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Influence of aluminum(III) hydroxide, magnesium(II) hydroxide and organophosphorus compounds on the flammability of epoxy materials

Wpływ wodorotlenku glinu (III) i wodorotlenku magnezu (II) oraz związków fosforoorganicznych na palność materiałów epoksydowych

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Abstract: The article presents the effect of Mg $(OH)_2$, Al $(OH)_3$, Roflam F5 and Roflam B7 on the flammability properties of hardened epoxy resin Epidian 5. After an analysis of the heat release rate in a cone calorimeter and executing a thermogravimetric analysis, it was found that the introduced additives are effective flame retardants of the tested epoxy materials. The lowest value of the maximum heat release rate was recorded for the sample consisting of Epidian 5 and 10 wt.% of Roflam F5 and 5 wt. $Al(OH)_3$.

Keywords: epoxy resins; fire-retardant modification; fire properties

Streszczenie. W artykule zaprezentowano wpływ $Mg(OH)_2$, $Al(OH)_3$ oraz Roflamu F5 i Roflamu B7 na właściwości palne utwardzonej żywicy epoksydowej Epidian 5. Po analizie szybkości wydzielania ciepła w kalorymetrze stożkowym oraz analizie termograwimetrycznej stwierdzono, że wprowadzone dodatki są skutecznymi antypirenami testowanych materiałów epoksydowych. Najmniejszą wartość maksymalnej szybkości wydzielania ciepła zanotowano dla próbki składającej się z Epidianu 5 oraz 10% wag. Roflamu F5 oraz 5% wag. $Al(OH)_3$.

Słowa kluczowe: żywice epoksydowe; modyfikacje uniepalniające; właściwości przeciwpożarowe.

Since the invention of epoxy resin in the 1930s, significant advances in its use have been made, allowing for an expansion of its application possibilities, e.g. in composite materials, cast floors, castings, adhesives, etc. However, materials formed of cured epoxy resins are relatively flammable and, as e.g. structural materials or as part of interior finishes and furnishings in escape routes, should be fire-modified [1]. The combustion of epoxy resins releases a large amount of heat and smoke per unit time, which can reduce the time to evacuate building occupants under fire conditions. Therefore, modifying epoxy resins to reduce their combustion without compromising their performance and negative environmental impact [2] is important for the fire safety of facilities. For environmental reasons, more attention is being focused on the introduction of flame retardants into epoxy resins, which, under fire conditions, reduce the amount of heat and smoke released and the toxicity of thermal decomposition and combustion products.

Originally, the way to modify fire retardant epoxy materials was to introduce halogen compounds during the synthesis of resins or into the finished polymer mass. Nowadays, the use of halogenated flame retardants is restricted or banned due to the release of large quantities of irritant and toxic gases, including bromodihydrogen, hydrogen chloride, dibenzodioxins and dibenzofurans [3], which are deemed to be harmful to man and to the environment [4]. Due to these limitations, there has been an intense increase in interest in halogen-free combustion reaction inhibitors designated for polymeric materials, which can reduce the rate of heat release from modified materials and typically reduce the emission of toxic thermal decomposition and combustion products [5]. In recent years, phosphorus-based non-halogen flame retardants [6,7] as well as those based on silicon [8, 9], boron [10 – 12], nanoadditives [13] have been extensively developed and used to modify epoxy resins. Among these, a particular role was played by the antipyrene DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) and its derivatives, which is found to have a high reactivity with resins, relatively high thermal stability and flame retardant effectiveness [14]. In contrast, modifications of epoxy resins with phosphorus-based compounds showed a significant decrease in their thermal stability, but reduced their flammability when permanent charred layers were formed on the surface of the polymer material. Furthermore, the flame retardant effectiveness of flame retardants on the flammability of epoxy resins was dependent on the concentration of the introduced flame retardant [15]. Currently, there is a trend towards developing a more complex modification of epoxy resins, which consists of several flame retardant components. Many flame retardant modifications of polymers containing,

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for example, phosphaphenanthrene and other functional groups contained, among others, in maleimide [16,17], phosphazene [18], triazine [19], triazine-trione [20] and silsesquioxane [21] also make epoxy resins less flammable. Furthermore, a synergistic effect was observed when different antipyrene groups were introduced into one polymer matrix, e.g. phosphazene and phosphaphenanthrene [22]. Flame retardants that contain a phosphorus atom can either act in the condensed (solid, polymer) phase, the vapour phase or simultaneously in both phases. Some phosphorus compounds, e.g. phosphine oxide, decompose in the condensed phase to form phosphoric or polyphosphoric acid. These can act as catalysts in dehydration reactions, reacting for example with cellulose or in the case of rigid polyurethanes. Polyphosphoric acid can also form a viscous, molten surface layer on the polymer surface. This layer can shield the polymer base from flame (heat) and oxygen from the air. The effect of forming intumescent layers with an acid, such as phosphoric acid, is to form layers of carbonisation on the polymer surface, protecting the polymer from heat and oxidation

For this reason, the article attempts to effectively modify the flame retardancy of these polymers and further analyses their flammability providing an explanation of the mechanism of action of the flame retardants used.

Experimental Studies

Description of Samples for Testing. The fireproof modification of materials formed from an epoxy resin that bears the trade name Epidian 5 comprised the addition of selected flame retardants to the polymer base at an appropriate concentration determined in an experimental way. To Epidian 5 commercially available halogen-free admixtures were added while stirring continuously with a mechanical stirrer (at V = 300 rpm): Roflam B7 (tert-butylphenyl phosphate) or Roflam F5 (phenyl-isopropylphenyl phosphate) in the range of 5 ÷ 10 wt. %, as well as nanofillers $Mg(OH)_2$ or $Al(OH)_3$ in the range of 5 ÷ 10 wt. %. Once all components were incorporated, the antipyrene and polymer mixture was stirred for further 20 min and afterwards the whole mixture was placed in an ultrasonic bath for 1 hrs. with continuous stirring on a stirrer. The polymer mixture was then degassed on a mechanical pump. Both the unmodified and the modified epoxy resin were then cured with the addition of hardener Z-1 at 12 parts by weight to 100 parts by weight of the resin. The curing process was carried out at room temperature and the gel time was approximately 15 minutes. Initial curing was achieved after about 3 hours, with a cure rate of about 80÷90% after 24 hours. For this reason, the cured samples were then post-cured by placing in an oven for a further 2 hours at 120°C. The composition and determination of the produced samples are shown in Table 1.

Table 1. Composition and characterisation of the samples analysed

Tabela 1. Skład i oznaczenie analizowanych próbek

No.	Sample name	Sample composition
1.	Ep5	Epidian 5
2.	5B	Epidian 5+5% wt. Roflam B7
3.	5A	Epidian 5+5% wt. $Al(OH)_3$
4.	5M	Epidian 5+5% wt. $Mg(OH)_2$
5.	5F	Epidian 5+5% wt. Roflam F5
6.	10F+5M	Epidian 5+10% wt. Roflam F5+5% wt. $Mg(OH)_2$
7.	10F+5A	Epidian 5+10% wt. Roflam F5+5% wt. $Al(OH)_3$
8.	10B+5M	Epidian 5+10% wt. Roflam B7+5% wt. $Mg(OH)_2$
9.	10B+5A	Epidian 5+10% wt. Roflam B7+5% wt. $Al(OH)_3$
10.	5F+10M	Epidan 5+5% wt. Roflam F5+10% wt. $Mg(OH)_2$
11.	5F+10A	Epidian 5+5% wt. Roflam F5+10% wt. $Al(OH)_3$
12.	5B+10M	Epidian 5+5% wt. Roflam B7+10% wt. $Mg(OH)_2$
13.	5B+10A	Epidian 5+5% wt. Roflam B7+10% wt. $Al(OH)_3$

Description of research methods

Cone calorimeter method. The fire behaviour of the analysed cured epoxy resin was established by using the cone calorimeter method according to the standard [23]. This method allows the simultaneous determination of HRR *(Heat Release Rate)* and smoke during the combustion of materials that have been exposed to a controlled thermal radiation power of 50 kW/m^2. The applied thermal radiation power simulated the first phase of the fire according to the standard curve 'fire temperature – combustion time". The cone calorimeter method is based on the calorimetry of oxygen consumption for combustion to determine the rate of heat release from the test materials. For most combustible materials, it is assumed that 13.1 MJ of heat is released per kilogram of oxygen consumed during the combustion of the material. Deviations from this average value are ±5%, depending on the material.

Thermogravimetric method. The thermal analysis of cured epoxy resin both unmodified and modified was performed with the use of a dynamic technique according to the standard [24]. This method involved recording the change in mass of the test sample undergoing decomposition as a function of temperature at a pre-programmed heating rate. A TA Instruments Q500 thermogravimetric analyser (USA) was used for needs of the study. During the testing, the change in mass of the tested materials was recorded as a function of temperature in the temperature range 20 ÷ 900ºC, at a heating rate of 2.5ºC/min. The test was carried out in an atmosphere of air at atmospheric pressure, achieved by a constant flow of air – 90 ml/min and nitrogen (as a carrier of combustion products) – 10 ml/min. The thermogravimetric method makes it possible to analyse the thermal decomposition of polymers.

Test results

Analysis of heat release rate results. A summary of selected fire parameters of epoxy materials (arithmetic averages from 5 measurements) derived from cured Epidian 5 with added flame retardants at the tested thermal exposure is presented in Table 2. The heat release rate curves at a thermal exposure of 50 kW/m^2 of the tested epoxy materials formed on the basis of Epidian 5 are presented in Figure 1. In the initial phase of testing of the cured Epidian 5 samples, it is possible to note the time interval (0 ÷ 16 s), which is characterised as the initial heating period of the sample. During this time interval, the absorbed he-

Table 2. Thermokinetic and thermophysical properties of cured epoxy resin Epidian 5 modified and unmodified with $Al(OH)_3$ or $Mg(OH)_2$ and organophosphate flame retardants under ignition conditions at an external heat flux density of 50 kW/m²
Tabela 2. Właściwości termokinetyczne i termofizyczne utwardzonej żywicy epoksydowej Epidian 5 modyfikowanej i niemodyfikowanej $Al(OH)_3$ lub $Mg(OH)_2$ oraz fosforoorganicznymi antypirenami w warunkach zapłonu przy zewnętrznej gęstości strumienia ciepła 50 kW/m²

No.	Sample	HRR_{max} [kW/m²]	HRR_{avg} [kW/m²]	THR* [MJ/m²]	SEA_{avg} [m²/kg]	TSP** [m²]	Time until		Sample remnants [% wt.]	Proper emission	
							ignition [s]	reaching HRR_{max} [s]		CO [kg/kg]	CO_2 [kg/kg]
1.	Ep5	1318	603	130	849	40,7	16	132	1,85	2,1	11,3
2.	5B	900	595	114	316	21,3	10	84	3,87	2,2	10,4
3.	5A	748	435	136	197	17,0	16	148	5,64	1,9	10,5
4.	5M	892	364	117	158	15,6	36	100	3,25	2,0	10,6
5.	5F	1011	446	77	655	33,6	38	82	5,74	2,9	10,6
6.	10F+5M	962	475	101	701	35,3	34	120	7,60	2,4	10,4
7.	10F+5A	539	353	84	693	35,0	16	118	16,47	2,3	10,1
8.	10B+5M	1162	584	121	476	27,1	30	104	5,57	2,2	11,6
9.	10B+5A	740	310	105	327	21,7	10	96	10,22	2,3	10,5
10.	5F+10M	1199	530	107	278	19,9	10	114	6,97	2,2	11,6
11.	5F+10A	570	369	104	926	43,5	36	190	9,28	2,1	10,0
12.	5B+10M	988	470	96	754	37,2	38	118	11,01	2,4	11,9
13.	5B+10A	693	405	87	547	29,7	30	136	9,80	2,7	11,3

* THR – Total Heat Release, ** TSP – Total Smoke Production

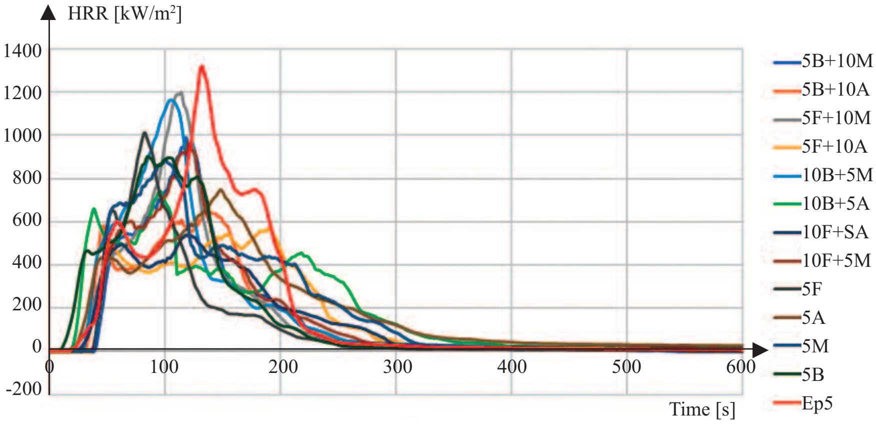

Fig. 1. Heat release kinetics of unmodified and modified epoxy material at a heat flux of 50 kW/m² in gas phase ignition conditions
Rys. 1. Kinetyka wydzielania ciepła przez materiał epoksydowy niemodyfikowany i modyfikowany w strumieniu ciepła 50 kW/m² w warunkach zapłonu fazy gazowej

at emitted from the irradiator by the samples leads to their thermal decomposition and the HRR values are low. Subsequently, a significant spike in HRR values (after 10 seconds) is observed for sample 5B and 10B+5A, due to the presence of phosphate flame retardants, which reduce the thermostability of the polymer material by forming a char layer, effectively acting as a solid-phase flame retardant. In contrast, homogeneous modification of Epidian 5 with Roflam F5 at 5 wt. % or mixed modification with Roflam B7 at 5 wt. % and $Mg(OH)_2$ at 10 wt. % resulted in the highest time to ignition of the sample of 38 seconds.

The test results have shown that the flame retardant additives introduced into Epidian 5 significantly reduce HRR_{max} (by 9 ÷ 59%) and HRR_{avg} (by 1 ÷ 49%), making them effective flame retardants. The highest HRR_{max} value of 1318 kW/m² was recorded for Epidian 5. Among the single-component additives, $Al(OH)_3$ allowed the biggest decrease of the HRR_{max} value of the tested resins. This effect was due to the release of water vapour and the formation of a glassy coating during the combustion process, protecting the material from heat and oxygen. When analysing the HRR_{avg} value, the highest value of 603 kW/m² was achieved with the cured, unmodified Epidian 5. This value was reduced to the lowest level of 310 kW/m² after the addition of 10 wt. % Roflam B7 and 5 wt. % $Al(OH)_3$. In the case of single-component additives, the value of HRR_{avg} was most effectively reduced by $Mg(OH)_2$, and allowed obtaining an HRR_{avg} value of 364 kW/m². By analysing the values of SEA_{avg} (mean specific extinction coefficient), it can be observed that the introduction of fire retardant additives causes a decrease in the value of this parameter. Among the mixtures with a single flame retardant, the lowest value of 158 m²/kg was recorded for the 5M sample. This value was 81% lower than that of the Epidian 5 sample. However, the simultaneous introduction of 5% wt. of Roflam F5 and 10% wt. of $Al(OH)_3$ resulted in an increase in the amount of smoke released and the SEA_{avg} value. It can be concluded that Roflam F5 accelerates the decomposition of the polymer by forming decomposition products together with aluminum(III) hydroxide, increasing the light attenuation surface area of the smoke particles. Taking into account the %wt. residue of the sample after combustion, it can be concluded that the effect of the phosphorus-based flame retardant additives in the combustion process of the cured modification of the epoxy resin Epidian 5 is mainly related to the gas phase. In the analysed thermal exposure, the introduction of additional hydroxides into Roflam B7 increased, as compared to Epidian 5, the time to ignition of the sample and the time to reach HRR_{max}, e.g. for sample 5F+10A, by 20 s and 58 s, respectively. Considering the values of CO released from 1 kg of material, it was observed that antipyrene-modified materials typically tend to release comparable amounts of CO at an average level of 2.3 kg/kg compared to unmodified cured Epidian 5. Epoxy material samples modified only with hydroperoxides produced lower amounts of CO per 1 kg of material from Epidian 5. Analysing the CO_2

release per 1 kg of material, it can be seen that sample 5F+10A achieves the lowest specific CO_2 emission value of 10.0 kg/kg, which is at the same time more than 12% lower in relation to Epidian 5. The mechanism of action of the mixed flame retardants was based on the synergistic effect. Phosphorus compounds acted as radical eliminators by evacuating free radicals in the gas phase at elevated temperatures during the combustion process, while inorganic compounds, i.e. $Mg(OH)_2$ or $Al(OH)_3$, caused the release of water vapour, effectively lowering the HRR_{max} value.

Thermogravimetric analysis. On the basis of TG and DTG thermogravimetric curves of the tested epoxy materials, the values of selected parameters describing the process of their thermal decomposition were read out and have been summarised in Table 3.

Figure 2a-b shows selected TG curves of cured modified and unmodified flame retardant epoxy resin samples based on Epidian 5 at a heating rate of 2.5°C/min.

Figure 2a-b suggests that all fire retardant modifications of Epidian 5 had a higher percentage sample residue after thermal decomposition as compared to the cured, unmodified epoxy resin. For example, among the single-component additives, the highest residue after thermal decomposition and combustion was recorded for sample 5M, and among the two-component additives for 5F+10M. These values were almost threefold and more than fourfold higher, respectively, as compared to Epidian 5. The values of the initial thermal decomposition temperature of the first phase of the cured, $Mg(OH)_2$ – modified epoxy resin samples (sample 5M) or 5 wt. % organophosphate compound and 10% wt. $Mg(OH)_2$ (samples 5B+10M and 5F+10M) were higher as compared to the cured, unmodified epoxy resin for these samples (e.g. by 1°C – 5M, by 18°C – 5B+10M, by 8°C – 5F+10M). The temperature of the maximum sample weight loss rate in the first phase of the transformation was the highest for sample 5M with a difference of 16°C as compared to the unmodified epoxy resin Epidian 5.

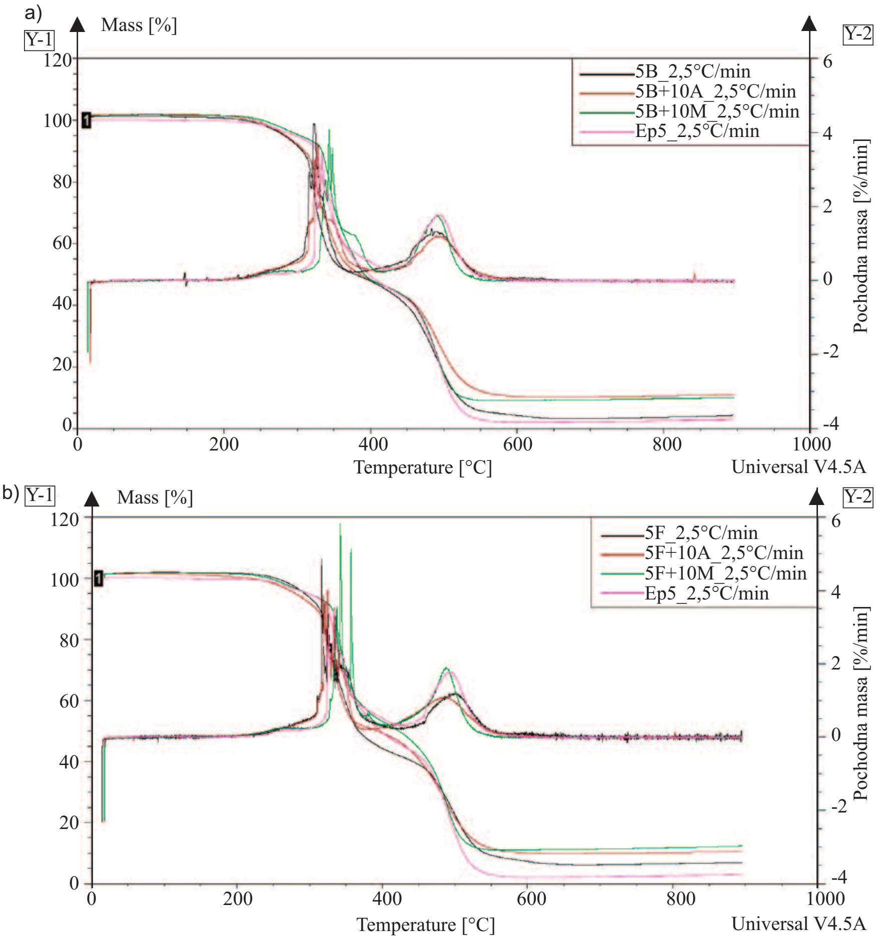

Fig. 2. Illustrative TG and DTG curves obtained during thermal decomposition of unmodified and modified Epidian 5 at a heating rate of 2.5°C/min: a) with Roflam B7 and $Mg(OH)_2$ or $Al(OH)_3$; b) with Roflam F5 and $Mg(OH)_2$ or $Al(OH)_3$

Rys. 2. Przykładowe krzywe TG i DTG uzyskane podczas rozkładu termicznego niemodyfikowanego i modyfikowanego Epidianu 5 przy szybkości ogrzewania 2,5°C/min: a) Roflamem B7 i $Mg(OH)_2$ lub $Al(OH)_3$; b) Roflamem F5 i $Mg(OH)_2$ lub $Al(OH)_3$

Table 3. Thermogravimetric test results of cured modified and unmodified epoxy resin

Tabela 3. Wyniki badań termograwimetrycznych utwardzonej modyfikowanej i niemodyfikowanej żywicy epoksydowej

No.	Sample	Heating rate of samples [ºC/min]	Temperature of		Maximum rate of mass loss of the 1st transformation phase [%/min]	Temperature of		Maximum mass loss rate in the 2nd transformation phase [%/min]	Sample mass after thermal decomposition [mg]; [%]
			commencement of thermal decomposition of the 1st transformation phase [ºC]	maximum sample mass loss in the 1st transformation phase [ºC]		50% sample mass loss [ºC]	maximum sample mass loss in the 2nd transformation phase [ºC]		
1.	Ep5	2,5	318	334	3,45	398	496	1,78	0,11; 2,96
2.	5B	2,5	311	323	4,25	379	483	1,40	0,15; 4,28
3.	5A	2,5	318	329	3,99	420	493	1,80	0,21; 6,52
4.	5M	2,5	319	350	2,88	383	462	3,41	0,27; 8,12
5,	5F	2,5	304	317	4,87	368	502	1,20	0,24; 6,88
6.	10F+5M	2,5	305	333	4,47	408	490	1,50	0,27; 8,69
7.	10F+5A	2,5	300	319	3,38	365	499	1,09	0,32; 8,52
8.	10B+5M	2,5	309	336	3,49	395	500	1,46	0,28; 7,99
9.	10B+5A	2,5	302	318	3,44	366	504	1,23	0,29; 8,69
10.	5F+10M	2,5	326	342	5,83	423	488	1,90	0,44; 12,30
11.	5F+10A	2,5	308	325	4,05	393	490	1,09	0,40; 10,50
12.	5B+10M	2,5	336	344	4,08	392	491	1,75	0,34; 9,98
13.	5B+10A	2,5	309	328	3,72	386	495	1,21	0,35; 10,90

Conclusions

On the basis of results of conducted tests of the combustion properties and heat and smoke release rates of the tested modifications of Epidian 5, as well as of the increase in the effect of the modifying agents on the improvement of the fire properties of the epoxy materials, the following conclusions can be drawn:

- the applied flame retardant additives to the epoxy resin Epidian 5 change fire properties of the epoxy materials being tested. These modifications decreased the heat release rate as compared to the unmodified flame retardant material, which implies that in real fires they would decrease the fire power, as both HRR_{max} and HRR_{avg} values of all flame retardant modifications are lower as compared to the respective HRR values of the unmodified Epidian 5 material in the analysed thermal exposures (HRR_{max} lower by 9 to 59%, HRR_{avg} lower by 1 to 49%);
- the obtained modifications of cured epoxy resin, forming layers of char, confirm the inhibitory effect in the solid phase of the applied flame retardants and their mixtures;
- for samples 5F and 5B+10M, the highest values of times to ignition of the gas phase were obtained at an external heat flux density of 50 kW/m^2 (38 seconds). The main action of the additives was recorded in the solid phase. This is also evidenced by the higher residue values after thermal decomposition and combustion (by 76÷790%) compared to the unmodified sample;
- the mechanism of action of the additives used tends to vary. The addition of 5% wt. $Al(OH)_3$ to cured Epidian 5 has a gas-phase action. This is evidenced by the relatively small residue of the char layer after burning (5.64 wt.%);
- the mixed compositions were found to have a lower temperature of onset of thermal decomposition of the first phase than Epidian 5;
- sample 5M exhibits the least amount of total smoke release of all the materials tested, and if this type of resin is used as a finishing and furnishing material, it is expected to release less smoke in a fire than Epidian 5, which would allow a better visibility in smoke and a safer evacuation.

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