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Using products of polyethylene recycling for the production of holding tanks

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Abstract. In this paper, the influence of recovered high-density polyethylene on the tensile strength at break, elongation at break, hardness Shore D, flexural strength, and charpy impact energy of the polymer compositions has been studied, as well as the process has been developed for rotational moulding of holding tanks made of products of polyethylene recycling. The developed compositions have satisfactory physical-mechanical properties, and they can be used effectively to make holding tanks from products of polyethylene recycling with modifying plasticizer. Notably, the products have a lower cost as compared to products made of virgin polyethylene. The developed technology of holding tank production from products of polyethylene recycling addresses the important environmental problem regarding the management of polymer waste and the transition to a circular economy.
Keywords: polyethylene recycling, holding tanks, rotational moulding, waste management

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1. Introduction

Nowadays, the consumption of polymer materials is continuing to grow. Thus far, the worldwide consumption of large-tonnage polymer materials exceeds 265 million tons. Polyolefins account for more than 65 % of the demand.

Recycling of used plastics is a major issue in the polymer industry [1-17]. As estimated by NITsPURO (Research and Development Center for Management of Resource Saving and Waste, Russia), 34 % of polymer waste in Russia is polyethylene (PE), 20.4 % – polyethylene terephthalate (PET), 13.6 % – polyvinyl chloride (PVC), 7.6 % - polystyrene (PS), 7.4 % – polypropylene (PP), and 17 % – mixed materials on paper or board base.

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Notably, PE waste has the highest collection and recycling rate (20 %), next are PP (up to 17 %), PET (12 %), PS (12 %), PVC (no more than 10 %) [18]. These materials can be stored in natural conditions for a long period of time due to their high environmental resistance. However, the recovery of polymer waste can be considered an important economic factor in terms of its environmental impact since the energy and materials are reused.

Polymer materials fit completely within the concept of a circular economy: the energy needed for the production of recycled granulate from waste averages only 10 % of the energy required for the production of virgin granulate. In this regard, the best polymers are polyethylene terephthalate and polystyrene, and the most challenging are polyolefins. An increase in the consumption of polyolefins and corresponding waste makes recycling a vital task in materials engineering.

2. Materials and methods

The components of the polymer compound were polymer composition RotoPol M115CB for rotational moulding (supplied by Polymer Corporation, Kazan, Russia) (Table 1); plasticizing masterbatchRevtol, grade PF0010/1-PE (made by the scientific and production company BARS-2, Saint Petersburg, Russia) (Table 2); recycled polymer composition RotoPol M115CB for rotational moulding (Fig. 1); pigment Iron Oxide Black 722 (made in PRC) (Table 3). The recycled composition was prepared in the following order: a collection of waste (used holding tanks and plastic water-filled barriers); washing of the waste to remove any external contaminations; crushing of the waste in the crusher (the size of a particle was 1-10 mm); grinding of the waste in MF-500 miller (the size of a particle was 0.1-0.5 mm); weighing of the components on the industrial scales. The recycled polymer composition consists of ground waste and pigment Iron Oxide Black 722; the components of the recycled polymer composition were mixed in the stirrer.

Table 1. Physical and mechanical properties of the polymer composition RotoPolM115CB

Index	Measurement method	Meaning
Melt flow index (190°C, 2.16 kg) g/10 min	ASTM D 1238	3.8
Density, g/cm^3	ASTM D 1505	0.938
Modulus of elasticity in bending, kgf/cm^2, not less than	ASTMD790	800
Izod impact strength at 23°C, J/m, not less than	ASTMD256	does not collapse

Fig. 1. Secondary polymer composition for rotational molding RotoPolM115CB (RotoPol M115CB) after grinding on a mixer

Table 2. Material properties: concentrate "BASCO"

The name of indicators	Norms according to TU 20.16.59-001-23124265-2018 with amendments. No. 7	Results
Granulometric composition	It is allowed to have granules smaller than 2 mm and more than 5 mm in amounts up to 1%	corresponds
Color (shade) of the colored polymer	Must match the color of a sample from an approved range or a control sample agreed upon between the manufacturer and the consumer	corresponds
Quality of staining	The sample must be evenly colored in tone without streaks and inclusions	corresponds
Bulk density of concentrate, g/cm^3	0.40-1.60	0.54
Conditions for determining the melt flow index of the concentrate		M-2.16 kgf, T-190°C, nozzle 2.095 mm
Melt flow rate g/10 min, not less	2,0	11
Heat resistance, °C, not less	200	240

Table 3. Physical and chemical parameters of iron oxide black pigment (IronOxideBlack 722)

The name of indicators	Specification
Appearance	Uniform black powder
Mass fraction of iron compounds in terms of Fe2O3, %	91.3
Mass fraction of substances soluble in water,%,	0.4
pH of water extract	5.0-8.0
Mass fraction of volatile substances, %	1.2
Residue after screening through a sieve No. 325, %	0.3
Light fastness	8 points
Relative coloring power, %	98.0

Six (6) different holding tank samples were made to study the properties of rotationally moulded products made of recycled polyethylene; to develop the best possible compositions to compensate for the shortcomings of recycled polyethylene; to develop the best possible rotational moulding process. Their compositions are given in Table 4. The amount of pigment for all the studied tanks was 15 g per tank (14 kg). The influence of pigment on the properties of the resulting materials was assumed as insignificant due to its small amount.

The holding tanks were made by rotational moulding using POLIVINIL rotational moulding machine. The optimum conditions of rotational processing were chosen empirically: primary starting rotational velocity within an oven was 3.7 rpm; primary secondary rotational velocity within an oven was 3.0 rpm; end primary rotational velocity within an oven was 3.7 rpm; end secondary rotational velocity within an oven was 3.7 rpm; clockwise rotation time was 3 minutes; counterclockwise rotation time was 3 minutes; moulding time was 43 minutes; moulding temperature was 260°C.

The following properties of the studied samples were determined: tensile strength at break, MPa (GOST 11262-2017 [19]); elongation at break, % (GOST 11262-2017 [19]); hardness, Shore D units (GOST 24621-2015 (ISO 868:2003) [20]); flexural strength, MPa (GOST 4648-2014 [21]); Charpy impact energy, kJ/m^2 (GOST 4647-15 [22]).

Testing for tensile strength at break and elongation at break according to GOST 11262 was performed on the samples of type 2. The tests were carried out using the universal testing machine LRXPlus. Testing for flexural strength according to GOST 4648 was performed on the samples of the recommended type: a length (*l*) of 80±2 mm, a width (*b*) of 10.0±0.2 mm, and a thickness (*h*) of 4.0±0.2 mm. The tests were carried out using the universal testing machine LRXPlus. Testing for Charpy impact energy according to GOST 4647 was performed on the unnotched samples of type 2. The tests were carried out using the impact test machine HIT 25P. Testing for Shore D hardness according to GOST 24621 was performed on the square samples of 30×30 mm. The tests were carried out using the hardness tester DigiTest. The structure of the samples was analyzed using the digital microscope Levenhuk DTX 700 LCD.

3. Results and discussion

One of the main problems with plastic waste is the presence of various additives: dyes, stabilizers, plasticizers, and special additives containing metals, mercury, lead, and cadmium. Incineration cannot solve the problem of disposal into the environment. Recycling may solve this problem. The main recycling methods are mechanical recycling, chemical recycling, and energy recovery. Land disposal restrictions play a significant role: landfill bans are in force in eight European countries out of eighteen where the polymer recycling rates are above the European average (28 %). In Japan, up to 83 % of polymer waste is recycled, mainly using energy recovery. In Russia, only 5-15 % of all household waste is subjected to recycling. The share of sorted useful fractions does not exceed 10-15 %, and one-fifth of them are polymers. In total, maximum of 350 kt of polymers go into recycling and more than 4.5 are buried. The ongoing reform of the legislation (amendments to Federal Law No. 89-FZ on Production and Consumption Waste) is promising fundamental changes in the management of municipal solid waste.

One of the base polymers is polyolefins – polymers of ethylene (PE). Products made of polyolefins are widely used in the construction and renovation of residential and non-residential buildings, as finish materials, for interior finishing of buildings and structures, for power and water supply utilities, for fabrication of various containers, and medical products. Polymer pipes are widely used in the public utility sector, pipeline construction, etc. Food and non-food packaging is an important application of polymers. The main methods of PE reprocessing into end products are injection moulding, extrusion moulding, rotational moulding, etc.

Holding tanks for portable toiler cubicles were selected as test objects. These tanks were made of PE, manufactured by rotational moulding, and had a capacity of a maximum of 250 l. Typically, these products are made from rotational moulding grades of virgin PE. The products shall meet the following requirements: satisfactory physical-mechanical properties; an operating temperature range of ±40°C; resistance to water and chemical media (human waste, detergents); light weight; high structural load capacity.

Recycled materials are known [1] to have different mechanical properties and ageing resistance as compared to virgin ones. Both recycled and virgin materials feature the same mechanism of degradation when subjected to mechanical forces, and physical and chemical effects, but with different reaction rates. For that reason, recycled materials are more sensitive to degradation when processed.

In view of this, the objective of this paper was to study the influence of recovered PE content in rotationally moulded compositions on the physical-mechanical properties, as well as to develop a process of rotational moulding for holding tanks using PE recycling products.

Table 4. Formulation and physical-mechanical properties of the studied samples

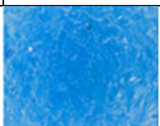
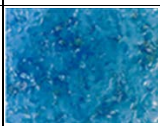
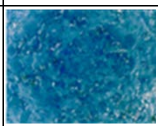
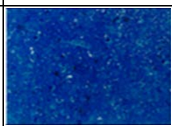
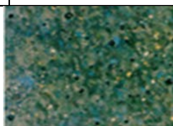
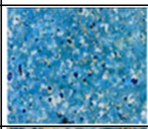
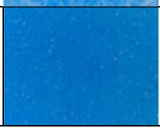
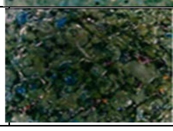
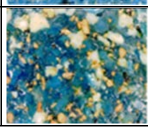
Sample	1	2	3	4	5	6
Formulation, mass fractions						
Virgin PE (RotoPol M115CB)	100	70	50	-	-	-
Recycled PR (RotoPol M115CB)	-	30	50	100	100	100
Plasticizing masterbatchRevtol, grade PF0010/1-PE 4	-	-	-	5	4	-
Physical mechanical properties						
Tensile strength at break (MPa)	16	16	16	16	16	15
Elongation at break (%)	81	80	74	73	74	28
Hardness (Shore D units)	22	22	22	22	22	22
Flexural strength (MPa)	16	16	18	17	18	20
Charpy impact energy (kJ/m^2)	51	51	42	46	52	35 Failure

Mechanical processing of PE is a very important segment of the recycling industry. The final properties and economic value of PE depend on the level of degradation during first use and on the recycling conditions. The main source of recovered high-density polyethylene (HDPE) is liquid containers. In this case, the molecular mass of used HDPE products remains quite high because degradation of materials of this type is rather low during short-term use. This factor means that the properties of recycled materials are close to the properties of virgin polymers.

Table 4 gives the formulations of the virgin and recycled HDPE compositions and their physical-mechanical properties.

The analysis of the macrostructures of the resulting compositions (Table 5) showed the formation of a heterogeneous structure for the recycled PE compositions (samples 4-6) as compared with the virgin PE samples.

Table 5. Micrographs of the sample surface

Sample	1	2	3	4	5	6
Outer side						
Inner side						

It is observed that the surface of the recycled PE samples has voids and air holes (samples 5 and 6), as well as different coloured inclusions, which may indicate the formation of a faulted macrostructure. Sample 6 has large different coloured inclusions, which is associated with the formation of a heterogeneous structure. Therefore, the important factor in getting high-quality recycled PE products is the introduction of additives to improve processing qualities and compatibility of broken-down particles.

Hence, mixtures of virgin and recycled polymers and mixtures to go to the waste are heterogeneous systems, which explains lower mechanical properties as compared to virgin materials. Phase separation in the melt and after cooling results from a poor interface between the components and local stress concentrations. Compatibilizers reduce interfacial tension in the melt by modifying the boundaries or by forming links between the phases. It induces the stabilization of a dispersed phase through its growth and agglomerating, increases the adhesion at the interface, and limits the phase separation in the solid state.

Table 4 shows that the majority of the physical-mechanical properties have relatively similar values as a result of the absence of significant degradation during production. Besides, there is a considerable difference in the elongation at break and the impact energy.

The properties-content curves for the mixtures of virgin PE/recycled PE were assessed. Figure 2 shows the dependence of the elongation at break, flexural strength, and Charpy impact energy on the content of recycled PE in the mixture. It should be noted that the values of both properties lie significantly lower than the values which have been calculated according to the rule of mixtures. It means that small quantities of recycled PE can cause a significant decrease in PE properties. It is known that the primary factors responsible for deviation from the rule of mixtures are the presence of other components in recycled PE, and differences in the morphology of the crystalline phase. Lower elongation at break (Fig. 2a) results from the degradation of PE, and weakening and discontinuity of the system followed by a negative impact on the properties. The impact properties (Fig. 2c) are more sensitive to the breakdown of polymer chains, which changes the morphology and causes a significant decrease in the impact properties. Notably, the products made of 100% recycled PE feature a catastrophic decrease in impact strength. The flexural strength increases slightly, which is associated with the formation of partially cross-linked structures (Fig. 2b).

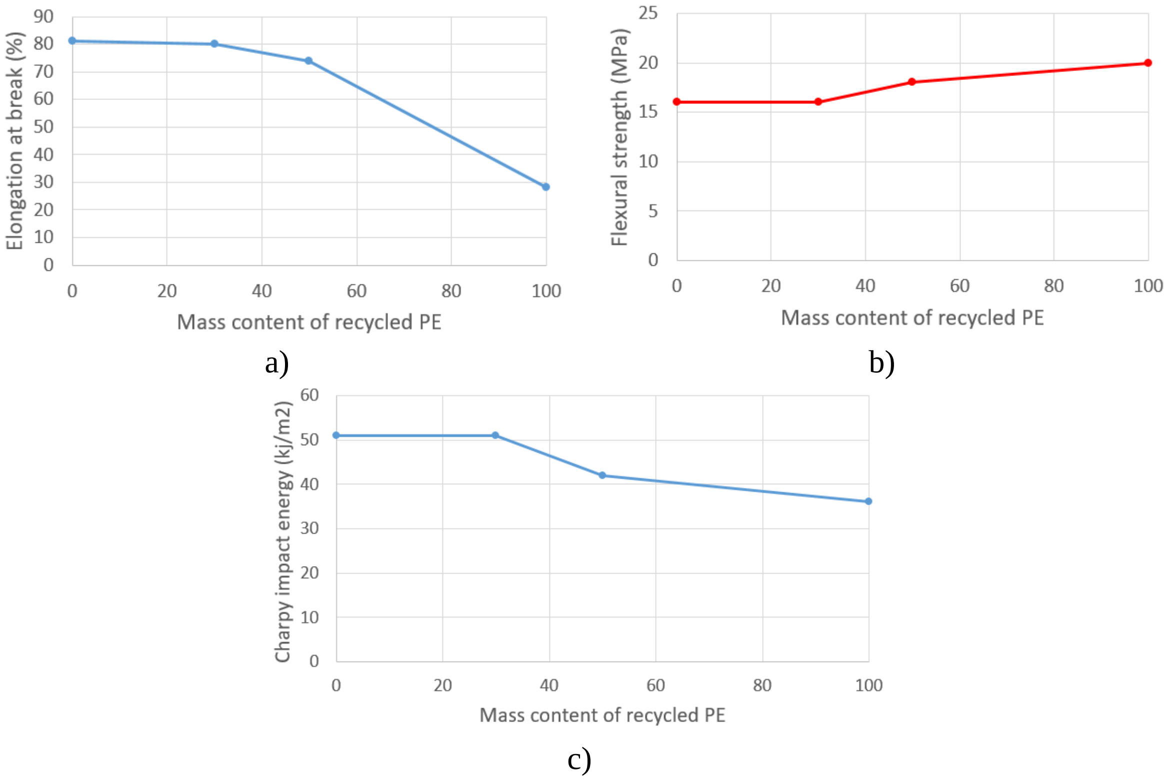


Fig. 2. Change in the properties due to an increase in the content of recycled PE: a) elongation at break; b) flexural strength; c) Charpy impact energy

Therefore, the differences in the physical-mechanical properties depending on the content of recycled PE result from the changes in the structure and morphology.

The addition of the compatibilizer by BARS-2 (plasticizing masterbatchRevtol, grade PF0010/1-PE 4) showed the effectiveness of this system. Notably, the physical-mechanical properties of the product made from recycled PE with 5 parts by weight of plasticizer (sample 5, Table 4) are not inferior to those of the products made of virgin PE (sample 1, Table 4).

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4. Conclusions

The comprehensive studies showed that it was possible to make holding tanks from recycled PE using modifying plasticizer (sample 4). The physical-mechanical properties of sample 4 are not inferior to those of samples 1-3 which were made from virgin PE. Ina ddition, sample 4 has high application properties. The specialists of Polymiz-Tara LLC (Russian Federation, Kazan) decided to introduce a polymer composition (sample 4) into the technology for manufacturing storage tanks from recycled PE by rotational molding (Fig. 3).

Fig. 3. Storage Tank (sample 4)

Therefore, the developed technology of holding tank production by rotational moulding using products of polyethylene recycling ensures high-quality products, a lower product cost as compared to the products made of virgin polyethylene, and addresses the important environmental problem regarding the management of polymer waste and transition to a circular economy.

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