

Research article

Modification of the used up polymeric materials and investigation thof e properties of the materials obtained

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ABSTRACT

The sources of scientific literature on the research have been investigated, various approaches to the processing and modification of polymers have been analyzed, and the main direction of the study has been identified. The changes in the properties of thin layers of industrially produced low-density polyethylene (LDPE) grades 10803-20 and 16603-01 operating under different climatic conditions have been studied having, and it has been determined that changes with different intensities occur in the structure and in this connection in the physical and mechanical properties of LDPE that was in operation at different time intervals and in different climatic conditions of the Absheron Peninsula and the Aran region: melt flow index of polymer alloy, tensile strength at break, relative extension, and values of the indicator sreredeteriorate ing, sreredeteriorate. In polymers, sample are as formed ~24,2 – 28,6% of the insoluble phase and as a result of oxidation up to ~ 12,3 – 16,8% carbonyl, HDD,,ox,y,l and other functional groups.

Keywords: Polyethylene, Modification, Mineral Filler, Physical and Mechanical Properties, Waste, Ecology.

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INTRODUCTION

The expansion of the production of polymers and composite materials based on them exacerbates the problem of drug of waste wings from the operation of polymer products. The solution to this problem is associated with the creation of low-waste or economically favorable non-waste production or the development of effective modification methods for reusing polymer waste, taking into account their structure and properties [1-4].

Most polymeric mat material materials retain their structure and properties from the beginning of the production process to the end of the open operational period used Using. Thqua The qualitative of polymeric material are of great practical importance and must be taken into account when processing polymeric materials [5-7].

The development of the production and processing of polymer materials, and the expansion of their use in various industries lead have led to an increase in environmental pollution, an increase in the share of polymer waste, and the emergence of new environmental problems [8].

Thus, an increase in the number of polymer materials used in various industries creates an economic incentive that allows you one to get obtain a significant profit for the use of polymer materials,

and, on the other hand, increases the amount of polymer waste and thus creates environmental problems [9].

As you know, polymer Polymer waste must be either recycled or destroyed to protect the environment from pollution. The solution to this problem showed that the destruction of waste polymer materials requires even more capital investments, and at the same time, the destruction of waste by incineration is not environmentally safe [10].

In the light of the foregoing in the presented paper, the structure and properties of the manufacturer thesen industry with state standards 16337-77 LDPE grades 10803-020 and 16603-011 were investigated, operated for 3 months and 1 year in the Aran zone of the Republic of Azerbaijan, as well as for 6 months on the Absheron Peninsula, in comparison with primary, unused polyethylene, restoration of lost properties as a result of modification using mineral fillers and compounds supporting functional groups during processing, obtaining composite compositions based on modified LDPE and studying their properties, the field of application of compositions obtained on the basis basonionnon DPE [11-12].

The study of the physicochemical, Physico mechanical, al

and rheologic properties of the used up LDPE showed that it is impossible to turn polyethylene waste into reusable raw materials without modification, which is associated with structural and chemical changes that occur in macromolecules during polymer processing and operation in natural climatic conditions. Therefore, to restore the original polymer properties, the recycling of polyethylene waste must be carried out along with the modification process.

Even though the disposal process is 8 times more expensive than the cost of processing industrial waste and 3 times more expensive than the processing of cost of processing household waste, the cost of polymer waste is 40-70% lower than the base price for the original polymers, while their overall quality is slightly different from the quality of the original polymer material.

Recycling paper waste cons considerable reduces the need for the original polymer and save financial and labor resources.

Hence, the recycling of polymer materials along with environmental problems also contributes to solving socio-economic problems – the socioeconomic problems—the conservation of natural resources [4]. One of the most common and widely used methods for producing polymer composites uses different obsolete polymer products, which can significantly change the properties of polymer mixtures and thereby expand their scope.

RESULTS AND DISCUSSION

High-density polyethylene LDPE is produced on an industrial scale, but the need for thermoplastic polymers in industrial areas is not fully satisfied. In the third world worldwide thousands of tons of waste polymeric materials are thrown into the environment, and their processing has not yet been organized at the proper level. This is clear evidence of landfills on the outskirts of cities caused by discarded waste (Figure 1).

Figure 1: Obsolete polymeric materials



In this land fill semi-finished ten products, at least shown in Figure 2, can be obtained in the easiest ways and used for the various purposes.

Figure 2: Compositions obtained from polymer waste obsolete polymer waste



Table 1: Properties of the original and obsolete LDPE grade 10803-020

Parameter name	Original LDPE	LDPE after 3 months of operation	LDPE after one year of operation
Density, kg/m ³	925,0	930,0	918,0
Melt flow index, 190°C, load 2,16 kg, gr/10 min	1,20	0,80	0,22
Crystallization rate, %	45,0	-	-
Tensile strength at break, MPa	15,5	11,4	4,6
Relative extension, %	500	170	115
Hardness, MPa	1,5	1,7	2,5
Number of >C=O groups, %	0,1	1,6	16,8
The amount of insoluble phase, %	0	20,0	28,6
Melting temperature, °C	105,4	110,0	119,2

Therefore, from an economic and environmental point of view, the most appropriate direction is the processing of polymer waste. Restoring's the ore basic properties of polymer arrester is possible by mechanochemical and physical modification of their structure and properties. Through recycling and modification of LDPE, which is a characteristic polymeric waste for the Republic of Azerbaijan, it is economically and environmentally viable to obtain multi-purpose purpose multipurpose site materials To investigate the properties change properties of LDPE grade 10803-020 during operation, the polymer samples were stored for 6 spring-summer months in the open air at a temperature of 30-45 °C, and their physical and mechanical properties change wasp was properties were studied the esresultsre. The results are presented in Table 1.

Table 1: Properties of the original and obsolete LDPE grade 10803-020

Parameter name	Original LDPE	LDPE after 3 months of operation	LDPE after one year of operation
Density, kg/m ³	925,0	930,0	918,0
Melt flow index, 190°C, load 2,16 kg, gr/10 min	1,20	0,80	0,22
Crystallization rate, %	45,0	-	-
Tensile strength at break, MPa	15,5	11,4	4,6
Relative extension, %	500	170	115
Hardness, MPa	1,5	1,7	2,5
Number of >C=0 groups, %	0,1	1,6	16,8
The amount of insoluble phase, %	0	20,0	28,6
Melting temperature, °C	105,4	110,0	119,2

As Table: 1 indicates, the initial properties of LDPE are changing dramatically, and the properties of LDPE of gradgrades3-011 under the same conditions after 6 months of storage are shown in Table2. The thermo physical properties of LDPE given in Table 3.

Table 2: Physical and mechanical properties of LDPE (grade 16603-011)

Parameter name	Original LDPE	LDPE after 6 months of operation
Density, kg/m ³	919,0	-
Melt flow index of polymer alloy, 190°C load 2,16 kg, gr/10 min	1,1	0,075
Crystallization rate, %	35-40	-
Tensile strength at break, MPa	9,3	-
Fracture resistance, MPa	12,2	7,7
Relative extension, %	600	260
Hardness, MPa	18-19	25
Modulus of elasticity	98	42

Table 3: Thermophysical properties of LDPE

Parameter name	Parameter value
Melting temperature, °C	103-108
Vick heat resistance, °C	100-105
Heat transfer, Vt/mK	0,32-0,36
K	-9,3
Coefficient of linear thermal expansion from 0°C to 100°C, 1/°C	(2,1-5,5) 10 ⁻⁴
Casting shrinkage, %	1,0-3,5
Brittle temperature, °C	-100

Given the formation of various functional groups in LDPE during its

operation, it has been modified with a reactive epoxy resin (ED-16, ED-20) capable of retaining functional groups, phenol-formaldehyde oligomer (PFO) modified with thiocarbamide and remainder of the alunite processing – sludge and natural mineral fillers – zeolite and shell limestone.

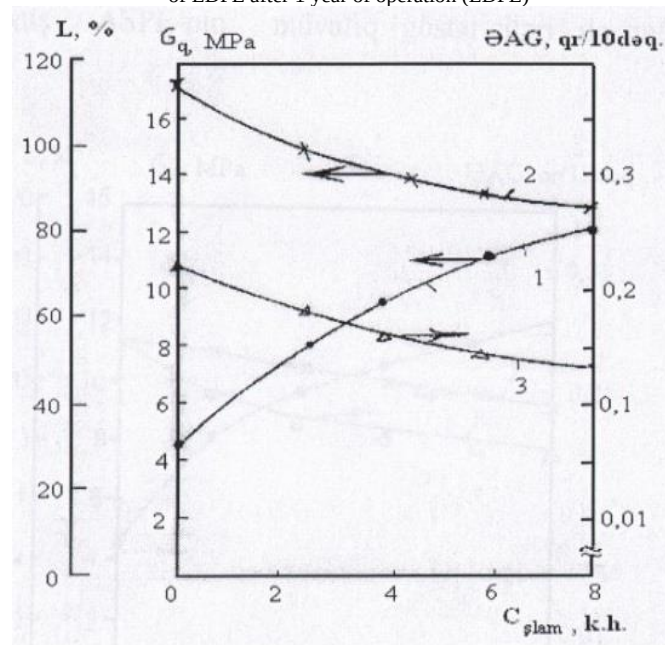
Table 4: Effect of the optimal amount of dolomite-filler and binder on the physical and mechanical properties of LDPEPE

Formulation compositions (1) and indicators (2) based on LDPE	Formulation compositions and property indicators		
	LDPE after 1-year exposure (LDPE)	LDPE	Composition based on RLDPE with ED-20 binder addition
The amount of oof20 (per 100 w/w of RLDPE), w/w	-	-	15,0
Dolomite filler, w/w	-	8,0	8,0
Dispersive-stearic acid, w/w	-	2,0	2,0
Tensile yield stress, MPa	7,1	4,8	8,2
Tensile strength at break, MPa	4,6	11,8	14,8
Extension elongation, %	115	100,0	150
Melt flow index-MFI, gr/10 min	0,22	0,15	0,52
Relaxation modulus, 25°C, ε=20%, MPa	2,7	2,8	2,2
Modulus of elasticity, MPa	80,2	72,8	70,0
Effective viscosity - η _e , 160°C, Pa·s	12,2	13,8	10,1

Table 5: Dependence of the thermal stability of RLDPE compositions on the amount of sludge

Formulation compositions, w/w	Half-life	Half-life t _{1/2} , sec	Initial decomposition temperature, T _{d,0.1} , °C
Original LDPE-100	65,4	39,5	143,8
Used up LDPE (RLDPE) - 100	69,1	61,9	148,2
RLDPE+sludge-100+2	78,2	65,6	190,2
RLDPE+sludge-100+4	86,2	71,4	225,4
RLDPE+sludge-100+6	111,5	76,5	238,2
RLDPE+sludge-100+8	121,9	82,4	254,1

Figure 3: The effect of the amount of sludge on the change in the properties of LDPE after 1 year of operation (LDPE)



It was shown that the restoration of the technological and physical-and-mechanical properties of LDPE, in which the amount of elastic phase decreased and brittleness increased as a reason that the operation is possible in the adjusting the numerous of dees and mineral fillers, wetting the filler particles, their distribution in the mixture, adding a filler-binder, chemical binder in the composition of used up LDPE. The obtained results are given in Tables 4, 5, 6 a, and 7, and Figure 3.

Table 7: Physical and mechanical properties of used and modified LDPE

Parameter name	Original LDPE	LDPE	Modified RLDPE				
			1	2	3	4	5
Melt flow index of polymer alloy, 190°C, load 2,16 kg, gr/10 min	1,1	0,075	0,4	0,4	0,3	0,18	0,12
Fracture resistance, MPa	12,2	7,7	8,1	8,4	9,6	10,3	10,7
Relative extension,%	600	260	340	340	320	300	290
Hardness, MPa	18	25	20	20	22	22	23
Modulus of elasticity, MPa	98	42	70	71	68	65	60
Vick heat resistance, °C	105	-	105	107	110	118	120

Improving the complex properties of sludge and zeolite filled with RLDPE, FFO, modified thiocarbamide and its mixture with ED-16 in a ratio of 60:40 is associated with the functionality of the binder and its ability to wet the filler particles. Because in the binders hydroxyl, epoxy, and thio groups coordinate the bond in the polymer-filler system, as well as carry out chemical bonding formed in the used polymer with hydroxyl, carbonyl, ether, and other substances, an improvement in the complex properties of the compositions is observed. The intensity and character of these relationships were confirmed by IR spectroscopy, DT, and analytical methods for the study of functional groups.

It was established that during the recycling of used up

LDPE modification of the structure and properties – restoration is possible only in the case of wetting particles of mineral filler and when dispersively mixing them with a polymer mass using mixtures ED-2, modified phenol-formaldehyde oligomer + ED-16, which support functional low molecular weight groups.

As a result, an efficient recycling process of LDPE was achieved, and the complex properties of RLDPE were addition it the obtained in compositions can be used not only to save raw materials but also to solve environmental problems and produce multipurpose products.

Table 8: Physical and mechanical properties of the obtained bitumen grade Baku 85/25, as industrial bitumen

Indicator	Units of measurement	Baku 85/25
Penetration at 25 °C	mm/10	20-30
Softening point (the ring and ball)	°C	80-90
Elongation at 25 °C	cm	2,5
Flashpoint	°C	246
tensile strength(France)	°C	- 10

Table 9: Formulation of the composition based on crumb rubber (CR)

Name of components	No of samples				
	1	2	3	4	5
	Content of the mass parts				
Bitumen	100	100	100	100	100
CR	2	4	6	8	10
Sulfur	-	-	-	1	2

Table 10: Physical and mechanical properties of a composition based on crumb rubber

Indicator	Samples				
	1	2	3	4	5
Needle penetration at 25 °C	38	72	100	71	The
The softening point, °C	49	68	82	56	75
Brittle temperature, °C	-10	-10	-26	-8	-20
Elongation at 25 °C	40	60	70	55	60
Density, g/cm ³	2,34	2,36	2,38	2,2	2,4
Temperature changes at T=65 °C within 5 hours	7	6	6	6	6
Tensile Strength M Pa at 20°C	2,4	3,0	3,5	3,1	3,4
at 50 °C	0,9	1,0	1,2	1,1	1,3

Table 11: Properties of bitumen-polymer compositions

Indicator	Sample values								
	Samples/1	2	3	4	5 Prototype model	6	7	8	9
Tensile strength, MPa,	4,5	10,0	6,0	6,5	Torn without load	7,0	8,0	5,0	9,5
Tensile strain, %	650	850	1100	780	-	900	900	700	830
Shore A hardness, conventional units	63	50	35	58	20	45	43	40	45
MFI at T=190 °C, P=49 N, g/10 min	18	20	40	35	100	30	35	30	25

At the same time, to study the possibilities of expanding the scope of use of obsolete tires, we have carried out a series of studies. Scientific studies have been conducted on the use of crumb rubber [1, 4, 8, 17], and it was found that the most profitable method of recycling obsolete tires is to modify them and obtain multipurpose compositions. To recycle obsolete tires after their grinding to dust with the size of particles 1-2 mm, it is possible to modify oil road bitumen and obtain a polymer bitumen binder. The resulting polymer bitumen was used for the manufacture of asphalt concrete. The results

obtained are given in Tables 8, 9, 10, 11, 1,2 and 13.

Studies have shown that complex properties may not be possible complex required in recycled low-density polyethylene (LDPE), which has been modified only by mineral filler. Although durability and indicators of thermal stability are improving, technological and plastic and elastic properties such as effective viscosity, elasticity, and melt flow index are deteriorating.

Table 12: Indicators of the physical and mechanical properties of asphalt mixtures

Item name	Samples			
	1	2	3	4
Compressive resistance, MPa, at temperature 20 °C and 50 °C	2,2, 0,9	- -	- -	- -
The coefficient of water resistance with prolonged water saturation, % by volume	0,86	0,90	0,94	Water-resistance
Water-resistance coefficient	0,90	-	0,95	0,89
Swelling, % by volume	0,6	0,9	0,5	1,0
Residual porosity, % by volume	2,1	2,4	2,0	2,3

Table 13: Physical and mechanical properties of stone mastic asphalt SMA-15 with the introduction of RTEP on stone materials

Parameter	GOST standards 31015-2002	RATE	0, 1% RTEP	0, 2% RTEP	0, 3% RTEP	0, 5% RTEP
Density, g/cm ³	-	2,38	2,39	2,395	2,406	2,410
Residual porosity, %	2,0-4,0	3,64	3,57	3,13	2,46	1,83
Water saturation, % by volume	1,5-4,0	3,07	2,68	2,52	2,33	2,05
Compressive resistance, MPa at temperature 20°C 50°C	2,5 0,70	3,51 0,72	4,08 0,78	4,26 0,85	4,59 0,89	Resistance coefficient
Resistance coefficient	-	0,85	0,88	0,90	0,92	0,94
The coefficient of water resistance with prolonged water saturation (15 days)	0,75	0,83	0,84	0,87	0,89	0,91
Crack resistance – ultimate tensile strength when split at temperature 0°C, MPa	3,0 – 6,5	3,95	4,36	4,58	4,75	4,66
Coefficient of internal friction, tg	0,94	0,91	0,92	0,92	0,93	0,93
Shear griptemperature at 50°C, MPa	0,20	0,20	0,32	0,55	0,59	0,63
Binder runoff rate, %	0,20	0,20	0,19	0,15	0,13	0,11

Improving the complex properties of RLDPE is observed in compositions obtained at optimal values of the binder.

The optimum quantity of binders per 100 w/w of LDPE has been shown: binders supporting functional groups –ED-20 modified PFO – 15-20 w/w, fillers – sludge and zeolite 6-8 w/w and shell limestone 20-25 w/w, and at established optimal amounts, it is possible to restore the basic properties of LDPE.

CONCLUSIONS

The changes in the properties of thin layers industrially produced low-density polyethylene (LDPE) grades 10803-20 and 16603-011 operating under different climatic conditions have been studied. The study revealed that in the structure and related physical and mechanical properties of LDPE that were in operation in natural climatic conditions in different periods (6-8 months) and conditions (May-September and December-March), various changes occur: tensile strength at break, relative elongation and other indicators of polymers and composite materials are deteriorating. In polymer, samples are formed ~ 24,2 – 28,6% insoluble phase and as a result of oxidation up to ~ 12,3 – 16,8% carbonyl, hydroxyl, and other functional groups.

The formation of various functional groups in used up LDPE has been modified with a reactive epoxy resin ED-16, ED-20 capable of retaining functional groups, PFO modified with thiocarbamide and remainder of the alunite processing – sludge and natural mineral fillers – zeolite and shell limestone. It was indicated that restoration of the technological and physical and mechanical properties of LDPE, in which the amount of elastic phase decreased

and brittleness increased as a result of the operation, is possible in the case of adjusting the number of binders and mineral fillers, wetting the filler particles, and their distribution in the mixture, providing chemical bonds in the LDPE-binder-filler system.

Studies have shown that when recycled low-density polyethylene (LDPE) is modified only with a mineral filler, it is impossible to obtain the necessary complex properties. Thus, even though material strength and indicators of thermal stability are improving, technological plastic and elastic properties including effective viscosity, elasticity, and melt flow index, are deteriorating. Improving the complex properties of RLDPE is observed in compositions obtained at optimal values of the binder. The optimum quantity of binders supporting functional groups partially provided the basic property recovery of RLDPE per 100 w/w of LDPE: ED-20 modified PFO 15-20 w/w, fillers – sludge and zeolite 6-8 w/w, and shell limestone 20-25 w/w.

Improving the complex properties of sludge and zeolite filled with RLDPE, FFO, modified thiocarbamide, and its mixture with ED-16 in a ratio of 60:40 is associated with the functionality of the binder, and its ability to wet the filler particles. When in the binders hydroxyl, epoxy, and thio groups coordinate the bond in the polymer-filler system, providing chemical bonding formed in the used polymer with hydroxyl, carbonyl, ether, and other groups, an improvement in the complex properties of the compositions is observed. The intensity and character of these relationships were confirmed by IR spectroscopy, DTA, and analytical methods for the study of functional groups.

Thus, the studies revealed that during the recycling of used up LDPE modification its structure and properties – restoration is possible only in the case of wetting particles of mineral filler and when dispersive mixing them with a polymer mass using mixtures – ED-20, modified phenol-formaldehyde oligomer + ED-16, which support functional low molecular weight groups. Efficient recycling of used LDPE and preparation of compositions provide improved complex properties of RLDPE, along with the production of multipurpose products, making it possible to save raw materials and solve environmental problems.

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