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GENERAL PURPOSE  
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# Thermal Deformation Properties of Dynamically Vulcanized Thermoplastic Elastomers Based on Random Polypropylene and Nitrile Butadiene Rubber

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**Abstract**—The thermal deformation properties of dynamically vulcanized thermoplastic elastomers based on random polypropylene and nitrile butadiene rubber (NBR) are studied. Exxelor PO1200, a graft polypropylene copolymer with a maleic anhydride, was used as a compatibilizer to improve the compatibility of polymer mixtures. The concentration of maleic anhydride in the grafted copolymer was 3.0 wt %. We showed that it is possible to improve the compatibility of bipolar mixtures through the incorporation of a compatibilizer, when there is no separation between the components of the mixture. We found that the polymer composition exhibits the properties of thermoplastic elastomers upon the introduction of 30 wt % NBR-18 and 40 wt % NBR-26 or NBR-40 into random polypropylene, so that the plastic deformation changes to a highly elastic one typical of rubbers. The temperature regions of the solid, highly elastic, and viscous-flow states are found. The polymer mixtures were vulcanized with crosslinking agents (dicumyl peroxide and sulfur) to exhibit the properties of rubber. We showed that the thermomechanical properties of dynamically vulcanized thermoplastic elastomers change significantly with an increase in concentration of dicumyl peroxide from 0.25 to 1.0 wt %. The vulcanized materials almost completely lose their ability to flow, and they transform from a highly elastic state to a glassy one after the introduction of 1.0 wt % of dicumyl peroxide. The melt flow index (MFI) of vulcanized thermoplastic elastomers remains unchanged after the introduction of sulfur in an amount from 1.0 to 10 wt %.

**Keywords:** thermoplastic elastomers, compatibilizer, dicumyl peroxide, sulfur, highly elastic deformation, glassy state

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## INTRODUCTION

The issues related to the development of composite materials based on incompatible polymers attract great attention [1–3]. This is due to the fact that it seems to be possible to combine the characteristic unique properties of components in a composition during the preparation of materials based on dissimilar polymers. This becomes possible, however, only if there is a required technological compatibility of mixed polymers with different polarities. This is not a thermodynamic compatibility, but is a satisfactory mixing or technological compatibility of polymer mixtures, which becomes possible when compatibilizers are used. The problem of using compatibilizers and their influence on phase transitions in the study of thermal deformation properties of thermoplastic

elastomers with various ratios of components, therefore, are mainly considered in this work. The problems related to the preparation of dynamically vulcanized thermoplastic elastomers with characteristic properties of rubber appear to be more urgent [4, 5]. The studies in this area are due to the fact that it is possible to obtain qualitatively new thermoplastic elastomers with rubber properties, but processed as thermoplastics on injection molding equipment or on an extrusion unit during the dynamic vulcanization of polymer mixtures according to a single technological scheme.

The aim of this work is to find the regularities of deformation of compositions and the region of their phase transitions depending on the temperature and the NBR grade.

## EXPERIMENTAL

Random polypropylene and nitrile butadiene rubber were used as the polymer objects.

Random polypropylene (RPP) or thermoplastic random copolymer of ethylene with a propylene extrusion grade RP2400 has the following properties: the breaking stress is 28.5 MPa, the elongation is 600%, MFR = 1.78 g/10 min, the density is 0.904 g/cm<sup>3</sup>, the melting point is 146°C, and the heat resistance is 131°C.

Nitrile butadiene rubber (NBR) with different amount of acrylic acid nitrile (NBR-18, NBR-26, and NBR-40) was also used.

An Exxelor PO1200 compatibilizer is used as a binding agent to improve the compatibility of polymeric materials and to improve the reactivity during interaction with inorganic fillers. This is achieved during a reactive extrusion process via graft copolymerization of polypropylene with maleic anhydride (MA). The concentration of MA in the compatibilizer is 3.0 wt %.

The vulcanization temperature of a composition in the presence of dicumyl peroxide (DP) is 140–170°C. Free radicals formed during the decomposition of dicumyl peroxide detach hydrogen from polymer macromolecules, and the resulting polymer radicals interact with each other to form C–C bonds. A peroxide radical attaches predominantly to it or detaches  $\alpha$ -methylene hydrogen in the presence of a double bond in a polymer chain. Moreover, the macroradicals appear to form crosslinks in both cases.

Sulfur is a widespread and multivalent chemical element with atomic number of 16. Elemental sulfur is a bright yellow crystalline solid at room temperature. Sulfur atoms form cyclic octatomic molecules with the chemical formula S<sub>8</sub> under normal conditions. Sulfur is used as a vulcanization agent for polymers.

The polymer mixtures were mixed on friction rollers at 160°C. An Exxelor compatibilizer was introduced into the mixture in an amount of 3.0 wt % after the RPP was melted. NBR and then a vulcanization agent were introduced into this melt, and it was mixed for 10–12 min.

A derivatographic analysis was performed with a Paulik–Paulik–Erdei system.

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

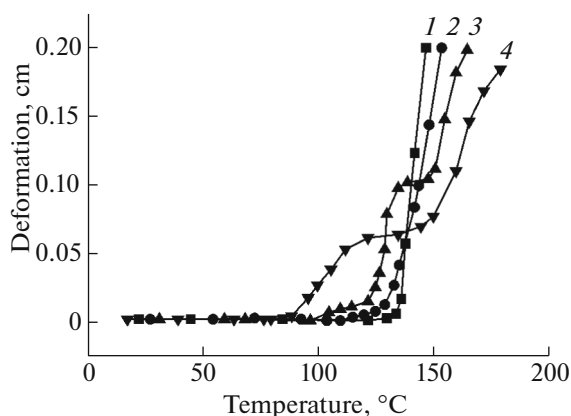
The thermomechanical properties were determined on a Kanavets unit. The deformation was measured at successively changed temperatures ( $T$ ) at a load of 0.3 kg/cm<sup>2</sup> and a heating rate of 50°C/h. It was very important to cover the entire temperature range of existence of a polymer (glassy (crystalline), highly elastic, and viscous-flow states) to construct a thermomechanical curve of a polymer  $\Delta = f(T)$ . Thermo-

mechanical curves reflect all possible physical, physicochemical, and chemical changes in a sample during the change in temperature of experiment and, therefore, allow obtaining reliable information on temperature transitions that are significant for processing of polymers.

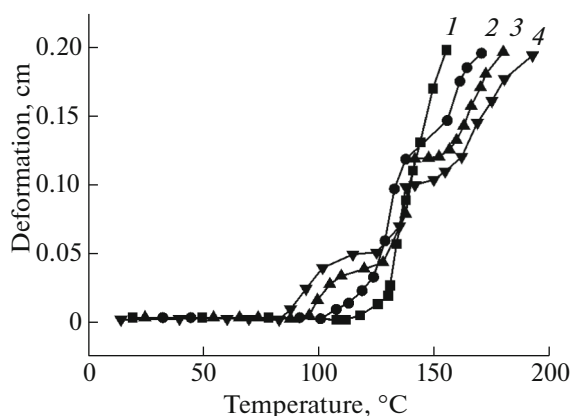
## RESULTS AND DISCUSSION

Thermomechanical measurements on a Kanavets unit make it possible to observe phase transitions with high accuracy: from a solid state to a highly elastic or viscous-flow one. The detection of such phase transitions allows the predetermination of temperature regions required for processing polymer materials by injection molding or extrusion [6, 7]. More fundamental are the problems related to the identification of temperature processing regions in a melt mode with subsequent cooling and transfer of a polymer to a solid state in the production of materials based on incompatible polymer compositions. Exxelor, which is a polypropylene modified with a maleic anhydride (PPMA), was used as a compatibilizer to improve the miscibility and technological compatibility of mixtures based on RPP and NBR. At the same time, it was important to reveal how this compatibilizer influences the thermomechanical properties of the polymer mixtures considered.

Figures 1–3 show the influence of the concentration of various NBRs on the thermomechanical curves of polymer mixtures based on RPP + NBR + Exxelor. It is clear that the introduction of NBR into the RPP composition significantly changes the relationship between temperature and deformation. The comparative analysis of thermomechanical curves indicates that there is a decrease in the softening temperature of the samples with an increase in the concentration of NBRs regardless of their brand. This is mainly due to the influence of the rubber component on the softening temperature of the polymer mixture. Figure 1 shows that the higher the concentration of NBR-18 in the RPP + NBR polymer mixture, the more distinct the “bulge” in the low-temperature region. Further increase in temperature leads to an increase in deformation of the sample. The area of highly elastic deformation appears only when amount of NBR-18 is 30 wt % and higher. It is characteristic that this region also appears in those samples where NBR-26 and NBR-40 were used as the rubber component (Figs. 2 and 3). The difference is in the fact that the region of highly elastic deformation in these samples appears when the amount of NBR-26 and NBR-40 is 40 wt %. All this indicates that the higher the concentration of acrylic acid nitrile (AAN) in the NBR composition, the higher its concentration in the RPP + NBR mixture the region of highly elastic deformation appears. There are also differences in the temperature range close to the onset of softening of a polymer composition. Indeed, the softening temperature for a starting



**Fig. 1.** Influence of concentration of NBR-18 on thermo-mechanical curves of RPP-based polymer mixtures in the presence of Exxelor compatibilizer: (1) initial RPP, (2) 20, (3) 30, and (4) 40 wt %.



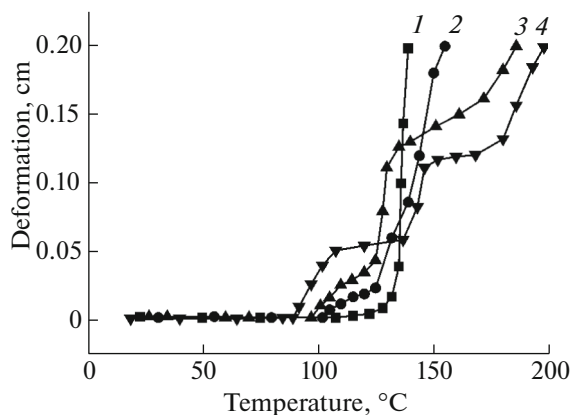
**Fig. 2.** Influence of concentration of NBR-26 on thermo-mechanical curves of RPP-based polymer mixtures in the presence of Exxelor compatibilizer: (1) 20, (2) 30, (3) 40, and (4) 50 wt %.

RPP begins at a temperature of 134°C, and the softening point decreases for the samples with the amount of NBR-18 of 20, 30, and 40 wt % in the following sequence, respectively: 112, 94, and 86°C. The softening point changes as follows 113, 102, 96, and 88°C in the RPP + NBR-26 samples with an increase in concentration of NBR-26 in the sequence of 20, 30, 40, and 50 wt %, respectively. The softening point changes as follows in the compositions based on RPP + NBR-40: 117, 105, 99, and 92°C. The comparison of the data indicates that the softening temperature of the samples increases at the same concentration of the rubber component upon going from NBR-18 to NBR-40. The fact that a region of highly elastic deformation appears on the temperature dependence of deformation when the amount of NBR is 30–40 wt % indicates that the transition from plastic deformation to highly elastic deformation characteristic of thermoplastic elastomers is observed exactly at this ratio of components in the polymer mixture. Further increase in temperature leads to the transition of the polymer composition from a highly elastic state to a viscous flow one.

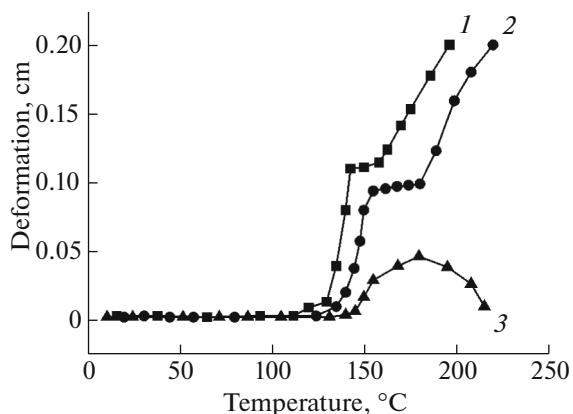
It seemed interesting to consider the influence of the concentration of various crosslinking agents on changes in thermomechanical properties so that thermoplastic elastomers would possess clear rubber properties [8, 9]. DP and sulfur were used as crosslinking agents. DP seems to be the most reactive among any other initiators in the crosslinking process of macromolecules. We used such an amount of DP that the crosslinking would lead to the region of a highly elastic state characteristic of rubbers in the samples. At the same time, such technological properties of a vulcanized composition as MFR should retain the ability of the composition to process them with injection molding and extrusion. It was important, therefore, to find the maximum concentration in the presence of crosslinking agents at which the technological processing fea-

tures of the samples would remain unchanged together with the improvement of their heat resistance.

Figure 4 shows the thermomechanical relationships between the deformation and temperature at different concentration of DP for the RPP + 40 wt % NBR-40 + 3.0 wt % Exxelor composition as an example. A comparative analysis of the curves (Fig. 4) indicates that the thermomechanical curves change significantly with an increase in concentration of DP from 0.25 to 1.0 wt %. The thermomechanical curves become typical of rubbers after the introduction of DP in an amount of 0.25–0.5 wt %. The polymer composition passes immediately from a highly elastic state to a glassy one at a concentration of DP of 1.0 wt %. The polymer is completely crosslinked in this state and almost completely loses its ability to flow, or the MFI becomes zero. The softening temperature changes as



**Fig. 3.** Influence of concentration of NBR-40 on thermo-mechanical curves of RPP-based polymer mixtures in the presence of Exxelor compatibilizer: (1) 20, (2) 30, (3) 40, and (4) 50 wt %.

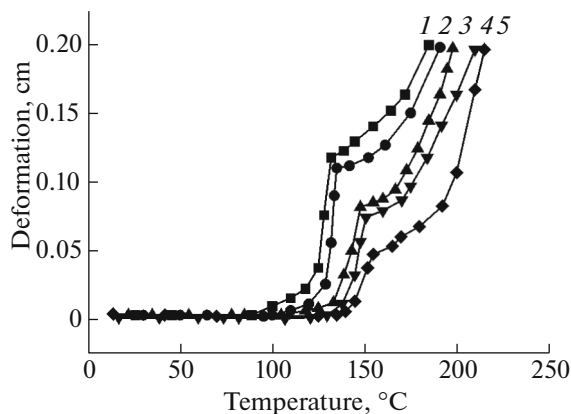


**Fig. 4.** Influence of concentration of DP on thermomechanical curves of dynamically vulcanized thermoplastic elastomers based on RPP + 40 wt % NBR-40: (1) 0.25, (2) 0.50, and (3) 1.0 wt %.

follows for the samples with the amount of DP of 0.25, 0.50, and 1.0 wt %: 114, 131, and 143°C. The area of highly elastic deformation for the vulcanizates containing 0.25 and 0.5 wt % of DP changes within 142–158 and 154–181°C, respectively. The transition from a highly elastic state to a glassy one proceeds at 180°C at a concentration of DP of 1.0 wt %.

The amount of gel fractions in crosslinked compositions was determined on a Soxhlet device. We found that the gel fraction in the crosslinked thermoplastic elastomers based on RPP + NBR-40 + Exxelor changes in the following order depending on the amount of DP (0.25, 0.5, and 1.0 wt %) during the washing of crosslinked samples in boiling toluene: 10, 29, and 82%. As expected, the gel fraction increases significantly with an increase in concentration of DP. High concentration of the gel fraction indicates that a densely reticulated spatial structure is formed after the introduction of 1.0 wt % DP, which increases the rigidity of the polymer matrix and leads to a complete loss of melt flow.

Figure 5 shows the thermomechanical curves of the relationship between the deformation and temperature for the RPP + 40 wt % NBR-40 + Exxelor composition at various concentrations of sulfur as a vulcanization agent. It is clear (Fig. 5) that the thermomechanical curves change regularly with an increase in concentration of sulfur. Firstly, there is an increase in the softening temperature of the vulcanizates in the following order with an increase in the concentration of sulfur (1.0, 3.0, 5.0, 7.0, and 10 wt %): 90, 96, 105, 111, and 125°C, respectively. Secondly, the area of highly elastic deformation changes within 132–140, 135–142, 148–167, 152–172, and 155–187°C. At the same time, the maximum deformation temperature is as follows at around 0.2 cm: 188, 193, 197, 211, and 215°C, respectively. The fact that there is a solid, highly elas-



**Fig. 5.** Influence of concentration of sulfur on thermomechanical curves of dynamically vulcanized thermoplastic elastomers based on RPP + 40 wt % NBR-40: (1) 1.0, (2) 3.0, (3) 5.0, (4) 7.0, and (5) 10 wt %.

tic, and viscous-flow state in the vulcanizates indicates that the obtained thermoplastic elastomers possess the properties of rubber.

## CONCLUSIONS

In summary, thermoplastic elastomers with rubber properties can be obtained after the introduction of 30 wt % NBR-18 and 40 wt % NBR-26 or NBR-40 into RPP.

We found that the most optimal amount of dicumyl peroxide in the composition is 0.5 wt %. The polymer composition transforms into a glassy state at a higher concentration of dicumyl peroxide, when it completely loses the ability to flow.

Such studies are much useful for specialists in the field of processing thermoplastic elastomers to produce cable products.

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