UDC 665

Jerzy Korol
Doctor of Science, Associate Professor
Department of Material Engineering, Central Mining Institute, Republic of Poland

Aleksander Hejna
Doctor of Science, Assistant Professor
Department of Polymer Technology, Gdańsk University of Technology, Republic of Poland

Mariusz Marć
Doctor of Science, Assistant Professor
Department of Analytical Chemistry, Gdańsk University of Technology, Republic of Poland

ASSESSMENT OF VOLATILE ORGANIC COMPOUNDS EMISSIONS FROM RECYCLED LOW-DENSITY POLYETHYLENE STREAMS

Abstract. *The recycling of plastics is currently one of the most significant industrial challenges. Due to the enormous amounts of plastic wastes generated by various industry branches, it is essential to look for the potential methods of their utilization. Nevertheless, it should not be forgotten that recycled plastics are not pure materials, and they still may show an unfavorable environmental impact. They may contain different contaminants accumulated during processing processes, as well as their use. Moreover, post-consumer plastics may be partially degraded due to the actions of stress, temperature, or environmental conditions. Therefore, it is imperative to investigate the actual environmental impact and eco-friendliness of recycled plastics. In the presented paper, we analyzed the volatile organic compounds emissions from recycled low-density polyethylene streams. Results indicated that the application of recycled plastics should not be indisputably considered the environmentally-friendly solution.*

Keywords: *Low-density polyethylene; recycling; volatile organic compounds; emissions*

Introduction

It is crucial to determine their environmental impacts for a full assessment of the benefits and drawbacks of various products and sustainable processes development. One category of the impact is the emission of volatile organic compounds (VOCs). Its determination is essential for human safety. However, this issue is not very often investigated and described in the literature. It should be, without any doubt, analyzed during the application of recycled and waste materials, which could be contaminated and partially decomposed as a result of consumer use. Such an effect may noticeably affect the environmental impacts of various materials, e.g., recycled plastics. Therefore, in the presented work, we aimed to assess the VOCs emissions from the recycled low-density polyethylene (LDPE) streams.

Figure 1. The appearance of analyzed recycled LDPE streams.

Materials and methods

In the presented research work, four types of recycled low-density polyethylene were investigated. These samples were obtained from the local recycling company.

Their appearance is presented in Figure 1. It can be seen that only one of the analyzed streams was relatively pure. Others contained a noticeable amount of impurities. In the case of samples 1 and 4, which originated from the recycling of agricultural films, the impurities probably included soil residues. Sample 3, characterized by the noticeably white color was probably containing chalk, often used as an inactive filler, which is applied to reduce the materials' cost.

The emissions assessment of representatives of volatile organic compounds (VOCs), as well as the total amount of VOCs (TVOC parameter – the sum of all organic compounds, eluting between n-hexane and n-hexadecane on non-polar or slightly polar stationary phases of a capillary column using GC-FID and quantifying as toluene equivalents) [1] released to the gaseous phase from the investigated samples of polymer composites, was performed employing the microscale stationary emission chamber – the Micro-Chamber/Thermal Extractor™ (μ-CTE™ 250, Markes International, Inc) [2].

The studied polymer composites were weighed on an analytical balance on the glass Petri dish and placed inside a single stainless steel chamber. The mass of investigated polymer samples was ~1.5 g. Each sample was investigated two times. The use of Petri dishes allowed to avoid potential contamination of the chambers' interior with potential residues of the studied samples and to minimize the impact of the wall-memory effect on the final result of the determinations. Before the emissions assessment studies, chambers were conditioned at temp. 150 ºC for 15 min under nitrogen gas flow rate to remove potential impurities.

The seasoning conditions of investigated samples of polymer composited using mentioned above the μ-CTE™ 250 system were as follows: seasoning/conditioning temperature – 100 ± 0.5 ºC; seasoning/conditioning time – 30 ± 0.5 min; inert (nitrogen, 2.2) gas flow rate continually passing through the chamber – 25 ± 0.5 ml/min. At the outlet of each chamber, the stainless steel tube filled with Tenax TA sorption medium (60/80 mesh, Merck KGaA, Darmstadt, Germany) was attached to collect the analyte samples emitted to the gaseous phase from the studied materials.

Table 1

General information about the operating parameters of applied GC-FID and GC-MSD system

Separation and identification of selected chemical compounds retained on the applied sorption medium		
Type of gas chromatograph	Agilent Technologies 6890	Agilent 7820A GC
Detector	Mass spectrometer (5873 Network Mass Selective Detector) working in a SCAN mode	Flame Ionization Detector Working temperature: 280 °C
Transfer line temperature	GC-MS transfer line: 300 °C TD-GC transfer line: 160 °C Ion source: 230 °C Quadrupole mass analyser: 150 °C	TD-GC transfer line: 180 °C
Type of capillary column	HP-1ms 30 m x 0.25 mm x 1 µm	DB-1 30 m x 0.32 mm x 5 µm
Helium flow rate	1.0 ml/min	2.0 ml/min
Oven temperature	50 °C by 1 min 10 °C/min to 120 °C, hold 2 min 15 °C/min to 280 °C, hold 10 min	45 °C by 1 min 15 °C/min to 120 °C, hold 2 min 10 °C/min to 250 °C, hold 5 min
Data collecting software	CHEMSTATION	OpenLAB CDS ChemStation Workstation VL

After the sampling stage, collected analytes were analyzed using two-stage thermal desorption (TD) system (Markes Series 2 Thermal Desorption Systems; UNITY/TD-100 - equipped with multibed microtrap that ensures the determination of terpenes) combined with gas chromatography equipped with flame ionization detector (GC-FID). Moreover, in addition to the TD-GC-FID analysis and better identification, the samples of analytes emitted from the studied samples collected on the sorption medium were analyzed using the TD-GC system combined with a mass spectrometry detector (MSD). Detailed information about the working parameters of applied analytical equipment was listed in Table 1.

Results and discussion

In Figure 2, there are presented values of the TVOC parameter for analyzed samples. It can be noted that sample 4 had the highest TVOC value by far, which means that it emitted the most VOCs. The measurement was conducted at 100 °C, which means that the emission at processing temperatures, which is usually higher by several tens of degrees, would remain at a similar or higher level. This indicates a significant environmental impact of this waste stream, which should be considered during application. The lowest emissions were observed for stream 2, which has the highest purity and lowest contaminants content. A relatively low emission value was also observed for stream 3, which is most likely contaminated with chalk, the presence of which allows some organic compounds to be absorbed.

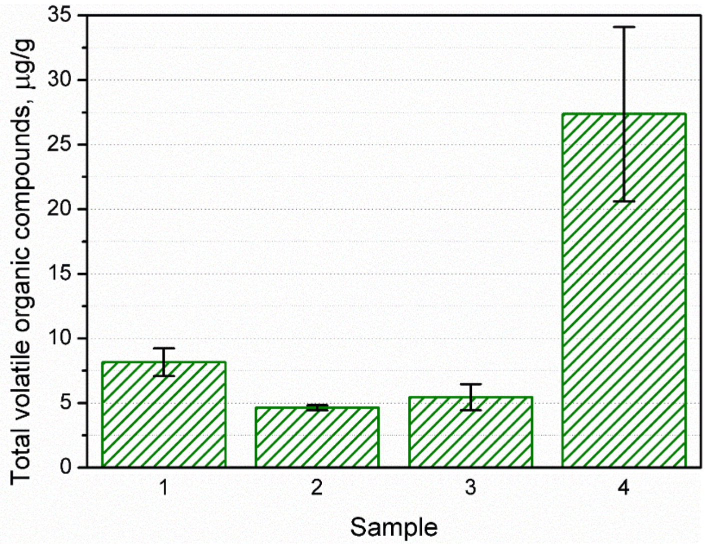

Figure 2. The values of TVOC parameter for analyzed recycled LDPE streams.

Table 2 presents the major compounds along with the area under the peaks on the chromatogram assigned to their presence. Most of the detected compounds can be classified as linear hydrocarbons, from decane to eicosane. They are often detected during the assessment of VOCs emissions from polyolefins [3]. According to literature data, their presence may be related to the polyethylene main chain's partial decomposition during processing [4]. Although the values of area under curve should not be treated as a quantitative measure of emitted VOCs, noticeably, the highest values, especially for lower molecular weight compounds, were observed for sample

4. Such an effect may indicate its highest degree of degradation or the presence of low molecular weight polyolefin fraction caused by contamination. The presence of compounds from the aldehyde group and carboxylic acids, which according to literature data, are polyethylene decomposition products, was also noted [5]. It may be related to the LDPE recycling, especially to those unit processes, during which external forces (mainly shredding) or temperature (plastic remelting) act on the material. Moreover, residual amounts of octanal, nonanal, and decanal may be associated with the application of LDPE as packaging material. They can be present in multiple food products and cosmetics.

Table 2

VOCs emitted from recycled LDPE streams

Compound	Chemical formula	The area under curve, %			
		121	124	125	126
Isopropyl alcohol	C_3H_8O	2.46	2.66	2.41	1.85
Acetic acid	$C_2H_4O_2$	2.00	0.82	-	2.21
Hexanoic acid	$C_6H_{12}O_2$	0.82	0.53	-	-
Decane	$C_{10}H_{22}$	1.50	0.51	0.74	1.16
Octanal	$C_8H_{16}O$	0.77	1.08	0.91	0.33
Limonene	$C_{10}H_{16}$	0.93	1.67	0.75	0.89
Heptanoic Acid	$C_7H_{14}O_2$	0.37	-	0.57	-
Acetophenone	C_8H_8O	1.05	1.18	0.68	0.97
Undecane	$C_{11}H_{24}$	3.00	3.09	3.43	5.82
Nonanal	$C_9H_{18}O$	3.31	4.74	4.68	1.74
Dodecane	$C_{12}H_{26}$	8.23	8.68	9.41	15.96
Menthol	$C_{10}H_{20}O$	0.35	0.61	-	0.46
Decanal	$C_{10}H_{20}O$	2.33	2.91	3.58	1.15
Tridecane	$C_{13}H_{28}$	6.30	6.61	5.07	17.12
Tetradecane	$C_{14}H_{30}$	9.54	5.19	7.99	8.69
Pentadecane	$C_{15}H_{32}$	3.21	2.25	2.31	1.14
2,6-di-*tert*-butyl-benzoquinone	$C_{14}H_{20}O_2$	1.05	1.75	1.49	1.10
2,4-di-*tert*-butylphenol	$C_{14}H_{22}O$	3.60	4.00	2.62	2.48
Hexadecane	$C_{16}H_{34}$	6.00	2.05	5.05	6.06
Heptadecane	$C_{17}H_{36}$	1.22	0.52	1.22	0.34
Octadecane	$C_{18}H_{38}$	2.12	0.51	2.39	1.93
Nonadecane	$C_{19}H_{40}$	1.04	1.67	0.60	1.13
Eicosane	$C_{20}H_{42}$	0.94	0.40	1.18	-

The presence of isopropanol may be related to the plastic washing processes during recycling since it is often applied during disinfection and degreasing of materials [6].

Acetic acid is commonly observed in the decomposition of plastics produced using vinyl acetate, including EVA copolymer, which shows excellent miscibility with polyethylene and can often be present in small amounts in PE regranulates. Moreover, vinyl acetate is often used as one of the components of adhesives for labels applied in packaging materials. In the case of sample 3, the lack of signal most likely indicates the presence of chalk in the waste, which confirms previous speculations, since due to its chemical structure ($CaCO_3$), chalk can interact with acetic acid to form calcium acetate, which will not be detected during the analysis performed.

The presence of limonene and menthol may be related to contaminants from food and cosmetics stored in recycled PE packaging.

The presence of 2,4-di-*tert*-butylphenol and 2,6-di-*tert*-butylbenzoquinone is related to their role in the polymerization process. They are used as stabilizer and inhibitor of the polymerization reaction, respectively, and their presence is frequently observed according to literature data. Moreover, the highest intensity of signals from these compounds may be a confirmation of the highest PE content in waste stream 2, which confirms its highest purity.

Conclusions

Generally, presented results revealed that recycled plastics, in this case, LDPE, can be characterized by the significantly different values of volatile organic compounds emissions. Depending on the origin and previous applications, different contaminants may be present in plastics. Moreover, as mentioned above, plastics can be partially decomposed during their primary use and recycling process. As a result, they can emit noticeable amounts of hydrocarbons, but also stabilizers or polymerization inhibitors, which can be considered as a threat towards human health. Therefore, assessment of VOCs emissions may be applied to investigate the decomposition level and determine the usefulness of recycled plastics in industrial processes, especially when coupled with other techniques.

Acknowledgments

This work was supported by The National Centre for Research and Development (NCBR, Poland) in the frame of POIR.04.01.04-00-0051/17 project – New polymeric

material based on waste for production of flame retardant film with highest strength and low environmental impact in the whole life cycle.

References:

1. Massold E, Bahr C, Salthammer T, Brown SK (2005): *Determination of VOC and TVOC in air using thermal desorption GC–MS—practical implications for test chamber experiments*. Chromatographia, 62, 75–85.
2. Marć M (2020): *Emissions of selected monoaromatic hydrocarbons as a factor affecting the removal of single-use polymer barbecue and kitchen utensils from everyday use*. Science of the Total Environment, 720, 137485.
3. Lattuati-Derieux A, Egasse C, Thao-Heu S, Balcar N, Barabant G, Lavédrine B (2013): *What do plastics emit? HS-SPME-GC/MS analyses of new standard plastics and plastic objects in museum collections*. Journal of Cultural Heritage, 14(3), 238-247.
4. Curran K, Underhill M, Gibson LT, Strlic M (2016): *The development of a SPME-GC/MS method for the analysis of VOC emissions from historic plastic and rubber materials*. Microchemical Journal, 124, 909-918.
5. Kułtys B, Waląg K (2018): *Application of headspace for research volatile organic compounds emitted from building materials*. E3S Web of Conferences, 28, 01019.
6. Slaughter RJ, Mason RW, Beasley DMG, Vale JA, Schep LJ (2014): *Isopropanol poisoning*. Clinical Toxicology, 52(5), 470–478.