

Comparative Analysis of Virgin and Recycled Thermoplastic Polymer based on Thermochemical Characteristics

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Plastics are among the most-used materials globally, with thousands of different grades and a wide range of applications. However, its end-of-life management is a common issue, despite most plastics produced today containing highly recyclable thermoplastics. The quality of recycled plastic material should be enhanced as it depends on several factors, such as cross-contamination, presence of additives, impurities and degradation rate. In this study, a comparative analysis of thermochemical characteristics of virgin and recycled commonly-used thermoplastic polymer, high-density polyethylene (HDPE), was performed to study the impact of recycling on the material properties. The proximate and ultimate analysis, identification of functional groups and thermal behaviour were performed to study the chemical changes in the recycled and virgin material. The results showed that recycled HDPE started to degrade at a lower temperature than virgin HDPE, with a lower degradation rate (92.7 wt.%) compared to virgin HDPE (99.6 wt.%) due to the presence of impurities and other factors. Calorific values of both samples were comparable, while the degree of crystallinity was 79.8 % for virgin HDPE and around 19 % lower for recycled HDPE samples. Significant differences between recycled and virgin material were also obtained in terms of melting and crystallisation enthalpies.

1. Introduction

Societies' daily activities are responsible for mishandling plastics and, notably, plastic waste, which has proven to be a very weak human trait in the last few years. Plastic pollution has become one of the pressing environmental problems. Around 400 Mt/y of plastics are produced globally, mainly from fossil hydrocarbons obtained from oil, natural gas and coal, and more than 50 % of the total production amounts to single-use plastics (Chen et al., 2021). Globally, less than 10 % of all produced plastic waste is recycled, leading to an enormous plastic waste footprint (Klemeš et al., 2021). In the EU, the figure is slightly better (32.5 % recycled) (European Parliament, 2021); however, the degree of circularity is still far from sustainable. The post-consumer plastic waste is usually not well-managed (Evode et al., 2021), as it is usually incinerated or accumulated in landfills and natural environments such as marine litter, posing a significant threat to the environment. High recalcitrance of most plastics results in their long persistence in the environment and thus in the accumulation of large amounts of plastic litter in the land and water environments (Moharir and Kumar, 2019) which slowly degrade into macro, meso, micro and nanoplastics (Boyle and Örmeci, 2020). There are, to date, no effective solutions for the rapidly growing production of plastic products. A major challenge is to develop waste management strategies, such as ten common circular economy strategies (10 R's) (Fan et al., 2021), to efficiently transit towards the circular economy.

Large quantities of plastic products are made from thermoplastic polymers, such as polypropylene (PP), high and low-density polyethylene (HDPE and LDPE) and others. HDPE is one of the most widely used semi-crystalline polymers in our daily life owing to its many desirable and beneficial physical properties, such as good

chemical resistance and mechanical strength (Xie et al., 2019). Other advantages are low price, easy processing, and resistance to abrasion and chemicals. It is used for bottles, toys, caps, plastic bags, and various packaging. The best advantage of this polymer is that it can be recycled several times, and consequently, it is among the most recycled polymers globally. Recycled HDPE (R-HDPE) represents the second-largest share of the plastic recycling market (James et al., 2019).

In one of the studies (ESE, 2018), it was found that HDPE can be recycled at least up to ten times. The study of the impact of mechanical and thermal properties of virgin HDPE over multiple (six) recycling processes (Vidakis et al., 2021) concluded that mechanical properties of R-HDPE polymer generally improved over the recycling repetitions for a certain proportion of recycling. The properties of virgin and R-HDPE obtained from milk bottles were proved to be similar (Adhikary et al., 2008), indicating that R-HDPE could be used for various applications. As HDPE is mainly produced from oil and natural gas by polymerisation, the reuse of recycled polymer would be a significant advantage in the circular economy. Several research studies were also performed dealing with various aspects of plastic materials, including the analyses of the thermal behaviour of HDPE (Mazloun et al., 2021). The effect of thermal and thermo-oxidative degradation conditions on the chemical and thermal properties of HDPE was also studied (Cuadri and Martín-Alfonso, 2017). However, in some other studies, a decrease in the mechanical properties was observed for R-HDPE in mixtures with virgin HDPE (Tesfaw et al., 2022). The disadvantage of plastic recycling, including HDPE, are huge amounts of toxic gases that are generated during the recycling process (Evode et al., 2021). Also, the market for recycled plastic materials experiences various challenges and barriers, including economic, technical, environmental and regulatory barriers (James et al., 2019). More intensive research on comparative analysis of recycled materials and their properties is needed to encourage their use.

The main goal of this study was to characterise the virgin and R-HDPE and to comparatively analyse their thermochemical properties. The HDPE quality was characterised by the determination of the following properties: moisture content, volatile matter, ash content, fixed carbon, elemental composition, calorific value, identification of chemical bonds/functional group by Fourier Transform Infrared (FTIR) spectroscopy and thermal behaviour by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The comparative analysis could shed light on the behaviour of HDPE used as new material or as a fuel in the combustion process. As comparative analyses on virgin and recycled HDPE materials are rare, this work brings valuable insights regarding its thermochemical properties and further use.

2. Materials and methods

This section describes the characterisation methods and analytical procedures and further the procedure for thermal analysis of virgin and recycled HDPE samples. Two samples of polymers, virgin HDPE (uncoloured granulate, size of 3 x 3 x 4 mm) and R-HDPE (blue coloured granulate from solid plastic packaging, size of 2 x 3 x 3 mm), were obtained from the local company that produces plastic packaging, were comparatively analysed for their thermochemical characteristics. An important limitation is that the previous uses of R-HDPE are not known in detail, and thus their impact on the material properties cannot be determined.

First, the basic characteristics, such as ultimate and proximate analyses, including moisture content, volatiles and ash content, were determined. A moisture analyser (Mettler Toledo HB43-S) was used to determine the moisture in the polymer samples. Approximately 4 g of sample was weighed on an aluminium pan and dried at 105 °C until constant weight. The analyses were performed in triplicate. Experimental higher heating value (HHV_e) was determined by combustion in a bomb calorimeter. The theoretical HHV_t was calculated using Eq(1) (Channiwala and Parikh, 2002):

$$HHV \left(\frac{MJ}{kg} \right) = 0.3491 \cdot C + 1.1783 \cdot H + 0.1005 \cdot S - 0.1034 \cdot O - 0.0151 \cdot N - 0.0211 \cdot Ash \quad (1)$$

where C, H, N, O, S, and ash are the weight percentages of carbon, hydrogen, nitrogen, oxygen, sulfur, and ash on a dry basis. Ash content was determined by the combustion of samples at 800 °C for 3 h. Volatile matter content (VM) was determined by measuring the weight loss by combustion of samples at 900 °C for 7 min. The elemental analysis was performed by PerkinElmer Analyser Series II 2400 (C, H, N, S content). The oxygen content was calculated by Eq(2):

$$O = 100 - C - H - N - S - Ash \text{ (all in wt.\%)} \quad (2)$$

The fixed carbon (FC) was calculated as (Eq(3)):

$$FC \text{ (wt.\%)} = 100 - VM - Ash \quad (3)$$

Chemical functional groups and chemical bonds of recycled and virgin HDPE were identified by FTIR analysis. The spectra of the samples were recorded in the range of 400 - 4,000 cm^{-1} using a Shimadzu IRAffinity FTIR spectrophotometer by attenuated total reflection infrared spectroscopy (ATR) method.

Thermal analyses were performed for the two samples by using TGA and DSC techniques. The TGA study was carried out using Mettler Toledo TGA/DSC (TGA/DSC1 STAR). Each sample (20 \pm 5 mg) was weighed into the aluminium pans and analysed. Measurements were performed in an air atmosphere in the temperature range from 30 to 600 $^{\circ}\text{C}$ with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ and with simultaneous recording of the signals.

For DSC measurements, the samples were first heated from 25 $^{\circ}\text{C}$ to 280 $^{\circ}\text{C}$ to obtain a molten phase, then cooled to 25 $^{\circ}\text{C}$ to achieve a crystallisation curve, and then reheated to 280 $^{\circ}\text{C}$ to obtain a melting curve. The objective of the first heating step was to eliminate the heat history of the sample. Crystallisation temperature (T_c) and crystallisation enthalpy (ΔH_c) were determined from the cooling step while melting temperature (T_m) and melting enthalpy (ΔH_m) were determined from the second heating sequence. All experiments were performed in triplicate at a constant nitrogen flow of 20 mL/min and at a constant heating and cooling rate of 10 K/min. Finally, the degree of crystallinity χ_c (%) for each sample was calculated following Eq(4). The degree of crystallinity of the polymer reflects the degree of structural order and strength of the polymer because, in the crystalline phase, the intermolecular bonding is more significant.

$$\chi_c(\%) = \frac{\Delta H_m}{\Delta H_{m,100\%}} \cdot 100 \quad (4)$$

where $\Delta H_{m,100\%}$ is the theoretical melting enthalpy for HDPE with 100 % of crystallinity, which is by (Cuadri and Martín-Alfonso, 2017) 290 J/g.

3. Results and discussion

The results obtained from the proximate and ultimate analysis of virgin and R-HDPE samples are shown in Table 1. The elemental analysis revealed high contents of C and H in the samples and smaller amounts of other elements. R-HDPE had almost 3 wt.% lower C content and, on the contrary, higher N, S and O contents. The ash content was much higher for R-HDPE (5.18 wt.%) than virgin HDPE (0.03 wt.%). The results from elemental analysis and ash content indicate that impurities appeared in the sample during the recycling process. Similar to this study, lower C and higher O contents were characteristic also for the coloured PE waste as compared to virgin PE, probably due to additives or dyes that were added to the polymer (Čolnik et al., 2021).

The moisture content and fixed carbon were negligible in both HDPE samples. The volatile matter content was 99.96 % in the virgin HDPE sample, while in the recycled sample, lower content was measured, 93.56 %. This confirmed that R-HDPE requires a longer residence time to achieve complete combustion. Differences between the samples were also noticed in the measurements of calorific values (HHV_e and HHV_t), where the HHV value of the recycled material was lower than that of virgin HDPE (44.75 vs 46.46 wt.% in the case of HHV_e). The calorific value obtained in this study was comparable to the calorific value of HDPE (46.48 MJ/kg) in one of the previous studies (Singh et al., 2019). The values show that HDPE materials possess a large amount of chemical energy for the end-of-life phase recovered by incineration or pyrolysis. Ultimate and proximate analysis showed significant differences among the samples, which could affect the quality of R-HDPE and its further use.

Table 1: The results of ultimate and proximate analysis of HDPE and R-HDPE samples

Parameter	HDPE	R-HDPE
Ultimate analysis		
C (wt.%)	85.03 \pm 0.75	82.25 \pm 0.92
H (wt.%)	14.29 \pm 0.13	11.48 \pm 0.47
N (wt.%)	0.18 \pm 0.03	0.26 \pm 0.03
S (wt.%)	0.42 \pm 0.02	0.64 \pm 0.01
O (wt.%)	0.05 \pm 0.01	0.19 \pm 0.03
Proximate analysis		
Moisture (wt.%)	0.07 \pm 0.01	0.07 \pm 0.01
Volatile matter (% of dry matter)	99.96 \pm 0.03	93.56 \pm 0.08
Ash (wt.%)	0.03 \pm 0.01	5.18 \pm 0.02
Fixed carbon (wt.%)	0.01 \pm 0.00	1.26 \pm 0.05
HHV_e (MJ/kg)	46.46 \pm 0.74	44.75 \pm 1.31
HHV_t (MJ/kg)	46.56 \pm 0.22	42.17 \pm 0.66

The FTIR spectra of the HDPE and R-HDPE are further presented in Figure 1a. The spectra of both materials showed similar peaks, although, in the case of R-HDPE, significantly lower intensities of peaks were observed, indicating the presence of impurities and contaminants. A peak at around $1,470\text{ cm}^{-1}$ is attributed to CH_2 scissoring vibrations of polyethylenes, while a peak at 700 cm^{-1} reflects C-H bend. Due to the crystallinity of polyethylene, the peak at 700 cm^{-1} is split, and an additional peak is seen at around 720 cm^{-1} . Peaks in the area between $2,800$ and $3,000\text{ cm}^{-1}$ result from aliphatic $-\text{CH}_x$ asymmetric and symmetric stretching, as the main component of HDPE are aliphatic hydrocarbons, alkanes and alkenes. The HDPE spectra are comparable to those reported in previous studies (Xie et al., 2019). Figure 1(b) further shows TGA and DSC curves of HDPE samples exposed to heating in an air atmosphere in the temperature range from 30 to $600\text{ }^\circ\text{C}$ (heating rate of $10\text{ }^\circ\text{C}/\text{min}$). TGA determines mass changes related to the degradation of the material, while DSC evaluates the effect of temperature in the variation of a material heat capacity due to structural changes of material, like phase transition or melting (Sorolla-Rosario et al., 2022). TGA curves showed that degradation of R-HDPE started at a lower temperature than virgin HDPE. The temperature at which R-HDPE starts to degrade was $\sim 441^\circ\text{C}$ and that of virgin HDPE $\sim 453^\circ\text{C}$. Similar to this study, waste polymers showed a lower degradation temperature than virgin polymers during the degradation of waste plastics under a non-sweeping atmosphere (Singh et al., 2019). Virgin HDPE sample in this study degraded almost completely ($99.61\text{ wt.}\%$), while in the case of R-HDPE, the residue of around $7.50\text{ wt.}\%$ of initial mass was observed, as the presence of contaminants in the recycled material leads to an increased amount of residue. The characteristics of TGA curves agree with those of HDPE (Mazloun et al., 2021) and other polymers such as PP and LDPE (Sorolla-Rosario et al., 2022) in the literature. From the DSC curve, the peak temperature of melting was $144.61\text{ }^\circ\text{C}$ for HDPE and $140.17\text{ }^\circ\text{C}$ for R-HDPE. The differences result from the composition of materials due to impurities and additives in R-HDPE. Several volatile compounds were identified in waste and R-HDPE in the past, such as alcohols, hydrocarbons, alkenes, phthalates, hydrocarbons, terpenes, and diverse sources for these volatiles were proposed, namely additives, residues, preservatives and cleaning agents (Strangl et al., 2018). The presence of additives, plasticisers, etc., was found to cause an early mass loss and reduction in the degradation temperature, also in the case of waste plastics (Singh et al., 2019). Multiple recycling processes adversely affect the physical properties and leads to a lower degradation temperature.

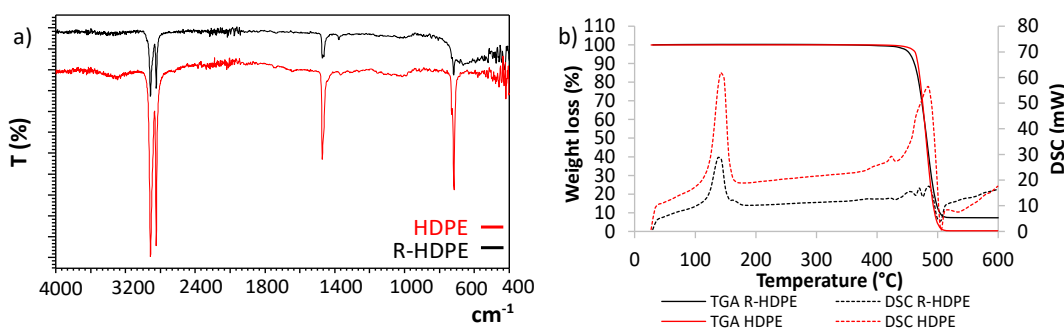


Figure 1: a) FTIR spectra and b) results of TGA and DSC measurements for HDPE and R-HDPE samples

Finally, DSC analysis was carried out to investigate the changes in crystallisation and melting temperatures in both HDPE samples, as well as their corresponding enthalpies and crystallinity. DSC curves in the temperature range of $25 - 280\text{ }^\circ\text{C}$ are presented in Figure 2, while Table 2 shows a summary of TGA and DSC experiments, including the crystallisation, decomposition and melting temperatures, and melting and crystallisation enthalpies for both samples. As shown in Figure 2, the three main zones can be recognised from the curves. Table 2 shows that crystallisation temperatures of R-HDPE and HDPE were quite similar ($111.14\text{ }^\circ\text{C}$ and $112.34\text{ }^\circ\text{C}$), but crystallisation enthalpies (ΔH_c) differed for more than 50 J/g . Similar was noticed for melting temperature and enthalpy, as ΔH_m of R-HDPE was lower (174.48 J/g) than that of virgin HDPE (231.42 J/g). HDPE is almost entirely composed of linear macro-molecules without any long branching chains, and it exhibits low melt strength (Xie et al., 2019). The degree of crystallinity $\chi_c(\%)$ of HDPE sample was 79.80% , while R-HDPE sample exhibited lower value, only 60.17% . Lower degree of crystallinity after recycling of polymers such as PP, HDPE and LDPE was also noticed in other studies (Hadi et al., 2014). The thermal properties of tested HDPE and R-HDPE samples are compared with the properties of polyolefins reported in other studies, including polypropylene (PP) (Mazloun et al., 2021) and low-density polyethylene (LDPE) (Čolnik et al., 2021), which are listed for the comparison. The discussed parameters are influenced by different factors such as the degree of

branching, the presence of impurities or additives, the particle size or the thermal history of the sample (Sorolla-Rosario et al., 2022). Plasticisers, antioxidants, lubricants, pigments, light and heat stabilisers, and thermo-stabilisers are the most commonly used additives (Čolnik et al., 2021) with a huge impact on their properties. The higher the content of additives and impurities in the recycled material, the lower the melting temperature.

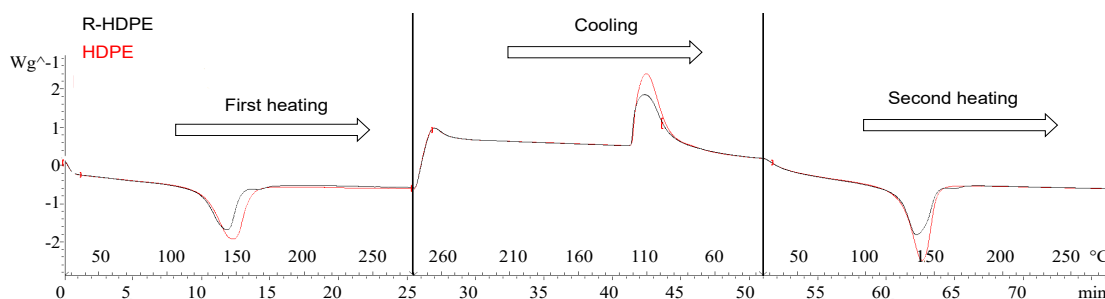


Figure 2: DSC curves of a virgin (red) and R-HDPE (black) in the temperature range of 25 - 280°C.

Table 2: Thermal properties of HDPE and R-HDPE samples from this study compared to other polymers

Sample	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	T_d (°C)	χ_c (%)	Reference
R-HDPE	111.14	193.77	132.92	174.48	441	60.17	This study
	/	/	131	/	/	68.2	(Hadi et al., 2014)
HDPE	112.34	253.42	134.50	231.42	453	79.80	This study
	116.76	214.68	142.71	213.56	/	/	(Čolnik et al., 2021)
	112.40	186.20	133.80	192.00	415	66.20	(Cuadri and Martín-Alfonso, 2017)
	/	/	139.00	/	478	/	(Sorolla-Rosario et al., 2022)
	/	/	140.00	130.00	/	/	(Mazloun et al., 2021)
R-LDPE	/	/	110	/	/	44.1	(Hadi et al., 2014)
LDPE	93.01	91.25	113.81	95.11	/	/	(Čolnik et al., 2021)
	/	/	109.00	/	463	/	(Sorolla-Rosario et al., 2022)
PP	/	/	157.50	69.00	/	/	(Mazloun et al., 2021)
	/	/	154.00	/	444	/	(Sorolla-Rosario et al., 2022)

4. Conclusions

This study presented the results of thermochemical characterisation of virgin and recycled commonly used thermoplastic polymer HDPE. The results showed significant differences between virgin and recycled polymer samples in terms of characteristics, such as elemental composition, volatiles, ash content and calorific value. FTIR analysis revealed lower peak intensities for recycled polymer. R-HDPE exhibited lower degradation temperature than virgin HDPE, most likely due to the presence of impurities. The recycling process, according to DSC analysis, significantly affected melting and crystallisation temperatures and enthalpies. Characterisation of the virgin and recycled polymer provides important information that could be used for conducting Life Cycle Assessment (LCA) and optimising the chemical recycling process. Sorting affects the presence of contaminants, additives and impurities, both in terms of quantity and quality, and more efficient waste recycling and recovery are crucial. Future work could include a comparative analysis of thermochemical characteristics of HDPE over multiple recycling processes and characteristics of other thermoplastic and thermoset polymers. It could as well evaluate plastic recycling by accounting for downgrading, sustainability and circularity considering cradle-to-cradle designs. Finally, it could evaluate the global environmental impact of various plastic materials considering their current and more intelligent waste management systems. The results could help make provision for more sustainable waste management strategies and the transition to a near zero-waste lifestyle.

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References

- Adhikary K.B., Pang S., Staiger M.P., 2008, Dimensional stability and mechanical behaviour of wood–plastic composites based on recycled and virgin high-density polyethylene (HDPE), *Composites Part B: Engineering*, 39(5), 807-815.
- Boyle K., Örmeci B., 2020, Microplastics and Nanoplastics in the Freshwater and Terrestrial Environment: A Review, *Water*, 12(9), 2633.
- Channiwalla S.A., Parikh P.P., 2002, A unified correlation for estimating HHV of solid, liquid and gaseous fuels, *Fuel*, 81(8), 1051-1063.
- Chen Y., Awasthi A.K., Wei F., Tan Q., Li J., 2021, Single-use plastics: Production, usage, disposal, and adverse impacts, *Science of the Total Environment*, 752, 141772.
- Čolnik M., Kotnik P., Knez Ž., Škerget M., 2021, Hydrothermal decomposition of polyethylene waste to hydrocarbons rich oil, *The Journal of Supercritical Fluids*, 169, 105136.
- Cuadri A.A., Martín-Alfonso J.E., 2017, The effect of thermal and thermo-oxidative degradation conditions on rheological, chemical and thermal properties of HDPE, *Polymer Degradation and Stability*, 141, 11-18.
- ESE, 2018, HDPE Multiple Recycling Proven in an Experiment, <ese.com/en/ese-world/ese-news/news-details/article/hdpe-multiple-recycling-proven-in-an-experiment/>, accessed 13.6.2022.
- European Parliament, 2021, Plastic waste and recycling in the EU: facts and figures, <europarl.europa.eu/news/en/headlines/society/20181212STO21610/plastic-waste-and-recycling-in-the-eu-facts-and-figures>, accessed 27.5.2022.
- Evode N., Qamar S.A., Bilal M., Barceló D., Iqbal H.M.N., 2021, Plastic waste and its management strategies for environmental sustainability, *Case Studies in Chemical and Environmental Engineering*, 4, 100142.
- Fan Y.V., Jiang P., Klemeš J.J., Liew P.Y., Lee C.T., 2021, Integrated regional waste management to minimise the environmental footprints in circular economy transition, *Resources, Conservation and Recycling*, 168, 105292.
- Hadi A.J., Najmuldeen G.F., Ahmed I., 2014, Quality restoration of waste polyolefin plastic material through the dissolution–reprecipitation technique, *Chemical Industry & Chemical Engineering Quarterly*, 20 (2), 163–170.
- James G., Whitley S., Sloggett J., Nichols J., 2019, The plastic landscape: Risks and opportunities along the value chain. <unpri.org/download?ac=10258> accessed 9.6.2022.
- Klemeš J.J., Fan Y.V. and Jiang P., 2021, Plastics: friends or foes? The circularity and plastic waste footprint, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 43(13), 1549-1565.
- Mazloum S., Aboumsallem Y., Awad S., Allam N., Loubar K., 2021, Modelling pyrolysis process for PP and HDPE inside thermogravimetric analyzer coupled with differential scanning calorimeter, *International Journal of Heat and Mass Transfer*, 176, 121468.
- Moharir R.V., Kumar S., 2019, Challenges associated with plastic waste disposal and allied microbial routes for its effective degradation: A comprehensive review, *Journal of Cleaner Production*, 208, 65-76.
- Singh R.K., Ruj B., Sadhukhan A.K., Gupta P., 2019, Thermal degradation of waste plastics under non-sweeping atmosphere: Part 1: Effect of temperature, product optimization, and degradation mechanism, *Journal of Environmental Management*, 239, 395-406.
- Sorolla-Rosario D., Llorca-Porcel J., Pérez-Martínez M., Lozano-Castelló D., Bueno-López A., 2022, Study of microplastics with semicrystalline and amorphous structure identification by TGA and DSC, *Journal of Environmental Chemical Engineering*, 10(1), 106886.
- Strangl M., Schlummer M., Maeurer A., Buettner A., 2018, Comparison of the odorant composition of post-consumer high-density polyethylene waste with corresponding recycled and virgin pellets by combined instrumental and sensory analysis, *Journal of Cleaner Production*, 181, 599-607.
- Tesfaw S., Fatoba O., Mulatie T., 2022, Evaluation of tensile and flexural strength properties of virgin and recycled high-density polyethylene (HDPE) for pipe fitting application, *Materials Today: Proceedings*. 62, Part 6, 2022, 3103-3113. doi: 10.1016/j.matpr.2022.03.385
- Vidakis N., Petousis M., Maniadi A., 2021, Sustainable Additive Manufacturing: Mechanical Response of High-Density Polyethylene over Multiple Recycling Processes, *Recycling*, 6(1), 4.
- Xie L., Liang X., Huang H., Yang L., Zhang F., Luo Z., 2019, Preparation and properties of long chain branched high-density polyethylene based on nano-SiO₂ grafted glycidyl methacrylate, *RSC Advances*, 9, 1123-1133.