

THERMOMECHANICAL PROPERTIES OF DYNAMICALLY VULCANIZED NANOCOMPOSITES BASED ON RANDOM POLYPROPYLENE, NITRIL BUTADIENE RUBBER AND BENTONITE

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Abstract. The influence of the concentration of bentonite nanoparticles on the regularity of thermomechanical properties of thermoplastic elastomers based on random polypropylene, nitrile butadiene rubber of various grades is considered. To improve the compatibility of the random polypropylene with nitrile butadiene rubber, a compatibilizer was used - a grafted copolymer of polypropylene with maleic anhydride. It was shown that with the loading of bentonite nanoparticles, the region of highly elastic deformation is most clearly manifested. The effect of vulcanizing agents - dicumyl peroxide and sulfur on the regularity of changes in thermomechanical curves was studied. It was found that at certain concentrations of crosslinking agents it seems possible to obtain dynamically vulcanized nanocomposites based on random polypropylene, nitrile butadiene rubber, compatibilizer and a crosslinking agent.

Keywords: vulcanization, compatibility, compatibilizer, random polypropylene, highly elastic deformation, thermomechanical properties.

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1. Introduction

Simultaneously with expanding the areas of practical use of polymeric materials and toughening operational requirements for their use, the scope of research and development aimed at improving modern methodological approaches to obtain new types of composites with a significantly improved set of physicomechanical properties has expanded significantly. To improve the properties of polymers, as a rule, various modification methods are used, which make it possible, to one degree or another, to obtain composites with improved specific characteristics. So, for example, the loading of a dispersed filler, plasticizer, stabilizer or the preparation of polymer mixtures, their physical or chemical modification made it possible to a certain extent to approach the preparation of composites with predetermined properties. The use of nanofillers also allowed introducing new concepts and a theoretical background to the interpretation of the supramolecular structure and properties of nanocomposites (Ashurov *et al.*, 2016; Osama *et al.*, 2009; Kodolov *et al.*, 2006; Kahramanov *et al.*, 2016; Vishnyakov *et al.*, 2013).

Truly revolutionary were the studies begun under the guidance of professor S.I. Wolfson, who proposed, in fact, a new approach to producing dynamically vulcanized composites. This line of research opens up new possibilities for the mechanochemical

synthesis of composites during reaction extrusion (Volfson, 2001; Volfson *et al.*, 2015). At the same time, very little information is given in the literature regarding the study of issues related to the regularities of phase transitions in dynamically vulcanized composites based on incompatible polymer mixtures, especially when transitioning from a solid to a highly elastic and viscous flow state.

In connection with the foregoing, the aim of the research was to study the thermomechanical properties of dynamically vulcanized nanocomposites, taking into account modern approaches in assessing their structural features and phase transitions.

2. Experimental part

2.1. Materials

Random polypropylene and nitrile butadiene rubber were used as the polymer object of study. Random polypropylene (RPP) or thermoplastic random copolymer of ethylene with propylene extrusion grade RP2400 is characterized by the following properties: ultimate tensile stress – 28.5 MPa, elongation at break – 600%, MFI = 1.78 g/10min., density 0.904 g/cm³, melting point 146°C, heat resistance 131°C.

SKN - nitrile butadiene rubber with different content of acrylic acid nitrile (SKN-18, SKN-26 and SKN-40).

Exxelor PO1200 compatibilizer is intended for use as a bonding agent in order to improve the compatibility of polymeric materials and to improve reactivity when interacting with inorganic fillers. This is achieved by reactive extrusion by graft copolymerization of polypropylene with maleic anhydride (MA). The concentration of MA in the compatibilizer is 3.0 wt. %.

Bentonite is a mixture of natural aluminosilicate minerals, the basis of which is montmorillonite $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot n\text{H}_2\text{O}$ (60-70%). As a result of the natural substitution of silicon atoms in the crystal lattice of bentonites by magnesium, iron, or other metal ions, they contain saponite - $\text{Al}_2\text{O}_3[\text{MgO}]4\text{SiO}_2 \cdot n\text{H}_2\text{O}$, nontronite - $\text{Al}_2\text{O}_3[\text{Fe}_2\text{O}_3]4\text{SiO}_2 \cdot n\text{H}_2\text{O}$, beidelite - $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$ and pyrophyllite - $\text{Al}_2[\text{Si}_4\text{O}_{10}](\text{OH})_2$. In bentonites, kaolinite and other minerals are present. Since montmorillonite predominates in the crystalline structure of bentonites, they are often called montmorillonites.

Bentonite nanoparticles were obtained in an A-11 analytical mill with a maximum rotor speed of 28,000 rpm.

The size of bentonite nanoparticles was determined on an instrument of the STA PT1600 Linseiz Germany model and amounted to 10-105 nm.

Dicumyl Peroxide (DP) - The vulcanization temperature in its presence is 140-170°C. Free radicals formed during the decomposition of dicumyl peroxide detach hydrogen from the polymer macromolecules, the polymer radicals formed in this way interact with each other with the formation of C–C bonds. In the presence of a double bond in the polymer chain, the peroxide radical binds predominantly to it or detaches α -methylene hydrogen. Moreover, in both cases the formation of macroradicals and the subsequent occurrence of cross-linking occur.

Sulfur is a chemical element with atomic number 16. It is widespread, multivalent. Elemental sulfur is a bright yellow crystalline solid at room temperature. Under normal conditions, sulfur atoms form cyclic eight-atom molecules with the chemical formula S_8 . Used as a polymer vulcanization agent.

2.2. Preparation of composites

The polymer mixtures were mixed on friction rollers at a temperature of 160°C. After the RPP was melted, an Exxelor compatibilizer in an amount of 3.0 wt. % and bentonite were added. After that, SKN and then a vulcanization agent were loaded into this melt, which were mixed for a total of 10-12 minutes.

2.3. Characterization of the composites

Derivatographic analysis was performed on a Paulik, Paulik, and Erdei brand instrument.

The melt flow index (MFI) was determined on a MELT FLOW TESTER, CEAST MF50 (INSTRON, Italy) brand rheometer at a temperature of 190°C and a load of 5 kg. Under these conditions, the MFI of the initial RPP was 3.6 g / 10 min.

Thermomechanical properties were determined on a Kanavets instrument. The deformation was measured at successively changing temperatures (T) at a load of 0.3 kg/cm² and a heating rate of 50°C/h. When constructing the thermomechanical curve of the polymer $\Delta = f(T)$, it is very important to cover, if possible, the entire temperature range of the polymer's existence - glassy (crystalline), highly elastic and viscous flow conditions. Thermomechanical curves reflect all possible physical, physicochemical and chemical changes that occur in the sample during the change in the temperature of the experiment and, thus, provide reliable information on the temperature transitions that are significant for polymer processing.

3. Results and Discussion

Before proceeding to the study of the thermomechanical properties of nanocomposites, it was necessary, first of all, to deal with issues related to the compatibility of miscible polymer components. In this case, incompatible polymer mixtures based on RPP and SKN of various grades are used as the object of study. In this connection, it became necessary to use a compatibilizer-combiner capable of ensuring the miscibility of the components of the mixture and their technological compatibility. For this purpose, Exxelor-grafted copolymer of polypropylene with maleic anhydride (PPMA) was used as a compatibilizer, the loading of which even at low concentrations contributes to a noticeable improvement in the properties of composite materials (Kahramanlyi, 2013). It is known that when mixed incompatible mixture components are mixed at a supramolecular level, a pronounced two-phase system is formed. The objective of the study was to achieve uniform dispersion of nanoparticles and compatibilizer throughout the volume of the polymer mixture. There is reason to believe that the main role of PPMA should be that, uniformly distributed mainly in the boundary zones of contact of the elastomer with RPP macrochains, contribute to the formation of relatively small elastomeric phases in which favorable conditions are created for miscibility and technological compatibility of the polymer components of the mixture. However, a simple mixing of the components of the mixture can not always contribute to the formation of the necessary structure of thermoplastic elastomer. The latter becomes possible only under those conditions when, at a certain ratio of polymer components, the plastic deformation of the polymer mixture is replaced by a highly elastic characteristic for thermoplastic elastomers. We experimentally found that this process is mainly possible when the concentration of SKN in the composition of the RPP is not lower than 40 wt. %. Earlier, in works (Guseynova *et al.*, 2019;

Kurbanova *et al.*, 2020), we also showed the proposed mechanism of the process of technological compatibility of mixed heteropolar components of the mixture, according to which the properties of thermoplastic elastomers in a two-phase system are formed depending on the ratio of rigid and elastic blocks of RPP and SKN. At the same time, hard RPP blocks after dilution in an elastomer medium and physical interaction between themselves form domains that play a peculiar role of multifunctional nodes responsible for the strength of thermoplastic elastomers. The lack of chemical bonds between the rigid blocks of the RPP contribute to the preservation of the fluidity of the melt at elevated temperatures, which is extremely important to ensure the processability of thermoplastic elastomers by injection molding and extrusion.

The advantage of dynamically vulcanized composites is that, at low concentrations of peroxide crosslinking agents, interchain crosslinking occurs mainly in the SKN phase due to the large number of double bonds and, accordingly, methylene groups located in the α -position to the vinyl groups. At higher concentrations of DP, interchain cross-linking occurs not only in the dispersed phase of SKN, but also in the hard domains of RPP along tertiary carbon atoms, which unconditionally contributes to the formation of a densely-mesh spatial structure, which prevents the possibility of processing cross-linked thermoplastic elastomer on standard equipment. Therefore, the task of the study was to determine the minimum concentration of DP at which the structure of a dynamically vulcanized composite is formed. In this structure, crosslinking proceeds predominantly along the elastomeric phase. In this case, the filler itself, which is nanosized bentonite, should be taken into account. The role of bentonite nanoparticles in this case is to increase the strength of the nanocomposite.

In order to understand the structural features of dynamically vulcanized nanocomposites, it seemed interesting to study the thermomechanical properties in two stages. At the first stage, the influence of the concentration of bentonite nanoparticles on the regularities of phase transitions from one state to another is studied. Next, at the second stage, the influence of the concentration of DP or sulfur on the process of vulcanization of nanocomposites is studied, as a result of which the permissible minimum concentration of crosslinking agents is established, which makes it possible to obtain dynamically vulcanized nanocomposites that can be processed by injection molding or extrusion.

As noted above, we first begin the implementation of the first stage of work on the production of dynamically vulcanized thermoplastic elastomers based on RPP and SKN of various grades (SKN-18, SKN-26 and SKN-40), the results of which are shown in figures 1-3. At the same time, when developing the material, PPMA in the amount of 3.0 wt. % was used as a compatibilizer. Such an analytical approach to the evaluation of experimental data will allow a more competent and consistent approach to the study of the qualitative characteristics of the developed materials and thereby make useful forecasts in relation to the technology of their processing.

In this regard, figures 1-3 show thermomechanical curves of the temperature dependence of deformation for compositions based on RPP + SKN + PPMA depending on the concentration of bentonite nanoparticles and SKN grade. When using SKN-18, SKN-26 and SKN-40, their concentration in the composition of the RPP was constant and amounted to 40 wt. %.

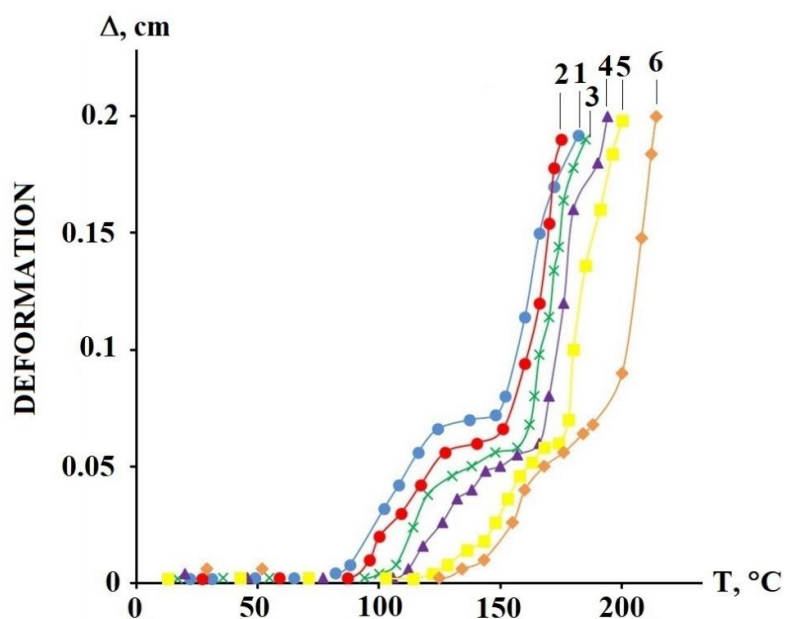


Figure 1. Effect of bentonite concentration on thermomechanical curves of the dependence of deformation on the temperature of composites: (1) - initial RPP + 40 wt. % SKN-18 + 3.0 wt. % PPMA; (2) - 1.0; (3) - 3.0; (4) - 5.0; (5) - 10 and (6) – 20 wt. %.

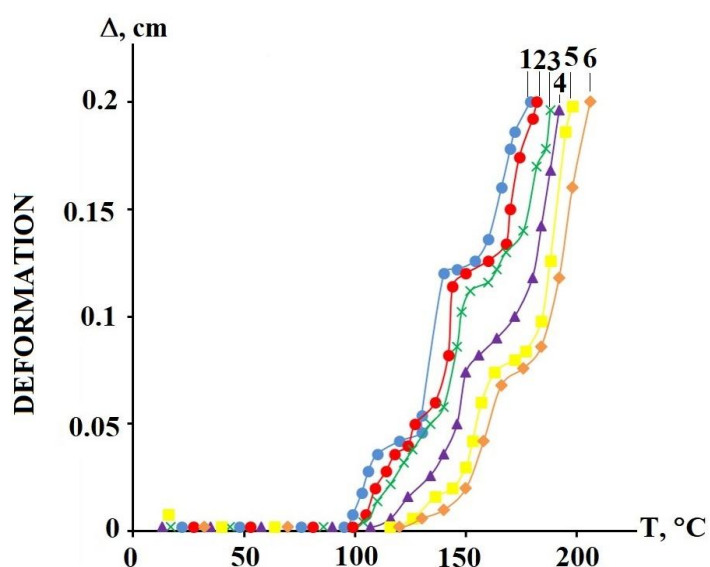


Figure 2. Effect of bentonite concentration on thermomechanical curves of the dependence of deformation on the temperature of composites: (1) - initial RPP + 40 wt. % SKN-26 + 3.0 wt. % PPMA; (2) - 1.0; (3) - 3.0; (4) - 5.0; (5) - 10 and (6) – 20 wt. %.

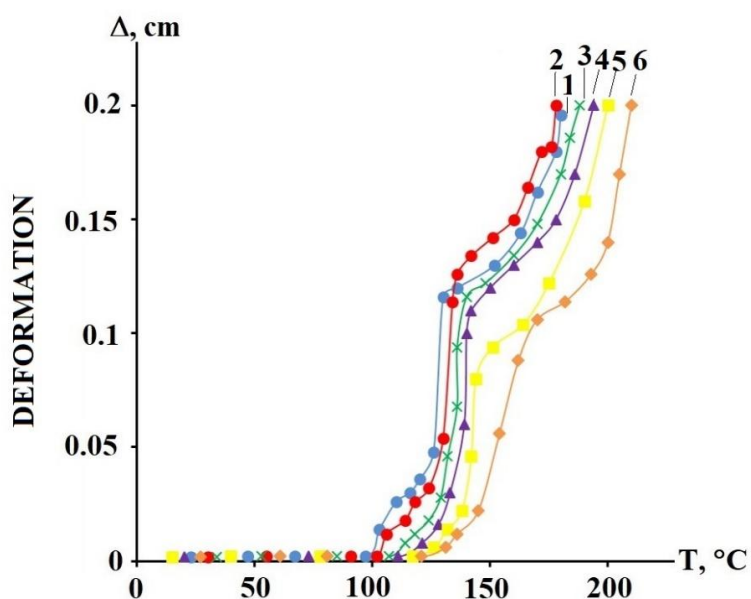


Figure 3. Effect of bentonite concentration on thermomechanical curves of the dependence of deformation on the temperature of composites: (1) - initial RPP + 40 wt. % SKN-40 + 3.0 wt. % PPMA; (2) - 1.0; (3) -3.0; (4) -5.0; (5) -10 and (6) – 20 wt. %

This is the threshold concentration of SKN in the composition of the RPP, when the polymer composition acquires the properties of thermoplastic elastomers. The concentration of bentonite nanoparticles in the composition of this composite was varied within 1.0; 3.0; 5.0; 10 and 20 wt. %. The objective of the study was to identify the role of the filler in the regularities of change in phase transitions from one physical state to another. If we pay attention to the thermomechanical curves in figures 1-3, we can see that the initial unfilled compositions of polymer mixtures RPP + SKN contribute to the formation of a peculiar hump at a relatively low temperature on the thermomechanical curve. This circumstance is due to the fact that SKN has a lower softening point than RPP. Therefore, the initial polymer mixtures RPP + SKN + PPMA, depending on the brand of SKN, melt at a relatively low temperature. The higher the content of nitrile groups in the composition of SKN, the more softening of the polymer mixture occurs at a higher temperature. From a comparative analysis of the data presented in these figures, it can be established that as the concentration of bentonite nanoparticles in the composition of the thermoplastic elastomer increases, a regular increase in the temperature of the onset of softening of the samples is observed with a simultaneous decrease in the hump in the low-temperature region of thermomechanical curves. It is characteristic that when SKN-18, SKN-26, and SKN-40 elastomers are loaded into composites, respectively, the more effective is the effect of bentonite nanoparticles on the nature of the change in strain with temperature. So, for example, when SKN-18 is loaded into the composition of the polymer mixture, then, depending on the concentration of bentonite, the softening temperature changes in the range of 83-98°C. With the loading of SKN-26, the softening temperature varies between 95-102°C, and with the loading of SKN-40 this temperature range changes between 99-122°C. If in figure 1 the most noticeable effect of bentonite nanoparticles on the regularity of changes in thermomechanical curves occurs at a concentration of 10 wt. % or higher, then in figure 2 this effect begins to appear at a concentration of 5.0 wt. %. In figure 3,

the most noticeable differences in the regularities of changes in thermomechanical curves can be established at a concentration of 10 wt. % and higher. From the thermomechanical curves shown in figures 1-3, it can be established that, regardless of the type of SKN and the concentration of bentonite, they are characterized by the appearance of 3 transitions from a solid to a highly elastic and viscous flow state. The presence of all three physical states is characteristic of thermoplastic elastomers.

After a detailed examination of the thermomechanical curves in figures 1-3, we proceed to the study of the second stage of research, based on the study of the effect of the concentration of crosslinking agents on phase transitions in dynamically vulcanized thermoplastic elastomers, the results of which are presented in figures 4 and 5. Figure 4 shows the thermomechanical curves of the temperature dependence of deformation for vulcanized nanocomposites, where in all cases the bentonite content was 5.0 wt. %. The starting material used was a RPP + 40 wt. % SKN-40 + 3.0 wt. % PPMA + 5.0 wt. % bentonite nanocomposite. DP was used as a crosslinking component, the concentration of which varied within 0.25–2.0 wt. %. As can be seen from this figure, with an increase in the concentration of DP from 0.25 to 0.75 wt. %, the region of highly elastic deformation characteristic of rubbers is most clearly manifested.

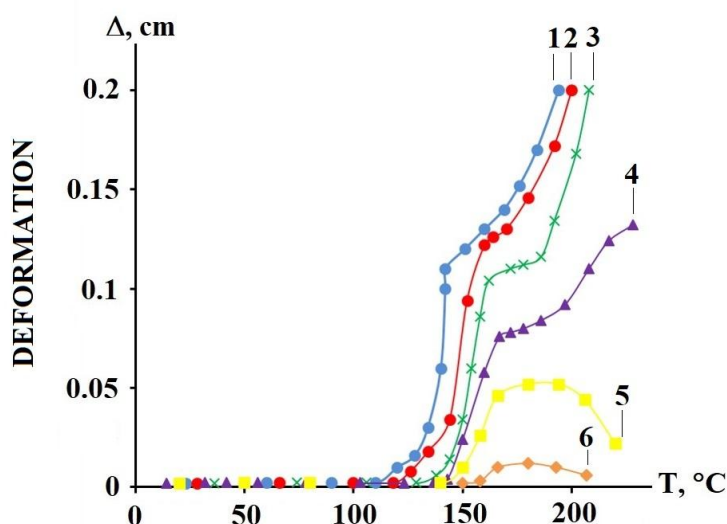


Figure 4. Effect of DP concentration on thermomechanical curves of the dependence of deformation on the temperature of composites: (1) - initial RPP + 40 wt. % SKN-40 + 3.0wt.% PPMA+5wt.% bentonite; (2)- 0.25; (3)- 0.5; (4)- 0.75; (5)- 1.0; (6)- 2.0 wt. %

With the loading of 1.0–2.0 wt. % DP, vulcanized nanocomposites are characterized by the fact that they transition from a highly elastic state to a glassy state. This is a condition in which the nanocomposite is completely crosslinked and loses its processability. In this case, the crosslinking process proceeds not only along double bonds and α -methylene groups, but also along tertiary carbon atoms with the formation of a high density of crosslinked structures. This type of nanocomposites is not of particular interest, since it is not possible to obtain coherent products based on them (Panfilova *et al.*, 2016; Kalistratova *et al.*, 2019; Nguen Min Tuan *et al.*, 2017). When 0.75 wt. % DP is loaded, nanocomposite, when exposed to high temperatures, forms spatially cross-linked structures with a very low MFI of 0.31 g/10 min. Nanocomposites obtained in the process of vulcanization 0.25-0.50 wt. % content of DP, to the greatest

extent possible to obtain dynamically vulcanized materials. According to thermomechanical curves 4.2 and 4.3, these materials possess properties characteristic of dynamically vulcanized nanocomposites, in which the MFI varies from 1.93 to 0.95 g/10 min, respectively.

Another direction of the second stage of the study was the use of sulfur as a curing agent. It should be noted that, in contrast to DP, sulfur consists of an 8-membered cycle, which during processing and thermomechanical action is destroyed with the formation of radicals. These radicals are most effective for curing elastomers at the site of double bond cleavage. Since the content of double bonds is much higher in comparison with RPP in SKN, we do not exclude that in this case it would be appropriate to assert the selectivity of the vulcanization process. If in the case of DP between the macrochains a rigid transverse bond is formed along the C–C bond, then in the case of sulfur this bond is formed with the participation of an 8 membered sulfur chain, which preserves the elasticity of the nanocomposite. Such a possible mechanism for the formation of the spatial structure allows us to state that crosslinking occurs mainly in the elastomeric phase of the nanocomposite, as a result of which a dynamically vulcanized nanocomposite is formed in a single technological process.

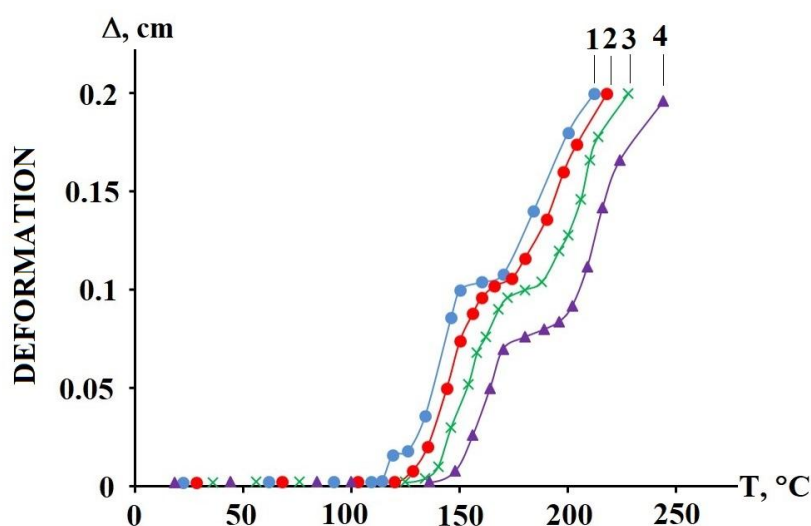


Figure 5. Effect of sulfur concentration on thermomechanical curves of the dependence of deformation on the temperature of composites based on RPP + 40 wt. % SKN-40 + 3.0 wt. % PPMA + 5.0 wt. % bentonite: (1)- 1.0; (2)- 3.0; (3)- 5.0; (4)- 10 wt. %

Figure 5 shows the thermomechanical curves of nanocomposites based on RPP + 40 wt. % SKN-40 + PPMA + 5.0 wt. % bentonite sulfur vulcanized. From a comparative analysis of thermomechanical curves in this figure, it can be noted that with an increase in sulfur concentration from 1.0 to 10 wt. %, a regular change in thermomechanical curves is observed, as a result of which the softening temperature rises accordingly from 109 to 137°C. All this testifies in favor of the fact that with increasing sulfur concentration the degree of crosslinking increases. It was found that the MFI of nanocomposites changes as follows: with an increase in sulfur concentration in the sequence of 1.0; 3.0; 5.0 and 10 wt. % the value of this indicator is reduced, respectively, in the following order - 2.71; 2.30; 1.96 and 0.91g/10min. From the data obtained it follows that the sulfur content in a dynamically vulcanized nanocomposite is

most effective - 3.0-5.0 wt. % using a higher sulfur content is not advisable. It can be seen from the thermomechanical curves presented that, with increasing sulfur concentration, the region of highly elastic deformation shifts to the region of high temperatures. For example, the temperature region of highly elastic deformation, respectively, changes as follows: 151-172°C, 159-173°C, 170-195°C and 172-203°C. As can be seen from figure 5, if at a sulfur concentration of 1.0–5.0 wt. %, highly elastic properties begin to appear approximately at a deformation of 0.09–0.1 cm, then with the loading of 10 wt. % sulfur, a highly elastic state begins to appear at a deformation of 0.07 cm.

4. Conclusion

Thus, based on the foregoing, we can come to the following conclusion:

The effect of various brands of SKN and the concentration of bentonite nanoparticles on the regularity of changes in the thermomechanical characteristics of thermoplastic elastomers based on RPP + 40 wt. % SKN + 3.0 wt. % PPMA was studied. It was shown that with an increase in the concentration of bentonite nanoparticles, an increase in the softening temperature of nanocomposites is observed.

It was found that at certain concentrations of such crosslinking agents and the ratio of polymer components, dynamically vulcanized nanocomposites can be obtained.

References

- Ashurov, N.R., Dolgov, V.V., Sadyikov, Sh.G., & Usmanova, M.M. (2016). Nanocomposites ethylene polymers filled with layered aluminosilicates. *Tashkent: "Fan." Academy of Sciences of Uzbekistan*, 183 (in Russian).
- Guseynova, Z.N., Kahramanov, N.T., Guliev, A.D., & Kurbanova, R.V. (2019). Thermomechanical properties of polymer mixtures based on thermoplastic polyolefins and butyl rubber. *All materials. Encyclopedic reference book*, 3, 2-9 (in Russian).
- Kahramanlyi, Yu.N. (2013). *Incompatible polymer mixtures and composite materials based on them*. Baku, Elm, 152 (in Russian).
- Kahramanov, N.T., Azizov, A.G., Osipchik, V.S., Mamedli, U.M., & Arzumanova, N.B. (2016). Nanostructured composites and polymer materials science. *Plastic masses*, 1-2, 49-57 (in Russian).
- Kalistratova, L.F., & Egorova, V.A. (2019). Ordering of the amorphous phase as one of the characteristics of the supramolecular structure of an amorphous crystalline polymer. *Materials Science*, 1, 3-5 (in Russian).
- Kodolov, V.I., Hohryakov, N.V., & Kuznetsov, A.P. (2006). To the question of the mechanism of the influence of nanostructures on structurally changing environments in the formation of "intelligent" composites. *Nanotechnology*, 3(7), 27–35 (in Russian).
- Kurbanova, R.V., & Kahramanov, N.T. (2020). Thermomechanical properties of hybrid nanocomposites based on functionalized high density polyethylene and bentonite. *Materials Science*, 4, 26-30 (in Russian).
- Min'Tuan, N., Chalaya, N.M., & Osipchik, V.S. (2017). Structure and physico-mechanical properties of mixtures of polypropylene and metallocene ethylene-propylene elastomer. *Plast. massy*, (9-10), 12-16.
- Osama, A.H., Osipchik, V.S., Petuhova, A.V., Kravchenko, T.P., & Kovalenko, V.A. (2009). Modification of filled polypropylene. *Plastics*, 1, 43-46 (in Russian).
- Panfilova, O.A., Volfson, S.I., Ohotina, N.A., Minnegaliev, R.R., Vahitov, I.I., & Karimova, A.R. (2016). The effect of the composition of the vulcanizing group on the properties of

- dynamically vulcanized thermoplastic elastomers based on styrene butadiene rubbers and polyethylene. *Bulletin of Kazan Technological University*, 19(17), 39-43 (in Russian).
- Vishnyakov, L.R., Petropolskiy, V.S., & Morozova, V.N. (2013). Polymer-based nanocomposites. *Bulletin of the Academy of Engineering of Ukraine*, 3-4, 202-205 (in Russian).
- Volfson, S.I. (2001). Thermoplastic elastomers - construction materials of a new generation. *Chemistry and Business*, 1, 30-40 (in Russian).
- Volfson, S.I., Ohotina, N.A., Panfilova, O.A., & Vahitov, I.I. (2015). Methods for producing thermoplastic vulcanizates based on a mixture of rubbers and polypropylene. *Bulletin of Kazan Technological University*, 18(14), 90-92 (in Russian).