National University of Science and Technology
POLITEHNICA Bucharest
Doctoral School Chemical Engineering and Biotechnologies

Ph.D THESIS

-SUMMARY-

Recovery of polyethylene terephthalate (PET) waste in the context of circular economy

Author: PhD.STUDENT Eng. Adriana-Cornelia Mârșolea (Cristea)
Supervisor: Prof. Cristina Orbeci

Special thanks

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INTRODUCTION

The need to approach this research topic derives from the adoption of mechanisms to ensure a long-term sustainable recovery, towards a circular economy, mainly aiming at the valorization of waste from plastic materials, an action aimed at reaching the optimal parameters towards a circular economy.

In an interconnected world, the adressing of this research area represents a challenge, due to the low level of the action toward a circular economy, explained by the financial difficulties, which led to an imbalance in achieving this path towards a circular economy. The novelty of this reserach aims in the valorization of plastic waste, in particulary polyethyleneterephtalate (PET), and another type of wastes like pyrite, red mud, fly ash and glass waste.

The thesis is formed by two parts entitled: literature study where the news in domain are presented, respectivelly the specific objectives for the sustenability concept and the original reserach.

Chapter 1 envisages the aspects of importance of the circular economy concept to the European and national level. Also, in Chapter 1, the aspects regarding the impact of the plastics to the human health, respectivelly to the enviroment are presented.

Chapter 2 presents the clasification and valorization of plastics from circular economy point of view.

In Chapter 3, the characteristics of PET, respectivelly the recycling and degradation methods are described.

In Chapter 4, the firts subchapter presents the justification of the topic choice, the aim and the objectives of the thesis, respectivelly the materials and methods used. Also, presents the synthesis and characterization of the PET depolymerized products.

Chapter 5 describes the migration and leaching tests of the organic contaminant Bisphenol A, the influence of temperature and storage time of non-carbonated water in

polyethylene terephthalate (PET) containers, while Chapter 6 presents the influence of storage conditions on polyethylene terephthalate (PET) containers.

The Chapters 7 and 8 present the synthesis and characterization of the new composites materials provided from the depolymerized PET with different filling agents that constitute industrial wastes as well.

Chapter 9 is dedicated to the general conclusions of the thesis resulting from the experimental studies that formed the basis of the original research.

The thesis concludes with the presentation of the original contributions, the further perspectives of research development, the list of published works and the conferences at which the experimental results were disseminated, as well as the bibliographic references.

The thesis contains 186 pages, 69 figures, 23 tables and 110 references.

The results of this work have been presented in 4 publications of which 2 articles in ISI rated journals and 1 article in the UPB Scientific Bulletin and 1 article in the process of publication. Also, the results were presented at 1 international conference.

I. LITERATURE STUDY

The concept of circular economy is a new model of approach to the production and consumption of products and the resulting waste.

The transition from a linear model: raw material - processing - consumption – waste, contributed to a rapid depletion of resources, but also to an explosive increase in the amount of waste, to a circular system is a complex process and with a strategic approach. Therefore, the concept of circularity is closely related to the efficiencient use of natural resources at system level, respectively with the entire product life cycle, as well as the transformation of waste into new products.

The importance of efficient waste management has as its general objective the prevention and reduction of the impact on the environment. Recycling and accounting for products will contribute to reducing the depletion of natural resources and significantly reducing the loss of biodiversity.

The circular economy aims to recycle waste instead of storing it, being known that effective management brings real benefits to the environment and human health, but also to the economy as a whole.

Poli(ethylene terephthalate) (PET)

Polyethylene terephthalate (PET) is a type of plastic that is smooth, transparent and relatively thin. Thus, PET is used for the production of drinking bottles and packaging material for different solid or liquid products. Also, this polymer acting as a gases barrier, prevents the contact between the oxygen and products [19]. PET can become dangerous in various severe environmental conditions, dut to the risk that certain contaminants, such as acetaldehyde, stidium, phthalates, etc., migrate into the packaged food.

In order to reduce the toxic effects of the plastic wastes on the enviromental and public health, the waste managment play an important role. Global reduction of plastic waste and ocean pollution requires improvements in the collection, treatment and proper disposal of plastic waste [32].

The recovery of waste from plastic materials in order to reduce environmental pollution can be achieved by encouraging their recycling for the manufacture of new products that comply with the quality. This initiative can lead to reducing of the negative impact on the environment and improving the quality of the population's health [37].

PET is obtaining by the reaction between bis (2 hidroxy ethyl terephthalate) and ethylene glycol. Due to the good resistance to the water, PET is used for bottles manufacturing for drinks. PET is easily recyclable and has the number "1" as the recycling symbol. According to a large number of reports worldwide, PET with an annual production of 56 metric tons, is the most used thermoplastic in the world. Textile Industry consumes about 60% of the amount of PET, other important consumers include the packaging and bottling industry with 30% [38].

PET degradation methods include: hydrolitic, thermic and biodegradation.

PET recycling include: chemical and mechanical methods.

Through the chemical recycling of PET, the macromolecular chains brake in the monomeric units or in oligomers [47]. Chemical recycling needs to be implemented on a large scale to become economically feasible. Compared to other recycling methods, chemical recycling is the only method that respects the principles of "sustainability" [48] because it produces original raw materials. Commercially available chemical recycling technologies [49] involve processes such as glycolysis, hydrolysis, methanolysis reactions and aminolysis.

Mechanical method of recycling

The most widely used is the mechanical recycling, which consists of obtaining clean PET flakes that are used directly or mixed with virgin polymer in the subsequent transformation process to obtain other end products [50]. After the plastic containers are sorted and separated from associated contaminants, washed and dried, they are ground (flaked), melted and reprocessed into plastic pellets by extrusion [51].

II. ORIGINAL CONTRIBUTIONS

The objectives of the research

The main objective of this work is to contribute to the rational and responsible use of resources, to achieve the secondary objectives that are the basis of the principles of sustainability and competitiveness, regarding the reduction of the amount of plastic waste. Also, the impact on human health and the environment and methods of valorization of plastic materials in the form of composite materials whose applications can contribute to the prevention of the generation of quantities of plastic waste have been investigated.

The main objectives of the thesis were:

1. Evaluation of the release of organic contaminants from PET containers;
2. The recovery of waste resulting from the consumption of drinks bottled in PET plastic containers.

Objective 1 was achieved by fulfilling the following 3 specific directions:

1a. Leaching tests of organic compounds from PET containers

1b. The influence of storage conditions of PET containers on the mobility of organic contaminants

1c. Migration and leaching of Bisphenol A from PET water containers

- ✓ Evaluation of migration and leaching of Bisphenol A
- ✓ The influence of temperature on the migration of Bisphenol A
- ✓ The influence of storage time on the migration of Bisphenol A
- ✓ Evaluation of the release of Bisphenol A from PET containers based on the Piringer migration model

The second objective assumed the fulfillment of two secondary directions, each with specific objectives:

1a. Utilization of depolymerized PET for the synthesis of composite materials

- ✓ Characterization of composite materials obtained

- ✓ Gel permeation cromatography
- ✓ FT-IR analysis
- ✓ SEM and EDX analysis
- ✓ Mechanical tests
- ✓ Thermal analysis

2a. Utilization of depolymerized PET for the synthesis of flexible composite materials

- ✓ Synthesis of composite materials
- ✓ Characterization of the obtained composite materials
- ✓ FT-IR analysis
- ✓ SEM and EDX analysis
- ✓ Mechanical tests
- ✓ Thermal analysis

CHAPTER 5 - MIGRATION AND LEACHING OF BISPHENOL A FROM PET WATER CONTAINERS

The objective of this chapter is to evaluate the release of Bisphenol A from several assortments of PET containers used for bottling non-carbonated mineral water through migration and leaching tests. The influence of temperature and storage time of non-carbonated mineral water in PET containers on the degree of release of Bisphenol A from them (migration tests) is also presented. The potential for water contamination with Bisphenol A, due to its long-term storage in PET containers was also evaluated (leaching tests).

5.2. THE INFLUENCE OF TEMPERATURE ON THE MIGRATION OF BISPHENOL A

The release of Bisphenol A from PET samples at two storage temperatures, i.e. 3°C, which is the typical temperature for food and beverage storage in cold, and 23°C, which is the temperature for room temperature storage, are presented in Fig. 5.1.

As can be seen, there is an important difference between the three PET brands in terms of BPA release. In the case of brand A (samples S1 and S2), apparently Bisphenol A is released from PET only at room temperature, its concentration in bottled water being 0.28 ng/L after two weeks of storage. For brand B (samples S3 and S4), the concentration of Bisphenol A in bottled water is below the limit of quantification (LOQ), regardless of the storage temperature. As for brand C (samples S5 and S6), Bisphenol A is released from PET at both storage temperatures, but more pronounced at room temperature. Thus, the concentration of Bisphenol A in bottled water is approximately three times higher for PET containers stored at room temperature compared to those stored at 3°C. Also, the concentration of Bisphenol A in the water in the C brand PET container stored at room temperature is more than five times higher than in the A brand PET container. However, the determined Bisphenol A concentrations are below the accepted limits according to Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption, which are up to 2.5 µg/L [64].

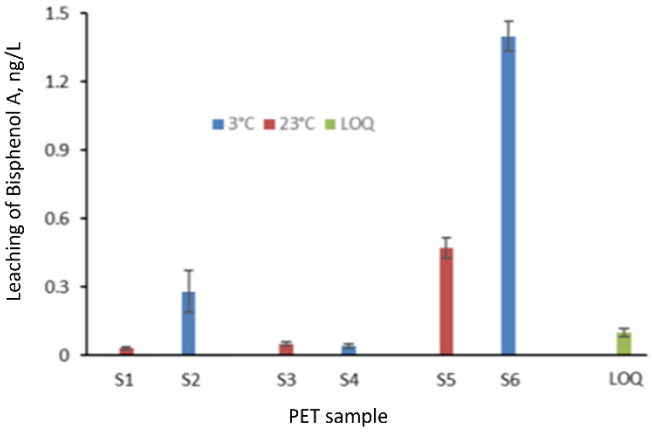


Fig. 5.1. Bisphenol A released from PET samples: brand A (S1 and S2); brand B (S3 and S4); brand C (S5 and S6); LOQ – limit of quantification

It should be noted that there is no information on the raw material from which PET containers are made, regardless of brand, in the sense that it is not known whether they were manufactured using virgin or recycled polyethylene terephthalate. Also, if the raw material comes from recycled PET, it is not known how many times it has been recycled. If Bisphenol A is present in PET only as a contaminant, then its presence in bottled water depends on the raw material and the manufacturing process of the PET containers. Also, the release of Bisphenol A from the PET container depends on the physico-chemical properties of the PET container as a product, but also on its stability in different environmental conditions. This statement could be supported by the different degree of release of bisphenol A from the containers of the investigated brands, containers stored under different storage conditions.

5.3. INFLUENCE OF STORAGE TIME ON BISPHENOL A MIGRATION

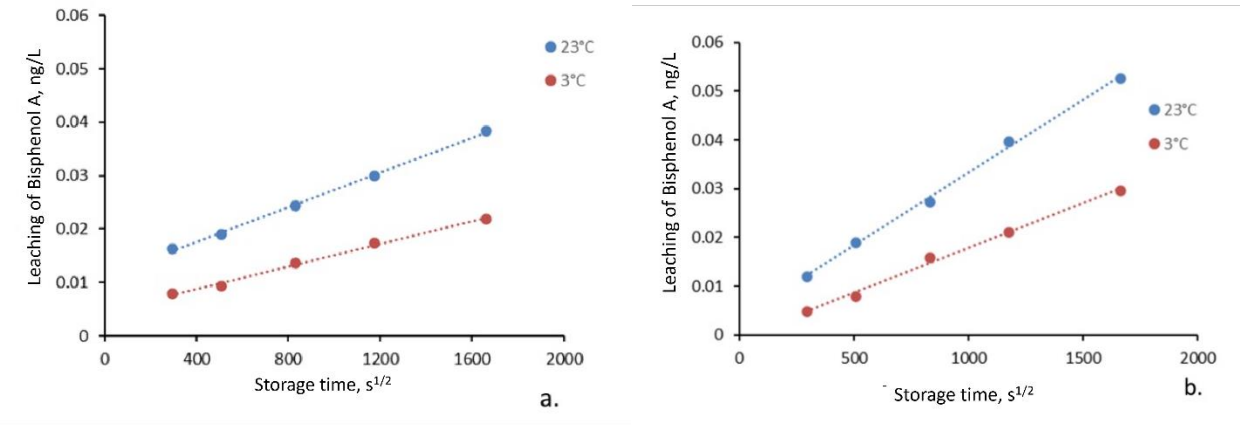


Fig. 5.2. Bisphenol A migration kinetics from PET bottles: a. PET brand D (not used); b. PET brand C (used)

Table 5.2. Co-logarithmic values of diffusion coefficients calculated from experimental data and predicted by the model (brand C: S7 and S8; brand D: S9 and S10).

Sample	S7	S8	S9	S10
pD_{exp}	12.83	11.90	12.64	11.58
pD_{mod}	12.8	11.52	12.80	11.52

The results obtained after the comparison between the co-logarithmic values of the diffusion coefficients predicted by the model and calculated from the results of the migration tests are shown in figure 5.3. As can be seen, the values of these co-logarithms are quite close to each other, with a slight underestimation of the model for sample S8. This result demonstrates once again that the mobility of the migrant is highly dependent on the physicochemical properties of the polymer matrix.

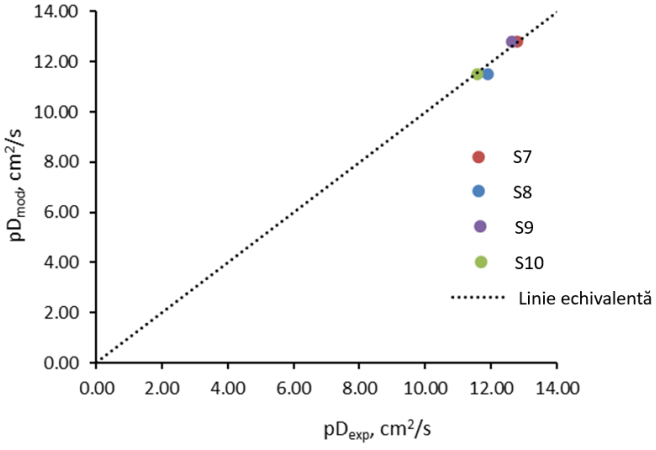


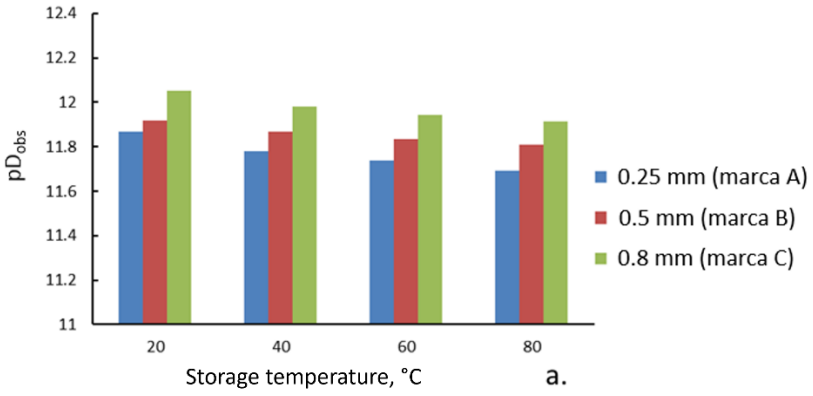
Fig. 5.3. Comparison between cologarithmic values of diffusion coefficients predicted by the model and calculated from migration test results (PET brand C: S7 and S8; PET brand D: S9 and S10)

CHAPTER 6 - LEACHING OF PET FROM WATER CONTAINERS

Figure 6.3 and Figure 6.4 show the mobility of organic compounds in PET containers as a function of storage conditions as well as the wall thickness of the PET containers. Mobility was calculated based on the results of TCLP leaching tests as well as by using a leaching model adapted for this type of leaching tests (equation 6.1) [67].

$$C_{TCLP} = C_0 \frac{M_P}{V_l} \frac{A_P}{V_P} \left(\frac{4D_{obs}}{\pi}\right)^{0,5} t^{0,5} \qquad (6.1)$$

Where: C_0 is the initial concentration of the organic contaminant in the solid (g/kg), Mp/Vl is the solid-liquid ratio corresponding to the TCLP leaching test, Ap/Vp is the area-volume ratio of the PET particles and D_{obs} (m^2/s) is the diffusivity observed that 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 the value, the lower the mobility of the contaminant.



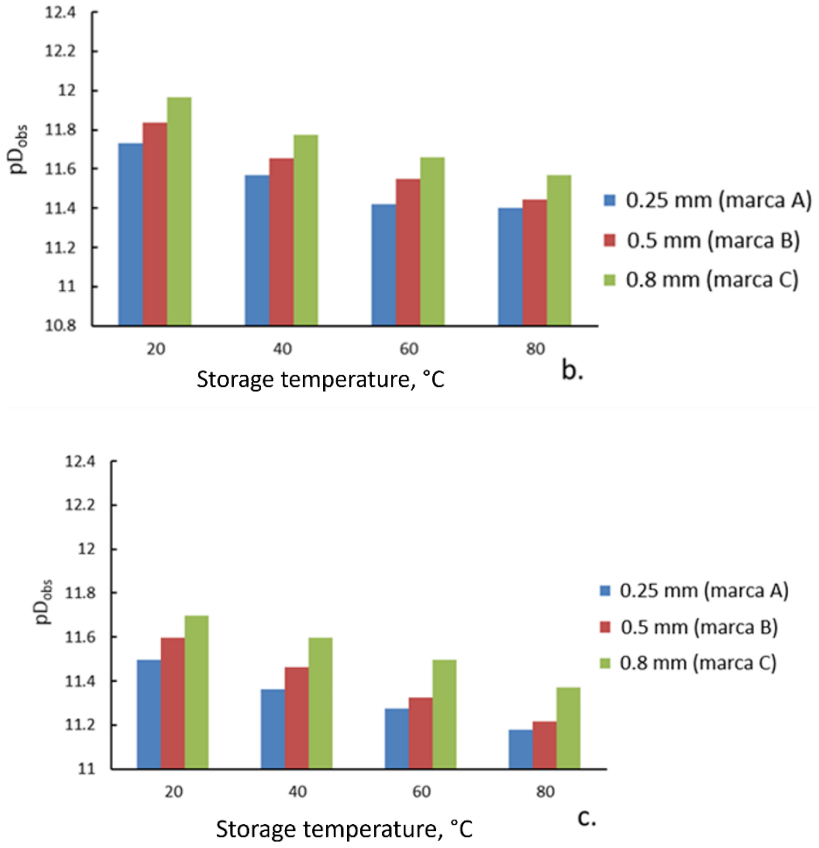
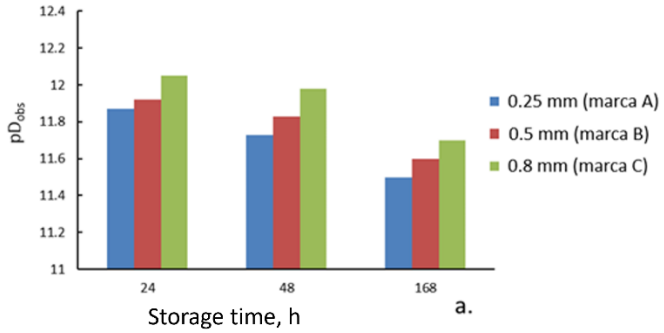


Fig. 6.3. Mobility of organic contaminants according to storage temperature: a. 24 h; b. 48 h; c. 168 h.



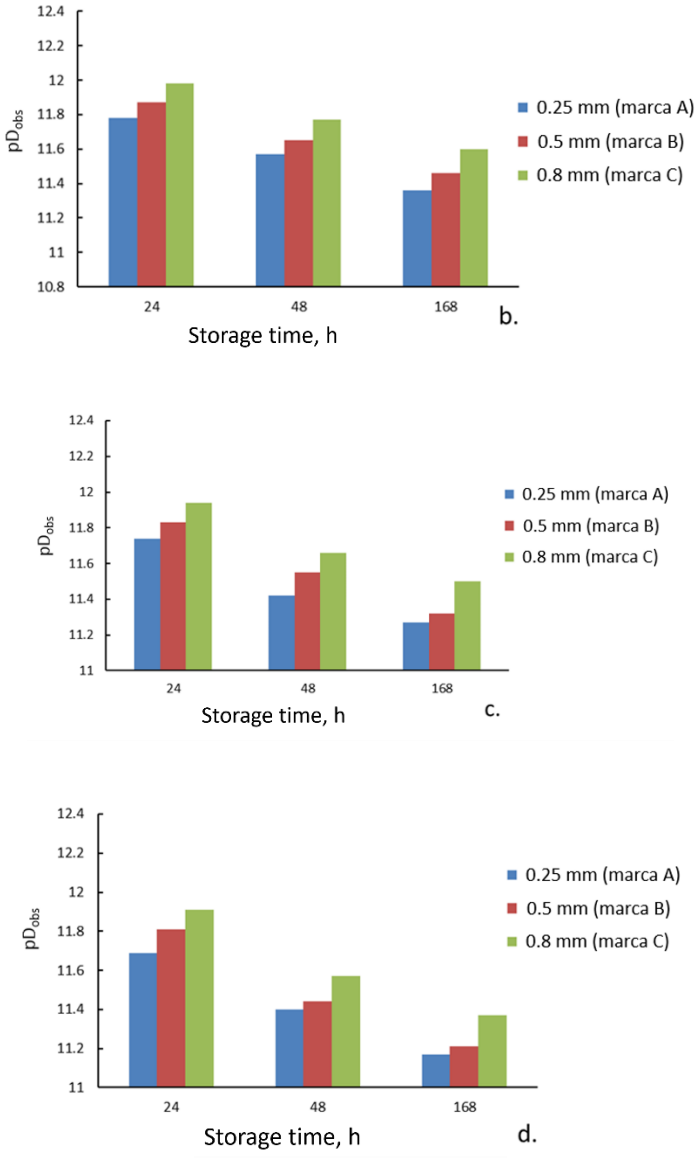


Fig. 6.4. Mobility of organic contaminants according to storage time: a. 20 °C; b. 40 °C; c. 60 °C, d. 80 °C.

CHAPTER 7 - RECOVERY OF PET WASTE IN COMPOSITE MATERIALS

The main purpose of this study was to valorize PET waste, by synthesizing and characterizing new composite materials based on polyurethane foam filled with two types of inorganic industrial waste: pyrite ash and red mud. Applications consider the retention of Hg^{2+} from contaminated water for the first category of polyurethane and pyrite based

composites, while the second category of polyurethane foam and red mud based materials may find applicability in pavement rehabilitation.

7.1.1. PET depolymerization

PET waste (brand C: used containers) from still water containers was ground after removing the cap into small pieces of 3 x 4 mm ± 1 mm. In a reactor equipped with a mechanical stirrer, condenser and thermostat, were added 240 g of polyethylene terephthalate, 150 g of diethylene glycol and 1.5 g of zinc acetate as a catalyst as detailed in figure 7.1.c Reaction was performed on a laboratory scale in a nitrogen atmosphere at a temperature of 220 °C under continuous stirring for 2 hours.

Catalytic depolymerization of polyethylene terephthalate in the presence of ethylene glycol led to the formation of bis-(2-hydroxydiethyl) terephthalate (BHDET) [68] as described in figure 7.2.

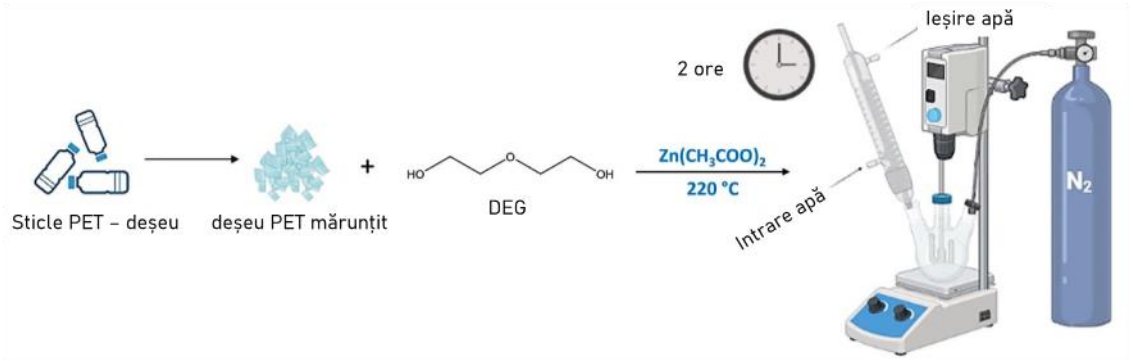


Fig. 7.1. Laboratory installation of polymerization of PET waste

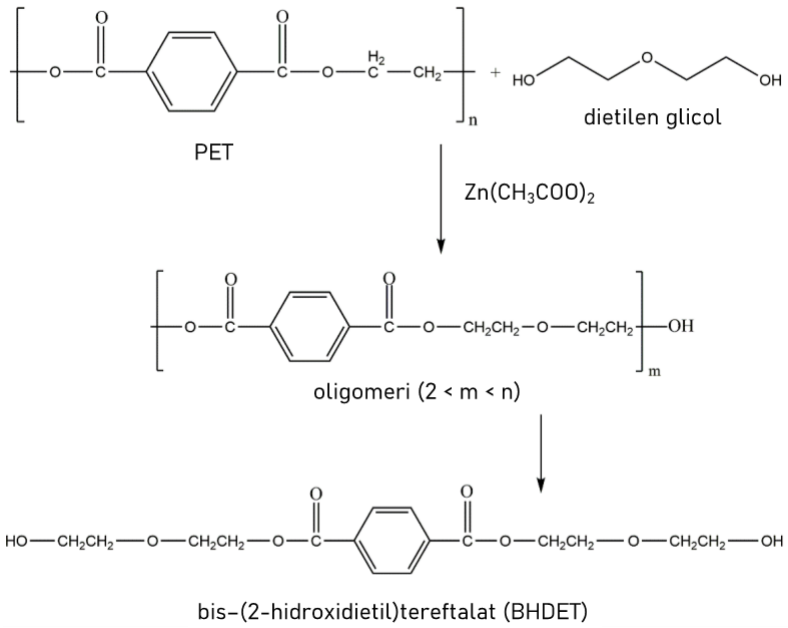


Fig.7.2. Depolymerization reactions for PET in the presence of DEG

7.1.2. Synthesis of the polyurethane foams

Table 7.2. presents the compositions of the synthesized materials

Sample	Polyol, g	MDI, g	Castor oil, g	Pyrite, g	Red mud, g
Blank sample	2	2	1	-	-
PUR-py-1	2	2	1	0,2	-
PUR-py-2	2	2	1	0,3	-
PUR-py-3	2	2	1	0,4	-
PUR-rm-1	2	2	1	-	0,2
PUR-rm-2	2	2	1	-	0,3
PUR-rm-3	2	2	1	-	0,4

7.2. Characterization of the polyurethane composite materials

7.2.2. Determination of the density of composite materials

The density of the synthesized composite materials was determined according to the standardized procedure ASTM D 7710-14, the values of the obtained densities being presented in table 7.3

Table 7.3. Density of polyurethane composite materials

Sample	Densities, kg/m^3
Blank sample	112
PUR-py-1 (0,2 g)	136
PUR-py-2 (0,3 g)	154
PUR-py-3 (0,4 g)	132
PUR-rm-1 (0,2 g)	143
PUR-rm-2 (0,3 g)	123
PUR-rm-3 (0,4 g)	126

7.2.3. SEM Microscopy and EDX Mapping for Polyurethane Foams

The SEM images shown in figure 7.8 revealed a porous structure for the blank foam (figure 7.8a), modified with pyrite (figure 7.8b-d) and modified with red mud (figure 7.8e-g). Although, the concentration of fillers increased in series PUR-py-1 to PUR-py-3 and PUR-rm-1 to PUR-rm-3, respectively, there was no significant change in pore size from one composite specimen to another.

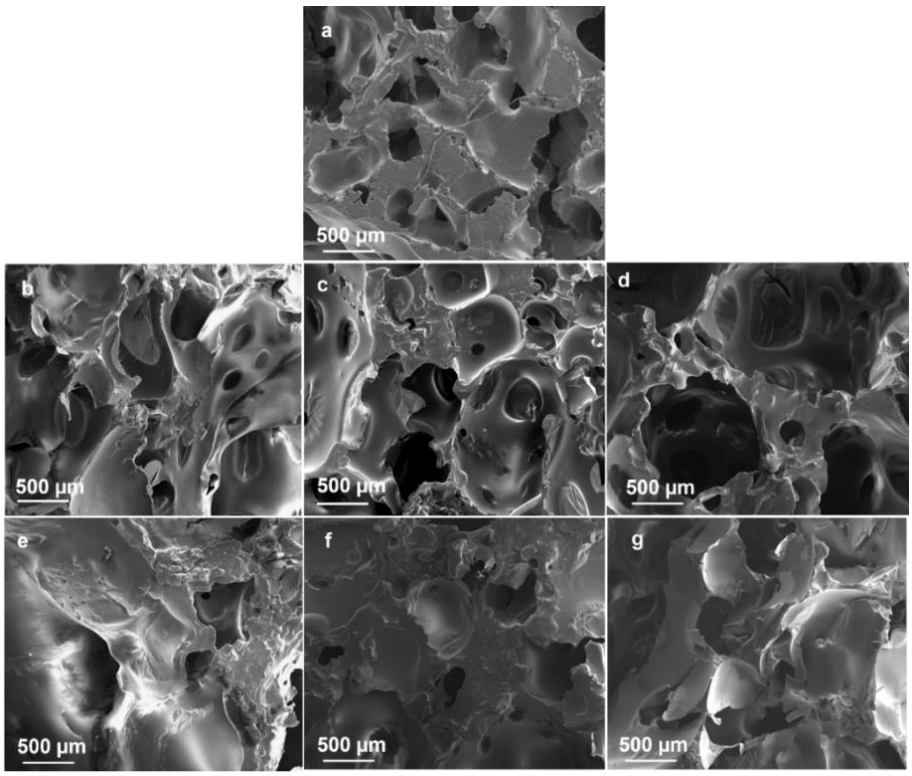


Fig. 7.8. SEM images of the control sample (a), polyurethane foams filled with pyrite (b: 0.2 g; c: 0.3 g; d 0.4 g), respectively with red mud (e: 0.2 g; f: 0.3 g; g 0.4 g)

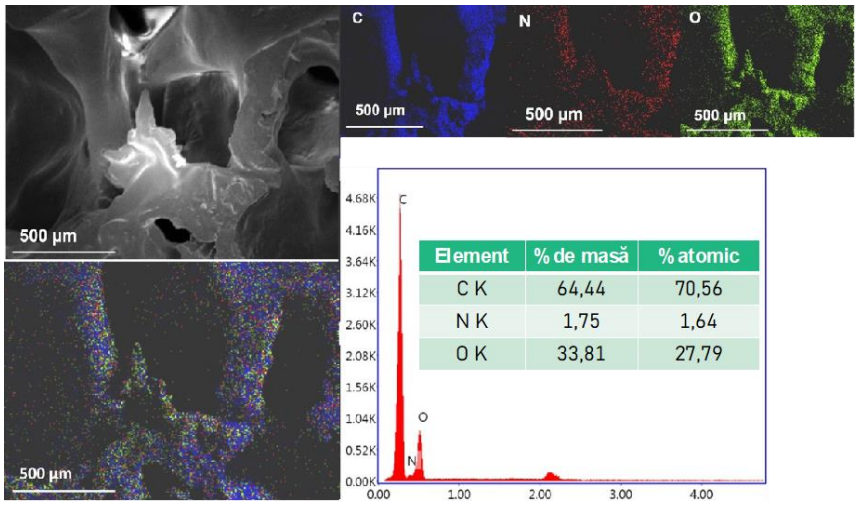


Fig. 7.11. EDX spectrum and EDX maps for the blank sample

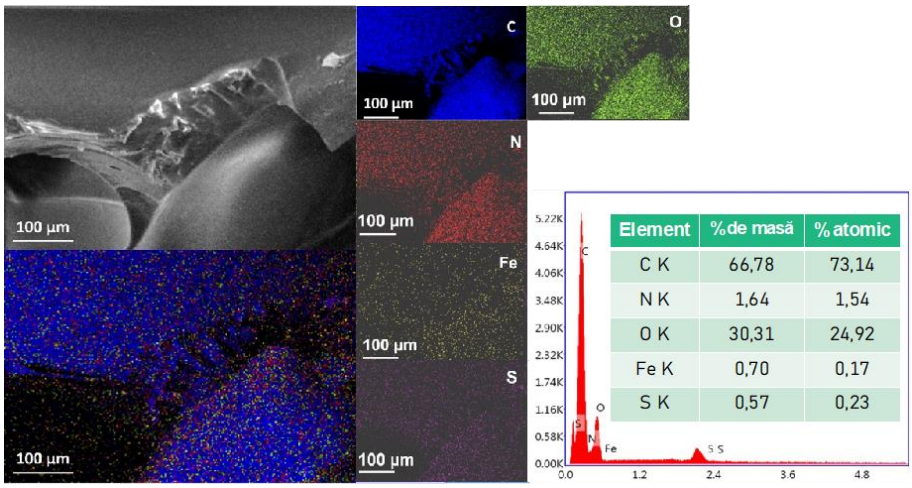


Fig. 7.12. EDX spectrum and EDX maps for sample PUR-py-1 (0.2 g)

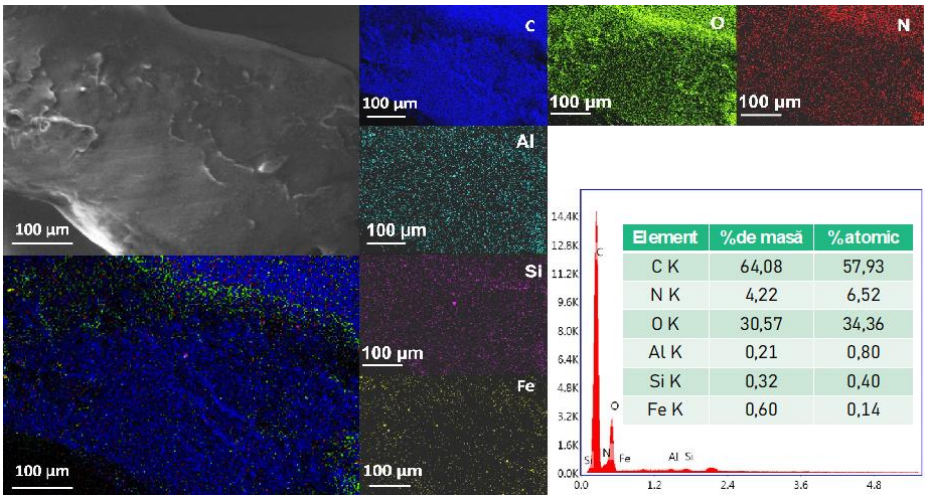
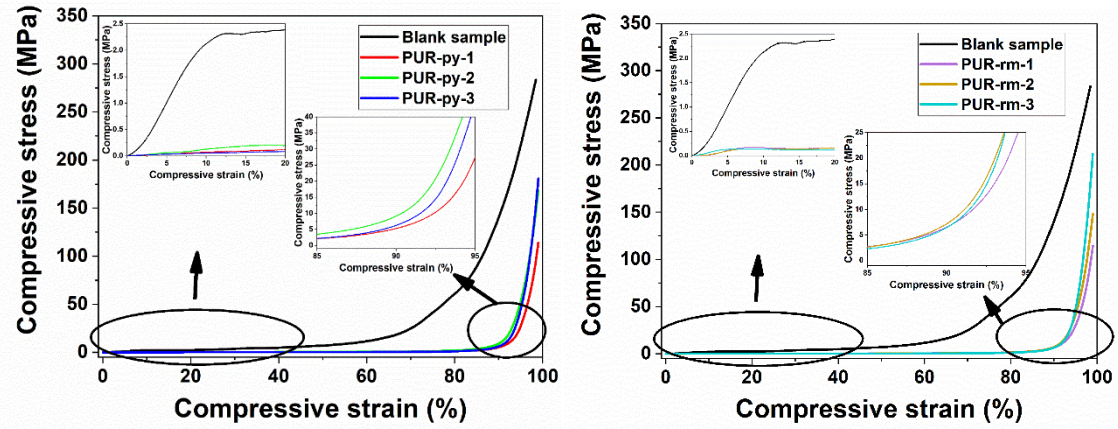


Fig. 7.15. EDX spectrum and EDX maps for sample PUR-rm-1 (0.2 g)

In conclusion, EDX mapping confirmed the uniform distribution of elements in all cases, agreeing with the SEM analysis which showed a good distribution of fillers in the 3D PUR foam structure.

7.2.4. Mechanical resistance

In figure 7.18, the compression force was graphically represented as a function of the compression deformation for the blank sample and the polyurethane foams filled with pyrite (figure 7.18A), respectively with red mud (figure 7.18B). Based on the shape of the curves, three regions (elastic zone, plateau zone and densification zone) were identified that characterize the mechanical behavior of all the samples and they are in agreement with the data from the specialized literature [77].



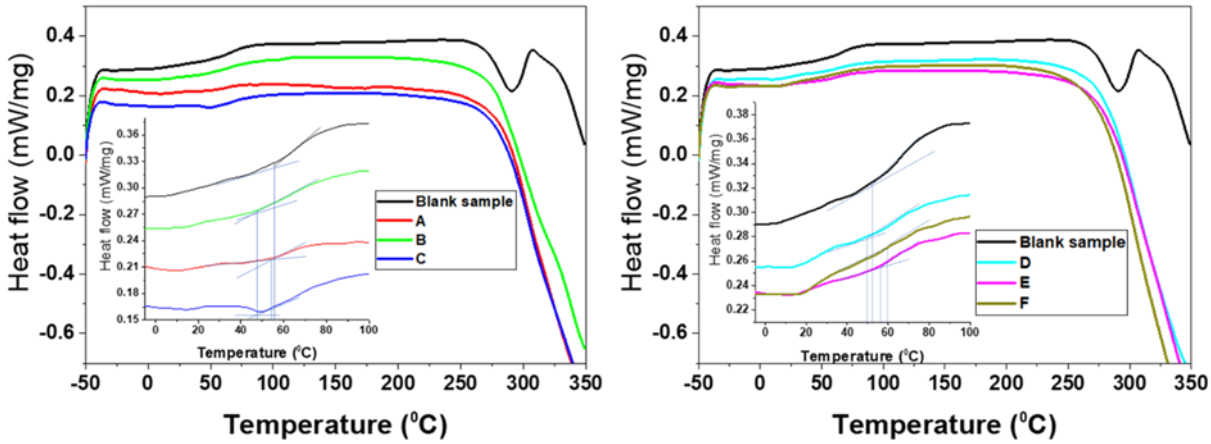
A B

Fig. 7.18. Compression tests for blank sample and polyurethane foams filled with pyrite (A), respectively red mud (B)

In conclusion, both types of samples recorded good compression performance regardless of the reinforcing agent type, but the establishment of a clear dependence with the density values was not possible due to the fact that the samples do not present a high homogeneity due to the difficult dispersion of the filler in component A (table 7.4) [92-94]. In all cases, regardless of the reinforcing agent used, the densification stage was achieved for compressive strain values greater than 95% (Figure 7.18A and Figure 7.18B).

7.2.5. Thermal resistance

The DSC (**Fig. 7.20**) was utilized to determine the glass transition temperature (Tg) for the synthesized materials (**Table 7.5**). It was determined that the Tg values decrease with the increase of the pyrite filler concentration (**Fig 7.19A**), while for the red mud containing samples the Tg varies: $Tg_{PUR\text{-}rm\text{-}3} > Tg_{PUR\text{-}rm\text{-}2} > Tg_{blank} > Tg_{PUR\text{-}rm\text{-}1}$. In the case of pyrite samples, the behavior can be attributed to flexibility of the macromolecular chain flexibility. Probably, given the more consistent shape and smaller particle size of the pyrite waste compared to the red mud, the pyrite particles have a more uniform distribution in the polymer matrix and the polymer chains are more susceptible to cover the pyrite particles or to flow between the reinforcing agent particles (**Fig 7.21**). For the red mud samples, aggregates with larger volume are formed and the polymer chain movement is impeded which results in a lower flexibility compared to the other samples (**Fig 7.21**).



A **B**

Fig. 7.20. DSC analysis for PUR foams modified with pyrite (A) and with red mud (B) PUR-py-1: 0.2 g; PUR-py-2: 0.3 g; PUR-py-3: 0.4 g; PUR-rm-1: 0.2 g; PUR-rm-2:0.3 g; PUR-rm-3: 0.4 g

Tabel 7.5. The values of the transition temperature, Tg, all samples.

Sample	Tg, °C	Sample	Tg, °C
Blank sample	**57**		
PUR-py-1 (0,2 g)	**55**	PUR-rm-1	**50**

PUR-py-2 (0,3 g)	**47**	PUR-rm-2	**57**
PUR-py-3 (0,4 g)	**49**	PUR-rm-3	**60**

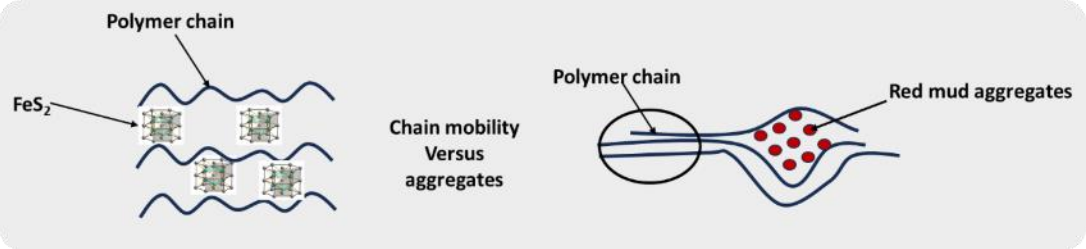


Fig. 7.21. Possible behavior of polymer chains in the presence of pyrite and red mud aggregates

CHAPTER 8 – PET VALORIZATION AS FLEXIBLE POLYURETHANE FOAMS

In this chapter are presented the synthesis and characterization of polyurethane foams (PUR) obtained using products from the depolymerization of poly(ethylene terephthalate) (PET) and two types of fillers: fly ash and glass waste.

Figure 8.1 presents the production procedure for the polyurethane foam.

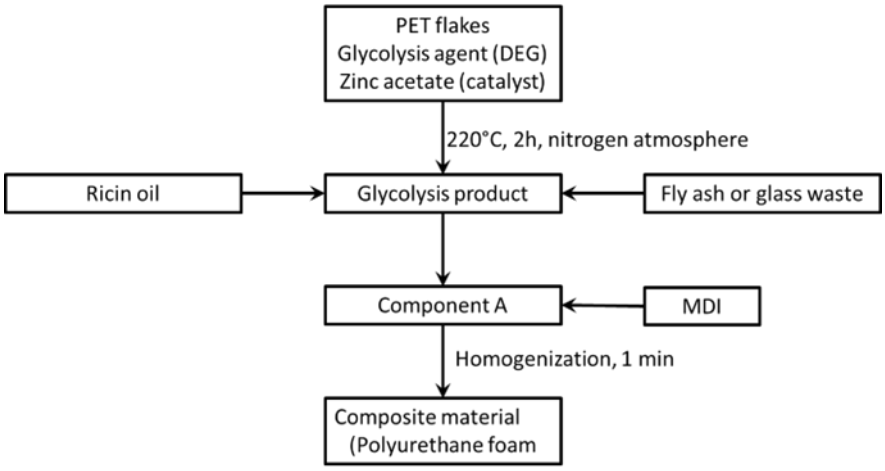


Fig. 8.1. Synthesis procedure for flexible polyurethane foams with fly ash or glass waste

In all compositions the molar ratio between the NCO/OH (1.3) was kept constant (Table 8.1). The concentration of the filling agent for the two types of materials varied between 4 and 8%, the code of the sample reflecting the amount of filler.

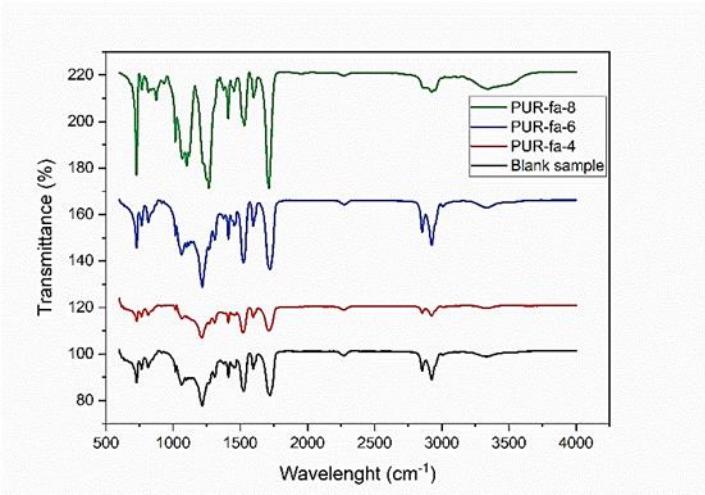
Tabel 8.1. Composition of the samples

Sample	Polyol, g	MDI, g	Castor oil, g	Fly ash, g	Glass waste, g
Blank	2	2	1	-	-
PUR-fa-4	2	2	1	0,2	-
PUR-fa-6	2	2	1	0,3	-
PUR-fa-8	2	2	1	0,4	-
PUR-gw-4	2	2	1	-	0,2
PUR-gw-6	2	2	1	-	0,3
PUR-gw-8	2	2	1	-	0,4

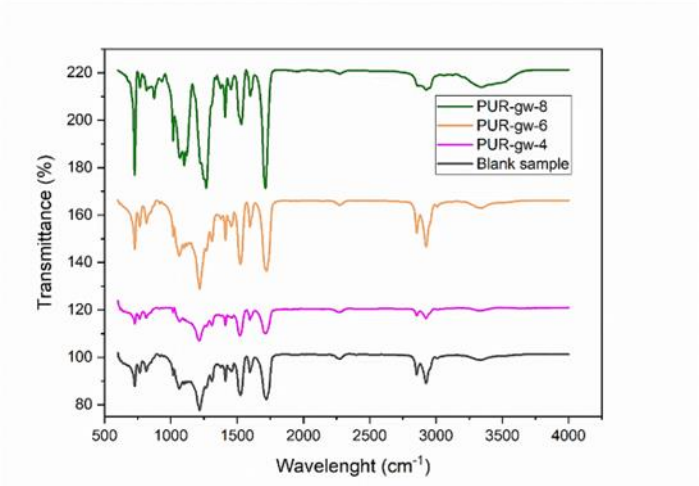
8.2.1. FT-IR analysis of the polyurethane foams

To demonstrate the efficient reaction between the PET derived polyol and the diisocyanate component (MDI), the PUR samples were investigated by FT-IR analysis (**Fig. 8.4.**).

In **Figure 1a and Figure 1b** the FT-IR analysis evidenced the characteristic vibrations of polyurethane structure for all samples filled with fly ash [73] and glass waste. The signal from 3332 cm^{-1} attributed to NH stretching and the signal from 1721 cm^{-1} assigned to C=O stretching confirmed the formation of urethane groups due to the reaction between the OH groups and NCO groups from MDI [73].



(a)



(b)

Fig. 8.4. FT-IR spectra of blank sample and polyurethane foams based on fly ash (a) and glass waste (b); PUR-fa-4: 0.2 g; PUR-fa-6: 0.3 g; PUR-fa-8: 0.4 g; PUR-gw-4: 0.2 g; PUR-gw-6: 0.3 g; PUR-gw-8: 0.4 g.

8.2.2. SEM and EDX analysis of the polyurethane foams

In **Fig 8.7**, the SEM micrographs indicate a close cellular structure specific to polyurethane foams [99]. It can be observed that as the filling agent concentration increases the size of the pores decreases. In the case of the polyurethane foams containing fly ash **fig 8.7b, c, d** the SEM images indicate that the pores of the PUR-fa-8

are smaller compared to the blank sample or the two other samples with fly ash (PUR-fa-4 and PUR-fa-6). The same behavior was observed for the glass waste samples (**Fig 8.7e, f, g**). Thus, the material in which the smallest pores were formed contains the highest concentration of filler (PUR-gw-8) compared to PUR-gw-4 and PUR-gw-6. At the same time, the number of pores increases with the increase of filler content. Thus, PUR-fa-8, respectively PUR-gw-8 presented the largest number of pores based on the SEM analysis (**Fig 8.7d**, respectively **Fig 8.7g**).

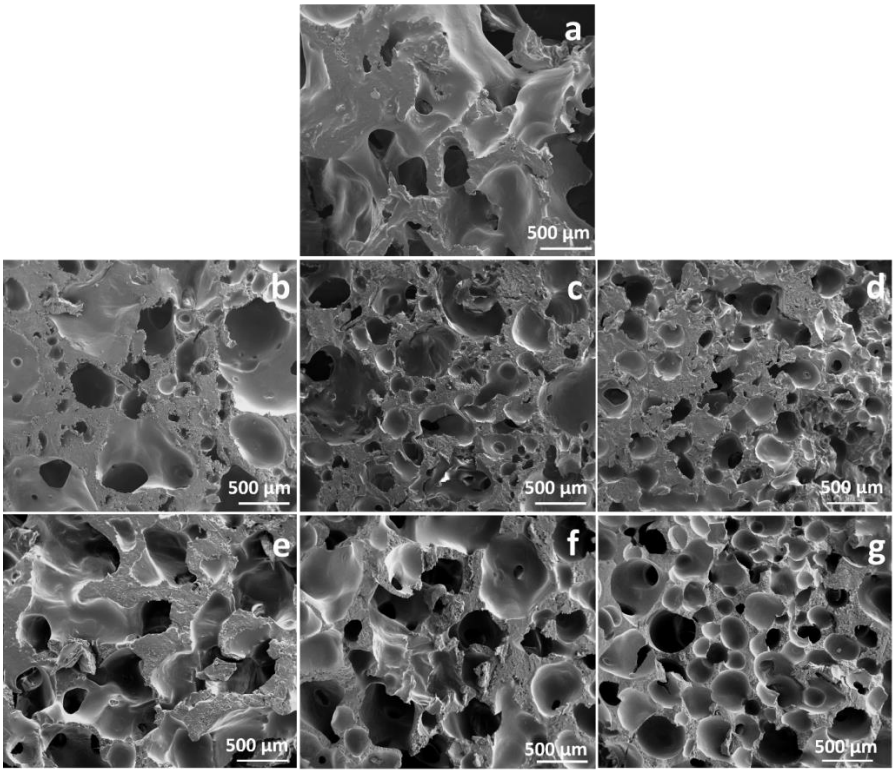
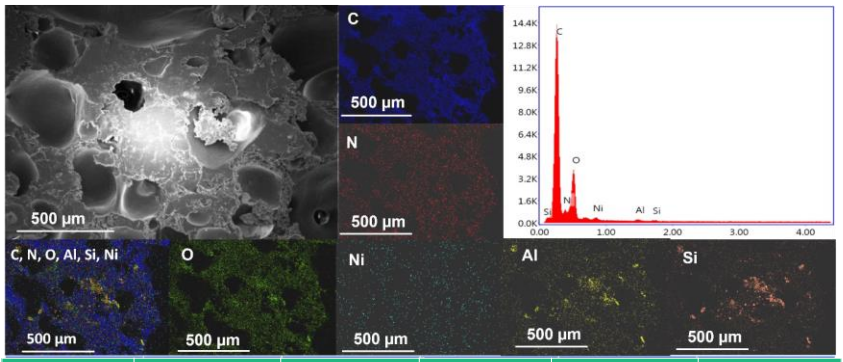


Fig. 8.7. SEM micrographs of the blank polyurethane foam (a) and polyurethane specimens filled with fly ash (Samples PUR-fa-4, PUR-fa-6, and PUR-fa-8) (b, c, d), respectively waste glass (Samples PUR-gw-4, PUR-gw-6, and PUR-gw-8) (e, f, g)

In the case of composite polyurethane foams containing the two types of filling agents, the mechanical properties can be drastically influenced by the distribution of the filler in the polymer matrix. For this reason, the EDX analysis of the sample was performed. The EDX spectra and the EDX mapping revealed the distribution of the most important constituents in the material with the most intense signal for the different metal

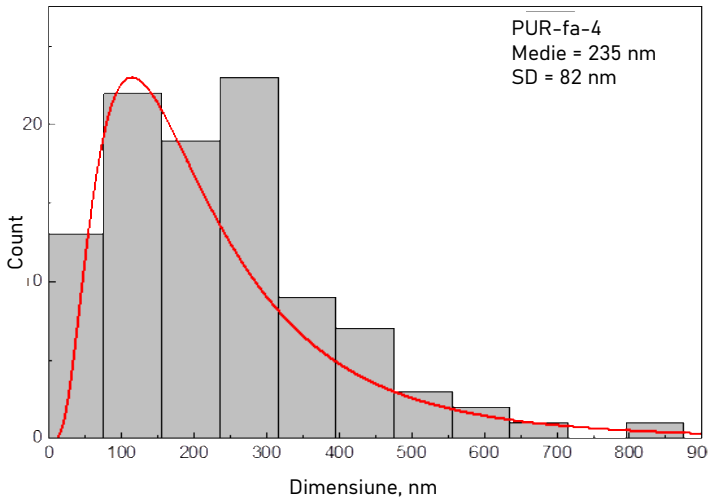
oxides identified in the two types of waste materials as presented by the XRF analysis (Table 4.3).

The pore size of the polyurethane foams containing fly ash – samples PUR-fa-4, PUR-fa-6 și PUR-fa-8 (**Fig 8.9, 8.10 and 8.11**) was determined based on the SEM analysis and they varied between 23 µm up to 800 µm (PUR-fa-4), 28 µm up to 750 µm (PUR-fa-6) and 30 µm up to 444 µm (PUR-fa-8). The highest percentage of pores were found to be within 98 – 302 µm, 46 – 198 µm, 51 – 202 µm diameter pore range having the mean diameter 235 ± 82 µm, 178 ± 65 µm, 178 ± 58 µm, respectively.



Element	%de masă	%atomic	Element	%de masă	%atomic
C K	58,97	65,73	Ni K	1,09	0,25
N K	6,43	6,14	Al K	0,34	0,17
O K	33,01	27,62	S K	0,17	0,08

(a)



(b)

Fig. 8.9. EDX spectrum and EDX mapping analysis of polyurethane foam filled with fly ash (a) and pore size distribution (b) for sample PUR-fa-4 (0.2 g).

In **Table 8.2** are presented the data obtained for the distribution of the pore size for all the samples in a concise manner to highlight the difference between the samples. To obtain a correlation between the porosity and density, the median values for these parameters were represented in a graphic for all the samples, as presented in **Fig 8.15.** The values for the density (according to the data presented in Table 8.3) in the case of the PUR modified with fly ash have increased as the filler content increased from sample PUR-fa-4 to PUR-fa-8 while the pore dimensions decreased. The same tendency was observed the glass waste. The density values for the polyurethane foams containing glass waste were lower compared to the fly ash samples, which can be attributed to the particle dimensions of the filler used (**Fig 8.16)**. It is worth mentioning that this correlation is in good agreement with literature data [101] and the values obtained for density ranging from 112 kg/m3 (Blank sample) to 168 kg/m3 (PUR-fa-8) are specific for flexible foams [102].

Tabel 8.2. Characterization of PUR foams - determination of pore size distribution

Sample	**Median value of the pores (μm)**	**SD (μm)**	**Min-Max (μm)**	**FWHM (μm)**
Blank sample	220	78	48 -635	100-255
PUR-fa-4 (0,2 g)	235	82	23-800	98-302
PUR-fa-6 (0,3 g)	178	65	28-750	46-198
PUR-fa-8 (0,4 g)	178	58	30-444	51-202
PUR-gw-4 (0,2 g)	259	95	36-561	89-269
PUR-gw-6 (0,3 g)	233	105	27-754	51-225
PUR-gw-8 (0,4 g)	182	75	49-523	63-201

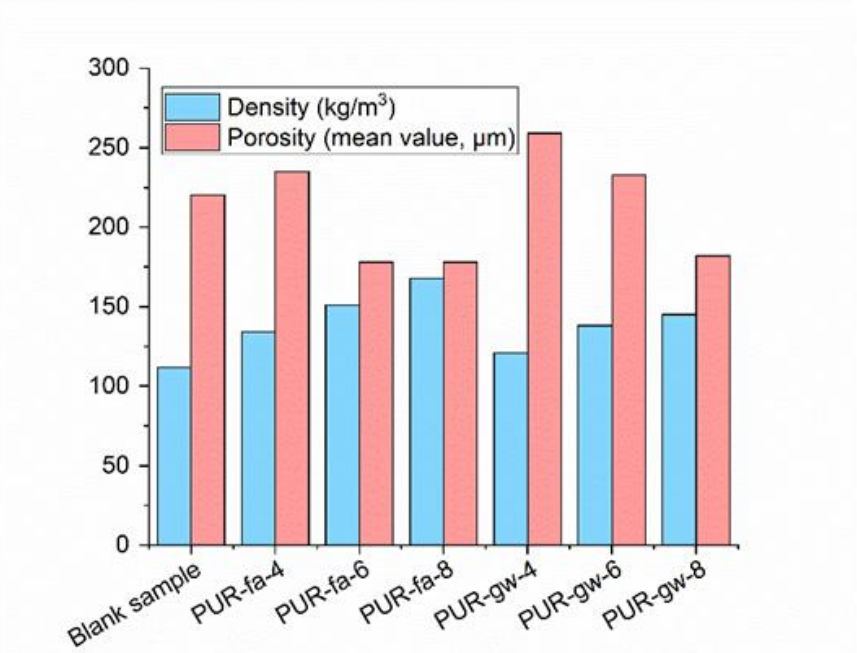
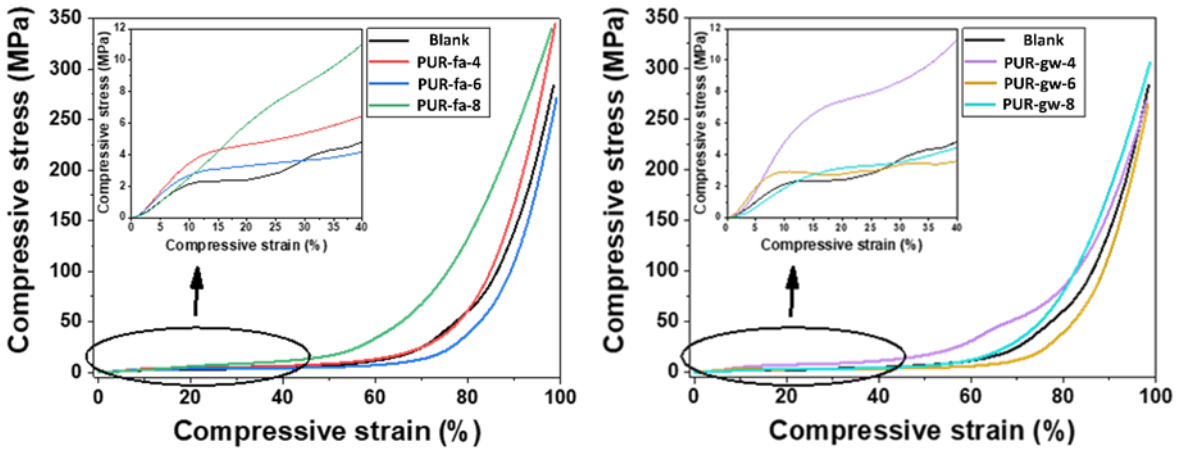


Fig. 8.15. The mean values for porosity and density for all PUR specimens; PUR-fa-4: 0.2 g; PUR-fa-6: 0.3 g; PUR-fa-8; PUR-gw-4: 0.2 g; PUR-gw-6:0.3 g; PUR-gw-8: 0.4 g

8.2.3. Mechanical test for polyurethane foams

In figure 8.17, the compression stress is graphically represented as a function of the compression strain for the blank samples and the PUR foams filled with fly ash (figure 8.17A), respectively with glass waste (figure 8.17B).

Mechanical compression tests of the PUR foam confirmed that the compressive stress and compressive strain increased for the samples where the lowest concentration of filler was added. Thus, the best mechanical performances were recorded for the sample PUR-fa-4 (figure 8.17A – detailed image), respectively PUR-gw-4 (Figure 8.17B – detailed image). Based on the shape of the curves, it can be seen that three regions characterize the mechanical behavior of all samples, namely the elastic zone, the plateau zone and the densification zone, zones also confirmed by Petrů and Novák [103].



(A) **(B)**

Fig. 8.17. Compression tests for blank sample and polyurethane foams filled with fly ash **(A)**: PUR-fa-4: 0.2 g; PUR-fa-6: 0.3 g; PUR-fa-8**,** respectively glass waste **(B)**: PUR-gw-4: 0.2 g; PUR-gw-6:0.3 g; PUR-gw-8: 0.4 g.

8.2.4. Thermal analysis

The DSC analyses (**Fig 8.19**) allowed the determination of the Tg (glass transition temperature) for the samples displaying the best mechanical properties (PUR-fa-4, respectively PUR-gw-4) which was compared to the blank sample.

In the case of sample PUR-gw-4, the value of the Tg increases in comparison with the blank sample. The highest value was registered for the composite with the lowest concentration of fly ash, PUR-fa-4.

Tg is a parameter that characterizes the mobility/flexibility of the polymer chain, the value being lower with the loss of chain mobility. The increase of Tg in the case of PURs reinforced with different filling agents can be explained by preventing the mobility of polymer chains (compacting effect) that determines a more loosened structure as the temperature rises.

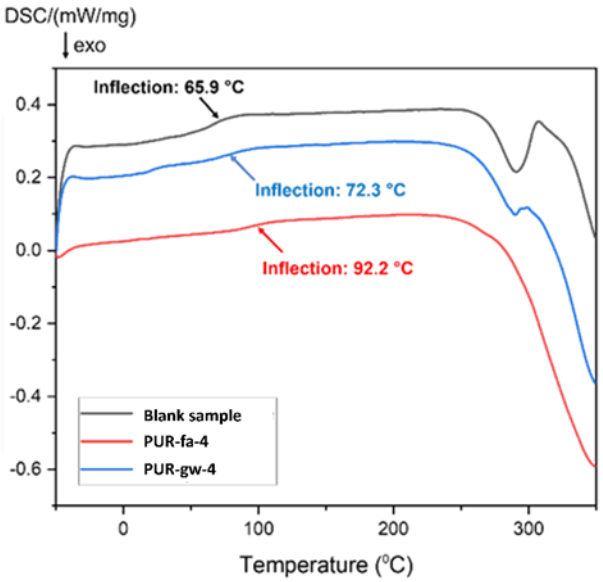


Fig. 8.19. DSC diagram for the Blank sample, PUR-fa-4 (0.2 g) și PUR-gw-(0.2 g).

In **Fig 8.20** is presented the influence size of the filler on the polymer chain mobility, a lower dimension of the particles (a higher specific surface) leading to a higher Tg [109]. In the case of fly ash (represented by red spheres in **Fig. 8.20**) the Tg value was 92.2 °C, while for glass waste (the green spheres) the value of Tg was lower (72.3 °C).

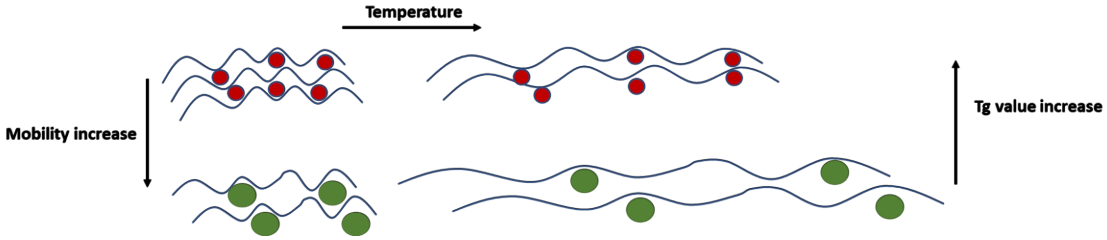


Fig. 8.20. Influence of mobility on glass transition temperature (Tg)

Thus, in terms of thermal characteristics, in our case the highest values of Tg were registered for the PURs modified with the lowest concentration of fly ash.

CHAPTER 9 – CONCLUSIONS

9.1. GENERAL CONCLUSIONS

In the last years the interest for the environment has risen considerably and a special “branch” of chemistry has been developed – “green chemistry”. Currently, an increasing number of studies aim to replace dangerous/toxic/pollutant compounds/materials with an environmentally friendlier alternative.

With the increase of demand for industrial products, flexible packages based on plastics have been used on a large scale due to their versatility. In the food industry, the packaging has the outmost impact on the commercial value of a product. Due to its chemical resistance, PET based materials are compatible with food packaging solutions.

Leaching/migration tests are defined as the transfer of chemical compounds from the packaging material into the food. The permeability of the packaging systems consists in the passing of the chemical substances into the food, and it is conditioned by a series of factors such as the storage temperature and duration of the food in the package.

The novelty and originality of this research topic resides in the valorization of plastic packaging materials, particularly PET to obtain new materials in combination with other types of waste materials as filling agents (pyrite, red mud, fly ash and/or glass waste).

The evaluation of the leaching/migration behavior of the organic compounds from the PET containers used for water bottling was performed using the TCLP procedure (Toxicity Characteristic Leaching Procedure). The obtained results highlighted the fact that the storage temperature and duration of the storage influenced the leaching of the organic compounds from the PET containers. The bisphenol A leaching from PET is more pronounced at room temperature compared to a cold room. The obtained results suggest that bisphenol A is concentrated in bottled water due to its migration from the PET bottle. Also, it was ascertained that bisphenol A diffusivity increased with the increase of storage temperature.

The leaching tests confirmed the potential for contamination with bisphenol A of the non-carbonated bottled water during long term storage in PET containers.

Experimental studies indicated that the release of bisphenol A from PET depends on the assortment/brand of PET. Moreover, as the thickness of the container wall increases the mobility of the compounds decreases resulting in a slower release of the contaminants during leaching. The observable diffusivities estimated based on the experimental data and modeling indicate a significant potential for leaching of organic compounds from PET containers composition.

As for the valorization of other types of waste materials alongside PET, 6 types of composite materials were synthesized using the glycolysis product from PET flakes, pyrite, and red mud. Thus, 3 types of polyurethane foams with different concentrations of pyrite and red mud were designed to retain Hg^{2+} from contaminated water (pyrite-based PUR) and for pavement rehabilitation (red mud). The FT-IR analyses confirmed the formation of urethane bonds from the reaction between the diol (PET glycolysis product) and MDI in all cases. The SEM and EDX analysis/mapping were employed to assess the porous structure of the foams and the distribution of the filling agents in the cellular walls.

The valorization of the 2 types of dangerous industrial waste materials was performed with success resulting in the production of polyurethane foams for future applications in decontamination of water and construction applications such as pavement rehabilitation. The rheological analysis the PET glycolysis product confirmed its tixotropic pseudoplastic characteristic. The TGA analysis demonstrated that the polyurethane foams with filling agents have an increased thermal stability compared to the blank sample for the red mud samples. DSC analysis indicated, for the pyrite samples, a decrease in Tg values up to 47 °C compared to the control sample (57 °C), while the Tg values for the red mud-based samples increased up to 60°C as the red mud concentration increased. This behavior was also reflected in the compression tests and can be attributed to a possible formation of pyrite aggregates. In the case of the red mud based polyurethane foam, the mechanical properties decreased with the increase of the filler concentration as reflected by the compression tests which can be attributed to the formation of aggregates.

To demonstrate that pyrite modified polyurethane composite material is a good candidate for materials that can contribute to the retention of Hg^{2+} from wastewater, the sample PUR-py-3, loaded with the highest concentration of pyrite, was contacted with an

aqueous solution contaminated with $HgCl_2$. The EDX spectrum and EDX mapping analysis confirmed the presence of mercury on the surface of the polyurethane foam based on pyrite, the absence of Fe being most likely due to the high ability of pyrite to retain mercury.

In the case of component A resulting from depolymerized PET, castor oil and fillers, the rheological behavior was not affected by filler type or filler concentration maintaining Bingham-type behavior. The polyol component was composed of glycolysis products resulting from the depolymerization of polyethylene terephthalate (PET) in the presence of diethylene glycol and castor oil. Rheological tests showed that the degraded PET is a non-Newtonian pseudoplastic fluid, while the addition of castor oil changed the behavior of the mixture into a Bingham fluid. After the critical shear rate, the mixture acts as a Newtonian fluid. FT-IR analysis revealed the reaction between polyols and diisocyanates, confirming the formation of the polyurethane structure without excess functional groups that could influence the mechanical properties of the final products. SEM analysis and EDX mapping indicated a cellular structure in which the fillers were uniformly incorporated. In all cases, the EDX results can be correlated with the XRF analysis performed for the fillers. The porosity of the samples decreased with increasing filler concentration. The density values ranged from 112 kg/m^3 to 168 kg/m^3 and an increasing trend was observed as the filler concentration increased. The values recorded for the density confirmed the formulation of the polyurethane foam with flexible characteristics, which were also confirmed by the mechanical compression tests, regardless of the filler. Mechanical compression tests confirmed that the best mechanical performance was recorded by the composites with the lowest concentration of filler, while the highest thermal resistance was obtained by the polyurethane foams with the highest concentration of reinforcing agent. TGA analysis indicated two stages of decomposition specific for urethane bonds and the Gram-Schimdt profile for volatile compounds. The residual mass was found to be higher for the modified polyurethane foams with the highest filler concentration, regardless of the filler used. The highest glass transition temperature (Tg) value determined by DSC analysis was obtained for the polyurethane foam modified with the lowest power plant ash concentration. The value of the glass transition temperature Tg increased up to 92.2 °C for PUR-fa-4 compared to PUR-gw-4

(72.3 °C), being influenced by the polymer chain mobility attributed to the morphology and size of the fillers. Thus, the obtained flexible polyurethane foams could be used in various applications such as automotive and civil engineering.

9.2. ORIGINAL CONTRIBUTIONS AND FUTURE PERSPECTIVES

The experimental studies regarding the release of bisphenol A from PET indicated that it largely depends on the brand of PET. The thicker the container wall, the lower the mobility of the compounds, so there is a slower release of contaminants into the leachate. The evaluation of the release of bisphenol A from PET containers was carried out based on the Piringer migration model, as an element of novelty.

Experimental studies allowed the synthesis and characterization of flexible polyurethane foams made from industrial waste. In this way, industrial waste such as PET, pyrite, glass waste and red mud can be recovered.

Three types of polyurethane foams with different concentrations of pyrite or red mud were designed for Hg^{2+} retention from contaminated waters (those with pyrite) and pavement rehabilitation (those with red mud).

This provided an alternative to address waste-generated problems by designing value-added composites/products with promising properties for materials used in Hg^{2+} ion retention, wastewater treatment, and construction applications such as paving or pavement rehabilitation.

Flexible polyurethane foams obtained from depolymerization products of PET and two types of fillers – fly ash and glass waste - could be used in various applications such as automotive and civil engineering.

It is also worth mentioning another direction of valorization of the materials resulting from the depolymerization of PET, castor oil and other filling agents can be made into films with potential applications in the fashion industry.

LIST OF PUBLICATIONS

1. Adriana Cornelia Mârșolea (Cristea), Cristina Orbeci, Edina Rusen, Paul Octavian Stănescu, Oana Brincoveanu, Roberta Irodia, Cristian Pîrvu, Adrian Dinescu, Constantin Bobirică, Alexandra Mocanu, Design of polyurethane composites obtained from industrial plastic wastes, pyrite and red mud, **Construction and Building Materials 405 (2023)** 133319

IF = 7.4

2. Adriana C. Mârșolea, Florentina L. Chiriac, Cristina Orbeci, Liliana Bobirică, Constantin 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**, 58, 5609–5615

IF = 3.3

3. Adriana C. Mârşolea, Cristina Orbeci, Liliana Bobirică, Constantin Bobirică, Leaching behavior of polyethylene terephthalate containers used for water bottling, **U.P.B. Sci. Bull., Series B, accepted**

IF = 0.5

IF cumulated = 11.2

4. Adriana Cornelia Mârșolea (Cristea), Alexandra Mocanu, Paul Octavian Stănescu, Oana Brincoveanu, Cristina Orbeci, Roberta Irodia, Cristian Pîrvu, Adrian Dinescu, Constantin Bobirică, Edina Rusen, Synthesis and characterization of polyurethane flexible foams provided from PET derivatives, fly ash, and glass wastes, **Heliyon,** submitted in June **2023**, **under review**

PARTICIPATION AT INTERNATIONAL CONFERENCES

- Mârșolea Adriana Cornelia, Chiriac Florentina Laura, Orbeci Cristina, Bobirică Constantin, Bobirică Liliana, Vasile Ion Iancu, Assessment of Bisphenol A Release from PET Water Bottles under Different Storage Temperature and Duration, 22nd Romanian International Conference on Chemistry and Chemical Engineering Sinaia, ROMANIA, September 7 – 9, 2022