Modification of Polymer Wastes and Obtaining Com Composites Based on Them Annotation

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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 have been identified. The changes in the properties of thin layers of industrially produced low-density polyethylene (LDPE) grades 10803-20 and 16603-011 operating under different climatic conditions have been studied. 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 other indicators are deteriorating. In polymer samples is formed ~24,2 – 28,6% of insoluble phase and as a result of oxidation up to ~ 12,3 – 16,8% carbonyl, hydroxyl and other functional groups.*

Keywords: *polymer, polyethylene, recycling, modification, mineral filler, physical and mechanical properties, waste, ecology, melting temperature, crumb rubber, polymer-bitumen, binder.*

I. INTRODUCTION

The expansion of the production of polymers and composite materials based on them exacerbates the problem of reusing of waste 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 of polymer waste, taking into account their structure and properties. Thus, an increase in the amount of polymeric materials used in various industries, on the one hand, with the replacement of metals with polymer composite materials creates an economic incentive allowing to make significant profits for the use of polymeric materials, and on the other hand, an increase in the amount of obsolete polymer waste increases environmental pollution. As is known, polymer waste must be either recycled or destructed to protect the environment from pollution. The feasibility study for solving this problem showed that destruction of waste polymeric materials requires even greater investment and along with this destruction of waste by burning is not environmentally friendly. In the light of the foregoing in the presented paper the structure and properties of manufactured in industry in accordance with state standard 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 of modified LDPE.

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Theory

Despite the fact that the cost of the polymer waste disposal process is 8 times more expensive than the cost of processing industrial waste, 3 times more expensive than the processing of household waste [1-6], the cost of polymer waste is 40-70% lower than the base price for original polymers, while their overall quality is slightly different from the quality of the original polymer material. Therefore, recycling of polymer materials is of great economic importance [7 - 10].

Recycling of polymer waste considerably reduces the need for original polymer and saves financial and labor resources. Hence, the recycling of polymer materials along with environmental problems also contributes to solving socio-economic problems – the conservation of natural resources [11]. One of the most common and widely used methods for producing polymer compositions is the use of different obsolete polymer products, which can significantly change the properties of polymer mixtures and thereby expand their scope [12-13].

II. RESULTS AND DISCUSSIONS

Therefore, from an economic and environmental standpoint, the most appropriate direction is the recycling of polymer wastes. And one of the major points of this direction is the maximum restoration of lost properties of obsolete polymer waste by mechanical and chemical and physical modification of its 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 composite materials. To investigate the properties change 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 was studied. The results are presented in Table 1.

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

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

As Table 1 indicates the initial properties of LDPE are changing dramatically. The change in the initial properties of LDPE of grade 16603-011 under the same conditions after 6 months of storage are shown in Table 2. Thermophysical properties of LDPE are given in Table 3.

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

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

Table 3. Thermophysical properties of LDPE

N	Parameter name	Parameter value
1.	Melting temperature, ^0C	103-108
2.	Vick heat resistance, ^0C	100-105
3.	Heat transfer, Vt/mK	0,32-0,36
4.	Specific heat capacity at 20^0C, J/(kgK)	-9,3
5.	Coefficient of linear thermal expansion from 0^0C to 100^0C, $1/^0C$	$(2,1\text{-}5,5)\ 10^{-4}$
6.	Casting shrinkage, %	1,0-3,5
7.	Brittle temperature, ^0C	-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. 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 result of operation is possible in the case of adjusting the amount of binders 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 Table 4-5, and Figure1 .

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

N	*Formulation compositions (1)* and indicators (2) based on LDPE	*Formulation compositions* and property indicators		
		LDPE after 1 year exposure (RLDPE)	Composition based on RLDPE	Composition based on RLDPE with ED-20 binder addition
1.	The amount of ED-20 (per 100 w/w of RLDPE), w/w	-	-	15,0
.2	Dolomite filler, w/w	-	8,0	8,0
.3	Dispersive-stearic acid, w/w	-	2,0	2,0
4	Tensile yield stress, MPa	7,1	4,8	8,2

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5	Tensile strength at break, MPa	4,6	11,8	14,8
6	Extension elongation, %	115	100,0	150
7	Melt flow index – MFI, gr/10 min	0,22	0,15	0,52
8	Relaxation modulus, 25^0C, ε=20%,MPa	2,7	2,8	2,2
9	Modulus of elasticity, MPa	80,2	72,8	70,0
10	Effective viscosity - η_{ε}, 160^0C, Pa·s	12,2	13,8	10,1

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

N	Formulation compositions, w/w	Activation energy of decomposition $\varepsilon_{act.en}$, kJ/mol	Half life $t_{1/2}$, sec	Initial decomposition temperature, $T_{d.b.}$, ^{0}C
1.	Original LDPE-100	65,4	39,5	143,8
2.	Used up LDPE (RLDPE) - 100	69,1	61,9	148,2
3.	RLDPE+sludge-100+2	78,2	65,6	190,2
4.	RLDPE+sludge-100+4	86,2	71,4	225,4
5.	RLDPE+sludge-100+6	111,5	76,5	238,2
6.	RLDPE+sludge-100+8	121,9	82,4	254,1

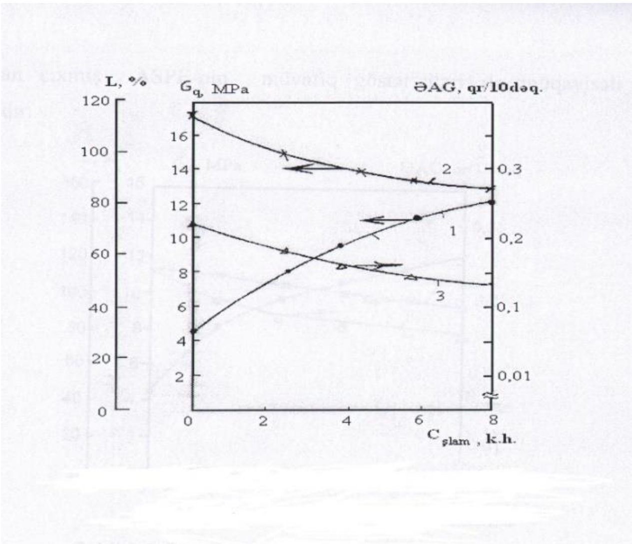

Figure1. The effect of the amount of sludge on the change in the properties of LDPE after 1 year of operation (RLDPE)

1 - σ_q; 2 - L_q; 3 – MFI

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, its ability to wet the filler particles. Due to the fact that 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 groups, an improvement in the complex properties of the compositions is observed. The intensity and character of these relationships was confirmed by IR spectroscopy, DTA 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-20, Modified Phenol Formaldehyde Oligomers(MFPO)

+ ED-16, which support functional low molecular weight groups.

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

At the same time to study the possibilities of expanding the scope of use of obsolete tires, we have carried out a series of researches. Scientific studies have been conducted in the use of crumb rubber [1, 4, 8, 17] and it was found that the most profitable method of obsolete tires recycling is to modify them and obtaining based on them multi-purpose compositions. In order 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 on its basis. The resulting polymer bitumen was used for the manufacture of asphalt concrete. The results obtained are given in Table 8-11, .

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 ^{0}C	cm	2,5
Flash point	°C	246
Ultimate tensile strength	°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

N	Indicator	Samples				
		1	2	3	4	5
1.	Needle penetration at 25 °C	38	72	100	71	96
2.	Softening point, ^{0}C	49	68	82	56	75
3.	Brittle temperature, ^{0}C	-10	-10	-26	-8	-20
4.	Elongation at 25 ^{0}C	40	60	70	55	60
5.	Density, g/cm^3	2,34	2,36	2,38	2,2	2,4
6.	Temperature changes at T=65 °C within 5 hours	7	6	6	6	6
7.	Ultimate tensile strength at 20 ^{0}C at 50 ^{0}C	2,4 0,9	3,0 1,0	3,5 1,2	3,1 1,1	3,4 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

Studies have shown that it is not possible to obtain the required complex properties in recycled low density polyethylene (RLDPE) which has been modified only by mineral filler – although durability, indicators of thermal stability are improving, technological and plastic and elastic properties – effective viscosity, elasticity, 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 per 100 w/w of used up 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 basic properties of RLDPE.

III. 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 the physical and mechanical properties of LDPE that was in operation in natural climatic conditions in different periods of time (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 is 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.

Having regard formation of various functional groups in used up LDPE, it 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 operation is possible in the case of adjusting the amount of binders and mineral fillers, wetting the filler particles, their distribution in the mixture, providing in the used up LDPE-binder-filler system chemical bond.

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Studies have shown that when Recycled Low Density Polyethylene (RLDPE) is modified only with a mineral filler, it is impossible to obtain the necessary complex of properties. Thus, despite the fact that material strength, indicators of thermal stability are improving, technological and plastic and elastic properties – effective viscosity, elasticity, 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 providing basic properties recovery of RLDPE per 100 w/w of used up LDPE: ED-20 modified PFO15-20 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, its ability to wet the filler particles. When in the binders hydroxyl, epoxy, and this 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 was 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, (MFPO) + ED-16, which support functional low molecular weight groups. Efficient recycling of used up LDPE and preparation of compositions providing improved complex properties of RLDPE, along with the production of multi-purpose products, make it possible to save raw materials and solve environmental problems.

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