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REVISITING THE ASSESSMENT OF POLYMERIC MATERIALS FIRE PROTECTION EFFICIENCY

The main requirements regulating the fire-safe application of plastics in construction, industry and transport were specified. The issues of the methodology for assessing polymeric materials (PM) fire protection efficiency in compliance with the existing normative and technical base were considered. It was demonstrated that, depending on the field of application and the functional purpose, various requirements are imposed on PMs as related to fire protection efficiency. It was established that, using comparative information on the processes of destruction and thermal decomposition of PMs in the presence of various flame retardants and their resistance to fire effect, it is reasonably likely to predict the behavior of a polymer composition under standard testing conditions. The results of experimental studies on the development of low combustible polymers were presented. The extreme relevance of studying the possibility of correlating the flammability parameters using small-scale and large-scale test methods for the development of the compositions presenting low fire hazards was found. The conclusions on the advisability of developing an integrated approach to the assessment of fire hazard properties of flame-retardant polymers at their laboratory production stage were drawn.

Keywords: normative base; fire-safe application of plastics; polymeric materials; fire hazard assessment methods; fire protection efficiency.

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Introduction

The development of polymeric materials (PM) production and their broad application in various sectors of construction, industrial production and transport are bringing the tasks of developing and creating materials having reduced fire hazards and the materials with predetermined fire hazard properties into a line with the prioritized ones.

The existing normative base of fire-safe application of PMs in Russia and abroad relies on their field of use and functional purpose. The assessment methods and fire hazard parameters of PMs selected depend on the requirements of regulatory documents regulating their use [1].

It should be noted that the various test conditions and classification criteria in the current standard methods for assessing the fire hazards of PMs allow the possibility of ensuring various degrees of their fire protection efficiency depending on their field of use [2].

The present paper includes an approach that is optimal in terms of selecting methods and determinable parameters for assessing the fire hazards of low combustible PMs by introducing flame retardants (FR) into their formulations. To validate formulation of tasks, the nomenclature of the effective test methods and indicative operational features of certain types of PMs was taken into account. The analysis of suitability of experimental techniques, the assessment of fire hazards of polymer compositions, the study of mechanism of inert fillers (by the example of aluminum composite panels for front systems) and flame retardants (by the example of the PVC-based materials) should be considered as the main tasks to be solved.

Methodological basis for assessing the fire hazards of PMs

Classification of construction, textile, tanning materials, as well as of building structures for fire hazards, was established by Federal Law No. 123-FZ "Technical Regulations on Fire Safety Requirements" (hereinafter referred to as FZ No. 123). The main properties of fire hazard, e. g. for construction materials (CM), are the groups of flammability, combustibility, surface flame propagation, smoke-generating capacity and combustion products toxicity determined in accordance with GOST 30402–95, GOST 30244–94, GOST R 51032–95 and GOST 12.1.044–89.

Some fire safety requirements for finishing polymeric materials, including the textile ones, not included in FZ No. 123, are reflected in the regulatory documents on fire safety. Particularly, SP 4.13130 sets out the requirements to the materials for seats in the stands of sports facilities and in the halls of cultural and entertainment facilities, in terms of combustibility and toxicity of combustion products.

The main fire safety requirements for PMs for railroad and subway cars are specified in the Technical Regulations of the Customs Union (TR CU) "On safety of railway rolling stock" (TR CU-001–2011), GOST R 54893–2012, GOST R 55183–2012, NPB 109 and are based on the results of a comprehensive assessment of materials by combustibility group, smoke-generating index, flame propagation index and combustion products toxicity. It should be noted that the test method for determining the combustibility of materials and their classification are established in accordance with GOST 12.1.044–89 (para. 4.3) and significantly deviate in terms of determining the flammability parameters of construction materials as per GOST 30244–94 (method 2). Therefore, polymeric materials varying in the fire resistance degree can be used at construction sites and in car building sector.

Materials used on marine vessels should comply with the requirements set forth in the International Code for Application of Fire Test Procedures as of 2010 (2010 FTP Code, IMO Resolution MSC.307(88)) [1], and be resistant to ignition and surface flame propagation.

Fire hazards of materials depending on their functional purpose (finishing and facing, floor coverings, curtains, upholstery, bedding items) is assessed using the relevant international test procedures (parts 1, 2, 5, 7–9 of the 2010 FTP Code), test equipment and determinable parameters of which substantially differ from the existing domestic standard methods for assessing the fire hazards of these materials.

The fire hazard of finishing materials and coatings used on inland waterways vessels is regulated by the Rules of the Russian River Register (Volume 2, Part X), according to the criteria such as surface flame propagation, smoke-generating capacity and combustion products toxicity determined by the methods specified in GOST 12.1.044–89.

Regulatory test requirements, for example, interior finishing materials for motor vehicles are based on determination of burning rate and are set out in GOST 25076–81.

Materials for special working clothes subject to thermal risks are tested in accordance with the requirements of TR CU 019/2011 "On the Safety of Protective Clothing".

Thus, the existing methodological basis for assessing the fire hazards of PMs largely depends on their field of use and functional purpose. This results in different approaches to the assessment of their fire hazards and, therefore, requires considering this fact when developing fireproof PM compositions.

Methods and materials

The actual task when creating low combustible materials is a well-founded choice of predictive small-scale methods for investigating the fire hazard properties of PMs and the criteria that will correlate or meet the standard criteria and the requirements that ensure the safe use of PMs in one field or another.

In the studies on the selection of flame retardants for PMs, the information on their efficiency in terms of the study of thermal decomposition can be obtained, for example, when performing thermal analysis according to GOST R 53293, using qualitative and valuable identification characteristics [3].

When obtaining the data on the parameters characterizing the processes of thermal destruction and thermal oxidation of PMs in the presence of FRs (particularly, over the temperature ranges in which these processes occur, according to the thermal effects by which they are accompanied), it is possible to estimate the degree of influence of FRs on these processes in gaseous and condensed states [4].

Significant identification thermal analytical characteristics include: temperatures at fixed mass losses, temperatures at maximum mass loss rates; mass loss rate; coke residue, which is determined at the end of the pyrolysis process in an inert atmosphere or at a fixed temperature; ash residue, which is determined after the thermal oxidation process at a fixed temperature; melting temperature and corresponding thermal effects, which can be used to compare the effectiveness of an FR used in PMs.

Results and discussion of them

The results of studies on the development of low-flammability polymers used as an internal layer of aluminum composite panels (ACP) applied in construction, particularly in air spaced curtain wall systems are of concern. To reduce the combustibility of such materials, the polymeric matrix is filled on the basis of a mixture of polyethylene and ethylene copolymers with components containing flame retardants of various types, including those developed and tested in recent years [5–10]. The development of formulations for such materials is a quite complex and multicomponent task, which must take into account the technological compatibility of a composite with the specific production equipment, as well as the cost, quality and availability of its constituents. For this very reason, it is advisable to make a reasonable selection of small-scale research methods at the stage of developing an optimal formulation of the polymer composition, the test results of

[1] International Code for Application of Fire Test Procedures, 2010 (2010 FTR Code, IMO Resolution MSC.307(88)).

Table 1. The combustion heat and thermo analysis characteristics material of internal layer for aluminum composite panels AKP with different level of fireproof

Sample number	Combustion heat, MJ/kg	Mass losses velocity, %/min (for temperature, °C)	Maximum of exo- and endothermal effects, °C/mg (for temperature, °C)	Relational heat emission, °C·min/mg	Coke residuum, %
1	2.7	3.0 (441)	0.25 (450)	0.89	68.5
2	8.2	4.3 (498)	0.83 (545)	3.90	48.9
3	15.7	54.9 (439)	0.58 (526)	0.92	1.1

which will allow predicting the behavior of materials, for example, when carrying out medium-scale tests in accordance with GOST 31251, which regulates the classification of front systems of buildings and structures in terms of fire hazard [11].

As a result of the undertaken studies [12] it was found that the assessment of such fire hazardous properties of a composite as combustion heat in accordance with GOST R 56027–14, and significant thermal analytical characteristics in accordance with GOST R 53293, allow reasonably likely to predict their behavior under fire exposure within the standard methods of testing. Tables 1 and 2 show the results of comparative complex experimental studies of fire hazard indices in the development of formulations of a low combustible polymer composite for ACPs manufacturing.

The analysis of thermal degradation characteristics obtained from the curves of the thermal analysis of a sample of the ACP inner layer (see Table 1) allows to identify the fact that the sample No. 1 is the least combustible composite material having a low heat combustion value (2.7 MJ/kg) with low heat emission values (up to 0.25 °C/mg) and thermal decomposition rate (3.0 %/min) and high coke residue (up to 68 %). Correspondingly, the material classified as highly combustible (combustibility groups G4) is characterized by high heat emission values and thermal decomposition rates, as well as a small amount (1.1 %) of coke residue.

Despite the fact that samples Nos. 1 and 2 refer to the same combustibility group (G1), the least flammable material can be identified by the heat combustion values.

Table 2 shows the summarizing results of numerous experimental and analytical studies on the assessment of heat combustion value, depending on the percentage of various types of FRs contained in composites and the comparison of their combustibility groups with the fire hazard classes of construction materials adopted in the European Standard EN 13501 (Part 1).

Thus, samples of type No. 1, having a polymer layer composition system filled with inert components and flame retardants of at least 80 %, are included into the group of fireproof materials of Class A2 according to the European Classification of fire hazards of construction finishing materials (with inner layer combustion heat of not more than 4 MJ/kg).

To assess the fire protection effect, developers of FRs for PMs typically use the most common small-scale comparative method for estimating the oxygen index (OI) (GOST 12.1.044, ISO 4589-2–1996, ASTM D 2863-13, ISO 4589-3-1996, [13–16]). However, according to the obtained value of OI for low combustible PMs, it cannot be concluded that its properties correspond to the regulatory requirements for fire-safe application. There are the papers known, which along with standard parameters present OI values that can be used to predict the PM's combustibility group, but they address a very limited list of construction materials [17]. Consequently, now, it seems to be highly relevant to conduct the work on investigation of the possibility of correlating the flammability parameters obtained by small-scale and large-scale test methods in the development of compositions having reduced fire hazard.

In particular, when developing fireproof polymeric materials for construction, the final assessment should be carried out according to the combustibility group in accordance with GOST 30244–94 (Method 2), which provides testing of samples of sufficiently large dimensions (1000×190 mm). Based on many years of experience in the experimental work, Fire Safety Research Institute obtained the data on correlation of test results with the methods of GOST 12.1.044–89 and GOST 30244–94 (Method 2), which indicate that, as a rule, the combustibility groups of construction materials G1, G2 correspond to the group of fire-resistant materials according to GOST 12.1.044–89.

Thus, when carrying out studies on the selection of an optimal composite formulation for the assessment of

Table 2. Comparative data of fire hazard for aluminum composite panels (ACP)

Sample number	Content of inert additives and fire-retardant agents in internal layer, %	Combustion heat of internal layer, MJ/kg	Combustibility group, GOST 30244–94 (method 2)	Class of fire hazard, EN 13501
1	More 85	Less 3.0	G1	A2
2	70–80	9.0–3.0	G1	B
3	Less 65	More 15.0	G4	C

Table 3. Experimental date of combustibility fireproof PVC film composition

PVC film sample	OI, GOST 12.1.044–89 (para. 4.14))	Combustibility group, GOST 12.1.044–89 (para. 4.3)			Combustibility group, GOST 30244–94 (method 2)
		Maximal temperature T_{max}, °C	Mass losses Δm, %	Burn time τ, sec	
Base	21.4	465	67	120	G4
No. 1	28.7	390	54	30	G4
No. 2	36.2	270	45	–	G3
No. 3	42.1	240	30	–	G2

their combustibility, it is advisable to use two methods collectively — the OI method and the method of experimental determination of the groups of fire-resistant and combustible substances and materials in accordance with GOST 12.1.044–89 (para. 4.14 and 4.3, respectively).

Experimental studies have also been carried out to determine the possibility of reducing the combustibility of plasticized polyvinyl chloride (PVC) by the use of reactive flame retardants and fillers [18]. An important condition in so doing was the effect of flame retardant in the processing of a polymer on its thermal stability, melting point and the quality of polymeric matrix formation. Therefore, to obtain a PVC composition with a reduced fire hazard and a set of required properties, it was required to produce a fairly large number of samples of experimental batches of PVC film of various formulations, both in laboratory conditions and on industrial equipment.

Table 3 shows experimental data on the flammability parameters of a number of samples of PVC compositions modified in a different ratio by magnesium hydroxide and a phosphorus-nitrogen-containing complex FR.

Experimental data set forth in Table 3 demonstrate a significant change in the oxygen index and flammability parameters, which indicates a decrease in the fire hazard of the PVC composition when FR is introduced. In addition, the studies made it possible to compare the results of laboratory and medium-scale test methods and establish an approximate value of the OI to predict the combustibility group of the samples developed; in this case a fire-resistant PVC film.

Fire resistance rating polymeric materials and products is often determined using the existing standard methods for assessing the resistance to ignition from low-calorie ignition sources. For example, for plastics, methods for determination of the combustion resistance in accordance with GOST 28157–89 or UL 94 are used, and for fabrics, flammability resistance is determined according to GOST R 53294–09 or GOST R 50810–96. A group of combustible highly flammable construction materials is identified using the GOST R 56027–14 method.

The procedure applied in GOST R 56027–14 allows to establish a group of combustible highly flammable construction materials, particularly, to identify a group of the most fire hazardous CMs, including those with the ability to cause a molten mass formation and burning dropping. Therefore, when carrying out studies on the fire protection efficiency of thermoplastic polymers using this method, one can estimate the effect of material carbonization, excluding the burning dropping process, as it was shown, for example, in the paper [19].

Conclusions

When conducting the work on selecting and optimizing PMs' formulations to achieve their effective fire protection, it is advisable to select laboratory (small-scale) research and testing methods, the results of which will allow to predict the behavior of PMs during medium- and large-scale tests, as well as under real fire conditions.

When justifying the selection of a test procedure for assessing the combustibility (flammability) of modified polymer systems, it is necessary to take into account the scope of application and functional purpose of the material along with the specified parameters.

It is reasonably likely to predict the behavior of a polymer composition under standard testing conditions using comparative information on the processes of destruction and thermal decomposition of PMs in the presence of various FRs and their resistance to fire effect.

Considering the lack of appropriate work, it is advisable to continue carrying out complex studies to introduce new approaches to assessing fire hazard properties of various flame retardant polymers at their laboratory production stage.

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