Fire resistant glass fabric-epoxy composites with reduced smoke emission (*Rapid communication*)

Rafał Oliwa[1), *)], Mariusz Oleksy[1)], Joanna Oliwa[1)], Aleksandra Węgier[2)], Sławomir Krauze[2)], Maciej Kowalski[2)]

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Abstract: In this article a preparation method of epoxy resin/glass fabric composites with reduced flammability and smoke emission was presented. For this purpose the two groups of powder-epoxy compositions containing: (1) melamine polyphosphate (MPP) and aluminum diethyl phosphinate (AlDPi); (2) ammonium polyphosphate (APP) and dipentaerythritol (DPE) were used as matrices in six-ply glass fabric reinforced composites. The flame retardants content was 25 wt %. In addition, the 10–15 wt % of zinc borate (ZB) as a smoke reducing agent was added to each compositions. The flame resistant and smoke emission of prepared laminates designed for application in public transport components were evaluated. It was found that with the increase of zinc borate content, the emission of fumes decreased. The lowest maximum of specific optical density ($D_s$max = 312.2), specific optical density in the first 4 minutes of the test [D_s(4) = 304.1] and cumulative specific optical densities in the first 4 minutes of the test (VOF_4 = 707.6 min) have been achieved for composite containing 10 wt % of MPP, 15 wt % of AlDPi and 15 wt % of ZB. Furthermore, this composite was characterized by V0 class by UL94 test, limiting oxygen index *LOI* = 36.8 % and maximum average rate of heat emission *MAHRE* = 80 kW/m^2.

Keywords: powder-epoxy resin, glass fiber, composites, fire resistant, smoke emission.

Ognioodporne kompozyty epoksydowe wzmocnione tkaniną szklaną o zmniejszonej emisji dymów

Streszczenie: Na osnowie z proszkowej żywicy epoksydowej otrzymywano kompozyty wzmocnione tkaniną szklaną, charakteryzujące się zwiększoną odpornością na płomień oraz zmniejszoną emisją dymów. Przygotowano dwie grupy kompozycji epoksydowych: (1) polifosforanu melaminy (MPP) i dietylofosfinianu glinu (AlDPi); (2) polifosforanu amonu (APP) i dipentaerytrytu (DPE), które wykorzystano jako osnowy w sześciowarstwowych kompozytach wzmocnionych tkaniną szklaną. Zawartość uniepalniaczy wynosiła 25 % mas. W celu zmniejszenia intensywności wydzielania dymów do kompozycji wprowadzano też 10–15 % mas. boranu cynku (ZB). Wyniki badań potwierdziły, że wraz ze zwiększaniem zawartości boranu cynku zmniejsza się emisja dymów z badanych materiałów. Najmniejsze wartości: maksymalnej właściwej gęstości optycznej ($D_s$max = 312,2), właściwej gęstości optycznej po 4 minutach badania [D_s(4) = 304,1] oraz łącznej wartości właściwych gęstości optycznych w pierwszych 4 minutach badania (VOF_4 = 707,6 min) wykazywał kompozyt wytworzony z 10 % mas. MPP, 15 % mas. AlDPi oraz 15 % mas. ZB. Kompozyt ten charakteryzował się klasą palności V0 wg testu palności UL94, indeksem tlenowym *LOI* = 36,8 % oraz maksymalną średnią szybkością emisji ciepła *MAHRE* = 80 kW/m^2.

Słowa kluczowe: proszkowa żywica epoksydowa, włókna szklane, kompozyty, odporność na ogień, emisja dymów.

The development of novel composite materials as well as their modification are a big challenge for most material engineers. In particular, the epoxy composites reinforced with glass or carbon fabrics have great potential and can replace traditional metallic materials. The railway industry offers considerable scope for the structural use of composites [1]. They are used for the production of train fronts (driver's cabs), evacuation doors, internal and external elements of train and toilet modules. They allow to obtain lighter structures which reduce fuel con-

1) Rzeszow University of Technology, Faculty Chemistry, Al. Powstańców Warszawy 12, 35-959 Rzeszów, Poland.

2) SZTK TAPS Maciej Kowalski, Borowa 4, 94-247 Łódź, Poland.

*) Author for correspondence; e-mail: oliwa@prz.edu.pl

sumption, increase speed, cargo volume, and improve passenger safety. For this reason, composites are becoming an attractive alternative to steel for mass transport applications [2]. The variety of railway infrastructure raises many challenges and opportunities for the composites industry. The main disadvantage of the polymer composites limiting their application in building primary and secondary structure in transportation means is the flammability of polymer matrix. On the other hand, the wider use of polymer fiber composites in public transport means requires adaptation to strict fire safety regulations. The improvement of fire resistance of polymer matrix is one of the crucial tasks for the development of the advanced polymer construction materials [3, 4]. At present, research on reducing the flammability of polymers focuses on seeking for environment friendly flame retardants containing preferably such elements as nitrogen, phosphorus, boron, and silicon. The most commonly used flame retardants additives are phosphorus and nitrogen compounds such as: ammonium polyphosphate [4–6], melamine polyphosphate [7, 8] and aluminum phosphinates [9, 10]. The addition in the range 10–20 wt % allow to obtain fire-resistant composites. However, the materials used as structural elements in public means of rail transport must be characterized by a suitably low-level smoke emission, according to ISO 45545-2. There are a few papers dealing with additives reducing the density of fumes. The most of these reports concentrated on the application of metal oxides [11, 12] and graphene [13, 14], as effective compounds that reduce toxicity of fumes and smoke release rate.

Therefore, the composites characterized by simultaneously increased flame resistance and reduced smoke emission are an interesting area of research. The objective of the present study was to investigate the influence of type of flame retardants and zinc borate content on the flammability, and smoke emission of epoxy-based composites with a glass fabric reinforcement used as the main structural elements of seats in public transport.

EXPERIMENTAL PART

Materials

The following materials were used in this study:

– one-component powder epoxy resin A.S.SET Powder 01 produced by New Era Materials Plant (Poland);

– halogen-free commercial flame retardants: melamine polyphosphate (MPP), zinc borate (ZB), ammonium polyphosphate (Addforce FR APP204; APP), dipentaerythritol (Dipenta D40; DPE) all produced by WTH GmbH (Germany) and aluminum diethyl phosphinate (AlDPi) produced by Clariant (Switzerland) were tested;

– glass woven roving fabric (2/2, 350 g/m^2) manufactured by Rymatex Sp. z o.o. was used as the main reinforcement.

T a b l e 1. Powder-epoxy resin compositions with flame retardants

Composition	Flame retardant content in epoxy compositions, wt %				
	AlDPi	MPP	ZB	APP	DPE
AS0	0	0	0	0	0
AS1	12.5	12.5	0	0	0
AS2	15	10	0	0	0
AS3	12.5	12.5	10	0	0
AS4	15	10	10	0	0
AS5	12.5	12.5	15	0	0
AS6	15	10	15	0	0
AS7	0	0	0	18	7
AS8	0	0	10	18	7
AS9	0	0	15	18	7

All the materials were used without further purification or modification.

Preparation of epoxy compositions

The powder resin was sieved through a screen with a mesh size of 0.06 mm, and then a composition was created by adding the flame retardants; their percentage content in each mixture is shown in Table 1. Each time after a flame retardant was added, the composition was blended with a high shear mixer (Dispermat CN40 produced by VMA-Getzmann, Gmbh) for 10 minutes, at velocity of 2000 rpm, where a propeller mixer was applied as a homogenising element.

Preparation of the laminates

The six-layer laminates were formed by applying a low-pressure molding method, with the use of a hydraulic press (Carver, USA). Each sheet of the fiber was covered by the 30 g of powder-epoxy composition. The whole structure was placed between two heated panels and subjected to a two-stage forming process, at the temperature of 120 °C and the pressure of 1 MPa applied for 1 min, and subsequently 4 MPa for 14 min. Samples for the study were cut using a milling machine from the obtained laminates with an approx. 50 wt % content of the reinforcement.

Methods of testing

The limiting oxygen index (*LOI*) for the laminates was determined according the EN ISO 4589 standard at room temperature using an instrument from Fire Testing Technology Ltd. (United Kingdom).

The flammability tests by using UL94 method were carried out in a chamber produced by FTT Ltd. (UK). The measurements were made according to PN-EN 60695-11-10

T a b l e 2. The results of flammability and smoke emission tests of the epoxy composites with glass fabric

Composition	*MAHRE* kW/m^2	*TTI* s	*PML* %	UL94 class	*LOI* %	$D_s$max	D_s(4)	VOF_4 min
AS0	203.0	56	41.3	HB75	22.5	> 700	> 700	1797.0
AS1	119.0	29	38.1	V0	36.8	> 700	> 700	1593.0
AS2	138.0	30	36.2	V0	35.9	> 700	> 700	1667.0
AS3	111.5	36	33.3	V0	36.6	382.1	356.8	1066.5
AS4	125.0	38	34.8	V0	36.3	358.3	342.9	912.0
AS5	74.5	26	27.8	V0	37.2	369.0	327.8	743.5
AS6	80.0	33	31.8	V0	36.8	312.2	304.1	707.6
AS7	110.8	42	35.8	V1	30.8	> 700	> 700	1312.0
AS8	143.0	28	32.0	V1	33.7	599.7	496.0	972.5
AS9	130.0	22	28.5	HB40	32.6	324.4	316.0	785.6

with vertical and horizontal sample beam positions and methane fed burner of 25 mm height.

The maximum average rate of heat emission (*MAHRE*) during sample combustion as well as other parameters (*TTI* – time to ignition, *PML* – percentage mass loss) characterizing flammability were evaluated for composite plates using a cone calorimeter from Sychta Laboratorium Sp.J. (Poland) according to ISO 5660-1:2015 by applying a heat flux of 50 kW/m^2 and the 25 mm distance from an ignition source.

The smoke emission intensity was determined according to EN ISO 5659-2 by applying a heat flux of 50 kW/m^2. The test was evaluated for composite plates with a size of 75 × 75 × 2.5 mm using a chamber – a product of Sychta Laboratorium Sp.J. (Poland). On the basis of the test the maximum of specific optical density ($D_s$max), specific optical density in the first 4 minutes [D_s(4)] and cumulative specific optical densities in the first 4 minutes (VOF_4) were determined.

RESULTS AND DISCUSSION

The results, *i.e.*, arithmetic means from three tests of flammability and smoke emission for each glass fabric-reinforced epoxy composites with flame retardants are collected in Table 2.

It was found that the addition of flame retardants improves flame resistant and decreases smoke emission of composites. Furthermore, the obtained results indicate that the values of *MAHRE* and *TTI* of composites decrease with zinc borate loading. The shorter time to ignition may be linked with faster decomposition of flame retardants, which form a sinter constituting a physical barrier between the high temperature flame and the polymer [15, 16]. Better results were obtained for composites containing melamine polyphosphate, aluminum diethyl phosphinate and zinc borate (AS3, AS4, AS5), in these cases the V0 flammability class has been achieved. In this group of the fire-retarded composites, the highest reduction of *MAHRE*, nearly three-fold (compared to the composite with unmodified matrix, AS0), was observed in the AS5 laminate matrix containing 12.5 wt % each of MPP and AlDPi and 15 wt % of ZB. This composite was also characterized by the largest *LOI* value, by 65 % compared to reference sample, exceeding 37.2 %. In the case of composites containing ammonium polyphosphate, dipentaerythritol and zinc borate (AS8, AS9) smaller change in the tested parameters was observed. In contrast to composites containing MPP, AlDPi and ZB, the *LOI* value of AS9 sample decreased by 1.1 % in comparison with AS8 composite with the increment of ZB loading and caused also the change of flammability class from V1 to HB40.

As expected, the smoke suppression increases with increase of zinc borate load. The curves presented in Fig. 1 indicate the differences in smoke emission for the tested composites. After ignition, the specific optical density of composites prepared with AS0, AS1, AS2 and AS7 matrices grows very fast reaching D_s = 700 after 100 s. After this time, the measurement was interrupted. The addition of zinc borate results in a reduce of the slope of the D_s curve. As a result, the maximum of D_s is shifted towards longer times. Again, the better results for composites prepared with the matrices containing MPP, AlDPi and ZB were achieved. In the group of mentioned materials, the smallest values of $D_s$max, D_s(4) and VOF_4 were recorded

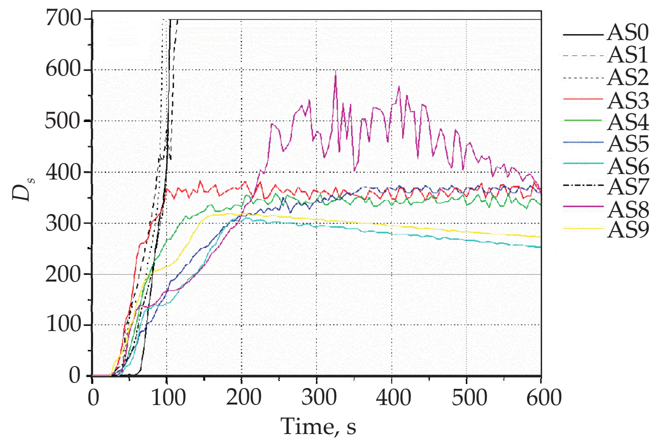

Fig. 1. Specific optical density (D_s) for the composites as a function of flammability tests duration

for AS6 composite. A decrement of AlDPi and MPP mass ratio (*i.e.*, from 1.5 : 1 for AS6 to 1 : 1 for AS5) led to a small increase of $D_s$max, D_s(4) and VOF_4 values. Similar relationship was observed in the case of AS3 and AS4 laminates comprising 10 wt % of zinc borate. Moreover, as can be seen in Table 2 the inverse relationship between flame resistance and smoke formation was obtained, *e.g.*, the AS9 composite with HB40 class exhibited lower values of $D_s$max (-46 %), D_s(4) (-36 %) and VOF_4 (-18 %) in relation to AS8 characterized by V1 flammability class.

CONCLUSIONS

In this work the powder epoxy resin/glass fabric--based composites with reduced flammability and smoke emission were obtained. A few commercial compounds containing phosphorus and nitrogen, as well as zinc borate have been used as flame retardants. The obtained results significantly revealed that zinc borate addition reduced smoke emission and *MAHRE* value, thus the materials fulfill the R6 requirements according to EN 45545-2:2013+A1:2015 (for hazard level of HL1). Furthermore, among the flame resistance systems applied to glass fabric reinforced epoxy-based composites the best results (V0 class by UL94, *LOI* = 36.8 % and *MAHRE* = 80 kW/m^2) were reached for the laminates with the matrix consisting of 60 wt % of epoxy resin, 10 wt % of MPP, 15 wt % of AlDPi and 15 wt % of ZB (AS6).

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