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DEVELOPMENT OF COMPOSITE MATERIALS BASED ON HIGH AND LOW DENSITY POLYETHYLENE, NANOCLAY AND LUBRICATING SYNTHETIC OIL

[1]Gulnara Sh. Gasimova, [1]Dilbar R. Nurullayeva, [2]Lala Kh. Gasimzade, [1]Fidan A. Aqayeva, [1]Aida L. Tagiyeva

[1]Institute of Polymer Materials of the Ministry of Science and Education Republic of Azerbaijan, S.Vurgun str., 124, Sumgait, AZ 5004
[2]Azerbaijan State Oil and Industry University
Azadlıq ave., 20, Baku, AZ 1010; e-mail: gulnara.qasimova.68@mail.ru

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Abstract: *In the paper, the results of research into the development of polymer composition materials with improved strength and antifriction properties based on high-density polyethylene (HDPE), as well as low-density polyethylene (LDPE) and modifying additives – Azerbaijani clays and synthetic lubricating oil are presented. It was established that the introduction of 5-25% nano-sized clays and 1-3% of the above-mentioned oil into the composition makes it possible to obtain thermoplastic materials with sufficiently high antifriction and other properties. In addition, in the paper the influence of the temperature regime and the pressure of melt extrusion in a material cylinder on the physical-mechanical properties of composites on the basis of propylene were examined. The optimal conditions of processing of multicomponent composites were shown.*

Keywords: *polymer,poliethylene,composite materials, strength and antifriction properties.*
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Introduction

In modern technology and industrial production technology, more and more attention of scientists is focused on the development of new types of materials which, according to their exploitation characteristics, are distinguished by high strength properties, wear resistance, thermal and heat resistance, resistance to hard climatic conditions, etc. At the same time, it is necessary that the polymer materials have appropriate high physical-mechanical and technological properties. To change the properties of polymers produced in the industry, the various methods of their modification are used: plasticization, introduction of fillers, stabilizers, creation of polymer mixtures, alloying additives, structure-forming agents, dressing of mineral fillers, etc [1-3].

Thus, as a result of the use of a whole set of existing modification methods, the wide opportunities are created for regulation of the structure and properties of polymer composites. This practice is widely used by specialists today, following which perspective opportunities for their implementation in various fields of industry are opened up [2-3].

In technologies related to the development of filled polymer composition materials for various purposes, a special attention is paid to the scientifically based selection of modifying additives to the polymer matrix, which eliminates the phenomenon of antagonism between them and ensures sufficiently high operational properties [1].

In recent years, with the development of nanotechnology, the wide possibilities have opened up for varying the physical-chemical and operational parameters of composition materials by impregnating various metals, their oxides, sulfides, montmorillonite, graphite and modifying substances in the structure of polymer matrices [4-7].

The processes occurring during impregnation have been studied in detail on the effect of nano-sized metal particles (NMP) or their cluster particles on the properties of traditional polymers (polyethylene -PE, polyvinyl chloride - PVC, etc.).

The processes mentioned above are explained by the ability of particles to form ionic and coordination cross-link limiting the mobility of molecular chains or their segments, cohesive and adhesive interactions and other reasons [3].

Often, in compositions based on PE, polytetrafluoroethylene (PTFE), etc., along with inert fillers, the reactive oligomers and cooligomers participating in the cross-linking process of polymer chains, with the formation of a material with high strength and antifriction properties are used. So, in the patent [8] it is proposed a new, cured composition consisting of 1% PTFE (particles of size 0.1-0.4 mcm), 57.5% reinforced fabric from carbon fiber and 48.5% phenol-formaldehyde resin. The cured material can be used in dry friction conditions, in the absence of any lubrication. Thus, to add the required additional properties to industrial polymers, various methods are used on the basis of the inclusion of filler particles and other modified additives into the composition and their processing in some known suitable way [9].

In addition to the above-mentioned, one of the important directions of scientific-technological development is the creation and implementation of new technologies, substances and materials ensuring resource-saving and meeting ecological requirements. In the general concept of "sustainable development of civilization" adopted by the UN, an emphasis is laid on the development of ecologically safe technologies, excluding the isolation of harmful substances into the atmosphere, the utilization of existing technogenic waste, the rational use of non-renewable natural resources, the possibility of recycling materials after their operational period.

At the "Ethylene-Polyethylene" plant (Sumgayit), heavy pyrolysis resin is obtained during the pyrolysis of low-octane gasoline and gas oil for the purpose of producing ethylene and propylene, which has not yet found its specialized field of application. This resin was subjected to vacuum distillation with the separation of the 200-245 °C fraction and a high-boiling residue. The 200–245°C fraction was subjected to alkylation with cyclohexene in the presence of an industrial catalyst at a temperature of 180°C. The yield of alkylate was 70 wt% per resin. The physical-chemical parameters of the obtained alkylate were determined as follows: B.p.°C = 150-200/0, T_{flash}=210°C, T_{congel} = -72 °C, ν_{40} = 11.99 mm^2/c, ν_{100} = 4.66 mm^2/c.

The resulting alkylate is a light yellow liquid with low solidification point, high flash point, good viscosity properties which can be used as synthetic lubricants oils for various (SLO) purposes [10,11].

In this paper the results of our investigations due to the development of new composition materials on the basis of high-density polyethylene (HDPE) and low-density polyethylene (LDPE), nano-sized Azerbaijani clays (Gizil-Dare deposits of the Republic of Azerbaijan) and synthetic lubricating oil are analyzed.

Also, the purpose of this analysis is to study the regularity of changes in the basic physical-mechanical, technological and tribological characteristics of composites during processing by injection molding and extrusion methods.

Experimental part

Main characteristics used in the work as polyethylene matrices are given in Table. 1.

Table 1. Characteristics of polyethylenes

Indices	LDPE	HDPE
Density at 20°C, kg/m^3	924	957
Melt flow index at 190°C, g/10min.	7.0	8.6

Melting temperature	105-110	124-132
Tensile strength, MPa	26.0	31.0
Specific elongation at break, %	170	190
Water absorption (30 days, 20°C)	0.020	0.005

Characteristics of modifying additives:

a) Nano-clay, being a sedimentary rock, pulverized in a dry state and plastic at moistening, consists of one or more materials of the kaolinite, montmorillonite or other layered aluminosilicates group. Composition, % mass.: SiO_2–47.0, Al_2O_3–39.0, H_2O –14.0.

The clay nanoparticles were obtained at the analytical mill A-11 at a maximum rotor rotation rate of 28.000 rev/min.

The size of nanoparticles was determined on the device of model STA PT1600 Linseiz Germany and was 14-110 nm.

b) Physical-chemical indices of SLO: B.p,°C = 150-200/0, T_{flash}=210 °C, $T_{congel.}$ = -72 °C, ν_{40} = 11.99 mm^2/c, ν_{100} = 4.66 mm^2/c.

The compositions were made with use of LDPE (or HDPE) and various quantities of filler (clay) and SLO (acting as structural plasticizer) as matrices. The samples were prepared on hot rollers at temperature 180°C and duration of 8-10 min. At first, the clay was impregnated with oil. The oil was dissolved in a benzene solution, then nanocline particles were added and stirred for 6 hours at temperature 50°C. Then the obtained heterogeneous solution was filtered out and dried in a vacuum cabinet at temperature of 60°C.

Preparation of polymer composite: The oil-containing clay particles were introduced into the polyethylene melt on rollers at temperature 180°C. For examination of the physical-mechanical properties of polymer composites, they were subjected to pressing at temperature 210°C. The samples were cut from pressed plates for determination of the breaking stress, specific elongation and flexural modulus of elasticity of filled composites. The samples are prepared without oil. The evaluation indices were the breaking tensile stress and specific elongation (on ГОСТ 17370-71), as well as the friction coefficient (on ГОСТ 11012-69)

Results and discussion

Table 2 presents the test results of filled composition materials obtained on the basis of polyethylene with nanoclay and oil (at their various mass ratios).

Table 2. Test results of compositions

Ratio of components, % mass	Breaking stress, MPa	Specific elongation, %	Melt flow index, g/10min	Friction coefficient
HDPE: nanoclay:SLO				
75:25:0	25.3	15.0	11.7	0.42
85:15:0	27.5	21.0	13.3	0.35
73:26:1	25.5	25.0	9.5	0.21
72:25:3	26.3	43.0	12.7	0.18
83:15:2	28.8	71.0	15.4	0.19
94:5:1	31.8	190	8.7	0.32
LDPE: nanoclay: SLO				
75:25:0	12.5	21.0	7.2	0.24
73:25:2	15.7	50.0	8.7	0.13
69:27:4	13.5	23.0	7.7	0.21
83:15:2	16.9	73.0	5.9	0.16
95.5:4:0.5	15.7	225	2.3	0.19

As can be seen from Table 2, the inclusion of nano-sized clays and oils (with viscosity of ~ 10 ml /s) in the composition of the polyethylene matrix makes it possible to create a composition filled material with high strength and antifriction properties. When using only HDPE filler (clay) in the composition, it is not possible to achieve a sufficiently low value of the friction coefficient.So, during testing of cured composition consisting of 75% HDPE and 25% of nanoclay, the friction coefficient is 0.42, then it is enough to introduce only 1% oil to reduce the friction coefficient to 0.21. As for the use of LDPE (95.5%), nanoclay (4%) and only 0.5% oil as a matrix, the composition material with friction coefficient 0.19 and a tensile elongation 225% were obtained. The composition consisting of 73% LDPE, 25% of clay and 2% oil has the lowest wear index: the friction coefficient at the same time is minimum 0.13. According to the values of the breaking stress of the sample, compiled on the basis of HDPE, they exceed those obtained on the basis of LDPE.

The results of experimental investigations allow confirming that the improvement of the wear resistance of nanocomposites has been largely connected with the peculiarities of changes in their per-molecular structure. The considered polyolefins are referred to the amorphous-crystalline or polycrystalline polymers, in which the structural factor is the determining factor in estimation of the physical-mechanical characteristics and wear resistance of nanocomposites based on them. The crystal phase consists of spherulite formations interconnected by "pass-through chains". As the size of the spherulites decreases, the number of pass-through chains formed during their formation and the probability of participation of one macrochain in the simultaneous formation of several crystalline formations grows [10,11].

Along with this, the appearance of a foreign body (nanoparticles) in the composition of the polymer matrix essentially influences on the formation of heterogeneous nucleation centers, which, together with homogeneous centers, favor the formation of small-spherulite crystal structures. As the crystals grow, the basic mass of the nanoparticles are ejected into the amorphous or inter-spherulite field [12,13]. The latter circumstance leads to additional reinforcement of amorphous areas, which, according to Table-1, favors the essential improvement in the properties of composite materials.

It should also be noted that the results of the experimental investigations confirm the fact that the simultaneous use of two or three components in the composition of the composite leads to obviously noticeable improvement in the properties of nanocomposites. All the results above allow confirming a "synergistic effect" in use of two mineral fillers. In this case, each filler contributes to the formation process of the permolecular structure and change of the complex properties of composite materials [14-16].

A comparative analysis of the data presented in this Table indicates that the introduction of nanoclay and synthetic lubricating oil into the composition of composites on the basis of polyolefins leads to quite serious changes in their physical-mechanical properties and the friction coefficient. As expected, comparatively the best indices for the friction coefficient are samples of oil-filled nanocomposites. There are reasons to believe that in the friction process in the contact zone the oil is constantly isolated from the composition of filler particles, which naturally influences on essential reduction in friction and wear of the material. This effect is observed on almost all composites.

It ought to be noted that during the study of the mixing process and processing of filled polymer composites, the selection of equipment is of no small importance. As a rule, the most optimal is the use of twin-screw extruders, favoring the almost uniform dispersion of the filler in the volume of the polymer matrix. In the considered case, for carrying out mechanical-chemical modification and preparation of a product using monotreme technology the processing on a universal single-screw injection-molding machine is the most perspective one. This construction of the injection molding machine allows not only thorough thermo-mechanical mixing of polymer composites, but also to carry out mechanical and chemical modification in it simultaneously. The mechanical-chemical modification is characterized by the fact that in the mixing process of a polymer mixture with mineral filler, it is possible to obtain filled composition materials with relatively uniform dispersion of solid components in the polymer volume. By regulation of the temperature of the material cylinder, injection pressure and mold temperature, it is possible to change the physical-mechanical and technological characteristics of composites to a certain extent. The optimal holding time under pressure is 10 sec. The versatility of this equipment is concluded in the fact that after heating of the polymer mass, the mixing process is accompanied not only by the rotation of the screw, but also by a partial progressive movement of the screw, following which the necessary pressure is created at the time of injection into the mold .

In Table 3 the results of analysis of the properties of composite from polyethylene clay and SLO (LDPE + 5% mass clay + 5% SLO), depending on the temperature regime of injection molding are presented. The selection of this composite was due to the fact that with this ratio of the considered components, sufficiently encouraging data are observed on one of the main indices – wear resistance. So, for example, if the wear in the first cycle was 134,55 mg for the initial PP, then for the considered composite, the value of this index decreased to the level of 21,32mg, i.e. in 6.3 times. In this case, it was important to find out how this composition of the composition material will affect the change in other physical-mechanical characteristics depending on the technological conditions of their processing.

Table 3. Influence of the temperature regime and casting pressure on properties of composites on the basis of LDPE +5% mass clay+5% SLO.

Temperature on zones, ^{o}C	Casting pressure, MPa	Breaking stress, MPa	Specific elongation, %	Shrinkage, %	Wear after the first cycle, mg
150-160-170-180		32.5	50	0.45	26.53
150-170-180-190		31.0	50	0.45	25.12
150-170-185-2	50	31.0	54	0.43	25.40
150-170-190-210		32.6	65	0.41	25.86
150-160-170-180		32.3	50	0.32	24.61
150-170-180-19		33.2	60	0.32	25.07
150-170-185-200	100	33.6	60	0.30	24.19
150-170-190-210		34.1	70		23.32
150-160-170-180		32.5	60	0.15	24.21
150-170-180-190		34.5	70	0.12	23.35
150-170-185-200	150	35.5	70	0.09	21.32
150-170-190-210		35.5	80	0.09	21.48

Comparison of the data in this Table is indicative that the casting pressure and the temperature regime of the material cylinder have a certain influence on the properties of the composition material. It becomes obvious that as the temperature of the material cylinder and the casting pressure increase, a natural increase in the breaking stress of the composite occurs. There is reason to believe that as a result of temperature rise, a decrease of the viscosity of the polymer matrix is observed, following which the probability of uniform dispersion of filler particles in the volume of the polymer matrix increases. On the one hand, the temperature rise and casting pressure favors an increase in the melt flow of the polymer mass and, correspondingly, a faster and more complete filling of the mold. On the other hand, clay and SLO particles, having a developed contact surface with the polymer matrix, are capable of additional creation of heterogeneous nucleation centers even in the process of thermal fluctuation and mixing in the material cylinder. The latter ones, as a result of crystallization and spontaneous growth of crystalline formations in a relatively cold mold, favor the formation of a small-spherulite permolecular structure. As a result, according to the data of Table, the temperature growth and casting pressure is accompanied by rise in the breaking stress and, to some extent, the relative elongation of the composite.

As expected, as the temperature and casting pressure grow, a definite decrease in the volume shrinkage of the composite is observed. A decrease of volumetric shrinkage is a very important factor, since it makes possible to eliminate the possibility of essential change in the volumetric and linear dimensions of the product during exploitation in various fields of technique.

When estimating the quantitative change in the composite wear from the above-mentioned processing factors, we have proceeded from the notion that all other things being equal, the value of this index depends mainly on their density and hardness . In other words, the higher the density of the same material, the greater its wear resistance should be. Indeed, at a relatively low temperature (150-160-170-180 ^{o}C) and low pressure (50 MPa), it has been established that the density of the composite is 953 kg/m^3 and, conversely, at a high pressure (150 MPa) and a processing temperature 150-170-190-210^{o}C, its density becomes equal to 961 kg/m^3.

Analyzing the data in Table, it can be seen that as the temperature regime and the casting pressure grow, a slight decrease in wear is observed, which, as shown above, apparently may be connected with an increase in the density of the composition material. In addition, it should be taken into account that the composition material has a nano-clay in its composition, which, as is known, is characterized by a layered structure largely determining the improvement of wear resistance and rheological characteristics. So, for example, at the lowest pressure and lower temperature regime of casting, the wear after the first cycle is 26.53 mg. At the highest values of the pressure and temperature regime of casting, the wear was 21.48 mg, i.e. decreased by 4.05 mg, i.e. in1.2 times.

Conclusion

Thus, based on the above, it can be said that the properties of the composite material are affected by the composition and ratio of the components of the mixture, as well as the technological aspects of their processing by injection molding. It was found that the mode of rise in the temperature of the material cylinder within the specified limits and the growth of the casting pressure are accompanied by a slight increase in the fracture shear stress and a significant decrease in the wear of the composite samples. The optimal conditions for keeping time under pressure are 10 seconds. It is also possible to create composite materials with high strength and anti-friction properties by changing the properties of industrial polyethylene with inexpensive inorganic additives.

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YUXARI VƏ AŞAĞI SIXLIQLI POLİETİLEN, NANOGİL VƏ SİNTETİK SÜRTGÜ YAĞI ƏSASINDA KOMPOZİT MATERİALLARIN HAZIRLANMASI

[1]G.Ş. Qasımova, [1]D.R. Nurullayeva, [2]L.X. Qasımzadə, [1]F.A. Ağayeva, [1]A.L. Tağıyeva

[1]Azərbaycan Respublikası Elm və Təhsil Nazirliyinin Polimer Materialları İnstitutu
AZ 5004, Sumgayıt, S.Vurğun küç., 124
[2]Azərbaycan Dövlət Neft və Sənaye Universiteti
AZ 1010 Bakı, Azadlıq pr, 20; e-mail: gulnara.qasimova.68@mail.ru

Xülasə: Məqalədə aşağı sıxlıqlı və və yuxarı sıxlıqlı polietilen, Azərbaycanın gili və sintetik sürtgü yağı kimi modifikasiyaedici əlavələr əsasında alınan yüksək möhkəmlikli, antifriksion xüsusiyyətlərə malik polimer kompozit materialların işlənib hazırlanmasının nəticələri verilmişdir. Göstərilmişdir ki, kompozisiyanın tərkibinə 5-25% gil və 1-3% yuxarıda göstərilən yağlar əlavə etməklə cox yüksək antifriksion və başqa xassələrə malik termoplastik materiallar almaq olar. Bundan başqa ərintinin ekstruziyasında material silindrin temperatur və təzyiqinin polietilen

əsasında alınan kompozitin xassələrinə təsiri öyrənilmişdir. Cox komponentli kompozitlərin emalı üçün opltimal şərait müəyyənləşmişdir.
Açar sözlər: polimer, polietilen, kompozit materiallar, xassələr

РАЗРАБОТКА КОМПОЗИЦИОННЫХ МАТЕРИАЛОВ НА ОСНОВЕ ПОЛИЕТИЛЕНА ВЫСОКОЙ И НИЗКОЙ ПЛОТНОСТИ, НАНОГЛИНЫ И СМАЗОЧНОГО СИНТЕТИЧЕСКОГО МАСЛА

[1]Г.Ш. Гасымова, [1]Д.Р. Нуруллаева, [2]Л.Х. Гасымзаде, [1]Ф.А. Агаева, [1]А.Л. Тагиева

[1]Институт полимерных материалов Министерства науки и образования Азербайджанской Республики
AZ 5004 Сумгайыт, ул С. Вургуна, 124
[2]Азербайджанский Государственный Университет Нефти и Промышленности
AZ 1010, Баку, пр. Азадлыг, 20; e-mail: gulnara.qasimova.68@mail.ru

Аннотация: В статье приводятся результаты исследований по разработке полимерных композиционных материалов с улучшенными прочностными и антифрикционными свойствами на основе полиэтиленов высокой (ПЭВП) и низкой плотности (ПЭНП) и модифицирующих добавок – азербайджанских глин и синтетического смазочного масла. Установлено, что введение в состав композиции 5-25% наноразмерных глин и 1-3% вышеуказанного масла позволяет получать термопластичные материалы с достаточно высокими антифрикционными свойствами. Кроме этого, в статье исследовано влияние температурного режима и давления экструзии расплава в материальном цилиндре на физико-механические свойства композитов на основе полиэтилена. Показаны оптимальные условия переработки многокомпонентных композитов.
Ключевые слова: полимер, полиэтилен, композиционные материалы, прочностные и антифрикционные свойства.