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The modification of polyolefin compositions based on thermoplastics

Influence of the nature and the behavior of nanofillers and microfillers on rheological and physico-mechanical properties of compositions on the basis of a polyolefin thermoplastic elastomer (ethylene-octene block copolymer) is studied. It is shown that modifying of a thermoplastic elastomer with nano- and microparticles of various chemical nature influences the structure and physico-mechanical properties of compositions: increases tensile strength, tear resistance, fatigue endurance at repetitive stretching, Shore A hardness.
Keywords: block copolymers, nanofillers, microfillers, rheological properties, physico-mechanical properties.

Modyfikacja kompozycji poliolefinowych opartych na termoplastach

Badano wpływ charakteru chemicznego i zachowania się nano- i mikronapełniaczy na właściwości reologiczne, fizyczne i mechaniczne kompozycji na podstawie poliolefinowego elastomeru termoplastycznego (kopolimeru blokowego etylenowo-oktenowego). Wykazano, że modyfikowanie elastomeru termoplastycznego nano- i mikrocząstkami różnej natury chemicznej wpływa na strukturę oraz właściwości fizycznych i mechanicznych kompozycji: zwiększa wytrzymałość na rozciąganie i na rozdzieranie, wytrzymałość zmęczeniową przy wielokrotnym rozciąganiu, twardość Shore'a A.
Słowa kluczowe: kopolimery blokowe, nanonapełniacze, mikronapełniacze, właściwości reologiczne, właściwości fizyczne i mechaniczne.

1. Introduction

The main allowances of change of physico-mechanical characteristics of polymeric materials consist in their purposeful modification and therefore, creation of the polymeric materials having a set of the improved or new properties.

One of the effective ways of regulation of composites rheology of is the introduction in the structure of a composite of the modifying additives of nanofillers and microfillers. From the point of view of polymeric materials science in case of the choice of the nanofiller it is necessary to consider availability of industrial production of the last in amounts necessary for real practical use.

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2. Experimental part

The purpose of this work was to study the influence of nature and the maintenance of nanofillers and microfillers on rheological and physico-mechanical properties of compositions on the basis of a polyolefin thermoplastic elastomer (TPE). To research polyolefin TPE, the ethylene-octene block copolymer (35 wt. % of elastic blocks) was chosen.

Physical characteristics of nano- and microfillers are given in Table 1.

As nanomodifiers were chosen:
- Technical carbon P-234;
- White soot BS-100.

As dispersed fillers were chosen:
- TRPN talc;
- GE-1 graphite.

Polymeric nanocomposites can be received by three main methods: solution, fusion, and in the course of polymer synthesis. In this work at producing polymeric nanocomposites the obtaining method by fusion was used.

Model mixtures were made in a laboratory internal mixer of periodic action at temperatures 120–150 °C, with a frequency of a rotor rotation 40–100 rpm. Samples for studies were formed on a molding machine KuASY 170/55. The uniformity of distribution of modifiers in a polymeric matrix was studied by means of the scanning electronic microscopy (SEM).

Physico-mechanical indicators of the thermoplastic elastomer were determined by GOST techniques established on these indicators: nominal tensile strength and relative elongation at break in accordance with GOST 270-75; tear resistance in accordance with GOST 262-93; Shore A hardness in accordance with GOST 263-75; melt flow index in accordance with GOST 11645-73.

The key stage of polymeric compositions technologies is distribution of components in a polymeric matrix. Those that are more effectively carried out at this stage, with bigger reliability can expect coincidence of properties of the polymeric compositions which are theoretically predicted by the experimentally received results. From this point of view the research of the factors influencing rheological and physico-mechanical properties of composition are of considerable practical interest.

3. Results and discussion

Physico-mechanical indicators of a thermoplastic elastomer are provided in Table 2.

According to Gianneli's works [1] process for generation of a nanocomposite proceed through a number of intermediate stages (Fig. 1).

At the first stage there is a formation of a tactoid — polymer surrounds nanomodifier agglomerates. At the second stage there is a penetration of polymer into interlaminar space of associates of the nanofiller, therefore there is a separation of layers to 2–3 nanometers

Table 1. Physical characteristics of nanofillers and microfillers
Tabela 1. Właściwości fizyczne nano- i mikronapełniaczy

Modifier	Size of particles	Specific adsorptive surface, m^2/g
Technical carbon P-234	29–32 nm	90
White soot BS-100	23–34 nm	85
GE-1 graphite	0.1–100 μm	77
TRPN talc	5–40 μm	17

Table 2. Physico-mechanical indicators of a thermoplastic elastomer
Tabela 2. Wskaźniki fizyczne i mechaniczne elastomeru termoplastycznego

Indicators	TPE of m 8420
Content of the elastic block (octen), wt. %	20
Melting point, °C	67
Melt flow index at 190 °C, freight of 2.16 kg, g / 10 minutes	2.6
Viscosity according to Mooney at temperature 120 °C	10.0
Density, kg/m^3	900
Shore A hardness, units	94
Nominal tensile strength, MPa	24.8
Relative elongation at break, %	730

[2]. At the third stage there is a partial stratification and a disorientation of layers of the nanofiller. At the last stage – their peeling off. Actually, at the received polymeric nanocomposites there can be all specified structures, it depends on the degree of homogenization of the nanofiller in a polymeric matrix. The peeling structure is the result of a very high distribution degree. Besides the nanofiller and little dispergating amount of agglomerates of the nanofiller at a polymeric matrix, it is possible that is confirmed by method of the scanning electronic microscopy (Fig. 2–4).

At reduction of particles of white soot BS-100 in TPE to 3–5 pts. wt. their best distribution of a matrix (Fig. 3) is reached. The smooth surface of a composite indicates lack of large agglomerates of particles of the filler, its rather homogeneous structure.

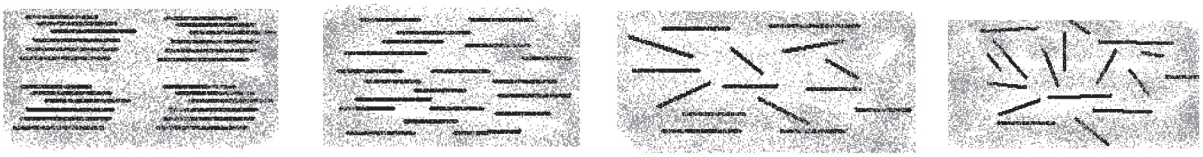

Fig. 1. Formation pattern of a polymeric nanocomposite
Rys. 1. Schemat formowania nanokompozytu polimerowego

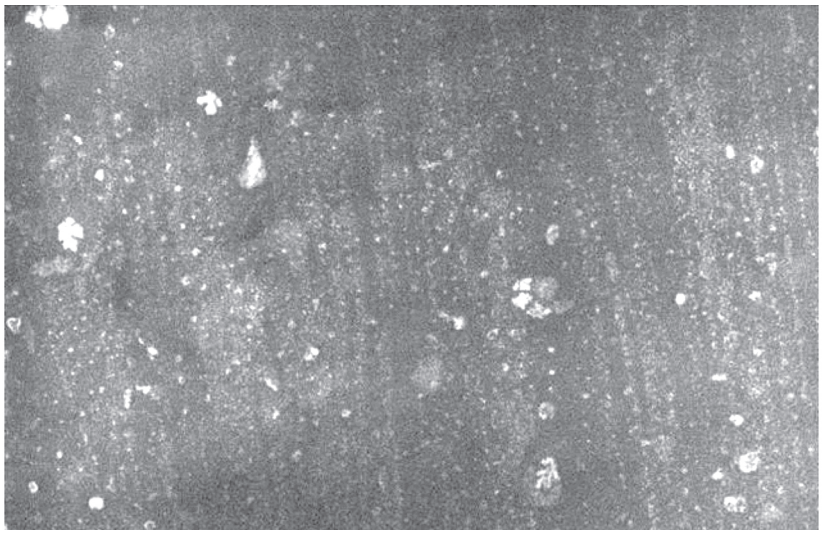

Fig. 2. SEM image of structure of TPE containing 10 pts. wt. of BS-100
Rys. 2. Obraz SEM struktury TPE zawierającego 10 cz. mas. BS-100

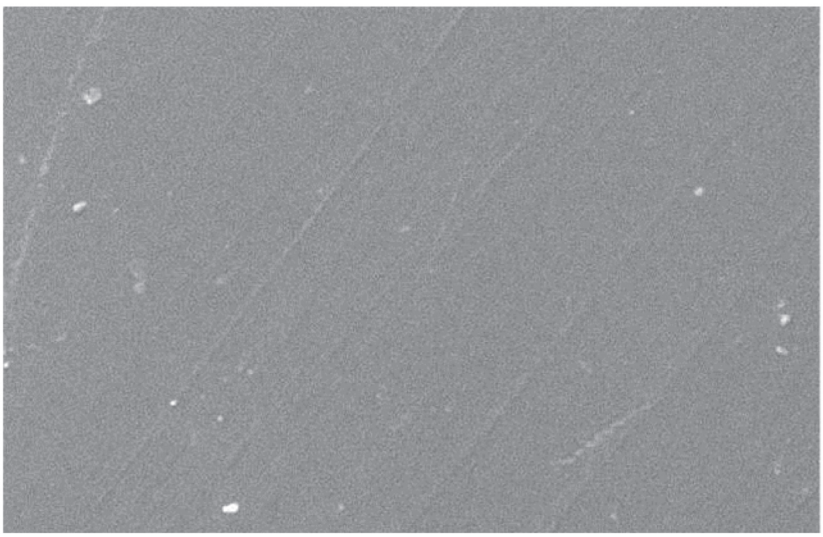

Fig. 3. SEM image of structure of TPE containing 3 pts. wt. of BS-100
Rys. 3. Obraz SEM struktury TPE zawierającego 3 cz. mas. BS-100

Distribution of talc in a polymeric matrix is shown on Fig. 4a, b).

a)

b)

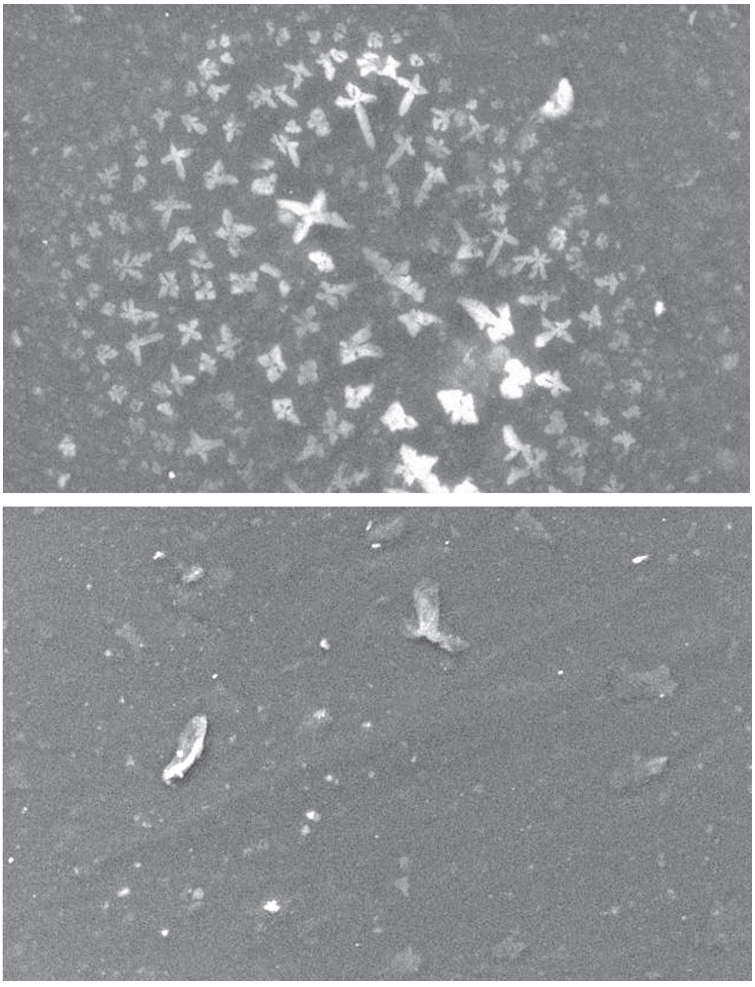

Fig. 4. SEM image of structure of TPE containing: a) 10 pts. wt. of TRPN talc.; b) 5 pts. wt. of TRPN talc
Rys. 4. Obraz SEM próbki TPE zawierającej: a) 10 cz. mas. talku TRPN; b) 5 cz. mas. talku TRPN

Table 3. Physico-mechanical characteristics of compositions on the basis of TPE with nanomodifiers
Tabela 3. Właściwości fizyczne i mechaniczne kompozycji na podstawie TPE z nanonapełniaczami

Indicators	TPE	Content of fillers at 100 pts. wt. of TPE							
		GE-1 graphite				TRPN talc			
		1	3	5	10	1	3	5	10
Melt flow index at temperature 190 °C, freight of 2.16 kg, g / 10 minutes	2.6	2.43	2.42	2.4	2.38	2.5	2.47	2.44	2.4
Density, kg/m^3	900	900	910	910	920	900	910	910	920
Shore A hardness, units	94	95	97	97	98	94	96	96	96
Nominal tensile strength, MPa	24.8	24.0	25.5	26.0	24.0	24.8	24.9	24.9	24.8
Nominal tension, MPa, at elongation:									
100%	6.0	6.4	6.6	6.0	6.0	6.0	6.0	6.0	6.0
200%	6.1	6.8	6.9	6.1	6.1	6.1	6.1	6.1	6.1
300%	6.6	7.0	7.3	6.6	6.6	6.6	6.6	6.6	6.6
400%	7.9	8.8	8.8	7.9	7.9	7.9	7.9	7.9	7.9
500%	10.2	10.6	11.2	11.1	10.4	10.3	10.4	10.5	10.5
Relative elongation at break, %	730	750	790	800	740	740	745	750	750
Viscosity according to Mooney at temperature 120°C	10	11	13	13	13	10	11	11	11
Tear resistance, N/mm	71	73	75	76	76	72	73	73	73
Wear endurance at repeated stretching for 150%, one thousand a cycle	270	520	560	620	600	320	320	310	310

Table 4. Physico-mechanical characteristics of compositions on the basis of TPE with microfillers
Tabela 4. Właściwości fizyczne i mechaniczne kompozycji na podstawie TPE z mikronapełniaczami

Indicators	TPE	Content of modifiers at 100 pts. wt. of TPE							
		BS-100				Technical carbon P-234			
		1	3	5	10	1	3	5	10
Melt flow index at temperature 190°C, freight of 2.16 kg, g / 10 minutes	2.6	2.47	2.45	2.4	2.36	2.4	2.38	2.2	1.92
Density, kg/m^3	900	900	910	910	920	900	910	910	920
Shore A hardness, units	94	95	96	96	97	97	98	98	98
Nominal tensile strength, MPa	24.8	24.7	25.0	25.4	24.8	25.0	25.6	26.0	24.9
Nominal tension, MPa, at elongation:									
100%	6.0	6.9	7.0	6.8	6.3	6.6	6.7	7.1	6.2
200%	6.1	6.9	7.2	7.1	6.5	6.9	7.2	7.4	6.7
300%	6.6	7.4	7.7	7.8	6.9	7.5	8.0	8.2	7.2
400%	7.9	8.6	8.9	9.0	8.4	9.0	9.5	9.8	9.8
500%	10.2	11.2	11.5	11.4	10.9	11.9	12.5	13.2	11.6
Relative elongation at break, %	730	720	790	800	740	760	790	810	750
Viscosity according to Mooney at temperature 120 °C	10	11	11	12	13	12	12	12	13
Tear resistance, N/mm	74	75	76	76	75	75	77	82	82
Fatigue endurance at repeated stretching for 150%, one thousand a cycle	270	280	295	240	170	290	315	230	150

The results of the research of physico-mechanical properties of composites are provided in Tables 3 and 4. The analysis of the obtained data shows that for the majority of TPE-composites their tensile strength increases in case of content of the modifier to 5 pts. wt.; in case of further increase to 10 pts. wt. it decreases. Increase in tensile strength is determined by intermolecular interactions of the particles of fillers which are well distributed in a matrix with macromolecules of TPE. In case of the overestimated amount of particles of fillers (10 pts. wt.) these intermolecular interactions aren't implemented because of agglomeration of particles, and tensile strength of the composite is equal to tensile strength of unmodified TPE.

The same dependency with a maximum in for 5 pts. wt. for all fillers is observed for nominal tension when samples were elongated for 100–500%. It confirms strengthening of intermolecular interactions in the modified composites in comparison with unmodified TPE in case of particles 1, 3 and 5 pts. wt.

Tear resistance also increases with the growth of intermolecular interactions in composites, therefore the tendency of increase in this indicator with growth of content of all modifiers in TPE matrix is also traced. On chained structures of fillers macromolecules TPE approach each other. Intermolecular interactions amplify that interferes with distribution of a cut. At the same time wear endurance in repeated stretching (in thousands of cycles) when entering nanoparticles of BS-100 and especially P-234 decreases by 150% since considerable intermolecular interactions interfere relaxations of tension in cycles loading – unloading that accelerates growth of microcracks in these composites of subjects more, than the dosage of nanoparticles is higher. On the contrary, larger particles of graphite (to 100 microns) and talc (to 40 microns) promote a relaxation of internal tension in composites, slow down formation and growth of microcracks and increase wear endurance in case of repeated stretching. Particles of graphite have

lamellar structure with a hexagonal form of crystals. The layers which are at distance ~ 0.34 nanometers from each other are connected among by weak van der Waals forces and under the influence of external acquiring mobility, i.e. are displaced from each other. Therefore particles of graphite perform function of internal lubricant.

The micro- and nanomodifying particles complicate a little reprocessing of composites in comparison with TPE. The fusion index decreases from 2.6 to 2.38 g / 10 minutes for grafite-and the talc-containing composites and to 2.36 to 1,92 g / 10 minutes for the composites containing the 0.10 wt. BS-100 and P-234. This results from the fact that though in fusion of composites at a temperature of 190 °C intermolecular relations are generally destroyed, however micro- and nanoparticles complicate sliding of macromolecules TPE and the speed of current fusions of composites are slowed down.

About strengthening of intermolecular interactions in the modified TPE composites, especially nanoparticles of BS-100 and P-234, and rapprochement of macromolecules TPE increase the density of materials since density of the modifying additives low (700–1800 kg/m^3, density of TPE of 900 kg/m^3) and the additive scheme TPE + the modifier doesn't work testifies.

Hardness on Blinders A significantly increases at introduction to TPE of microparticles of GE-1 graphite, TRNP talc and especially nanoparticles of BS-100 and P-234. It can also be explained with denser structure of composites in comparison with TPE.

4. Conclusions

Thus, modifying TPE micro- and nanoparticles of various chemical nature, it is possible to regulate its supramolecular structure and behavior in the field of mechanical forces. Nanoparticles of technical carbon and white soot in dosages 1–5 pts. wt. increase tensile strength and stability to a large extent to composites break due to strengthening of intermolecular interactions in them and consolidation of materials. Microparticles of talc and especially graphite, performing function of structural softener, increase a relaxation of internal tension at dynamic loadings, slow down formation and growth of microcracks, increase number of cycles before destruction.

References

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