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INVESTIGATION OF THE THERMOPHYSICAL PROPERTIES OF METAL OXIDE NANOCOMPOSITES IN THE PROCESS OF THERMAL AGING

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Abstract. The article presents research data on isotactic polypropylene (PP) and PP nanocomposites with a metal oxide nanoadditive ZrO2 before and after long-term thermal aging. After heat treatment, the supramolecular structure changes. It was found that an increase in the percentage of nanoadditives promotes the formation of nucleation and this leads to the appearance of cracks between the matrix chains. It turned out that, with the process of long-term 60-hour heat treatment, the thermophysical parameters of the initial PP and nanocomposite change, which leads to thermal fluctuation destruction.

Keywords: *Nanocomposite, thermal aging, polymer degradation, enthalpy, derivatographic analysis.*

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1. Introduction

The role of polymer composite materials in modern industry, science and technology is well known. PCMs are used in the various branches of the mechanical engineering, building materials industry, chemical industry, medicine, etc. The literature data show that introduction of fillers into the polymer causes significant changes in the supramolecular structure and properties of the interfacial layer of the composite material, and this leads to a change in the physico-mechanical, electrophysical as well as thermophysical characteristics of the composite (Oladele *et al.*, 2020; Wang *et al*., 2014; Srivastava & Kalam, 2019; Rubino *et al.*, 2020; Ramazanov *et al.*, 2021). In this regard, the purchase and study of functional materials is very relevant (Mammadov *et al.*, 2020; Dashdemirov *et al.*, 2021; Asadullayeva *et al.*, 2019; Kamal & Bhuiyan, 2018; Asadullayeva *et al.*, 2022; Mukhtarova *et al.*, 2022; Tagiyev *et al.*, 2009). In our study, the choice of PP as a matrix is due to the fact that among polyolefins, the most sensitive to degradation processes is PP, which has specific macromolecular and supramolecular structures. Through the combination of their properties, metal-containing polymer composite materials are the subject of intensive research in connection with the prospects for their research in various fields of engineering and technology. Under various operating conditions of insulating materials, the aging processes in them develop slowly and the insulation fails after a long period of time. Therefore, the direct determination of

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the service life of insulation under operating conditions is laborious, since the study of insulation in natural conditions requires an extremely long time. In this connection, artificial methods are usually used to speed up insulation tests. The proposed scientific work presents the results of studies of derivatographic analysis of the features of changes in the thermophysical properties of isotactic polypropylene and PP+ZrO_2 nanocomposites based on it subjected and not subjected to thermal aging.

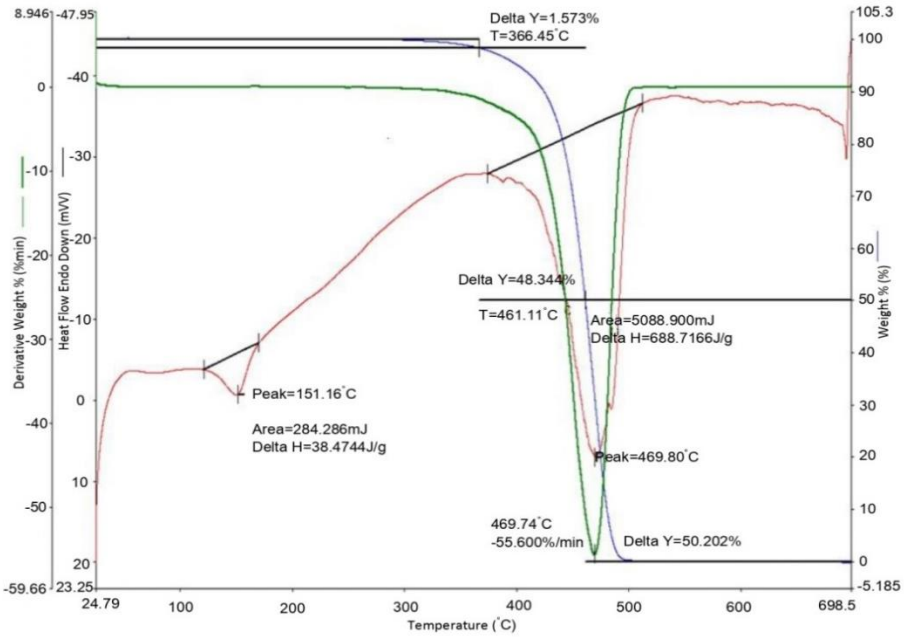
2. Experimental part

In our experiment, nanocomposites based on PP+ZrO_2 have been obtained by introducing ZrO_2 nanoparticles into the polymer solution (Ramazanov & Ibrahimova, 2020). The size of nanoparticles in the nanocomposite was 20-30 nm. The compositions have been prepared by hot pressing at the melting temperature of the polymer matrix under a pressure of 15 MPa for 3 min. Films with a thickness of 70-100 μm have been obtained. The method of differential thermal analysis makes it possible to detect changes in the temperature characteristics of the polymer and composite during degradation. This method always provides enough information for unambiguous conclusions when studying the processes of degradation and stabilization of polymeric and composite materials. Using this method, it is possible to obtain information about the processes of melting, oxidation and degradation of the material. The thermophysical properties of the samples (TG/DTG/DTA) were studied by a PerkinElmer STA-6000 instrument. Samples weighing 5-8 mg were heated in a nitrogen atmosphere (20 ml/min) in the temperature range from 25 to 700 °C at a given constant rate of 25 °C per minute.

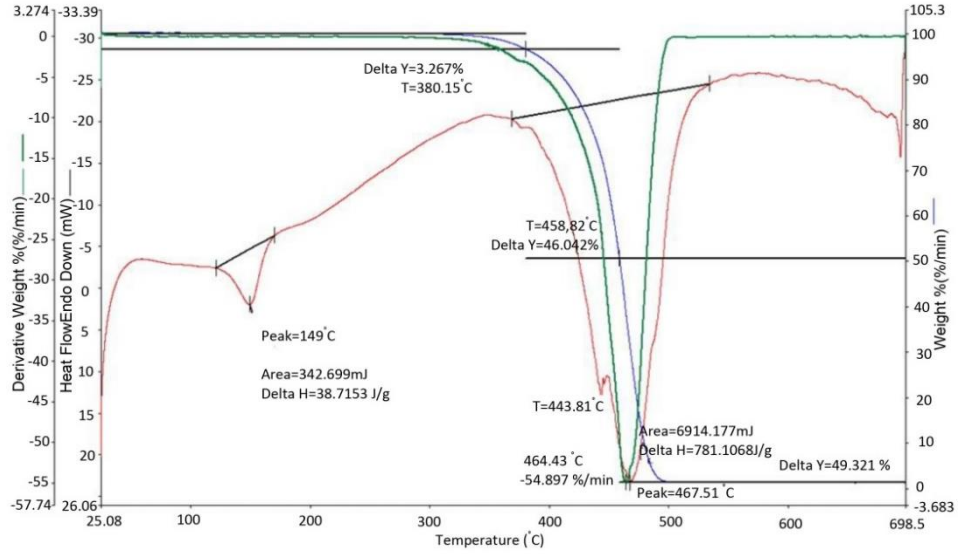
3. Results and discussion

Processing and operation of composite materials based on PP as a rule, is accompanied by exposure to high temperatures in the air. Therefore, it is advisable to study the effect of nanoadditives and thermal aging on the thermal-oxidative resistance of PP and nanocomposites based on it. Figure 1 (a, b) shows DTA, TG and DTG curves for PP without additive before and after thermal aging (aging time is 60 hours). It is seen that in the derivatograms in pure PP in the region of 151.16 °C and 469.80 °C, an endothermic peak characterizing the melting temperature appears, respectively, the energy spent on this melting is 284.286 mJ and 5088.900 mJ, and at 469.8 °C the degradation of the polymer begins. An increase in temperature leads to a linear increase in the melting point of the polymer under study, and the enthalpy also increases. In our view, this is due to the fact that, with an increase in temperature, phase transformations occur, i.e. there is a transition from the crystalline phase to the amorphous phase (Peram *et al.*, 2022). It can be seen from the DTG curves that, at a temperature of 469.74 °C, the rate of mass change is 55.600 %/min and at a temperature of 366.45 °C, the polymer loses 1.573 % and at 469.74 °C, 50.202 % of its mass is lost. At 500 °C, the polymer completely gets degraded. After 60 hours of thermal aging, the initial PP without additive has the following temperature characteristics: a new peak appears at 93.05 °C with an energy of 9.882 mJ and an enthalpy of 1.646 J/g, the other two peaks appear at temperatures of 151.16 °C and 469.80 °C. With an increase in temperature, the enthalpy of the initial PP increases from 16.3174 J/g to 666.6699 J/g. We believe that, this is due

to the separation of some part of the amorphous phase into a separate fraction. The melting of this particular phase corresponds to a wide endo-effect on the thermogram. The sample loses mass at a rate of 55.368 %/min. Thermal degradation starts at 382.92 °C and ends at 464.97 °C. According to the DTA curve, endo-effects are observed at 133 °C, and at 270 °C – exo-effects. At 253 °C, a gradual process of degradation begins, depending on the composition of the sample. At 359.2 °C and 386 °C endo-effects are observed, and at 373.1 °C – exo-effects. After the degradation process, endo peaks were observed at 463.9 °C and exo peaks at 526.1 °C.

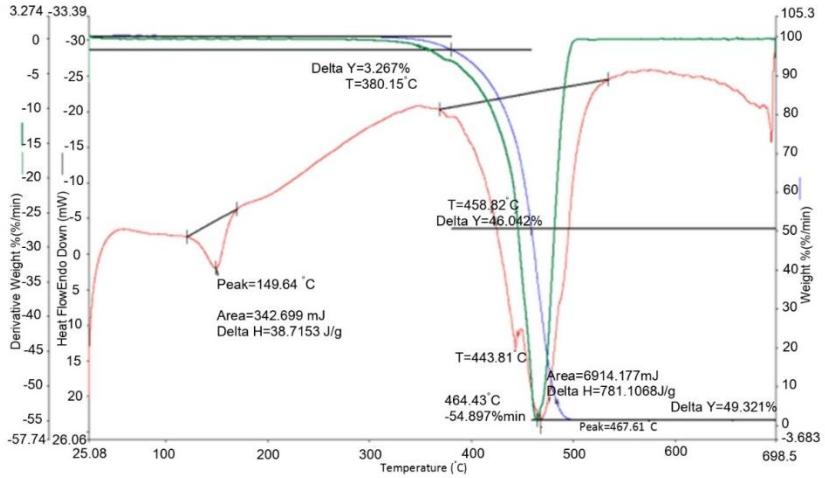


a)

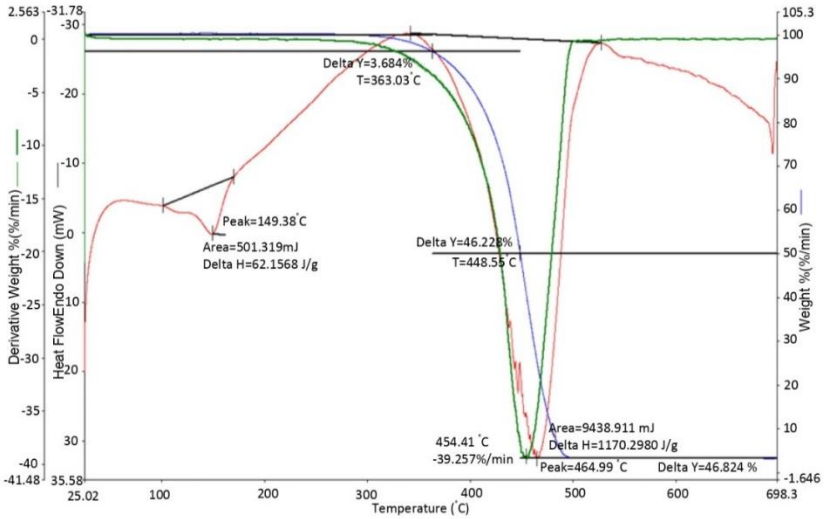


b)

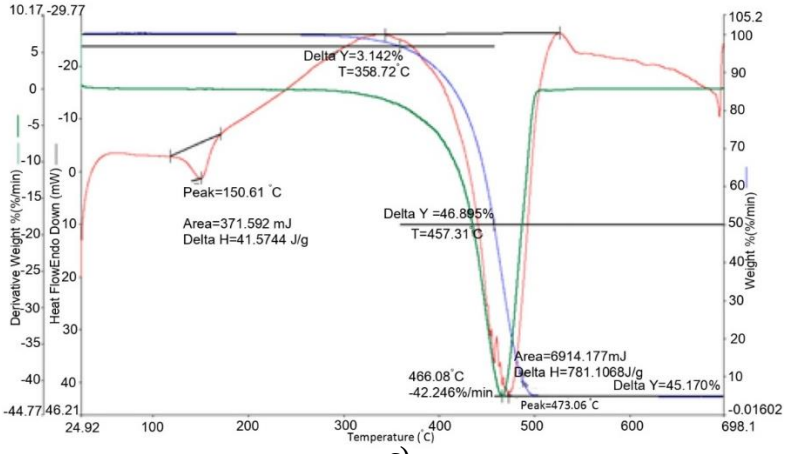
Fig. 1. DTA, TG and DTG curves for PP without additive before (*a*) and after (*b*) thermal aging (aging time is 60 hours)



a)



b)



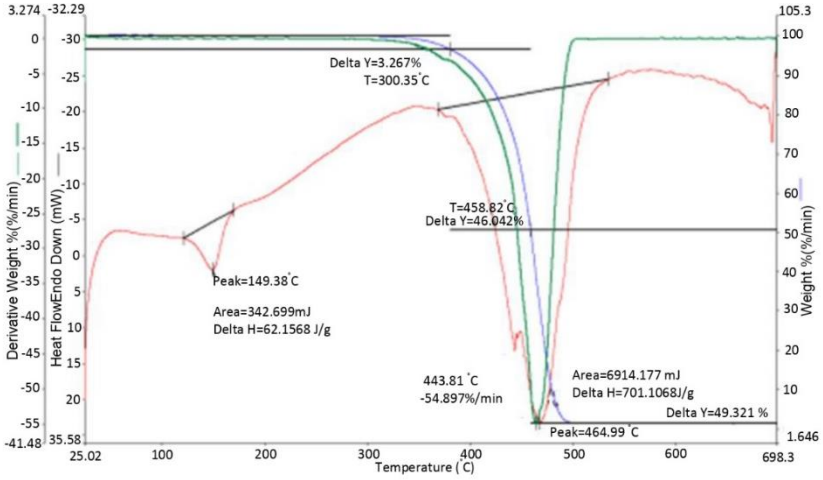
c)

Fig. 2. DTA, TG and DTG curves for nanocomposites PP+1%ZrO_2(*a*), PP+5%ZrO_2(*b*), PP+10%ZrO_2(*c*)

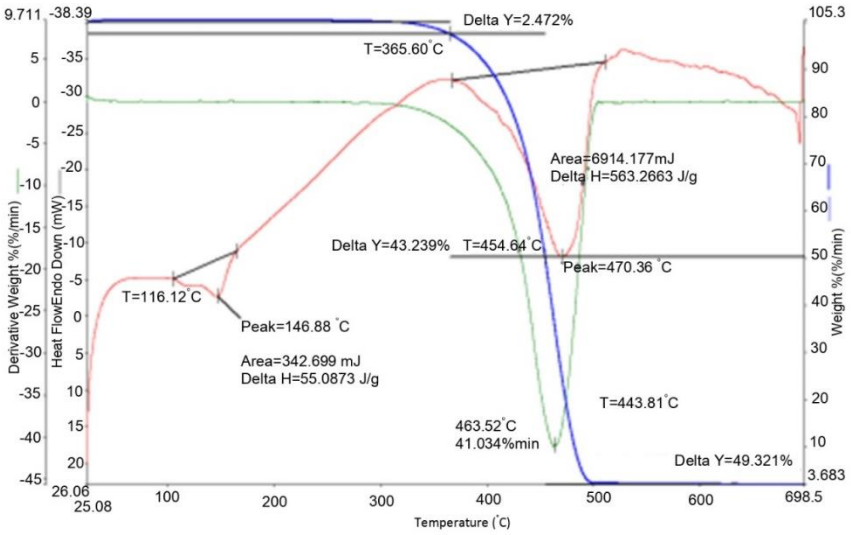
The thermograms (Fig. 2) show STA data for nanocomposites based on PP with different ZrO_2 contents.

As can be seen, the thermal stability of nanocomposites and their thermophysical parameters do not unambiguously change depending on the concentration of zirconium oxide. It can be seen that the presence of ZrO_2 reduces its thermal stability of the polymer. Since if in polypropylene without additives it is 151.16 °C, then in the PP+1% ZrO_2 nanocomposite the melting point is 150.27 °C and in the PP+3% ZrO_2 nanocomposite it is 149.64 °C. In the PP+5% ZrO_2 nanocomposite, there is an increase in thermophysical parameters, but this increase does not exceed the matrix.

Figure 3 (*a*, *b*) represents the curves for the PP+ZrO_2 composition before and after 60 hours of thermal aging.



a)



b)

Fig. 3. (*a*, *b*) DTA, TG and DTG curves for the PP+3%ZrO_2 composition before and after 60 hours of thermal aging

The first peak was found at a temperature of 146.88 °C and the second peak at a temperature of 470.36 °C; the enthalpy increases from 55.0873 J/g to 588.2653 J/g and the second peak shifts towards lower temperatures. At a temperature of 463.52 °C, the mass change occurs at a rate of 41.034 %/min. As can be seen, the modification of PP causes a slight decrease in the melting temperature of the initial PP and a shift in the onset temperature of the melting peak towards lower temperatures.

4. Conclusions

In our opinion, the metal oxide nanoadditive ZrO_2, when it enters the polymer matrix of the polyolefin, does not penetrate into the composition of its spherulites and thereby does not change the structure and size, but is located in the intercrystallite regions of the supramolecular structure of PP, increasing the free volume of the crystallizing system. The change after thermal aging can be explained by the appearance of relaxation processes at the level of intermolecular formations during processing. This can be assumed as the mobility of kinetic units, such as $–CH_2$ or $–CH(CH_3)$- included in the link of the PP polymer chain.

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