



Epoxy composites of reduced flammability



Rafal Oliwa^{*}, Maciej Heneczkowski, Mariusz Oleksy, Henryk Galina

Department of Industrial and Materials Chemistry, Rzeszow University of Technology, PL-35-959 Rzeszow, Poland

ARTICLE INFO

Article history:

Received 21 September 2015

Received in revised form

16 February 2016

Accepted 25 March 2016

Available online 5 April 2016

Keywords:

A. Flame resistance

A. Carbon fibre

A. Resins

A. Laminates

D. Thermal analysis

ABSTRACT

The effect of the so called environment friendly hybrid flammability reducing fillers, i.e. the halogen/antimony-free ones containing phosphorous, nitrogen and silicon on the utility properties of carbon reinforced epoxy laminates was studied. The total content of the fillers did not exceed 23 wt.%. The flame resistance of the laminates aimed as parts of aircraft construction was determined. The fire retardancy mechanism of the hybrid fillers was investigated by SEM/EDS examination of partially burned laminates. The best combination of flammability reducing fillers for the epoxy composite matrices consisted of 15 wt.% ammonium polyphosphate, 5 wt.% dipentaerythritol, and 3 wt.% organophilized bentonite. The synergy of silicon and phosphorus in this composition provided material of UL-94 flammability class V-0.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The excellent strength to density ratio of fiber reinforced polymer composites brought about wide application of these materials in many branches of technology, in the aviation industry, in particular. The contemporary planes built up from composites have their weight reduced by 25–45% and, hence, they reach longer distances having reduced fuel consumption. Epoxy laminates reinforced with carbon fibers constitute an important group among the composites used in the aviation industry [1]. The carbon fibers are preferred for their high specific tensile modulus and lower weight compared to glass fibers. The epoxy matrices, on the other hand, are advantageous because of their high chemical and thermal resistance and ease of processing. The main disadvantage of the epoxies limiting their application in building transportation means (aircrafts, boats, railway cars, buses, motorcars and other vehicles) is the flammability of this material, often failing to meet safety regulations [2]. Furthermore, the reinforcing fibers tend to exhibit a candlewick effect by bringing the fuel into the burning material by capillary forces thus accelerating the material thermal decomposition and burning process [3]. The improvement of fire resistance of the advanced composite laminates is therefore a crucial task. Halogen fire retardants, chlorine and bromine compounds along with antimony oxides were successfully used for many years to

reduce flammability of various polymer based materials. These compounds, however, are now replaced by new combinations of products because in the case of fire the halogen based flame retardants produced highly toxic fumes seriously endangering life or health of fire casualties [4].

The contemporary efforts aiming at making polymer materials less flammable focus on seeking for environment friendly and effective flame retardants containing preferably such elements as nitrogen, phosphorus, boron and silicon.

There are many phosphorous-containing flame retardants described in the literature, including those introduced into epoxy resin structure on the condensation stage through reactions of epichlorohydrin with phosphorous oxides [5], phosphates [6], or DOPO (i.e. 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) [7,8], by copolymerization of diglycidyl ether of bisphenol A, mostly with DOPO derivatives [9,10], or by using phosphorous containing amino curing agents [11–20].

Another group of phosphorous fire retardants constitute the fillers added to the composite matrix polymer precursor and thoroughly mixed with it before hardener is added. The most commonly used products of this group are ammonium polyphosphate (APP) [21–29] and melamine polyphosphates (MP) [22,23]. On fire, these compounds produce foamed coke of multi-cellular structure by interacting with the intumescent component of the system. Among these intumescent components there are acidic or acid forming compounds, e.g. ammonium polyphosphate, carbonizing agents, e.g. pentaerythritol, and gas releasing compounds, e.g. melamine.

^{*} Corresponding author.

E-mail address: oliwa@prz.edu.pl (R. Oliwa).

There are numerous papers dealing with hybrid flame retardants, the components of which would interact and better protect materials by joint action. The most of these reports concentrated on a synergetic effect obtained by modifying DOPO with silanes or siloxanes [30–33] or by introducing both DOPO and silicon-rich modifiers [34,35]. The latter solution, however, cause some problems in the modified material processing.

In our studies on the effect of organophilized layered aluminosilicates on the mechanical properties and flame resistance of epoxy based glass or carbon fiber reinforced composites [36], we attempted to reach a synergetic effect in reducing flammability of these composites by modifying of the epoxy resin with a bentonite treated with quaternary phosphonium salts and with commercial flame retardants containing phosphorous and nitrogen.

2. Experimental section

2.1. Materials

The epoxy resin and the curing agent used in this work were Epidian® 6 (EP6) containing mostly diglycidyl ether of bisphenol A and triethylenetetramine (Z1) respectively, both commercial grade products of Ciech-Sarzyna Plant, Poland. Halogen-free commercial flame retardants used are listed in Table 1. Unidirectional carbon fabric 200 g/m² (TC) was purchased from Havel Composites. All these materials were commercial grade and used without further purification or modification. The organoclay, bentonite “Specjal” (Zebiec SA Plants, Poland) was modified with a butyl-triphenylphosphonium chloride (BSQPS, Xiamen Pioneer Technology Inc., China).

2.2. Modification of bentonite with quaternary phosphonium salt

The modification procedure of smectic clays with quaternary ammonium or phosphonium salts has been previously patented [37,38] and described in detail in our previous papers [36,39]. It consists of introducing aqueous solution of quaternary salts to a suspension of a montmorillonite-rich bentonite in water, removal of supernatant liquid, drying, grinding and sieving modified

bentonite to obtain organophilized layered aluminosilicate (BSQPS) of grain sizes below 60 μm.

2.3. Preparation of epoxy compositions

In our previous research on the applications of organophilized aluminosilicates we have found these products to substantially reduce flammability of polymers when used as fillers and act as environment friendly flame retardants [39]. Epoxy resin compositions were prepared containing 3 wt.% of bentonite modified with quaternary phosphonium salt and commercial flame retardants so that total amount of filler did not exceed 23 wt.%. Preparation of the compositions started with introducing modified bentonite to the resin and homogenizing the mixture. Then, the remaining flame retardants were introduced and the composition homogenized. After introducing each component, the four-stage homogenization procedure was applied [37]. In the choice of type and amount of fillers, suggestions of producers were taken into account. The mechanisms of flame retardancy of each component were also considered in order to find possibly a synergetic effect. The compositions selected are listed in Table 1.

2.4. Preparation of carbon fiber/epoxy compositions laminates

The epoxy composition based on EP6, containing mixtures of flame retardants as shown in Table 1, were used to prepare four-layer laminates with unidirectional carbon fabric (200 g/m²) acting as reinforcement. The contact method was used. Successive sheets of fabric were laid on a Teflon film and impregnated with epoxy composition containing amine curing agent using a grooved roller. The top layer, after removing the excess of resin, was covered with another Teflon film before the sample was placed between two steel plates of dimensions 200 × 300 mm which acted as a mold. The plates were pressed to exert a pressure of about 10 MPa. The laminates were left to cure at room temperature overnight and then post-cured in an oven with hot air circulation at 100 °C for 6 h. The resulting laminates contained ca. 40% of carbon fabric by weight. The samples were cut from the laminates in the direction parallel to the direction of fibers with an oscillating cutting disk. The samples were used in flammability tests as well as to measure their thermal properties.

2.5. Characterization of carbon fibre/epoxy compositions laminates

The thermal decomposition of laminates was followed in a thermogravimeter TG 209 (Netzsch, Germany) in temperature range 0–800 °C with heating rate 10 deg/min.

The limiting oxygen index (LOI) for the samples was determined according the standard EN ISO 4589-3 at room temperature using an instrument of Fire Testing Technology Ltd. (United Kingdom).

The flammability tests by using UL-94 method were carried out in a chamber produced by FTT Ltd. (United Kingdom). The measurements were made according to standard PN-EN 60695-11-10 with vertical sample beam position and methane fed burner of 25 mm height.

The heat release rate (HRR in kW/m²) during sample combustion as well as other parameter characterizing flammability were evaluated for composite plates 100 × 100 × 2 mm in size using a cone microcalorimeter, a product of FTT Ltd. (United Kingdom), according to standard ISO 13927, by applying the heat flow 25 kW/m² and the distance from ignition source 25 mm.

To verify the assessments of flame resistance of laboratory samples made by specialized instruments, direct flammability tests were made for reinforcing plates of unmanned plane (DRON) stabilizer. The plates were formed in a vacuum mold from carbon

Table 1
Epoxy compositions with flame retardants.

Composition	Percentages of component of epoxy compositions [%]						
	BSQPS ^a	APP ^b	DPER ^c	MPYP ^d	TEP ^e	EG ^f	ATH ^g
K0	3	–	–	–	–	–	–
K1	3	10	10	–	–	–	–
K2	3	15	5	–	–	–	–
K3	3	–	10	10	–	–	–
K4	3	–	5	15	–	–	–
K5	3	10	5	5	–	–	–
K6	3	5	5	10	–	–	–
K7	3	7.5	5	7.5	–	–	–
K8	3	–	10	–	10	–	–
K9	3	–	5	–	15	–	–
K10	3	–	–	–	15	5	–
K11	3	15	–	–	5	–	–
K12	3	15	–	–	–	3	–
K13	3	–	–	–	–	–	20
K14	–	17	6	–	–	–	–
K15	–	–	6	17	–	–	–

^a Bentonite modified with buthyltriphenylphosphonium chloride [36].

^b Aluminum trihydroxide, APYRAL 200 SM, (Nabaltec, Germany).

^c Melamine polyphosphate, Ecoret MPP (Alwernia Poland).

^d Amonium polyphosphate, (Tecnosintesi S.p.A., Italy).

^e Dipentaerythritol, (Sigma–Aldrich).

^f Triethyl orthophosphate, (Sigma–Aldrich).

^g Expanded graphite EG096, (Sinograf, Poland).

Download English Version:

<https://daneshyari.com/en/article/7212645>

Download Persian Version:

<https://daneshyari.com/article/7212645>

[Daneshyari.com](https://daneshyari.com)