Metal-Containing Nanocomposites on the Basis of Isotactic Polypropylene and Butadiene-Nitrile Rubber

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Abstract**—** *One and two-step methods for the synthesis of saccharin-6-carboxylic acid triglyceride were studied. The reesterification reactions of 2-hydroxypropyl-1,3-bis-ethersulfoimide of this acid and glycerol with some aliphatic saccharin-6-carboxylic acid esters were carried out. The resulting products are characterized by elemental analysis and IR spectroscopy and size exclusion chromatography. It was found that when using a two-step method, the end product is obtained with the highest yield (85%). The influence of additions of nanofillers (NF) containing nanoparticles of the copper oxide, stabilized by polymer matrix of maleinized polyethylene of high pressure (MPE), obtained by mechano-chemical method on peculiarities of structure and properties of metal-containing nanocomposites on the basis of isotactic polypropylene (PP) and butadiene-nitrile rubber (BNR) by methods of X-ray phase (RPhA) and differential-thermal analyses (DTA) and scanning electron microscopy (SEM) has been investigated. It has been revealed an improvement of the strength, deformation and rheological indices and also the thermal-oxidative stability of the obtained nanocomposites, which has been apparently connected with the synergetic effect of the interaction of the zinc-containing nanoparticles with maleic groups of MPE. It has been shown that the nanocomposites on the basis of PP/BNR/HF can be processed both by pressing method and by methods of casting under pressure and extrusion, which expands the sphere of its application.*

Keywords**— *butadiene-nitrile rubber, DTA, isotactic polypropylene, metal-containing nanocomposites, nanoparticles of zinc oxide, RPhA, SEM – analyses, thermal properties.***

I. INTRODUCTION

The modern stage of development of chemistry and technology of the composition materials is largely determined by the search for ways of creation of materials with an improved complex of properties. The intensive development of the world petrochemical industry intends a constant search for new materials possessing high consumer properties, ecological safety and simplicity of processing. Such materials are not without reason the thermoplastic elastomers (TPE). The creation of TPE is a priority direction of work in the field of polymer materials science [1, 2].

The most perspective direction of preparation of new types of TPE is the mixing of elastomers with plastics with simultaneous vulcanization of the elastomer, which leads to a high degree of dispersity of the rubber phase in the materials. TPEs obtained by this method were called thermoplastic vulcanizates (TPV). A distinctive peculiarity of TPV is the combination of the properties of vulcanized rubbers during exploitation and thermoplastics in the processing. Owing to the complex of high physical-mechanical properties, wide temperature range of working capacity, lower cost of finished products, TPVs are considered one of the most perspective classes of the polymer composite materials. Their application areas are very various [3, 4].

A large number of works on TPE and TPV has been obtained with use of polypropylene (PP) as a thermoplastics, and SKEPT, natural rubber, butadiene nitrile rubber (BNC), etc. – as elastomers. In use of various fillers or compatibilizers for improvement of the compatibility, physical-mechanical and technological properties of the compositions [5-8].

The use of solid nanoparticles (NP) of various form and chemical nature as fillers of the polymer materials opens up new possibilities of modification of the latter ones, since the surface properties of the nano-sized substance are differed by high surface energy and adsorption activity. The composition materials containing NP have a high adhesive strength of the polymer matrix with NP [9].

The creation of the metal-polymer composition materials possessing specific physical-mechanical and exploitation properties: higher heat- and electrical conductivity, high magnetic susceptibility, ability to screen ionizing radiation, etc. favored the development of investigations of nano-sized and cluster metal-containing particles in polymer matrices in many ways [10, 11].

It was known that the use of nanoparticles of d-valence metals (copper, zinc, cobalt, nickel, etc.) in polymers allows obtaining principally new materials, which are widely used in radio- and optoelectronics as magnetic, electric-conducting and optical media [9-11].

In this work, we have studied the influence of small NF additives containing NP of the metal oxides on the properties of mixture TPE based on isotactic PP and BNR.

II. EXPERIMENTAL

The following materials were used in work: isotactic PP "Kaplen" (Russia) of mark 01 030 with a molecular weight ~ 2-3×10^5, polydispersity index – 4.5, MFI – 2.3-3.6 g/10 min.

BNR – butadiene nitrile copolymer of mark NB 192 HF, containing 27% of acrylonitrile, firm BSL Olefinverbund GmbH Shckopau, d=0.98g/cm^3 (Germany).

Nanoparticles (NP) of the zinc oxide (ZnO) stabilized by polymer matrix of maleinized high-pressure polyethylene manufactured of firm Olenta (Russia), obtained by a mechano-chemical method in a polymer melt, were used as NF. A content of nanoparticles – 5 mass %, size – 26±1.0 nm, degree of crystallinity – 35 ÷ 45% [12]. A ratio of components of composition (mass %): PP/BNR/NF=50/50/(0.3; 0.5; 1.0)

The nanocomposite polymer materials have been obtained by mixing of PP with BNR and zinc-containing NF on laboratory rollers at temperature 160-165°C for 15 min. For carrying out of mechanical testing, the obtained mixtures were pressed in the form of plates with a thickness of 1 mm at 190°C and a pressure of 10 MPa.

The physical-mechanical indices of the obtained compositions were determined on the device PMI-250.

The melting flow index (MFI) was determined on the device IIRT at T=230°C, load – 5.0 kg.

The X-ray phase (RPhA) of the obtained compositions has been carried out on the device “D2 Phaser” of firm Bruker (Germany).

Thermal stability of the investigated samples of thermoelastoplasts was studied on the derivatograph of mark Q-1500D of firm MOM (Hungary). The tests were carried out in the air atmosphere in the dynamical regime at heating of the samples 5 degr·min^{-1} from 20 to 500°C, weight – 100 mg, sensitivity of the channels DTA-250mcV, TG-100, DTG-1 mV.

SEM – analysis of the obtained compositions has been carried out on the device JEOL (USA).

III. RESULTS AND DISCUSSION

The nanocomposite polymer materials on the basis of PP/BNR with zinc-containing nanofiller have been obtained. A ratio of the initial components (mass %): PP/BNR/NF = 50/50/(0.3; 0.5; 1.0).

The physical-mechanical, rheological, heat-physical and thermal properties of the obtained nanocomposites have been investigated.

In Table 1 the physical-mechanical and rheological indices of the obtained nanocomposites are presented.

TABLE 1
PHYSICAL-MECHANICAL AND RHEOLOGICAL INDICES OF THE COMPOSITION MATERIALS

Composition (mass %.), PP/BNR/NF ПП/БНК/НН	Tensile strength at break, MPa	Specific elongation, %	Vicat heat stability, °C	MFI, g/10 min
50/50/0	5.04	16	87	0.089
50/50/0.3	6.65	36	125	0.127
50/50/0.5	6.94	40	120	0.135
50/50/1.0	6.51	32	115	0.287

As is seen from data of Table 1, an introduction of 0.3 –0.5 mass % of NF into composition leads to an increase of strength index from 5.04 to 6.94 MPa. An increase of concentration of NF more than 1.5 mass % leads to the decrease of the composite strength (6.51 МПа), which has been probably stipulated by aggregation of nanoparticles leading to the formation of microdefects in a volume of the polymer matrix. An increase of NF concentration from 0.3 to 0.5 mass % leads to the decrease of deformation value at break of the composite in 2.25÷2.5 times, which has been apparently connected with the synergetic effect connected with availability of zinc-containing nanoparticles in matrix of MPE containing maleic groups, the mutual influence of which favors an increase in both deformation value and strength index. The investigation of Vicat heat stability of the obtained compositions showed that an introduction of nanofiller into composition of PP/BNR leads to the increase of heat-resistance index from 87 to 127°C in introduction of 0.5 mass % of NF, a further increase of quantity of NF leads to some decrease of heat-resistance index, which has been probably stipulated by microdeficiency of the obtained composite. At the same time, an increase of content of nanofiller (0.5-1.0 mass %) favors the increase of melting flow index (MFI) to 0.155 (0.5 mass %) and 0.287(1.0 mass %) g/10 min, which evidences about improvement of composition fluidity and possibility of its processing by casting under pressure and extrusion.

Fig. 1, 2 presents the diffractograms of RPhA of the initial PP/BNR and PP/BNR with zinc-containing nanofiller. There have been shown the reflexes corresponding to PP: d_{hkl} 6.19929; 5.17135; 4.73608; 4.48713; 4.17687; 4.03424; 3.47038; 3.11297; 2.11651 Å and a halo image is given for an amorphous BNR. On the diffractogram of the sample PP/BNR/NF (Fig. 2) there are also observed reflexes characteristic for zinc-containing NP: d_{hkl} 2.46563; 2.12992; 1.50595; 1.28812 Å, which corresponds to the series of d_{hkl} of zinc oxide – ZnO according to ASTM card file. [d-Spacings (20) – 01-071-3645 (Fixed Slit Intensity) - Cu Kα1 1,54056 A. Entry Date: 11/19/2008 Last Modification Date: 01/19/2011].

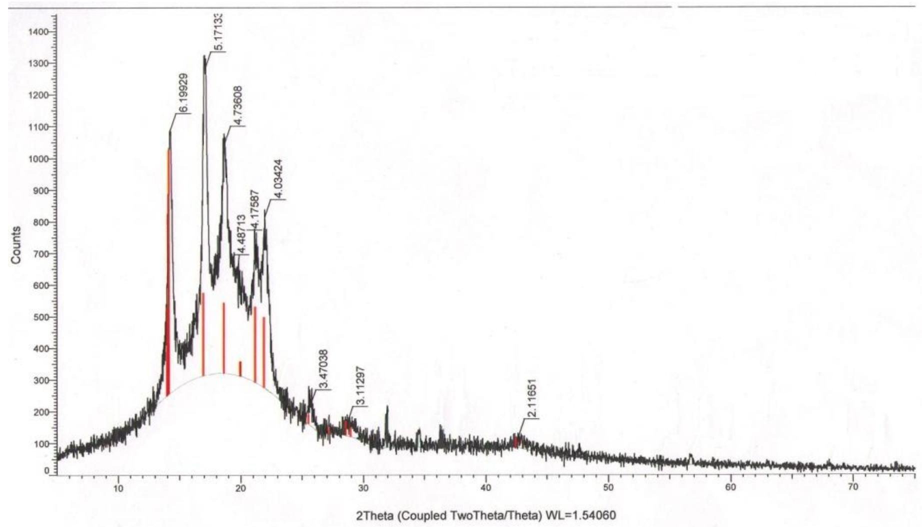

FIGURE 1: Diffractogram of PP/BNR sample

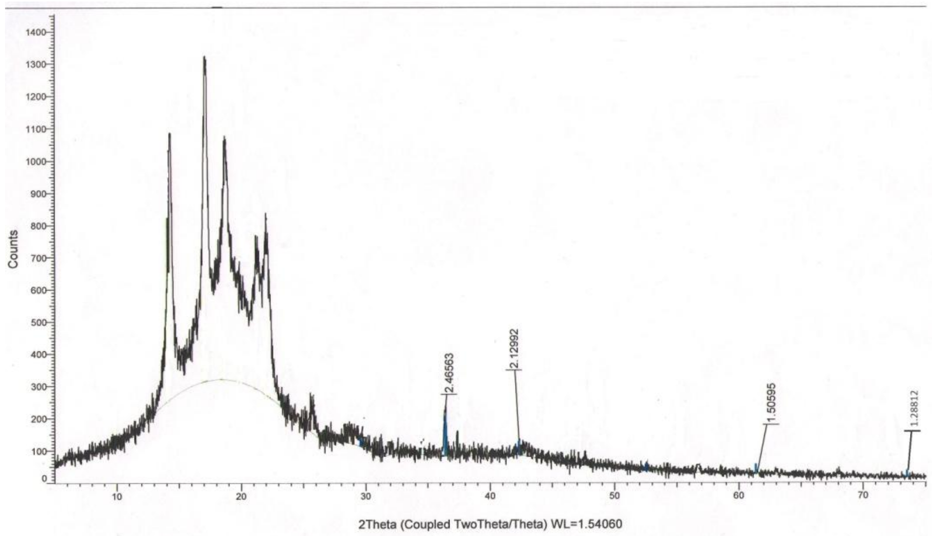

FIGURE 2: Diffractogram of PP/BNR/NF sample

Thermal stability of the investigated samples of mixed TPE on the basis of PP/BNR and PP/BNR/NF containing NF with NP of zinc oxide was estimated on activation energy (E_a) of thermal-oxidative destruction calculated by a method of double logarithm on TG curve on methodology [13], on temperature of 5% (T_5), 10% (T_{10}), 20 (T_{20}), 50% (T_{50}) decay of the investigated samples of TPE and also on their half-decay time – $\tau_{1/2}$. The data obtained as a result of derivatographic investigations are presented in Table 2.

TABLE 2
THERMAL PROPERTIES OF THE INVESTIGATED SAMPLES OF TPE

Composition (mass %.) of PP/BNR/NF	M.p., °C	T_5, °C	T_{10}, °C	T_{20}, °C	T_{50}, °C	$\tau_{1/2}$, min.	E_a, kJ·mol^{-1}
50/50/0	150	210	225	250	300	62.8	124.48
50/50/0.3	150	240	260	305	370	75.1	186.32
50/50/0.5	150	250	270	315	380	80.3	204.77
50/50/1.0	150	235	255	300	365	72.4	172.45

As can be seen from the data in Table 2, an introduction of HF containing NP of the copper oxide into the composition of mixed thermoelastoplasts favors the considerable increase of decay temperature of the samples: T_5 at 30-40°C, T_{10} at 35-45°C, T_{20} at 55-65°C, T_{50} at 70-80°C; half-decay time $\tau_{1/2,}$ is increased from 62.8 to 80.3 min., and activation energy (E_a) of decay of thermal-oxidative destruction of the obtained nanocomposites is increased by 52-80 kJ/mol, while T_m is maintained on the level 150°C. The derivatographic investigations showed that an introduction of HF containing NP of the zinc oxide into the composition of mixed thermoelastoplasts favors the improvement of thermal-oxidative stability of the obtained nanocomposites.

The numerous experimental data on mechanical, strength, relaxation and other properties of polymer-polymer and polymer-filler mixtures are explained within the framework of the concepts of the availability of interphase layer [14].

The permolecular structure of the polymer (size of spherulites, degree of crystallinity, availability of C=O groups and various branches, etc.) and the interphase interaction at the interface influences noticeably on properties of the polymer composites.

The metal-containing nanoparticles used in this work, being located at the interface of the interphase layer of the structural elements of PP, BNR and MPE favor the formation of composition of heterogeneous nucleation centers in a melt, which in the process of stepwise cooling of the nanocomposite favor the increase in crystallization centers, leading to an improvement in the crystallization process and the formation of a relatively fine-spherolite structure on the whole.

SEM analysis of the obtained composites has been carried out (Fig.3, 4).

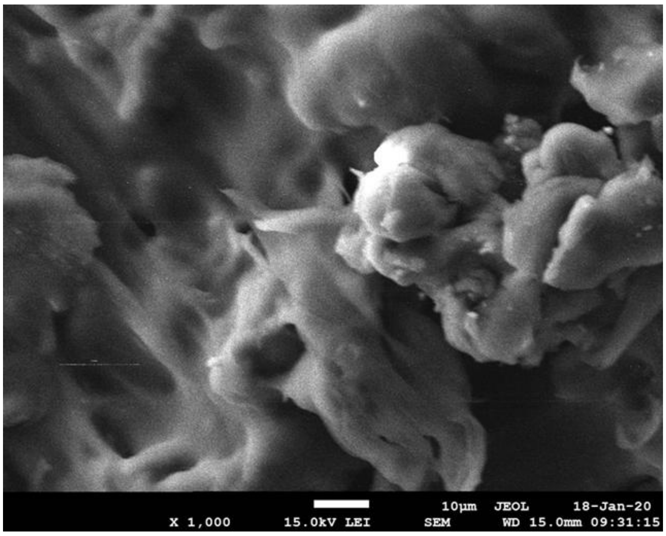

FIGURE 3. MICROPHOTOGRAPH OF PP/BNR SAMPLE

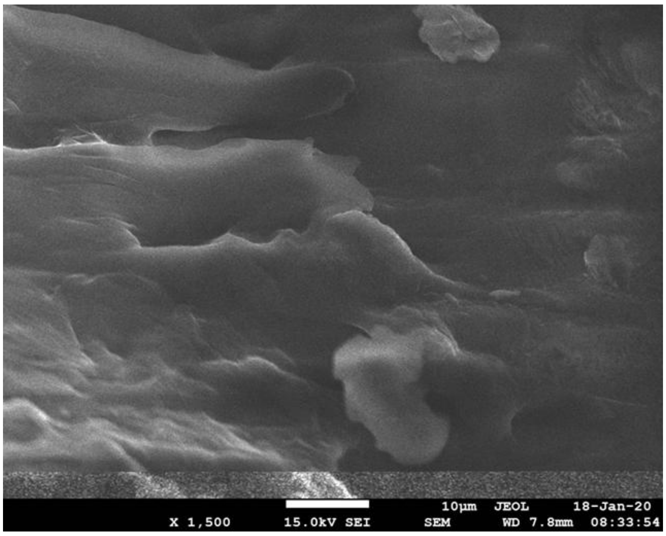

FIGURE 4. MICROPHOTOGRAPH OF PP/BNR/NF

In Fig.3, a micrography of the PP/BNR sample is presented. It is seen that the structure of the composite is quite loose with large shapeless formations. An introduction of nanofiller into the PP/BNR composition favors the formation of a fine-spherulite layered structure, which leads to an increase in the fluidity of the nanocomposite (Fig.4).

SEM-analysis of the obtained nanocomposites showed that small amounts of nanofillers (0.3 – 0.5 mass %) introduced into the polymer, obviously play the role of structure-forming agents – artificial nuclei of crystallization, which favors the appearance of a fine-spherulite layered structure in the polymer, characterized by improved physical-mechanical, rheological and thermal properties of the obtained nanocomposite [15, C.80,328].

IV. CONCLUSION

The influence of nanofiller containing nanoparticles of the zinc oxide stabilized by matrix of maleinized polyethylene (MPE), obtained by mechano-chemical method on properties of composites on the basis of PP/BNR has been investigated

The RPhA diffractograms confirm the availability of the zinc oxide nanoparticles in the composition of composites on the basis of PP/BNR.

It has been revealed the improvement of the strength, deformation and rheological indices and also the thermal-oxidative stability of the obtained nanocomposites, which has been apparently connected with the synergetic effect of the interaction of the zinc-containing nanoparticles with maleic groups of MPE.

It has been shown that the nanocomposites on the basis of PP/BNR can be processed both by pressing method and by methods of casting under pressure and extrusion.

It has been shown the prospectivity of use of the nanofiller containing zinc oxide NP, stabilized by a matrix of maleinized polyethylene, obtained by a mechano-chemical method as an additive to PP/BNR, which favors the creation of a fine-crystalline structure of the composition, in connection with which its properties are improved and thereby the areas of application of the obtained nanocomposite is expanded.

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