Для створення вогнезахисного покриття, що може бути застосоване в умовах вуглеводневої пожежі, синтезовано нанокомпозити співполімера етилену з вінілацетатом (EVA) з монтморилонітом (MMT), терморозширеним графітом (EG) та досліджено структуру, фізико-хімічні та термічні властивості. Методами ІЧ-спектроскопії та рентгенофазового аналізу встановлено, що нанокомпозити EVA з монтморилонітом та графітом, отримані в розчині та розплаві, мають ідентичну структуру.

Досліджена термоокислювальна деструкція співполімеру EVA та нанокомпозитів на його основі в інтервалі температур 100–700 °C. Доведено, що наноглина та нанографіт у складі нанокомпозитів підвищують теплові характеристики вихідних полімерів. Термічна стабільність досліджених сполук підвищується у ряду: полімер < полімер-EG < полімер-MMT < полімер-MMT-EG. Показано, що присутність в полімерній матриці наночастинок знижує швидкість термічного розпаду EVA при температурі вище за 450 °C та підвищує масу коксового залишку після температури початку деструкції вихідного співполімеру EVA – 250 °C. Встановлено синергічну дію суміші MMT/EG на процеси уповільнення термічної деградації співполімера EVA.

Вивчено вплив графіту та органомодифікованого монтморилоніту у складі нанокомпозитів EVA на термодеструкцію інтумесцентної системи поліфосфат амонію/меламін/пентаеритрит. Встановлена синергічна дія суміші наночастинок глини та графіту в гібридному нанокомпозиті. Синергізм полягає у підвищенні межі вогнестійкості металевих конструкцій майже на 20 % в порівнянні з покриттям, що містить нанокомпозит полімер/наноглина чи полімер/нанографіт.

На основі отриманих результатів розроблено інтумесцентну основу вогнезахисної фарби для сталевих конструкцій, яка рекомендується до застосування для підвищення межі вогнестійкості металу в умовах вуглеводневої пожежі

Ключові слова: органомодифікований монтморилоніт, терморозширений графіт, нанокомпозит, інтумесцентне покриття, вуглеводнева пожежа

DEFINITION OF THE THERMAL AND FIRE-PROTECTIVE PROPERTIES OF ETHYLENE-VINYL ACETATE COPOLYMER NANOCOMPOSITES

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1. Introduction

Fire protection of building structures by treatment with special fire retardants is a mandatory measure, regulated by national construction standards. The development of new technologies of intumescent coatings [1, 2] should solve a number of urgent problems:

– increase reliability and efficiency of fire retardant coatings of critical building and infrastructure facilities in compliance with the requirements for fire safety of facilities in accordance with the Regulation (EU) No. 305/2011;

– ensure the environmental safety of coatings (especially in the fire) by excluding prohibited or restricted chemicals and preparations from their composition in accordance with REACH.

It should also be noted that, in addition to fire protection efficiency and environmental parameters, new generation coatings must be resistant to the environment, moisture,

weathering, etc. [3, 4]. This, on the one hand, significantly extends the life of fire retardant coatings, and, on the other hand, keeps its original fire protection efficiency. Maintaining of fire-protective properties of coatings during operation is especially important for objects of strategic importance, which potentially can be a source of hydrocarbon fire.

The necessity and urgency of creating reliable fire retardant coatings with increased efficiency are also due to the recently increased threats of terrorist attacks and wars with the use of heavy and explosive weapons.

2. Literature review and problem statement

The traditional intumescent system, which is the basis of fire retardant coatings, consists of three main components:

– acid donor – phosphates, ammonium polyphosphates (APP);

– carbonizing agent – polyalcohols, as a rule, pentaerythritol (PER) or its analogs;

– gasifier – derivatives of melamine (MA), dicyan diamide, urea.

The most common and studied theoretically, as well as applied commercially, is the intumescent system ARP/PER/MA [1, 2].

An important component of the intumescent system, as shown by recent studies [5, 6], is the polymer component of the fire retardant coating. The polymer matrix in the required temperature range should provide the formation of a strong and volumetric insulating coke layer [7] with a satisfactory adhesion to the metal substrate [8, 9]. The thermal stability of the binder of the polymer intumescent composition directly affects the coke formation mechanism, the strength of adhesion to the substrate and the intensity of burnout under fire conditions [7]. Given such requirements for the polymer component of fire retardant coatings, the range of polymers applicable for fire protection is quite limited [1, 2].

The most preferred for environmental water-based fire retardant paints are vinyl acetate homopolymers, vinyl acetate, ethylene and vinyl chloride copolymers, vinyl acetate and vinyl ether copolymers, vinyl acetate and acrylic acid ether copolymers [1, 2]. But these polymers, as a rule, cannot be used to create reliable coatings for the hydrocarbon fire. They have moderate fire-resistant characteristics: formation of the coke layer in the temperature range of 200–450 °C and its disintegration at temperatures above 600–700 °C [10]. Coatings with such thermal characteristics are inoperative under conditions of "thermal shock" of hydrocarbon fire. In addition, they have a short lifetime and require the use of an additional protective layer [11].

To improve the fire resistance and durability of polymer intumescent systems, nanostructured fire retardants are used – graphites [12], nanooxides [13, 14], nanoclays [10], etc. [15]. The results of studies on the effect of nanoimpurities on the intumescent fire protection efficiency allow highlighting the general features of the action of nanoparticles at high temperatures. This is the strengthening of the protective coke frame by structuring the polymer matrix with MeO particles or B and Si atoms and increasing the thermal stability of the polymer component of the fire retardant coating [1].

Considering the economic feasibility of using nanomaterials in industrial intumescent technologies, nanoclays and thermally expanded graphite (EG) are the most attractive.

Nanoclays are mainly bentonite clays – natural layered silicates. The most studied and promising ones are montmorillonite (MMT) [16, 17] and its close analogs (smectite, attapulgite), which in the form of organomodified derivatives (oMMT, organoclays) [18] are widely used in nanotechnologies and synthesis of nanocomposites [19]. Thermally expanded graphite is also a low-cost nanomaterial, which forms polymer-based organic-inorganic compounds. In addition, EG is used for the production of fire retardant coatings [12].

The analysis of [12, 18] shows that the necessary condition for the positive effect of nanoimpurities on the fire protection efficiency of the intumescent coating is to obtain a stable nanocomposite matrix – polymer/MMT or polymer/EG. Therefore, the study of the effect of nanoclay and nanographite on the thermal destruction of the corresponding nanocomposites, as well as intumescent compositions (IC) with them, have considerable scientific and practical interest for the design of new formulations of intumescent coatings for the hydrocarbon fire. This type of fire [20] is typical not only for petrochemical and gas complexes, chemical plants, ammunition depots, but also may occur in gas line accidents in civil construction. The need for research on improving the effectiveness of fire protection means is also due to the global problem of increasing the fire safety of critical facilities in the face of strengthening terrorist threats and wars.

3. The aim and objectives of the study

The aim of the study is to explore the effect of the nanocomposites based on the ethylene-vinyl acetate (EVA) copolymer on the fire protection efficiency of the intumescent system ammonium polyphosphate/pentaerythritol/melamine (APP/PER/MA).

The aim provides for accomplishing two blocks of related objectives:

– to obtain nanocomposites of EVA with MMT and EVA with EG and to determine their thermal properties;

– to study the effect of the obtained nanocomposites on the formation and physical characteristics of the coke layer of the intumescent system in the temperature range of 200–700 °C and in the conditions of fire tests.

4. Materials and methods of studying the effect of nanocomposites on the fire protection efficiency of the intumescent system

4. 1. Materials and equipment used in the experiment

The dispersion of the Mowilith LDM 1780 ethylene vinyl acetate copolymer (Clariant, Germany), CEVA copolymer (Exxon Mobil Chemical, Belgium), type II ammonium polyphosphate – CF APP 201 (Shifang Changfeng Chemical Co., Ltd., China), RN-P micronized pentaerythritol, RN-M 40 melamine (Roshal Group, Russia), DCP dicumyl peroxide (Arkema, France), TAC triallylcyanurate (Evonik Performance Materials GmbH, Germany) was used in the study. As nanoimpurities to obtain nanocomposites, montmorillonite modified with cations of thallium bis-hydroxyethyl methylammonium, Garamite 7303 (MMT) manufactured by BYK Additives & Instruments (Germany) and thermally expanded graphite, EG-250 (BeijingGreatWallCo., Ltd., China) were used.

IR spectroscopy tests were performed on Specord 75 IR and Bruker Tensor 37 FT-IR devices in the range of 400–

4,000 cm^{-1}. X-ray phase analysis was performed on the DRON-2 diffractometer. Thermogravimetric studies were performed on the Thermoscan-2 device. Determination of the swelling coefficient of intumescent compositions K (cm^3/g) and coke residue mass (m, %) is detailed in [18].

4. 2. Synthesis of ethylene vinyl acetate-montmorillonite (EVA-MMT-I) and ethylene vinyl acetate-graphite (EVA-EG-I) nanocomposites in solution

During stirring, 6 g of Garamite 7303 nanoclay was added in portions to 200 g of the ethylene-vinyl acetate copolymer (EVA, 50 % dispersion of Mowilith LDM 1780). The mixture was stirred in a low-speed mixer (~200 rpm) for 5 hours until obtaining a homogeneous liquid containing the EVA-MMT-I nanocomposite.

For the synthesis of the EVA-EG-I nanocomposite, graphite (EG-250), triallycyanurate (TAC), dicumyl peroxide (DCP) and tetrahydrofuran at a ratio of 1:0.01:0.01:1 were pre-mixed in a ball mill for 30 min. Then, 12 g of this mixture was added in portions to 200 g of the ethylene-vinyl acetate copolymer while stirring. The mixture was stirred in a low-speed mixer (~200 rpm) for 5 hours.

EVA-MMT-EG-I nanocomposite was prepared by mixing 200 g of the EVA copolymer, 3 g of Garamite 7303 nanoclay and 6 g of EG-250 graphite with TAC and DCP in tetrahydrofuran for 5 hours.

Solutions of the nanocomposites were applied with a thickness of 1-2 mm on Teflon substrates and dried in air for 3 days. The resulting films were kept in vacuum at 60 °C to a constant weight.

4. 3. Synthesis of ethylene vinyl acetate-montmorillonite (EVA-MMT-II) and ethylene vinyl acetate-graphite (EVA-EG-II) nanocomposites in the melt

50 g of the ethylene-vinyl acetate copolymer (CEVA) was heated to 120 °C while intense stirring. After the polymer melting, a certain amount of Garamite 7303 nanoclay or EG-250 graphite was added. The mixture was stirred in an extruder at a temperature of 120–130 °C for 1 hour.

For the synthesis of EVA-MMT-EG-II, a certain amount of Garamite 7303 nanoclay and EG-250 graphite was added to the CEVA polymer melt at a ratio of 1:1 by weight.

From the melts of the nanocomposites, 1–2 mm thick films were formed for further research.

4. 4. Preparation of the intumescent composition (IC)

The components of the intumescent system: ammonium polyphosphate (APP), pentaerythritol (PER), melamine (MA), titanium oxide (TiO$_2$) at a ratio of 3:1:1:0.5 (pts. wt.) were placed in a bead mill. The mixture was stirred for 30 min, separated from the beads. 2 (pts. wt.) solution of the nanocomposites was added to the resulting paste. From the finished composition, samples of films were prepared by filling the aluminum foil boxes and dried to a constant mass at room temperature.

For fire tests, based on the IC APP/MA/PE/TiO$_2$/EVA or EVA nanocomposite fire retardant paints (with rheological and other impurities) were obtained. The paint was applied on a (200×200×3) mm primed metal plate with a dry layer thickness of (2±0.2) mm, dried for 21 days. The tests were carried out in a small-scale furnace in the hydrocarbon fire.

5. Results of obtaining nanocomposites and studies of fire protection efficiency of intumescent systems

5. 1. Physico-chemical characteristics of ethylene-vinyl acetate copolymer nanocomposites

Depending on the nature of the components (nanomaterial, polymer matrix), method and conditions of synthesis, hybrid organic-inorganic substances of three basic types can be obtained:

a) microcomposites – micron-size layered silicate particles;

b) intercalated nanocomposites, where the macromolecule is introduced into the interlayer space of agglomerated particles of layered silicate;

c) exfoliated nanocomposites, where nanosized layers are evenly distributed throughout the polymer matrix [24].

On the example of the "polymer-nanoclay" nanocomposite (EVA-MMT, EVA-EG), conditions for obtaining nanocomposites of two structures were modeled:

– intercalated nanocomposites (EVA-MMT-I, EVA-EG-I) – stirring of the EVA dispersion with Garamite 7303 nanoclay or EG-250 graphite respectively;

– exfoliated nanocomposites (EVA-MMT-II, EVA-EG-II) – method of copolymer and nanoimpurity melting.

Hybrid nanocomposites EVA-MMT-EG-I and EVA-MMT-EG-II were obtained by the same methods (mixing in solution and melt).

The structure of the nanocomposites obtained was investigated using IR spectroscopy (Fig. 1–3).

The data of the X-ray phase analysis of the EVA polymer and nanocomposites are given in Table 1. The average size of the basal interval d (interlayer distance between nanoimpurity particles and polymer fragments) was calculated using the Wulff-Bragg's formula and diffraction patterns.

The obtained results allow us to make some generalizations regarding changes in the physico-chemical characteristics of the EVA copolymer when transformed into nanocomposite:

– shift of the absorption band of the C=O group of the nanocomposites to the more short-wave region (Fig. 1–3). This situation is the result of interaction of carbonyl oxygen of the polymer with the electron-acceptor centers of clay (Al^{3+} and Fe^{3+} ions –Lewis sites);

– absence of the absorption band of OH groups of the EVA copolymer – 3,447 cm^{-1} in the nanocomposites with MMT, which is the result of interaction of the hydroxyl group with proton-acceptor centers of clay (Bronsted site Si$^{\sigma+}$–O$^{\sigma-}$);

– increase of interlayer distances in layered silicates in the transition from organoclay to nanocomposite.
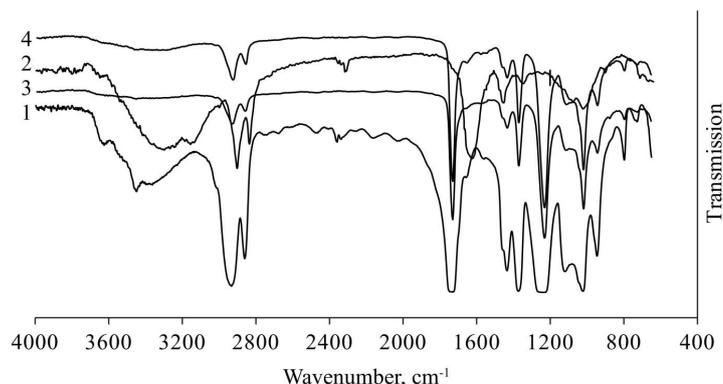

Fig. 1. IR spectra of ethylene vinyl acetate-montmorillonite copolymer nanocomposites: 1 – EVA; 2 – MMT; 3 – EVA-MMT-I; 4 – EVA-MMT-II
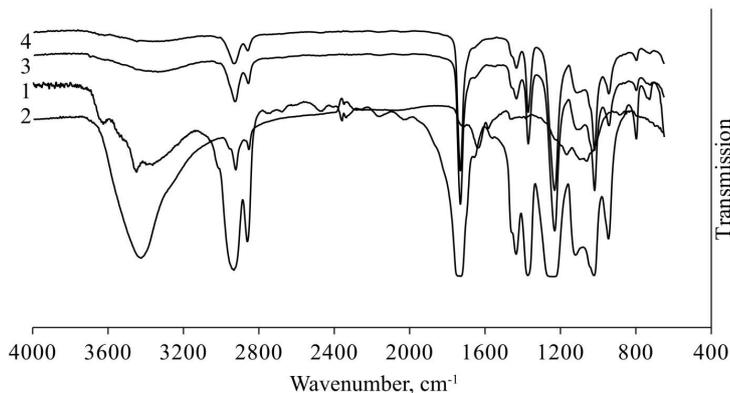
Fig. 2. IR spectra of ethylene vinyl acetate-thermally expanded graphite copolymer nanocomposites: 1 — EVA; 2 — EG; 3 — EVA-EG-I; 4 — EVA-EG-II
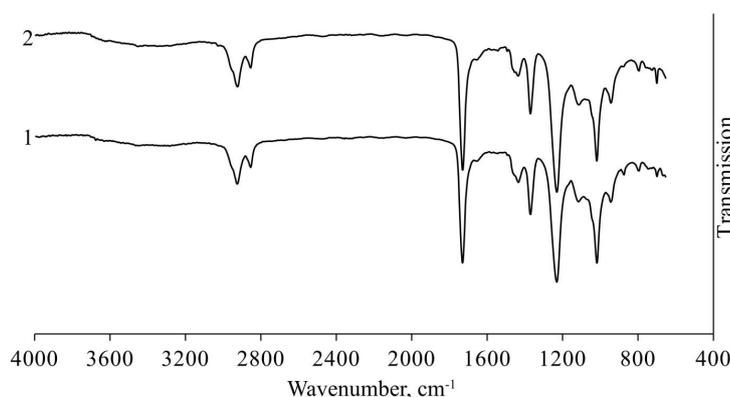

Fig. 3. IR spectra of ethylene vinyl acetate-montmorillonite-thermally expanded graphite copolymer nanocomposites: 1 — EVA-MMT-EG-I; 2 — EVA-MMT-EG-II

Table 1

Physico-chemical characteristics of the EVA polymer and nanocomposites

No.	Substance	Wave number C=O, cm^{-1}	Interlayer distance, d, nm
1	MMT (Garamite 7303)	–	2.25
2	EG (EG 250)	–	3.37
3	EVA	1,735	–
4	EVA-MMT-I	1,723	3.21
5	EVA-MMT-II	1,720	3.45
6	EVA-EG-I	1,731	3.49
7	EVA-EG-II	1,730	3.37
8	EVA-MMT-EG-I	1,732	3.64
9	EVA-MMT-EG-II	1,731	3.60

The thermal oxidative degradation of the nanocomposites was investigated using the Thermoscan-2 TG-analyzer under atmospheric conditions. The results of the thermogravimetric analysis of the EVA nanocomposites with MMT and EG are shown in Table 2: T_{pr} – temperature of the beginning of thermal destruction of the polymer or nanocomposite, and $T_{20\%}$, $T_{50\%}$, $T_{80\%}$ correspond to the mass loss of the sample – 20, 50 and 80 %, respectively.

The general conclusion from the results presented in Table 2 is that the presence of nanoimpurities in the system (MMT, EG or mixture) shifts the oxidative decomposition of EVA to the more high-temperature region. The values of these shifts are insignificant – 10–25 °C, but indicate a change in

the chemical mechanisms of polymer decomposition. This circumstance can play a significant role in the replacement of the EVA polymer with the corresponding nanocomposite in the intumescent system.

Table 2

Thermogravimetric analysis of the EVA polymer and nanocomposites

Substance	T_{pr}, °C	$T_{20\%}$, °C	$T_{50\%}$, °C	$T_{80\%}$, °C	% m, 700 °C
EVA	249	374	412	475	0.3
EVA-MMT-I	255	382	415	501	3.8
EVA-MMT-II	261	385	413	504	3.9
EVA-EG-I	264	387	417	492	4.1
EVA-EG-II	262	385	415	494	3.4
EVA-MMT-EG-I	265	391	416	490	4.1
EVA-MMT-EG-II	264	394	418	498	4.0

The dependence of the temperature of maximum weight loss of the EVA nanocomposites on the nanoimpurity content is presented in Fig. 4.

The comparison of the effect of impurity content in the EVA nanocomposites on the temperature of maximum weight loss during oxidative degradation is very informative. Optimum thermal stabilization is observed at the filler content of 2–4 wt % for MMT and EG and 2.5–6.5 wt % for their mixture. Below these values, as well as with increasing the nanoimpurity content, the thermal stability of the nanocomposites is reduced. This behavior can be explained by changes in the relative share of exfoliated and intercalated nanocomposites. Low nanoimpurity content is not enough to affect the heat-resistant properties of the polymer. With an increase in the filler content, the exfoliation degree of nanoparticles, and, accordingly, the degree of interaction with EVA polymer chains are reduced. Proceeding from Fig. 4, for further experiments on the effect of the inorganic component of the nanocomposite on the thermal properties of the IC, the nanoimpurity content of 3 % was used.
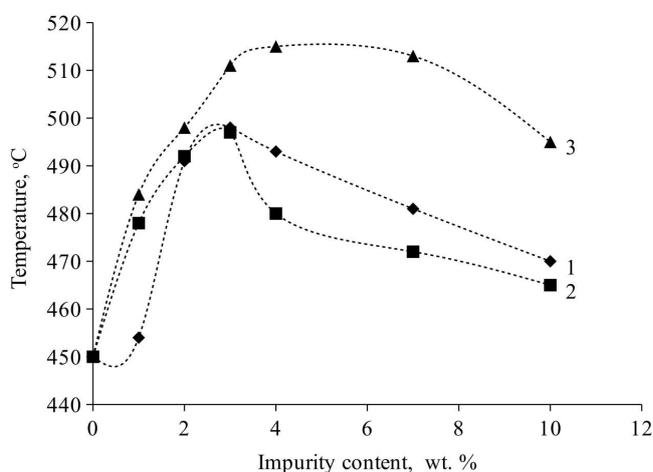

Fig. 4. Dependence of temperature of maximum weight loss of EVA nanocomposites on impurity content: 1 — EVA-MMT-I; 2 — EVA-EG-I; 3 — EVA-MMT-EG-I

The obtained data on the study of the physical and chemical properties of the obtained EVA nanocomposites confirm the formation of new polymer materials with properties differing from those of the original polymer. In this case, it should be noted that the structure of the nanocomposites obtained in solution practically does not differ from the structure of the nanocomposites obtained in the melt.

5. 2. Determination of the swelling coefficient and mass loss of intumescent compositions in the temperature range of 200–700 °C

In the work, a step-by-step study of the characteristics of the IC coke layer was used, which consists in holding the samples of IC films at a certain temperature from 200 to 700 °C [18]. Unlike the con-calorimetric method of studying the combustibility of polymer materials [21], the proposed approach gives a more or less complete picture of physical-mechanical properties. Namely, it allows estimating the level of swelling, destruction temperature, density, adhesion of the coke layer formed as a result of chemical interactions of the components of the intumescent system to the substrate. These characteristics are very important for the long-term fire rating of building structures under fire conditions, especially in the hydrocarbon fire.

Since it is more convenient to use solutions of nanocomposites in IC, only the nanocomposites obtained by the solution method will be further considered. The prepared IC samples were kept in a furnace at a given temperature for 10 minutes, the volumetric swelling coefficient (K, cm^3/g) and the mass of the coke residue (m, %) were determined. Fig. 5 shows the dependences of K of intumescent compositions APP/MA/PER/TiO$_2$ containing the EVA copolymer and nanocomposites (EVA-MMT-I, EVA-EG-I, EVA-MMT-EG-I) as polymer components, on temperature.

Thermogravimetric studies of IC with different nanocomposites are given in Table 3. These data in the first approximation coincide with the values of the mass of the coke residue (m, %) obtained by the step-by-step study of the characteristics of the IC coke layer (Fig. 6). The difference in temperatures ($\Delta T_{80\%}$, °C), at which there is an 80 % mass loss of the coke residue of IC with the nanocomposite and IC with the EVA copolymer can be noted. The presence of EVA-MMT-EG-I nanocomposite in the IC (No. 4, Table 3) slows the disintegration of the coke layer at 84 °C.

the temperature range above 400 °C, the value of the coke residue mass increases in the series: EVA<EVA-EG-I<EVA-MMT-I<EVA-MMT-EG-I.
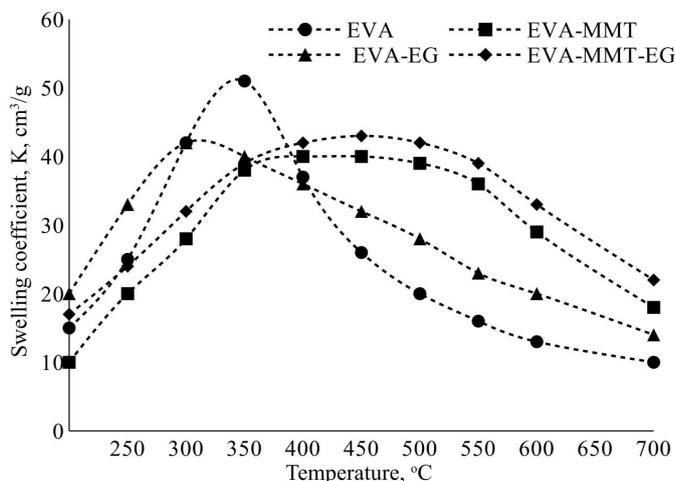

Fig. 5. Dependence of the swelling coefficient K (cm^3/g) of intumescent compositions in the nanocomposite variation on temperature T (°C)
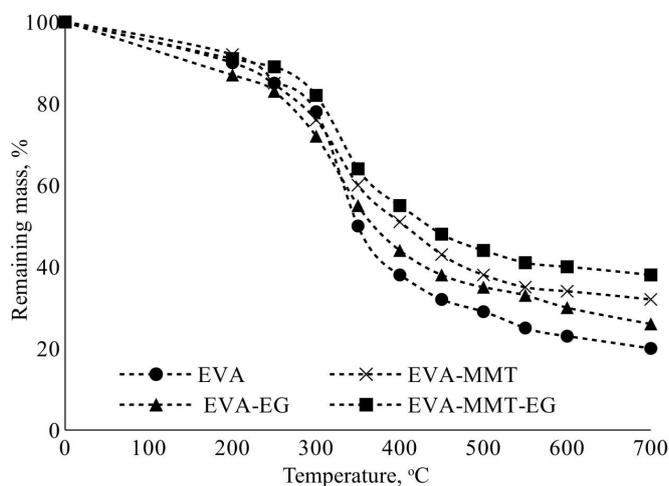

Fig. 6. Dependence of the mass of the coke residue (m,%) of intumescent compositions in the nanocomposite variation on temperature T (°C)

Fig. 7 shows the data of fire tests of intumescent paints of APP/MA/PER/TiO$_2$/EVA(nanocomposite) of composition. These data allow us to compare the effect of the inorganic nanocomposite component on the fire rating of the coating. The fire rating (R, min) was the time from the beginning of fire action until the critical temperature of metal (500 °C). The obtained R values given in Table 3 confirm that the highest fire resistance is demonstrated by the fire-retardant intumescent coating with hybrid nanocomposite EVA-MMT-EG-I.

Based on the results of determining the swelling coefficient and mass loss of IC in the temperature range of 200–700 °C, as well as fire tests, it is possible to draw the conclusion important for the development of effective fire protection coatings for the hydrocarbon fire. EVA hybrid nanocomposites, which simultaneously contain MMT and EG nanoimpurities, are optimum polymer components of fire retardant intumescent coatings.

Table 3

Thermogravimetric analysis and fire rating (R, min) of intumescent compositions APP/MA/PE/TiO$_2$/polymer (nanocomposite)

No.	Polymer/ Nanocomposite	$T_{20\%}$, °C	$T_{50\%}$, °C	$\Delta T_{80\%}$, °C	m, % 700 °C	R, min
1	EVA	305	360	0	20.0	37
2	EVA-MMT-I	300	422	62	35.6	42
3	EVA-EG-I	292	390	35	23.9	40
4	EVA-MMT-EG-I	311	450	84	40.1	47

From Fig. 6, it also appears that the replacement of the EVA copolymer in the IC with EVA-MMT-EG-I nanocomposite increases the coke residue mass 2 times at 700 °C. In
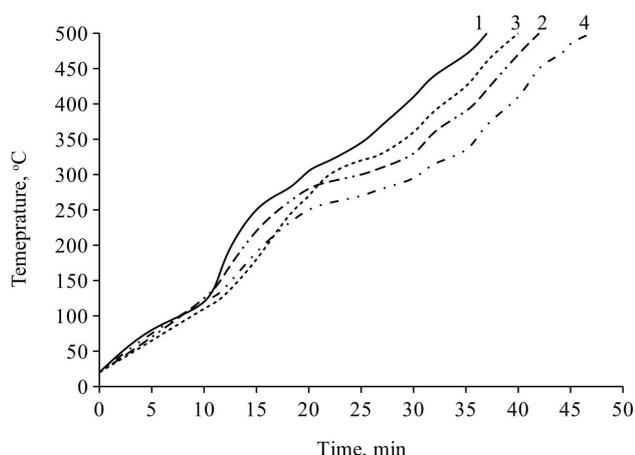
Fig. 7. Dependence of the temperature of the metal plate (T, °C), protected by the APP/MA/PER/TiO$_2$/polymer intumescent coating, on the flame exposure time: 1 — EVA; 2 — EVA-EG-I; 3 — EVA-MMT-I; 4 — EVA-MMT-EG-I

6. Discussion of the results of the study of the effect of nanocomposites on the intumescent fire protection efficiency

6. 1. Identification of the structure of EVA nanocomposites

The aim of this study is to apply the EVA nanocomposites as film formers of intumescent fire-retardant paints. Therefore, one of the important aspects of achieving the aim is to prove the "in situ" formation of nanocomposite in the process of paint production by mixing the components of the EVA polymer and MMT (or EG). Despite the considerable difference in the chemical nature of MMT and EG, these nanoimpurities have common features in their layered nanostructure.

It is known [22] that the melting method is the most common, cost-effective and productive method for obtaining nanocomposites with a high degree of exfoliation. In this case, layered nanomaterial (nanoclay or expanded graphite) is mixed with a polymer matrix in a molten state during intense mixing (grinding). In the process of obtaining a nanocomposite, a polymer enters the intermediate spaces or galleries of nanoparticles, forms intercalates through intermolecular and ionic interactions with subsequent exfoliation. It should also be emphasized that, according to the authors [23], the melting method allows obtaining completely exfoliated nanocomposites, in which nanomaterial is distributed at the level of individual layers up to 1 nm.

According to the method of polymer and nanoimpurity mixing, nanomaterial stratification, the degree of which depends on the nature of solvents or requires additional effects (temperature, ultrasound, shear grinding, etc.), occurs in solution. This method is called exfoliation-adsorption, since the dissolved polymer is adsorbed onto layered fragments, forming nanocomposite material. It is obvious that the degree of nanoimpurity exfoliation in the nanocomposite obtained by this method is the result of a whole complex of factors, both chemical and physical-mechanical.

IR characteristics of the nanocomposites (Fig. 1–3), as well as X-ray phase analysis data (Table 1) of EVA-MMT, EVA-EG and EVA-MMT-EG nanocomposites confirm the formation of the nanocomposites under conditions

of their mixing in solution. According to their structural characteristics (IR spectra 3 and 4, Fig. 1, IR spectra 1 and 2, Fig. 3), the obtained organo-inorganic hybrid compounds practically do not differ from the analogs obtained in the melt. The IR spectra of the nanocomposites (Fig. 1–3) have bands in the region of wave numbers 2,800–900 and 1,100–1,500 cm^{-1} characteristic of the alkyl groups $-CH_3$, $-CH_2-$, as well as characteristic bands of the carbonyl groups of polymers with maxima at 1,740–1,720 cm^{-1}. The intense absorption band in the EVA copolymer range (Fig. 1, 2) – 3,447 cm^{-1} belongs to the $-OH$ groups present in the starting copolymer. The presence of graphite in the nanocomposites is confirmed by the bands at 1,641 cm^{-1} ($-C=C-$). The presence of silicates in the investigated compounds is indicated by the bands at 1,005 cm^{-1} (stretching vibrations of Si–O–Si), as well as the bands at 610–605, 512–505 and 465–458 cm^{-1} (deformation vibrations of Me–O bonds).

In this case, the values of the interlayer distances (d, Table 1, No. 2, 6, 7) show that the exfoliation degree of EG graphite in the EVA-EG-I nanocomposite obtained in solution is even higher than in the similar EVA-EG-II nanocomposite, obtained by the melting method. There are no changes in the intervals between the EG galleries after mixing the EVA and EG melt (No. 2 and No. 7, Table 1) and a slight increase in the interlayer distances in the EVA-EG-I nanocomposite obtained in solution. This is evidence that the EVA chains in the conditions of obtaining nanocomposites enter the gaps between the EG plates, and not in the graphite interplanar space. The same result is presented in [13], where the structure of the EVA nanocomposites with thermally expanded graphites was studied.

A noticeable increase in the interlayer distances (d, nm) for the nanocomposites with MMT (No. 1 and No. 4, 5, Table 1), regardless of the method of obtaining, indicates a high degree of clay exfoliation.

The identity of the structures obtained in solution and melt is indicated by the data of the TGA analysis of the EVA copolymer and hybrid organic-inorganic substances shown in Table 2. In the temperature range of 200–700 °C, no significant difference in the mass loss of the samples between nanocomposites I and II was observed. Only the shift of the main endothermic processes to the more high-temperature region (10–25 °C) is observed, due to the presence of nanoimpurities.

In the framework of this study, the mechanism of thermal decomposition of EVA in the presence of nanoclay and thermally expanded graphite is not studied in detail. From the literature data, it is known [24] that thermal degradation of EVA occurs in two stages. First, there is removal of acetic acid with a rupture of polymer chains (300–350 °C) and formation of ethylene and acetylene copolymers. Further, the polymer is dehydrated with the formation of alkanes, alkenes and diene hydrocarbons (400–500 °C), as well as with the accidental generation of radical particles. It was shown [10, 19, 25] that nanoclays, oxides (Al_2O_3) and hydroxides $Mg(OH)_2$ act as catalysts of cyclic processes, contributing to the formation of EVA degradation products with a decrease in the number in the series – alkene>diene>alkane. In turn, the number of EVA degradation products in the absence of nanoimpurities looks as follows – alkane>diene>alkene. The question of the impact of nanographite or other carbon nanomaterials on the EVA thermal degradation mechanism is open. In some studies [12, 13], there is only a statement of the fact of improved thermal prop-

erties of polymer hybrid organo-inorganic materials with the participation of nanostructured graphites, graphenes, carbon tubes. There is also information that graphites are fairly inert compounds and do not affect the chemical processes associated with thermal degradation of polymers [13].

However, one can single out the main directions of inhibition of combustion processes of polymers in the presence of nanoimpurities:

– deceleration of radical processes by the formation of scavengers of radicals formed during dehydration and rupture of polymer chains;

– formation of barrier screens by flat nanoclay and nanographite nanoparticles that prevent the flow of oxygen into the combustion zone;

– formation of rigid coke residues due to the coal-forming ability of the investigated nanoimpurities.

The proven identity of the studied EVA nanocomposites is of great practical importance for the technology of intumescent fire retardant coatings. The use of EVA-MMT-I, EVA-EG-I and EVA-MMT-EG-I (in the form of solution) nanocomposites allows developing formulations of intumescent coatings based on the in-situ obtained stable nanocomposite matrix, which does not require additional technological lines for obtaining nanocomposites.

6. 2. Effect of the EVA nanocomposites on the formation of the coke layer of the intumescent composition

The swelling coefficient (K, cm^3/g) of IC is one of the main characteristics of intumescent fire protection, the essence of which consists in the formation of a heat-insulation layer of the coating under the influence of fire. The nature of changes in K for the APP/MA/PE/TiO$_2$ system with temperature increase in the range of 200–600 °C (Fig. 5) demonstrates the effect of the nature of the nanoimpurity in EVA according to the following parameters:

– change in the temperature of the beginning of swelling – the samples containing graphite in the EVA nanocomposite swell in the more low-temperature region. The temperature of swelling increases in the row: EVA-EG-I< <EVA<EVA-MMT-EG-I<EVA-MMT-I;

– length of the stabilization site – the temperature interval, where K has conditionally maximum values (the dotted line in Fig. 5). From Fig. 5, it turns out that the swelling coefficient is maximum at the following temperatures: EVA (280–415 °C); EVA-MMT-I (320–585 °C); EVA-EG-I (250–445 °C); EVA-MMT-EG-I (300–610 °C);

– shift of temperature of intense destruction of the coke layer, which coincides with the conditional end of the stabilization site.

The analysis of the results for the mass loss of the investigated IC (m, Table 3, Fig. 6) also indicates the positive effect of the nanocomposites: at 700 °C, the mass of the coke residue of IC with the EVA nanocomposites is 1.5–2 times higher compared with the same indicator of IC with the EVA polymer. And at temperatures above 400 °C, the smallest mass loss is observed for IC containing the hybrid nanocomposite EVA-MMT-EG-I.

Based on the results of determining the swelling coefficient and mass loss of IC in the temperature range of 200–700 °C, one can conclude about the synergistic effect of nanoclay and nanographite in the intumescent system APP/MA/PER/TiO$_2$. Synergy in this case should be considered as an excess of K and m for the EVA-MMT-EG nanocomposite over the values that could be expected based on K and m for EVA-MMT and EVA-EG.

Such a dependence of the process of formation of the heat-insulation coke layer on the nature of the inorganic component of the nanocomposite indicates its direct involvement in the chemical and physical processes of coke formation. We can offer the following mechanisms of nanoimpurity effect in IC:

– catalysis or inhibition of chemical processes between IC components;

– creation of barriers for oxygen in the zone of combustion and migration of released gases;

– participation in carbonization processes with coke layer formation.

Within this study, it is impossible to explain the nature of the synergism of MMT and EG nanoimpurities. Nevertheless, the synergistic effect of nanoclay and nanographite is confirmed by fire tests of the intumescent coating (Fig. 7).

From Fig. 7, it appears that the fire rating R (Table 3) for the intumescent paint containing the EVA-MMT-EG nanocomposite is 47 min, which exceeds the value for EVA-MMT (42 min) and EVA-EG (40 min). Given that fire tests were conducted in the hydrocarbon fire, one should consider the promising application of hybrid nanocomposites with inorganic nanoimpurities such as nanoclays and nanographites for the development of special fire-retardant coatings. It should also be understood that certain values of the fire rating R are not values that are determined according to generally accepted world or national standards. But there is a clear indication of the trend of increasing fire protection efficiency of intumescent fire-retardants when using polymer organic-inorganic nanocomposites instead of traditional polymer binders.

7. Conclusions

1. The nanocomposites of the EVA copolymer with MMT and EVA with EG, obtained in solution and melt, have the same structure. It was proved that 2–4 % (by mass) of nanoclay and 2.5–6.5 % (by mass) of nanographite in the EVA nanocomposites increase the temperature of oxidative decomposition of EVA by 10-25 °C.

2. The use of the nanocomposites instead of the EVA copolymer in the intumescent compositions APP/MA/PE/TiO$_2$ positively affects the formation of the coke layer in the temperature range of 400–600 °C and increases the coke residue mass 2 times at 700 °C. It was determined that the simultaneous presence of nanoclay and nanographite in the hybrid nanocomposite EVA-MMT-EG shows the synergistic effect. The intumescent paint containing the EVA-MMT-EG nanocomposite ensures an increase in the fire resistance of metal by almost 20 % compared with the paint containing the EVA copolymer.

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