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**THE INFLUENCE OF MASTERBATCHES OF FILLERS
AND STABILIZERS ON POLYETHYLENE'S THERMOSTABILITY**

The article presents the influence of joint and separate introduction of fillers (ADDITIVE 13169, TALC MB, EFPE 1001, VC PE 175) and stabilizers (RA10) masterbatches on the thermal aging of polyethylene's composites. It was estimated the thermal stability of polyethylene compositions by determining dynamics change of strength properties during thermal aging. The activation energy of thermal oxidative degradation of polyethylene compositions was calculated. The content of carbonyl groups in the IR spectra was determined. Compositions with high thermal stability containing masterbatches chalk (VC PE 175) and talc (TALC MB) and masterbatch stabilizer PA10 were developed.

Key words: masterbatch, stabilizer, filler, thermostability, polyethylene, heat aging, polymer composite material.

Introduction. Currently, composite materials based on polymers are widely used. Such materials have a number of advantages in comparison with unfilled plastics. They combine several components with specific properties, and their joint action is reflected in the synergetic effect [1]. However, the polymeric materials as well as pure polymers are affected by various external factors; e.g. temperature, sunlight, radiation, air oxygen. Therefore there is a need in stabilization of such composites. The content and stabilization of polymers processes are well studied separately. When creating compositions containing two or more components, sometimes the products properties deteriorate due to possible antagonism phenomena [2–10]. Previously we have studied the mutual influence of fine-dispersed fillers and stabilizers in their joint introduction to the polymer matrix [11]. The present work continues the series of studies on the subject.

Main part. The aim of this work was to study the effect of industrial masterbatches fillers and stabilizers in the separate and joint use on the thermal stability of compositions of polyethylene (PE).

The use of masterbatches fillers and stabilizers compared to the use of additives in powder form has several advantages: uniform distribution of the additives in the polymer matrix, no additives losses as a result of shedding powder in the forming equipment, little equipment weariness, no agglomerates of filler particles, leading to possible fault articles, etc.

In this work, we used the following masterbatches fillers:

- granular talc filler masterbatch ADDITIVE 13169 by “Cromex” company (Brazil): base-polymer – polyethylene, maximum temperature resistance 300°C, non-toxic, talc contents – 60 wt %;
- talc filler masterbatch MB TALC “Prayag-Polytech” company (India): base-polymer – polyethylene, maximum temperature resistance 280°C, high dispersion, non-toxic, talc contents – 60 wt %;
- chalk filler masterbatch EFPE 1001 E-Filler (Europlast, Vietnam): base-polymer – polyethylene,

non-toxic, calcium carbonate contents 75 wt %, melting point – 110°C;

– chalk filler masterbatch VC PE 175 E-Filler (Europlast, Vietnam): base-polymer – polyethylene, non-toxic, calcium carbonate contents 75 wt %.

Granulated filler masterbatch PA10 produced by JSC “Globalcolor” (Russia) was used to stabilize the compositions: thermal stability at 200°C – not less than 5 min, the heat stabilizers contents 10 wt %. 3 wt % of the stabilizer masterbatch was introduced to the composition.

It should be noted that the exact composition of fillers and stabilizers masterbatches is a commercial secret of the manufacturers, and in addition to the carrier polymer and the main additives they may contain different compounds that improve the distribution of the material and external appearance of products.

IR-spectroscopy was used to assess tentatively the masterbatches composition. Fig. 1 presents the IR spectrum of the stabilizer RA10. There were fluctuations of the hydroxyl groups in the area 3,600–3,650 cm^{-1} , as well as fluctuations in the area 1,080–1,150 cm^{-1} , typical for phenols. The absorption bands in the spectrum area 2,412 and 2,289 cm^{-1} determine the valence bonds PH fluctuations, the absorption band in 2,662 cm^{-1} belongs to valence fluctuations of the group of ROON. Absorption bands in 772, 642, and 723 cm^{-1} belong to the deformation bonds fluctuations at $\text{C}_{\text{ar}}\text{--H}$. Thus, we can assume that the stabilizer PA10 is a mixture of phenolic and phosphate stabilizers.

Investigation of PA10 with energy dispersive x-ray analysis (Fig. 2) allowed us to detect Calcium (0.10%) and Nickel (0.11%), which might be due to the dispersing or slipping agents [12].

Samples for testing were obtained by molding under pressure at molding machine BOY 22A (Dr. Boy, Germany). Test samples of type 2 (paddle, GOST 11262-80) were performed according to GOST 11262-80 on the tensometre T2020 DC10 SH (AlphaTechnologies UK, USA). There were 5 samples in each test.

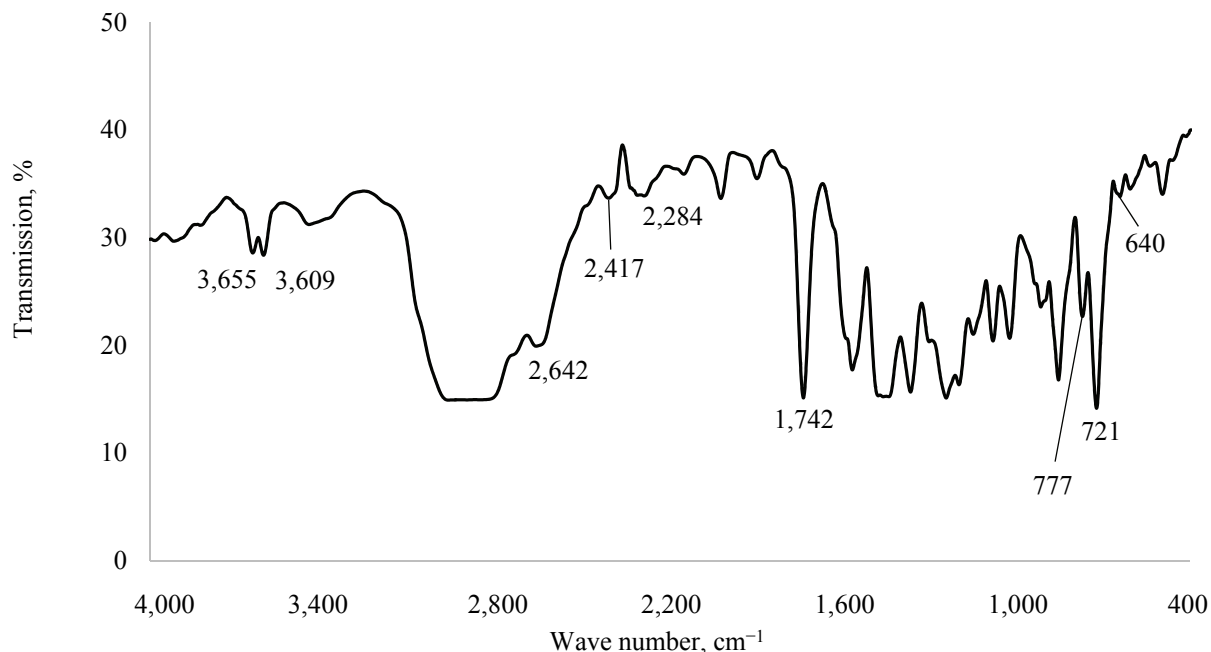


Fig. 1. The IR spectrum of the concentrate stabilizer PA10

Accelerated thermal aging of samples was conducted in an oven in air at 100°C. Resistance to increased temperatures was estimated by indicators change of relative elongation at break and tensile strength due to thermal aging. The exposure time of the samples in an oven was 150 and 300 h. The samples conditioning according to GOST 12423-66 was carried out for 6 hours at $(23 \pm 1)^\circ\text{C}$ to determine deformation and strength characteristics. There were 10 samples in each test. Calculation of activation energy of thermo-oxidative degradation of the compositions was carried out according to

the method [13] along the curves of TGA designed at TGA/DSCI (MettlerToledo, Switzerland). IR spectroscopy (Nexus ESP, ThermoNicolet, USA) was used to identify compounds.

An important parameter in determining the quality of polymeric composites is uniform distribution of the fillers and stabilizers in the polymer matrix. The agglomerates of filler particles resulting from poor dispersion lead to defective areas in the composite structure, concentration stress and contribute to the deterioration of deformation and strength properties of materials.

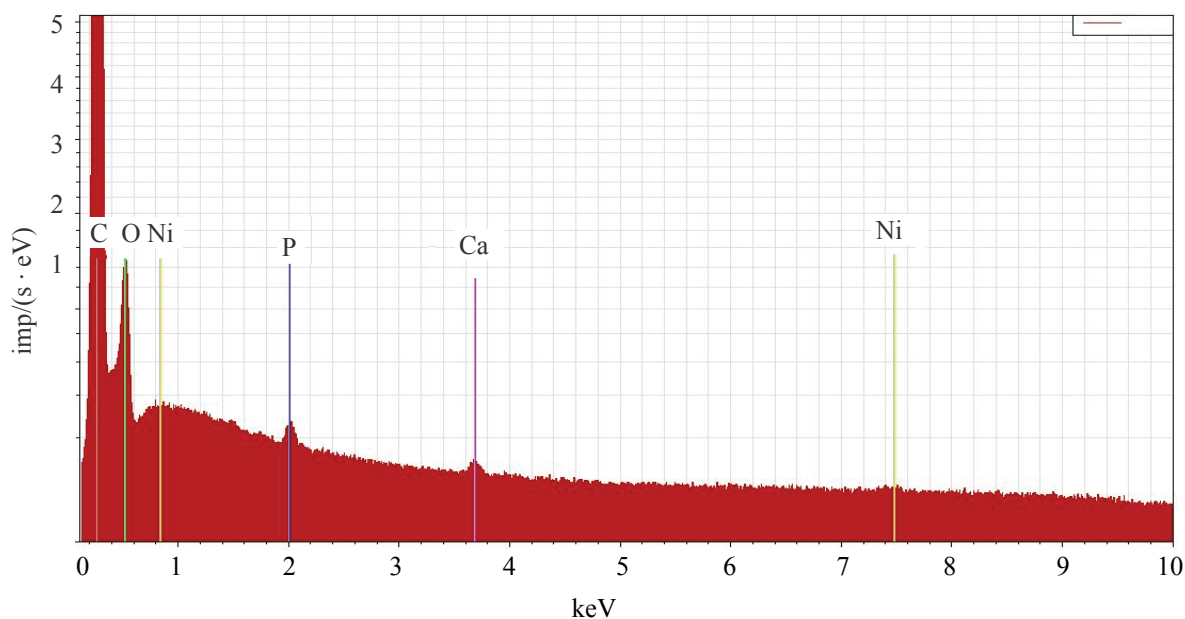


Fig. 2. X-ray analysis of the stabilizer masterbatch PA10

The uniformity of distribution of filler particles in the polymer matrix was evaluated with electron microscope. Fig. 3 presents the images obtained for PE containing 10 wt % VC PE 175. Fig. 3 shows a uniform distribution of the filler, absence of particles agglomerates in the composite; it is due to a good distribution of the masterbatch in the polymer.



Fig. 3. An image of the surface of PE, containing 10 wt % filler VC PE 175 (magnification – 250 times)

The results of the study of the compositions stability to heat aging, depending on the exposure duration are presented in Table 1.

For unstabilized PE after 300 h ageing the values of elongation are reduced up to 70%, the use of

masterbatch thermostabilizer can slow the process of degradation, resulting in maintaining the properties at 79%.

With increasing the aging time from 0 to 150 hours there is a gradual increase in the tensile strength for all studied compositions that is associated with the predominant development of crosslinking processes over degradation processes. With further increasing the aging time up to 300 hours durability is reduced, which testifies the active development of destructive processes.

From the literature [1] it is known that the introduction of dispersed fillers in relatively small amounts (up to 10 wt %), contributes to maintaining or even some increase of strength polymeric material. It is also known that chalk in the amount up to 20 wt % is introduced into the polyolefins, in particular polypropylene, that is used for plastic furniture production [14]. Therefore, in this paper, the used polymer compositions were with 10 and 20 wt % filling degree in terms of pure filler. The reduction of properties of compositions containing EFPE 1001 and 13169 ADDITIVE (10 wt %) is the most intense. With increasing filling degree of compositions up to 20 wt % the intensity of the oxidative processes increases if compared to pure polyethylene. The most intense process of aging is with the use of filler ADDITIVE 13169.

Table 1

The change of deformation and strength properties of the composites as a result of their heat aging

Filler	Concentration, wt %	Stabilizer	ε , %			σ , MPa		
			Aging time, h					
			0	150	300	0	150	300
Without filler	–	–	97.3	77	70	11	14.1	13.2
		3% PA10	91.6	94	79	10.57	13.42	12.7
TALC MB	10	–	95.6	84	80	11.86	13.04	12.4
		3% PA10	103.6	98.2	98	11.44	12.54	12.04
	20	–	90	74	71	12.4	12.8	12
		3% PA10	95	84.4	87.2	12.06	12.92	12.26
ADDITIVE 13169	10	–	88	83.2	62	12.08	13.38	11.96
		3% PA10	102	97.6	100	12.3	12.9	12
	20	–	82	51	31	12.42	12.6	12.2
		3% PA10	85	80.8	62	9.5	13.25	12.7
EFPE 1001	10	–	84.4	70	55.3	12.86	13.75	11.3
		3% PA10	87	88	79.6	11.4	11.82	12.48
	20	–	84.7	73.2	52	12.6	13.02	11.28
		3% PA10	80.4	78.5	70	11.76	12.8	10.86
VC PE 175	10	–	88	84	80	10.6	13.1	12.2
		3% PA10	88.5	93	84	11.08	13.26	12.3
	20	–	80	70	55	10.52	13.56	11.44
		3% PA10	80.8	77.6	76	10.3	13.18	12.44
TALC MB + VC PE 175	5 + 5	–	94.8	88	89.2	12.71	13.48	12.36
		3% PA10	95	92	90	12.42	12.72	12.4
TALC MB + EFPE 1001	5 + 5	–	96.4	87	86.8	12.3	12.7	11.68
		3% PA10	100.4	85.6	86.4	12	12.5	11.9

Thus, with increasing degree of the filling composites, the intensity of oxidizing processes increases, which is reflected in strength and elongation decrease.

When filler and stabilizer are introduced together, there may be either the mutual reinforcing effect, or a reversed effect that was noted in our previous publication [11]. However, the earlier studies were performed with the use of powdery stabilizers and fillers. In production in most cases masterbatches are added in convenient technological form of granules. It facilitates dosage and allows you to distribute evenly the additive throughout polymer matrix volume. Therefore, the present paper examines the impact of joint use of stabilizers and fillers masterbatches on the stability of the compositions to heat aging.

Table 1 shows that compositions containing 10 wt % VC PE 175, the values of ε equal to 80% after 300 h of aging. The application of heat stabilizer PA10 leads to the conservation values of relative elongation at 84%. The use of the stabilizer in the filling degree 20 wt % allows you to keep ε at 76% after 300 h of aging compared with 55% non-stabilized compositions. In the compositions containing the filler EFPE 1001, PA10 use of stabilizing additives allows you to reduce significantly the oxidative processes resulting in the properties preservation after 300 h of aging compared to unstabilized samples. It should be noted that unstabilized compositions containing 10 and 20 wt % filler EFPE 1001, are more susceptible to develop oxidative degradation than the compositions containing VC PE 175, as demonstrated by the values of elongation after 300 h of aging. Thus, we can conclude that use of the studied chalk containing additives significantly affects the properties of the compositions, and their replacement in the products manufacture will affect the final product characteristics. Use of PA10 allows you to slow down destructive processes, which testify the effectiveness of these additives. Comparison of the received results on studying the dynamics of change of deformation and strength properties of the composites as a result of their aging shows the differential impact of ADDITIVE 13169 and TALC MB masterbatches in resistance to heat aging. Use of ADDITIVE 13169 leads to acceleration of aging processes compared with pure PE. Application of 10 wt % ($\varepsilon = 80\%$ after 300 h of aging) TALC MB slows down degradation during thermal aging. The introduction of the masterbatch stabilizer PA10 can significantly improve the resistance to thermo-oxidative degradation, which is manifested in the preservation the values ε after 300 h of aging at 16% (at 20 wt %) and 20% (at 10 wt %).

When using mixtures of talc containing masterbatch MB and chalk containing VC PE 175 or

EFPE 1001 at the ratio 1 : 1 (10 wt %) increased thermal stability was observed as compared to pure PE and PE containing all the analyzed fillers masterbatches separately. Perhaps, this is due to a different mechanism of each filler action on the inhibition of oxidation processes. Fine particles of chalk can act as nuclei of crystal formation, leading to the crystalline structure formation that is more resistant to temperature. The larger particles of talc are displaced into the amorphous portion, where the observed inhibitory effect of solid surface on the chain oxidation processes and decomposition of macromolecules under the action of temperature. Thus, it is possible that the observed inhibitory effect of fillers on the two mechanisms lead to higher resistance to thermocycling [15]. However, this effect is observed at relatively low contents of fillers, 10%, while increasing their content, we installed the reverse amplification effect in decomposition rate.

To study the stability of the investigated compositions to heat aging an independent method was used to determine activation energy of thermooxidation degradation. The calculated values of the effective activation energy of thermooxidation degradation is presented in Table 2. The initial PE has low thermal stability; the calculated value is 108 kJ/mol.

Table 2

The values of the activation energy of thermooxidation degradation

Composition	E_j , kJ/mol
PE (100 wt %) initial	108
PE + PA10	160
PE + 10% TALC MB	146
PE + 10% TALC MB + PA10	159
PE + 10% VC PE 175	131
PE + 10% VC PE 175 + PA10	169
PE + 5% VC PE 175 + 5% TALC MB	186
PE + 5% VC PE 175 + 5% TALC MB + PA10	178

The use of stabilizer PA10 can slow the development of destructive oxidation processes, as it was testified by increasing E_j values up to 160 kJ/mol. The use of chalk containing fillers VC PE 175, talc containing TALC MB in 10 wt %, and their mixture in the ratio 1 : 1 (5% VC PE 175 : 5% TALC MB) has a pronounced stabilizing effect, which is manifested in a significant increase in the values of E_j , especially in the case of fillers mixture ($E_j = 186$ kJ/mol). The use of stabilizer PA10 with PE is effective for compositions containing fillers separately (9% for TALC MB, to 23% for VC, PE 175), which correlates with data on studying deformation and strength properties.

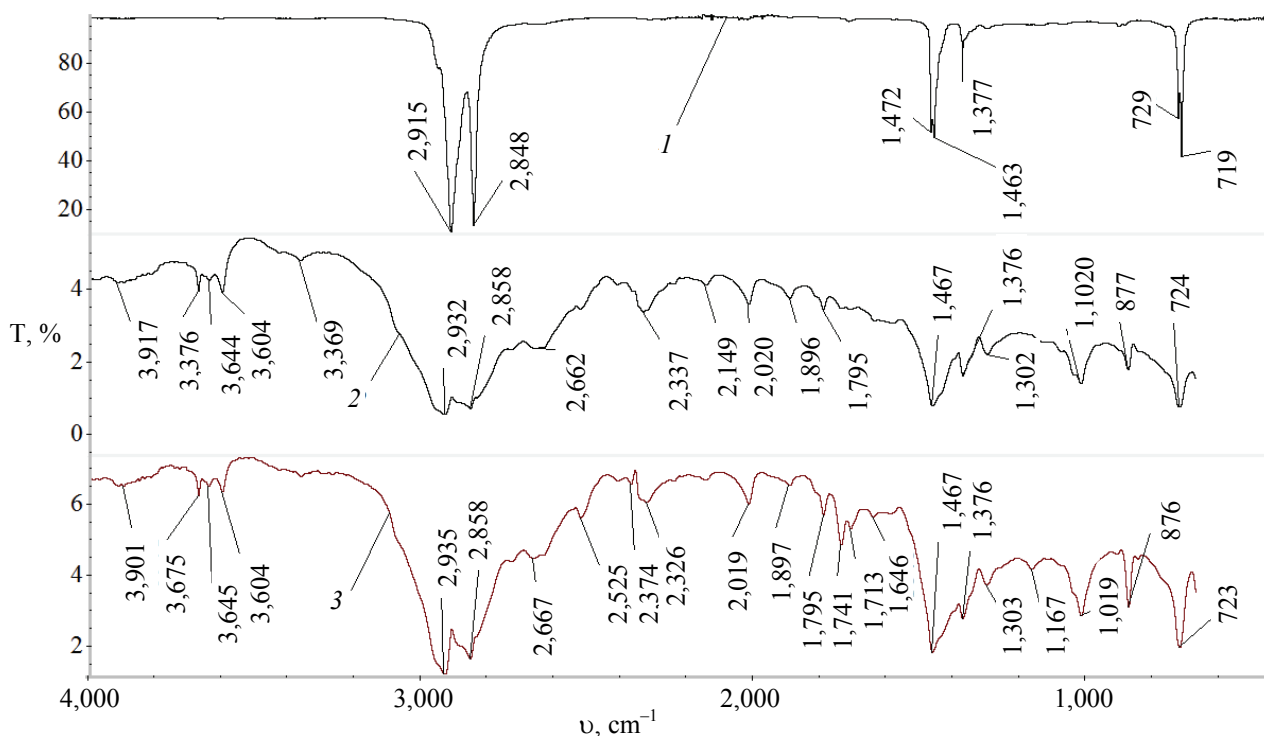


Fig. 4. IR spectra of the PE containing fillers and stabilizer:

1 – PE; 2 – PE + a mixture of fillers VC PE 175 (5 wt %) + TALC MB (5 wt %) + stabilizer PA10 (3 wt %);
3 – PE + a mixture of fillers VC PE 175 (5 wt %) + TALC MB (5 wt %)

In the case of introducing PA10 in the composition containing a mixture of fillers, the value of E , decreases to 178 kJ/mol. This effect can be explained by the possible interactions between the stabilizer, fillers and the presence of organic compounds forming part of the investigated masterbatches fillers.

To confirm this assumption, the obtained absorption spectra of the stabilized and unstabilized compositions of PE containing a mixture of fillers 5 wt % TALC MB and 5 wt % VC PE 175 (Fig. 4).

Fig. 4 shows that in the spectrum of PE containing a mixture of fillers without stabilizer (spectrum 2), there is an intense peak in the area $1,741\text{ cm}^{-1}$ (it determines the presence of C=O). The band in $1,741\text{ cm}^{-1}$ is also observed in the spectrum of the masterbatch of the stabilizer PA10 (Fig. 1). On the spectrum of PE containing a mixture of fillers and

PA10, instead of the expected increase in the intensity of absorption band in $1,741\text{ cm}^{-1}$ is observed a decrease, which indicates the interaction between the stabilizer PA10 and compounds included in the composition of fillers masterbatches.

Conclusion. Stability of the compositions of PE to thermal aging, depending on the applied masterbatches fillers and stabilizers, and their combinations was studied. The best chalk (10 wt % VC PE 175) and talc (10 wt % TALC MB) masterbatches were defined, which allows us to increase the thermal stability of the compositions of PE by 21 and 35%, respectively, and their combination with stabilizer masterbatch. Combinations of three masterbatches demonstrated the antagonistic effect. The necessity to consider the mutual influence of the components of the compositions was determined.

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