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Investigation of the Effect of Fillers on the Properties of the Expanded Coke Layer of Epoxyamine Compositions

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Abstract. Intumescent fire-retardant coatings based on epoxy resins, compared to traditional fire-retardant compositions, have improved performance properties – high strength, chemical and atmospheric resistance, adhesion to many materials. However, unmodified epoxy polymers are combustible and to obtain IFR based on them, flame retardants and mineral fillers are added to their composition. Intumescent systems for flame retardant coatings based on epoxy oligomers (non-halogen-containing) usually consist of ammonium or ammophos polyphosphate as an acidic agent and a wide range of fillers, both inert and gaseous, or which are an additional source of carbon. Each component of the fire-retardant intimate coating in different ways affects the processes of coke formation, which determines the requirements for their choice. Thus, the aim of this work is to conduct experimental studies of the dependence of the characteristics of the expanded coke layer on the composition of the intumescent epoxyamine composition.

The results of experimental studies of the effect of ammonium polyphosphate and binary mixtures of ammonium polyphosphate (APP) with aluminum hydroxide (AH), sodium tetraborate decahydrate (STD), titanium oxide TiO_2 (TO), pentaerythritol (P), aerosil (A) and expandable graphite are presented (EG) on the multiplicity of expanding and weight loss of epoxy compositions at study temperatures of 350, 400 and 450°C.

Studies have shown that the production of intumescent flame retardant coatings based on epoxy oligomers is possible provided they are filled with ammonium polyphosphate in an amount of more than 20 mass parts. The most effective in terms of expanding are additives titanium oxide and aluminum hydroxide in an amount of 20 mass parts, which allows to obtain intumescent fire-retardant coatings with a linear coefficient of expanding 30-32 and 24-27, respectively, throughout the range of temperatures. The obtained data are useful in the development of fire-retardant coatings based on epoxy oligomers.

Introduction

The problem of ensuring the appropriate level of fire resistance of building structures, utilities and communications is an important component in the field of construction, industry and transport. Among the methods used to increase the fire resistance of building structures [1-5], the most common is the use of intumescent (reactive) fire-retardant coatings (IFRC). The fire-retardant effect of such coatings is associated with two main factors – chemical and physical [6]. The chemical factor is caused by endothermic reactions of system components with the formation of a strong coke layer and the release of volatile non-combustible substances that slow down or inhibit combustion. The physical factor is the thermal insulation of the protected surface with the help of the formed coke layer. The multiplicity of expanding of the IFRC reaches values 20-80.

Intumescent systems (IS) for fire protection, which are used today in world practice, mainly consist of the following main components: acid donor, carbonizing agent and gasifier [6, 7]. Pentaerythritol (PE) and polysaccharides are most often used as carbonizing agents in traditional

flame retardant compositions, and phosphates and ammonium polyphosphates (APP) are used as donor acids, as well as melamine or urea as a gasifier [6]. An important point in the development of fire-retardant compositions is the choice of film former – polymeric binder. Acrylic dispersions and copolymers, dispersions based on polyvinyl acetate and its copolymers, silicone rubbers, phenol-formaldehyde and epoxy resins are traditionally used as film formers [5, 8]. Since film formers [9, 10] differ in viscosity, fluidity, adhesion, strength, heat resistance and flammability, the operational and technological properties, advantages and disadvantages of fire-retardant coatings depend primarily on the nature of the polymeric binder.

Water-based film formers have obvious advantages in their environmental friendliness. In [10] one of the methods of preliminary evaluation of water-based IVP efficiency is given, comparison of such characteristics of fire-retardant coating as weight loss, expanding coefficient, heat-insulating efficiency for polyvinyl acetate, acrylic and styrene-acrylic water dispersions with fixed content of components is made (pentaerythritol, titanium oxide (II) TiO_2, ammonium polyphosphate, melamine). The results are to inform you about the efficiency of the quality control in the flammable warehouses based on the polyvinyl acetate dispersion of the DF 51/10C brand, which will provide a multiplicity of up to 84.6. However, the IFRC on a water basis is sensitive to the climatic factors from the hour of application and during operation, there may be corrosion of metals applied to an unprepared surface and strong until the components of the system are imbued with power, at the same time.

Crossings in fire-rated pokrittiv on the basis of plivkotvoryuvachiv on organic razchinnikov є the ability to apply for low temperatures, reducing the atmosphere and water resistance. The main general disadvantage of flame retardants based on ammonium polyphosphate, pentaerythritol, melamine and organic film former is the toxicity of their thermal decomposition products due to the presence of halogen-containing components (including chloroparaffins) [5].

Fire-retardant compositions based on epoxy oligomers should be singled out. If we compare intumescent fire-retardant coatings based on epoxy resins with other film formers, we can say that these IFRC have improved performance properties - high strength, chemical and atmospheric resistance, adhesion to many materials [12]. However, unmodified epoxy polymers are combustible and to obtain IFRC based on them, flame retardants and mineral fillers are introduced into their composition. The influence of the chemical nature and content of phosphate fillers and bromine-containing flame retardants on heat resistance, flammability and smoke-forming ability is presented in [13], it is shown that from the point of view of flammability bromine-containing flame retardants are more effective. However, recently, both in the EU and in Ukraine, there are some restrictions on the use of halogen-containing materials aimed at ensuring human safety and environmental protection. Therefore, the use of halogen-containing flame retardants to obtain IFRC based on epoxy materials is not desirable. As a result of the analysis of the scientific literature it is established that fire-retardant epoxy polymers (non-halogen-containing) are obtained by introducing phosphates, pentaerythritol, melamine, alkaline earth metal hydroxides, graphite into their composition [2, 4-8, 12-18].

A feature of IFRC based on epoxy oligomers is also that the source of carbon for the formation of a swollen coke layer under thermal effects is the polymer itself. Previous studies have shown that modification of epoxy polymers with monoammonium phosphate, activated basaltic scales and oxides of transition valence metals allows to obtain a fire-retardant composition for wood with an oxygen index of 27-33% [14-16] and with acceptable performance characteristics. To reduce the flammability of epoxy polymers, the authors [18] proposed the use of silicon compounds both by introducing silicon atoms into the structure of epoxy polymers and by filling them with inert flame retardants. In [19], the authors used inert quartzite and dinas with a high SiO_2 content to modify epoxy composite materials. The flammability of the polymers was evaluated by the oxygen index. It is known from the literature [20, 21] that intumescent systems for flame retardant coatings based on epoxy oligomers usually consist of ammonium polyphosphate or ammophos as an acid agent [4, 14, 20, 21] and a wide range of fillers as inert (silicon oxide) [18], basalt scales [16], metal compounds [12, 22] and those that intensify gas formation (borax, aluminum hydroxide) [4, 20] and

are an additional source of carbon [4, 7].

The possibility of using modified non-combustible epoxy polymers as fire-retardant coatings for building structures is of interest in the study of such a characteristic of IFRC as the expanding rate.

Unresolved Issues

The development of fire-retardant coatings that swell under the influence of high temperatures is a complex scientific and practical task that requires a clear understanding of the role of each of the components in the intumescent system. The given researches of influence of the basic components of epoxy fire-retardant coverings give idea of multiplicity of expanding, flammability, operational and technological characteristics of the specified coverings. However, these studies were conducted in a complex that does not allow to assess the effect of each of the components on the formation of a protective coke layer. It should be noted that each component of the fire-retardant intimate coating has a different effect on the processes of coke formation, which determines the requirements for their selection. Thus, the aim of this work is to conduct experimental studies of the dependence of the characteristics of the expanded coke layer on the composition of the epoxyamine compound.

Main Part

As the object of the study used compositions based on epoxy oligomer ED-20 (DSTU-2093-92), hardened with a hardener polyethylene polyamine (PP) (TU 2413-357-00203447-99). To reduce the flammability of epoxy polymers and to form a porous coke layer during thermal exposure to their composition was introduced ammonium polyphosphate (APP) in an amount of 10-40 mass parts (m.p). Modification of the APP-filled composition to study the characteristics of the swollen coke layer was performed by introducing aluminum hydroxide (AH), sodium tetraborate decahydrate (STD), titanium oxide TiO_2 (TO), pentaerythritol (P), pyrogenic silicon dioxide – aerosil (A) and expandable graphite (EG).

To study the characteristics of the swollen coke layer, tests were performed on samples to determine the linear coefficient of expanding K_L, carried out on the basis of the method DSTU-N-P B B.1.1-29: 2010 [23] and determined the weight loss of samples after these tests.

The essence of the method of determining the linear coefficient of expanding is to determine the ratio of the thickness of the coating applied to the steel plate, measuring 50x50 ± 1 mm and a thickness of 2.0 ± 0.2 mm, before and after temperature exposure. In contrast to DSTU-N-P B B.1.1-29: 2010, the study was conducted not at a fixed temperature of 340°C, but at temperatures of 350°C, 400°C and 450°C ± 5°C. Measurement of the thickness of the swollen layer after temperature exposure was performed using a caliper depth gauge at five points for each sample, located: the first - in the geometric center of the sample, and four more – equidistant from the central point diagonally at a distance of 0.25 length of this diagonal.

To estimate the linear coefficient K_L expanding we used the following relationship:

$$K_L = \frac{h_{c1} + h_{c2} + h_{c3} + h_{c4} + h_{c5}}{d_c} \quad (1)$$

where h_{c1}, … h_{c5} – the results of measuring the thickness of the expanded coating at the appropriate points, mm.

d_c – e thickness of the coating layer before the test, determined by a caliper as an average of four points.

Samples were prepared as follows. A layer of test epoxy polymer with the appropriate content of components was applied to the prepared steel plate. The samples were dried at 20 ± 5°C for 48 hours and at 70 ± 5°C for three hours according to the requirements [23].

The study was performed in a muffle furnace СНО30/1100И4ПР.

The weight loss of the samples Δm (%) was determined by the ratio:

$$\Delta m = \left(1 - \frac{m_t + m_{pl}}{m_c + m_{pl}}\right) \cdot 100 \quad (2)$$

where m_t – is the mass of the coated plate after the test, g;

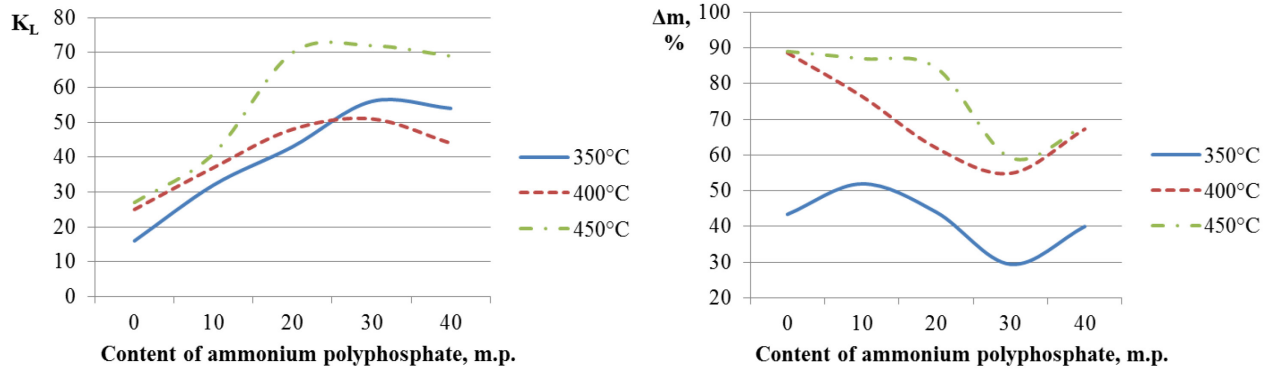
m_c – is the mass of the coated plate after drying, g;

m_{pl} – mass of the plate, g.

The tests were performed K_L and Δm on two samples for each experiment and took the arithmetic mean.

Determination of mass was carried out to the nearest 0.01 g using scales REDWAG PS 4500.R2.M.

The results of the study of the linear coefficient of expanding of K_L and weight loss Δm (%) of epoxy polymer from the content of ammonium polyphosphate in tests at a temperature of 350, 400 and 450°C are presented in Fig. 1.



a. b.

Fig.1 Dependence of the linear expanding coefficient K_L (a) and weight loss Δm (%) (b) on the content of ammonium polyphosphate in tests at 350°C, 400°C and 450°C.

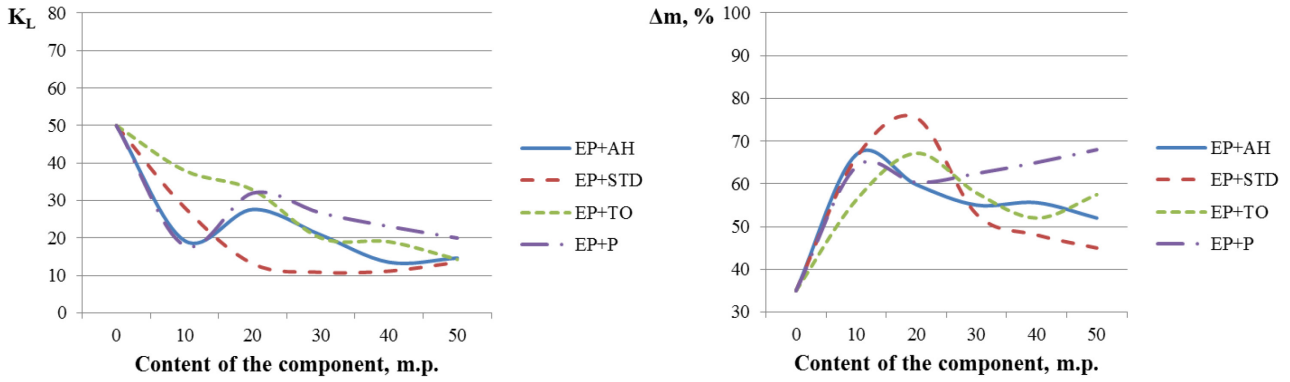
From the dependences of the expanding ratio on the APP content presented in Fig.1 a, it can be seen that with increasing the content of the component, the linear expanding coefficient increases to a value of 72 when the APP content is 25 mass parts and test temperatures of 450°C. At temperatures of 350°C and 400°C, the maximum value of K_L was obtained at an APP content of 30 mass parts and is 60 and 51, respectively.

The weight loss of the test samples decreases with increasing APP content to 30 mass parts after which there is a slight increase in weight loss. It is expected that at higher temperatures the weight loss is greater. When filling the epoxy polymer APP in the amount of 30 mass parts the lowest values of weight loss of 30, 54 and 54% are observed at temperatures of 350, 400 and 450°C, respectively.

From fig.1 a, b shows that the introduction of APP into the polymer matrix in an amount of 20-30 mass partss allows to obtain a coating with the highest value of the expanding ratio for all ranges of the studied temperatures. In [15] the results of studies of flammability of epoxy polymers on the index of oxygen index from the content of impurities are presented. According to the results of these studies, the introduction into the epoxy polymer of ammophos (the main component - ammonium dihydrogen phosphate) allows to obtain a "self-extinguishing" composition with LOI 26 and 31% when filled with 20 and 30 mass parts in accordance.

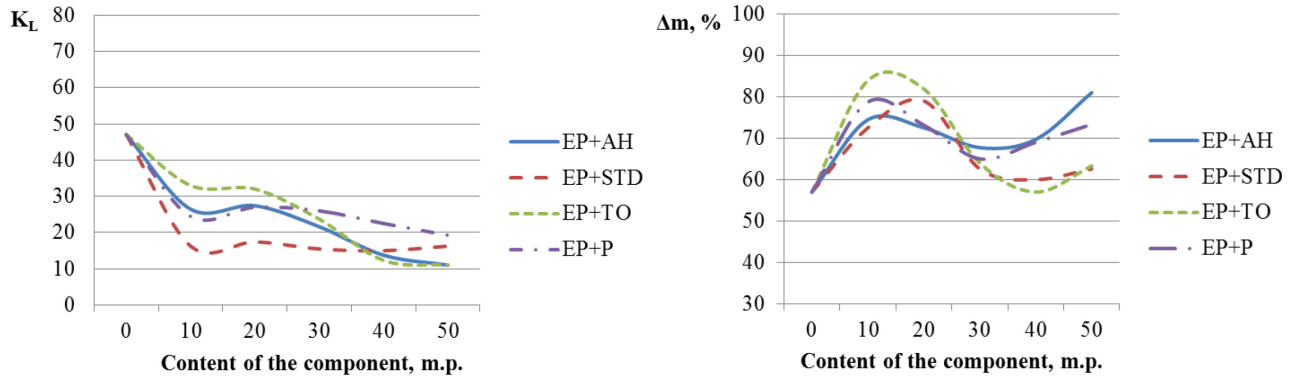
Thus, further studies were performed on binary mixtures, one of the components of which was chosen APP in the amount of 25 mass parts (EP), and the second aluminum hydroxide (AH), sodium tetraborate decahydrate (STD), titanium oxide (TO), pentaerythritol (P) in amounts of 10-50 mass parts and aerosil (A) and expandable graphite (EG) in an amount of 2-10 mass parts.

The results of the study of the linear coefficient of expanding K_L and weight loss Δm (%) of epoxy polymer from the content of these components in tests at a temperature of 350, 400 and 450°C are presented in Fig.2-7.



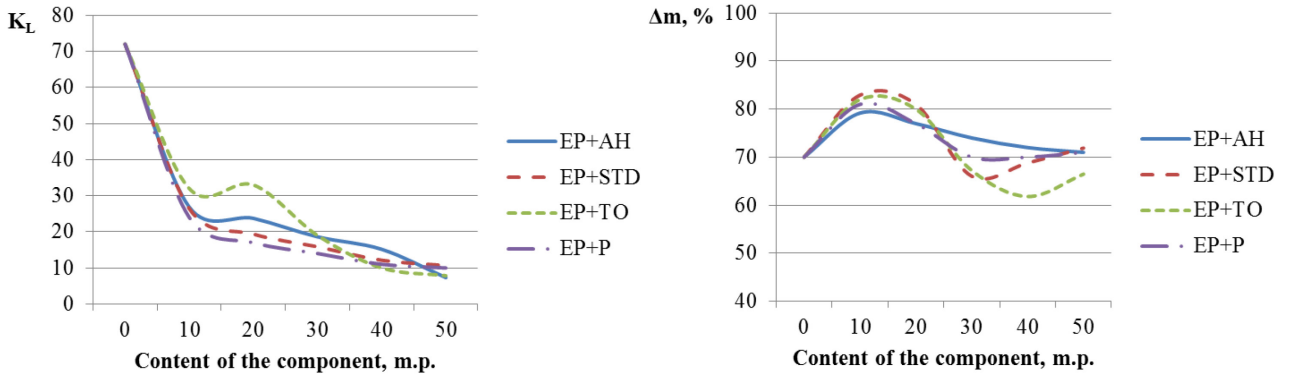
a. b.

Fig.2 Dependence of the linear coefficient of expanding K_L (a) and weight loss Δm (%) (b) of the epoxy polymer on the content of the component (alumina trihydrate, sodium tetraborate, titanium oxide (IV) and pentaerythritol) when tested at 350°C.



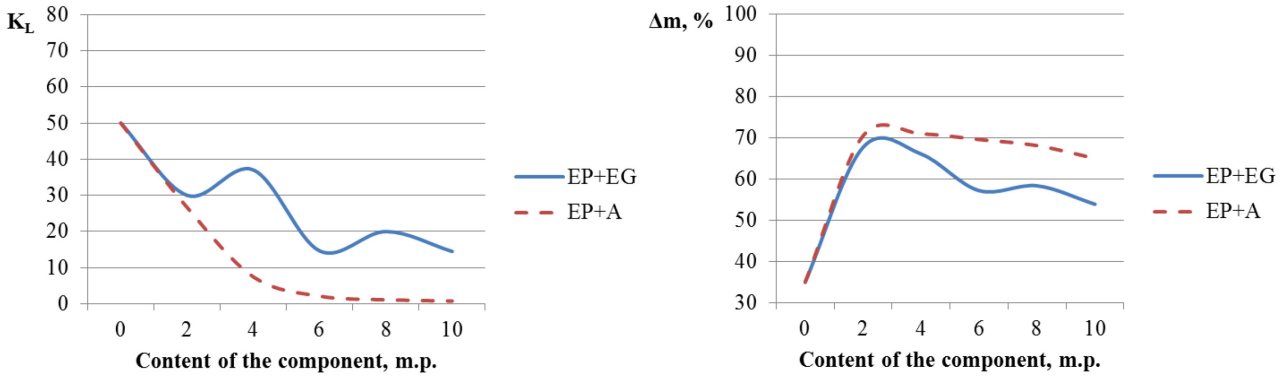
a. b.

Fig.3 Dependence of the linear coefficient of expanding K_L (a) and weight loss Δm (%) (b) of the epoxy polymer on the content of the component (alumina trihydrate, sodium tetraborate, titanium oxide (IV) and pentaerythritol) when tested at 400°C.



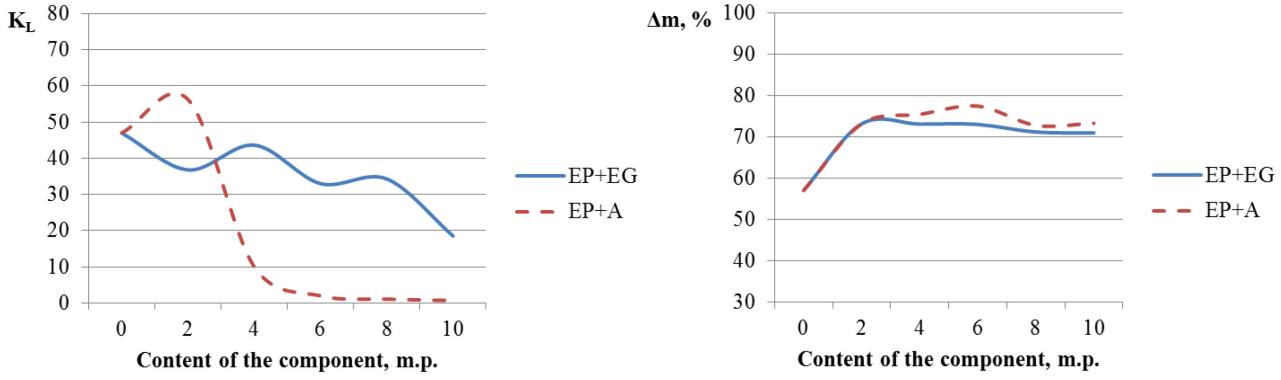
a. b.

Fig.4 Dependence of the linear coefficient of expanding K_L (a) and weight loss Δm (%) (b) of the epoxy polymer on the content of the component (alumina trihydrate, sodium tetraborate, titanium oxide (IV) and pentaerythritol) when tested at 450°C.



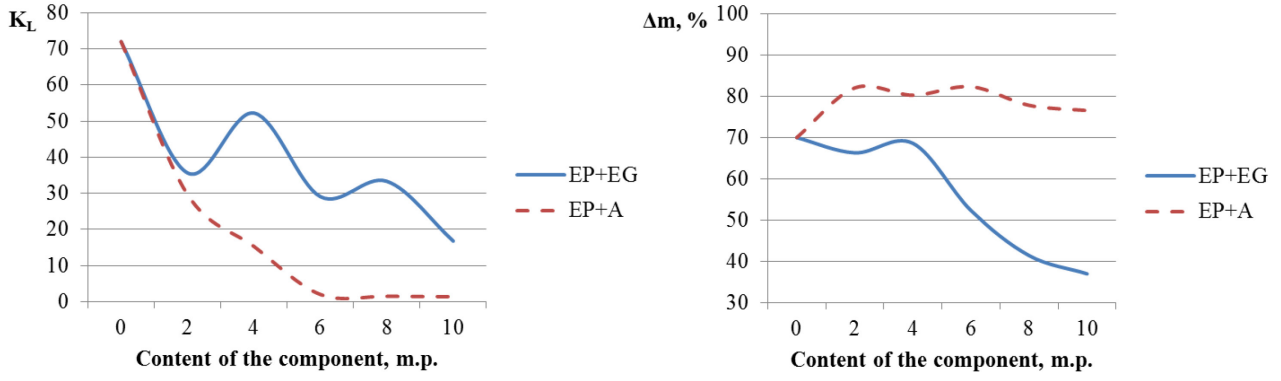
a. b.

Fig.5 Dependence of the linear coefficient of expanding K_L (a) and weight loss Δm (%) (b) of the epoxy polymer on the content of the component (graphite and aerosil) when tested at a temperature of 350°C



a. b.

Fig.6 Dependence of the linear coefficient of expanding K_L (a) and weight loss Δm (%) (b) of the epoxy polymer on the content of the component (graphite and aerosil) when tested at a temperature of 400°C.



a. b.

Fig.7 The dependence of the linear coefficient of expanding K_L (a) and weight loss Δm (%) (b) of the epoxy polymer on the content of the component (graphite and aerosil) when tested at a temperature of 450°C.

Analysis of the results showed that the introduction of additives leads to a decrease in the multiplicity of expanding and to an increase in weight loss compared to the composition filled only with APP. Addition of TiO_2 in the amount of 20 mass parts stabilizes K_L at the level of 30-32 in all range of the investigated temperatures. A similar effect is observed when adding 20 mass parts including aluminum hydroxide for temperatures of 350 and 400°C (K_L = 27), but at a temperature

of 450°C is a decrease in K_L to 24. The introduction into the composition of EPP pentaerythritol allows to obtain K_L to 32 when tested at 350°C, but with its growth, the effectiveness of the additive decreases. Sodium tetraborate decahydrate significantly reduces the expanding rate of epoxy polymer.

The use of graphite and aerosil in the amount of 2-10 mass parts stabilizes the weight loss of the samples when tested at temperatures of 350 and 400°C at the level of 55-75% and 70-80%, respectively. At a temperature of 450°C, the weight loss of the samples filled with graphite decreases, which depends on the type of increase in the content of graphite. The multiplicity of expanding reaches the highest values with the introduction of 4 mass parts graphite. The introduction of aerosil more than 2% is not advisable, as it leads to a sharp decrease in the multiplicity of expanding, although the effect of stabilizing the weight loss of the sample is maintained even at a temperature of 450°C. This is obviously due to the increase in the melt viscosity of the epoxy polymer during heating with the introduction of aerosil.

Summary

Thus, the paper presents the results of experimental studies of the effect of ammonium polyphosphate and binary mixtures of ammonium polyphosphate with alumina trihydrate, sodium tetraborate, titanium oxide (IV), pentaerythritol, aerosil and graphite on the expanding rate and weight loss of epoxy compositions in tests at 350, 400 and 450°C.

Studies have shown that the production of intumescent flame retardant coatings based on epoxy oligomers is possible provided they are filled with ammonium polyphosphate in an amount of more than 20 mass parts. The most effective in terms of expanding are additives titanium oxide and aluminum hydroxide in an amount of 20 mass parts, which allows to obtain intumescent fire-retardant coatings with a linear coefficient of expanding 30-32 and 24-27, respectively, throughout the range of temperatures. The obtained data are useful in the development of fire-retardant coatings based on epoxy oligomers.

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