

New Approaches for the Interpretation of the Structure and Phase Transitions in Nanocomposites Based on Modified Polyolefins and Technical Carbon

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Summary: The results of the investigation of the thermomechanical characteristics of maleinized polyolefine-based nanocomposite materials with different carbon black content are presented. The high density polyethylene, low density polyethylene and polypropylene were used as polyolefins. Highly structured amorphous carbon black of the Printex XE 2B brand with a nanoparticle size of 20 nm, introduced into the composition of the polyolefin in an amount of 1.0–20 wt%, was used as technical carbon. To improve the compatibility of polyolefins with technical carbon, a compatibilizer was used – high-density polyethylene graft copolymer with 5-6 wt% maleic anhydride (PEMA) brand Exxelor PO1040 and polypropylene graft copolymer with 5-6 wt% maleic anhydride (PPMA) brand Exxelor PO1020. The compatibilizer was introduced into the composition of polyolefins in the amount of 2.0 wt%. An electron microscopic, derivatographic and X-ray diffraction analysis of nanocomposites with different technical carbon content was carried out. Thermomechanical studies were carried out on a Kanavets instrument. It was found that with an increase in the content of technical carbon within 1.0, 5.0, 10, 20 wt%, the regularity of change in the thermomechanical curves undergoes significant changes. At a technical carbon concentration of 10 and 20 wt%, an area as a plateau appears on the thermomechanical curves. The most thermally stable plateau appeared for nanocomposites based on maleinized LDPE* and PP* with 20 wt% technical carbon content. New scientific approaches are presented for interpreting the discovered regularities, taking into account modern theoretical concepts of the supramolecular crystal structure of nanocomposites and the interfacial amorphous region.

Keywords: Thermomechanical curves, Crystallinity, Supramolecular structure, Derivatogram, Interfacial region, Technical carbon.

Introduction

As the technique and technology of industrial production improve, more and more stringent requirements are imposed on the quality of polymeric materials intended for use in such areas as mechanical engineering, automobile production, shipbuilding, electronics, aircraft building, military and space technology [1]. In this regard, a number of measures are being taken aimed at conducting research to improve the properties of industrial polymers by loading plasticizers, fillers, compatibilizers, stabilizers into their composition, as well as chemical modification of macromolecules with various polar monomers [2]. In recent years, there has been a significant increase in interest in the development of nanocomposite polymeric materials using nanofillers with a particle size of less than 105 nm, which can significantly affect their final properties [3, 4]. The interest in the use of nanofillers is due to the fact that the nanoparticles have a developed surface and are commensurate with the globular structures of

polymers in the melt, as a result of which there is a unique opportunity to obtain thermally stable heterogeneous “nucleation centers” [2, 5]. In this regard, many scientists began to show considerable interest in the problems associated with the preparation and investigation of polymer nanocomposites filled with special grades of technical carbon (TC) nanoparticles and nanotubes [6–8]. Interest in these investigations is due to the fact that TC-filled nanocomposites based on polyolefins have fairly good electrical conductivity and physical-mechanical properties, which opens up a promising possibility for their practical use in the electronic and electrical industries as conductors, semiconductors or antistatic agents, etc. [9]. Along with this, the literature provides very limited information on the thermal deformation characteristics of nanocomposites filled with TC based on polyolefins, the establishment of a relationship in the polymer-nanoparticle-structure-property system [10–12]. In total, all these

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circumstances create certain difficulties associated with the establishment of a systematic scientific approach to identify the first-order phase transition, as well as the temperature regions of physical states (crystalline, highly elastic and viscous-flow), which could be very useful for predicting the temperature regime of nanocomposite processing by methods extrusion and injection molding.

Based on the foregoing, the purpose of this work was, using the example of maleated polyolefin nanocomposites, to carry out the investigations of the thermal deformation characteristics of nanocomposites, to establish the role of TC nanoparticles in the process of formation of their structural features at the micro- and macro-levels, allowing, in general, to obtain fairly complete information about the nature of the change in deformation from temperatures in various physical states.

Experimental

Materials

The following initial materials were used in the course of the research:

High density polyethylene (HDPE) - brand PETİLEN YY I668 (UV) - (Turkey) is characterized by the following properties - ultimate tensile stress 31.3 MPa, elongation at break 1135%, density 965kg/m³, melting point 145°C, crystallinity 82%, melt flow index MFI = 5.6g / 10 min.

Low density polyethylene (LDPE) grade 108-14 (SOCAR-polymer company, Sumgayit city) with an average molecular weight of 125000, density of 923 kg/m³, ultimate tensile stress of 9.6 MPa, elongation at break of 360%, degree of crystallinity of 59%, MFI - 7.8 g/10 min. at a load of 5 kg.

Isotactic polypropylene (PP) grade HP500M (SOCAR-polymer company, Sumgayit city) is characterized by the following properties: ultimate tensile stress 33.0 MPa, elongation at break 30%, Vicat softening point 160°C, melting point 169°C, density 903 kg/m³, crystallinity 65%, MFI is 3.6g/10min.

Compatibilizer (PEMA) – high-density polyethylene functionalized with maleic anhydride (MA) – Exxelor PO1040 (PEMA) for modification of all grades of polyethylene and Exxelor PO1020 (PPMA) for modification of PP. The degree of MA grafting in compatibilizers is 5-6 wt%.

Technical carbon (TC) brand Printex XE 2B is produced in the USA by Orion Engineered Carbons company as nanoparticles 20 nm in size and is a highly structured amorphous carbon black. The chemical composition of the TC, carried out on an ICP MS 7700 e mass spectrometer, is as follows: V- 0.88; S- 0.53; Ni- 0.45; Fe- 0.37; Ca- 0.05; P- 0.05; Si- 0.02; Zn- 0.0068; K- 0.0039; Mo- 0.0038; Cu- 0.0035; Co- 0.0003; Cr- 0.0002; C- 97.55 wt%.

The TC particle size was determined on a Malvern Mastersizer-3000 instrument, which allows one to determine the particle size from 10 nm to 3000 μm.

Preparation of composites

Previously, it is shown in [13-15] that when studying the physical-mechanical properties of nanocomposites based on polyolefins and TC, the concentration of compatibilizers did not exceed 2.0 wt %, since at higher concentrations, a noticeable deterioration in their properties is observed. This is due to the fact that the used compatibilizers are based on low molecular weight HDPE and PP, which, at a concentration of more than 2.0 wt %, exhibit the properties of potent plasticizers that reduce strength characteristics.

In order to preparation a nanocomposite based on HDPE and LDPE and TC, the process of mixing the components of the mixture was carried out as follows: the initial HDPE or LDPE was mixed on a roller with 2.0 wt% PEMA for 7 minutes at a temperature of 150°C (for LDPE) and 170°C (for HDPE), then TC nanoparticles were loaded in the amount of 1.0, 5.0, 10 and 20 wt%. The mixture of the initial HDPE with 2.0 wt% content of PEMA will be abbreviated in the article as HDPE*. A blend of initial LDPE modified with 2.0 wt% PEMA will be abbreviated as LDPE*. Mixing of PP with PPMA was carried out at a temperature of 180°C, then TC nanoparticles were loaded in the amount of 1.0, 5.0, 10, and 20 wt%. A mixture of initial PP modified with 2.0 wt% PPMA will be abbreviated PP*.

Based on the obtained polymer nanocomposites, tablets 8 mm thick and 20 mm in diameter were pressed at a temperature of 190°C. During the cooling of the samples under the press from 190 to 50°C, the pressing pressure was constant and amounted to 90 MPa.

Characterization of the composites

The melt flow index (MFI) was determined on a MELT FLOW TESTER, CEAST MF50

rheometer (INSTRON, Italy) at a temperature of 190°C and a load of 5 kg.

Thermomechanical tests were carried out on a Kanavets instrument [10]. The deformation was measured under the condition of successive increase in the temperature of the sample at a rate of 1°C per minute. When constructing the thermomechanical curve of the polymer $\Delta = f(T)$, it is very important to cover, as far as possible, the entire temperature range of the polymer - solid (crystalline), highly elastic and viscous-flow state. Thermomechanical curves reflect the physical, physicochemical and chemical processes occurring in the polymer matrix, providing useful information about temperature transitions that are significant for polymer processing.

The derivatographic analysis of the nanocomposites was carried out on a STA 6000 synchronous thermal analyzer from Perkin Elmer company in the temperature range 20–750°C in a nitrogen gas medium.

Electron microscopic images were taken on the Leo 912 AB Omega transmission microscope.

X-ray diffraction analysis of the nanocomposites was carried out on a Rigaku Miniflex 600 instrument. The total degree of crystallinity was determined on the diffraction pattern by measuring the area under the crystalline peaks (S_{cr}) and amorphous holo (S_{am}) in a certain limited range of Bragg angles, taking into account the correction for the background, and the ratio of these areas was found. The areas were measured by the gravimetric method: by weighing the cutout areas. The total crystallinity degree (CD) was determined from the ratio:

$$CD = \frac{S_{cr}}{S_{cr} + S_{am}} \cdot 100\%$$

Results and Discussion

In the process of investigation of the thermomechanical characteristics of nanocomposites based on polyolefins* and TC, the task of the investigation was to identify the temperature ranges of transitions from one physical state to another. The term "thermomechanical properties" of polymers refers to their mechanical behavior under various temperature conditions. So, for example, it was important to find out how the concentration of TC in the composition of HDPE* affects the regularity of change in deformation with temperature. The concentration of TC in the composition of HDPE* was changed in the range of 1.0-20 wt%. The thermomechanical properties of the considered

HDPE* nanocomposites are shown in Fig 1. Analyzing the curves in this Fig, it can be seen that with an increase in the content of TC in the composition of HDPE*, a change in deformation with temperature is observed according to a certain regularity. If for the initial HDPE* the softening temperature or phase transition from solid to viscous-flow state is 136°C, then for nanocomposites with a content of TC of 1.0, 5.0, 10, 20 wt%, the value of this indicator, respectively, changes in the following sequence: 138, 139, 142 and 134°C. It follows from the data obtained that with the introduction of up to 10 wt% TC into HDPE*, an increase in the softening temperature is observed. At 20 wt% TC content, on the contrary, there is a noticeable decrease in the softening temperature to 134°C, i.e. becomes lower than HDPE*.

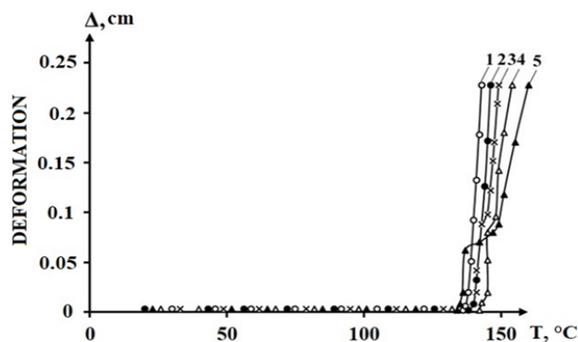


Fig. 1: Thermal deformation curves of dependence of deformation on temperature for initial HDPE*(1) and its nanocomposites with different content of TC: 2-1.0; 3-5.0; 4-10; 5-20 wt%.

There is reason to believe that polyolefins are characterized by the formation of homogeneous nucleation centers in the melt. When TC is introduced, its nanoparticles participate in the formation of heterogeneous nucleation centers in the polymer matrix melt. As a result, the growth of crystalline formations simultaneously from homogeneous and heterogeneous nucleation centers leads to the formation of a finely spherulite supramolecular structure. It should be noted that, as crystalline formations grew, another part of the nanoparticles was displaced into the interspherulitic amorphous space [6, 16, 17], contributing to an increase in its density. Apparently, this circumstance becomes one of the main steric factors hindering the formation of a long-range order in the arrangement of macrochains, simultaneously increasing the rise in the defectiveness of the crystalline phase of the nanocomposite.

For comparative analysis, the melting points of HDPE* and its nanocomposites were determined by derivatography method in a nitrogen gas medium. At the

same time, it was found that with an increase in the concentration of TC in the composition of HDPE* within 1.0, 5.0, 10 and 20 wt%, the value of the melting temperature changed in the following sequence: 148, 146, 149, 143°C. The melting temperature of the initial HDPE* was 145°C. A comparative analysis shows that the loading of TC leads mainly to an increase in the melting temperature of nanocomposites. The exception is a sample with 20 wt% TC content in the composition of HDPE*, whose melting point is 143°C, i.e. lower than that of the initial HDPE*. The obtained data of derivatographic analysis are in good agreement with the data of thermomechanical studies. According to the derivatographic analysis for HDPE*, the onset of melting occurs at a temperature of 115°, the melting peak is 145°C and the end of the melting region is 170°C. Thus, the temperature region of HDPE* melting varies within 55°C. At the same time, the softening temperature of HDPE* according to thermomechanical studies is 136°C.

Derivatographic analysis of HDPE* nanocomposite with 10 wt% TC showed that the beginning of the melting temperature range corresponds to 125°C, the melting peak corresponds to 149°C, and the end of the melting range corresponds to 160°C. In total, the melting temperature range varies within 35°C. In this case, as shown above, according to thermomechanical tests, the softening point of this nanocomposite is 142°C, i.e. it comes within the melting temperature range.

Thus, when considering the thermomechanical curves in Fig. 1, it can be argued that the results of the investigations carried out are in good agreement with the data of the derivatographic analysis. However, during investigation of thermomechanical curves in the region of a viscous-flow state, the moments are revealed that can be interpreted only on the basis of the structural features of nanocomposites. In particular, at first glance, the appearance of some anomalous temperature-dependent changes in the regularities of deformation can be seen on the thermomechanical curves of nanocomposites containing 5.0 wt% and more TC. So, for example, at a temperature of 142°C and at a deformation of 0.09 cm, nanocomposite containing 5.0 wt% TC exhibits some bends of the thermomechanical curve in the region of the viscous-flow state. This effect becomes even more noticeable as the TC content in the HDPE* composition increases. It has been established that the higher the TC content, the lower the deformation value, the formation of a plateau on the thermomechanical curve in the region of the viscous-flow state begins. In this case, the plateau is a section of the thermomechanical curve in which any deformation processes slow down or stop altogether. If for a sample with 10 wt% TC content, the process of the

appearance of a plateau on the thermomechanical curve is fixed at a deformation of 0.08 cm and a temperature of 146°C, then for a nanocomposite with 20 wt% TC this process begins at a deformation equal to 0.062 cm and a temperature of 140°C. If you pay attention to curves -3, 4 and 5 in Fig. 1, then it can be established that for nanocomposites with 5.0, 10 and 20 wt% TC content, the plateau covers the temperature range at 143-145°C, 145-148°C and 140-152°C, respectively. It follows from the obtained data that the widest plateau is observed in the nanocomposite with 20 wt% TC content, i.e. the width of the plateau increases with an increase in the TC concentration. To clarify the causes associated with the formation of a plateau, it would be appropriate to refer to the data on the determination of the MFI of nanocomposites. For example, it was found that with the introduction of 1.0, 5.0, 10, and 20 wt% TC, the MFI value decreases, respectively, in the following sequence: 5.1, 2.6, 1.1, and 0.2 g/10 minutes. It follows from the obtained data that at 20 wt% TC, the melt viscosity increases to such an extent that, in the region of the viscous-flow state, the deformation processes associated with the softening and melting of the crystal structure of the nanocomposites are significantly slowed down.

To elucidate the reasons causing such a noticeable change in the properties of nanocomposites, it seemed interesting to carry out X-ray phase analysis of its structure using the example of a nanocomposite with a 20 wt % TC content in HDPE*. Fig. 2 shows the results of X-ray diffraction analysis of the initial HDPE* and nanocomposite with 20 wt% TC content. From a comparative analysis of the diffractograms, it can be seen that a shift in the characteristic reflections of HDPE* is observed in the nanocomposite. As can be seen from this Fig, with the loading of TC, the intensity of the reflection of the initial HDPE* at $2\theta=21^{\circ}46'$ shifts to $2\theta=21^{\circ}25'$ and at $2\theta=24^{\circ}27'$ to $2\theta=23^{\circ}50'$. The shift of the characteristic reflections of HDPE* allows us to state that there is a physical interaction between the TC nanoparticles and the polymer matrix. In all likelihood, it is expressed in the fact that the developed surface of TC nanoparticles promotes adhesion and, accordingly, adsorption of HDPE* macrochains and the occurrence of orientation processes on it, followed by the formation of heterogeneous nucleation centers [17–19]. In addition, the intensity of the characteristic reflections of the nanocomposite is somewhat lower, which indicates a decrease in the degree of its crystallinity. In particular, it was found that with the loading of 20 wt% TC, the total degree of crystallinity of HDPE* decreases from 82% to 73%.

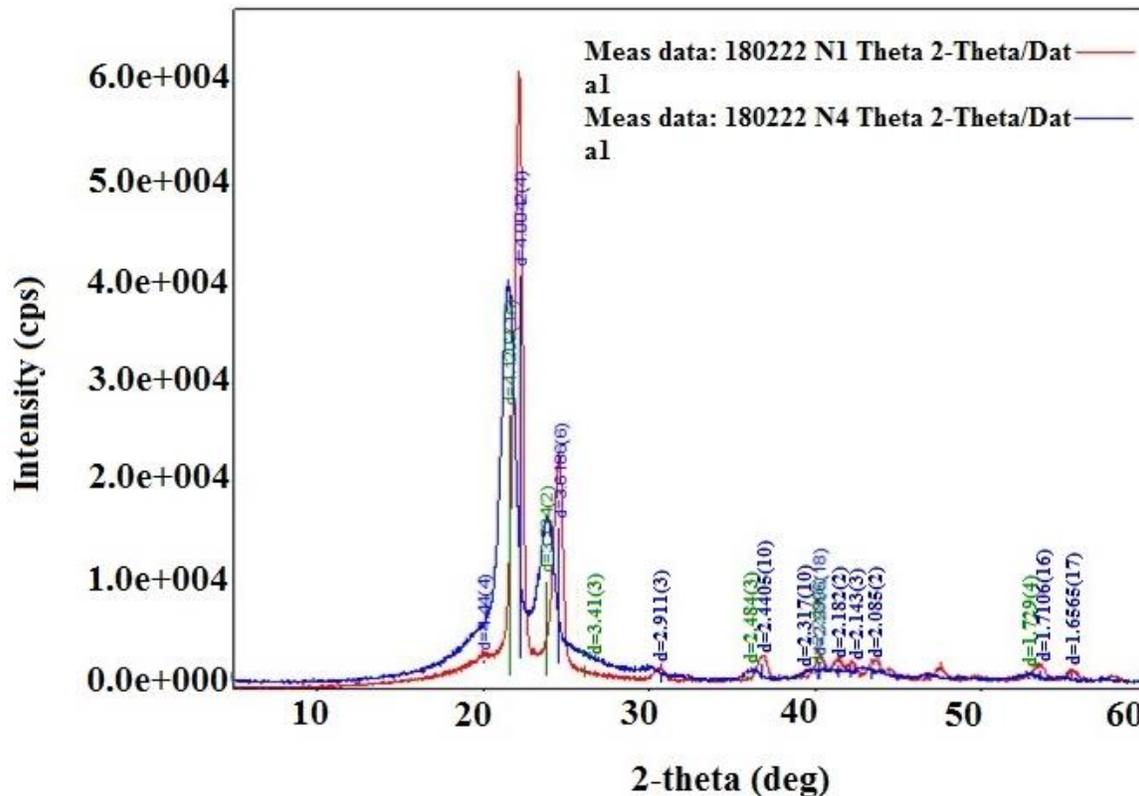


Fig. 2: X-ray diffraction patterns of the initial HDPE* (red) and HDPE*+20 wt% TC nanocomposite (blue stripe).

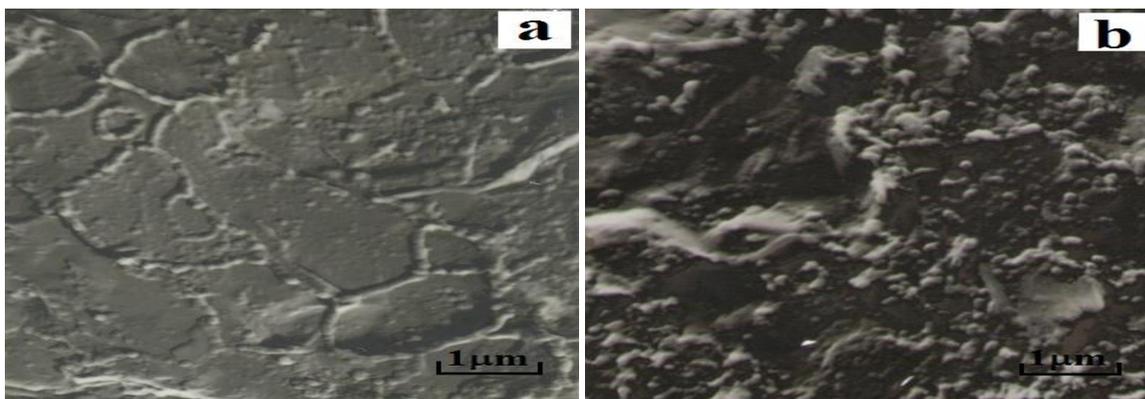


Fig. 3: Electron microscopic images of HDPE* + 5.0 wt% TC (a) and HDPE* + 20 wt% TC (b) nanocomposites. Magnification x10000.

For clarity, Fig. 3(a, b) shows electron microscopic images of nanocomposites with 5.0 and 20wt% TC content. Comparing these images, it can be seen that at 5.0wt% TC content, nanoparticles are distributed along the perimeter of spherulite formations, forming a kind of chain of nanoparticles. As can be seen from Fig. 3(b), at 20 wt% TC content in HDPE*, nanoparticles almost completely envelop and block the crystal structure of HDPE*, thereby

hindering any deformation processes. The presented electron micrographs clearly demonstrate the role of nanoparticles and their concentration in the formation of the supramolecular structure of nanocomposites.

Figs 4 and 5 show thermomechanical curves of nanocomposites based on LDPE* and PP*. Analyzing the curves in Fig. 4, it can be seen that as the TC concentration in the composition of LDPE*

increases, there is a general tendency to increase the softening temperature of the nanocomposite. Suffice it to note that when TC is introduced in an amount of 1.0, 5.0, 10 and 20 wt%, the softening point value changes, respectively, in the following sequence: 105, 111, 129 and 109°C. The initial LDPE* has a softening point of 103°C. It follows from the data obtained that with an increase in the TC content to 10 wt%, an increase in the softening temperature of nanocomposites by 26°C is observed. An exception is the nanocomposite with 20 wt% TC content, in which the softening point drops sharply to 109°C. At the same time, very unexpected results were obtained associated with anomalous changes in the thermomechanical curves of LDPE* nanocomposites containing 10 and 20 wt% TC. Comparing the thermomechanical curves in Fig. 4, it can be established that, in contrast to HDPE*, in nanocomposites based on LDPE*, the process of plateau formation proceeds at a higher temperature and in a fairly wide temperature range. Thus, in nanocomposites with 10 wt% TC, the formation of a plateau begins at a deformation of 0.09 cm and a temperature of 155°C and continues up to 178°C with a slow increase in deformation to 0.12 cm. Further, there is again a sharp increase in deformation, which is characteristic of the region of the viscous-fluid state.

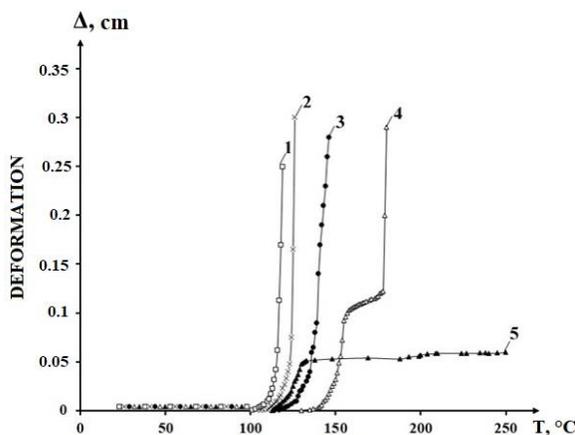


Fig. 4: Thermomechanical curves of the dependence of deformation on temperature for the initial maleized LDPE*(1) and its nanocomposites with different content of TC: 2-1.0, 3-5.0, 4-10, 5-20 wt%.

An analysis of the thermomechanical curve of the LDPE* nanocomposite with 20 wt% TC content shows that at a softening temperature of 109°C it passes from a solid to a viscous-flow state, then, at a deformation of 0.05 cm at 130°C, a very wide plateau appears, on which practically no deformation is recorded up to 250°C.

For a comparative assessment by derivatographic analysis, it was found that for the initial LDPE* and its nanocomposites with 10 and 20 wt% TC, the melting temperature changes in the following sequence: 115, 113, and 112°C, and the thermal destruction temperature: 471, 505, and 502°C. Thus, unlike nanocomposites based on HDPE*, with an increase in the TC content in LDPE*, a slight decrease in the melting temperature and a noticeable increase in the temperature of thermal degradation of nanocomposites are observed. Comparing the obtained data, it becomes obvious that TC nanoparticles have a significant effect on the process of formation of the crystal structure, the interfacial region and, accordingly, the first-order phase transition. The appearance of a plateau on the thermomechanical curve indicates the occurrence of serious changes in the supramolecular structure, which affect the formation of the crystal structure and interspherulitic region in nanocomposites.

To interpret the discovered regularities, let us turn to some known facts and possible variants of the plateau formation mechanism. In the experimental part, we have shown that the CB contains 0.53 wt% of S. Based on this, it can be assumed that the resulting plateau may be the result of a partial cross-linking of macro-chains with the participation of sulfur, followed by the formation of a characteristic region of a highly elastic state. This assumption with the formation of a spatially cross-linked structure is confirmed by data on a sharp decrease in the MFI of samples with a high content of TC. With an increase in TC in the composition of LDPE* within the limits of 1.0, 5.0, 10 wt%, the MFI of nanocomposites decreases in the following sequence: 8.1, 3.4, 1.2 g/10 minutes. For a nanocomposite with a 20 wt% TC content, the MFI value becomes equal to zero.

It can also be assumed that in LDPE*+10 wt% TC nanocomposites, the melting process itself proceeds in two stages. At the first stage, melting of spherulite formations formed on homogeneous nucleation centers takes place. The second stage ends at a relatively higher temperature and is accompanied by the melting of crystalline structures formed on the basis of heterogeneous nucleation centers, which are more resistant to thermal fluctuation decay [13, 17, 19].

And, finally, another version is that the accumulation of the main mass of TC nanoparticles in the interfacial amorphous region contributes to a significant increase in its density, as a result of which the mobility of "through" macrochains along the entire perimeter of spherulites is blocked, thereby creating

additional difficulties for melting crystalline formations [13, 17].

Then, how can one explain the appearance of such a difference in the regularities of change in the thermomechanical curves of nanocomposites based on LDPE*+20 wt% TC and HDPE*+20 wt% TC? What is the effect of the degree of crystallinity of the initial polymer matrix on the change in thermal deformation curves? As noted above, the degree of crystallinity of the initial HDPE* is 82%, and LDPE* is 59%. Based on this, it can be argued that the degree of amorphism for HDPE* is, respectively, 18%, and for LDPE* 41%. It is clear that the softening of the supramolecular structure begins with the melting of the crystalline phase of polymers. Since there is relatively more crystalline phase in HDPE*, a high degree of crystallinity is the main factor that allows maintaining the ability of the polymer matrix to soften and melt. Above, according to X-ray diffraction analysis, it was shown that the loading of 20 wt% TC leads to a decrease in the degree of HDPE* crystallinity from 82 to 73%. And since the bulk of the nanoparticles accumulate in the interfacial amorphous region, which is 27% in this nanocomposite after filling, their effect on the suppression of the sample melting process becomes minimal. In the LDPE* nanocomposite with 20 wt% TC, the bulk of the nanoparticles is also distributed in the amorphous space, which makes up 41% of the polymer matrix. This amorphous space filled with TC nanoparticles turns out to be quite sufficient to block the mobility of through macrochains and completely suppress the process of softening and melting of the crystalline phase of the nanocomposite after the formation of a plateau on the thermal deformation curve [13, 14].

In all likelihood, in the highly filled nanocomposites under consideration, the first-order phase transition, i.e. the first phase of the transition from a solid to a viscous-flow state is carried out due to the softening of crystalline formations located in the surface layer of the test sample. After the formation of a plateau in nanocomposites with 5.0 and 10 wt% TC, the second phase of the transition to a viscous-flow state in LDPE* becomes possible after the melting of crystalline formations located in areas relatively remote from the sample surface.

Based on the foregoing, it can be assumed that, first, at high concentrations of TC, the density of the interfacial amorphous phase increases sharply. Secondly, according to Fig. 2 and 3(b), the accumulation of a significant amount of nanoparticles in the amorphous region affects the decrease in the degree of crystallinity of HDPE* and, accordingly, the

increase in the amorphism of nanocomposites. Thirdly, the value of the MFI of highly filled LDPE* is practically equal to zero, which is expressed in the absence of a region of a viscous-flow state.

Similarly, the thermomechanical curves of nanocomposites based on PP* and TC were studied in a similar way, the results of the study, which are shown in Fig.5. Analyzing the curves in this Fig, one can notice that in this case, too, anomalous changes in the regularities of deformation of nanocomposites with temperature are manifested. As in the case of LDPE*, these characteristic changes in deformation with temperature appear mainly on PP* nanocomposites with 10 and 20 wt% TC. The initial PP* and nanocomposites with 1.0, 5.0, 10, and 20 wt% TC content are characterized by the softening temperature in the following sequence, respectively: 158, 160, 164, 169, and 160°C. Thermomechanical curves of PP*+10 or 20 wt% TC nanocomposites change approximately according to the same regularity as LDPE* samples with 10 or 20 wt% TC content. It can be established from a comparative analysis of the curves in Fig. 5 that for PP*+10 wt% TC sample, the softening temperature and the transition from a solid to a viscous-flow state begins at a temperature of 169°C. Then a plateau appears with a deceleration of the deformation rate in the temperature range of 178°C - 204°C. Above this temperature, the second phase of the transition to a viscous-flowing state occurs, but with a much lower deformation rate.

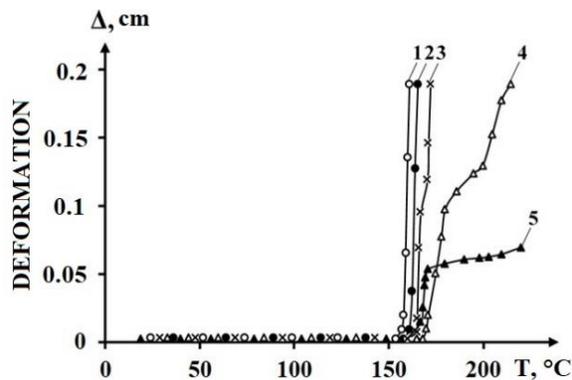


Fig. 5: Thermomechanical curves of the dependence of deformation on temperature for the initial maleized PP*(1) and its nanocomposites with different content of TC: 2-1.0, 3-5.0, 4-10, 5-20 wt%.

When the concentration of TC in PP* in an amount equal to 20 wt%, the softening process begins at a relatively low temperature equal to 160°C and the transition to a viscous-flow state continues up to a

temperature of 171°C. A further increase in temperature to 250°C leads to the appearance of a plateau with a slight change in the thermal deformation dependence of the nanocomposite. Only a slight increase in deformation is observed. The data obtained once again testify in favor of the fact that TC nanoparticles have the ability to adhesion and adsorb polyolefin macrochains on their surface, thereby significantly increasing the density and thermal stability of the interfacial region. It is this feature of the interfacial region that is one of the important criteria explaining the reasons for the formation of a plateau on thermomechanical curves. Based on the fact that PP* is characterized by a degree of crystallinity equal to 65%, which is lower than that of HDPE*, then the occurrence of a thermally deformation-resistant plateau in the PP* nanocomposite with 20 wt% TC content should be understandable.

Conclusions

The thermomechanical curves of nanocomposites based on TC and maleated polyolefins (HDPE*, LDPE* and PP*) have been studied. The concentration of TC nanoparticles varied within the limits of 1.0, 5.0, 10, and 20 wt%. It is shown that in the investigation of nanocomposites with 10 and 20 wt% TC content, anomalous changes in the regularities of thermomechanical curves have been established.

A comparative change in the degree of crystallinity of the HDPE* +20 wt% TC nanocomposite and the initial HDPE* was carried out by X-ray diffraction analysis. A decrease in the degree of crystallinity of HDPE* from 82 to 73% is shown. A shift in the characteristic reflexes of the nanocomposite was found, confirming the existence of a strong physical interaction between nanoparticles and the polymer matrix.

A derivatographic analysis of nanocomposites containing TC in HDPE* from 1.0 to 20 wt% was carried out. The melting and thermal degradation temperatures were determined. It has been established that with an increase in the concentration of TC in the composition of HDPE* within the limits of 1.0, 5.0, 10, and 20 wt%, the melting point changes in the following sequence: 148, 146, 149, 143°C. Depending on the concentration of TC, the temperature of thermal degradation changes as follows: 503, 507, 506, 503°C.

It was found that the degree of crystallinity of the polyolefin has a significant effect on the nature of

the plateau formation. At a 10 wt% TC content, the process of transition from a solid to a viscous-flowing state proceeds in two stages with the intermediate formation of a heat-resistant plateau. In LDPE* and PP* nanocomposites with 20 wt% TC, the softening temperature occurs at a relatively low temperature, at which a transition from a solid to a viscous-flowing state occurs, followed by the formation of a solid heat-resistant plateau.

New approaches to the interpretation of the deformation of nanocomposites with temperature, taking into account modern concepts of a first-order phase transition and processes occurring in the interfacial region are presented.

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