REPUBLIC OF AZERBAIJAN

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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

OBTAINING AND RESEARCH OF NEW TYPES OF NANCOMPOSITES WITH HIGH PHYSICOMECHANICAL PROPERTIES BASED ON COPOLYMERS OF ETHYLENE WITH BUTENE, ETHYLENE WITH HEXENE AND NATURAL MINERALS OF AZERBAIJAN – CLINOPTILOLITE AND VESUVIAN

Speciality: 2318.01 – Chemistry and technology of composite materials

Field of science: chemistry

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SUMGAIT – 2024

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INTRODUCTION

Relevance and approbation of the topic. The intensification of the global industrial production of polyolefins is directly related to the expansion of their use in various fields of engineering and technology. This circumstance, in turn, contributed to a significant expansion of developments in the field of producing composite materials, especially nanocomposites based on polyolefins and mineral fillers. This is due to the fact that large-scale research in the field of materials science began to open up new and promising opportunities for the practical use of polymer composites This is due to the fact that large-scale research in the field of materials science began to open up new and promising opportunities for the practical use of polymer composites[1]. In this regard, research that allows a more in-depth approach to the study of the basic principles of obtaining polymer nanocomposites has become of paramount importance[2]. At the same time, it is important not only the complex of studies carried out by scientists to improve the final properties of polymer composites, but also to obtain sufficiently voluminous information about the mechanism of formation of the interphase region and, in general, the microheterogeneous structure in incompatible segregated mineral-polymer systems. In accordance with the above, developments aimed at the possibility of using nanoparticles of layered natural aluminosilicates as a polymer reinforcing filler, the prominent representatives of which are vesuvian (VS) and clinoptilolite (CTL), are of particular interest.

In this regard, it would be appropriate to note that despite the large number of works in the field of producing composites based on polyolefins, research on modifying the structure and properties of composites and vulcanizates based on copolymers of ethylene with α-olefins is very limited. Research on the effect of nanoparticles on

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[1] Берлин, А.А. Принципы создания композиционных материалов / А.А. Берлин, С.А. Вольфсон, В.Г. Ошман – Москва: Химия, – 1990. – 240 с.

[2] Симонов-Емельянов, И.Д. Построение структур в дисперсно-наполненных полимерах и свойства композиционных материалов // Пластические массы, – 2015. No. 9-10, – p. 29-36.

the thermal deformation properties of the above copolymers is completely limited. A separate consideration of the thermomechanical characteristics of nanocomposites allows us to analyze all processes occurring in the solid, highly elastic and viscous states[3].

Analysis of the state of the problem shows that the creation of new promising composite materials based on classical methods of modifying polyolefins with traditional fillers and ingredients has completely exhausted itself.

Research conducted in recent years has shown that revolutionary breakthrough solutions can only be achieved using nanotechnology using nano-sized dispersed fillers based on natural minerals[3]. At the same time, the contribution of nano-sized filler particles is that it helps to enhance the strength characteristics of nanocomposite materials and the formation of a new level of supramolecular structure and properties. It is this approach to the development of nanocomposites that allows us to come close to obtaining structural materials with predetermined structural features and performance characteristics. In this case, ethylene-butylene copolymer (EBC) and ethylene-hexene copolymer (EHC) were used as prominent representatives of ethylene copolymers with α-olefins.

Object and subject of research. The objects of the study are EHC and EBC, natural mineral nanofillers – vesuvian and clinoptilolite, compatibilizer – graft copolymer of HDPE with methacrylic acid (PEMAA), lubricant – calcium stearate, structure former - alizarin, cross-linking agents - dicumyl peroxide (DP) and sulfur. The subject of the research is the development of high-strength nanocomposites based on EHC, EBC and vesuvian, clinoptilolite nanoparticles. To increase heat resistance and strength properties, cross-linking agents – DP and sulfur – were used.

The purpose and objectives of the research. The purpose of this

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[3] Марков, В.Ф. Наноматериалы: получение, свойства и применение: Учебное пособие для студентов вуза, обучающихся по направлению подготовки 18.03.01, 18.04.01 «Химическая технология» / В.Ф. Марков, Л.Н. Маскаева – Екатеринбург: Уральский федеральный университет им первого Президента России Б.Н. Ельцина, – 2023. – 160 с.

dissertation is to obtain and study the structure and properties of new types of high-strength nanocomposites based on ethylene-hexene copolymer (EHC), ethylene-butene copolymer (EBC) and natural minerals of Azerbaijan - clinoptilolite and vesuvian.

Research objectives are:

- in the process of mechano-chemical modification, develop nanocomposites based on EBC and EHC sing nano-sized particles of the natural minerals clinoptilolite (CTL) and vesuvian (VS);
- to study the influence of the particle size of KTL and VS, as well as various ingredients and cross-linking agents on the structure, physicomechanical, thermal deformation and thermophysical properties of composite materials;
- to investigate the rheological features of the flow of nanocomposites in a wide range of temperatures (190-250 °C) and loads of 2.16-21.6 kg, study the dependence of shear rate on shear stress, determine the dependence of viscosity on shear stress and temperature, estimate the activation energy of viscous flow;
- using the dilatometric method of stepwise cooling to study the pattern of crystallization of nanocomposites depending on the content and type of filler and polymer matrix, determination of phase transitions of the first and second order; to investigate the interfacial region, the mechanism of crystallization, as well as the patterns of changes in the occupied and free specific volumes of nanocomposites depending on temperature and the ratio of mixture components;
- to research and test at the METAC LLC the technological features of processing nanocomposites based on EHC and EBC using injection molding and extrusion methods in a wide range of temperatures and pressures.

Research methods. The following research methods were used in the dissertation work: IR spectroscopy, derivatography; X-ray phase analysis, SEM analysis, Vicat softening point, flexural modulus, ultimate tensile stress, tensile yield strength, elongation at break, flexural strength, thermomechanical analysis according to Kanavets, MFR, rheology, and step dilatometry.

Basic provisions for defense:

1. experimental data, theoretical conclusions and scientific principles related to the mechano-chemical modification of EBC and EHC with natural nanofillers and ingredients during the process of mixing components in the melt mode;
2. results of the study of physical-mechanical, thermophysical, rheological properties, kinetic patterns of crystallization and the mechanism of growth of crystalline formations;
3. scientific principles and conclusions concerning the mechanism of formation of the interphase region and the establishment of the structure-property relationship;
4. experimental data, scientific statements and conclusions regarding the study of the vulcanization process and mechano-chemical synthesis of EBC and EHC nanocomposites;
5. experimental data and scientific conclusions on the influence of technological parameters of processing nanocomposites by injection molding on their basic physical and mechanical properties.

Scientific novelty of the research. The scientific novelty of the dissertation work lies in the fact that for the first time,

- nanocomposites with high physical, mechanical and technological properties have been developed based on EBC, EHC and natural minerals of Azerbaijan (vesuvian and clinoptilolite);
- the influence of filler dispersion (particle size) from 20 to 4500 nm on the process of formation of the interphase region and the pattern of changes in the strength characteristics, heat resistance and MFR of nanocomposites was studied;
- The thermomechanical properties of nanocomposites based on EHC and EBC were studied depending on the VS and CTL content, the influence of the DP and sulfur content on the pattern of changes in deformation, the first-order phase transition, the process of glass-transition and the formation of a region of highly elastic deformation was considered;
- using the step dilatometry method, the temperature dependence

of the specific volume, occupied volume and free volume of the nanocomposites under consideration was studied, the kinetic pattern of crystallization and the mechanism of growth of crystalline formations were determined depending on the nanofiller content;

- in the process of mechano-chemical modification, optimal technological conditions for processing nanocomposites based on copolymers EBC and EHC and natural minerals CTL and VS were developed. Test certificates for nanocomposites were obtained using injection molding and extrusion methods on industrial units.

Theoretical and practical significance of the research. The theoretical analysis, the developed main provisions and conclusions, as well as the obtained experimental data can be used by scientists, teachers, undergraduates and dissertation students at other research objects. The practical significance of the work lies in the fact that using standard injection molding equipment METAC LLC, a technology for producing and processing nanocomposites based on EBC and EHC was developed and tested (test certificate is available). Varying the ratio of mixture components and cross-linking components makes it possible to obtain a whole set of materials for structural purposes intended for use in special fields of technology.

Approbation and application of research. Based on the dissertation materials, 35 scientific works have been published, including 1 Patent of the Republic of Azerbaijan, 20 conference materials and abstracts, 14 articles, of which 9 were published abroad and 2 mono-articles. The main results of the work were presented and reported at the following conferences, symposiums and meetings: International Conference dedicated to the 94th anniversary of National Leader H.A. Aliyeva (Ganja, 2017); International Scientific and Technical Conference on "Petrochemical synthesis and catalysis in complex condensed systems" (Baku, 2017); International Scientific Conference on "Functional monomers and polymer materials with special properties: problems, prospects and practical views" (Baku, 2017); International Conference "Actual problems of modern natural and economic sciences" (Ganja, 2018); Republican

Scientific and Technical conference on "Youth and scientific innovations" (Baku, 2018); International Scientific and Practical Conference on “Prospects for innovative development of oil refining and petrochemistry”, dedicated to the 110th anniversary of academician V.S. Alieva (Baku, 2018); Republican Scientific-Practical conference on "Ways of applying scientific innovations in the teaching process" (Lankaran, 2019); International scientific and technical conference on “Polymer composites and tribology” Polycomtrib – 2019, (Belarus, Gomel 2019); International scientific conference on “Current issues of modern chemistry”, dedicated to the 90th anniversary of the Institute of Petrochemical Processes named after academician Y. Mamedaliev (Baku, 2019); International Scientific Conference on "Innovative Development Perspectives of Chemical Technology and Engineering" (Sumgait, 2019); All-Russian scientific and practical conference on "Perspective technologies and materials" (Sevastopol, 2020); XVII International Conference of Young Scientists, National Academy of Sciences of Belarus (Minsk, 2020); 15th international conference of young scientists, students and postgraduates Kirpichnikovsky readings on "Synthesis and investigation of properties, modification and processing of high-molecular compounds" (Kazan, 2020); International Scientific and Practical Conference on "Perspective Technologies and Materials" (Sevastopol, 2021); International scientific and technical conference of young scientists on "Innovative materials and technologies" (Minsk, 2021); MSF 2022 Materials Science Of The Future: Research, Development, Scientific Training (Nizhny Novgorod, 2022); Republican Conference on "Environmental protection, industrial and household waste recycling" (Ganja, 2022).

The name of the institution where the dissertation work was performed. The dissertation work was carried out in accordance with the plan of research works of the Institute of Polymer Materials of the Ministry of Science and Education Republic of Azerbaijan.

The author's personal involvement. In the process of completing the dissertation, the author took a direct part in setting the task, summarizing and discussing the obtained results, conducting experimental studies. This work represents the completed scientific work of the applicant, which allowed her to summarize the complex of conducted studies in the scope of the dissertation work.

The volume and structure of the work. The dissertation is presented on 193 pages (222702 characters), consists of an introduction (13030 characters), V chapters (205216 characters) and main conclusions (4456 characters), includes 27 tables, 45 figures, a list of cited scientific literature (37491 characters), consisting from 183 titles.

In the introduction, the relevance of the topic is substantiated; the goal and main tasks of the research, scientific novelty and practical value of the dissertation work are formulated.

In the first chapter (37084 characters), a detailed analysis of the state of the problem of obtaining and studying composites and nanocomposites is given, problems related to the study of the interphase region, the formation of their structure and properties are considered. After each section, conclusions are given, and at the end of the literature review, there are conclusions and promising directions for research.

In the second chapter (19341 characters), the methods of experimental studies on the mechano-chemical synthesis of polymer composite materials are given, the characteristics of the raw materials and materials used in the dissertation work are given, various methods of evaluating the structure and properties of polymer materials are described, and the technological aspects of the processing of polymer materials are given in detail.

In the third chapter (68947 characters) of the dissertation work, in the part "results and their discussion", the results of the study of structural features, a complex of physical-mechanical and thermophysical characteristics, as well as kinetic regularities of the crystallization process, rheological properties of nanocomposites depending on the type and content of the natural filler are given.

In the fourth chapter (53792 characters) detailed studies of kinetic regularities of crystallization of nanocomposites of EBC and EHC with natural minerals are given. The task of the study included determining phase transitions of the first and second order, free and occupied volume, as well as the mechanism of crystallization of nanocomposites during the continuous formation of crystallization centers. Also, in this chapter, attention is focused on the study of rheological characteristics of nanocomposites based on EBC and EHC and natural minerals. Flow curves, dependence of viscosity on shear rate and temperature were determined; activation energy of viscous flow was calculated.

The fifth chapter (26052 characters) focuses on studying the influence of technological features of processing nanocomposites using injection molding and reaction extrusion methods. The influence of the temperature regime of the material cylinder, injection pressure, mold temperature and holding time under pressure on the basic physical, mechanical and technological properties of nanocomposites has been established.

The work is summarized by conclusions on the work done, which presents the main results of the research conducted on the structure, properties and processing technology of nanocomposites, and predetermines the main innovative and promising directions for the practical use of the resulting nanocomposites. The dissertation ends with a list of cited literature.

The appendix contains a test certificate for nanocomposites in a specialized and leading plastics processing company, "METAK" LLC, Baku.

MAIN CONTENT OF THE WORK

1. Physical and mechanical properties of nanocomposites based on EBC, EHC and natural minerals

In this section, the main attention is paid to the study of the influence of the content and particle size of natural minerals – clinoptilolite (CTL) and vesuvian (VS) on the main physical and mechanical and thermophysical properties of nanocomposites based on EBC and EHC. The choice of these research objects was due, first of all, to their insufficient knowledge in the polymer-mineral filler system, the results of which are shown in Table 1.

Based on the experimental data obtained, it was found that with increasing filler content, the strength properties of nanocomposites change according to a certain pattern. The maximum value of the ultimate tensile stress of nanocomposites is achieved at VS content within 5.0 wt % and is 30.8 MPa. It should be noted that even with the loading of 2.0 wt % VS, the ultimate tensile stress of nanocomposites based on EBC increases from 27.1 to 29.7 MPa while maintaining the elongation at break at the level of the initial EBC.

Table 1.

Physical and mechanical properties of nanocomposites based on EBC and VS with nanoparticle sizes in the range of 20-110 nm

№	Composition formulation, wt %	Ultimate tensile stress, MPa	Elongation at break, %	Flexural modulus, MPa	MFR g/10min	Vicat softening point, °C
1	EBC	27.1	880	532	4.6	116
2	EBC + 2 % VS	29.7	880	571	5.2	118
3	EBC + 5 % VS	30.8	515	612	6.1	118
4	EBC + 10 % VS	30.0	185	658	7.0	122
5	EBC + 15 % VS	28.4	95	705	8.5	123
6	EBC + 20 % VS	26.6	70	724	9.6	125
7	EBC + 30 % VS	24.5	35	755	6.2	128

Such a noticeable increase in the ultimate tensile stress at minimum filler content (5.0 wt %) clearly supports the assertion that VS nanoparticles can simultaneously perform the function of a nucleating agent, ultimately promoting the formation of a fine spherulite supramolecular structure and the strengthening of nanocomposites. According to the data in Table 1, the introduction of VS leads to an increase in the MFR of nanocomposites. This is apparently due to the fact that most natural minerals, including VS, contain nanoclay (9-10 wt %), which, as is known, is characterized by a layered structure. The interlayer space of nanoclay contains polar liquids, surfactants, glycerin, etc. We believe that when mixing the components of the mixture on hot rollers and as a result of thermal deformation, intercalation of macrochains of the polymer matrix occurs into the interlayer space of the nanoclay, followed by exfoliation of its structure. During the decomposition of the layered structure of nanoclay, polar liquids migrate into the polymer matrix, which, like a lubricating agent, help improve the rheological properties of nanocomposites. This fact was important, as it allowed us to verify that the improvement in MFR is associated with the presence of an organic component in the composition of the natural VS, which is responsible for improving the rheological properties of polymer composites.

To obtain more complete information about the processes occurring in nanocomposites, it seemed interesting to study the influence of the size factor of dispersed VS particles on the main physical, mechanical and thermophysical properties of composites. The size of VS mineral particles above the nanoscale level varied in the following grinding fractions: 350-840 nm, 1420-2000 nm, 2210-4430 nm. It was found that, in comparison with nanosized particles (up to 110 nm), the loading of relatively larger VS particles into the composition of the EBC is accompanied by a change in the ultimate tensile stress with a maximum at 10 wt % content in the composite. The flexural modulus changes according to a certain pattern.

Similar studies were carried out on composites based on EBC + CTL, EHC + VS and EHC + CTL. And in these nanocomposites, it was found that the maximum value of the ultimate tensile stress is achieved in samples with 5.0 wt % content of mineral filler.

Identification of temperature transitions from one state to another in polymer composites makes it possible to make the most accurate choice of technological regime for their processing. In this regard, the thermomechanical research method allows us to obtain the most complete understanding of phase transitions from one state to another. In this regard, using the example of EBC, EHC and mineral fillers – vesuvian and clinoptilolite, the thermomechanical properties of nanocomposites based on them were studied. Figure 1 shows thermomechanical curves of deformation versus temperature. From the comparative analysis of the data in this figure, it can be noted that in the thermomechanical curve of the nanocomposite EBC + 5.0 wt % VS forms a small plateau in the temperature range of 120-125 °C.

As the VS content increases within 5.0; 10 and 20 wt % in the composition of EBC, the softening temperature of nanocomposites increases accordingly in the following sequence: 115; 120 and 125

°C. With an increase in the VS content from 0.5 to 20 wt %, the temperature range of measurements at 2 mm deformation mark in the viscous-flow state stretches, respectively, to 116; 121; 140; 171 and 189 °C.

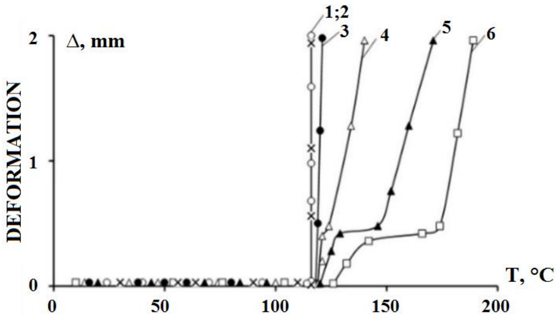

Figure 1. Regularity of changes in deformation depending on temperature for nanocomposites based on EBC + VS: 1 – initial EBC; 2 – EBC + 0.5 wt % VS; 3 – EBC + 1.0 wt % VS; 4 – EBC + 5 wt % VS; 5 – EBC + 10 wt % VS; 6 – EBC + 20 wt % VS

Further in this chapter, we present the results of a study of the influence of the dicumyl peroxide (DP) content on the vulcanization process of the considered nanocomposites based on EBC + VS and EBC + CTL. As can be seen from Table 2, with an increase in the DP content and, accordingly, the degree of cross-linking, an increase in the strength characteristics, melting temperature and heat resistance of nanocomposites is observed with a maximum at 0.5 wt % of the cross-linking agent. At a higher DP content, the nanocomposite is almost completely cross-linked and the MFR value becomes zero.

The influence of sulfur content on the vulcanization process and the properties of nanocomposites based on EBC + 5.0 wt % VS and EBC + 5.0 wt % CTL were studied. It has been established that, regardless of the type of filler, with increasing sulfur content, a noticeable change in the ultimate tensile stress is observed with a maximum at 5.0 wt % content of the vulcanizing agent – sulfur. At the same time, the most noticeable advantage of sulfur vulcanizates over peroxide ones is maintaining the elongation at break and MFR at a satisfactory level.

Figure 2 shows the effect of DP content in EBC and EHC nanocomposites on the pattern of changes in thermomechanical curves. Using the example of EBC + 5.0 wt % CTL nanocomposite, the effect of DP content on the pattern of changes in deformation depending on temperature is shown.

Table 2.
Effect of DP content on the properties of nanocomposites based on EBC + VS and EBC + CTL

№	Composition formulation, wt %	Ultimate tensile stress, MPa	Elongation at break, %	MFR, g/10 min	Vicat softening point, °C	Melting point, °C
1	EBC	27.1	880	4.6	116	128
2	EBC + 5.0 VS	30.8	515	6.1	116	124
3	EBC + 5.0 VS + 0.25 DP	31.9	375	3.4	118	128
4	**EBC + 5.0 VS + 0.5 DP**	**33.5**	**265**	**1.5**	**129**	**134**
5	EBC + 5.0 VS + 1.0 DP	29.7	85	–	147	149
6	EBC + 5.0 VS +2.0 DP	24.3	30	–	156	156
7	EBC+ 5.0 CTL	31.2	400	6.7	115	124
8	EBC + 5.0 CTL + 0.25 DP	32.0	345	3.9	118	128
9	**EBC + 5.0 CTL + 0.5 DP**	**33.9**	**225**	**1.7**	**131**	**135**
10	EBC + 5.0 CTL + 1.0 DP	28.2	80	–	148	150
11	EBC + 5.0 CTL + 2.0 DP	23.5	30	–	159	159

As can be seen from Figure 2, with the loading of DP in an amount of 0.25 wt % the region of highly elastic deformation (plateau) changes in the temperature range of 122-139 °C; with a DP content of 0.5 wt %, this region appears in the temperature range of 143-164 °C.

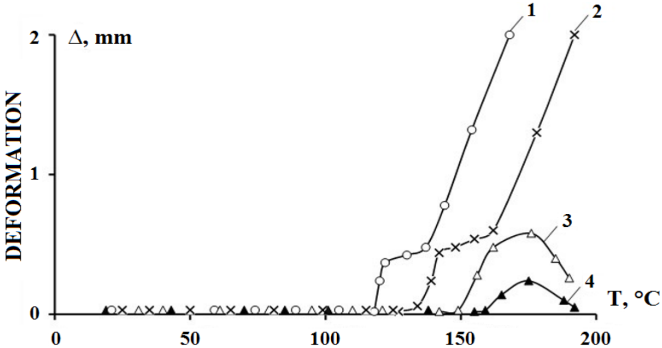

Figure 2. Effect of DP content on the thermomechanical properties of the EBC + 5.0 wt % CTL nanocomposite, wt %: (1) ○ – 0.25; (2) × – 0.5; (3) Δ – 1.0; (4) ▲ – 2.0

With an increase in the DP content above 0.5 wt %, the samples lose their plasticity and melt fluidity and become vitrified. For glassy nanocomposites cross-linked with 1.0 and 2.0 wt % DP, the maximum temperature is 176 and 178 °C.

2. Kinetic patterns of nanocomposites crystallization

The cooling process is one of the critical moments in polymer processing technology; since as a result of the correct choice of cooling mode or crystallization of the melt, it is possible to obtain high-quality structural products. And, as the results of research carried out in this direction have shown, the method of dilatometric measurements of specific volume depending on temperature in stepwise cooling mode allows one to obtain fairly detailed information about the patterns of nanocomposites crystallization. Analysis of the crystallization process of nanocomposites opens up additional possibilities for regulating their cooling mode in a mold or forming head. For example, Figure 3 shows the dependence of the specific volume on temperature for the original EHC and its nanocomposites with CTL.

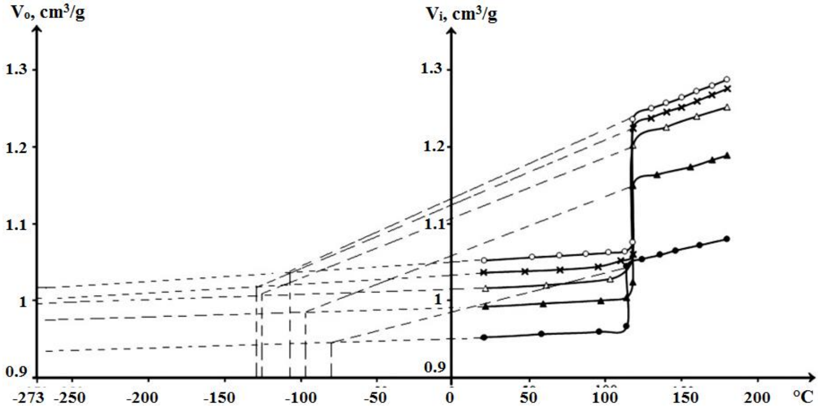

Figure 3. Effect of CTL content on dilatometric curves of dependence of specific volume on temperature for nanocomposites based on EHC, in wt %: ○ – initial EHC, × – EHC + 1.0 CTL, Δ – EHC + 5.0 CTL, ▲ – EHC + 10 CTL, ● – EHC + 20 CTL

Comparing the dilatometric curves in Figure 3, it can be established that, regardless of the CTL content in the composition of EHC, a general pattern appears for all nanocomposites, which consists in a first-order phase transition at the crystallization temperature. In other words, the phase transition from a viscous flow to a solid state is accompanied by a characteristic abrupt decrease in specific volume. For the initial EHC and nanocomposites with CTL content of up to 10 wt %, this phase transition occurs at 117 °C. At 20 wt % CTL content, the phase transition occurs at a relatively low temperature of 114 °C. The decrease in the temperature of the first-order phase transition can be interpreted based on the features of the formation of the crystal structure in nanocomposites. A decrease in the phase transition temperature from 117 to 114 °C indicates that at very high filler contents, relaxation processes and conformational mobility of macrochains are hampered, and therefore, to a certain extent, crystallization processes that affect the decrease in the phase transition temperature are blocked. In addition, during the crystallization process and growth of spherulitic formations, filler particles are pushed into the interspherulitic and amorphous region. Since the amorphous region is characterized by the presence of "passing" chains, the accumulation of nanoparticles in this region will help block the mobility of passing chains, accompanied by inhibition of the rate of crystallization processes.

Along with this, the dilatometric measurement method makes it possible to determine the "occupied" (V_o) and "free" (V_f) specific volume in the polymer mass. According to the dilatometric curves in Figure 3, by extrapolating the lower branch of the curves to the region of absolute zero (-273 °C), it is possible to estimate the value of the occupied specific volume. From a comparative analysis of the experimental data obtained, it can be noted that an increase in the CTL content in the composition of EHC is accompanied by a decrease in the occupied volume and, accordingly, an increase in the density of the samples.

The influence of temperature on the pattern of changes in the free specific volume of nanocomposites depending on the degree of filling has been studied. When studying the kinetic laws of the crystallization process, the Avrami-Kolmagorov model was used, which repeatedly confirmed the applicability of this theory for polymer materials in the region of first-order phase transition. According to Avrami theory, the crystallization process proceeds in accordance with the expression:

$$\varphi = e^{-K\tau^n} \qquad (1)$$

where φ – the part of the polymer that has not yet undergone transformation into the crystalline phase; K – the generalized constant of crystal nucleation and growth; τ – crystallization time at the temperature of a first-order phase transition, s; n – constant, ranges from 1-4 and depends on the nucleation mechanism and the shape of the growing crystals.

After taking the double logarithm of the Avraami-Kolmagorov equation, we obtain the following expression:

$$\lg(-\ln\varphi) = \lg K + n\lg\tau \qquad (2)$$

According to the resulting equation, this dependence is a straight line in lg(-lnφ) coordinates from lgτ. The results of experimental studies showed the applicability of the Avrami-Kolmagorov theory for studying the mechanism of crystallization of the considered nanocomposites based on EHC. We found that at low filler contents the rate of crystallization increases. Figure 4 shows the kinetic patterns of crystallization of nanocomposites in which the CTL content varied within 1.0; 5.0; 10 and 20 wt %. As can be seen from Figure 4, at a low filler content, the crystallization rate increases, since, as shown above, filler particles play the role of crystallization nuclei. As the content of the filler increases, this process slows down, since, in this case, the predominant influence began to have an increase in the viscosity of the system. The analysis results showed that the *n* value for EHC was 2.1, and for nanocomposites EHC + 1.0 wt % – 2.3, for EHC + 5.0 wt % – 2.0, for EHC + 10 wt % – 1.4 and for EHC + 20 wt % – 1.21. Based on the data obtained, it can be established that at the minimum CTL content, the value of *n* is higher than that of the initial EHC. The data obtained allow us to come to the conclusion that the initial EHC and nanocomposites with a low

CTL content (1.0-5.0 wt %) are characterized by a lamellar (two-dimensional) type of crystal growth, and nanocomposites with 10-20 wt % CTL are characterized by linear (one-dimensional) type of crystal growth with the continuous formation of crystallization centers. The obtained research results once again confirm that the Avrami index provides qualitative information about the nature of the process of nucleation and growth of crystals, i.e. expressed by the sum of the number of measurements, under isothermal conditions.

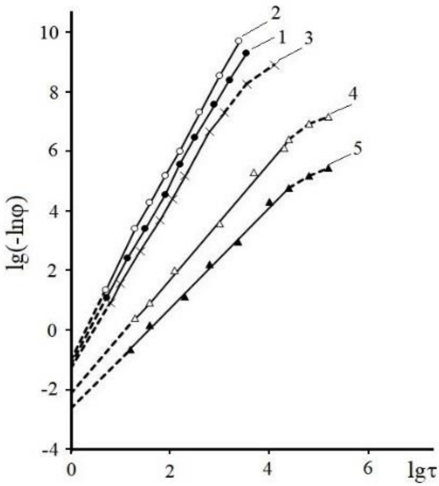

Figure 4. Influence of CTL content on the kinetic patterns of crystallization of nanocomposites based on EHC in Avrami coordinates, in wt %: 1 – initial EHC, 2 – EHC + 1.0 CTL, 3 – EHC + 5.0 CTL, 4 – EHC + 10 CTL, 5 – EHC + 20 KTL

Similar studies were carried out with nanocomposites based on EBC using VS and CTL as fillers. It can be argued that the introduction of CTL or VS into EBC or EHC is accompanied by the formation of a polymer material with a relatively new structural organization. This is a result of the existence of interfacial interactions at the polymer-nanoparticle interface. These include, first of all, adsorption or molecular interactions in the boundary contact zone in the interphase zone. The consequence of these interactions is a noticeable improvement in the physicochemical and physicomechanical characteristics of polymer composite systems. In other words, interfacial interactions predetermine the structural features of the boundary layer, the nature of the molecular orientation on the surface of solid particles, molecular conformational mobility, supramolecular structure and its other properties.

3. Rheological properties of nanocomposites

The formation of the microstructure of the polymer matrix in the presence of nanosized filler particles is fundamentally different from the structure formed by conventional fine particles. It is possible that nanoparticles interact with the polymer matrix somewhat differently than larger particles. Apparently, it would be appropriate to state that the distance at which this interaction occurs is commensurate with the size of the nanoparticles.

In this regard, for a comparative analysis of data on rheological studies, Figure 5 (a, b) shows the flow curves of the original EHC and its nanocomposite EHC + 5 wt % VS in logarithmic coordinates.

From the obtained flow curves it can be noted that at the same shear stress, an increase in the experimental temperature is accompanied by a natural increase in the shear rate. Moreover, over the entire range of temperatures and shear stresses, the flow curves do not have a break in the upper and lower parts of the branches. This is due to the fact that in the considered range of temperatures and shear stresses there are no largest and smallest Newtonian flow regions, i.e. the rate of destruction of associates of macrosegments in the melt is equal to the rate of their recovery. In addition, from a comparative analysis of the data in this figure, it is clear that the loading of 5.0 wt % of the VS into the composition of the EHC is accompanied by an increase in the shear rate by 1.8-2.0 times. The discovered effect of increasing the shear rate in the nanocomposite melt is interpreted by the fact that the natural mineral (vesuvian) contains nanoclay with a layered structure, the interlayer space of which contains various polar liquids, glycerin and surfactants. During processing and thermomechanical action on the composite melt, shear stresses promote the intercalation of macrosegments into the interlayer space of VS nanoparticles. Apparently, after intercalation of macrosegments into the interlayer space, strong shear stresses cause “exfoliation” of layer structures into even smaller ones. As a result of the decomposition of layer structural units, surfactants, glycerin and polar liquids are released directly into the composite melt, which, like lubricating agents, contribute to such a sharp increase in the fluidity of the melt.

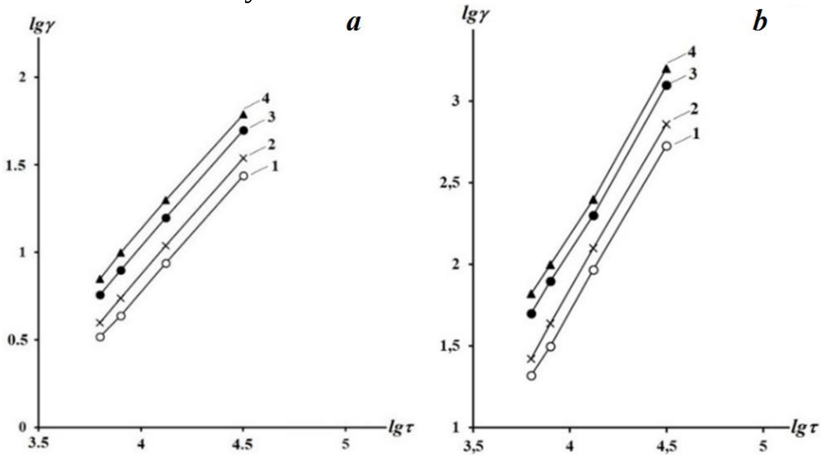

Figure 5. Flow curves of the initial EHC (a) and EHC + 5 wt % VS (b) at different temperatures: ○ – 190 °C, × – 210 °C, ● – 230 °C, ▲ – 250 °C

The rheological curves of the dependence of the effective melt viscosity on the shear rate for EHC and its nanocomposite with 5 wt % VS content were studied. The main difference is in the pattern of changes in the curves, which manifests itself at a temperature of 250 °C. The sharp decrease in melt viscosity, apparently, can be interpreted with the partial occurrence of thermo-oxidative destruction of EHC at such a high temperature. Unlike initial EHC, such a sharp decrease in viscosity is not observed in nanocomposites at 250 °C. Apparently, in this case, it would be appropriate to state that the VS nanoparticles shield and, thereby, restrain the process of thermal-oxidative destruction of the polymer matrix. This was confirmed by the data of derivatographic analysis, according to which, if for the initial EHC thermal oxidative destruction occurred at 242-272 °C, then for nanocomposites this process was recorded in the temperature range of 265-285 °C.

Curves of the dependence of viscosity on inverse temperature are presented in semilogarithmic coordinates. Analyzing the curves in Figure 6a, it can be established that at a constant shear stress they change according to a certain pattern. The difference is manifested in the fact that if at a shear stress of lgτ = 4.52 Pa (Figure 6a) the viscosity value on temperature is expressed by an almost linear dependence, then at a shear stress of 4.19 Pa and below the linear dependence is violated at a temperature of 210 °C.

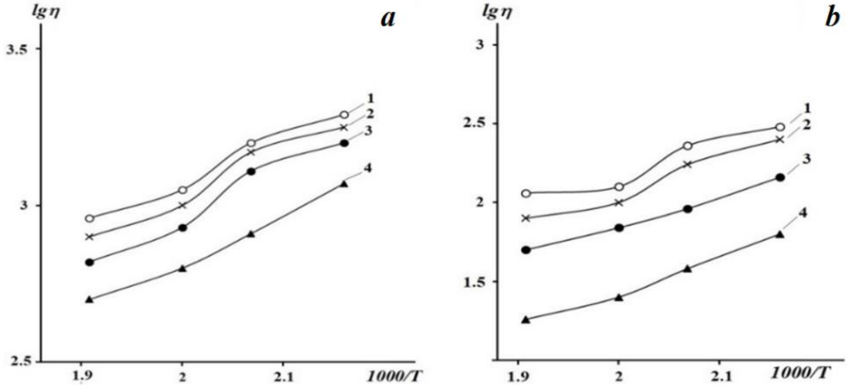

Figure 6. Dependence of the effective viscosity on the inverse temperature in Arrhenius coordinates for the initial EHC (a) and the EHC + 5 wt % VS nanocomposite (b) at different values of shear stress, Pa: ○ – 3.77; × – 3.88; • – 4.19; ▲ – 4.52

In the case of nanocomposites, a change in the nature of the curves is also observed at 210 °C only at shear stress of 3.88 Pa and below. According to the data obtained, an increase in shear stress is characterized by a sharp decrease in melt viscosity. This decrease is especially pronounced at shear stress of 4.54 Pa. It should be noted that the violation of the linear dependence of viscosity on the inverse temperature in Arrhenius coordinates, first of all, indicates the occurrence of complex physical and physicochemical processes in the EHC melt. In this case, we are talking about a special mechanism of destruction and restoration of macrochain associates in homogeneous nucleation centers in the polymer melt.

4. Technological features of processing nanocomposites based on EHC and EBC by injection molding

When assessing the influence of the technological regime on the properties of nanocomposites, EBC + 5.0 wt % KTL, EHC + 5.0 wt % KTL, EBC + 5.0 wt % VS and EHC + 5.0 wt % VS were used as the object of study. The influence of molding temperature on properties in the range of 130-200 °C is presented. The molding pressure is adjustable within the range of 50-150 MPa. As an example, Table 3 examines the influence of temperature conditions and molding pressure on the physicomechanical characteristics of nanocomposites based on EBC + 5.0 wt % VS.

Table 3.

Influence of temperature conditions and molding pressure on the properties of nanocomposites based on EBC + 5 wt % VS

Temperature by zones, T, °C	Molding pressure, MPa	Ultimate tensile stress, MPa	Flexural modulus, MPa	Shrinkage, %
140-150-160-170	50	30.3	1407	0.56
140-150-170-180		30.5	1425	0.56
140-150-180-190		31.0	1436	0.55
140-160-190-200		31.0	1445	0.52
140-150-160-170	100	30.7	1425	0.32
140-150-170-180		30.7	1438	0.32
140-150-180-190		31.4	1503	0.30
140-160-190-200		31.6	1510	0.27
140-150-160-170	150	31.0	1433	0.17
140-150-170-180		31.5	1440	0.17
140-150-180-190		32.2	1489	0.11
140-160-190-200		32.2	1517	0.11

As can be seen from Table 3, as the temperature of the material cylinder increases in zones, a slight increase in the ultimate tensile stress and flexural strength is observed. With increasing molding pressure, the strengthening effect of nanocomposites increases noticeably. This circumstance is interpreted by the fact that with increasing molding pressure and temperature, the sample is compacted to the maximum extent in the mold, which results in an improvement in the strength and shrinkage of the nanocomposites. At the same time, the advantage of screw cylinders in injection molding machines is that when transporting composites from the hopper to the nozzle, the material in the dosing zone is intensively mixed, melted and evenlyheated throughout the entire volume to a given temperature before injection into the mold. In the studied temperature conditions and molding pressure, volumetric shrinkage decreases from 0.56 to 0.11 %, i.e. 5.1 times. At higher molding temperature conditions, a "reverse flow" was observed, which affected an increase in energy consumption and a decrease in equipment productivity, while the effect of further improvement in properties was not observed. At lower molding temperature conditions, there was a danger of underfilling the mold sample, which is extremely unacceptable. Thus, in the chosen technological mode, the permissible high temperature and molding pressure contributed to the improvement of the ultimate tensile stress, flexural strength and shrinkage of the nanocomposites. The influence of mold temperature and holding time under pressure on the properties of nanocomposites was studied.

The dissertation examines in detail the influence of molding technological parameters on the basic physicomechanical properties of nanocomposites based on various combinations of EBC, EHC with mineral fillers such as VS and KTL. The optimal conditions for their processing have been determined.

5. Extrusion method of nanocomposites processing

It is known that the extrusion method of plastic processing makes it possible to obtain not only specific types of structural products, but is also an effective way to modify polymers in the process of mixing mixture components. The advantage of reaction extrusion is that in the process of cross-linking nanocomposites based on ethylene copolymers EBC and EHC, new types of polymer materials are synthesized, in which forced compatibility of nanoparticles with the polymer matrix is achieved. This compatibility occurs as a result of the retention of filler particles by spatially cross-linked structures of the polymer matrix. Previously, we showed in Table 2 that for the production of cross-linked nanocomposites, the most optimal was a composition based on EHC or EBC, consisting of filler in an amount of 5.0 wt % and DP – 0.5 wt %. The use of relatively small amounts of vulcanization agents promotes the formation of a rare network spatial structure of a nanocomposite with fairly high physicomechanical properties.

Table 4 provides experimental data on the influence of extrusion technological parameters on the main properties of nanocomposites based on EBC.

Table 4.
The influence of the temperature regime of the extruder material cylinder on the basic physicomechanical properties of nanocomposites based on EBC, natural minerals (KTL and VZ) and 1.0 wt % alizarin (AL), 1.0 wt % calcium stearate (CS)

№	Temperature regime of the material cylinder, °C	Melt dwell time in the extruder, s	Ultimate tensile stress, MPa	Elongation at break, %
93 wt % EBC + 5 wt % CTL + 1 wt % AL + 1 wt % CS				
1	140-160-170-180-185*	153	29.2	395
2	140-165-175-185-190*	141	30.3	410
3	140-165-175-190-200*	118	32.9	480
4	140-165-180-195-210*	97	28.7	455
5	140-170-185-210-230*	114	28.0	410
93 wt % EBC + 5 wt % VS + 1 wt % AL + 1 wt % CS				
6	140-160-170-180-185*	145	30.0	490
7	140-165-175-185-190*	134	31.7	500
8	140-165-175-190-200*	112	32.3	515
9	140-165-180-195-210*	95	31.8	515
10	140-170-185-210-230*	124	29.5	475

Note: * – temperature in the extruder head

Comparing the data in Table 4, it can be noted that, regardless of the type of filler, comparatively better performance in terms of ultimate tensile stress and elongation at break are achieved by nanocomposites at a material cylinder temperature of 140-165-175-190-200*°C and a dwell time of 112-118 seconds. As can be seen from Table 4, with an increase in the extrusion temperature, a natural decrease in the dwell time of the nanocomposite in the material cylinder is observed. The very fact of reducing the residence time of the nanocomposite in the material cylinder is due to the fact that with increasing extrusion temperature, the viscosity of the melt decreases, which helps to increase the productivity of the extruder. The exception is the temperature regime No. 5 and No. 10, which, on the contrary, helps to increase the dwell time of the material in the material cylinder. This circumstance is extremely important and indicates that at a relatively high extrusion temperature, regardless of the type of copolymer and natural filler, during the rotation of the screw, the viscosity in the material cylinder decreases so much that a “counterflow” of the nanocomposite melt occurs in the dosing zone.

The occurrence of a counterflow of the melt helps to reduce the rate of supply of the polymer material to the forming head, i.e. there is a decrease in the productivity of the extruder and, accordingly, an increase in the dwell time of the material in the material cylinder.

The work similarly investigated the influence of the temperature regime of extrusion of nanocomposites based on EHC and natural minerals CTL and VZ. Based on the results of technological research, METAC LLC received test certificates.

RESULTS

1. For the first time, the structural features and physicomechanical characteristics of nanocomposites based on ethylene copolymers (EBC and EHC) and natural minerals KTL and VS with particle sizes up to 110 nm have been studied. It has been shown that the maximum values of the strength properties of nanocomposites are achieved with the loading of 5.0 wt % nanoparticles of minerals into the composition of ethylene copolymers. The ultimate tensile stress and flexural modulus increase by 13-16 %. The additional use of ingredients such as alizarin and calcium stearate further increases the strength properties of nanocomposites by 20-22 %. The strengthening mechanism of nanocomposites is considered taking into

account the processes occurring in the interphase region [1, 6, 9, 13, 18, 22].

2. For the first time, it was established that at the same filler content, nanocomposites based on EBC and EHC are characterized by relatively higher deformation-strength characteristics and melt fluidity compared to its dispersed-filled composites (with a particle size of 300-4000 nm). It has been shown that, regardless of the particle size, with increasing filler content (KTL and VS) from 1.0 to 20 wt %, there is a general tendency towards an increase in the heat resistance of composite materials by 6-10°C [2, 4, 9, 10, 11, 15, 22, 23].
3. For the first time, the separate influence of cross-linking agents (DP and sulfur) on the physicomechanical properties of nanocomposites was studied. Establishing the optimal amount of cross-linking agents (0.5 wt % DP and 3.0-5.0 wt % sulfur) made it possible to obtain nanocomposites with relatively high values of heat resistance and ultimate tensile stress while maintaining the MFR of the samples at a satisfactory level. The most probable mechanism for the formation of a supramolecular structure in polymer-mineral systems and their vulcanizates is considered [8, 20, 21, 33, 34].
4. Using the Kanavets method, the thermomechanical properties of nanocomposites based on EHC, EBC and mineral fillers were studied, making it possible to determine temperature transitions from the solid to the viscous-flow state. It has been shown that with an increase in the VS or CTL content in the composition of ethylene copolymers from 5.0 to 20 wt %, a slight increase in the heat resistance of nanocomposites is observed from 2 to 11°C [12, 16, 24, 28].
5. The thermomechanical properties of DP vulcanized nanocomposites based on ethylene copolymers and mineral fillers have been studied. It has been shown that with an increase in the DP content from 0.25 to 2.0 wt %, significant differences are observed in the pattern of changes in the deformation of nanocomposite samples depending on temperature. At DP content of 0.25-0.5 wt %, 3 phase states are

observed on the thermomechanical curves of nanocomposites: solid, highly elastic and viscous. A further increase in the DP content in the composition of nanocomposites up to 2.0 wt % reveals 2 states characteristic of densely cross-linked samples on the thermomechanical curves: solid and glassy. When sulfur was used as a vulcanizing agent, regardless of its content, all samples were characterized by three physical states: solid, highly elastic and viscous [13, 14, 16, 21, 24, 28, 32, 35].

6. The rheological properties of nanocomposites based on ethylene copolymers were studied, depending on the temperature and CTL and VS content. The flow curves of nanocomposites in a wide temperature range of 190-250 °C and a load of 2.16-21.6 kg, the dependence of melt viscosity on shear rate and temperature, and the activation energy of viscous flow were determined. The study of the universal temperature-invariant characteristic by determining the dependence of the reduced viscosity ($\log\eta_e/\eta_o$) on the reduced shear rate ($\log\gamma\cdot\eta_o$) made it possible to predict the melt viscosity of nanocomposites that is close to the conditions of their processing by extrusion and injection molding methods [3, 5, 7, 8, 13, 17, 20].
7. The dependence of the specific volume, free and occupied specific volume of nanocomposites on temperature was studied using the step dilatometry method. Phase transitions of the first and second order are determined, which make it possible to estimate the onset temperatures of crystallization and the glass transition temperature of nanocomposites depending on the filler content. It has been shown that with an increase in the CTL and VS content, there is a noticeable decrease in the free specific volume and an increase in the glass transition temperature of the nanocomposites. The crystallization mechanism of nanocomposites has been established. It is shown that when CTL and VS content exceeds 5.0 wt %, the growth mechanism of spherulites changes from the plate-type growth of crystalline formations to one-dimensional with the continuous formation of crystallization centers [13, 14, 15, 19,

26, 29].

8. In accordance with the agreement concluded with the METAK LLC, experimental studies were carried out on industrial plastic processing units, which made it possible to evaluate the influence of temperature, molding pressure, mold temperature and holding time under pressure on the ultimate tensile stress, elongation at break and volumetric shrinkage of nanocomposites. The optimal technological regime for the reaction extrusion of nanocomposites has been established. A test certificate for nanocomposites has been received, confirming the promising possibility of their practical use in the production of high-quality structural products for technical purposes (the contract and test report are attached) [6, 22, 25, 27, 30, 31].

The main provisions of the dissertation are published in the following scientific works:

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The defense will be held on « 20 » September 2024 at 10^{00} at the meeting of the Dissertation council FD 1.28 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at the Institute of Polymer Materials of the Ministry of Science and Education Republic of Azerbaijan

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Abstract was sent to the required addresses on: « 2 » July 2024

Signed for print: 24.06.2024
Paper format: 60×90 1/16
Volume: 40024
Number of hard copies: 20 copies