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Eco-Friendly Synergetic Processes of Municipal Solid Waste Polymer Utilization

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The synergetic approach for eco-friendly efficient utilization of Polymer Solid Waste is presented. It is accounting for chemical processes in polymers during the use of the original product and at the stage of its waste recycling. The study of the polymer photoconductive degradation based on analysis of chemical reactions in the polymer film is presented. It is discussed how to predict the properties of the polymer after its use and to develop the efficient technique for its recycling. The recycling technique is demonstrated on examples of recycling polyethylene film by chemical foaming and injection moulding methods. The results of factorial experiments on the influence of different process parameters on process intensity and secondary product quality are presented. The results are used for developing modern technologies for the processing of polymer solid wastes into useful secondary products.

1. Introduction

As estimated by the World Bank report (Hoornweg and Bhada-Tata, 2012) about 1.3 x 10^9 t of Municipal Solid Waste (MSW) was generated worldwide in 2012, with a projection to increase to 2.2 x 10^9 t in 2025. Generally, over 10 % of this amount is polymer plastics. Current waste-to-energy technologies are well suitable for sustainable waste management and mitigation of environmental effects (Fodor and Klemeš, 2012) by increasing energy efficiency in the area (Touš et al., 2014). However, incineration of plastic solid waste (PSW) is a major source of air pollution by toxic gases like Dioxins, Furans, Mercury, Polychlorinated Biphenyls, Halogens, and other hazardous substances that are posing a threat to the environment and human health (Verma et al., 2016). Besides, the initial production of new plastics requires 4 % of the world's crude oil production that is equivalent to 1.3 10^9 barrels a year (Kreiger et al., 2014) and recycling of plastic solid waste is contributing to limiting of crude oil consumption. Sustainable recycling of PSW enables reduction of crude oil usage, while reducing environmentally hazardous carbon dioxide, other toxic emissions and landfill waste disposal. It gives opportunities to manufacture new products without consumption of new materials in this way contributing to sustainable development (Mwanza and Mbohwa, 2017). The economically and environmentally beneficial utilization of PSW requires a synergetic approach combining different methods of its treatment to obtain the optimal solution.

As it is discussed in the review by Singh et al. (2017), the main families of plastic polymers encountered in PSW are Low and High-Density Polyethylene, Polypropylenes, Polystyrene, Polyethylene Terephthalate and Polyvinyl chloride. All of them belong to the polyolefin class of polymers which are sufficiently thermostable materials and their re-processing by extrusion or injection moulding does not cause difficulties but has some features requiring closer attention. Recycling of plastics mainly depends on its type and before recycling the compatibility issue must be analysed and resolved. The degradation of polymers in PSW should be considered, including thermal degradation, photodegradation, biodegradation and degradation from mechanical stress (Ammala et al., 2011). There is also required proper characterization of polymer waste for recycling (Hu et al.,

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2013). To recycle PSW, different methods are used, including mechanical and chemical recycling. The survey of these methods is presented in a paper by Ragaert et al. (2017). The choice of PSW recycling method depends on specific waste streams and characteristics of the product which is aimed to be obtained after recycling. One of the mechanical ways of polymer recycling is foaming. It represents the technique for the production of low density, highly thermal and acoustic insulating, shock adsorbing materials (Greco et al., 2005). One of the promising ways to produce polyethylene foams is extrusion through different foaming agents. The properties of obtained products are determined by nature and degradation characteristics of recycled PSW, extrusion process parameters and additives (Wu et al., 2017).

The traditional for Eastern Europe chaotic technology of handling solid waste at the stage of collection does not leave the possibility of their qualitative, purposeful processing into secondary materials. The necessity to classify the polymer part of solid waste implies the identification of structural and chemical changes at all stages of operation and the selection of scientifically grounded new synergetic methods for modifying technological and physical-mechanical properties, in particular of secondary polyethylene. In this paper are presented the results of experimental study of polyethylene part in PSW at some municipalities in Eastern Europe. The discussion concerns the possible chemical reactions in the process of polymer degradation and the ways to recycle this PSW. The results of experiments on polyethylene recycling with analysis of obtained polyethylene foams, their properties and effects of different recycling process parameters are presented. The main attention is paid to PSW with reduced to a critical minimum physical-mechanical, physical-chemical, rheological, molecular, structure and other characteristics. It concerns polymer waste that lost some of its quality for various reasons of exploitation or being a mixture of different grades and compositions of polymers and other materials. The research is aimed at studying such issues as the development of modern high-performance models of synergistic recycling-modification of polyolefin polymeric solids in order to produce innovative secondary polymers.

2. Chemical reactions during polymer life

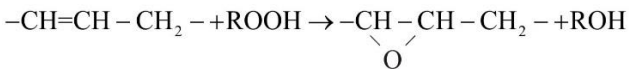
To develop technology for the recycling of PSW, it is necessary to study the changes in composition and structure of the original product which occur during its lifetime. On this basis, the technology of obtaining recycled secondary materials from PSW can be developed. Such technology can provide an increase in operational properties of the material, as well as the expansion of areas of its use. It is necessary to consider structural and chemical changes of the polymer during its use as an original product. There are expected three types of reactions of the interaction of polymers with oxygen: oxidation as a process of separate molecular reactions, the oxidation on the chain mechanism, thermal decomposition of the polymer and oxidation of decay products. All of these types of reactions are observed in real conditions but most often the interaction of polymers with oxygen occurs on the chain mechanism. By analogy with the processes of the interaction of oxygen with low molecular weight hydrocarbons, this process is called auto-oxidation. It is initiated by light and thermal influences.

The study of the process of auto-oxidation of polyolefin during the operation is performed accounting for three stages: the period of induction, which accompanies the stage of nucleation of the molecular chains; acceleration period, which corresponds to the growth stages of the chains; the deceleration period corresponding to the stage of the chain breaks. The analysis of all these processes chemical mechanisms is performed. The development of all oxidative processes starts from the polymer surface and the introduction of oxygen deep into the material is determined by the rate of diffusion of oxygen into polymers. Therefore, film materials, according to this research, are most prone to photoconductive degradation. The synergy of inhibitors for the oxidation of polyolefin in our studies is associated with chain free radical fat oxidation processes (possible end products) schematically expressed by the sequence of reactions:

$$R^{\cdot} \xrightarrow{O2} RO_2^{\cdot} \xrightarrow{RH} ROOH^{\cdot} \xrightarrow{RH} R^{\cdot} \quad (1)$$

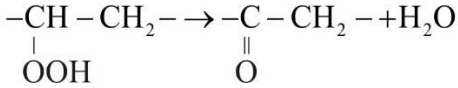
To achieve synergistic effects, information is used on the types of interactions of the components. One of the most common ways to achieve synergistic interactions in polymeric utilization/modification systems is the so-called "restorative synergism" - the oxidized form is restored by less active, and therefore more stable, so-called "antioxidant". In the study, it was considered that in the reactions of saturated hydrocarbons the probability of oxygen attack is the same for all methylene groups, whereas in olefins mainly methylene groups are oxidized which are in the α-position to the double bond (Bukhkalo, 2017). Hydroperoxides are thermally unstable and decompose under heating not by chain mechanism but in the usual molecular mechanism, with the formation of stable oxygen compounds. The final simplified forms of chemical reactions are as follows.

The interaction of a hydroperoxide with oxidized fragments of polymeric chain:



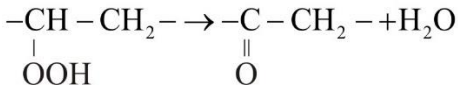
(2)

The formation of carbonyl groups is possible with reactions:



(3)

With further oxidation carbonyl compounds can transform into carboxyl compounds:



(4)

The presence of a different oxygen-containing groups in PSW at different locations is confirmed by data of polyethylene film analysis after its usage in different regions presented in Table 1.

Table 1: The change of polyethylene film properties during its usage (Bukhkalo, 2017)

The place	Time of operation d	Content, %				Breaking stress on stretching, MPa	Relative elongation on breaking, %
		polyether groups	carboxyl groups	hydroxyl groups	gel fraction		
Kharkiv,	60	1.53	0.31	0.19	35.3	9.6	221
Ukraine	120	0.19	1.15	0.44	34.8	9.4	182
Sochi, Russian	60	2.0	0.72	0.91	29.4	9.4	130
Federation	120	–	1.28	1.21	40.8	9.3	212
Olayne, Latvia	60	1.10	0.57	0.30	28.5	9.7	134
	120	0.04	0.90	0.61	39.4	9.5	151
Livny, Ukraine	60	1.20	0.20	0.28	22.8	9.8	340
	120	0.03	1.10	1.26	29.7	9.5	300

All these reactions are associated with the breaking of chains and are related to destructive processes, but along with them there are aggregative processes, in which double bonds of parallel chains take part, and also chain reactions simultaneously in two or more points of the macromolecule. As a result of the crosslinking process, spatially crosslinked structures are formed. At the first stage of the study the assumption is made that in the ageing processes under the influence of oxygen and light, the cross-linking takes place mainly by forming oxygen bridges between branched chains. And then these bridges can be peroxide, ester and polyester. The development of all oxidative processes occurs from the surface, the intrusion of oxygen into the interior of the material is determined by the rate of diffusion of oxygen into the polymers. Therefore, the film materials (as shows results of the study presented in Table 2) are most susceptible to photo-oxidative degradation.

Table 2: The variation with time of the number of unsaturated groups in polyethylene film

The time of operation, d	The content of unsaturated groups on 100 atoms of carbon				
	Vinyl group	Vinylidene group	Transvinyl group	Sum	Methyl group
0	0.0142	0.0974	0.0113	0.1230	5.6720
30 summer	0.0I92	0.0620	0.0125	0.0940	5.0910
62 summer	0.0583	0.0558	0.0290	0.1430	4.5210
128 summer	0.1385	0.0400	0.0300	0.2085	3.6980
30 autumn	0.0164	0.0769	0.0154	0.1087	4.9520
90 autumn	0.0111	0.0636	0.0145	0.0892	4.9630

Based on analysis of chemical processes in polyolefin during natural exploitation, the algorithm is developed for determining the change in the polyolefin properties in the course of natural usage. It was found that oxygen diffuses mainly into amorphous regions, where the free volume is greater than in the crystalline regions. Amorphous regions occupy 40 to 50 % of the volume and they can be distributed throughout the mass, permeating the film throughout the film thickness.

3. The recycling technique

As an example of a synergetic approach to polymer utilization, the chemical foaming method of the polyethylene waste is developed. The experiments to determine the influence of process parameters on the characteristics of polyethylene obtained after recycling process were performed. As the controlling parameters (factors) are taken: X_1 is the relative amount of foaming chemicals, %; X_2 is the temperature of foaming, ºC; X_3 is the time of treatment at foaming temperature, min. The characteristics of the obtained polymer are: Y_1 is the number of created cells per 1 cm^2 of the obtained polymer cross-section; Y_2 is the relative volume of gas phase in a process of secondary polymer production, %; Y_3 is average diameter of cells; Y_4 is the density of the secondary polymer. The experiments with two-level factorial design are performed at following range of factors: X_{10} = 3 %, Δ X_1 = 1 %; X_{20} = 170 ºC, Δ X_2 = 10 ºC; X_{30} = 10 min, Δ X_3 = 5 min. The resulting functions are presented in Table 3. More detailed discussion of the specific factors influence is not presented in this paper.

Table 3: The effect of process parameters on secondary polymer properties in foaming

Characteristic	Function
Y_1	$Y_1 = 2{,}987.50 + 237.50x_1 + 362.50x_2 + 337.50x_3 + 12.50x_1x_2 + 37.50x_1x_3 - 187.50x_2x_3 + 12.50x_1x_2x_3$
Y_2	$Y_2 = 44.91 + 6.58x_1 + 7.27x_2 + 9.45x_3 - 0.28x_1x_2 + 1.82x_1x_3 - 5.12x_2x_3 - 5.22x_1x_2x_3$
Y_3	$Y_3 = 0.17 + 0.0004x_1 + 0.0007x_2 + 0.0009x_3 + 0.0001x_1x_2 + 0.00013x_1x_3 - 0.0004x_2x_3 - 0.0009x_1x_2x_3$
Y_4	$Y_4 = 0.280 - 0.083x_1 - 0.120x_2 - 0.130x_3 - 0.002x_1x_2 - 0.007x_1x_3 + 0.050x_2x_3 + 0.073x_1x_2x_3$

Secondary polyethylene with synergistic foaming processes was obtained from a long operated polyethylene film. It was, further controlled by the amount of gel fraction, carbonyl, carboxylic and ester groups. The activation complex of the foaming process includes azodicarbonamide, zinc oxide, stearic acid and calcium stearate. The size of the cells of foamed polymers significantly influences their properties. With decreasing bubble size of the gas phase (i.e., with an increase in their amount per unit volume) the strength significantly increases as also the value of the limiting deformation at stretching.

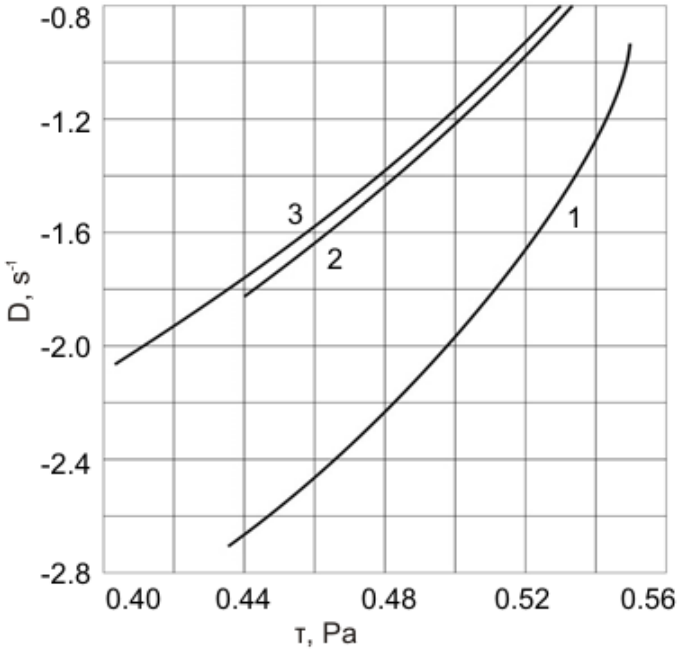


Figure 1: The rheological curves for SPE compositions: 1 – 0 % BS; 2 – 1 % BS; 3 – 2 % BS.

To characterize the processes of secondary polyethylene obtained with modification by barium stearate (BS) the melt flow index Y_5 was chosen. With the production of the secondary polyethylene by injection moulding and modification of its properties with dicumyl peroxide, the fracture toughness Y_6 in MPa was determined. Factors chosen are: X_1 is injection moulding temperature in the last zone, °C; X_2 is the duration of the casting cycle, s; X_3 is the relative amount of dicumyl peroxide, %. The initial data for the experiment were selected as follows:

X_{10} = 190 ºC, Δ X_1 = 20 ºC; X_{20} = 75 s, Δ X_2 = 10 s; X_{30} = 0.25 %, Δ X_3 = 0.15 %. The resulting functions obtained in experiments with two-level factorial design are presented in Table 4.

Table 4: The effect of process parameters on secondary polymer properties in moulding

Characteristic	Function
Y_5	$Y_5 = 17.40 - 0,09T - 0.38G + 6.07C + 0.002T \cdot G - 0.03T \cdot C - 0.16G \cdot C + 0.0008T \cdot G \cdot C$
Y_6	$Y_6 = -15.21 - 0.23T - 0.58\tau - 173.85C + 0.003T \cdot \tau + 0.91T \cdot C + 2.32\tau \cdot C - 0.012T \cdot \tau \cdot C$

Synergistic processes of recycling-modification of the composition of secondary polyethylene (SPE) with barium stearate (SB) were studied and analyzed by the change in rheological curves presented in Fig.1. A characteristic feature is the practically directly proportional dependence of the shear stress (τ = 0.4 ÷ 0.56 Pa) on the shear rate (*D* = -2.8 ÷ -0.8 s^{-1}), which indicates the possibility of facilitating material processing and allows it to be carried out in more wide range of technological parameters.
It was established a general increase in technological properties (P – productivity, %) with the introduction of a modifier (C – 0 - 5 %), which leads to an increase in productivity during the granulation process (Fig. 2), as well as to improving the quality of products.

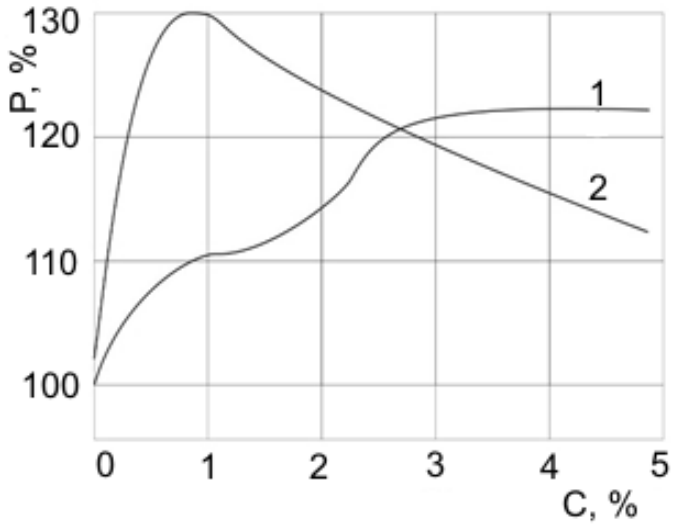


Figure 2: The productivity of the granulation process of compositions: 1 – SPE + SB; 2 - SPE + polyethylhydrosiloxane

The results are implemented in the technologies of modern high-efficiency methods for the processing of polymer solid wastes into products in the industry. Synergy for the formation of secondary polymer raw materials in the process of utilization-modification can be considered as the use of the features of chemical transformations in the polymer, taking into account that the main segmental movements, diffusion processes and chemical interactions occur in the amorphous phase of the polymer.

4. Conclusions

The eco-friendly efficient utilization of Polymer Solid Waste requires the synergetic study of processes in polymers during the use of the original product and on the stage of its waste recycling. The approach to study the polymer degradation based on analysis of chemical reactions of photoconductive degradation in the polymer film is proposed. It enables to determine the properties of the polymer after its use and develop the efficient technic of its recycling. The development of recycling technic is demonstrated on examples of recycling the polyethylene film. The methods of polymer chemical foaming and injection moulding are considered. The influence of different factors on process intensity and quality of secondary polymer is investigated experimentally and correlations are obtained. It enables to develop technologies of modern high-efficiency methods for the processing of polymer solid wastes into products in the industry.

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