ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 5, pp. 1068–1074. © Pleiades Publishing, Ltd., 2011.
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Ways of Providing Fire Safety of Aviation Materials

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Received December 1, 2009

Abstract—Influence of various fire-retardant additives, as well as thermostability and chemical structure on polymer flammability is analyzed, and nonfire-resistant and fire-resistant polymer materials are compared. An essential influence of these factors on flammability, smoke density, heat release rate, and limit oxygen index is shown.

DOI: 10.1134/S1070363211050422

Human existence is always associated with fire: This is either use offire for household and industrial needs or protection from it in the case of natural or technogenic disasters. Victims of fire amount annually up to tens of thousands of people and losses amount to billions dollars. The losses of fires in various countries are estimated at 0.5–1.0% of GDP [1, 2].

The overwhelming majority of materials (organic compounds, including natural, artificial, and synthetic polymers, and inorganic compounds, including many metals) can enter oxidation reactions. It these reactions involve a high heat release, proceed very fast, and are capable of self-sustaining, then, as a rule, light or fire emissions are observed. At present we still cannot, for a number of reasons (required mechanical parameters, convenience, etc.), completely obsolete flammable materials. The demand for polymers for industrial and household use is constantly growing, but simultaneously the fire safety requirements to these materials are getting more and more rigid. Therefore, there is an urgent need in developing new, fire safe materials and in providing protection of already existing materials, including traditional ones, from fire and other fire hazard factors.

Over a long time the search for ways to protect materials from fire has been performed empirically, and it is only in the middle of the 20th century that a scientific approach to this problem started to be developed.

Polymer Combustion and Fire Hazard Factors

Combustion is a multistage and branched process, involving both positive and negative feedbacks. For convenience in analysis, the combustion process is divided into space zones, each involving its specific physicochemical processes [3]:

– zone of the starting material;

– heating zone;

– zone of chemical transformations in the condensed phase;

– preflame zone;

– high-temperature reaction zone in the flame;

– zone of evolution of gaseous combustion products.

In the heating zone, polymer is heated until physicochemical transformations are initiated. In the next zone, sublimation, vaporization, and exo- or endothermal chemical decomposition occur. The resulting vaporous and gaseous products pass through the carbonized layer into the gas phase. Condensed-phase reactions lead in fact to two principal types of products: gaseous (flammable and nonflammable) and solid (carbon-containing and mineral). The preflame zone involves further oxidative pyrolysis of comparatively low-molecular flammable products. In the flame combustion zone, most redox reactions occur; and this zone has a maximum temperature. The heat released in in-flame redox reactions is transferred (by radiation, convection, and heat conduction) to the surface of the unburned fuel layer.

To enhance the fire safety of materials, one can act upon any combustion zone: to slow down condensed- and gas-phase reactions, decrease heat fluxes incident

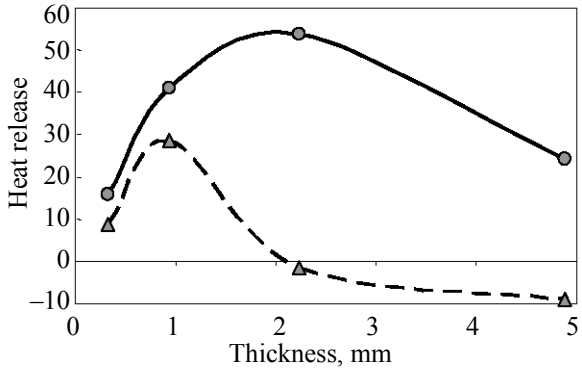

Fig. 1. Effect of glass plastic thickness (phenol binder) on heat release characteristics: (●) maximum heat release (peak), kW m^{-2}; and (▲) total heat release over the first two minutes, kW min^{-1} m^{-2}.

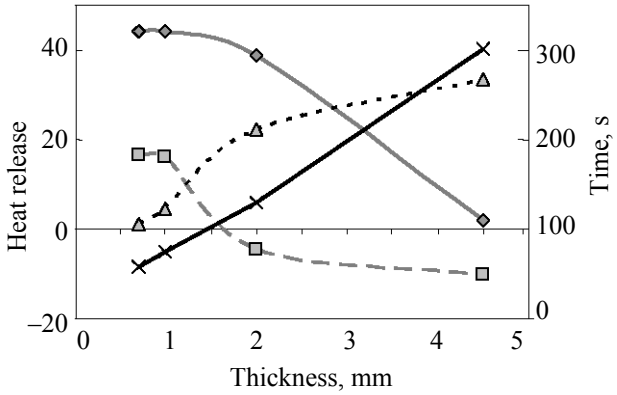

Fig. 2. Effect of the aluminum support thickness on the characteristics of heat release on combustion of a PVC polymer film: (◊) maximum heat release (peak), kW m^{-2}; (□) total heat release over the first two minutes, kW min^{-1} m^{-2}; (×) ignition time, s; and (Δ) maximum heat release time, s.

upon the polymer and passing inside the material, decrease heat release on combustion, or increase heat losses.

Fire has a number of hazard factors [3, 4] which can be arbitrarily divided into two groups: direct and indirect. The first group involves such factors as effect of open fire, elevated air temperatures, heat flux on the surface, toxic combustion products, and low oxygen concentration. The second group of factors involves smoke formation which disorients people and causes panic, short circuits in power systems and equipment failure, mechanical traumatization of people, and damage of expensive technics. Over the past decades the rates of fire incidents and total mortality, as well as material losses have tended to decline. Along with that, the distribution of fire hazard factors in terms of maximum hazard has changed essentially. If previously more than 60% of fire-ravaged people died of thermal traumas, at present their share is 15–20%, whereas the share of people died of poisoning toxic combustion products comprises 70–80 % of the total number of victims, which is associated with a wide use of polymers containing chlorine, fluorine, and other fire retardants [4–8].

Fire Hazard Characteristics of Materials

For assessment of fire safety of materials (basic components, aggregates, articles), regulated hazard factors should be measurable and modelable, i.e. the possibility of instrumental monitoring of exposure parameters and reproducibility of experiment should be provided. It is to be noted that fire hazard characteristics (flammability, self-extinguishing upon removal from flame, rate of flame propagation over the surface, release of heat, smoke, toxic compounds, etc.) are not infrequently contradictory, and an improvement of one of them is accompanied by a worsening of others. Moreover, fire-retardant additives in polymer materials usually slightly adversely affect physicomechanical, dielectric, or other performance and engineering characteristics, and increase the cost of the material. Therefore, to reduce the fire hazard of polymer materials is an intricate multidimensional task involving optimization of a complex of parameters. According to the "Aviation Rules" (AP-25) [9], the regulated parameters of decorative materials for passenger cabins include flammability, smoke formation, and heat release on combustion.

The fire hazard of a material depends on such characteristics as its thickness and surface mass, as well as the thermophysical properties of the support. Figure 1 shows the effect of the thickness of glass plastic on heat release on combustion, and Fig. 2 shows the elect of the thickness of aluminum support on the heat release of polymer film. On the one hand, for objective comparisons of the properties of materials it is desirable that the samples have the same thickness and weight but from the other, by varying these characteristics one can control the fire hazard of the construction.

Table 1. Properties of certain phenol–rubber adhesives

Parameter	Adhesive brand			
	VK-3	VK-32-200	VK-25	VK-50
Working temperature range, °C	–60 to +80	–60 to +200	–60 to +80	–60 to +150
Shear strength τ_s, MPa	15	13,5	23	25±5
Tearing strength σ_t, MPa	–	–	22	25±5
Delamination strength S_{delam}, kN m^{-1}	–	–	5– 6	10
Percentage elongation γ, %	–	–	140– 200	135– 150
Durability σ_{ls}, MPa (on the time basis, h)	–	–	18.5 (500)	17 (500)
Fatigue resistance τ_{max}, MPa (on the cycle basis, $N = 10^7$ cycles)	–	–	9	10

Table 2. Fire hazard characteristics of a phenolic glass plastic with a phosphorus-containing fire retardant. Sample thickness ~2 mm

Material	Flammability τ_{res}, s	Smoke-forming capacity (combustion mode)		Heat release on combustion	
		D_4	D_{max}	peak, kW m^{-2}	total over 2 min, kW min m^{-2}
No fire retardant	32	16	27	97	89
With phosphorus-containing fire retardant	0	12	14	68	46

Combustion Inhibitors

The simplest and, at the same time, the least effective way to reduce the fire hazard of a material is to reduce the fraction of its flammable component. Glass fibers or other inert fillers can reduce release of gaseous substances from polymers at the same total weight of the sample, according to the additivity law. However, such fire hazard parameters as the afterflame residual combustion time (τ_{res}, s), flame propagation rate, critical ignition flux, and others vary in a non-additive fashion with the inert additive fraction, and for positive effect quite high fractions of inert fillers (50–90%) are required. Low filler concentrations (2–5%) sometimes (due to decrease of thermal stability, effect of melt rheology, heat capacity and conductance) may prove to have an adverse effect, i.e. increase the rate of flame propagation, residual combustion time, and burn-out length, or decrease the self-ignition temperature.

The fire safety of flammable organic materials has long been provided by using, along with nonflammable fire-proof coatings, fire retardants (combustion inhibitors) [10]. The most common fire retardants, principles of their actions, and methods of their use are described in [11–13].

The most common fire-retardant agent are halogen-containing organic compounds [14]. Their efficiency increases in the order: F < Cl < Br < I. As polymer is heated and degrades, halogen atoms pass into the gas phase, where they interfere in radical reactions of flammable products with each other and with air oxygen. As a result, oxidation is slowed down and organic conglomerates form. This decreases the flame temperature, combustion completeness level (heat release), and simultaneously increases flame luminosity (the share of a luminous heat flux and surface heat losses increase) and the quantities of incomplete combustion products, toxic components, and soot. The influence of halogen-containing fire retardants on the principal fire hazard parameters of aviation materials is presented in Table 1.

Another type of fore-retarding agents includes phosphorus-containing compounds. These agents act primarily in the condensed phase and affect degradation processes by changing their direction, increasing coke residue and decreasing the quantity of

Table 3. Effect of aluminum hydroxide on the fire hazard characteristics of a phenolic microspherical Textolite. Sample thickness ~3 mm

Material	Flammability τ_{res}, s	Smoke-forming capacity (combustion mode)		Heat release on combustion	
		D_4	D_{max}	peak, kW m^{-2}	total over 2 min, kW min^{-1} m^{-2}
No fire retardant	4	11	28	107	84
With aluminum hydroxide	0	5	14	38	5

Table 4. Fire hazard characteristics of a textile material with a nitrogen-containing fire retardant

Material	Flammability τ_{res}, s	Smoke-forming capacity (combustion mode)		Heat release on combustion		Oxygen index, %
		D_4	D_{max}	peak, kW m^{-2}	total over 2 min, kW min^{-1} m^{-2}	
Wool fabric	55	105	113	125	89	27
Wool fabric treated with fire retardant	4	54	75	50	32	33

gaseous flammable products [2]. The foamed glassy polyphosphoric acid layer formed on the polymer surface has a low heat conductance, and it hinders prevents heat penetration into the polymer. Certain phosphorus-containing fire retardants decompose into gaseous substances, and in this case phosphorus favors formation of soot agglomerates, which decreases combustion completeness and increases flame luminosity (Table 2).

Inorganic compounds, specifically hydroxides and salts, including salt hydrates (aluminum and magnesium hydroxides and hydrocarbonates), too, are used as fire retardants. On heating they decompose with a high endothermic effect and evolve inert gaseous products (carbon dioxide and water) which dilute the gaseous component. Salts that are law-melting glasses (borates, silicates), like phosphorus-containing fire retardants, form a foamed glassy protective layer on the surface. An example of changing fire hazard characteristics in response to aluminum hydroxide is presented in Table 3.

One more group of fire-retardant agents is formed by nitrogen-containing organic compounds (Table 4).

There are more than ten chemical elements which exhibit a fire-extinguishing effect. The efficiency of fire retardants is not infrequently enhanced, when a mixture of different elements is added: halogens + antimony, phosphorus + halogens, phosphorus + nitrogen, etc. It is desirable that the decomposition temperature of the fire retardant were lower or the same as that of the base polymer. Otherwise, the fire retardant does not reach the flame zone and does not affect combustion processes.

Depending on the material, different techniques for introduction of fire retardants are used: surface treatment, impregnation, chemical modification of the polymer chain, or copolymerization. It should be taken into account that different types of fire-retarding additives differently affect different polymers. Thus, for instance, phosphorus- and nitrogen-containing fire retardants are poorly effective for polyolefins. The preferable choice of fire retardants for polymers of different chemical compositions is presented in [2].

Microencapsulated fire retardants and nanoparticles can be referred to as separate classes of fire retardants in terms of both the mode of introduction and the character of action.

Microencapsulated fire retardants [3]. Microcapsules are usually 50–200 μm is size and comprise a polymer shell (gelatin, polyvinyl alcohol, etc.) filled with a liquid fire-retarding agent. Of the greatest interest are fire retardants with a fairly low boiling point, by 100–200°C lower the capsule breakdown point, like carbon tetrachloride, dibromotetrafluoroethane, and other freons. In this case, by the moment when the capsule breaks down, the encapsulated liquid is overheated, and then microexplosion occurs, which disperses polymer particles blown out of the flame zone. However, this mechanism of action of

Table 5. Effect of thermal stability on heat release characteristics of glass plastics on the basis of thermoplastic binders

Polymer binder brand	Thickness, mm	Mass, g m^{-2}	Combustion heat, kJ g^{-1}	Thermal degradation point, °C	Heat release	
					peak, kW m^{-2}	total over 2 min, kW min^{-1} m^{-2}
PK-N	1.9	3100	29.66	400	56	47
Udel P 1700NT11	2.1	3150	30.78	460	60	37
PSF-150	1.9	3050	30.29	500	45	32
PES	1.9	3230	25.30	530	14	–3
Radel K 5000TE	1.9	3200	28.18	540	14	–8

Table 6. Fire hazard characteristics of glass plastics on the basis of different polymers [24]. Sample thickness ~ 2 mm

Binder	Flammability[a]	Smoke evolution by State Standard 24632	Heat release[b]
Epoxide	Flammable	Strongly smoking	120…180[c]
Epoxide brominated	Self-extinguishing	Strongly smoking	90…120
Phenol	Self-extinguishing	Low smoking	15…70
Polyester	Flammable	Strongly smoking	100…150
Polyimide	Low-flammable	Virtually smoking	10…35
Polyethylene	Flammable	Strongly smoking	280
Polycarbonate	Self-extinguishing	Essentially smoking	60…90
Polysulfone	Self-extinguishing	Low smoking	60…75
Polyestersulfone	Low-flammable	Virtually nonsmoking	15
Polyester Ester Ketone	Low-flammable	Virtually nonsmoking	5…10

[a] Testing method and classification by Tentative Standard 1 90093 (exposure time to furnace flame 60 s). [b] Peak heat release in kW m^{-2}, testing according to AP-25, Annex F, Part IV. [c] Depending on the thermal stability of a concrete binder brand.

fire retardants is effective only in the case of low-calorie flame sources. When the flame is powerful, polymer remains in the flame zone, and the efficiency of encapsulated fire retardants decreases to a normal level.

Nanocomposites. Nanoparticles are capable of enhancing the fire safety of materials [15–17]. At present the most frequently used are carbon nanoparticles (nanotubes, fullerenes, etc.), as well as nanosilicates. Nanoparticles reside between polymer macromolecules, do not introduce additional defects to the structure, and, therefore, do not decrease the thermal stability of the polymer matrix. However, on thermal exposure and thermal degradation these particles can act as coke nucleation centers. Sometimes the surface of nanoparticles is hydrophobized by organic fluorine compounds as fire-retardant agents which work to increase coke residue and decrease combustion completeness, thereby enhancing the positive effect of nanoparticles. For better compatibility nanoparticles are frequently modified by functional reactive groups, and, therewith, the number of such groups per one particle can be fairly high [4–8]. Such nanoparticles provide a high degree of cross-linking, thus enhancing the thermal stability of the polymer and increasing coke residue.

Effect of Polymer Composition and Structure on Its Fire Safety

The fire safety of a material can be enhanced by enhancing the thermal stability (thermal degradation temperature) of the polymer [18] by changing the chemical composition and structure of the polymer chain to decrease the number of bonds with a low

dissociation energy or forming or increasing the number of interchain cross links (ladder and cross-linked polymers). The effect of thermal stability on the heat release of glass plastics is exemplified in Table 5 [19].

Fire hazard is also decreased by decreased combustion heat, increased coke residue and pyrolysis heat, as well as increased inert gas evolution.

In practice the effect of different components is impossible to separate, since the combustion heat, thermal degradation temperature, and coke formation vary together with the chemical composition of the polymer. Combustion heats can be calculated from the structural formulas of polymers by the Konovalov–Hendrik equation [20]. The quantity of coke residue, too, is calculated from the structural formula of the polymer [13]. The heat release process on combustion can be described in terms of the material layer-by-layer heating–thermal degradation–combustion mathematical model [19, 21–23]. This model allows the heat release kinetic curve and effect of different factors (thermal stability, combustion heat, coke number, emissivity, heat capacity, heat conductance, etc.) to be fairly accurately assessed from the thermophysical and thermochemical characteristics of the material.

Table 6 lists the fire hazard characteristics of polymer composites of different classes. As seen, depending on the type of the polymer binder, the maximum heat release can vary over an order of magnitude, the smoke-forming capacity, more than two orders of magnitude, and the residual combustion time, from 0 to hundreds of seconds.

Table 6 lists materials grouped in terms of residual combustion time and burn-out length: respectively, 0 s and ≥ 152 mm (low-flammable material); ≥ 15 s and ≥ 152 mm for glass plastics and structural elements and ≥ 203 mm for fabrics, coatings, etc. (self-extinguishing material); and flammable materials (does not relate to the previous two groups). At horizontal tests, one more group is recognized, viz. slowly combusting materials having the flame propagation rate of no more than 60 mm/min (used for materials for special functional applications, such as rubbers, organic glasses, etc.). In terms of smoke evolution, a material is considered virtually nonsmoking, if the maximum specific optical density of smoke D_{max} is < 5; low-smoking, $D_4 < 16$ (specific optical density of smoke after 4 min) and $D_{max} < 50$; medium-smoking, $D_4 < 100$ and $D_{max} < 200$; essentially smoking, $D_2 < 100$ and $D_4 < 200$; and strongly smoking, $D_2 > 100$ and $D_4 > 200$.

Thus, fire hazard characteristics can be affected, depending on the task assigned, in different ways, and, with the progress in knowledge of the mechanisms of in-flame reactions and in production technologies, a possibility for the development of new materials with enhanced fire safety arises.

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