Epoxy resin compositions containing liquid phosphorus flame retardants used in infusion technology (*Rapid communication*)

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Abstract: This study investigates the impact of the type and amount of liquid phosphorus flame retardant additive on the flammability and mechanical properties of epoxy compositions dedicated to the infusion process. To this purpose, epoxy resin (EP) compositions containing 10 and 20 wt % of liquid ammonium polyphosphate (APPL) and dimethyl methylphosphonate (DMMP) were obtained. Mechanical properties and flame resistance of obtained epoxy compositions were determined in terms of their use as a matrix in laminate infusion technology. Based on the results obtained, it was found, that the flame resistance increases, while the mechanical properties decreases with flame retardant loading. The best flame resistance results were obtained for a composite containing 20 wt % APPL: limiting oxygen index LOI = 23.9% instead of 19.8% – EP, peak of heat release rate $pHRR$ = 427.3 kW/m^2 instead of 1046.3 kW/m^2 – EP.

Keywords: composites, epoxy resin, infusion, liquid flame retardants.

Kompozycje żywic epoksydowych z dodatkiem ciekłych uniepalniaczy fosforowych stosowane w technologii infuzji

Streszczenie: Zbadano wpływ rodzaju i ilości dodatku ciekłych uniepalniaczy fosforowych na palność i właściwości mechaniczne kompozycji epoksydowych przeznaczonych do zastosowania w procesie infuzji. Wytworzono kompozycje żywicy epoksydowej (EP) zawierające 10 i 20% mas. ciekłego poli(fosforanu amonu) (APPL) oraz metylofosfonianu dimetylu (DMMP). Określono właściwości mechaniczne oraz odporność na płomień otrzymanych kompozycji epoksydowych w kontekście ich zastosowania w charakterze osnowy w technologii infuzji laminatów. Na podstawie uzyskanych wyników stwierdzono, że wraz ze zwiększaniem zawartości uniepalniaczy zwiększała się odporność na płomień, natomiast pogarszały się właściwości mechaniczne kompozycji. Najlepszą odporność na płomień wykazywał kompozyt z udziałem 20% mas. APPL: graniczny indeks tlenowy LOI = 23.9% (w odniesieniu do wartości LOI żywicy epoksydowej 19.8%) oraz maksymalna szybkość uwalniania ciepła $pHRR$ = 427.3 kW/m^2 (w porównaniu do $pHRR$ żywicy 1046.3 kW/m^2).

Słowa kluczowe: kompozyty, żywica epoksydowa, infuzja, ciekłe uniepalniacze.

In recent years, epoxy resins have found use as construction materials in the automotive and aerospace industries. Due to good performance and low viscosity, they are often used to obtain composites using infusion technology. Therefore, to increase the potential use of epoxy resins, they are modified through the use of effective flame retardants, which include compounds containing phosphorus, silicon, bromine or nitrogen. As phosphorus based flame retardants, to reduce the flammability of epoxy resins, reactive substances are used, which are incorporated into the structure of the epoxy network [1, 2]. However, the presence of -P-O- groups in the main or side chain of epoxy resin significantly reduces the thermal stability of composites in the initial stages of decomposition (by up to 150°C) and causes a decrease in the glass transition temperature of composites by up to 90°C compared to commercial epoxies [3]. Until recently, resins derived from tetrabromodian and epichlorohydrin remained among the many different products on the market. Currently due to the tendency to exclude bromine compounds as potentially harmful to the environment, epoxy resin with the addition of phosphorus flame retardants are starting to compete with them [4, 5]. Undoubtedly, the addition of reactive compounds improves flame resistance, but their

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synthesis and method of application makes their use in processing very difficult. Phosphorus additive flame retardants in the form of phosphates, phosphinates or phosphine oxides are also effective compounds improving flame resistance of epoxy composites. Their effectiveness depends mainly on the proportions used and appropriate mixing in the epoxy matrix. However, the main disadvantage of this type of flame retardants, limiting their application as a laminate matrix in pressure-vacuum technologies such as infusion or RTM (Resin Transfer Molding), is a significant increase in the viscosity of epoxy compositions. Additive liquid phosphorus flame retardants can be an alternative to additive powder flame retardants. Dimethyl methylphosphonate (DMMP) is known as an effective synergistic agent in reducing the flammability of polyester resins [6], epoxy resin [7] and polyurethane foam [8]. However, there is no information on the effect of the addition of liquid additive flame retardants such as DMMP and APPL (ammonium polyphosphate), on the flame resistance and mechanical properties of epoxy resins.

Therefore, the purpose of this work is to investigate the effect of the amount and type of phosphorus based liquid flame retardants on the flammability and mechanical properties of epoxy composites in the context of their use as a matrix of laminates obtained by pressure or vacuum methods. The results presented in the article are an extension of research on composites with increased flame resistance using halogen-free flame retardants.

EXPERIMENTAL PART

Materials

The following materials were used in this study:
– Epoxy resin Epidian® 624 – epoxy resin containing mostly diglycidyl ether of bisphenol A (EP) and the curing agent triethylenetetramine (Z1), both commercial grade products of Ciech-Sarzyna Plant, Poland.
– Halogen-free liquid flame retardants: ammonium polyphosphate (APPL) and dimethyl methylphosphonate (DMMP), produced by WTH (GmbH, Germany)

Preparation of test samples

A flame retardant was added to the epoxy resin (Epidian® 624) in amounts of 10 or 20 wt % and mixed for 10 minutes using a high speed turbine homogenizer (Dispermat CN40 produced by VMA-Getzmann, Gmbh). The stirrer speed was about 1500 rpm. Then, the compositions were degassed using a VAKUUM UHG 400 chamber (Schuechl, Germany). Then, after adding 12 wt % hardener, the compositions were cast into silicone molds prepared in accordance with ISO 527-1:1998. The samples were cured at room temperature for 24 h and then at 100°C for 6 h. After two days, the fittings were tested in accordance with the relevant standards.

Methods of testing

– The bending strength was determined in accordance with PN–EN ISO 178 using the INSTRON 5967 testing machine. The bending speed was 2 mm/min. The strength test was performed using the three-point bending method for a support spacing of 64 mm.
– Tensile strength was determined in accordance with ISO 527-1:1998 using the same tensile machine equipped with a video extensometer. Elongation speed was 2 mm/min.
– Rockwell hardness was determined using a ZWICK 3106 hardness tester in accordance with EN 10109-1. An indenter load of 358 N was used. The final result was an arithmetic mean of at least 10 measurements.
– Charpy impact strength was determined in accordance with PN-EN ISO 179-1 with Ceast 9050 Impact Pendulum (Italy), using hammer impact energy of 1 J.
– Limiting oxygen index (*LOI*) was determined according to the standard EN ISO 4589-1 at room temperature using an instrument of Fire Testing Technology Ltd. (United Kingdom).
– The UL-94 flame tests were carried out in a chamber produced by FTT Ltd (UK). The measurements were made according to the UL-94 test standard with horizontal sample beam position and a methane fed burner of 20 mm height.
– The maximum heat release rate (*pHRR* in kW/m^2) during sample combustion and other parameters characterizing flammability were evaluated in composite plates, $100 \times 100 \times 2$ (mm^3) in size, using a Mass Loss Calorimeter (MLC) from FTT Ltd, according to ISO 13927, by applying a heat flux of 50 kW/m^2 and the distance from the ignition source of 25 mm.

RESULTS AND DISCUSSION

Based on the results summarized in Table 1, it was found that with increasing content of liquid flame retardants, the mechanical properties of epoxy composites decrease. The flexural strength and flexural modulus of composites containing 10 wt % of APPL and DMMP were reduced by an average of 18 and 12%, compared to the unmodified resin. Increasing the content of flame retardants to 20 wt % caused even a double decrease of these parameters. Similar relationships were observed in the case of tensile strength and Young's modulus. Only the value of the tensile strength of composites containing 10 wt % flame retardants slightly decreased, by an average of 7%, compared to the reference sample. However, the content of 20 wt % has already caused a significant decrease of this parameter, by 47 and 42%, for a composite containing ammonium polyphosphate and dimethyl methylphosphonate, respectively. In turn, the Young's modulus decreased by 1.54 and 1.37 GPa, respectively, in relation to epoxy resin (Young's modulus = 2.52 GPa). In the case of Charpy impact tests, a clear, 50%, decrease in

T a b l e 1. Mechanical properties of epoxy resin and epoxy composites with liquid flame retardants

Symbol of sample	Ultimate flexural strength MPa	Flexural modulus GPa	Ultimate tensile strength MPa	Young modulus GPa	Charpy impact kJ/m²	Rockwell hardness MPa
EP	89.01 ± 7.2	2.22 ± 0.35	22.6 ± 2.1	2.52 ± 0.40	11.3 ± 1.2	127.2 ± 3.8
EP10APPL	73.4 ± 6.7	1.98 ± 0.30	20.8 ± 2.6	1.88 ± 0.15	9.0 ± 2.1	93.1 ± 3.5
EP20APPL	44.9 ± 2.6	1.05 ± 0.41	11.9 ± 3.0	0.98 ± 0.31	5.8 ± 1.5	69.0 ± 2.5
EP10DMMP	70.6 ± 3.9	1.91 ± 1.31	21.2 ± 3.2	1.84 ± 0,20	9.1 ± 1.6	117.2 ± 1.9
EP20DMMP	32.8 ± 2.6	0.92 ± 0.17	13.0 ± 1.6	1.15 ± 0.11	5.4 ± 1.2	51.2 ± 2.7

± – standard deviation

T a b l e 2. The results of flammability tests of epoxy resin and epoxy composites with liquid flame retardants

Symbol of sample	TTI s	pHRR kW/m²	THR MJ/m²	EHC MJ/kg	PML %	Vertical burning rate mm/min	UL-94 class	LOI %
EP	31	1046.3	57.4	64.3	94.2	32	HB 40	19.8
EP10APPL	29	548.2	48.9	54.8	86.1	-	HB 40b	21.8
EP20APPL	25	427.3	42.6	50.4	83.6	-	HB 40b	23.9
EP10DMMP	27	605.7	50.5	57.6	82.4	24	HB 40	21.9
EP20DMMP	21	515.7	40.1	56.3	78.8	12	HB 40	23.6

TTI – time to ignition, *pHRR* – peak heat release rate, *THR* – total heat released, *EHC* – effective heat of combustion, *PML* – percent mass loss, *LOI* – limiting oxygen index

this parameter was observed for composites containing 20 wt % flame retardants (Table 1). As could be expected, Rockwell hardness also significantly deteriorated in line with the relationship observed during impact tests. In short, the liquid flame retardants significantly reduced the mechanical properties of the epoxy composites. Decrease in the mechanical properties is greater than the our results obtained for glass fiber reinforced composites [9] as well as literature data where ammonium polyphosphate was used in powder form [10, 11]. What's more, the Rajaei [10] and Lim [12] teams achieved an increase in the flexural and Young's modulus of epoxy compositions containing solid ammonium polyphosphate (APP).
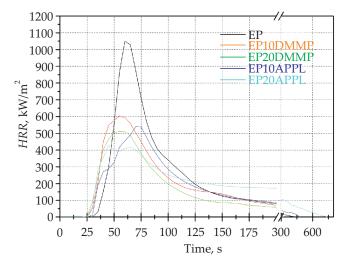

Fig. 1. Heat release rate (*HRR*) curves as a function of time during flammability tests performed in the mass loss calorimeter of unfilled epoxy resin and epoxy composites

The results of tests for determining the flammability of epoxy composites using a mass loss calorimeter are given in Table 2. The results are the arithmetic mean of three measurements for each composite. In turn, Fig. 1 shows representative curves of the dependence of heat release rate as a function of time recorded during the test.

Based on the Fig. 1, it was found that the addition of phosphorus flame retardants changes the burning process of epoxy composites compared to unmodified epoxy resin. In the case of unfilled epoxy resin, the ignition time was 31 s, followed by a sharp and rapid increase in heat release, as a result of which the recorded average *pHRR* value was 1046 kW/m². In turn, the addition of flame retardants caused faster ignition of the sample, which is associated with their faster distribution [13] and a significant, by half, reduction of the maximum heat release rate. With APPL loading, the maximum heat release rate decreased by 48 and 59%, respectively, compared to the unmodified resin, while the composite containing DMMP stood out for the reduction in the *pHRR* value, by 42 and 50%. The addition of 10 and 20 wt % APPL causes a decrease in *THR* by 15 and 26%, compared to the unfilled resin, and a percentage mass loss of 83.6 and 86.1%. In turn, composites with 20 wt % DMMP were characterized by the largest reduction of *THR* by 30%, compared to the reference sample and the lowest mass loss (*PML*) of 78.8%. The analysis of the reduction of the *EHC* value and the increase in residue of composites containing flame retardants, carried out in accordance with our previous works [5] and literature data [14] indicates that the gas-phase effect plays a major role in the reduction of *THR* as confirmed by the calculated values (83.5, 78.4, 70.0 and 73.3% for 10%

APPL, 10% DMMP, 20% APPL, 20% DMMP, respectively). In turn, the decrease in *pHRR* was also determined by the protective barrier effect. Among the flame retardants used, the calculated additional protection effect of the char layer was larger for composites with the addition of APPL and was 37 and 41%, which showed a intumescence of char during the test.

The results obtained from the UL-94 and limiting oxygen index tests are shown in Table 2. The flammability class for unfilled epoxy resin was defined as HB 40, which means that the burning rate of the sample did not exceed 40 mm/min at a distance of 75 mm. The burning rate for this sample was the highest and amounted to 32 mm/min. Unexpectedly, the addition of flame retardants slightly changed the flame resistance in the UL-94 test, because regardless of the type and amount of flame-retardant additives applied, the composites also achieved HB 40 flammability class, which is a much weaker result compared to composites filled with standard ammonium polyphosphate - the addition in the range 10–15 wt % allow to obtain V0 flammability class of composites [15, 16]. Only the burning rate changed, which for the composite with 10 and 20 wt % DMMP was 24 and 12 mm/min, respectively. On the other hand, the composite with APPL was impossible to measure because the flame front didn't reach the 75 mm distance. Also much worse results compared to the literature data [17] were obtained in the case of the oxygen index, which reached the value of about 21.8 and 23.9% for composites containing 10 and 20 wt % of flame retardants, respectively.

SUMMARY

The paper presents the results concerning the influence of the application of liquid phosphorus flame retardants on utility properties of epoxy composites. For this purpose, liquid ammonium polyphosphate and dimethyl methylphosphonate were used. The obtained results indicate that the addition of liquid flame retardants in an amount of up to 20 wt % significantly reduces the mechanical properties compared to the addition of standard flame retardants in the form of powder. Also the degree of flame retardancy turned out to be much lower as the composites containing 20 wt % of flame-retardant additives were characterized by HB 40 flammability class according to UL-94 and an *LOI* of 23.8%. In turn, tests in a mass loss calorimeter showed a significant reduction, by more than 50%, in the value of the maximum heat release rate, compared to the reference sample, which was associated with the activity of flame retardants in the gas phase and, to a lesser extent, the additional protective barrier effect.

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