Polyethylene/Layered Aluminosilicate Nanocomposites: Investigation of Thermal Stability under Static and Dynamic Conditions

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Abstract

Based on linear low-density polyethylene and maleated polyethylene a polymer nanocomposites containing modified montmorillonite have been obtained, structure is investigated by XRD analysis. In turn, by the methods of thermal analysis in static and dynamic modes, the resistance of polymer nanocomposites to oxidative destruction it was investigated. In parallel with this, a comparative analysis of the thermal stability of polymer nanocomposites and polymer compositions containing commercially available organic antioxidants for stabilization of materials based on polyolefins. By results of the analysis carried out in a dynamic mode, for a series of polymer composites the activation energy of thermooxidative destruction was calculated. It is shown that the nanocomposites based on polyethylene, containing the modified montmorillonite not only not concede to polymer compositions with antioxidants in to thermal stability, but also exceed their. Accelerated tests, carried out at relatively high temperatures allowed evaluate the durability of polymer nanocomposites to thermooxidative destruction. Received results allow approve about a long-term thermal stability of these materials in the processing, and in the exploitation conditions.

1. Introduction

For the purpose of prevention of thermooxidative destruction of polyethylene in the course of processing or exploitation at certain temperatures, used organic stabilizers of various mechanisms of an action. At the same time, their efficiency is limited within temperatures 200–250 °C an above which stabilizers are destructed and, respectively, lose the activity, long before the beginning of the thermooxidative destruction of polyethylene which begins in air oxygen presence at 270–300 °C [1].

The nanocomposites based on polyethylene with montmorillonite are characterized by the increased melting temperature, heat deformation temperature, thermal stability [2–5]. Thermal stability of polymer nanocomposites in the conditions of the continuous temperature growth were investigated rather intensively while there are no publications related with studying of stability of such materials under conditions of long thermal influence. Thereby, in this paper we present the results of investigation directed to studying of thermal stability of

nanocomposites based on linear low-density polyethylene filled with layered aluminosilicate at the static and dynamic modes of tests.

Such characteristics are especially important for materials (for example, constructional, technical and electro-technical application) which have to possess the increased rigidity and wear resistance in the wide temperatures range [6].

2. Experimental

The linear low-density polyethylene (LLDPE), F-0320 with a melt flow index 3.0 g/10 min (Shurtan Gas Chemical Complex of the Republic of Uzbekistan) and the maleated polyethylene (MAPE) received based on the same polyethylene, containing ~5 wt.% of the grafted maleic anhydride, were used.

The modified montmorillonite $((C_{18})_2N\text{-MMT})$, the known as «Cloisite 20A» (Southern Clay Product Inc.), the modified N,N'-dimethyl-N'',N'''-dialkylammonium chloride, with the various length of a normal structure of the aliphatic radical (65 wt.% –

$[(CH_3)_2(C_{18}H_{37})_2N]Cl$, 30 wt.% $- [(CH_3)_2(C_{16}H_{33})_2N]$Cl and 5 wt.% $- [(CH_3)_2(C_{12}H_{25})_2N]Cl]$ has been used as a filler. The general maintenance of the modifier into modified clay was made 39 wt.%.

The following antioxidants: octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate the known as «Irganox 1076» (Sigma-Aldrich), and also a mixture with tris (2,4-ditert-butylphenyl)phosphate, the known as «Irgafos 168» (Sigma-Aldrich) also were used. The antioxidants mass ratio of Irganox 1076 and Irgafos 168 was made 0.075 : 0.150.

Polymer composites were prepared using Brabender mixer (Plasticorder Brabender OHG Duisburg, Germany), at 180 °C and the rate 50 rpm. The mixing time of components established the following: 20 min – composition of polymer(s) with the modified montmorillonite, 10 min – composition of polymer with the stabilizers. A mass ratio of MAPE to $(C_{18})_2N$-MMT was made 4 : 1.

X-ray diffraction analysis of the polymer composites containing montmorillonite carried out using automatic X-ray DRON-3M diffractometer (Burevestnik, Russia), with the monochromatic CuK_α-radiation (λ = 1.548 nm), at a rate of move the counter 2 deg · min^{-1}, in the range from 2 to 10° at the 2θ scale. About intercalation and/or exfoliations of layered aluminosilicate in a polymer matrix, namely by intensity and the position of the reflex 001 (or his absence) of montmorillonite by a X-ray diffractograms have judged. The thermogravimetric analysis under air atmosphere was carried out by using Paulik-Paulik-Erdei derivatograph (MOM, Hungary), under dynamic (at temperatures range – 20–800 °C and at heating rate – 10 °C/min) and isothermal (at temperature – 180 °C and of time of thermal aging – 100 h) modes.

3. Results and Discussion

3.1. Structural characterization

About degree of exfoliations of layered aluminosilicate in polymer matrix was judged by the intensity change of a reflex [001] in the angle range 2–10°, as well as by comparing the spectrum of air-dry organically-modified montmorillonite (($(C_{18})_2N$-MMT) with the spectra of micro-($PE/(C_{18})_2N$-MMT) and nanocomposites ($MAPE/(C_{18})_2N$-MMT and $PE/MAPE/(C_{18})_2N$-MMT). In the spectrum of the sample air-dry modified montmorillonite are present two reflexes: first reflex [001] strong intensity at 3.83° (d_{001} = 2.32 nm) and second reflex [002] by weak intensity at 7.50° (d_{002} = 1.18 nm).
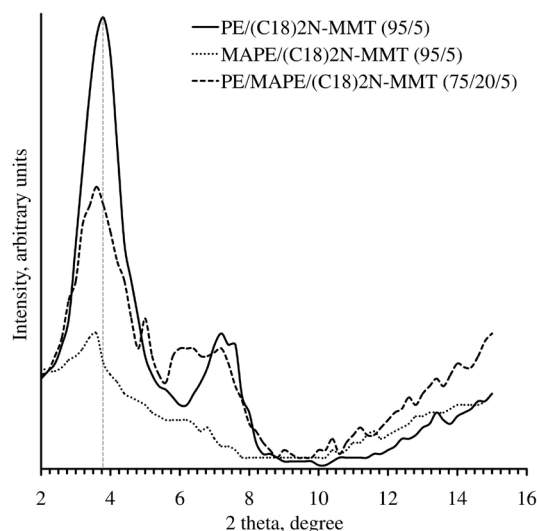

Fig. 1. XRD spectra of polymer composites containing 5 wt.% modified montmorillonite.

On Fig. 1 X-ray diffractograms of polymer composites containing 5 wt.% modified montmorillonite and differing by polarity a polymer matrix are presented. Offset of montmorillonite basal reflex to side smaller 2θ angles was caused by broadening of the distance between the layers into aluminosilicate, owing to partial intercalation of polymer chains. In turn, the reduction in the intensity of the basal reflex [001] was caused by a partial delaminating of layered aluminosilicate to form individual layers and/or particles, in which the number of layers is much less.

3.2. Thermal stability of nanocomposites under dynamic mode

Thermooxidative stability (thermal stability) of polymer is the characteristic of chemical stability of polymer at high temperatures and the air atmosphere conditions. Thermal stability is estimated at the beginning of decomposition temperature of polymer after which the changes it's of chemical structure and properties is observed.

Results of an assessment of thermal stability (at the temperatures, at which a weight loss 5, 10 and 50 wt.% is observed) of the polymers and composites based there, differing with the type of the polymer matrix and the composite structures, are presented in Table 1. In parallel with composites, the polymer composites containing widely used organic antioxidants and their mix were investigated. At the same time, used such ratio of stabilizers at which their considerable efficiency, which characterized from efficiency of separately taken antioxidants is observed. Thermal stability of samples was evaluated on the temperatures difference corresponding

Table 1
Decomposition temperatures and activation energy values of the polymers,
composites and polymer composites, containing antioxidants

Sample name	Composition, wt.%	Temperature, °C			E_a, kJ · mol^{-1} ($T_{3\%}$, °C)
		5%	10%	50%	
LLDPE	100	356	372	440	109.6 (330)
MAPE	100	327	350	440	–
PE/MAPE	50/50	307	358	440	–
PE/(C$_{18}$)$_2$N-MMT	95/5	361	392	445	96.3 (345)
MAPE/(C$_{18}$)$_2$N-MMT	95/5	359	420	460	34.9 (310)
PE/MAPE/(C$_{18}$)$_2$N-MMT	75/20/5	408	426	460	198.1 (360)
PE/Irganox 1076	99.775/0.225	390	415	448	102.1 (350)
PE/[Irganox 1076+Irgafos 168]	99.775/0.225	380	400	440	212.1 (365)

to the certain weight loss of unfilled polymer (or polymer-polymer blend) and a composite.

Judging by values of decomposition temperatures of the polymers and polymer composites presented in Table 1 it is visible that among composites, the nanocomposite PE/MAPE/(C$_{18}$)$_2$N-MMT possesses rather bigger thermal stability ($\Delta T_{5\%}$ is 101 °C, concerning of PE/MAPE blend). Also, is of interest compare thermal stability of a microcomposite (PE/(C$_{18}$)$_2$N-MMT) and of the nanocomposites (MAPE/(C$_{18}$)$_2$N-MMT and PE/MAPE/(C$_{18}$)$_2$N-MMT) with polymer composites containing of the antioxidants (or a mixture of antioxidants). Apparently from Table 1, in thermal stability the nanocomposite not only doesn't concede, but even surpasses the composites with antioxidants (compare the $T_{5\%}$, $T_{10\%}$, $T_{50\%}$).

On Fig. 2 curves of the thermogravimetric analysis (TG-curves) of polyethylene and the polymer composites containing the modified montmorillonite or antioxidants are presented.
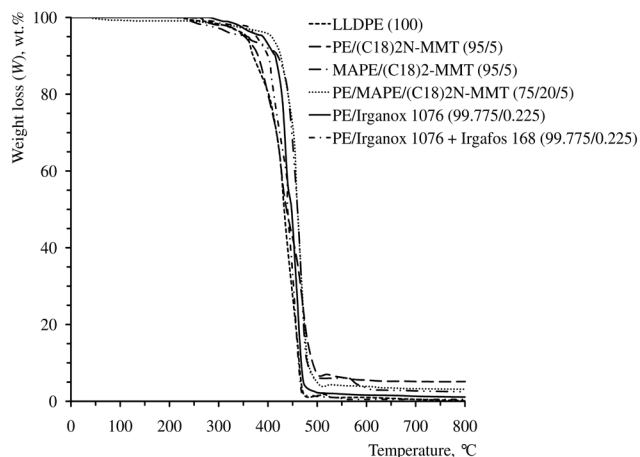

Fig. 2. TG-curves of polyethylene and polymer composites containing modified montmorillonite (or antioxidants).

In addition to results of an assessment of thermal stability, the activation energy of thermooxidative destruction (E_a) of linear low-density polyethylene, and also the polymer composites containing the modified montmorillonite or organic stabilizers was calculated.

Activation energy of thermooxidative destruction this is an excess of energy (a potential barrier) needed for destruction of the chemical bonds forming the main chain of polymer at the influence of temperature, oxygen and ozone of air. For calculation of kinetic parameters was used of a method of double logarithm which consists in definition of a tangent of angle of an inclination of a straight line in coordinates $\ln\{\ln[100/(100-\Delta w)]\} - 1/T \cdot 10^3$. Further E_a was calculated to the equation:

$$E_a = \text{tg}\alpha RT$$

where Δw is the weight loss, wt.%; T is the destruction temperature, K; R is the gas constant (8.31 · 10^{-3} kJ · (mol · K)$^{-1}$).

Apparently from Table 1, close values E_a have a polyethylene, microcomposite and composite with the antioxidant (Irganox 1076) while, for a nanocomposite and composition PE/[Irganox 1076 + Irgafos 168] the values of activation energy exceed twice that indicates their considerable thermal stability.

3.3. Thermal stability of nanocomposites under isothermal mode

Above results of investigation thermooxidative stability of nanocomposites at the conditions of the continuous temperature growth which the rate made 10 °C/min were discussed. In turn, the study thermooxidative destruction of nanocomposites under isothermal (the static) mode, gives useful information concerning material stability as in course

of processing, and in use at the conditions of long thermal influence.

Destruction of polyethylene begins with the moment of oxygen sorption from air that leads to formation of considerable number of hydroperoxides, the accelerating destructive processes owing to what there is a decrease in polymer molecular weight. The sorption of oxygen with a polymer proceeds in the first 5 h tests (an induction period) during whom occurs increase in a sample weight. In the course of long thermal influence the oxygen sorption and polymer destruction which is followed by formation of low-molecular gaseous products pass successively. The thermal stability has evaluated at weight loss for the entire period of tests (or ΔW_{100}) which for polymers increases in the following row: LLDPE (2.80%) < MAPE (2.09%) < PE/MAPE (1.63%); for polymer compositions increases in the following row: MAPE/$(C_{18})_2$N-MMT (1.57%) < PE/$(C_{18})_2$N-MMT (1.28%) < PE/MAPE/$(C_{18})_2$N-MMT (1.21%).

On Fig. 3 kinetic curves of weight loss (W) polyethylene and composites based on its, containing the modified montmorillonite depending from time (τ) of thermal influence are presented. Apparently from Fig. 3, low intensity of weight loss is observed only for micro- and a nanocomposite.

In parallel with polyethylene, with maleated polyethylene and with composites based on their, also the polymer composites containing antioxidants were analyzed; the efficiency of which (in the rate deceleration of thermooxidative destruction of polymer) can be evaluated from the weight losses each of polymer composites, at the constant value of time. Investigation of thermal aging of such composites allows concluding that curves W–τ for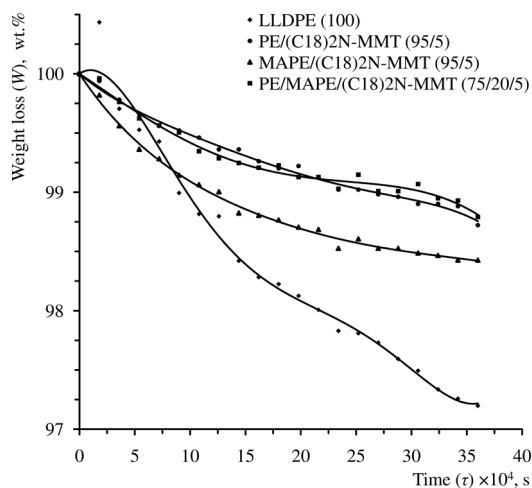 the composites containing antioxidants have a similar appearance and practically don't differ from curve a polyethylene (see the Fig. 4). An exceptional advantage in comparison, for example, with PE/MAPE/$(C_{18})_2$N-MMT nanocomposite, has the polymer composite containing the antioxidants mix for which change of weight during 20 h isn't observed. On the other hand, in comparison with ΔW_{100} polyethylene, a considerable difference in weight losses for two composites antioxidants containing isn't observed (for composite with Irganox 1076 $\Delta W_{100} = 2.98\%$ and with Irganox 1076 + Irgafos 168 $\Delta W_{100} = 2.71\%$). Such insignificant difference in values ΔW_{100} is probably related with almost the complete deactivation of antioxidants in polymer. The mechanism of action of mixture of such the antioxidants is known consists in breakage of radical chain reactions: the sterically hindered phenols are chain-breaking donor antioxidants; esters of phosphites (the triphenyl phosphite derivatives) – are substances causing the stoichiometric decomposition of peroxides and hydroperoxides.

In general, weight loss both for polyethylene, and for polymer composite with antioxidants proceeds twice more intensively, in comparison with a nanocomposite. In our opinion, the similar difference is caused by the decreasing viscosity of polyethylene and the stabilized polymer composite (owing to destruction of macromolecules and of reduction of molecular weight); that allows with ease to diffuse for molecular oxygen into polymer melt increasing the rate of the destruction reactions. While, increase of nanocomposite viscosity (owing to specific interactions of functional groups of polymer with the active centers of aluminosilicate, and because of formation of branched and cross-linked structures) and availability of a barrier in the form of flat particles of aluminosilicate leads to the slowing of the diffusion of oxygen molecules to the deeper layers of the polymer sample. And, as already it has been told earlier, according to low values of weight loss it is possible to judge about domination of reactions of intermolecular cross-linking, over the destruction reactions (in the process of which low-molecular hydrocarbons are formed).

Observations over process of thermal aging of samples have shown that unlike from microcomposites, nanocomposites can retain a form, in view of their comparably high of the viscosity which continues to increase in the course of long thermal influence. After total the tests period, samples of nanocomposites were characterized by rather rigid structure in comparison with microcomposites and with unfilled polymers which structure is comparable with structure of wax.
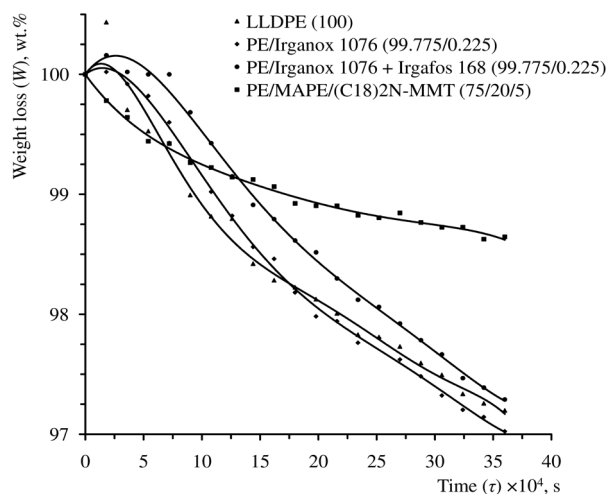

Fig. 3. Kinetic curves W–τ of polyethylene and polymer composites containing modified montmorillonite.

Fig. 4. Kinetic curves $W–\tau$ of polyethylene, nanocomposite and composites containing antioxidants.

Formation of volatile products in the entire period of tests makes 1–3 wt.% at the same time a polyethylene, maleated polyethylene and their a blend are capable the lose a weight continuously during long the period of tests (exceeding 100 h). In turn, the rate of thermooxidative destruction of nanocomposites by the end of tests considerably decreases. In process of thermal influence, nanocomposites change color from weak-yellow to black. This indicated the formation in the polymer of compounds with multiple bonds. Apparently, it is occurring because of transfer of hydrogen from a macromolecule not to a macromolecule (as case of disproportionation reaction), and on an active the center of the aluminosilicate.

4. Conclusions

Resistance of the nanocomposites to the thermooxidative aging, not only the chemical nature of polymer is defined, but also intercalated and exfoliated structures of aluminosilicate. At the time of thermal exposure, exfoliated nanoparticles of the aluminosilicate in polymer nanocomposite one hand create additional physical barrier, thereby retarding the diffusion of molecular oxygen in polymer volume, on the other − render catalytic effect on structuring processes of the polymer (is formed the cross-linked and branched polymer structures).

It is shown also that in comparison with the polymer composites, containing traditional organic antioxidants thermal stability of polymer nanocomposites is much higher.

As a result, long thermal influence leads to carbonization of polymer in the nanocomposite. Excepting of the specific interactions (arising between polymer functional groups and active centers of the aluminosilicate) and increase in a volume fraction of a filler (owing to the exfoliation), increase of the nanocomposites viscosity, is also due by availability of the branched and cross-linked structures which under long thermal influence are formed.

Thus, judging by the results of tests carried out at a temperature of 180 °C, can be assumed that at moderate exploitation temperatures (50–100 °C) or in the processing, polymer nanocomposites will have long-term resistance to thermooxidative destruction.

Acknowledgements

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