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THE EFFECT OF METAL-CONTAINING NANOPARTICLES ON THE THERMO - OXIDATIVE PROPERTIES OF THERMOPLASTIC ELASTOMERS BASED ON ISOTACTIC POLYPROPYLENE AND ETHYLENE PROPYLENE DIENE RUBBER

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Abstract. The effect of nanofillers containing nanoparticles of metal oxides (Cu_2O, NiO) stabilized by various polymer matrices on the thermo-oxidizing properties of non-vulcanized (TPE) and dynamically vulcanized (TPV) thermoplastic elastomers based on isotactic polypropylene and ethylene propylene diene elastomer has been studied. A DSC – TGA/T combined analysis of the studied compositions was carried out. It has been shown that the samples of the studied TPEs are thermally stable in air up to 300°C, and TPE with nanofillers are thermally stable up to 350°C; TPV is stable up to 350°C, and TPV with nanofiller is stable 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 (Ea) of the decomposition of thermal oxidative degradation increases by 29–48 kJ/mol, which indicates a high thermal stability of the obtained nanocomposites.

Keywords: *thermoplastic elastomers, isotactic polypropylene, ethylene propylene diene elastomer, metal-containing nanofillers, DSC – TGA/T analysis.*

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1. Introduction

In recent years, there has been considerable interest in composite materials based on polymer matrices and nanosized metal particles, which is due to a wide range of their applications - from catalysis to nanotechnology in information technology.

The unique properties and improved characteristics of nanomaterials are due to their size, surface structure and interfacial interaction. The role played by particle size is comparable to the role played by the chemical composition of particles, adding another parameter for designing and behavior control (Koo, 2019; Pomogailo, 2000; Suzdalev & Suzdalev 2001).

The use of solid nanoparticles (NP) of different shapes and chemical nature as fillers of polymer materials opens up new possibilities for modifying the latter, since the surface properties of a nanoscale substance are characterized by high surface energy and

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adsorption activity. Composite materials containing NP have a high adhesive strength of the polymer matrix with NP (Mikhailin, 2009).

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 move on to the creation and use of promising polymeric materials for sensors, catalysis, nanoelectronics, which have specific physical-mechanical and operational properties: increased thermal and electrical conductivity, high magnetic susceptibility, ability to shield ionizing radiation (Mikhailin, 2009; Pomogailo *et al.* 2000; Tretyakov, 2003).

The use of nanoparticles of metals of variable valence (copper, cobalt, nickel, etc.) in polymers makes it possible to obtain fundamentally new materials that are widely used in radio and optoelectronics as magnetic, electrically conductive, and optical media (Cubin *et al.* 2005; Pomogailo, et al. 2000).

Mixtures based on polyolefin and rubbers occupy an important place among polymer compositions. At a rubber content of up to 50–90%, fundamentally new materials are formed - thermoplastic elastomers (TPE), which combine the mechanical properties of rubber at normal temperatures with the processing ability characteristic of linear thermoplastic polymers above their melting point (Medintseva *et al.,* 2008; Prut *et al.,* 2008). Creation of TPE is a priority area of work in the field of polymer materials science. (Alimirzayeva, 2020; Guliyeva *et al*., 2021; Huseynova *et al.*, 2018; Kurbanova *et al.*, 2021).

Previously, we studied the effect of small additives of nanofillers (NF) containing nanoparticles (NPs) of copper, nickel and iron oxides stabilized by a polymer matrix on the property features of thermoplastic blended elastomers (TPE) and dynamically vulcanized elastomers (TPV) based on isotactic polypropylene (i- PP) and ethylene propylene diene elastomer (EPDM). It is shown that a small addition of NF in the amount of 1 wt. h. practically does not affect the crystallinity and dielectric constant of TPE and TPV, but reduces their modulus of elasticity while maintaining strength and rheological properties (Kurbanova *et al.,* 2016; 2019).

The present work is devoted to the study of the effect of metal-containing nanoparticles (NPs) on the thermal-oxidative properties of blended (TPE) and dynamically vulcanized (TPV) thermoplastic elastomers based on isotactic polypropylene (i-PP) and ethylene propylene diene rubber (EPDM).

2. Experimental part

The following were used in the work: isotactic polypropylene (i-PP) of the brand 21030-16 (Russia) with $M_п$=7.7x10^4 and Mw=3.4xl0^5; density p=0.907 g/cm^3; degree of crystallinity 55%; melting point T_{melt}=165 °C; MFR =2.3 g/10 min at T =190°C and a load of 2.16 kg; ethylene propylene diene rubber (EPDM) brand Dutral TER 4044 (with the amount of propylene units 35%, Mooney viscosity 44 (at 100°C); in the composition of EPDM the diene component was 5-ethylidene-2-norbornene in the amount of 4-5%.

Metal oxide nanoparticles (NPs) stabilized by different polymer matrices were used as nanofillers (NFs): copper oxide I (Cu_2O) NPs and nickel oxide (NiO) NPs were stabilized with a polyethylene matrix obtained using a titanium-phenolate catalytic system (NPCu_2OPE) – NF-1 and (NPNiOPE) – NF-2, NPs of copper oxide I (Cu_2O) - stabilized by the matrix of ABS-acrylonitrile butadiene thermoplastic (NPCu_2OABS) – NF-3, obtained in a polymer solution (“claspol” method) (Pat. İ20110058. Az. 2011. Alieva et al) of 1 wt. pt. per polymer mixture. The content of nanoparticles in the polymer matrix: copper oxide NPs - 3.9%, nickel oxide NPs - 18%, NP sizes 11-15 nm, the degree of NP crystallinity 25-45%. The ratio of the initial components (wt. parts): i-PP / EPDM / NF = 50/50/1 (Kurbanova *et al.*, 2017).

The thermo-oxidative properties of the obtained nanocomposites were tested on the STA PT 1600 LINSEIS device (Germany) under the following conditions:
Temperature, ˚C - 1000; time, min. - 59; heating rate ˚C - 20; atmosphere - air; furnace initial temperature, ˚C - 24; sample initial temperature ˚C – 21.

3. Results and discussion

The properties of mixed and dynamically vulcanized nanocomposites based on i-PP/EPDM containing fillers with nanoparticles of oxides of various metals have been studied. The resulting thermograms are shown in the Fig.1.

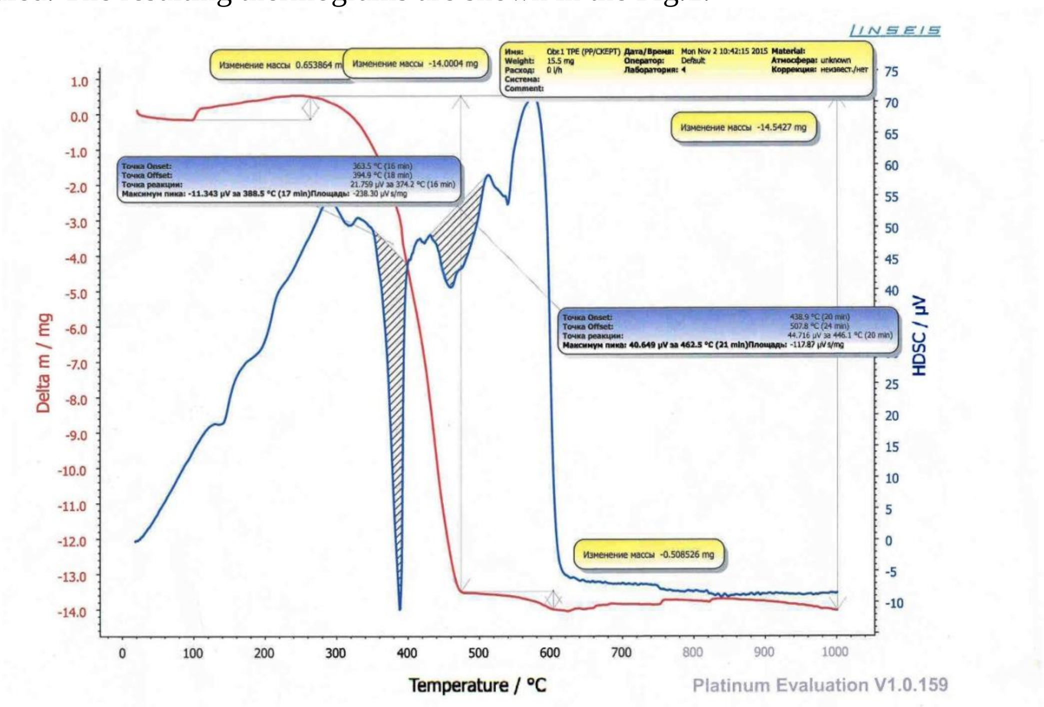

Fig. 1. DSC – TGA/T thermograms of composites: TPE (PP/EPDK)

It should be noted that all DSC-TGA/T thermograms had the same character for all test conditions and for all samples of thermoplastic elastomers.

The analysis of DSC curves on DSC – TGA/T thermograms showed that for all the studied samples of thermoplastics (TPE and TPV), the melting point (T_{melt}) is the same and equal to 140°C.

In the case of TPE (Fig. 1), with increasing temperature, the DSC curve smoothly rises to 140°C, then follows a sharp endothermic peak (heat absorption), corresponding to T_{melt} of TPE, then a smooth rise to 300°C - the polymer chain oxidation related exothermic processes. Then weight loss begins: at 320°C (10%), then the curve slowly drops to 350°C (20%), then a sharp endothermic peak is the process of sublimation or evaporation of degradation products, reaching a maximum at 388.5°C (weight loss 40%). At the same time, the weight loss rate on the DTA thermogram is also maximum, and at 465°C, the weight 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 release up to 420°C, then up to 600°C - competition of endo-exo processes and then a sharp endothermic peak with a gradual attenuation of the process until the complete release of degradation products from the experimental cell.

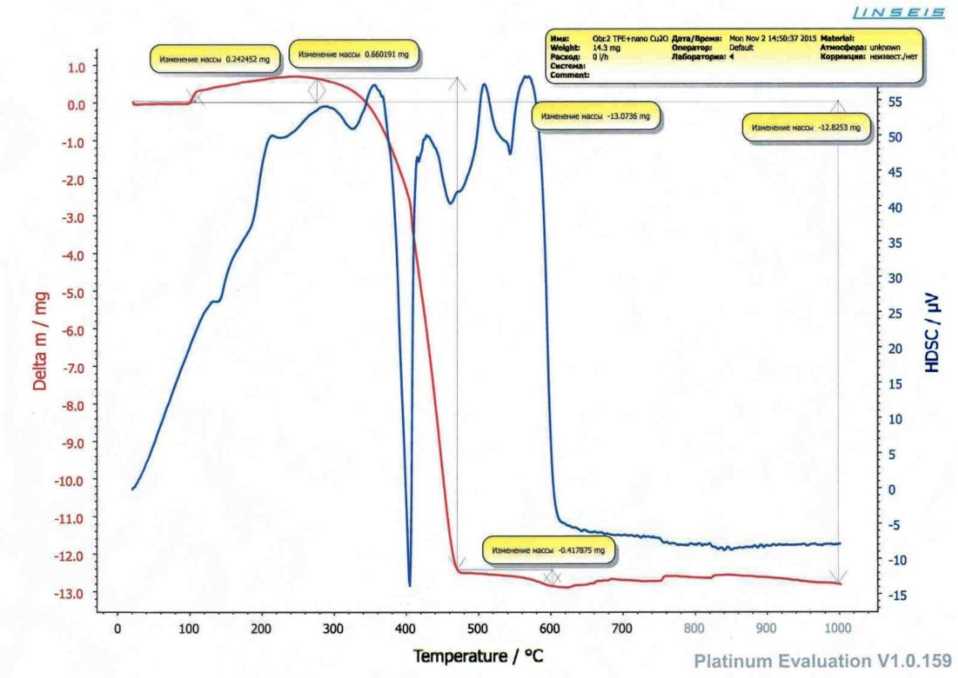

Fig. 2. DSC – TGA/T thermograms of nanocomposites TPE/NF-1

In the case of TPE with NF-1 (Fig. 2), also with increasing temperature, the DSC curve smoothly rises to 140°C, then follows a sharp endothermic peak (heat absorption), corresponding to T_{melt} of TPE, then rises to 350°C - the polymer chain oxidation related exothermic processes. After 360°C, weight loss (4-5%) begins, then a sharp endothermic peak - the process of sublimation of degradation products, reaching a maximum at 410°C (weight loss 20-23%). In this case, the weight loss rate on the TGA thermogram is also maximum, and at 485°C the weight loss corresponds to 90%. Approximately in the middle of the process of thermo-oxidative degradation at 400°C, there is a sharp transition from heat absorption to its release up to 420°C, then up to 600°C, competition of endo-exo processes and then a sharp endothermic peak with a gradual attenuation of the process until the destruction products are completely released from experimental cell.

In the case of TPV (Fig. 3), the DSC curve has a form similar to the curve for TPE, however, the temperature indicators change.

In the case of TPV with NF (Fig. 4.), the DSC curve looks similar to the curve for TPE with NF-1, however, the temperature indicators change.

An analysis of the DSC–TGA/T thermograms of the obtained mixed nanocomposites showed that the samples of the studied TPEs are thermally stable in air up to 300°C, while TPEs with NF containing copper oxide NPs are stable up to 350°C. The original TPE at 320°C loses 10% of the mass, at 360°C - 20% of the mass, and TPE with NF - 10%. At 388.5°C, the initial TPE loses 40% of its mass, and TPE with NF loses 18÷20%, i.e. 2 times less; at 465°C, the weight loss corresponds to 95.5%.

Analysis of the DSC – TGA/T thermograms of the obtained vulcanized nanocomposites (TPVs) showed that they are thermally stable in air up to 350°C, while

TPVs with NFs containing copper oxide NPs are stable up to 400°C. The initial TPV after 360°C loses 10% of the mass, at 410°C - 25% of the mass, and TPV with NF - 18÷20%, at 485°C the weight loss corresponds to 90%.

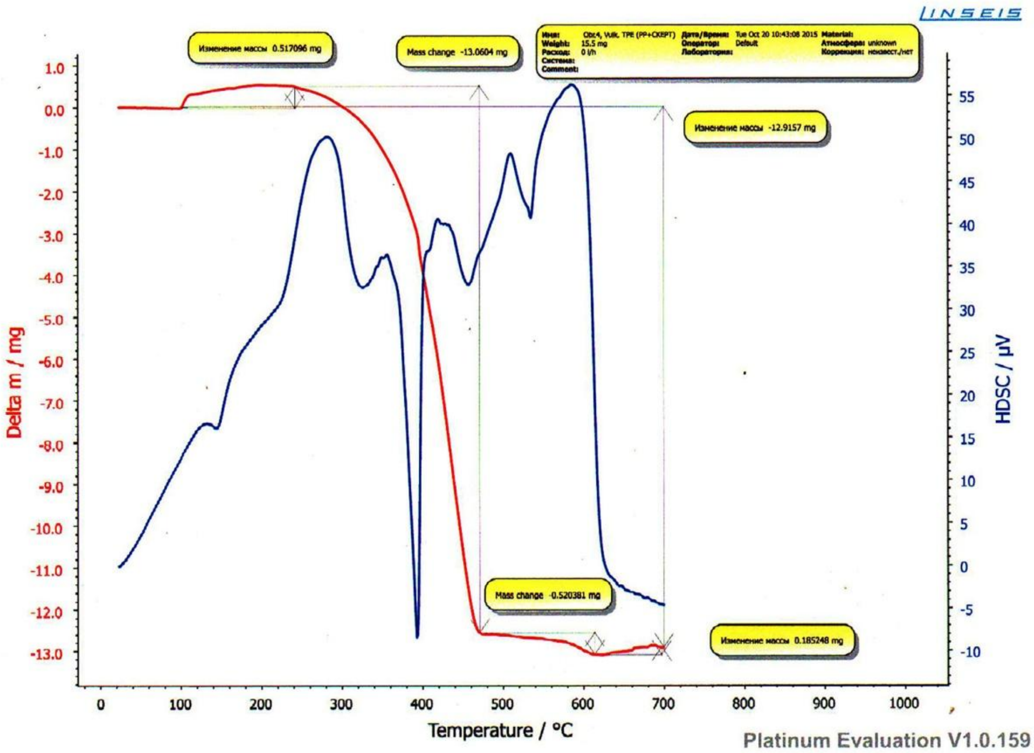

Fig. 3. DSC – TGA/T thermograms of composites TPV (vulcanized)

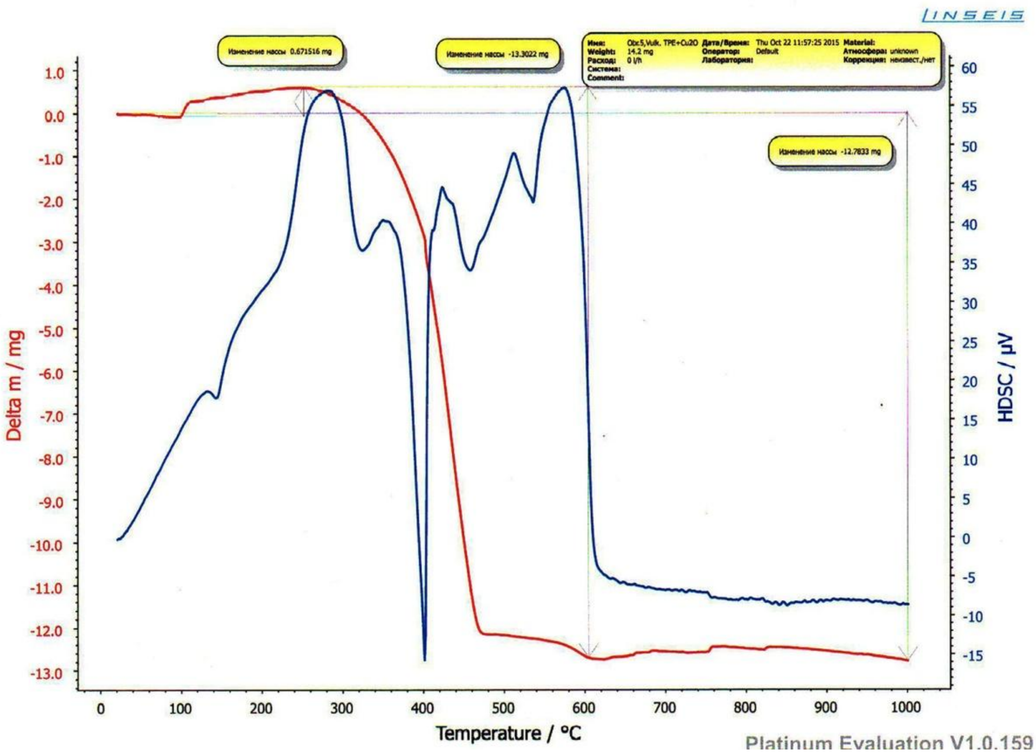

Fig. 4. DSC – TGA/T thermograms of nanocomposites TPV / NF-1(vulcanized)

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

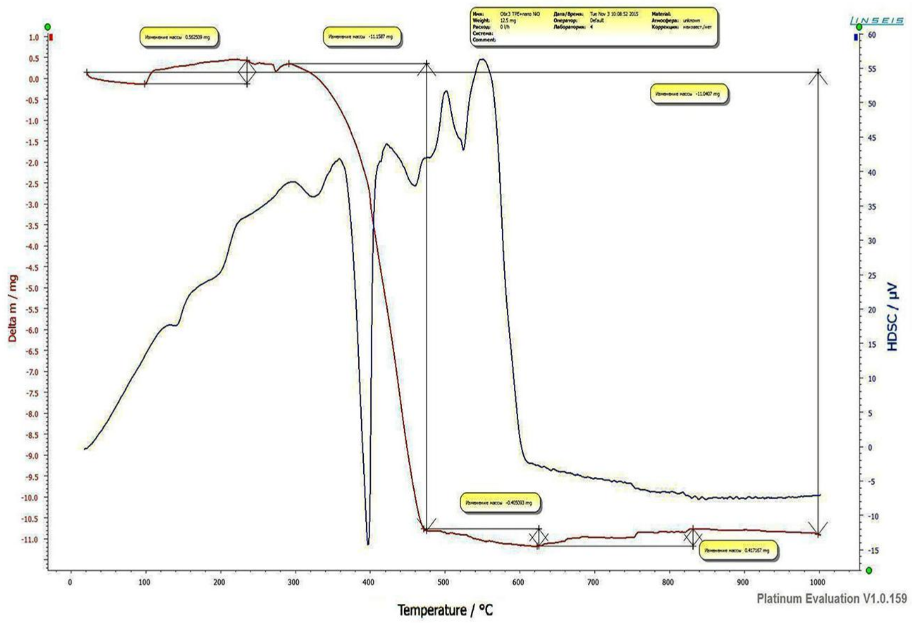

Fig. 5. DSC – TGA/T thermograms of nanocomposites TPE/NF-2

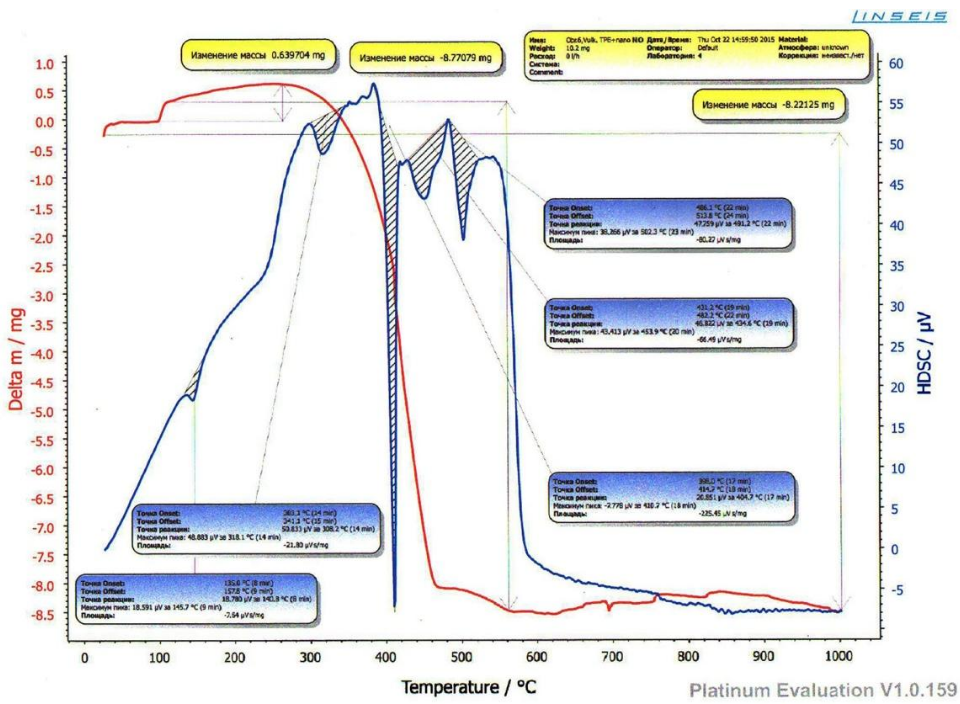

Fig. 6. DSC – TGA/T thermograms of nanocomposites TPV/NF-2

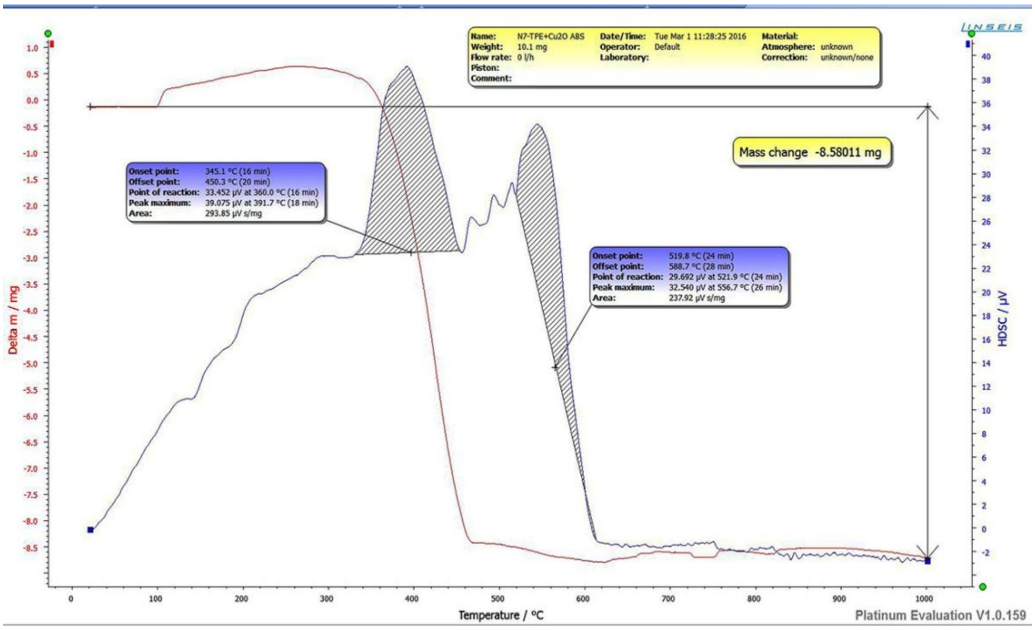

Fig. 7. DSC – TGA/T thermograms of nanocomposites TPE/NF-3

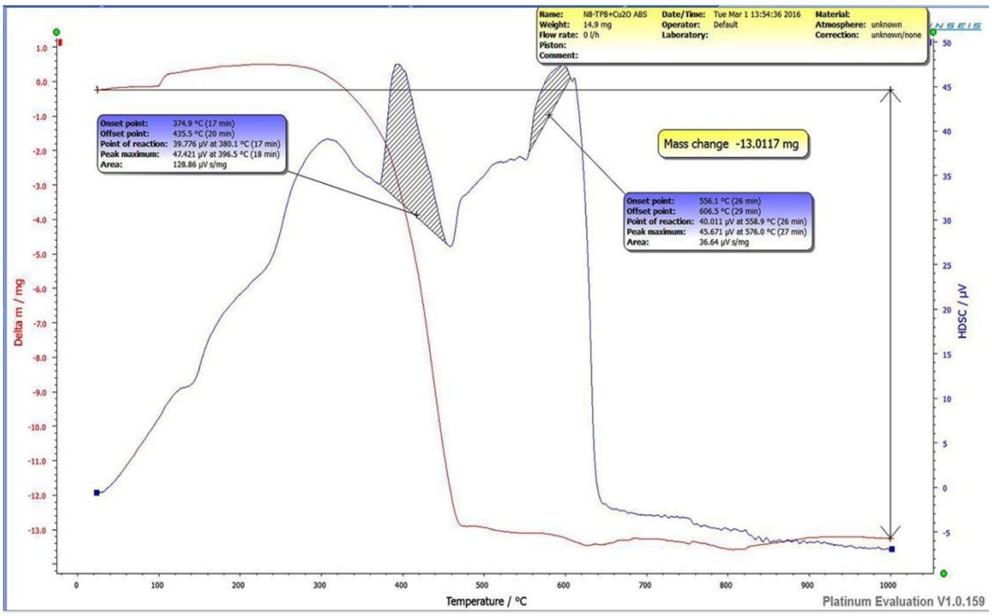

Fig. 8. DSC – TGA/T thermograms of nanocomposites TPV/NF-3

The shape of the curves of the DSC-TGA/T thermograms of nanocomposites with the participation of copper- and nickel-containing nanofillers is similar (Fig.5-8).

The thermophysical and thermal properties of the obtained samples of nanocomposites were also studied using the TGA curve.

The thermal stability of the studied samples was estimated from the activation energy (E_a) of the decomposition of thermal oxidative degradation, calculated by the double logarithm method according to the TGA curve, well as from the temperatures of 10% (T_{10}), 20% (T_{20}) and 50% - th (T_{50}) decomposition of the studied samples of TPE and TPV, and by their half-life period - $\tau_{1/2}$. The obtained data of thermogravimetric studies are given in the table.

Table. Thermal-oxidative properties of TPE and TPV nanocomposites\

Composition	**T_{10},%**	**T_{20},%**	**T_{50},%**	**$\tau_{1/2}$, min**	**Ea, kJ/mol**
TPE					
TPE	320	350	420	64	194.11
TPE / NF-1	360	390	480	72	235.47
TPE / NF-2	355	385	475	70	223.86
TPE / NF-3	365	395	485	73	242.35
TPV					
TPV	360	400	440	68	215.38
TPV/ NF-1	390	450	490	78	257.13
TPV/ NF-2	385	445	485	76	244.76
TPV/ NF-3	390	455	495	79	263.17

As can be seen from the data in the table, the T_{50}, $\tau_{1/2}$, and E_a values for the original TPV are higher than the corresponding data for the TPE. This can be explained by the fact that as a result of vulcanization of TPE, a vulcanization grid is formed, intermolecular cross-links, the structure of the TPV sample is strengthened and thus the thermal-oxidative properties are improved.

The introduction of nanofillers containing metal oxide nanoparticles into TPE and TPV compositions contributes to an increase in the decomposition temperature T_{10}, T_{20}, T_{50}, half-life $\tau_{1/2}$, and activation energy (E_a) of thermal oxidative destruction for all the studied nanocomposites; apparently, metal oxide nanoparticles contribute to the creation of strong intermolecular interaction between the components of the composition.

The data on the thermal-oxidative properties of composites obtained using NF with NiOPE NPs are inferior to the corresponding indicators of composites obtained with the participation of NF with Cu_2OPE NPs and Cu_2OABS NPs, which can be explained by the fact that the surface of Cu2O NPs is more active in intermolecular interaction between the components of the composition than the surface of NiO NPs.

At the same time, the temperature characteristics and E_a for Cu_2OABS NPs exceed the corresponding data for Cu_2OPE NPs. The highest thermal stability of the TPV/Cu_2OABS NP composition can apparently be explained by the fact that, along with intermolecular crosslinks, cyclic groups are formed, such as ABS domains, which contribute to the thermal stability of the composite.

As can be seen from the data in the table, the introduction of a filler containing nanoparticles of metal oxides into the composition of mixed thermoplastic elastomers contributes to an increase in the decomposition temperature of the samples: T_{10} by 35-45°C, T_{20} by 35-45°C, T_{50} by 55-65°C; half-life period $\tau_{1/2}$, increases from 64 to 73 min for TPE, and for vulcanized thermoplastic elastomers, an increase in the temperature of sample decomposition is observed: T_{10} by 25-30°C, T_{20} by 45-55°C, T_{50} by 45-55°C; the half-life period $\tau_{1/2}$ increases from 68 to 79 min for TPV, the activation energy (E_a) of the decomposition of the thermooxidative degradation of the obtained nanocomposites increases by 29–48 kJ/mol.

Thermogravimetric studies have shown that the introduction of fillers containing metal oxide nanoparticles into the composition of mixed and vulcanized thermoplastics improves the thermal oxidative stability of the obtained nanocomposites.

4. Conclusion

The study of the thermophysical and thermal properties of the obtained nanocomposites by the DSC-TGA/T method showed that the samples of the studied TPE are thermostable in an air atmosphere 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 beginning of thermo-oxidative destruction increases for TPE and TPV by 50°C, and the activation energy (E_a) of the decomposition of thermo-oxidative destruction increases by 29÷48 kJ/mol, which indicates the high temperature resistance of the obtained nanocomposites.

The conducted studies have shown that the introduction of nanofiller into the composition of 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.

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References

Alieva, R.V., Azizov, A.Q., Gahramanov, N.T. et.al. (2011). Pat. İ20110058. Az. 2011.

Alimirzayeva, N.A. (2020). Metal-containing nanocomposites on the basis of isotactic polypropylene and ethylene-propylene-diene rubber. *Azerbaijan Chemical Journal*, 1, 41-45.

Gubin, S.P., Yurkov, G.Y., & Kosobudsky, I.D. (2005). Nanomaterials based on metal-containing nanoparticles in polyethylene and other carbon-chain polymers. *International Journal of Materials and Product Technology, 23*(1-2), 2-25.

Guliyeva, T.M., Kurbanova, N.I., Mamedov B.A., & Nurullayeva D.R. (2021). Metal-Containing Nanocomposites on the Basis of Isotactic Polypropylene and Butadiene-Nitrile Rubber. *International Journal of Engineering Research & Science, 7(*3), 11-15. https://dx.doi.org/10.5281/zenodo.4647611

Huseynova, Z.N., Kakhramanov, N.T., Mamedov, B.A., Osipchik, V.S., & Mamedli U.M. (2018). Thermoplastic elastomers based on thermoplastic polyolefins and butyl rubber. *Perspektive Materials*, 7, 33–42.

Koo, J.H. (2019). *Polymer Nanocomposites: Processing, Characterization, and Applications*. McGraw-Hill Education, 289.

Kurbanova, N.I., Guliyeva, T.M., & Ishenko, N.Ya. (2021). Preparation and Properties of Metal-Containing Nanocomposites Based on Isotactic Polypropylene and Butadiene–Acrylonitrile Rubber. *Russian Journal of Applied Chemistry, 94*(1), 17−21.

Kurbanova, N.I., Alimirzoeva, N.A., Kuliev, A.M., Kuznetsova, O.P., Medintseva, T.I., Prut, E.V., & Shevchenko V.N. (2017). The effect of metal-containing nanofillers on the properties of blended and dynamically vulcanized thermoplastics based on isotactic polypropylene and triple ethylene-propylendiene elastomer. *International Polymer Science and Technology*, *44*(7), T49-T53.

Kurbanova, N.I., Alimirzoeva, N.A., Kuliev, A.M., Kuznetsova, O.P., Medintseva, T.I., Prut, E.V., & Shevchenko V.N. (2016). Influence of metal-containing nanofillers on the properties of mixed and dynamically vulcanized thermoplastics based on isotactic polypropylene and triple ethylene-propylendiene elastomer. *Plastic Masses*, *5*(6), 48-51.

Kurbanova, N.I., Alimirzoyeva, N.A., Arzumanova, N.B., & Kakhramanov, N.T. (2019). Influence of Metal-Containing nanofiller ob rheological properties of mixed Thermoplastic elastomers on the basis of isotactic polypropylene and ternary ethylene-propylene-diene elastomer. *Processes of Petrochemistry and Oil Refining*, *20*(4), 417-423.

Medintseva, T.I., Erina, N.A., & Prut, E.V. (2008). Specifics of the structure and mechanical properties of blends of isotactic polypropylene with ethylene-propylene-diene elastomer. *Polymer Science Series A*, *50*(6), 647-655.

Mikhailin, Y.A. (2009). Polymer nanocomposite materials. *Polymer materials*, 7, 10-13.

Pomogailo, A.D. (2000). Hybrid polymer - inorganic nanocomposites. *Russ. Chem. Rev*., *69*(1), 60-89

Pomogailo, A.D., Rosenberg, A.S., & Uflyand, I.E. (2000). Metal nanoparticles in polymers. *Chemistry*, 672.

Prut, E.V., Erina, N.A., Karger-Kocsis, J., Medintseva, T.I. (2008). Effects of blend composition and dynamic vulcanization on the morphology and dynamic viscoelastic properties of PP/EPDM Blends. *Journal of Appl. Polym. Sci.*, 109, 1212–1220.

Suzdalev, I.P., Suzdalev, P.I. (2001). Nanoclusters and nanocluster systems. *Russ. Chem. Rev*., *70*(3), 203-240.

Tretyakov, A.O. (2003). Polymer nanocomposites - materials of the XXI century. *Equipment and Tools for Professionals*, *2*(37), 18-20.