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Complex Approach to the Processing of Polymer Waste into Fuel, Lubricant Materials and Construction Materials for the Oil Refining Industry

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Abstract

The article describes a complex approach to the disposal of solid polymer waste produced in the cities of Ukraine through their technological pro-cessing into various types of fuel, lubricants and construction materials. This approach is supposed to have positive environmental effect in big cities and on the outskirts. Fuel fractions (bp.-200°C; 200-300°C and 300-360°C) were produced by thermal destruction. According to their characteristics and octane (66-72 units) and cetane (42-60 units) numbers in particular, these fractions are recommended for the production of motor fuels and preservative plastic lubricants (NLGI 3/4/5) and for combined processing of polymer waste with other waste - antifriction (NLGI 00/0/1/2/3) and sealing (NLGI 3/4/5) plastic lubricants; protective coatings with a softening temperature index value in the range of 80-130 °C, penetration at 25 °C in the range of 10-40 mm×10^{-1}. New structural materials were obtained from secondary polymers and mineral fillers using the technology of thermal compounding and pressing under pressure. These materials are characterized by high resistance to chemical reagents (loss of mass 0.11-4.60% by mass), water resistance (0.11% by mass); compressive strength (27.3 MPa). They have prospects for designing new waste water disposal systems for oil refining enterprises.

Keywords*: Solid domestic waste; Polymers; Sorting; Technological processing; Destruction; Compounding; Motor fuels; Plastic lubricants; Building materials.*

1. Introduction

One of the main problems of big cities is accumulation and utilization of solid domestic waste (SDW) and polymers in particular. Today polymers are quite widely used everyday life due to their availability, cheapness and operational properties. According to the amount of polymer waste generated annually in large cities of Ukraine, it ranks third (up to 13% of the total amount of MSW) after food waste, paper and cardboard. Up to 80% of all polymer waste is disposed of by burying at landfills which is harmful considering their high biological stability (the term of decomposition of polymers is more than 300 years). On the other hand, polymer waste should be considered not only as a significant environmental threat but also as a source of valuable feedstock for production of a big variety of domestic goods.

According to the data of the State Statistics Service of Ukraine, more than 40,000 tons of polymer waste are accumulated annually 31% of this amount is polyethylene, 10% is poly-propylene, and 8% is polystyrene. Nowadays only of Ukrainian polymer waste are processed into secondary feedstock. This can be explained by the lack of a clear, balanced state policy of systematic waste management and by low awareness of the population about the separate gathering of domestic waste. As a result, there is a deficit of domestic waste that can be processed into the secondary feedstock. Overcoming this deficit is solved by creating a system for sorting polymer waste by type, which is a key element in a comprehensive approach to their technological processing.

Considering all the given facts a comprehensive approach to the technological processing of polymer waste was proposed (see Fig. 1). It includes sorting it by type, primary preparation (shredding, cleaning, drying) and the direction of its further processing that depends on the properties of the polymer waste and the final product.

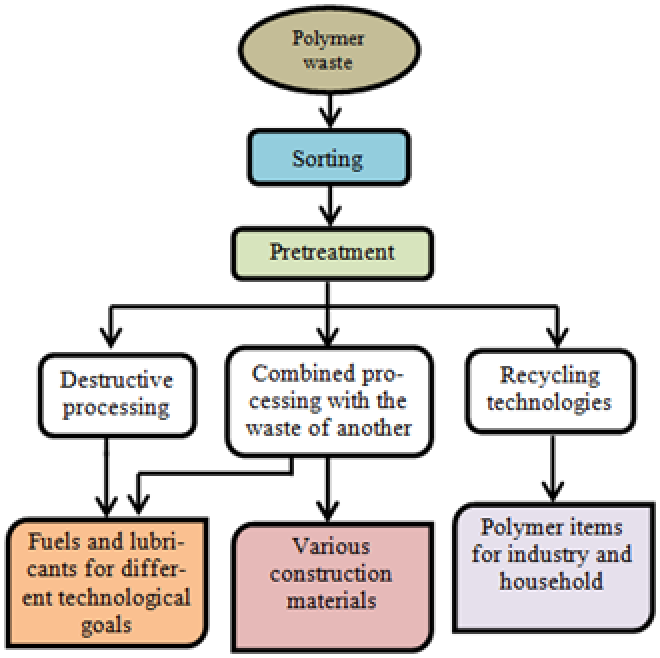

Figure 1. A comprehensive approach to the technological processing of polymer waste was proposed

Therefore most polymer waste (for example, low- and high-density polyethylene, polypropylene, polystyrene) can be used for production of fuel and lubricant materials without involving cleaning of neutralization systems both for final product and for gaseous emissions of production. The main method of processing is destructive thermal or thermocatalytic processing [1-7]. Moreover, thermal processing makes it possible to produce components of motor fuels, while thermocatalytic processing, due to a more stable hydrocarbon composition, provides receiving of final commodity items. Nowadays destructive processing becomes more relevant in Ukraine, especially considering the lack of classic petroleum raw materials which are used for production of fuel and lubricants.

It is known that fuels and lubricants may contain harmful sulfur- and chlorine-containing components [8-9]. There is an internal sulfur which can be present as a part of polymer waste, and external sulfur, caused by various impurities (for example, dyes) entering the raw materials. Sulfur in the amount of up to 200 ppm can be contained in feedstock such as ethylene, propylene or butylene.

Considering polymer feedstock it should be noticed that sulfur can be involved in production of new types of polymer materials - chlorosulfonated polyethylene (CSP). CSP is secondary polyethylene produced by treating of polyethylene with sulfur dioxide in the presence of chlorine. The amount of sulfur in CSP reaches 0.8-2.2%, and the amount of chlorine in these polymer materials can reach 27-45% [10-11]. Polyvinyl chloride (PVC) is another polymer based on ethylene and sodium chloride, which is widely used for production of multifunctional construction materials. Chlorine content in PVC reaches 57%. Chlorine released during thermal processing of PVC causes corrosion of technological equipment and is very harmful for the environment [12].

It is known that the main product of thermal destructive processing of sulfur-containing hydrocarbons (like thermal or catalytic pyrolysis) are fuels and lubricant materials. Moreover, the heavier the fractional composition of the product, the more sulfur-containing compounds it contains (for example, cycloalkyl derivatives of benzo- and dibenzothiophene) [13]. As a result of its harmful effect (on equipment during the production and direct use of fuels) and considering modern requirements for Euro-5 and Euro-6 motor fuels, the sulfur content in fuels (gasoline and diesel) is limited by 5-10 ppm [14-15]. In addition, sulfur and chlorine are catalytic poisons for catalytic destructive processes like cracking and pyrolysis. Therefore, the processing of the above-mentioned polymeric feedstock into fuels and lubricants inevitably involves additional stages of cleaning and pretreatment [16-17]. This obstacle significantly complicates production and increases the cost of produced fuels or their components.

From an economic point of view for the feedstock with high sulfur content it is sensible to replace thermal destructive processes with recycling technologies that provides producing of secondary materials with the same properties as a feedstock itself. Recycling technologies (for example, mechanical processing and extrusion technologies) are currently the most commonly useed in the world and are based on heating polymers to a viscous state, followed by obtaining finished products or semi-finished products for further processing [18-20]. Products obtained by such technologies can be used in the production of garden equipment, packaging containers, drainage systems, etc.

Another direction of the processing of such polymer waste can be their combined processing with other types of waste, which are generated in big cities. Such waste can be spent petroleum products and tires, which are generated in significant amount as a waste of transport infrastructure, and ash waste - residues from the burning of fuel (including fossil) at cogeneration power plants (CPP).

It is known that used petroleum lubricants may cause significant environmental harm because of the toxicity for all components of the natural environment - surface and underground waters, soil and plant cover, atmospheric air [21-22].

Used tires are a case of long-term environmental pollution. In addition, rubber is flammable and does resistant to biological decomposition and a pile of rubber tires is quite a convenient place for entire colonies of rodents and insects, many of which are a source of infectious diseases [23].

Ash from CPP has a size of up to 0.15 mm, consists of SiO_2 (30-40%), Al_2O_3 and Fe_2O_3 and cause a significant environmental pollution [24]. Therefore, in terms of the dangerousness and high tonnage of the waste described above, their combined processing with solid polymer waste can significantly improve the environmental situation in Ukrainian cities, reduce the area of landfills and become a valuable construction material (curbstones, pavement tiles, products for underground communications), which are used quite high demand on the building materials market. The current research describes a comprehensive approach to the processing of solid polymer waste and covers consists of interconnected spheres - communal and industrial. Polymer waste can be considered as a source for the wide range of commodity products for different areas of industry and infrastructure. And these directions of processing of polymer waste into construction and fuel and lubricants materials, in comparison with recycling technologies, in our opinion, are quite promising but still not studied enough. Considering this, processing of polymer waste was thoroughly described

2. Experimental

Industrial implementation of any technology is always based on laboratory re-search that defines choosing the technological parameters of production and determine the level of product. Low and high density polyethylene (LDPE and HDPE), polypropylene (PP), polystyrene (PS) were chosen as a feedstock in the current research.

Pretreatment is a quite important stage of any processing technology as well as sorting. Sorting considers grinding the polymers into particles no larger than 2-3 mm in size, washing from impurities and drying (residual moisture content up to 0.3%). This stage is necessary, on the one hand, to intensify further processing processes, and on the other hand, to reduce the overall dimensions of the devices.

Further stage is thermal destructive processing by heating it in a reactor-type apparatus to 400-480°C at a pressure of 0.1-0.14 MPa that provides producing of fractions used as motor fuels (automobile gasoline and diesel fuel) and plastic lubricants. The characteristics of the obtained products are given in tables 1-2.

Table 1. General characteristics of quality for fuel fractions produced by processing of LDPE, HDPE, PP and PS

Characteristics	Units	Value		
		b.p.-200°C	200-300°C	300-360°C
Density at 15°C	kg/m^3	767-779	784-797	805-827
Kinematic viscosity at 40°C	mm^2/s	0.61-1.88	2.00-3.45	4.3-6.9
Cetane number	-	-	42-49	51-60
Octane number	-	66-72	-	-
Flash point	°C	49	49-64	75-110
Self-ignition point	°C	333-293	289-267	252-229
Cloud point	°C	-31÷-25	-23÷-11	-10÷9
Pour point	°C	-35÷-28	-27÷-15	-13÷5
Corrosion of a copper plate (3 hours at 50 °C)	Class	1a-1b		
Sulfur content	ppm	<10		

Table 2. General characteristics of quality for fuel fractions produced by processing of LDPE, HDPE, PP and PS

Characteristics	Units	Value
Boiling point of a fraction	°C	Fraction > 320°C
Appearance	-	Homogeneous paste, beige or light brown color
Correspondence to NLGI	Class	3/4/5
Dropping temperature	°C	50-110
Flash point	°C	237-268
Acid point	mg KOH/g	0.05-0.50
Corrosion activity, 24 hours at 100°C	Class	1a-1b
Penetration at 25°C, within	mm.10^{-1}	145-249
Adhesion properties, at velocity	rpm	4000-8000

Combined processing of the prepared polymer raw materials with other wastes performs by compounding them at a temperature of 130-180°C and a velocity of the mixing device of 100-1000 rpm, for 60-120 minutes. By compounding polymer raw materials with used lubricating oils and automobile tires in this way, plastic lubricants (anti-friction and sealing) and protective coatings (mastics) can be obtained. The characteristics of the obtained products are given in Table 3.

Table 3. Characteristics of plastic lubricants (antifriction) without filler

Characteristics	Units	Amount
Disperse area	-	Waste motor oil SAE10W-40, SAE15W-40 SAE75W-140
Content of polymer material	% mass.	3.0-8.0
Correspondence to NLGI	Class	00/0/1/2/3
Drip temperature	°C	80-145
Penetration at 25°C	mm.10^{-1}	485-220
Strength limits at 50°C	Pa	120-195
Effective viscosity at 0°C and average gradient of deformation speed 10 s^{-1}	Pa.s	21-220
Colloidal stability	%	2-20
Tribological characteristics at (20±5) °C, wear rate at constant load 196H	mm	0.35-0.70

Combined processing of polymers and different domestic and industrial waste provides obtaining of wide range of commodity fuels and plastic lubricants. Along with it, it is possible to obtain valuable materials that can be used in the construction of oil refineries to create a sewage and wastewater treatment system.

The technology of such processing includes mixing polymer raw materials, waste motor oils and ash at a temperature of 200-270°C (depending on the properties of the polymer, in particular its melting point) for 30-60 minutes. Next, the resulting mixture is formed under a pressure of 15-30 MPa thanks to a hydraulic press.

To give the final product a commercial appearance, at the stage of mixing the prepared components, a dye can be added to the composition, and a reinforcing material (metal or fiberglass) can be added to increase strength. The quality characteristics for the obtained materials have the characteristics shown in Table 4.

Table 4. Characteristics of construction materials

Characteristics	Units	Value
Average density	kg/m^3	1845
Compressive strength	MPa	27.3
Water absorption	% mass.	0.11
Mass fraction of water absorbed by the material after final drying	% mass.	0.051
Wearing	mm^3/m	4.76
Frost resistance	Un.	550
Resistance to aggressive environments:		
1. Change in the mass of the sample (Keeping the sample in 30% H_2SO_4 solution for 72 hours)	% mass.	0.16
2. Change in the mass of the sample (Keeping the sample in 30% aqueous KOH for 72 hours)	% mass.	4.60
3. Change in the mass of the sample (Keeping the sample in diesel fuel for 72 hours)	% mass.	0.11

The obtained data (see Table 4) testify to the high operational characteristics of such materials due to the presence of polymers in their composition. In particular, this is manifested in resistance to the action of chemical reagents. Such reagents are always present in the wastewater of oil refining enterprises and cause corrosion of metal pipes of the water drainage system. The reliability of operation of such systems can be significantly increased by using the proposed materials.

3. Conclusions

Solid domestic and industrial waste in the form of polymeric materials is a significant environmental threat, but at the same time it should be considered as a valuable technological feedstock of a wide range of products for industrial and household use. The practical implementation of the proposed integrated approach to the processing of solid polymer waste generated in the cities of Ukraine will allow increasing the degree of processing of solid household waste that will have positive environmental effect. During the destructive and compatible processing of household polymer waste with other waste, it is possible to produce fuel fractions (bp.-200°C; 200-300°C and 300-360°C) which can be used for the production of motor fuels; antifriction (NLGI 00/0/1/2/3), sealing (NLGI 3/4/5) and conservation (NLGI 3/4/5) plastic lubricants; protective coatings with a softening temperature of 80-130 °C; penetration at 25°C within 10-40 mm×10^{-1}. New structural materials were obtained from secondary polymers and mineral fillers using the technology of thermal compounding and pressing under pressure. These materials are characterized by high resistance to chemical reagents (loss of mass 0.11-4.60% by mass), water resistance (0.11% by mass); compressive strength (27.3 MPa). They have prospects for designing new waste water disposal systems for oil refining enterprises.

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