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Дослідження проводили з використанням потрійної інтумесцентної системи, яка базується на Exolit AP 740 F і представляє собою синергетичний систему на основі поліфосфатів амонію з додаванням азот-вмісних сполук. В якості зв’язуючого використовувався стирол-акриловий полімер, роль пігменту виконував діоксид титану. Пластифікатори в дослідженні були обрані таким чином, щоб оцінити вплив їх молекулярної маси на структуру піни. В якості пластифікаторів були обрані: дибутилфталат і полібутенові олігомери: Indopol H 1200, Indopol H 6000 і Indopol H 18000.

Результати представлені у вигляді зображень електронної мікроскопії, часу досягнення критичних температур при випробуванні пальником Бунзена, коефіцієнти спучування композиції, а також графіків термогравіметричного аналізу.

Встановлено вплив пластифікаторів на пористу структуру і вогнестійкість вуглецевих пін інтумесцентних покриттів. На прикладі полібутенових аліфатичних матеріалів були визначені температурні інтервали термоокислювальної деструкції пластифікаторів, встановлена залежність їх стабільності при термічній обробці від значення молекулярної маси. Показано, що застосування пластифікаторів різної молекулярної маси дозволяє змінювати розміри комірок пін, шляхом зниження показника границі текучості розплаву, що призводить до збільшення розмірів цих комірок. При збільшенні молекулярної маси здатність пластифікатора формувати асоціативні структури зростає, що підвищує межу текучості розплаву і знижує значення середнього діаметра комірки піни, а також змінювати характер утворювання контракційних тріщин в структурі. Встановлено, що показник вогнестійкості покриттів залежить від типу і молекулярної маси використовуваних пластифікаторів. Для розглянутої інтумесцентної системи на основі стирол-акрилового полімеру виявлена залежність вогнестійкості від молекулярної маси пластифікатора.

Результати дослідження можуть бути використані при розробці рецептур інтумесцентних систем для протипожежного захисту

Ключові слова: інтумесцентне покриття, вуглецева піна, пластифікатор, термоізоляція, структура вуглецевого шару, вогнезахист

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INFLUENCE OF PLASTICIZERS ON FIRE RETARDING PROPERTIES OF CARBON FOAMS OF INTUMESCENT COATINGS

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1. Introduction

Intumescent coatings are a relatively new, but at the same time a very extensive class of materials used as passive fire protection. In 2017, their market volume amounted to about USD 900 million, every year the market is growing by 4–6 % on average [1]. The basic principle of operation of this protection is formation of porous coal foam when covering an open flame. The thickness of the foam layer exceeds the thickness of the original coating by 15–50 times. This causes a sharp decrease in thermal conductivity and delays the moment of reaching the temperature of softening of a steel structure, protected by the coating.

Up to now, the coatings with such an effect have been developed based on different polymers, including epoxy, polyurethane, and acrylic. The materials based on both organic solvents and aqueous dispersions are available [2]. However, most industrial intumescent coatings are based on the same operating system, including three main components: the acid donor, carbonized component, as well as pore forming agent. The interaction of these components was studied sufficiently well, however, the properties of the final product are also influenced significantly by other components of the system.

Since intumescent coatings are a conversion system, the important factor is not only the structure of the original thin-layer composite, but also the foam structure, which determines heat protective properties. In addition to structural features, such as general porosity, distribution of pores by dimensions, and their nature, mechanical strength of the foam and its adhesion to the base are important for fire retardant properties. The influence of additives on these indicators has been studied only partially so far, but their use enables fine adjustment of thermal insulation properties of a foam layer within a wide range.

Thus, studying the role of additives in the formation of heat protective properties of foams is an important task, the fulfillment of which will allow the creation of a general model of relation between the composition of the original composite, foam structure and ultimate fire-retarding properties of intumescent coatings.

Plasticizers are an additive that is widely used in the industry of paint and varnish coatings. Their effect involves an increase in the mobility of macromolecular polymer chains, which leads both to a decrease in melting temperature of the material, and the change in viscosity of its melt. Potentially, this makes plasticizers one of the effective regulators of the structure of fire-retardant foam, and, therefore, a means of improving the indicators of fire resistance of intumescent coatings.

This tool of the ultimate optimization of the structure of the insulating layer is not sufficiently explored in existing scientific publications. This increases the gap between the properties of the model systems explored in studies and those of actual industrial products. Lack of knowledge about the influence of plasticizers, in turn, leads to weak substantiation of the application of these components that are widely used in technological solutions.

2. Literature review and problem statement

During coal foam formation, a polymeric binder changes the rheological properties of the melt in the intumescent system so as to ensure its stability and strength. The impact of this component has been studied well enough.

Paper [3] explores the influence of molecular weight of the epoxy binder on the insulating properties of the foam of coating. It was shown that there is a certain optimum of the length of the molecular chain, at which a high foaming coefficient is reached with retaining the uniformity of the structure. An increase in this value causes a decrease in the foam height and its non-uniformity, which is probably caused by the complexity of bubbles formation under conditions of increased viscosity of the melt. These conclusions are supported by viscometry data, however, in the framework of this article, the authors are limited to the factor of molecular weight while studying the influence of viscosity on the foam structure.

In paper [4], the effect of binders of various nature on thermal oxidation processes of the system was studied. It was shown that when using hybrid silicone-acrylate polymer, oxidation resistance increases, which naturally leads to an increase in the foam weight after annealing. The use of these binders is one of the most promising ways to improve the stability of carbon layer, as during annealing, the formed carbon-containing foam eventually loses this component and transfers to the less solid mineralized phase. However, the authors do not take into consideration the parameters of porosity of the system, which that does not make it possible to assess adequately the effect of the binders of this class on general fire resistance of the coating.

Article [5] showed that some burning inhibiting additives decrease viscosity of the melt in the course of its formation, thereby reducing the general fire resistance of the coating. However, the authors consider only a decrease in viscosity of the system as a negative factor.

The largest number of papers is devoted to the influence of fillers on general fire resistance of the coating. Thus, article [6] explores the unique role of titanium dioxide, which involves the formation of phosphates of mixed composition (using polyphosphate as an acid donor). Its use enhances adhesion of residual foam to the steel substrate and strengthens the coating in general, which affects the resulting fire-resistance of coatings.

Paper [7] discusses the use of talc as a structuring plate filler. An increase in the overall fire-retardant capacity, which is associated with the increased content of mineral components in the coating and a change in the foam morphology, was shown. In paper [8], the simultaneous influence of two types of fillers with nanodimensional particles of the lamellar form – montmorillonite and graphene – was explored. It was shown that the latter significantly changes the chemical composition and the configuration of coal foam cells, which increases the thermal ability of the intumescent coating by 13 %, compared with the standard. Article [9] notes the effect of the surface of kaolin, used as a filler, inhibiting thermal oxidation. This is achieved by chemical interaction of the binder in the annealing process with the active groups on the surface of the clay mineral. A similar effect is described in [10], using montmorillonite as an example. In particular, the interactions with silicone organic polymer with the surface hydroxyl groups of the aluminosilicate were proved. In addition, the fillers have a strengthening effect on the foam structure, which is particularly expressed for fibrous particles. For example, in article [11], multi-layer carbon nanotubes are used in article [11] and basalt fibers in paper [12].

Thus, when considering the influence of the filler, two main effects are usually separated: a change of the morphology of foam cells and inhibition of carbon layer oxidation. The first effect, obviously, comes at the expense of changing the rheological properties of the melt, and the second is due to the guiding force of the mineral surface. It is noteworthy that a change of cells morphology is also achieved due to regulation of rheological properties of the polymer melt, as shown previously.

However, both the polymer part, and the filler are often the means of regulating a series of additional properties of a coating: strength, water resistance and so on. It causes the necessity of introduction in the composition of a component that would be suitable for fine regulation of rheological properties. This component of melt can be a plasticizer, the role of which was not studied at the sufficient level in modern studies.

3. The aim and objectives of the study

The aim of this study is to establish the possibilities of the regulation with the help of the plasticizers of the structure, thermal behavior, and general fire retarding properties of carbon foams of intumescent coatings.

To accomplish the aim, the following tasks have been set:

– to assess the influence of plasticizers on the structural features of the formed foams;

– to determine the influence of plasticizers with different molecular weight on the thermal character of formation of foams of intumescent systems;

– to establish the change in the fire-resistance of coatings with different content of plasticizers.

4. Materials and methods for studying the influence of plasticizers on the features of carbon foams of intumescent coatings

4. 1. Studied materials and equipment that was used in the experiment

The studies were conducted using the triple intumescent system Exolit AP 740 F (Clariant, Switzerland), which represents a synergetic system based on ammonium polyphosphate with addition of nitrogen-containing compounds. Styrene-acrylic polymer Neocryl 880 B (DSM Neoresins, Netherlands) was used as a binder, titanium dioxide Kronos 2043 (United States of America) acted as a pigment, Solsperse 26000 (Lubrizol, United States of America) acted as a dispersion agent. Xylene was used as solvent.

The ratio of components in the coating is given in Table 1.

Table 1

Basic formulation of coating

Component	Content, weight, %
Xylene	24.66
Dispersion agent	1.5
Polymer	12.34
Intumescent system	53
Pigment	8.5

Plasticizers in the study were selected to assess the influence of their molecular weight on the structure of foams, because it was expected that it could be an additional tool of controlling the rheological indicators of the melt. On this basis, dibutyl phthalate and polybutene oligomers Indopol H 1200, Indopol H 6000 and Indopol H 18000 (Ineos Oligomers, United Kingdom) were selected as plasticizers. Molecular weight of these substances was 278, 2100, 6000 and 4200 g/mol, respectively.

4. 2. Preparation of samples

The compositions were prepared by mixing using high-speed laboratory dissolvers of brand GFS-RN (Qinhungdao Pengyi Chem-Industry machinery co., Ltd, China). At the first stage, acrylic polymer was gradually added to the estimated amount of xylene at a low rate (400–600 rpm). At the end of the introduction of the polymer, the number of rotations increased to 2,000 and mixing was carried out until a transparent homogeneous solution was obtained. The dispersant was added to this solution, followed by the introduction of titanium dioxide, which was additionally dispersed at the rate of 3,500–4,000 rpm within 15 minutes. Then, the dissolver was switched to a low rate (250–330), the system was cooled to room temperature and degassed. The intumescent system was gradually introduced in the dispersion at the rate of up to 1,200 rpm. After the introduction, the composition was additionally stirred for 5 minutes to homogeneity.

Plasticizers were introduced to the same portions selected from the basic composition in the amount of 6 % by weight at stirring at the rate of 600 rpm for 15 minutes. The obtained homogeneous systems were degassed and cooled to room temperature before applying. The samples were marked according to Table 2.

Table 2

Marking of samples

Plasticizer	Marking of samples
–	Sample 1
Dibutyl phthalate	Sample 2
Indopol 1200	Sample 3
Indopol 6000	Sample 4
Indopol 18000	Sample 5

The samples of the compositions were applied on the smooth substrate from polytetrafluorethylene and dried at the temperature of 80 °C at a laboratory furnace for 12 hours. The obtained films were ground to conduct the thermal analysis.

To test fire resistance, the samples were applied on the steel plate with the thickness of 6 mm. The thickness of the coating in this case was 1.6 mm. The coatings were dried in the exhaust chamber for three days at room temperature and then in the drying chamber at the temperature of 80 °C for 24 hours.

The coated plate was mounted vertically on a tripod and was exposed to a controlled flame from burning propane gas. The temperature was maintained at about 1,000 °C. The distance from the nozzle and the coated plate was 15 cm. The setup consisted of a cylinder with propane, the holder for coated plates and the surface thermocouple, which was attached on the back side of uncoated metal plates.

The value for the coefficient of expansion factor (K) was determined as the ratio of the thickness of the original coating (mm) to the thickness of the coal foam layer (mm), obtained after fire resistance testing. To account for non-uniform thickness of the foam, the measurements were taken at six points of each sample, and the total thickness was calculated as arithmetic mean of these measurements.

To obtain the images of electron microscopy, the samples in the form of carbon foam after annealing were cut with the microtome knife DB 80 (Leica, Germany) into slices of the thickness of about 1 mm and fixed on the conductive adhesive. The scanning electron microscope Quanta SEM (Thermo Fisher Scientific, United States of America) was used in the research. Thermogravimetric analysis was performed on the setup TAG (SETARAM, France).

The electron microscopy images were processed in program ScopePhoto (ScopeTec, China): the dimensions of bubbles (120–150 pcs) were determined for each sample using the programming lineup, mean values of this indicator were calculated. It was impossible to use the integrated functions of the program for counting the particles due to the complex relief of the foam layer.

5. Results of research into the influence of plasticizers on the properties of foams of intumescent coatings

5. 1. Estimation of the influence of plasticizers on the structural features of the formed foams

Fig. 1 shows the results of electron microscopy of the foams of all samples with the same magnification. The photographs were made on the section of undamaged foam bubbles.

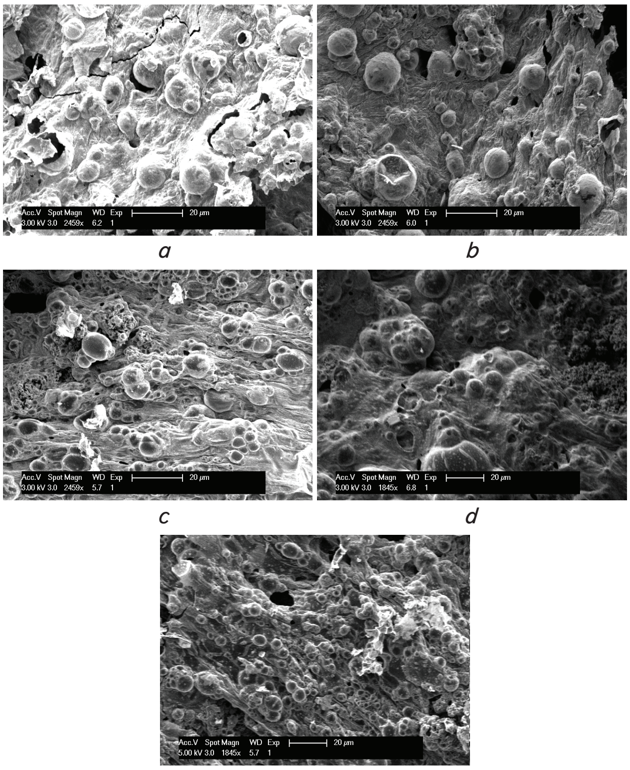

Fig. 1. The structure of foams of intumescent compositions: *a* — sample 1, *b* — sample 2; *c* — sample 3; *d* — sample 4; *e* — sample 5

While there are contraction cracks in the non-plasticized composition, they are not found in all samples with plasticizers. Two effects are observed when increasing the molecular weight of the plasticizer: a decrease in the average size of a single bubble, which occurs in all cases except for sample 2 and an increase in the number of joint bubbles.

5. 2. Determining the influence of plasticizers on the thermal character of the formation of foams of intumescent systems

The nature of the loss of weight of the plasticized samples at heating (Fig. 2) is very close to the nature of the original composition. However, the residual weight is decreased at an increase in the molecular weight of the plasticizer. It is noteworthy that for sample 5 (most high-molecular plasticizer), the difference between the weight loss of sample 1 is 6 % by weight, which is equivalent to the content of this plasticizer in the sample. The loss of the remaining samples is smaller, therefore, the products of the plasticizer oxidation are not removed completely.

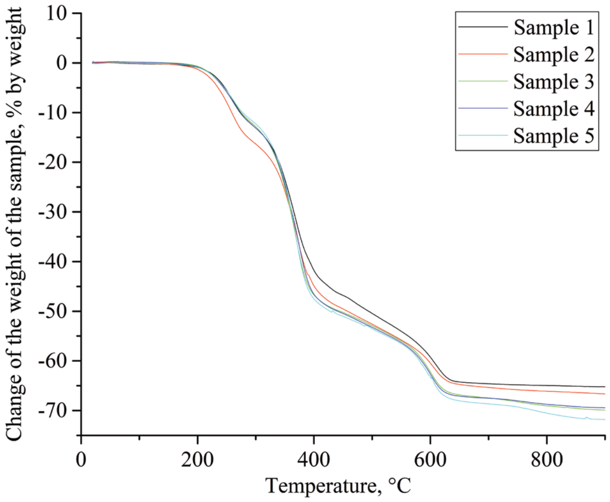

Fig. 2. Loss of weight by samples at heating

The difference in the behavior of the plasticizers becomes more evident from consideration of the differential thermal curves of weight loss by samples (Fig. 3).

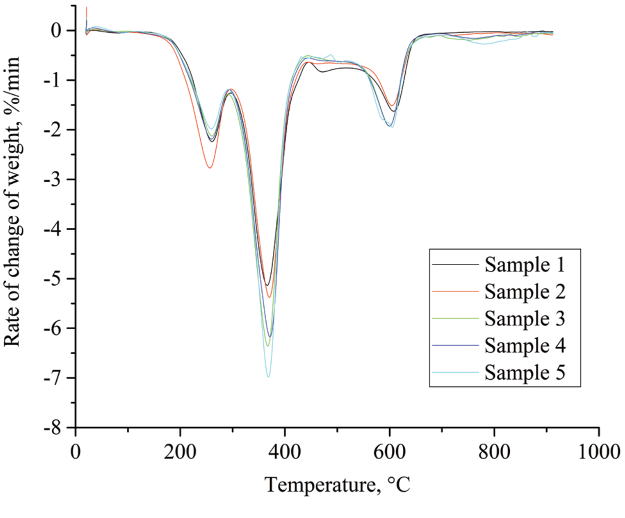

Fig. 3. DTG of compositions

The sample with low-molecular dibutyl phthalate loses much more weight that the other samples at the temperature of 260 °C, which corresponds to thermal decomposition of the acid donor (ammonium polyphosphate). The second effect, corresponding to the carbonation of the melt components at a temperature of 366 °C does not change its position, but increases intensity at an increase in molecular weight of the plasticizer. And, finally, the third weight loss peak that occurs at the temperature of around 600 °C and corresponds to thermal oxidation of carbon residue shifts a little to the left and significantly increases for the samples containing high molecular plasticizer.

5. 3. Determining the influence of plasticizers on the indicators of fire-resistance of coatings

Coefficient of expansion factor of compositions (Fig. 4) at the change of the type of the plasticizer does not change within the measurement error. However, it is by 20–25 % higher for the plasticized compositions than for the original composition that does not contain the plasticizer.

Despite this, the introduction of plasticizers significantly affects the general fire resistance of the composition, as shown in Fig. 5.

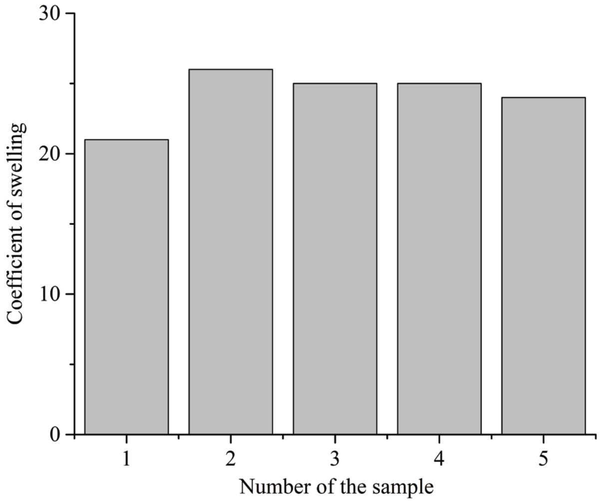

Fig. 4. Coefficients of expansion factor of the composition

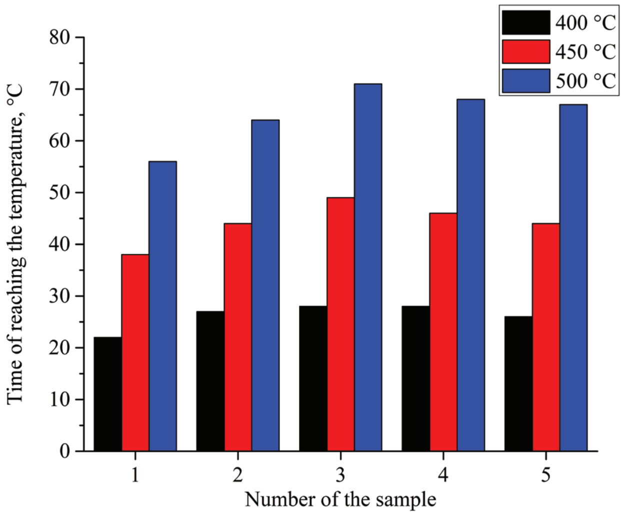

Fig. 5. Assessment of general fire resistance of the composition by the time of reaching the temperature limits under conditions of testing

Thus, fire resistance of the composition does not change linearly at an increase in molecular weight of the plasticizer, therefore. This dependence is characterized by the existence of an extremum: the highest values are achieved at the molecular weight of polybutene at the level of 2,100 and 4,200 g/mol. The general increase in fire resistance at the addition of these plasticizers amounted to 21–27 %. In this case, both low molecular dibutyl phthalate, and more high-molecular Indopol 18000 are less effective.

6. Discussion of results of studying the influence of molecular weight of the plasticizer on the structure and properties of foams of intumescent coatings

The change in the structure of foam bubbles (Fig. 1) is a natural effect of the regulation of viscosity of the polymer melt. In sources [13, 14], it is indicated that there is a relationship between viscosity of the medium during foam formation and the dimensions of the bubbles. It is alleged that this dependence is inversely proportional – at an increase in viscosity of the medium, the dimensions of a bubble decrease and vice versa. Partly, this is indirectly proved by the example of the additive of dibutyl phthalate, which due to its low molecular weight decreases the indicator of the melt fluidity limit, which leads to an increase in the dimensions of the bubbles. At an increase in molecular weight, the ability of the plasticizer to form associative structures grows, which increases the yield limit of the melt, and hence reduces the value of the average diameter of a foam cell.

In addition to the geometry of micro-bubbles, the plasticizer also significantly affects the distribution of dimensions of macropores, for example, in paper [15], it is shown that the use of volatile plasticizers (low molecular chlorine paraffins) leads to the formation of caverns of considerable sizes.

Dibutyl phthalate is one of the most volatile of the studied plasticizers. However, increased porosity of the sample (an increase in coefficient of expansion factor) is almost the same, which is evident when analyzing the data in Fig. 4. The noticeable decrease in coefficient is observed only for the most of high-molecular plasticizer, but this decrease is within the limit of the error of parameter measurement.

General fire resistance of the compositions (Fig. 5) is determined not only by the values of coefficient of expansion factor, but also by the features of the structure of the formed foams. A finer structure of cells in the case of plasticizers with average molecular weight ensures the most significant increase in the time of heat insulation. In sample 5, a decrease in this parameter occurs, probably at the expense of a decrease in general porosity (Fig. 4).

Decreased fire resistance of the system with the addition of dibutyl phthalate can be explained by both a more heat conductive structure at a comparative increase in dimensions of pores, which is proved by the data [16], and probably an increased level of macroporosity of the samples.

Thermal behavior of the samples is quite unusual (Fig. 3): an increase in molecular weight leads to a significant decrease of carbon residue of the plasticizer until it completely disappears in sample 5. Similar behavior can be explained by the influence of competing mechanisms of the thermo-oxidative decomposition, as it was shown, for example, in [17] for silicon organic oligomers of different molecular weight. It is an interesting fact that at increased weight loss during carbonization at 366 °C, the compositions with high-molecular aliphatic plasticizers lose the increased amount of carbon at the temperature of 600 °C. This suggests a greater degree of amorphousness compared with the product containing low molecular plasticizers. This is proved in article [18], where the authors point out the possibility of existence of carbon residues of varying degrees of graphitization (and consequently, temperature resistance) in the product of combustion of fire-retardant systems.

Thus, it was shown that plasticizers can be used as a means for regulating the structure of foams of intumescent coatings. However, it is necessary to take into account the thermal stability of the systems with their addition, and the content of these additives must also be balanced.

To obtain a more complete picture of the structure regulation, it is required to conduct further studies, which will include determining the rheological parameters of melts of the systems. This will make it possible to model qualitatively and then numerically the porous structure with the necessary cell diameter and coefficient of expansion factor.

To obtain a more complete characteristic of porosity, it is planned in the future to examine it additionally at the macrolevel by the method of slices or using X-ray tomography in the joint application of the systems of automatic image processing.

The results of this research can be used in developing intumescent fire protection systems, specifically, in developing and finalization of their formulations.

The use of plasticizers to regulate the porous structure of carbon foams is a challenge of material science – to obtain materials of the specified structure based on their composition, and can be used as an illustration of the principle in the academic courses.

An important issue when using plasticizers is the composition of the products of their thermal decomposition, which becomes particularly relevant when using chlorine-containing substances. The answer to this particular question within the broader study of the composition of the products of thermo-oxidative decomposition of intumescent systems and their impact on human health is a relevant direction of further research.

7. Conclusions

1. The temperature intervals of thermo-oxidative destruction of plasticizers were determined, taking polybutene aliphatic compounds as an example, the inverse dependence of their stability during thermal treatment on the value of molecular weight was established: low molecular plasticizers give the highest yield of non-volatile residue at carbonization. Besides, at the destruction of the formed amorphous carbon at the temperature of about 600 °C, a decrease in the weight of the composition is equivalent to the content of the plasticizer in the case of high molecular polybutene and is by 2–3 times less in the compound with low molecular weight.

2. It was shown that the application of plasticizers makes it possible to change foam cell dimensions in a wide range: at an increase in the molecular weight, the plasticizer's ability to affect the rheological properties of the system increases, which decreases the value of the average diameter of a foam cell by 1.5–2 times. In addition, application of plasticizers makes it possible to decrease the formation of contractional cracks in the structure, which is associated with a decrease in fragility of the film forming agent during the formation of these foams.

3. It was found that the integrated indicator of fire resistance of coatings depends on the type and molecular weight of the used plasticizers. The extreme dependence of fire resistance on the molecular weight of polybutene plasticizer was found for the explored intumescent system based on styrene-acrylic polymer. Application of polybutene oligomers: Indopol H 1200 with the molecular weight of 278 g/mol showed the best results: it took a steel substrate 71 minutes to reach the temperature of 500 °C, while the original material reached it in 56 minutes.

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CONSTRUCTION AND INVESTIGATION OF THE COMPUTER MODEL OF DISTRIBUTION OF THE COMPOSITION OF PRODUCTS FROM EQUILIBRIUM CONDENSATION TELOMOMERIZATION

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На основі механізму перебігу поліконденсації складена схема реакції рівноважної конденсаційної теломеризації, як поліконденсаційного процесу з обривом ланцюга монофункціональним телогеном. Виходячи з цієї схеми складені рівняння матеріального балансу за структурними елементами, що містять нескінченну кількість членів. При виконанні принципу Флорі про однакову реакційну здатність кінцевих груп нескінченні суми являють собою геометричні прогресії з однаковим знаменником. Це дозволяє згорнути модель процесу в замкнуту систему з чотирьох нелінійних алгебраїчних рівнянь.

В результаті досліджень властивостей моделі шляхом математичного аналізу і комп'ютерних експериментів встановлено наступне:

– розподіл продуктів теломеризації представляє суперпозицію геометричних розподілів базових структурних компонентів з одним і тим же знаменником прогресії, але різними величинами вихідних концентрацій. Розподіл Флорі для гомополіконденсації можна розглядати, як окремий випадок цього розподілу;

– система рівнянь моделі може мати до 4 дійсних коренів. При одиничному рішенні системи при випадковому виборі початкового наближення в ~74 % випадків виходить помилковий позитивний корінь. Для перевірки істинності кореня розроблений критерій на основі величини знаменника збіжної геометричної прогресії, запропонована процедура комп'ютерного рішення системи, що дозволяє знайти істинний корінь;

– на моделі виявлені закономірності впливу концентрації реагентів на склад рівноважної суміші при сталості концентрації побічного низькомолекулярного продукту конденсації. Показано, що при прагненні цієї концентрації до нуля склад перестає залежати від значень констант рівноваги.

Розроблена модель дозволяє розраховувати склад рівноважної суміші олігомерів в залежності від співвідношення концентрацій мономерів, телогена і низькомолекулярного продукту конденсації. Це робить її корисною на практиці для попередньої чисельної оцінки складу рівноважних сумішей олігомерів при плануванні синтезів методом конденсаційної теломеризації

Ключові слова: рівноважна конденсаційна теломеризації, нелінійні алгебраїчні рівняння, комп'ютерне моделювання, склад олігомерів

1. Introduction

Polycondensation is one of the main methods for obtaining polymers. An important kind of polycondensation is the condensation telomerization, which proceeds in accordance with a general pattern:

$$(n+1)\mathrm{H}-\mathrm{A}-\mathrm{H}+n\mathrm{X}-\mathrm{B}-\mathrm{X}+2\mathrm{RX} \rightleftarrows \rightleftarrows \mathrm{R}-\mathrm{A}-(\mathrm{B}-\mathrm{A})_n-\mathrm{R}+2\cdot(n+1)\mathrm{HX}. \tag{1}$$

Condensation telomerization can be regarded as heteropolycondensation with a chain disruption due to the