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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

OBTAINING AND STUDY OF PROPERTIES OF THERMOPLASTIC ELASTOMERIC COMPOSITES BASED ON ISOTACTIC POLYPROPYLENE AND METAL-CONTAINING NANO-FILLERS

Speciality: 2304.01 – "Chemistry of macromolecules"

Field of science: chemistry

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The work was performed at "Nanopolymer composites" laboratory of the Institute of Polymer Materials of Azerbaijan National Academy of Sciences

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GENERAL OVERVIEW OF THE WORK

Relevance and level of progress of the research It is known that the problem of creating composite materials with improved complex properties is preferable to solve by searching for optimal combinations of large-capacity polymers. An effective way to obtain new materials with the necessary performance properties is to mix two or more polymers. A significant advantage of this method of producing polymer compositions is the ability to create compositions having a stable set of properties that surpass traditional polymer blends in a number of parameters. The conditions for the preparation and processing of mixtures, the introduction of various additives are essential in the formation of their structure and properties.

Intensive development of the global petrochemical industry involves a constant search for new materials with high consumer properties, environmental safety and ease of processing. These materials not without reason are thermoplastic elastomers (TPE).

A distinctive feature of TPE is the combination of the properties of vulcanized rubbers during operation and thermoplastics during processing.

Due to its properties, TPE can be repeatedly processed without significantly changing the characteristics in the same ways as thermoplastic polymers: injection molding, blow molding, extrusion, etc., which allows full use of production waste and waste products. The creation of polymer mixtures that are processed without waste is also an important environmental challenge.

TPE based on polyolefins (polyethylene, polypropylene and their copolymers) and elastomers are one of the promising materials for practical use, as they have low cost and a wide temperature range of performance. Heterophase mixtures based on polypropylene (PP) and ethylene propylene diene copolymer (EPDM) obtained by dynamic vulcanization have the highest physical and mechanical properties.

One of the most promising directions in the development of modern science is nanotechnology - the production and use of materials containing nanoparticles. The development of nanotechnology has opened up the possibility of conducting research in the field of composite nanomaterials and has now made it possible to proceed to the creation and use of promising polymer materials for sensors, catalysis, nanoelectronics, etc.

The use of solid nanoparticles (NPs) of various shapes and chemical nature as fillers for polymer materials opens up new possibilities for modifying the latter, since the surface properties of a nanosized substance are characterized by high surface energy and adsorption activity. Composite materials containing NPs have high adhesive strength of the polymer matrix with NPs.

In recent years, the number of works devoted to the production and study of nanocomposite thermoplastic elastomers containing nanoparticles of layered silicates, Na^{+} -montmorillonites, has been intensively growing.

The relevance of the work is that for the first time we propose the use of metal-containing nanoparticles stabilized in a polymer matrix as nanofillers (NF) of thermoplastic elastomers based on isotactic PP and EPDM, which will allow us to obtain fundamentally new materials with improved properties that can be widely used in various areas of technology.

Object and subject of research. The object of the research is to obtain and study the properties of thermoplastic elastomeric composites based on isotactic polypropylene and metal-containing nanofillers. The subject of this research is the production of blended and dynamically vulcanized thermoplastic elastomers based on isotactic polypropylene with ethylene propylene diene elastomers of various types with high rheological and thermophysical properties by using metal-containing nanofillers, studying the structure, a complex of physical-mechanical, electrical, thermophysical and rheological properties of the obtained nanocomposites.

The purpose and objectives of the study. The aim of the research work is to study the influence of the type and content of nanofillers, as well as the vulcanizing system on the structure, physical-mechanical, electrical, thermophysical and rheological properties of composites based on isotactic polypropylene with ethylene-propylene diene elastomers of various types. To achieve this goal, the following tasks were solved:

- development of thermoplastic elastomeric composites based on isotactic polypropylene with ethylene propylene diene elastomers using nanofillers containing nanoparticles of oxides of various metals (Cu_2O, NiO, Fe_3O_4);
- study of the composition and structure of the obtained nanocomposites;
- study of the effect of the type of nanofiller and its content on the physical and mechanical properties of nanocomposites;
- study of the effect of the type of nanofiller on the electrical properties of nanocomposites;
- study of the effect of the type of nanofiller on the thermophysical properties of nanocomposites;
- study of the effect of nanofiller on the crystallization process of thermoplastic elastomeric composites by the dilatometric method;
- study of the effect of nanofiller on the rheological properties of nanocomposites;

Research methods

The structure and composition of polymer nanocomposites were investigated by IR spectroscopy, thermal (thermal gravimetric analysis, TGA and differential scanning calorimetry, DSC). The phase composition and microstructure of nanocomposite samples were studied using X-ray diffractometry (XRD) and electron microscopy.

Studies of the mechanical characteristics of samples of polymer mixtures of TPE and their vulcanizates TPV were performed on the test machine "Instron-1122" (Great Britain) at room temperature and a constant speed of movement of the upper traverse of 50 mm/min. The melt flow rate (MFI) was determined using IIRT-5 (Russia) at a temperature of 190° C and loads of 2.16, 5.00 and 10.6 kg.

X-ray phase analysis (XRD) of the obtained compositions was carried out on the "D2 Phaser" device of the Bruker company (Germany). The study of the IR spectra of the obtained compositions was carried out on the device “IR-Fourier spectrometer ALPHA” of Bruker (Germany), ZnSe crystal, wave number range 400 – 4000 cm^{-1}. The dielectric properties of the obtained materials were measured using the Concept 40 measuring system from Novocontrol (Germany). The measurement accuracy of dielectric permittivity is $1x10^{-2}$, the dielectric losses is $1x10^{-5}$. The measurements were carried out at room temperature, limited to the frequency range of 10^{-2} Hz÷10^{6} Hz. The thermophysical properties of the obtained nanocomposites were studied by the DSC / T method on the device "Thermo electron Corporation" (USA) 2006, Q-20-DSC. The studies were carried out in an atmosphere of nitrogen or air at a heating rate of 10° C/min.

The main provisions submitted for defense:

1. Obtaining of blended and dynamically vulcanized thermoplastic elastomers based on isotactic polypropylene with ethylene propylene diene elastomers of various types by using metal-containing nanofillers.
2. Influence of the type and content of nanofillers, as well as the vulcanizing system on the structure and physical and mechanical properties of the obtained nanocomposites.
3. Results of the study of dielectric and thermophysical properties of nanocomposites.
4. Results of studying the crystallization process and rheological properties of nanocomposites.
5. Possibilities of practical use of the obtained nanocomposites in various areas of the national economy.

Scientific novelty of the study. For the first time, we obtained new TPEs using metal-containing nanofiller, and studied the structure and properties of mixtures of isotactic polypropylene with unvulcanized and dynamically vulcanized ethylene propylene diene elastomers of various types. The effect of the vulcanizing system and metal-containing nanofillers on the properties of the obtained nanocomposites has been studied.

It was found that the introduction of metal-containing nanofiller into PP / EPDM changes the crystallization process of PP in its mixture with EPDM, promotes the formation of a fine-crystalline structure and thereby improves its properties.

New thermoplastic elastomers based on isotactic polypropylene and ternary ethylene propylene diene elastomer of different composition (with and without oil) have been developed using nanofiller containing nanoparticles of oxides of various metals. It is shown that a small addition of nanofiller has practically no effect on the crystallinity and dielectric constant of thermoplastic elastomers, but decreases their modulus of elasticity. The size of nanoparticles significantly affects the mechanical properties of materials.

As a result of the conducted studies, it was revealed that not only the type of metal nanoparticles, but also their stabilizing matrix affect the final properties of the obtained nanocomposites that can be explained by their compatibility or incompatibility with the structure of the PP/EPDM mixture.

For the first time, it was revealed that copper oxide nanoparticles partially interact with the components of the vulcanizing system to form a complex adduct, the structure of which is confirmed by the data of XRD and IR spectral analysis.

Theoretical and practical significance of the study

In our work, we first studied the effect of nanoparticles of metal oxides stabilized on polymer matrices on the properties of thermoplastic elastomers based on isotactic polypropylene and ethylene propylene diene elastomer. As a result of the research carried out, new nanocomposite materials have been obtained and the structure and physicomechanical properties of polymer nanocomposites have been studied. These new materials, in comparison with conventional composites, have new or improved physical and mechanical, rheological, thermal, barrier, optical, and other special properties, which makes them a commercially promising and interesting class of engineering plastics.

For the first time, we propose the use of metal-containing nanoparticles stabilized by a polymer matrix as nanofillers of thermoplastics based on isotactic PP and EPDM, which will allow us to obtain fundamentally new materials with improved properties that can be widely used in various fields of the national economy

The results obtained in this work are important for understanding the structure of mixed and dynamically vulcanized TPE based on PP/EPDM/NF, and the created new thermoplastic elastomers with an improved set of properties can be used in various fields of the national economy: in construction, in the food, medical, electrical, automotive and petrochemical industries

Approbation and implementation of research. According to the results of the dissertation work, the author has 32 scientific publications, including 15 articles (of which 2 are in mono authorship) in journals of the AAK list and 17 abstracts of reports at international and republican conferences.

The main results of the thesis were presented at international and national conferences: 1st, 2st International Scientific Conference of Young scientist and specialist (Baku, 2014, 2020); Akad.S.C.Mehdiyevin 100 illik yubileyinə həsr olunmuş respublika elmi-praktiki konfransı (Bakı, 2014); 1st International Turkic World Conference on Chemical Schience Tecnologies(Sarayevo, 2015); Всероссийская школа- конференция молодых ученых: «Органические и гибридные наноматериалы» (Иваново, Россия, 2015, 2017); Конференция, посвященная 90-летнему юбилею академика Т.Н.Шахтахтинского (Баку, 2015); Monomerlər və polimerlər kimyasının müasir problemləri III Respublika konfransının materialları (Sumqayıt, 2015); Polimer Materialları İnstitutunun yaradılmasının 50-illik yubileyinə həsr olunmuş «Makromolekullar kimyası, üzvi sintez və kompozit materiallar» mövzusunda respublika elmi konfransının materialları (Sumqayıt, 2016); Бакинская международная Мамедалиевская конференция по нефтехимии (Баку, 2016); M.Nağıyev adına Kataliz və Qeyri-Üzvi Kimya İnstitutunun 80-illik yubileyinə həsr olunmuş Respublika Elmi Konfransının materialları (Bakı, 2016); 3st International Turkic World Conference on Chemical Sciences and Technologies. (ITWCCST, Baku, 2017); Материалы Международная научно-техническая конференция «Нефтехимический синтез и катализ в сложных конденсационных системах», посвященная 100-летнему юбилею академика Б.К.Зейналова (Баку, 2017); Материалы Межд. науч.-тех конф. «Поликомтриб - 2017» (Гомель, Беларусь, 2017); 5th International Caucasian Symposium on Polymer &. Advansed Materials (Georqia, Tbilisi, 2017); Beynəlxalq elmi konfrans.”Funksional monomerlər və xüsusi xəssəli polimer materiallar: problemlər, perspektivlər və praktiki baxışlar”(Sumqayıt, 2017); Тезисы докладов Международной научно-практической конференции "Инновативные перспективы развития нефтепереработки и нефтехимии", посвященной 110-летию академика В.С. Алиева, 2018 г,; Akademik M.Nağıyevin 110 illiyinə həsr olunmuş "Nağıyev qiraətləri" elmi konfransının materialları, 2018; 6th International Caucasian Symposium on Polymer &. Advansed Materials (Georqia, Batumi, 2019)

The work was performed at the Institute of Polymer Materials of the National Academy of Sciences of Azerbaijan (IPM ANAS) in accordance with the plan of scientific research (State Registration No. 0111Az2160) with financial support from the Science Development Fund under the President of the Republic of Azerbaijan - (Grant No. EIF-Mob-1-2013-1 (7) -16/13/4) in the framework of the Agreement on scientific and technical cooperation on the topic: "Development of polymer composites based on modified polyolefins and dynamic thermoplastic elastomers using metal-containing nanofillers" between the laboratory "Chemical Modification of polymers " of IPM ANAS and laboratory "Physical and chemical processes in polymer systems " of N.N. Semenov Chemical Physics Institute of RAS.

Personal involvement of the author: The author has a leading role in the implementation of the work, including the statement of the problem, the main ideas and directions of research, conducting experiments, interpreting the results and formulating conclusions..

The structure and scope of the dissertation. The dissertation work consists of an introduction, 3 chapters, conclusions, a list of cited literature of 165 titles, 10 tables and 41 figures, includes a total of 171495 characters

In the introduction, the relevance is justified; the goals and objectives of the research, the scientific novelty and the practical significance of the dissertation work are formulated.

The first chapter provides a detailed analysis of the current state of the problem according to the literature data on thermoplastic elastomer compositions, their preparation, structure and properties, the data of Russian and other foreign works on the development and research of the properties of thermoplastic elastomers based on PP/EPDM (EPM) are considered. Contains a review of the literature on the preparation and study of the properties of nanomaterials, some prospects for their application in various fields of technology, medicine, etc. are considered.

The second chapter contains the selection of the initial components: isotactic polypropylene (PP) and ethylene propylene diene elastomers (EPDM, EPM) and metal-containing nanofillers, the ratio of the components, and the description of experimental methods.

The third chapter is devoted to the discussion of experimental results on the study of the process of obtaining thermoplastic elastomers based on isotactic polypropylene and ethylene propylene diene elastomer using metal-containing nanofillers.

The main content of the work

1. Obtaining nanocomposite thermoplastic elastomers based on PP/EPDM using nanofillers (NF), incorporating various metal-containing nanoparticles (MCN)

1.1. Determination of optimal component ratios in the obtaining and study of the properties of metal-containing nanocomposites based on PP/EPDM

The following were used in the work: isotactic PP of the TPPF79FB brand (Russia) with a melt yield strength of 10 ÷ 15 g /10 min, Vicat softening T (10H) not more than 150 ° C; Hüls EPDM with ρ = 0.86 g / cm^3 containing 8% ethylidene norbornene;

NPs of copper oxide I (Cu_2O), stabilized in the polymer matrix of industrial high-pressure polyethylene obtained by the mechanochemical method in polymer melt, were used as NF. The ratio of the components of polymer mixtures (parts by weight): PP/EPDM/ NF = 50/50/(0.3; 1.0; 3.0)

Nanocomposite polymeric materials were obtained by mixing PP with EPDM and copper-containing NF on laboratory rollers at a temperature of

160 - 165 °C for 15 minutes. For mechanical testing, the resulting mixtures were pressed in the form of plates 1 mm thick at 190°C and a pressure of 10 MPa.

Physico-mechanical parameters of the obtained compositions were determined on a RMI-250 device. The melt flow rate (MFR) was determined on an IIRT device at T = 200°C, load 5.0 kg.

X-ray phase analysis (XRD) of the obtained compositions was carried out on a "D2 Phaser" instrument from Bruker (Germany).

The physicomechanical and rheological properties of mixed TPE based on PP/EPDM containing NF with nanoparticles of copper oxide are presented in Table 1.

Table 1

Physico-mechanical and rheological parameters of nanocomposites

Composition	σ_p, МПа	ε_p, %	Vicat softening point, °C	MFR, g/10min
PP/EPDM	13.1	440	135	2.8
PP/EPDM /NF(0.3)	13.7	420	140	3.7
PP/EPDM/NF(1.0)	13.5	400	145	4.0
PP/EPDM/NF(3.0)	12.6	380	140	5.6

As can be seen from the data in table. 1, the introduction of 0.3 - 1.0 wt. % NF into the composition leads to some increase in the strength index from 13.1 to 13.7 MPa. The increase in the concentration of NF more than 1.0 mass. % leads to a decrease in the strength of the composite (12.6 MPa), which is probably due to the aggregation of nanoparticles, leading to the formation of microdefects in the bulk of the polymer matrix. An increase in the NF concentration leads to a decrease in the strain at break of the composite, which is apparently due to the blocking of the mobility of polymer segments by nanoparticles at the nanoscale.

A study of the Vicat softening temperature of the obtained compositions showed that the introduction of a nanofiller into the PP/EPDM composition leads to an increase in the heat resistance index from 135 to 145 ° C, a further increase in the number of HF leads to a decrease in the softening temperature index, which is probably due to the microdefectiveness of the obtained composite. At the same time, an increase in the content of HF (1.0 - 3.0 parts by weight) contributes to an increase in the MFR to 4.0 (1.0 parts by weight) and 5.6 g / 10 min (3.0 parts by weight), which indicates an improvement in the fluidity of the composition and the possibility of processing it by injection molding, extrusion, which extends the scope of its application.

1.2. Study of the effect of copper oxide nanoparticles on the crystallization process of thermoplastic elastomer based on PP/EPDM using dilatometric method

The effect of copper oxide (NP) on the crystallization process of thermoplastic elastomer based on isotactic PP and EPDM taken in the ratio (parts by weight): 50/50 was studied. As NF, copper oxide NPs stabilized on a matrix of industrial high-pressure polyethylene, obtained by the mechanochemical method in polymer melt without the use of solvents, were used.

Data on some physical states of polymers can be obtained from studies of dilatometric characteristics of polymer materials. Dilatometric studies consist in studying the temperature dependence of the density or specific volume of various polymers and composite materials

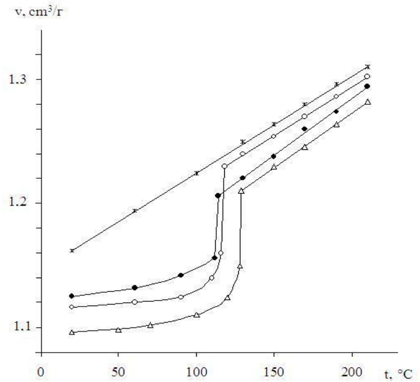


Fig. 1. Temperature dependence of the specific volume of the compositions: Δ- initial PP, *□ - initial EPDM, • - PP/EPDM = 50/50, o- PP/EPDM/NF (1.0)

Figure 1 shows the results of a study of the temperature dependence of the specific volume of the initial PP, EPDM and their mixtures in a ratio of 50/50. Analyzing the curves in this figure, it can be seen that during the stepwise cooling of the PP sample, as a representative of the class of semi-crystalline polymers at a crystallization temperature of 128 ° C, there is a characteristic sharp decrease in the specific volume from 1.21 to 1.14 cm^3/g, i.e. by 0.07cm^3/g. Such a sharp jump towards a decrease in the specific volume at the crystallization temperature is characterized as a first-order transition, i.e. transition from one state of aggregation to another. In this case, this transition is carried out from a viscous flowing state to a crystalline one. The value of this parameter is important for the process of processing polymer materials, since it approximately reflects the cooling (crystallization) process that takes place in the mold of an injection machine or in the molding head of an extruder. In addition, it allows evaluating the shrinkage of the material during the obtaining of structural products in the mold.

As expected, the initial EPDM, as an amorphous material, does not have a first-order phase transition and is characterized by a linear temperature dependence of the specific volume. However, introduction of synthetic rubber in the composition of PP leads to a significant change in the dependence of the dilatometric curve of the PP/EPDM composition, leading to a 13 ° C decrease in the temperature of the first-order phase transition. A decrease in the phase transition temperature in polymer mixtures is quite possible and is explained by the fact that the amorphous component, in this case, EPDM, slows down or interferes with the complete and free course of PP crystallization process.

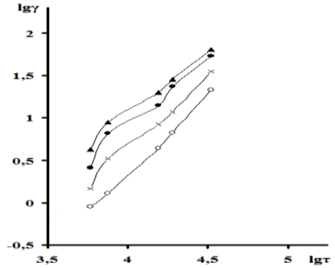
As a result of the studies, it was shown that the introduction of copper NPs contributes to an increase in the phase transition temperature by 3°C. At the same time, it was found that at the crystallization temperature the specific volume decreases from 1.231 to 1.159 cm^3/g, i.e. by a value of 0.072 cm^3/g. In fact, the introduction of NPs into the composition of the polymer mixture helps to restore the crystallization process and its full course. The data obtained can be interpreted as follows: NPs contribute to the formation of heterogeneous nucleation centers in the composition melt, which, during the stepwise cooling of the sample, increase the crystallization centers, which generally lead to an improvement in the crystallization of PP and the formation of a relatively fine spherulite structure.

1.3. Study of the effect of a nanofiller containing copper oxide nanoparticles on the rheological properties of mixed thermoplastic elastomers based on PP/EPDM

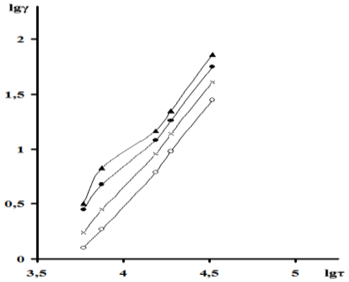
With the enhancing of the possibilities of producing large-sized automotive parts by high-speed injection molding, requirements for the rheological characteristics of polymer compositions are in the forefront.

Fig. 1 (a, b) shows the flow curves of the PP/EPDM polymer mixture and the PP/EPDM/NF composite based on it.

From the rheograms shown in Fig. 1 (a, b) it can be seen that, at low temperatures, the flow curves are linear, and at relatively high temperatures the linear dependence of the shear rate on the shear stress is broken. From a comparative analysis of the flow curves, it can be seen that when the PP/EPDM polymer mixture is filled with copper oxide nanoparticles at low temperatures, a regime close to the Newtonian regularity of the melt flow is observed, which is broken with increasing temperature. An analysis of the rheograms showed that when the content of NP of copper oxide (1.0 part by mass) in the PP/EPDM mixture is observed, the shear rate of the composite melt increases.



a)



b)

Fig. 2. The dependence of shear rate on shear stress: a) PP/EPDM; b)PP/EPDM/NF at various temperatures: ○ -190 ° C; × -210 ° C; ● -230 °; ▲ -250 ° C

Thus, a study of the rheological properties of the obtained nanocomposites showed that the insertion of nanoscale filler in a polymer composite improves the melt flow and other rheological properties, which facilitates their processing by high-speed injection molding and creates the opportunity for the producing of large-sized automotive parts.

1.4. Study of the effect of nanofillers containing copper oxide nanoparticles on the structure and properties of mixed TPE based on PP/EPDM (EPM).

The effect of nanofillers containing NPs of copper oxide on the properties of mixed TPEs based on PP/ EPDM (EPM) under optimal conditions found is studied. The nanocomposite polymeric materials are obtained as described above in paragraph 1.1.

Physicomechanical and rheological properties of mixed TPE based on PP/EPDM (EPM) containing nanofillers with nanoparticles of copper oxide are presented in table 2.

Table 2

Physico-mechanical and rheological parameters of nanocomposites

Composition	σ_p, MПa	ε_p, %	Vicat softening point, °C	MFR, g/10min.
PP/EPDM	13.1	440	135	2.8
PP/EPDM /NF	13.5	400	145	4.0
PP/EPM	7.7	60	137	does not flow
PP/EPM/NF	8.6	120	145	does not flow

On the DSC thermogram during heating of TPE in the O_2 atmosphere (Fig. 4a), a weak exothermic peak is observed at T = 160.57 ° C, corresponding to the melting of TPE. At 232.18 ° C, the endothermic process of sublimation of degradation products begins, reaching a maximum at 378.25 ° C (ΔH = 89.34 J / g). Further, the competition of the endothermic effects of dry distillation or sublimation of degradation products with exothermic oxidation processes leads to the formation of an apparent or "false" peak at 384.95 ° C. The maximum of endothermic processes occurs at 397.15 ° C (ΔH = 205.5 J / g), then there is a sharp transition from heat release to its absorption - a sharp endothermic peak, then two peaks: an exothermic peak at 403.02 ° C and an endothermic peak at 403.99 ° C, related to the competition of endo - exothermic processes, and then the gradual attenuation of the process of thermal oxidative degradation until the complete exit of the degradation products from the experimental cell.

As follows from Table 2, in mixed TPE based on PP/EPDM, the use of NF containing NPs of copper oxide leads to a slight increase in the tensile strength from 13.1 to 13.5 MPa and the MFR by 1.43 times, while the relative elongation decreases from 440 up to 400%, and Vicat softening point increases from 135 to 145°C.

As shown by studies in mixed TPE based on PP/EPDM, the use of NF containing NPs of copper oxide leads to an increase in tensile strength by 1.12 times, relative elongation by 2 times, and Vicat softening point by 8°C, however, the composition does not flow. The introduction of metal-containing NF in PP/EPDM in an amount of 1.0 parts by weight, apparently, does not affect the viscosity of the composition.

SEM analysis of the obtained nanocomposites Fig. 2 (a-d) was carried out. Figure 2 (a) shows a micrograph of the PP/EPM sample. It is seen that the structure of the composite is loose, shapeless. The introduction of nanofiller into the PP/EPM composition promotes the formation of a spherulite structure, but does not increase the fluidity of the nanocomposite in Fig. 2 (b).

Figure 2 (c) shows a micrograph of the PP/EPDM sample. It can be seen that the composite structure is compact spherulitic. The introduction of nanofiller into the PP/EPDM composition promotes the formation of a finer spherulitic structure, which leads to an increase in the fluidity of the nanocomposite Fig. 2 (d).

It was shown that small amounts of nanofiller (1.0 parts by weight) introduced into the polymer obviously play the role of structure-forming agents - artificial crystallization nuclei, which contributes to the formation of a fine- spherulitic structure in the polymer, characterized by improved melt flow rates, as well as physicomechanical and thermal properties of the obtained nanocomposites.

As a result of the studies, it was shown that composite TPEs based on PP/EPM / NF can be processed only by pressing, and on the basis of PP/EPDM/NF both by pressing and injection molding and extrusion.

The prospects of using a nanofiller containing NPs of copper oxide stabilized by a high-pressure polyethylene matrix obtained by the mechanochemical method as an additive to TPE based on PP/EPDM is shown, that contribute to the creation of a fine-crystalline structure of the composition, and therefore its properties are improved and thereby extend areas of application of the obtained nanocomposite.

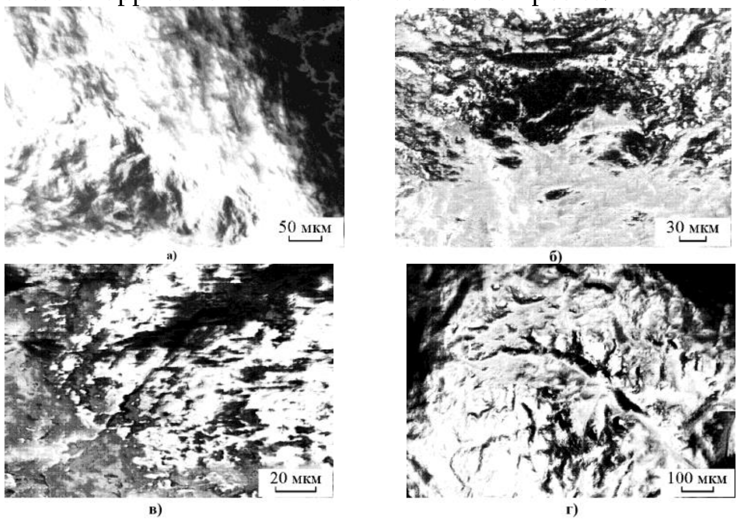


Fig. 2. Micrographs of PP/EPDM (a), PP/EPM/NF (b), PP/EPDM (c), PP/EPDM/NF (g)

The effect of NF containing NPs of copper oxide on the structure of mixed TPEs based on EPDM was studied by the X-ray phase method. In fig. 3 (a) a PP/EPDM diffractogram is presented, on which reflections corresponding to the PP are visible: d_{hkl} 6.19929; 5.17135; 4.73608; 4.48713; 4.17687; 4.03424; 3.47038; 3.11297; 2.11651 Å. For an amorphous EPDM, a halo image is given. The diffraction pattern of the PP/EPDM/NF sample (Fig. 3 (b)) also shows reflections characteristic of copper-containing NPs: d_{hkl} 3.02053; 2.46466; 2.13683; 1.74331; 1.51025; 1.28812 Å, which corresponds to the d_{hkl} series of copper (I) oxide - Cu_2O in the ASTM file cabinet.

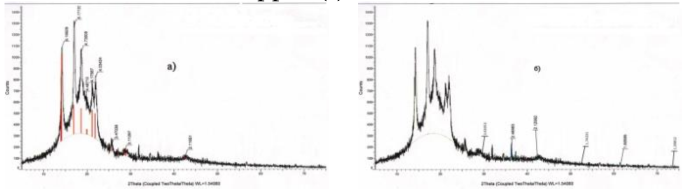


Fig. 3. Diffraction patterns of samples (a) PP/EPDM and (b) PP/EPDM/NF

1.5. Study of the thermophysical and thermal properties of the obtained nanocomposites by the DSC/T method

The thermal and thermophysical properties of the obtained nanocomposites were studied using a “Thermoelectron Corporation” (USA) 2006, Q-20-DSC instrument. The studies were carried out in an atmosphere of nitrogen or air at a heating rate of 10 ° C / min.

Many difficulties in thermal analysis arise when various processes associated with the release or absorption of energy occur simultaneously and overlap one another.

As is known, thermo-oxidative degradation of an open system is a combination of three processes accompanied by thermal effects:

$$Q_{\Sigma} = -Q_D + Q_O - Q_S$$

where Q_{Σ} is the total thermal effect, $-Q_D$ is the endothermic effect of the destruction (destruction) of the chains; Q_O - exothermic effect of oxidation of chains and thermal decomposition products; - Q_S - endothermic effect of sublimation or evaporation of degradation products.

In accordance with the above equation, competition of the endothermic effect of sublimation or sublimation of degradation products with an exothermic oxidation process can lead to the formation of apparent or “false” peaks.

It was shown that the introduction of nanoparticles into the polymer leads to the retention of thermal degradation products, i.e. a nanoparticle plays a role of a “trap” for free radicals formed during destruction.

Figure 4 (a-d) shows the DSC/T curves of TPE, TPE /NPsCuPE, TPV, TPV/NPsCuPE samples.

On the DSC thermogram during heating of TPE in the O_2 atmosphere (Fig. 4a), a weak exothermic peak is observed at T = 160.57 ° C, corresponding to the melting of TPE. At 232.18 ° C, the endothermic process of sublimation of degradation products begins, reaching a maximum at 378.25 ° C (ΔH = 89.34 J / g). Further, the competition of the endothermic effects of dry distillation or sublimation of degradation products with exothermic oxidation processes leads to the formation of an apparent or “false” peak at 384.95 ° C. The maximum of endothermic processes occurs at 397.15 ° C (ΔH = 205.5 J / g), then there is a sharp transition from heat release to its absorption - a sharp endothermic peak, then two peaks: an exothermic peak at 403.02 ° C and an endothermic peak at 403.99 ° C, related to the competition of endo - exothermic processes, and then the gradual attenuation of the process of thermal oxidative degradation until the complete exit of the degradation products from the experimental cell.

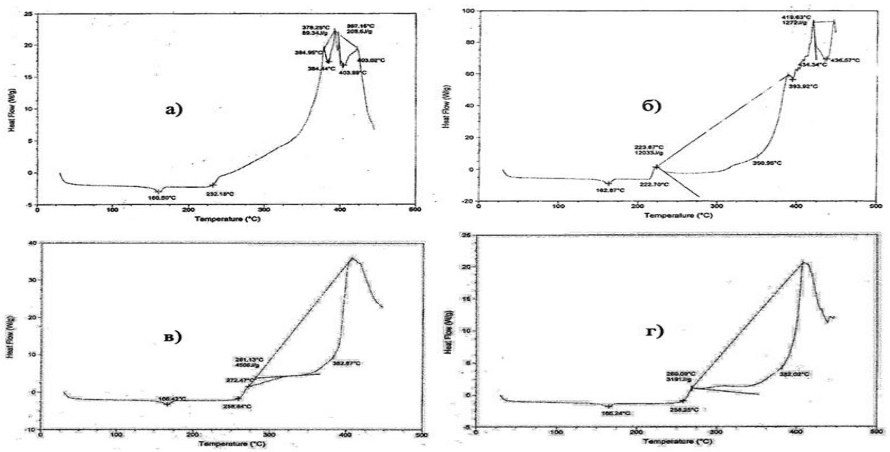


Fig. 4. DSC thermograms during heating of thermoplastic elastomers in an oxygen atmosphere: TPE (a), TPE/NPsCuPE (b), TPV (c), TPV/NPsCuPE (d).

When a TPE sample with copper nanoparticles is heated in an O_2 atmosphere (Fig. 4b), a weak exothermic peak is observed at 162.87°C, corresponding to T_{melt} TPE; at 222.70°C, the endothermic process of sublimation of degradation products begins, reaching a maximum at 223, 67°C (ΔH = 12.033 J / g). Up to 350.95°C - a smooth curve, as a result of competition of the endothermic effects of the sublimation of degradation products with exothermic oxidation processes. Then there is a sharp endothermic process with a maximum at 419.63°C (ΔH = 1272 J / g) and then a sharp transition from heat release to its absorption at 434.34 °C, and then another endothermic peak at 436.57°C, and then a sharp transition from heat release to its absorption associated with the attenuation of the process of thermal oxidative degradation.

With the insertion of copper nanoparticles into the composition of TPE, the melting point of the composite slightly increases from 160.57 to 162.87 °C. The temperature of thermo-oxidative degradation rises from 403.99 °C to 436.57 °C. The “false” peak at 384.95°C resulting from the superposition of endo - exothermic processes of thermo-oxidative degradation of chains and sublimation of degradation products disappears, due to the fact that the presence of nanoparticles in the system leads to retention of thermal degradation products, i.e. the nanoparticles play the role of a “trap” of free radicals formed during destruction.

On the DSC thermogram during heating of the TPV in the O_2 atmosphere (Fig. 4c), a weak exothermic peak is observed at T = 166.42°C, corresponding to the melting of the TPV. Further, oxidative processes of the chain proceed to 258.84°C, then a “false” peak appears at 272.47 ° C, and at 281.13°C (ΔH = 4508 J / g) the endothermic process of sublimation of degradation products begins, which transforms into a powerful endothermic process at 382.87 °C, reaching a maximum at 406.25 ° C, then the transition from heat release to its absorption, with a gradual attenuation of the process of thermal oxidative degradation.

When a TPV sample is heated with copper nanoparticles in an O_2 atmosphere (Fig.4d), a weak exothermic peak is observed at 165.24°C, corresponding to a TPV T_{melt}, oxidative processes of the chain proceed to 258.25 °C. Then begins the endothermic process of sublimation of degradation products at 269.09 °C (ΔH = 3191 J / g). From 382.02°C - a powerful endothermic process, reaching a maximum at 407.15°C, then a sharp transition from heat release to its absorption, with a gradual attenuation of the process of thermal oxidative degradation.

With the insertion of copper nanoparticles into the composition of the TPV, the melting point of the composite remains almost unchanged: 166.42 °C and 165.24 °C. The temperature of thermo-oxidative degradation also remains almost unchanged: 406.25 °C and 407.15°C. The “false” peak at 272.47°C, resulting from the superposition of endo - exothermic processes of thermo-oxidative degradation of chains and sublimation of degradation products disappears, which is explained by the fact that the presence of nanoparticles in the system leads to retention of thermal degradation products, i.e. nanoparticles play the role of a “trap” of free radicals formed during destruction.

1.6. Study of nanocomposites containing NPs of copper oxide stabilized by different polymer matrices: non-polar - PE (NF-1) and polar - ABS (NF-2), on the properties of TPV based on PP /EPDM

The effect of NFs containing NPs of copper oxide on the structure of vulcanized TPEs based on PP/EPDM was studied by the X-ray phase method. The Fig. 5 shows the diffraction pattern of the PP/EPDM/NF-1 sample, on which the reflections corresponding to the PP are visible: d_{hkl} 6.19929; 5.17135; 4.73608; 4.48713; 4.17687; 4.03424; 3.47038; 3.11297; 2.11651Å, a halo image was given for amorphous EPDM, reflections characteristic of copper-containing NPs were observed: d_{hkl} 3.02053; 2.46466; 2.13683; 1.74331; 1.51025; 1.28812 Å, which corresponds to the d_{hkl} series of copper (I) oxide - Cu_2O in the ASTM file cabinet.

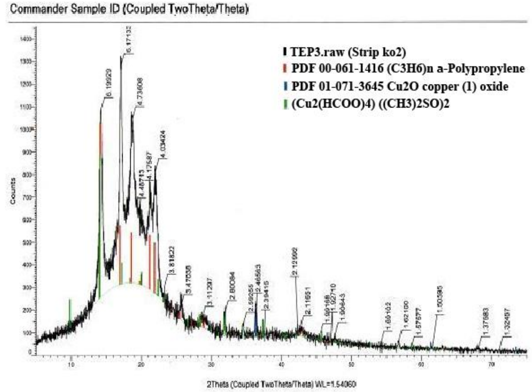


Fig. 5. The diffraction pattern of the PP/EPDM/NF-1 nanocomposite

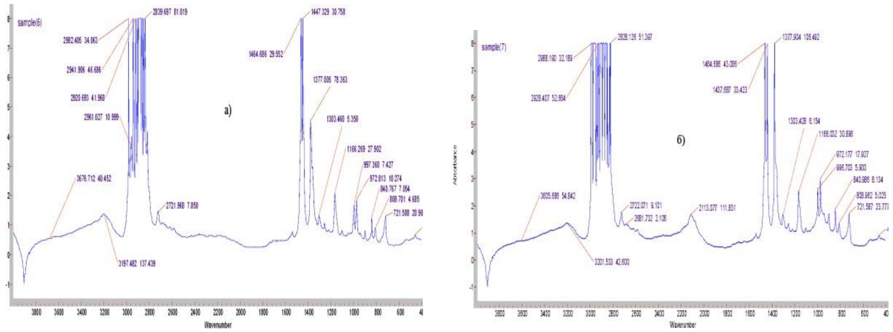


Fig. 6. IR spectra of PP/EPDM (a) and PP/EPDM /NF-1 (b)

Studies have shown that Cu_2O NPs partially interact with components of the vulcanization system to form the adduct $[Cu_2(HCO)_4\ ((CH_3)_2SO)\ _2]$, while Cu^{+} is oxidized to Cu^{2+}. This is evidenced by the data of the XRD analysis (Fig. 5), as well as the appearance of absorption bands on the IR spectra of the sample: 1377 cm^{-1}, which refers to the $((CH_3)_2SO)\ _2$ fragment; 2830cm^{-1} - characteristic of the CH_3-O- group; 1437 cm^{-1}, corresponding to the COO^- anion, which is not on the IR spectra of the initial thermoplastic elastomer (Fig. 6). Similar XRD data were obtained for the PP/EPDM/ NF-2 sample.

The properties of mixed TPEs and dynamically vulcanized TPVs based on PP/EPDM containing NFs with copper oxide NPs are presented in Table 3.

Table 3.

Properties of the studied TPE and TPV.

Composition	E, MPa	σ_p, MPa	ε_p, %	MFR, g/10min			C, %
				2.16 kg	5.00 kg	10.60 kg	
TPE							
PP/EPDM	395	11.0	170	0.9	3.7	14.8	53.7
PP/EPDM/NF-1	260	9.3	150	1.1	4.3	18.0	49.9
PP/EPDM/NF-2	269	8.6	110	1.0	4.0	16.2	50.7
TPV							
PP/EPDM	215	13.2	370	-	-	-	49.4
PP/EPDM/NF-1	165	14.0	390	-	-	0.15	52.1
PP/EPDM/NF-2	115	12.0	350	-	-	-	54.8

It is seen that the dynamic vulcanization of the PP/EPDMmixture slightly decreases its crystallinity (C) from 53.7 to 49.4%. It should be noted that the introduction of NF into the composition of TPE leads to a decrease in crystallinity from 53.7 to 49.9 (NF-1) and 50.7%. (HF-2), and in the case of TPV - to increase the crystallinity index from 49.4 to 52.1 (HF-1) and 54.8%

(HF-2).

The insertion of NF-1 and NF-2 into the composition of mixed TPEs contributes to an increase in the MFR index by 1.1–1.2 times at a load of 10.6 kg. In the case of TPV, fluidity is observed only for the PP / EPDM / NF-1 composite.

The use of NF in the mixed TPE based on PP /EPDM leads to an improvement in the MFR with a slight decrease in the elastic modulus and the preservation of the tensile strength and elongation at break. The dynamic vulcanization of the PP / EPDM mixture leads to a significant decline in its elastic modulus and an increase in ultimate mechanical properties.

As can be seen from the data in table 3, the TPE and TPV with the use of NF-1 are higher than when using NF-2.

With the insertion of NF-1 into the PP / EPDM composition, a partial compatibility of the components is likely to occur, since PE, on which copper NPs are stabilized, and the polymer matrix are non-polar. It is known that PP and PE, cooled from the melt, do not form joint crystals. PP has a higher crystallization temperature and will crystallize first, and PE will be distributed in the intercrystalline spaces of the PP, which can lead to both an increase and a decrease in the crystallinity of the obtained polymer, as well as a change in the strength characteristics of the system. It is shown that the insertion of small amounts of PE into PP does not cause a decrease in strength. PE has a lower melting point and plays the role of a plasticizer. Simultaneously with an increase in the degree of crystallinity, a decrease in the size of crystalline formations occurs.

Apparently, NF-1 plays the role of a builder and contributes to the creation of a fine-crystalline structure of the composition, in connection with which its fluidity and thermo-oxidative stability are increased.

It is known that ABS is a polar plastic; therefore, it does not combine well with the polymer matrix of the PP/EPDM/NF-2 mixture. Apparently, the ABS macromolecules are located as separate domains in the PP / EPDM matrix, which leads to a deterioration in the physicomechanical properties of the composition upon the addition of NF-2.

1.7. Study of the effect of metal-containing nanofillers on the properties of mixed and dynamically vulcanized thermoplastic elastomers based on isotactic PP and EPDM

The properties of mixed TPE and dynamically vulcanized TPV based on PP/EPDM containing NFs with NPs of oxides of various metals are presented in Tables 4 and 5. It can be seen that the dynamic vulcanization of the PP/EPDM-4044 mixture slightly reduces its crystallinity *K* from 54 to 49%. It should be noted that the introduction of NF of various nature has practically no effect on the crystallinity of the studied TPE and TPV.

Table 4.

Properties of TPE (crystallinity K, dielectric constant $\acute{\varepsilon}^1$, elastic modulus E, tensile strength σ_p, elongation at break ε_p, MFR).

Sample	*K*, %	$\acute{\varepsilon}^1$	*E*, MPa	σ_p, MPa	ε_p, %	MFR, g/10min		
						2.16 kg	5.00 kg	10.60 kg
PP/EPDM-4044	54	2.0	395	11.0	170	0.9	3.7	14.8
PP/EPDM-4044/NPsCuPE	50	2.2	260	9.3	150	1.1	4.3	18.0
PP/EPDM-4044/NPsNiPE	50	2.2	263	8.7	110	1.1	4.4	16.8
PP/EPDM-4044/NPsCuABS	51	1.7	270	8.6	110	1.0	4.0	16.2
PP/EPDM-4044/NPsFeSKS	50	2.4	200	7.6	40	1.2	4.6	16.8
PP/EPDM-4535	-*	-*	35	3.4	155	1.0	7.6	56.0
PP/EPDM-4535/NPsCuPE	-*	-*	38	2.6	140	0.9	6.0	45.0

Note: Dash — no flow observed; - * - measurements were not performed.

Table 5.

TPV properties (crystallinity K, dielectric constant $\acute{\varepsilon}^1$, elastic modulus E, tensile strength σ_p, elongation at break ε_p, MFR).

Sample	*K*, %	$\acute{\varepsilon}^1$	E, MPa	σ_p, MPa	ε_p, %	MFR, g/10min		
						2.16 kg	5.00 kg	10.60 kg
PP/EPDM-4044	49	2.0	215	13.2	370	-	-	-
PP/EPDM-4044/NPsCuPE	52	2.1	165	14.0	390	-	-	0.15
PP/EPDM-4044/NPsNiPE	50	2.4	115	12.8	340	-	-	-
PP/EPDM-4044/NPsCuABS	55	2.4	115	12.0	350	-	-	-
PP/EPDM-4044/NPsFeSKS	52	2.1	140	7.5	100	-	-	-
PP/EPDM-4535	-*	-*	43	6.9	460	-	0.3	5.5
PP/EPDM-4535/NPsCuPE	-*	-*	45	7.1	420	-	0.2	5.4

Note: Dash — no flow observed; - * - measurements were not perform

It is known that the dielectric constant исходного $\acute{\varepsilon}^1 = 2.2 \div 2.4$ for the initial PP. As our studies have shown (Tables 4 and 5), for TPE and dynamically vulcanized TPV based on EPDM-4044 that do not contain LV, $\acute{\varepsilon}^1 = 2.0$ and this value does not change with an increase in the research frequency from 10^{-2} to 10^7 Hz. When NN containing various NPs is introduced into mixtures, έ1 practically does not change and is constant in the entire studied frequency range. The obtained έ1 values for the investigated mixed and dynamically vulcanized TPEs correspond to the data for ordinary dielectrics.

It is known that for the initial PP the dielectric permittivity is $\acute{\varepsilon}^1$= 2.2 ÷2.4. As shown by our research (table. 4 and 5) for TPE, and dynamically vulcanized TPV based on EPDM-4044, not containing NF, $\acute{\varepsilon}^1$= 2.0 and with increasing testing frequency from 10^{-2} to 10^7 Hz, this value is not changed. When introducing into the composition of mixtures of NF containing different NPs, the value of $\acute{\varepsilon}^1$ practically does not change and is constant throughout the studied frequency range. The $\acute{\varepsilon}^1$ values obtained for the studied mixed and dynamically vulcanized TPE conform to that of conventional dielectrics.

The use of NF in composite TPEs based on EPDM-4044 leads to a certain decrease in the elastic modulus, tensile strength, and elongation at break (Table 4). The dynamic vulcanization of the PP / EPDM-4044 mixture leads to a significant decrease in its elastic modulus and an increase in the ultimate mechanical properties (Table 5). The insertion of NF of different composition into the TPV leads to a further decrease in the elastic modulus of the mixtures while maintaining their ultimate strength and elongation at break. The decrease in the elastic modulus of the materials is probably due to aggregation of NPs, leading to the formation of microdefects in the bulk of the polymer matrix.

It should be noted that the use of NF containing NPsFeSKS significantly reduces the mechanical characteristics of TPE and TPV. Probably, this is explained by the fact that the size of NPs of this type is quite large, and they introduce additional defects in the structure of the mixtures.

The melt flow rate of TPE with NF is practically the same as TPE PP/EPDM-4044 (Table 4). However, the MFR values of mixtures obtained at a maximum load of 10.6 kg slightly increase compared to TPE indicators that do not contain NF. Dynamically vulcanized TPVs do not exhibit fluidity at all the studied loads (Table 5). An exception is a mixture with the addition of NPsCuPE, which is very important for the processing.

The mechanical parameters of TPE based on oil-filled EPDM-4535 are lower, and the MFR is higher (with the exception of the values obtained at a load of 2.16 kg) than for mixtures containing EPDM-4044 (Table 4). Dynamic vulcanization increases the mechanical properties of oil-filled TPEs, but impairs their fluidity. The addition of NF to TPE and TPV based on EPDM-4535 does not change their mechanical characteristics and MFR.

Apparently, NF is localized in the oil-filled elastomer phase and does not affect the properties of the mixture.

1.8. Study of the influence of metal-containing NP additives stabilized on a polymer matrix on the specific thermophysical and thermal properties of mixed TPEs and dynamically vulcanized TPVs based on isotactic PP and EPDM

The thermophysical and thermal properties of the obtained nanocomposites are studied using combined thermal analysis, including DSC and TGA methods. All DSC - TGA/T thermograms were of the same nature for all test conditions and all samples of thermoplastic elastomers (Fig. 7).

The analysis of DSC curves on DSC - DTA thermograms showed that for all studied samples of thermoplastic elastomers (TPE and TPV), the melting temperature (T_{mlt}) is the same and equal to 140 °C.

In the case of TPE (Fig. 7a), with increasing temperature, the DSC curve smoothly rises to 140°C, then there follows a sharp endothermic peak (heat absorption) corresponding to T_{mlt} TPE, then a gradual rise to 300 ° C - exothermic processes associated with oxidation of the polymer chain . After 320 ° C, mass loss begins (5%), then the curve slowly drops to 350°C (10%), then a sharp endothermic peak - the process of sublimation or evaporation of degradation products, reaching a maximum at 388.5°C (weight loss 40%). Along with that, the mass loss rate on the DTA thermogram is also maximum and at 465°C the mass loss corresponds to 95.5%. Approximately in the middle of the process of thermo-oxidative degradation at 394°C, there is a sharp transition from heat absorption to its generation to 420°C, then to 600˚C-competition of endo-exoprocesses and then comes a sharp endothermic peak with a gradual attenuation of the process until the destruction products completely exit experimental cell. In this case, occurs a decrease in mass by 0.5 mg.

In the case of TPE with NF (Fig. 7b), as well as TPV and TPV with NF, the DSC curve has a similar form, however, the temperature indexes change.

The study of the thermophysical and thermal properties of the obtained nanocomposites showed that the samples of the studied TPEs are thermostable in an atmosphere of air up to 300 ° C, and TPE with NF - up to 350°C; TPV is stable up to 350°C, and TPV with NF - up to 400°C. The temperature of the onset of thermal oxidative degradation increases for TPE and TPV by 50°C, which indicates a high heat resistance of the obtained nanocomposites.

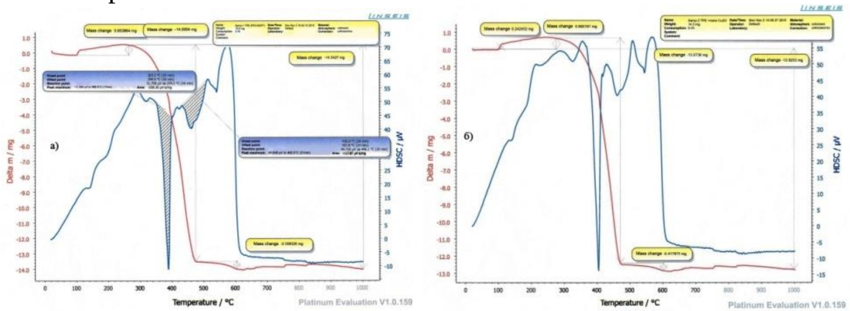


Fig. 7. Thermogram of the initial TPE (a) and TPE with NF (b)

A study of the thermophysical and thermal properties of the obtained nanocomposites samples was also carried out along the TGA curve.

The thermal stability of the studied samples was evaluated by the activation energy (E_a) of the decomposition of thermal oxidative degradation, by the temperature of 10% (T_{10}), 20% (T_{20}) and 50% (T_{50}) decay of the studied TPE and TPV samples, as well as by time their half-life time $\tau_{1/2}$. The data obtainedare shown in table 6.

Table 6.

Thermostability of TPE and TPV nanocomposites

Composition	T_{10}, %	T_{20}, %	T_{50}, %	$\tau_{1/2}$, min	E_a, kJ/mol
TPE					
TPE	320	350	420	64	194.11
TPE/CuPE	360	390	480	72	235.47
TPE/NiPE	355	385	475	70	223.86
TPE/CuABS	365	395	485	73	242.35
TPV					
TPV	360	400	440	68	215.38
TPV/CuPE	390	450	490	78	257.13
TPV/NiPE	385	445	485	76	244.76
TPV/CuABS	390	455	495	79	263.17

As can be seen from the data in Table 6, the insertion of a filler containing metal oxide nanoparticles into the composition of thermoplastic elastomers increases the T_{10}, T_{20}, T_{50}, and $\tau_{1/2}$, E_a of the obtained nanocomposites increases by 29-48 kJ / mol.

Conclusions

1. New thermoplastic elastomers, mixed and vulcanized on the basis of PP/EPDM, have been developed using metal-containing nanofillers containing nanoparticles (NPs) of metal oxides Cu_2O, NiO, Fe_3O_4, stabilized by various polymer matrices: NPs of copper oxide I (Cu_2O), stabilized by a HPP matrix,NPs of Cu_2O and NiO, stabilized by a matrix of polyethylene obtained using a titanium-phenolate catalytic system, NPs of (Cu_2O) stabilized by ABS matrix- acrylonitrile butadiene thermoplast and NPs of iron oxide (Fe_3O_4), stabilized by a matrix of SRS-divinyl styrene elastomer. The sizes of NPs of Cu_2O, and Nps of NiO – 11÷15 nm, NPs of Fe_3O_4 -100 nm, the degree of crystallinity of NPs 25-45% [1-7, 9-11, 13-15, 30].
2. New nanocomposites based on PP/EPDM with the use of a copper-containing nanofiller obtained by a mechanochemical method, stabilized by a polymer matrix of a high-pressure polyethylene, with improved strength index and melt fluidity, have been obtained. The studies of rheological properties have shown that the injection of a nanofiller into the composition leads to an increase in the flow rate of the polymer melt, which facilitates the process of processing it by injection molding and creates the possibility of obtaining high-dimensional products, thereby opening up prospects for the production of products of a wide range of applications: in automotive, aviation, shipbuilding, construction, in the oil and petrochemical fields [1, 2, 17, 18, 21, 25-28, 32].
3. The crystallization process of the obtained nanocomposite by the dilatometric method was studied. It is shown that copper oxide nanoparticles introduced into the PP/EPDM composition contribute to the improvement of the crystallization of the system, while forming a relatively fine spherulitic structure [3, 20, 22, and 28].
4. SEM analysis of the obtained nanocomposites showed that small amounts of nanofiller (1.0 parts by weight) introduced into the polymer obviously play the role of structure-forming agents - artificial crystallization nuclei, which contributes to the formation of a fine-spherulite structure in the polymer, characterized by improved

melt flow rates , rheological, physical, mechanical and thermal properties of the obtained nanocomposites[23-26].

5. Thermophysical and thermal analysis of the obtained nanocomposites using the DSC/T method was carried out. The data obtained made it possible to interpret the "false" peaks characterizing the processes of thermal and thermooxidative degradation, as well as the sublimation of degradation products[1-3].
6. The study of the thermophysical and thermal properties of the obtained nanocomposites by the DSC-DTA/T method showed that the samples of the studied TPEs are thermostable in an atmosphere of air up to 300 ° C, and TPE with NF - up to 350 °; TPV is stable up to 350 ° C, and TPV with NF - up to 400 ° C. The temperature of the onset of thermal oxidative degradation increases for TPE and TPV by 50 ° C, and the activation energy (E_a) of the decomposition of thermooxidative destruction increases by 29–48 kJ / mol, which indicates a high heat resistance of the obtained nanocomposites. The studies have shown that the injection of nanofiller into the composition of the TPE and TPV can significantly increase the thermal stability of the obtained compositions, which increases the temperature limits of use, as well as the possibility of finding new areas of their application [8, 16, 19, and 29].
7. New thermoplastic elastomers based on isotactic polypropylene and triple ethylene propylene diene elastomer of various compositions (with and without oil) using nanofillers containing nanoparticles of oxides of various metals (Cu_2O, NiO, Fe_3O_4) have been developed. It is shown that a small addition of nanofiller (1.0 part by weight) practically does not affect the crystallinity and dielectric constant of thermoplastic elastomers, but reduces their modulus of elasticity while maintaining strength characteristics. The nature of the nanoparticles significantly affects the physicomechanical and thermophysical parameters, as well as the fluidity of the composites. The introduction of nanofillers in a mixture based on oil-filled elastomer does not affect their properties [4-7].
8. Using radiothermoluminescence (RTL), the molecular mobility features in the temperature range of 77–300 K were studied for the

polypropylene (PP) /ethylene propylene diene elastomer SKEPT-4044 with NiO, Cu_2O, and Fe_3O_4 nanoparticles (NPs) based on ABS-acrylonitrile butadiene or SCS-divinyl styrene matrices. It has been shown that the introduction of nanofillers in PP significantly affects the nature and of γ- and β-relaxation processes, while the region of manifestation of the β process noticeably shifts to the region of low temperatures. Composites with Cu_2O NPs have a higher β-transition temperature T_β than composites with other NPs. It has been found that PP/SKEPT-4044 composites with Cu_2O NPs with a dispersion of 11–15 nm and acrylonitrile butadiene thermoplastics have optimal frost resistance compared to other compositions [30, 31].

9. As a result of the conducted studies, it was revealed that not only the type of metal nanoparticles, but also their stabilizing matrix affects the final properties of the obtained nanocomposites based on PP/EPDM. Identical copper(I) oxide nanoparticles stabilized by different polymer matrices: non-polar and polar, such as high-pressure polyethylene (HPP), linear polyethylene obtained using a titanium-phenolate catalytic system (LPE) and an acrylonitrile butadiene copolymer (ABS) matrix have different effects on the properties of the obtained nanocomposites. Nanocomposites with the participation of Cu_2O NPs, stabilized by a HPP matrix, have the best physico-mechanical and rheological properties, somewhat worse - by a LPE matrix, even worse-by an ABS matrix. This can be explained by the fact that the structure of the HPP matrix is similar to the structure of the PP/EPDM mixture and is well combined with it, partial compatibility of the components of the mixture occurs with the LPE matrix. ABS is a polar plastic, so it does not fit well with the polymer matrix of the mixture. Apparently, the ABS macromolecules are arranged as separate domains in the PP/EPDM matrix, which leads to a deterioration in the properties of the composition. [12, 14].
10. The prospects of using a nanofiller containing NPs of copper oxide stabilized by a high-pressure polyethylene matrix obtained by a mechano-chemical method as an additive to TPE based on

PP/EPDM are shown, which contributes to the creation of a fine-crystalline structure of the composition, in connection with which its properties are improved and thereby the areas of application of the resulting nanocomposite are expanded [1, 2, 28, 32].

The main results of the dissertation are presented in the following publications:

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5. Курбанова Н.И., Алимирзоева Н.А. Cu-содержащие нано-композитные полипропиленовые термоэластопласты. Конференция, посвященная 90-летию юбилея академика Т.Н.Шахтахтинского, – Баку, – 2015, – с. 245.
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