wall thickness of 0.5 mm and that of 0.8 mm (it is approximately 1.1 times higher). This trend is maintained for all storage conditions.

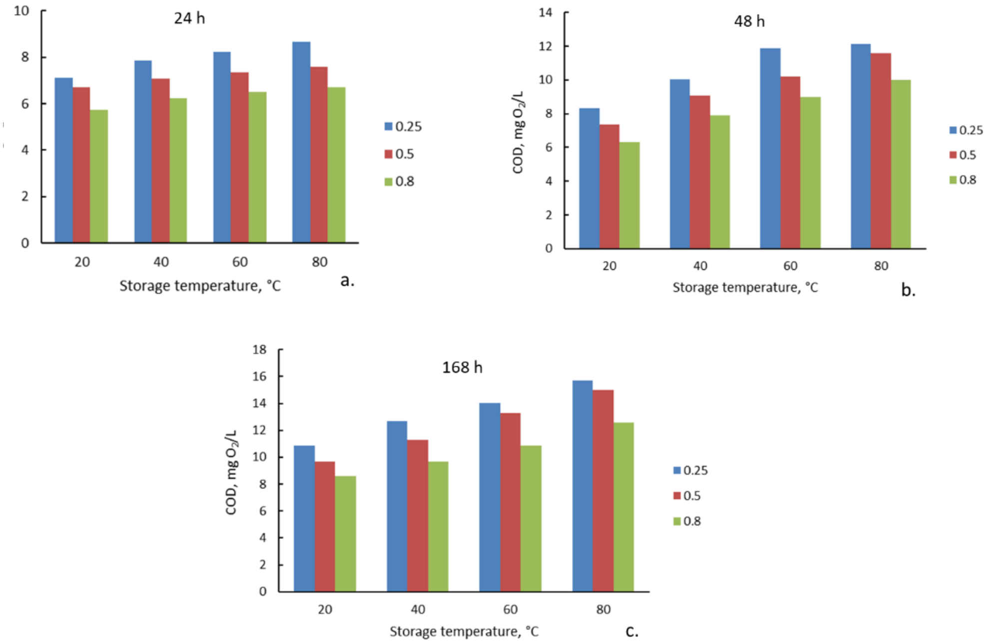

Fig. 1. Leaching behavior of PET containers depending on the storage temperature and analytical time: a. 24 h; b. 48 h; c. 168 h.

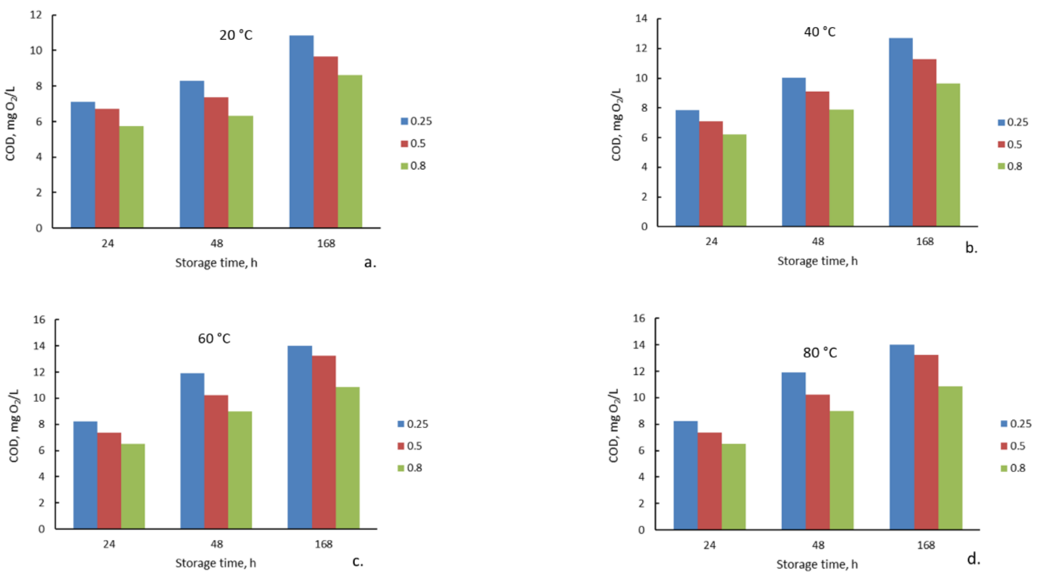

Fig. 2. Leaching behavior of PET containers depending on the storage time and temperature: a. 20 °C; b. 40 °C; c. 60 °C, d. 80 °C.

Fig. 3 and Fig. 4 show the mobility of organic contaminants in PET containers as a function of storage conditions as well as the thickness of PET containers wall. The mobility was calculated based on the results of the TCLP leaching tests as well as by using a leaching model adapted for this type of leaching tests (equation 1) [14].

$$C_{TCLP} = C_0 \frac{M_p}{V_l} \frac{A_p}{V_p} \left(\frac{4D_{obs}}{\pi}\right)^{0.5} t^{0.5} \tag{1}$$

where C_0 is the initial organic contaminant concentration into solid (g/kg), M_p/V_l is the solid-to-liquid ratio corresponding to the TCLP leaching test, A_p/V_p is the aria-to-volume ratio of PET particles and D_{obs} (m^2/s) is the observed diffusivity which expresses the mobility of organic contaminants. It should be noted that mobility is usually expressed as the negative logarithm of the observable diffusivity (-log D_{obs} or pD_{obs}), and therefore the higher its value, the lower the mobility of the contaminant.

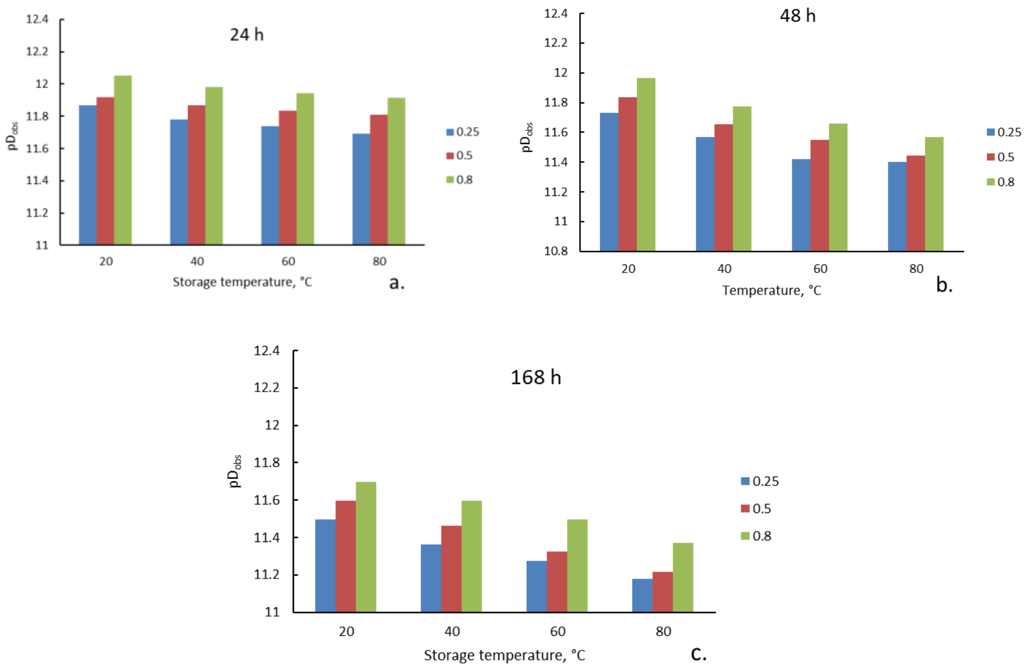

Fig. 3. The mobility of organic contaminants depending on the storage temperature and analytical time: a. 24 h; b. 48 h; c. 168 h.

The obtained results clearly indicate an increasing mobility of organic contaminants in PET, regardless of its thickness, under the influence of temperature and storage time. It should be taken into account that the observable diffusivity of organic contaminants is a characteristic that describes the long-term mobility of these contaminants in PET containers. Therefore, the results indicate that the tendency to increase the concentration of organic contaminants in the leachate with the increase in temperature and storage time of PET, regardless of the thickness of its walls, can be also long-term maintained, normally until the equilibrium is reached for the organic compounds (added during the manufacture of PET or entered into its composition through contamination during the recycling process) susceptible to leaching. susceptible to leaching. The fact that the mobility increases with the decrease in the thickness of the PET walls could indicate a predominantly diffusive mechanism for leaching of the organic contaminants.

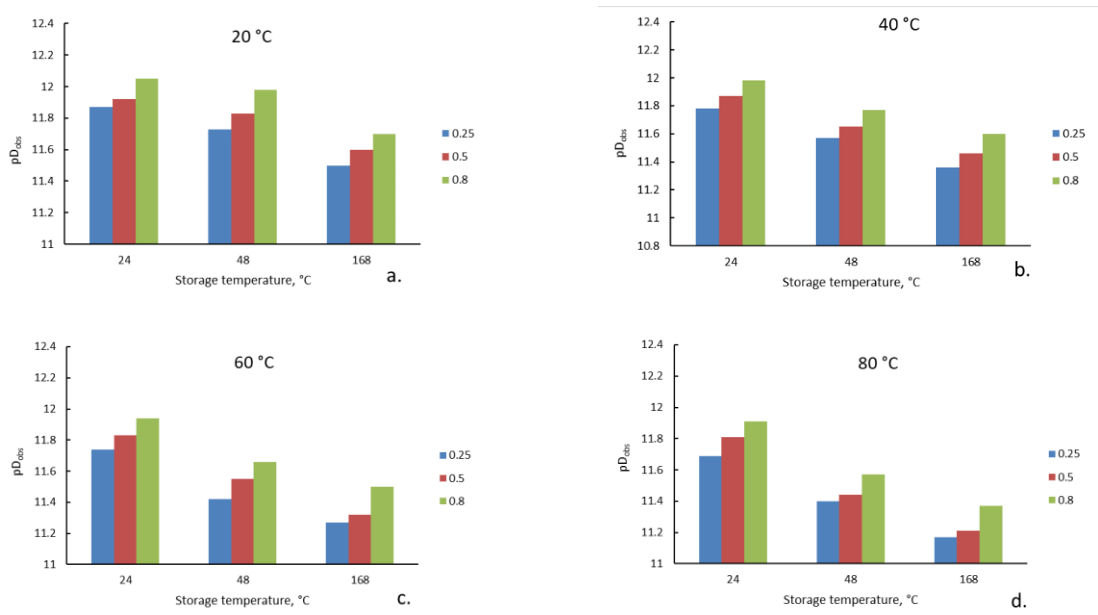

Fig. 4. The mobility of organic contaminants depending on the storage time and temperature: a. 20 °C; b. 40 °C; c. 60 °C, d. 80 °C.

The above hypothesis is also supported by the fact that the results obtained in this study regarding the mobility of organic contaminants (in general) in PET containers are closely related to the results obtained in a similar study that aimed to establish the mobility of Bisphenol A (a common contaminant of recycled PET containers) through dynamic leaching tests [15]. Thus, for PET with a wall thickness of 0.25 mm, an observable diffusivity (in terms of pD_{obs}) of Bisphenol A of 11.58 was established through dynamic leaching tests at a temperature of 20 °C, while for the same type of PET it was established through TCLP leaching tests an observable diffusivity of organic contaminants (in general) of 11.87 at the same temperature. However, the experimental results indicate a medium mobility ($11 < pD_{obs} < 12.5$) of organic contaminants in PET in all situations [16].

4. Conclusions

The main findings of the current work are:

1. The obtained results indicate an accentuated long-term leaching potential of organic contaminants from PET depending on their storage conditions.
2. The mobility of organic compounds susceptible to leaching from PET containers is influenced both by the PET storage conditions and by the thickness of their walls.
3. The increase in the mobility of organic contaminants along with the decrease in the thickness of the PET container walls indicates a predominantly diffusional leaching mechanism.

Acknowledgment:

This work has been funded by the European Social Fund from the Sectoral Operational Programme Human Capital 2014-2020, through the Financial Agreement with the title "Training of PhD students and postdoctoral researchers in order to acquire applied research skills - SMART", Contract no. 13530/16.06.2022 - SMIS code: 153734.

R E F E R E N C E S

[1]. *P. Sarda, J.C. Hanan, J.G. Lawrence, M. Allahkarami*, Sustainability performance of polyethylene terephthalate, clarifying challenges and opportunities, Journal of Polymer Science, **vol. 60**, 2022, 7-31.

[2]. *T.N. Tsironi, S.M. Chatzidakis, N.G. Stoforos*, The future of polyethylene terephthalate bottles: Challenges and sustainability, Packaging Technology and Science, **vol. 35**, 2022, 317-325.

[3]. *M.T. de A. Freire, A.P. Damant, L. Castle, L., F.G.R. Reyes*, Thermal stability of polyethylene terephthalate (PET): oligomer distribution and formation of volatiles, Packaging Technology and Science, **vol. 12**, 1999, 29-36.

[4]. *M. Mutsuga, T. Tojima, Y. Kawamura, K. Tanamoto*, Survey of formaldehyde, acetaldehyde and oligomers in polyethylene terephthalate food-packaging materials, Food Additives and Contaminants, **vol. 22,** 2005, 783-789.

[5]. *R.K. Foolmaun, T. Ramjeeawon*, Disposal of post-consumer polyethylene terephthalate (PET) bottles: comparison of five disposal alternatives in the small island state of Mauritius using a life cycle assessment tool, Environmental Technology, **vol. 33**, 2012, 563-572.

[6]. SW-846 Test Method 1311: Toxicity Characteristic Leaching Procedure, United States Environmental Protection Agency (USEPA), 1992.

[7]. *S.E. Musson, Y.-C. Jang, T.G. Townsend, I.-H. Chung*, Characterization of Lead Leachability from Cathode Ray Tubes Using the Toxicity Characteristic Leaching Procedure, Environmental Science and Technology, **vol. 34**, 2000, 4376-4381.

[8]. *V. Intrakamhaeng, K.A. Clavier, J.G. Roessler, T.G. Townsend*, Limitations of the Toxicity Characteristic Leaching Procedure for Providing a Conservative Estimate of Landfilled Municipal Solid Waste Incineration Ash Leaching, Journal of the Air and Waste Management Association, **vol. 69**, 2019, 623-632.

[9]. *K. Lewin*, Leaching tests for waste compliance and characterization: recent practical experiences, Science of The Total Environment, **vol. 178**, 1996, 85-94.
[10]. *Dhaka, V., Singh, S., Anil, A.G., Naik T.S.S.K., Shashank Garg S., Samuel J., Kumar M., Ramamurthy P.C., Singh J.* Occurrence, toxicity and remediation of polyethylene terephthalate plastics. A review. Environmental Chemistry Letters, **vol. 20**, 2022, 1777-1800.
[11]. *Bach C., Dauchy X., Chagnon M.C., Etienne S.* Chemical compounds and toxicological assessments of drinking water stored in polyethylene terephthalate (PET) bottles: a source of controversy reviewed. Water Research, **vol. 46**, 2012, 571-583.
[12]. *Keresztes S., Tatár E., Czégény Z., Záray G., Mihucz V.* Study on the leaching of phthalates from polyethylene terephthalate bottles into mineral water. Science of The Total Environment, **vol. 458-460**, 2013, 451-458.
[13]. *Y. Peng, J. Yang, C. Deng, J. Deng, L. Shen, Y. Fu*, Acetolysis of waste polyethylene terephthalate for upcycling and life-cycle assessment study, Nature Communications, **vol. 14**, 2023, 3249.
[14]. B. *Batchelor*, Leach models: theory and application, Journal of Hazardous Materials, **vol. 24**, 1990, 255-266.
[15]. *A.C. Mârşolea, F.L. Chiriac, C. Orbeci, L. Bobirică, C. Bobirică*, Migration and leaching behaviour of Bisphenol A from polyethylene terephthalate water bottles under different storage conditions, International Journal of Food Science and Technology, 2023, In Press.
[16]. Netherlands Normalisation Institute Standard (NNIS), Determination of leaching of inorganic components with the diffusion test. EA NEN 7375:2004, 2005, Bristol