Flame resistant hybrid epoxy composites *(Rapid Communication)*

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Abstract: Studies were conducted of epoxy composites with modified bentonites with quaternary phosphonium salts (QPS) and aluminium trihydrate (ATH). The content of the modified bentonite was 3.0 wt %, and ATH 5.0 or 10.0 wt %. It has been found that the basic mechanical properties of hybrid composites have been improved and achieved much greater resistance to flame.

Keywords: epoxy resin, quaternary phosphonium salts, modified bentonite, aluminium trihydrate, hybrid polymer composites, mechanical properties, fire retardancy.

Ognioodporne hybrydowe kompozyty epoksydowe

Streszczenie: Przeprowadzono badania kompozytów żywicy epoksydowej (EP) z bentonitami modyfikowanymi czwartorzędowymi solami fosfoniowymi (QPS) i z wodorotlenkiem glinu (ATH). Udział modyfikowanego bentonitu w kompozycie wynosił 3,0 % mas., natomiast ATH 5,0 lub 10,0 % mas. Stwierdzono, że podstawowe właściwości mechaniczne hybrydowych kompozytów uległy poprawie, a ich odporność na płomień wyraźnie wzrosła.

Słowa kluczowe: żywica epoksydowa, czwartorzędowe sole fosfoniowe, modyfikowany bentonit, wodorotlenek glinu, hybrydowe kompozyty polimerowe, właściwości mechaniczne, ognioodporność.

Due to increasing requirements for the environmental impact of polymer composites and auxiliaries introduced to them, particular attention is recently paid to inorganic flame retardants, especially such as aluminium trihydrate [1—3], modified bentonite (MB) [4, 5] and layered double hydroxides (LDH) [6, 7]. The advantage of using ATH is small smoke production and toxicity, insignificant corrosivity and low price. During heating ATH in the temperature range 190—230 °C, it begins to decompose with emission of water vapour at 350 °C and loses 35 % of the initial mass. ATH is an excellent inhibitor of polymer combustion, where the temperature of processing does not exceed 200—220 °C [8]. Emitted vapour results in cooling of the burned polymer, which reduces the speed of pyrolysis and diluting volatile pyrolysis products of the polymer, reducing the concentration of flammable gases below the lower limit combustion. One disadvantage of ATH is using its high concentration as a flame retardant, which worsens process ability and mechanical properties of the final product.

Due to its layered structure, MB may act as a thermal insulator and barrier to moving gaseous products of pyrolysis because while a flame is acting on the composite it is possible that a relatively tight layer of scale is created on the surface of the material which ensures two-way effect of a barrier to diffusion of gases originating during combustion and preventing an access of oxygen from the surrounding atmosphere to the surface of the ash and combustible volatile components of the pyrolysis of the polymer to the flame front [9]. When these two processes are severely impeded diffusion, the material may show self-extinguishing capacity [10]. Secondary mechanism of flame inhibition consists in the fact that at high temperatures inorganic fillers act like radical absorbers due to their nature of Lewis acid which results in deactivation of the flame. The level of diminishing combustibility of the polymer by adding nanofillers depends on the applied chemical, normally flammable modifier of bentonite. In recent years, many studies were devoted to the development of flame retardants containing phosphorus atoms [11, 12]. In this regard, also bentonites modified by quaternary phosphonium salts (QPS) are of great interest [13, 14]. The advantage of these nanofillers is combined effects of flame retardants according to two different mechanisms for flame retarding.

Experience gained in work devoted to nanocomposites based on synthetic resins [15—19], prompted us to undertake work on developing new epoxy compositions with addition of mixed fillers: modified bentonite QPS and ATH, which are resistant to fire.

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EXPERIMENTAL PART

Materials

The following materials were used in the research:

— bentonite from Russian resources (provided by a representative of Bento Group Minerals Poland Sp. z o.o., Gdynia, labelled **B**);

— quaternary phosphonium salts (QPS) modifiers of bentonite: butyltriphenylphosphonium chloride (labelled **Q1**), DishmanGroup, India and tetraphenylphosphonium bromide (labelled **Q2**), Alfa Aesar GmbH, Germany;

— Epidian 6 epoxy resin, the product of Chemical Plant „Ciech-Organika-Sarzyna" in Nowa Sarzyna, labelled **EP**;

— triethylenetetramine, a technical product of Chemical Plant „Ciech-Organika-Sarzyna" in Nowa Sarzyna, labelled **Z-1**;

— aluminium trihydrate $Al(OH)_3$ with trade names: APYRAL 100 SM labelled **A1** and APYRAL 200 SM labelled **A2,** products of Nabaltec (Germany).

The present research made use of procedure for modifying smectic clays applying phosphonium salts previously patented [18, 19], and described in the literature [15—17].

Thus prepared MB in an amount of 3.0 wt % with ATH in an amount of 5 or 10 wt % was added respectively to a mixture of liquid synthetic resin (Table 1) and then homogenized in a multistage process. Firstly modified bentonite was added to epoxy resin and dispersed until a homogeneous suspension was achieved, then ATH was added and dispersed.

In both cases a three-stage homogenization was applied consisting in: pre-mixing by means of slow-speed mechanical stirrer at room temperature for 20 minutes and subsequently a multistage stirring by: ultrasonic homogenizer (for 15 minutes), high speed mixer with a turbine stirrer (at a rotational speed of the stirrer of 8 000 min^{-1} for 30 min) and a cylinder-cylinder type grinder (where a rotation speed of the movable cylinder equals 6 000 min^{-1} for 15 min). The ingredients of the formulated compositions are given in Table 1. Thus prepared compositions were stored at a temperature of approx. 4 °C to prevent possible sedimentation of fillers.

Compositions based on Epidian 6 resin were cured by Z-1 (13 wt %), according to instructions of the resins manufacturer. The compositions were subsequently vented in a laboratory vacuum chamber VAKUUM UHG 400 (by Schuechl, Germany) and was cast at 40 °C to silicone moulds prepared in accordance with ISO 527-1:1998. Compositions were hardened at room temperature for 24 h and then re-hardened at 100 °C for 6 hours. After two days mechanical properties and flame resistance of prepared specimens were tested according to relevant standards.

Methods of testing

— Tensile strength was studied according to ISO 527-1:1998 standard using INSTRON 5967 testing machine equipped with a video-extensometer. Elongation speed was 2 mm/min and measuring temperature was 23 °C.

— Rockwell hardness was tested with ZWICK 3106 hardness tester, in accordance with EN 10109-1 standard. Indenter load equalled 358 N. Arithmetic mean of at least 10 measurements was accepted as the final result.

— Charpy impact strength was specified in accordance with PN-EN ISO 179-1 standard with PSW4J type tester, made by Gerhard Zorn (Germany) using a hammer with impact energy of 1 J with digital display of results.

— The morphology of brittle fracture of composites was analyzed using a transmission electron microscope (TEM) type Tecnai G2 SpiritTwin 12 (at an accelerating voltage of 120 kV). Ultra-thin scraps were made at room

T a b l e 1. Ingredients of tested compositions made on the base of epoxy resin, mechanical properties and flame retardancy of tested hybrid composites and the initial epoxy resin

Symbol	Content of filler used in composition, wt %				Tensile strength MPa	Young's modulus GPa	Charpy impact strength kJ/m^2	Rockwell hardness MPa	*LOI*, %	Flammability class UL 94
	BQ1	BQ2	A1	A2						
EP	-	-	-	-	46.9±1.1	2.99±0.23	4.21±0.49	144.9±1.2	19.0±0.3	combustible
EPBQ1A1-5	3.0		5.0		52.3±0.8	3.16±0.11	5.92±0.36	145.1±1.2	25.1±0.2	V2
EPBQ1A1-10	3.0		10.0		56.3±1.4	2.83±0.19	6.33±0.18	163.2±1.1	31.3±0.2	V1
EPBQ2A1-5		3.0	5.0		50.1±1.2	3.00±0.17	5.05±0.23	148.3±1.0	24.8±0.2	V2
EPBQ2A1-10		3.0	10.0		53.7±1.3	3.01±0.11	7.11±0.15	178.8±1.2	29.2±0.1	V1
EPBQ1A2-5	3.0			5.0	50.1±2.1	3.04±0.14	5.42±0.21	146.0±0.6	24.8±0.3	V2
EPBQ1A2-10	3.0			10.0	57.4±1.6	3.12±0.17	7.38±0.24	147.5±1.1	28.2±0.2	V1
EPBQ2A2-5		3.0		5.0	48.9±1.6	2.86±0.11	4.73±0.18	148.7±1.6	24.2±0.1	V2
EPBQ2A2-10		3.0		10.0	57.7±1.1	3.05±0.12	6.98±0.14	154.1±2.1	27.9±0.2	V1

temperature using Tesla ultra-microtome with glass knives. They were collected on the surface of a 10-percent aqueous acetone and placed on standard microscope copper grids.

— Morphology and elemental analysis of composite scale samples was made with a scanning electron microscope (SEM), HITACHI S-3400N equipped with an adapter EDS for microanalysis of chemical composition. A secondary electrons detector (SE) and a backscattered electrons detector (BSE) was applied, the accelerating voltage was 15 kV and the spot size <10 nm.

— Determination of the limiting oxygen index (*LOI*) was done at 25 °C according to EN ISO 4589-3 standard, using apparatus made by FireTesting Technology Ltd., UK.

Flammability test by UL-94 method was determined in a flammability test chamber made by FireTesting Technology Ltd. UK. Measurements were made in accordance with PN-EN 60695-11-10 standard.

RESULTS AND DISCUSSION

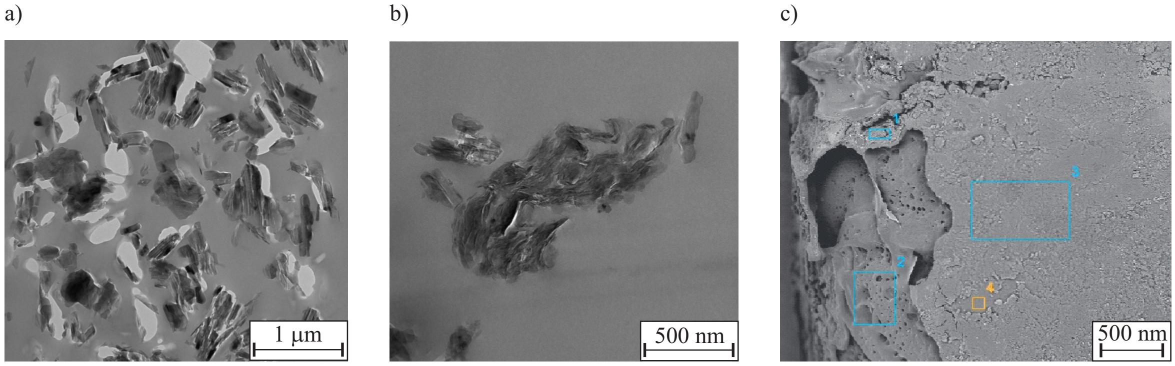
TEM micrographs of ultra-microtome scraps showed significant differences in morphology of EP composites containing tested fillers. In TEM micrographs one can see evenly distributed lamellar structure derived from AP, and among them galleries of sheets of MB (Fig. 1a). Unfortunately, in 10 % of the ATH composite formation of agglomerates can be seen (Fig. 1b).

Tagged mechanical properties of tested composites in relation to the unfilled EP are summarized in Table 1: tensile strength, Young's modulus, Charpy impact strength and Rockwell hardness.

As is evident from the data presented in Table 1, adding modified bentonite QPS1 and QPS2 to the resin along with ATH significantly influenced improvement in tensile strength (in the range of 4 to 23 %). Rockwell hardness of the samples (in the range of from 4 to 24 %), and impact strength without notch (in the range of from 5 to 68.9 %). Young's modulus of composites improved slightly (by a few percent). Thanks to applying different combinations of fillers, it was possible to improve all tested mechanical properties at the same time, which is not always possible when they were used individually.

The results of the *LOI* and flammability test with UL 94 method are collated in Table 1. *LOI* measurement showed that adding modified bentonite QPS and ATH to polymer matrix favourably influenced the value of that index, resulting in its increase. The biggest increase of oxygen index was observed in the hybrid composite EPBQ1A1-10 for which *LOI* was 31.3 % and flammability class UL 94 was V1. It should be noted that the oxygen index of unfilled EP resin was 19.0 %, and this improvement is due to synergistic activity of the modified bentonite (BQ1) and flame retardant with a different mechanism of action — ATH (A1).

Analysis of EP samples and hybrid composites (Table 1) after flame tests studied using SEM equiped with an instrument for elemental analysis EDS showed that in case of composites containing the MB and ATH, a porous char is formed in the charred part (Fig. 1c). One can also notice an increased silicon content in the charred part of the sample (Fig. 1d), which may indicate a possible formation of a glassy layer of silicon carbide. Such a glassy-porous structure reinforces the process of the composite flame retardancy, because hinders the access of oxygen



d)

Field number	Content of chemical elements, %					
	C	N	O	Si	Al	Cl
1	93.5	4.0	2.0	2.1	0.7	0.04
2	88.4	3.9	7.0	3.4	1.3	0.03
3	92.4	5.9	1.0	0.6	0.4	0.02
4	91.7	7.1	0.5	0.6	0.1	0.02

Fig. 1. TEM micrographs of ultra-microtome scraps of hybrid composites: a) EPBQ1A1-5, b) EPBQ1A1-10; c) SEM microphotography with marked fields, on which was made EDS elemental analysis of a charred sample of EPBQ1A1-10, d) results of EDS elemental analysis of different pieces of char of tested composite EPBQ1A1-10

necessary to sustain a flame and inhibits the outflow of exhaust gases slowing down the combustion process. A visible highly porous layer forms a thermal insulation of burning composite EPBQ1A1-10.

CONCLUSIONS

Adding a combination of modified fillers QPS bentonite and aluminium trihydrate to epoxy resin distinctly influenced on the improvement of mechanical properties. The greatest improvement in flame retardancy was achieved for a hybrid composite EPBQ1A1-10 which had *LOI* = 31.3 and flammability class V-1.

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REFERENCES

[1] "Fire Retardant Materials" (Eds. Horrocks A.R., Price D.), Woodhead Publishing Limited, Cambridge, England, 2001.

[2] Lomakin S.M., Zaikov G.E.: "Modern Polymer Flame Retardancy", VSP Publishers, Netherlands 2003.

[3] Levchik S.: "Flame Retardant Polymer Nanocomposites" (Eds. Morgan A.B., Wilkie C.A.), Wiley, Hoboken 1, 2007.

[4] Osman M.A., Rupp J.E.P.: *Polymer* **2005**, *46*, 8202. http://dx.doi.org/10.1016/j.polymer.2005.06.101

[5] Beyer G.G.: *Fire Materials* **2002**, *25*, 193. http://dx.doi.org/10.1002/fam.776

[6] Costantino U., Gallipoli A., Nocchetti M. *et al*.: *Polymer Degradation and Stability* **2005**, *90*, 586. http://dx.doi.org/10.1016/j.polymdegradstab.2005.05.019

[7] Hsueh H.B., Chen C.Y.: *Polymers* **2003**, *44*, 1151. http://dx.doi.org/10.1007/s10965-005-3982-8

[8] Zhubanov B.A., Nazarova S.A.: *Vysokomolekulyarnye Soedineniya* **1976**, *18*, 150.

[9] Chen-Yang Y.W., Yang H.C., Li G.J.: *Journal of Polymer Research* **2005**, *11*, 275. http://dx.doi.org/10.1007/s10965-005-3982-8

[10] Biswas M., Ray S.S.: *Advanced in Polymer Science* **2001**, *155*, 167. http://dx.doi.org/10.1007/3-540-44473-4_3

[11] Levchik S., Weil D.: *Polymer International* **2005**, *54*, 11. http://dx.doi.org/10.1002/pi.1663

[12] Xie A., Yan W., Zeng X. *et al*.: *Bulletin of the Korean Chemical Society* **2011**, *32*, 1936. http://dx.doi.org/10.5012/bkcs.2011.32.6.1936

[13] Wu T., Xie A., Tan S-Z., Cai X.: "Antimicrobial effects of quaternary phosphonium salt intercalated clay minerals on Escherichia coli and Staphylococci aureus", Elsevier 2011.

[14] Patel H., Somani R., Bajaj H., Jasra R.: "Preparation and characterization of phosphonium montmorillonite with enhanced thermal stability", Elsevier 2007.

[15] Oleksy M., Oliwa R., Heneczkowski M. *et al*.: *Polimery* **2012**, *57*, 228.

[16] Oleksy M.: *Polimery* **2012**, *57*, 212.

[17] Oleksy M., Galina H.: *Industrial and Engineering Chemistry Research* **2013**, *52*, 6713. http://dx.doi.org/10.1021/ie303433v

[18] *PL Pat.* 395 821 (2013).

[19] *PL Pat*. 407 020 (2014).

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