

Influence of reprocessing by melt-mixing and thermo-formation of polyolefin fractions, separated from wastes, on their calorific power

L. Costiuc¹, L. Baltes², S. Patachia^{3*}, M. Tierean², A. Lunguleasa⁴

¹Transilvania University of Brasov, Mechanical Engineering Department, 29 Eroilor Blvd., 500036 Brasov, Romania

²Transilvania University of Brasov, Materials Engineering and Welding Department, 29 Eroilor Blvd., 500036, Brasov, Romania

^{3*}Transilvania University of Brasov, Product Design, Mechatronics and Environmental Protection Department, 29 Eroilor Blvd., 500036, Brasov, Romania, st.patachia@unitbv.ro

⁴Transilvania University of Brasov, Wood Engineering Department, 29 Eroilor Blvd., 500036, Brasov, Romania

Polyolefins recycling is a desideratum, imposed by the actual environmental protection regulations that take into consideration the very high amounts of polyolefin utilization, their non-biodegradability and the rapidly diminishing of the fossil energetic resources. Calorimetric studies, performed on fractions obtained from municipal polymeric waste, from Brasov, Romania, separated by flotation, evidenced that their calorific power is comparable with that of fossil combustibles, meaning that polymeric waste could be incinerated for energy recovery. However, polymers incineration generates environmental concerns, especially for air pollution, remaining one of the last choices in polyolefins recycling. Thermal re-processing of polymeric fractions, by melt-mixing and thermoforming implies thermo-degradation processes that could influence the calorific power of re-used polymers. This paper aims to compare the calorific power of polymeric fractions separated from municipal polymeric waste with that of the re-processed polymers, obtained from the former fractions, by melt-mixing and thermoforming. A critical analysis of the efficiency of polymers recycling versus incineration, in different life cycles, is presented.

Keywords: polyolefin, waste, recycling, calorific power, melt-mixing, thermoforming

INTRODUCTION

Finding of new sources of energy, reducing of energy consumption and energy recovery are some of the most important issues of nowadays society due to the exponentially increase of the energy need.

Plastics are well-known as energy efficient materials considering their whole life-cycle, due to their easiness to be transported, installed and maintained, their high versatility and cost-effectiveness. For example, when comparing with traditional building and construction materials, plastics require 85% less energy to manufacture, generate 95% less CO₂ and use minimal water during production process [1]. However, most of plastics generate, at their end of life cycle, non-biodegradable waste that may have a serious impact on the environment and health. New strategies in the EU countries concerning the plastic products design, their use and recycling have been adopted on the 16th of January, 2018, in Brussels [2]. The use of plastics in circular economy imposes well controlled collection, separation and washing processes [3].

Often, the complexity of the plastic waste composition, due to their contamination during the

use, associated with current low prices of raw materials renders recycling un-economic compared with landfilling [1]. In this context, trying to avoid environmental concerns, the options are: the increase of the plastic biodegradability [1] and energy recovery by pyrolysis [4] or incineration.

One of our former studies showed that fractions separated from Municipal Solid Waste (MSW) from Brasov County, Romania, in 2010, showed a high calorific power that recommend them for recycling by incineration with energy recovery [5-7]. The higher the polyolefin content, the higher the calorific power of the waste is, the last one being comparable with that of the superior coal.

Other studies showed that the re-processing of these fractions by melt-mixing and thermoforming, allows obtaining secondary materials with acceptable mechanical and antimicrobial properties [8-10].

It is well-known that the thermal treatment of polymers as well as their exposure to the ambient conditions (temperature, light, moisture variations) lead to their properties alteration, due to oxidative processes, chain breaking, crosslinking, additives release, phase separation [11].

The aim of the present study is to determine the calorific power of the secondary materials obtained

* To whom all correspondence should be sent:
lmllldy@126.com

from the separated fractions coming from MSW from Brasov in 2010 and processed in the same year by melt-mixing and thermoforming. The influence of the thermal processing and time (assimilated with a second life cycle) on the calorific power of secondary polymers will be discussed in comparison with that of the polymers obtained at the end of the first life cycle. A critical analysis of the efficiency of polymers recycling versus incineration, in different life cycles, is presented.

MATERIALS

Polymeric waste coming from MSW collected in 2010 from Brasov County, Romania, has been separated by flotation in alcohol and alcohol-water solutions, based on density differences, in 13 fractions, described in papers [12-13].

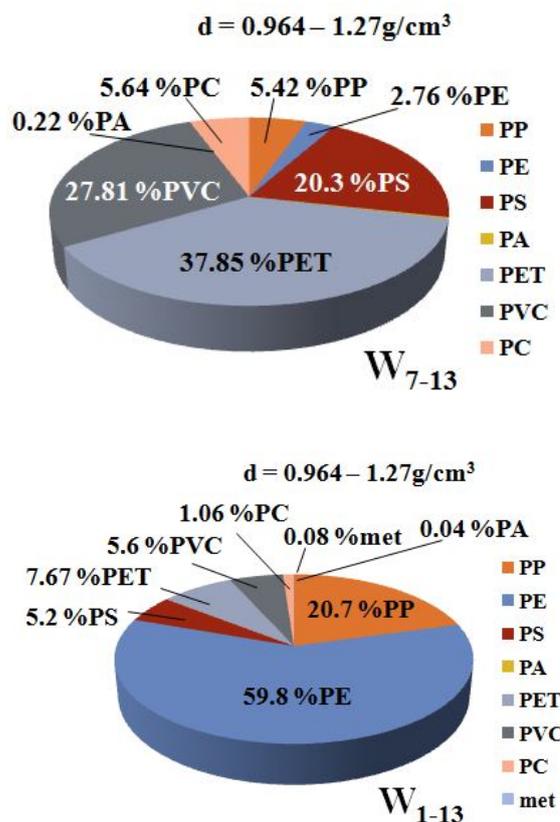
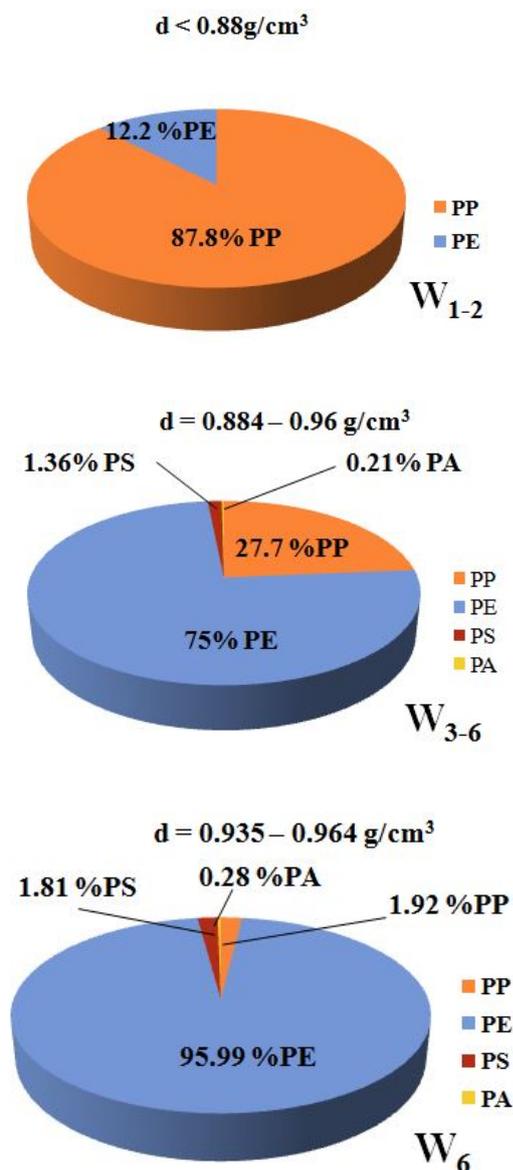


Fig.1. Composition of the fractions under present study, separated from polymeric municipal solid waste (MSW) from Brasov county, Romania in 2010 [12]

The composition of each fraction has been determined by correlating the mass-fraction obtained by FT-IR spectroscopy with the image analysis made by CIELab method [11-12].

Then, different fractions containing similar polymers have been mixed again and coded: W1-2; W3-6; W7-13 and respectively W1-13, where W means waste and the attached number represents the code of mixed density fractions. These narrow fractions were cooled up to -5°C , grinded up to 0.5-1 mm flakes dimensions, by using a centrifugal mill ZM200, melt-mixed by using a Brabender mixer with co-rotating twin screw extruder that allows the setting of the temperature, the mixing speed (60 rpm) and the duration of the mixing (10 minutes). The mixing temperature has been chosen as 10°C higher than the melting temperature of the dominating polymer in the fraction: for fractions with major polyolefin content (PE and PP) the work temperature has been set at 180°C and for fractions containing other polymers than polyolefin, the work temperature has been set at 220°C . The obtained melt mix has been cooled, cut and pressed in a Carver hydraulic press to obtain homogeneous sheets, without air bubbles, having the following

dimensions: L x l x h: 150 x 150 x 1 mm. These samples have been submitted to different analyses to evaluate the opportunity of mechanical polymers recycling.

The composition of the recycled fractions is presented in Fig.1.

The samples have been kept in laboratory conditions for 7 years. Major properties alteration has been noted. The mechanical properties dramatically decreased and the initial bacteriostatic character disappeared (unpublished own results). Considering the storage period as a second life cycle, once the material properties decreased making it unusable for a new life-cycle, another alternative of recycling could be incineration with energy recovery. In this context, the samples were submitted to calorimetric analysis.

METHODS

The obtained waste samples were weighed using the 0.1 mg precision analytical balance (Kern & Sohn ABJ 220-4M). Each weight of the sample was about 1.1 to 1.3 grams to obtain an acceptable temperature increase in calorimeter of 2.0 to 4.0°C for heat value measurements according to standards [14]. The bath temperature was monitored and recorded during the combustion process in a XRY-1C oxygen bomb calorimeter device with data acquisition software (XRY-1C Oxygen Burner Calorimeter, Shanghai Luheng Instrument Co.). Before determination of the heat of combustion, the calorimeter was calibrated using a standardized benzoic acid sample (Parr Instruments Co.). The thermal capacity of the calorimeter was about 12762 J/K. Following the standard procedure [14], the each weighed sample was placed inside the oxygen bomb. On the bottom of the bomb was added 1 ml of deionized water to investigate acid formation. The fuse wire was connected to the electrodes in the vessel and was brought into contact with the sample. The bomb was then assembled, sealed and the air content was removed, by twice pressurizing to 0.5 MPa with pure oxygen. Prior to determination, it is pressurized again with pure oxygen at 3.0 MPa. The increase of bath water temperature was measured by using a precision sensor with a temperature resolution of 1.0 mK. The temperature was recorded, during the test, by the data acquisition system at every 30 seconds.

RESULTS AND DISCUSSIONS

The samples obtained by melt-mixing and thermoforming of fractions coming from separation

of polymeric MSW, collected from Brasov county, Romania, were firstly visually compared, after 7 years of storage in the laboratory conditions, with the same samples evaluated immediately after preparation. The first observation was that they loosed their mechanical resistance, becoming very brittle. The W3-6 initial samples showed a good mechanical resistance, close to that of the virgin PE [15], allowing their application in similar ranges. After 7 years, the samples brittleness makes these materials unusable. Possible ageing processes (oxidation, crosslinking, phase separation) occurred.

In the present study, the heat of combustion was determined for the mentioned samples (2010 samples and 2017 samples) and its value was compared with that obtained for the separated fractions at the end of their first life cycle.

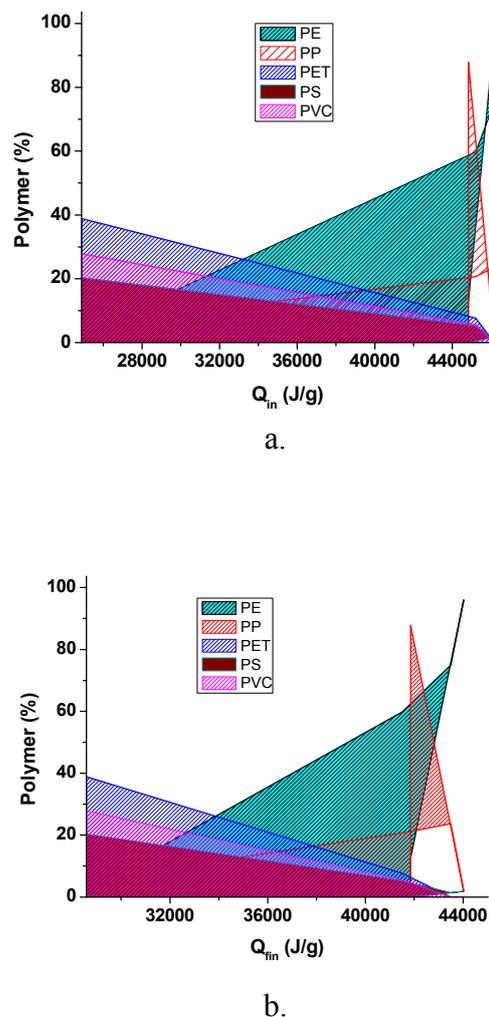


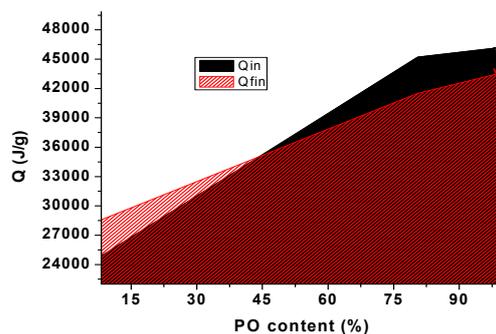
Fig.2. Influence of the composition of the polymeric fractions from MSW on their heat of combustion: (a) initially separated fractions; (b) recycled materials by melt mixing and thermoforming

The differences between the obtained heat of combustion values for the two series of samples will allow us to conclude on the dominating chemical or physical processes that occurred in the tested materials during their thermal treatment and storage for 7 years. Also, these values will give an image on the heat of combustion alteration during a second life cycle of polymeric materials under study, answering to the question: is it better to mechanically recycling polymeric wastes or to incinerate them at the end of the first life cycle?

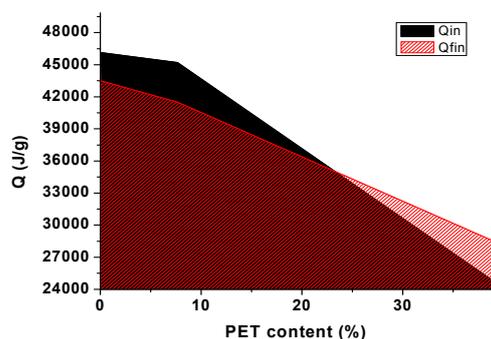
Calorimetric data obtained for both series of samples (initially separated ones and that recycled by melt mixing, thermoforming and kept in the laboratory conditions for 7 years) were compared and graphically represented as function of fractions composition, aiming to evidence the individual influence of each polymer on the energy content of the obtained materials.

Negative influence on the fractions' heat of combustion was recorded for PET, PVC and PS. Higher the PET, PVC and PS content in the polymer fractions, lower the heat of combustion is. This could be explained by the lower Q value of PET (21600 J/g [17]), and of PVC (18000-19000 J/g [16]), and by the low PS content in the MSW fractions, up to 20.7 % in W7-13. PS has a high Q value (41600 J/g) [17], but its low percent in the fractions has the dominating influence on their heat of combustion, as it can be seen in Fig. 2.

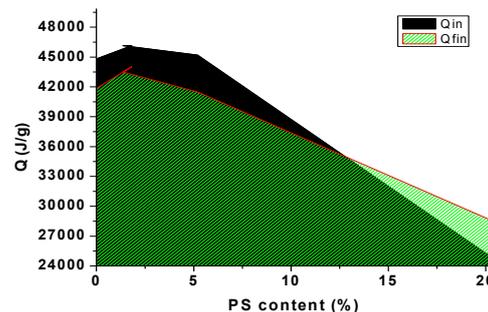
Similar behaviour is revealed in case of recycled fractions by melt mixing, thermoforming and then, stored for 7 years (Fig.2 b). The only differences are: (1) the lower Q values obtained for fraction having higher polyolefin content by comparing to that of fresh separated fractions. This behaviour is normal, taking into account the degradation processes occurring during thermal treatment and storage. Intermediate oxidized compounds have generally lower combustion heat than that of un-oxidized compounds. (2) Higher Q values were obtained for fractions with higher content of PET, PVC and PS by comparing to the same fresh separated fractions. This fact could be explained by PVC degradation during the thermal treatment and storage, releasing HCl. This led to the unsaturated polymeric chains formation. The last ones have higher heat of combustion by comparing to the chlorinated compounds. Also, they could react with thermal degradation compounds coming from PET, PS, PA and contaminants leading to compounds with higher heat of combustion.



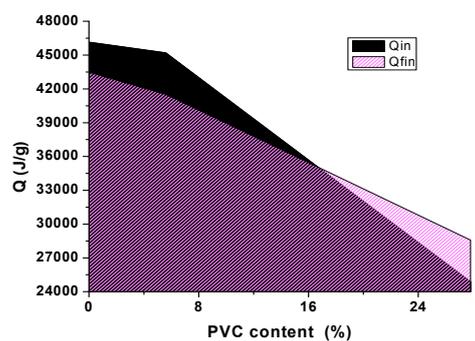
a.



b.



c.



d.

Fig.3. Comparison between the heat of combustion of fractions at the end of first life cycle and at the end of the second life cycle: (a) influence of PO-s content; (b) influence of PET content; (c) influence of PS content; (d) influence of PVC content

From Fig.3 it could be observed also that fresh separated fractions have higher heat of combustion

for higher content of PO-s; the recycled fractions by melt mixing, thermoforming and after storage evidenced lower heat of combustion for fractions with higher PO-s content. For fractions having lower content of PO-s (<45%) the Q-values for recycled fractions increased by comparing to fresh separated fractions (Fig.3.a).

Fig.3.b, 3.c and Fig.3.d show that the increase of the PET, PVC and PS content determines the Q-values decrease in both series of samples, but an increase of the Q-values by comparing the fractions at the end of the second life cycle with the fresh separated ones could be noted for mixtures containing higher PET content than 22% and higher content of PS than 13% and higher PVC content than 17%.

Variations of Q_{fin} by comparing to Q_{in} are presented in Fig.4.

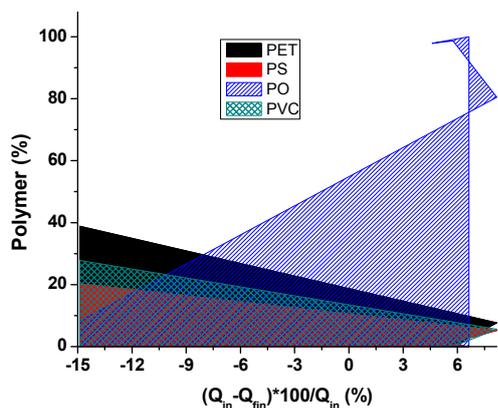


Fig.4. Quantification of abatements of Q_{fin} from Q_{in} as a function of fractions composition

Higher percent of PO-s in fractions increases the mixture instability (PO-s oxidation) and as consequence, decreases the Q_{fin} values and increases the differences ($Q_{in}-Q_{fin}$) up to 6%.

On contrary, the presence of PET, PVC and PS in the mixture, increases the density of the fractions, favoring a better retaining of the degradation products, increasing the Q_{fin} values and making the above mentioned differences negative, up to 15%.

This mechanism is consistent with the ash content measured after samples combustion. Fig.5. shows that the ash content is zero for samples with very high PO-s content while the increase of the PET, PVC and PS determines the increase of the residue. Decreasing PE and PP content will lead to the increase of the ash content. The obtained results are partially consistent with that reported by [18]. Based on the proximate and ultimate analysis results

and heat of combustion values, Zhou H and al. classified plastics from MSW in three clusters: (1) PE, PP and PS; (2) PVC and (3) PET, each containing polymers with similar properties.

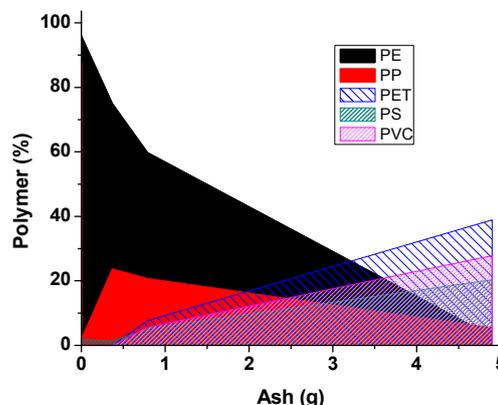


Fig.5. Variation of the ash content obtained after incineration of the polymeric fractions at the end of their second life cycle

1) PE, PP and PS have C+H content nearly 100%, O, N, S, Cl content almost zero, and they are completely volatile plastics, forming no char. Their heat of combustion is high, decreasing in the decreasing sequence: PP>PE>PS. [18-19].

2) The second cluster refers to PVC that contains Cl in the range of 50-60% and as consequence the C and H content diminished to 38-42% C and 4-6% H, variable content of ash, probably due to additives, up to 15%, volatiles are in the range of 71-95% and fixed carbon between 4% to 21%. Its heat of combustion is approximately half from that of PP, PE and PS, respectively.

3) The third cluster contains PET. It has approximately 62% C, up to 5% H and a high content of O approximately 33%. Volatiles are around 90-94%, ash very low, 0.09-0.31% and fixed carbon is 5.6-9.45%. The heat of combustion is low, around half from that of the first cluster and close to PVC.

Based on our results, both PVC and PS seems to behave similar to PET, decreasing the fraction's heat of combustion and increasing the ash content, while PE and PP, decrease the ash content and positively contribute to the fraction's heat of combustion.

Negative contribution of PS, PVC and PET content to the heat of combustion of fractions containing them, could be explained by the simultaneous decrease of the PO-s content of those fractions.

In spite of their very low ash content as individual polymers, PS and PET contribute to the increase of

the ash content of waste fractions. This behavior could be explained by PS and PET higher melting temperature (240°C for PS and 212-265°C for PET) when comparing them with PO-s. This characteristic draws near PS to PET, excluding it from the cluster (1), including PE and PP, proposed by using other criteria. PE and PP have lower melting temperature (HDPE: 120-135°C; LDPE: 70-100°C and PP: 130-171°C). This aspect possibly determines the including of PO-s and PVC intermediate combustion products or fillers into a sticky mass of melted PS and PET, finally affecting the waste fractions' combustion mechanism and consequently, the ash content.

Probably, this is the cause for that many researchers reported a higher content of ash for polymeric waste fractions, by comparing to individual polymer ones. For example, analysis of MSW in Piyungan Landfill, Yogyakarta, Indonesia, led to an ash content of plastic fraction of about 10%, while elemental analysis shows a high percent of O, meaning a possibly high percent of PET [20]. Also, analysis of the organic fraction of MSW collected from Hyderabad city of Pakistan, contained a plastic fraction with a high percent of O that generates approximately 5% of ash [21].

Proximate analysis of municipal solid waste in Ado-Ekiti, Ekiti State, Nigeria, shows for polymeric fraction, an ash content about 12% [22].

Pedersen et al. [19] reported a significantly different behavior of PET by comparing to PE and PP, when they were burnt in an electrically heated rotary drum furnace. Almost immediately after the injection, the PET pellets stuck to the drum wall, where they stayed during the devolatilization and char combustion. Van Der Geld et al. evidenced also important differences in combustion regression rate of PS and PE [23].

CONCLUSIONS

All the obtained results led to the following conclusions:

Chemical structure alteration of the polymers, during their second life cycle, is not very high. More important that degradation of individual polymers in the recycling process is the polymers separation effectiveness. This one seems to be the dominating influence both on the energy content and on mechanical properties of the recycled material. The last ones are mainly due to the polymers' incompatibility and as result to phase separation. Calorimetric measurements reveal that chemical degradation during polymeric waste reprocessing by

melt mixing and thermoforming is minor, fact that allows multiple recycling of PO-s. After that, when mechanical properties will no more attain the requested values for specific application, due to the chain scission, oxidation, or contamination, the recycling by incineration could be applied, due to very low decrease of combustion heat during the reprocessing and new life cycles.

Keeping with the actual classification of polymers in wastes, based on proximate and ultimate analysis, our results found similar behaviour for PE and PP (class 1) and PET (class 3) in the complex fraction mixtures. PS, initially included in class 1, behaves different from PE and PP, being closer to PET (which is closer as melting temperature): negatively influencing the fractions Q-values and participating to the increase of the ash content. Incineration of the complex mixture of polymers has to take into consideration the reciprocal influence of the mixture components types and concentration as well as of their T_g and T_m values on the burning mechanism.

NOMENCLATURE

- Q-values - Heat of combustion, J/g;
- Q_{in} - Heat of combustion of freshly separated fractions, J/g;
- Q_{fin} - Heat of combustion of fractions, after processing, J/g;
- T_g - glass transition temperature, °C;
- T_m - melting temperature, °C.

Abbreviations

- HDPE - High density polyethylene
- LDPE - Low density polyethylene
- Met - metal traces
- PA - Polyamide
- PC - Polycarbonate
- PE - Polyethylene
- PET - Poly (ethylene terephthalate)
- PO - Polyolefin
- PP - Polypropylene
- PS - Polystyrene
- PVC - Poly (vinyl chloride)

ACKNOWLEDGEMENTS

This research was funded by FP7 Grant 212782, Magnetic Sorting and Ultrasound Sensor Technologies for Production of High Purity Secondary Polyolefins from Waste, acronym W2Plastics.

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