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D. Matykiewicz, B. Przybyszewski, R. Stanik, A. Czulak

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Modification of glass reinforced epoxy composites by ammonium polyphosphate (APP) and melamine polyphosphate (PNA) during the resin powder molding process.

D. Matykiewicz[1], B. Przybyszewski[2], R. Stanik[2], A. Czulak[2]

[1]Poznan University of Technology, Institute of Materials Technology, Polymer Processing Division, Piotrowo 3, 61-138 Poznań

[2]Technische Universität Dresden, Institut für Leichtbau und Kunststofftechnik, Holbeinstr. 3, 01307 Dresden, Germany

Corresponding author: danuta.matykiewicz@put.poznan.pl

Abstract

The aim of the studies was to manufacture glass reinforced epoxy composites using technology based on hot pressing with improve flame resistance with good mechanical properties. Ammonium polyphosphate (APP) and melamine polyphosphate (PNA) were used as flame retardants with ranging from 5 to 20 wt. %. The thermal and mechanical properties of the composites were determined in the course of TGA analysis, flammability UL-94 test, limiting oxygen index (LOI) technique, Fourier Transform Infrared Spectroscopy, ultrasonic test and static tensile test. The flame retardancy of modified composites was significantly improved with addition of ammonium polyphosphate and melamine polyphosphate. Moreover, in most cases addition of flame retardants increased strength of composites. This study confirmed that fast and highly efficient Resin Powder Molding manufacturing process allows to produce high quality composites.

Key words Structural composites^{A}, Powder processing^{E}, Glass fibres^{A}, Thermal properties^{B}, Mechanical properties^{B}

Introduction

Epoxy resins are popular thermosetting matrices in construction materials used in the automotive, aircraft and shipbuilding industry [1-4]. In view of their organic structure, they mostly are flammable. Therefore, epoxy resins' application in many fields requires their modification by flame retardants. Improving the flame retardancy of epoxy resins may be achieved introducing to polymer halogen and non-halogen flame retardants [5,6]. However, generation of many toxic substances during the burning process is the main disadvantage of halogen flame retardants. Thus, non-halogen flame retardants are reported to be more friendly for natural environment and human health [7,8]. Moreover, the intumescent flame retardants (IFRs), where inorganic acids or precursor of the acids are used as an acid source, are a promising group. Additionally, their structure is composed by a carbonizing and blowing agent [9]. The acid compound decomposes releasing mineral acid, the carbonizing agent provokes char formation by dehydrating the carbonific, and the blowing agent produces gaseous foams. These mechanisms protect the polymeric material against external heat and fire [10,11]. Commonly applied IFRs are ammonium polyphosphate (APP) [12-14] and expandable graphite (EG) [15-16]. The efficiency of different phosphorous flame retardants have been reported in a variety of polymers [17-20]. According to Lim et all., introducing APP into epoxy/glass fiber composites effectively prevents fire mishaps without significantly affecting their mechanical and thermal properties [21]. The polyphosphoric acid from APP may react with the OH groups in epoxy resin and produce crosslinked phosphate ester which under heat creates phosphorus-rich layer and transforms into intumescent char protecting the material [22,23]. Other group of compounds used as flame retardants are melamines and their derivatives, such as: melamine oxalate, melamine phosphate, melamine phthalate and melamine cyanurate [21,25]. In epoxy system, melamine phosphate can be used as a hardener and flame retardant, forming protective layer which prevents epoxy matrix decomposition during combustion [21]. Melamine polyphosphate remains in the residue during thermal degradation and forms polyphosphate esters with the polymer, which result in an increased char formation [26].

Epoxy resin is often used as the matrix for fibre-reinforced composites with high stiffness, strength, dimensional stability, corrosion resistance, selective electrical properties and lightness [27,28]. These composites may be prepared using different methods, such as:, Pultrusion, Vacuum Assisted Resin Infusion and Resin Transfer Molding [29]. The recent possibility of epoxy resin application in new Resin Powder Molding process significantly reduces the final production time [30,31].

The aim of the studies was to manufacture glass reinforced epoxy composites using technology based on hot pressing with improve flame resistance with good mechanical properties. Ammonium polyphosphate (APP) and melamine polyphosphate (PNA) were used as flame retardants.

Experimental

Materials

The following components were used in this study: epoxy powder resin A.S.SET POWDER 01 (New Era Materials), flame retardants: ammonium polyphosphate (APP), melamine polyphosphate (PNA) both produced by Nordmann Rassmann (Nord-MIN JLS APP and Nord-MIN JLS PNA). Glass woven roving fabrics (Köper 2/2; 390 g/m^2, Panda^{TM}, R&G Faserverbundwerkstoffe GmbH) were used as a reinforcement.

Composites manufacture

In order to achieve high dispersion of flame retardants in the polymeric matrix, APP and PNA were mixed with A.S.SET powder using a high speed rotary mixer Retsch GM200 (2 min, 2000 rpm) [32]. The epoxy resin compositions with the 5, 10 or

20 wt% of flame retardants, respectively to their total weight, were produced. The composites were fabricated in a mould with glass woven roving fabrics (Kőper 2/2; 390 g/m^2), six sheets of 280mm x 280mm were cut from woven fabrics and covered by A.S.SET powder, layer by layer. Each sheet of the fiber was covered by the same amount of epoxy powder. The fiber content in composites was approximately 50 wt% .

The Resin Powder Molding parameters were chosen on the basis of our previous works [30,31] (T= 120°C, t= 8 min, F= 20kN). Composite samples have been manufactured using hydraulic press Rucks KV284. The reference sample was prepared from neat A.S.SET powder. The samples names are presented in Table 1.

Table 1. The samples names

Name	APP wt %	PNA wt %
ASET	0	0
5APP	5	0
10APP	10	0
20APP	20	0
5PNA	0	5
10PNA	0	10
20PNA	0	20

Measurements

Ultrasonic test

The quality of epoxy/glass composites were determined by ultrasonic analysis. The study was conducted using a generator with a frequency 250kHz and a receiver located at a distance of 100mm from the generator. The size of tested area was 300x 300mm with resolutions of 500 µm. The signal gain was 70dB while the measured level of attenuation -30 to 0dB.

Thermogravimetry (TGA)

The thermal properties of modified epoxy/glass composites were determined by thermogravimetric analyses (TGA) with temperature range between 30°C and 900°C at a heating rate of 10°C/min under nitrogen and air atmospheres using a Netzsch TG 209 F1 apparatus. Approximately 5 mg samples were placed in ceramic pans. The initial decomposition temperature $T_{5\%}$ was determined as a temperature at which the weight loss was 5%. The residual mass (W%) was defined at 900°C.

UL-94 Horizontal Burning Test

Tests were carried out with the horizontal burning method (HB) using barrel-shaped samples with dimensions of 125x10x2 mm as per PN-EN 60695-11-10 standard. Burning time was measured and the dripping of burning material was monitored. According to the above observations, the samples' burning rate V was calculated and on this basis the materials were classified (using UL 94 HB classifications).

Limiting oxygen index

LOI was measured on a limiting oxygen index chamber (Dynisco, Germany) according to ASTM D2863-77. The specimens used for the test were of dimensions 125x10x2 mm.

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR analysis were conducted by means of a Fourier transform spectrometer Bruker Vertex 70, at an ambient temperature (23°C). To analyze the composites' surfaces, the Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) was applied, total of 64 scans at a resolution of 1 cm^{-1} was used to record the spectra.

Static tensile test

The planar composite specimens have been cut from plates characterized by the highest manufacturing quality. For static tensile testing specimens with dimension of 250 mm x 25 mm x 2 mm, according to DIN EN ISO 527 norm have been prepared. The static tensile test was carried out on a universal machine “Zwick/Roell 1475” at ILK, TU Dresden. The pre-load of the test specimen was 25 N and the traverse speed was 2 mm/min. Each tensile test has been performed at room temperature (23 °C).

Results

Ultrasonic test

In order to assess the quality of manufactured composite plates ultrasound tests were conducted. The results allowed the pre-estimate the distribution of flame retardant additives and the presence of possible agglomerates. Moreover, this study allows to identify non-infiltrated areas as well as voids, defects and air bubbles in the composite structure. The figure 1 shows ultrasonograms of investigated materials. The sonograms confirm the high quality of manufactured composite plates. No pores, dry contacts and non-infiltrated area in the structure of investigated composites was observed.

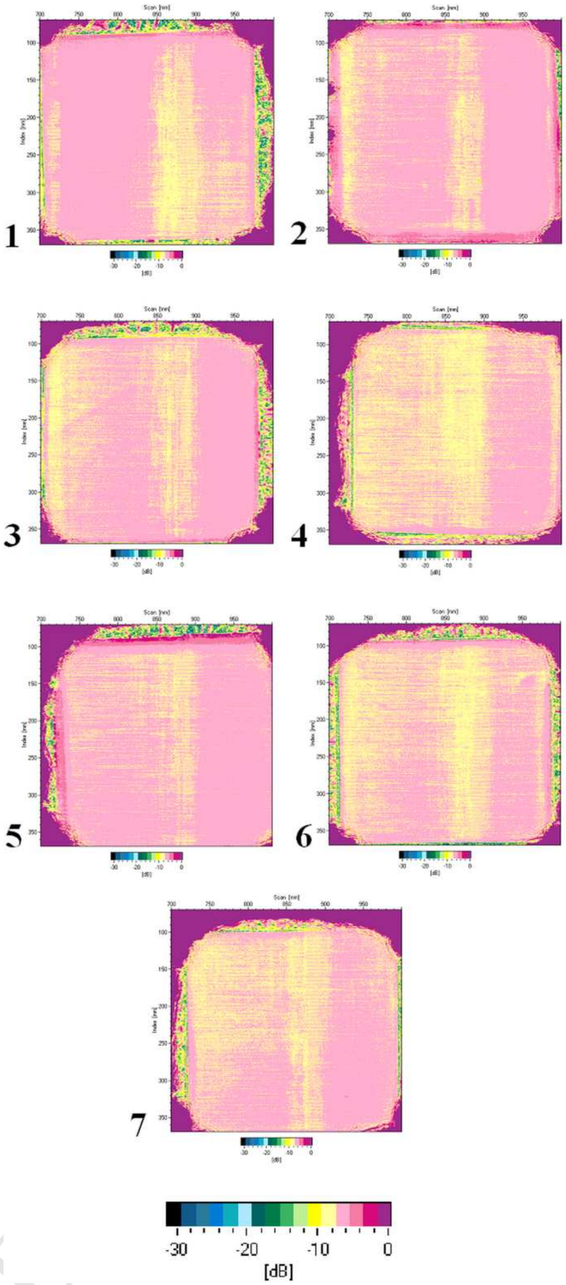

Fig. 1. Sonograms of investigated composites manufactured in RPM process: 1- ASET, 2- 5APP, 3-10APP, 4- 20APP, 5-5PNA, 6-10PNA, 7- 20PNA.

Furthermore, there was no displacement of the reinforcement layers to each other. These observations confirm the correctness of samples preparation process. By analyzing sonograms of specimens with flame retardants, there was no visible agglomerate of additives, what confirms the uniform distribution of the fillers in the polymer matrix. On the basis of ultrasound test results, areas with best quality were selected for samples for structural and strength tests.

Thermogravimetry (TGA)

The thermogravimetric analysis results of composites registered in nitrogen and air atmospheres, as plots of weight loss versus temperature and their derivatives, are presented in Figures 2. Detailed information on the degradation process, such as: 5% weight loss temperatures ($T_{5\%}$), maximum intensity of thermal degradation temperatures (T_{DTG}), and residual mass, are collected in Table 2 and 3. For composites with flame retardants, a two-step decomposition process was observed under nitrogen atmosphere, in contrast to the reference sample, where single-step process occurred. Moreover, for modified composites the value of $T_{5\%}$ and T_{DTG} decomposition rates were lower than in case of the reference sample. This fact arises from different mechanisms of APP and PNA degradation which enable the production of char to protect polymer matrix [9,24]. This phenomenon was confirmed by high amount of residual mass of the composites, ranging from 69 to 72 wt. %. In oxidizing atmosphere, the trend described above was also observed. Although, a tri-step decomposition process was noticed for all samples. The 20APP sample indicated the highest amount of residual mass in air atmospheres. According to literature, APP first decomposes to polyphosphoric acid, water and ammonia. Next, the polyphosphoric acid could react with the hydroxyl of cured epoxy resin to produce crosslinked phosphate ester [8].

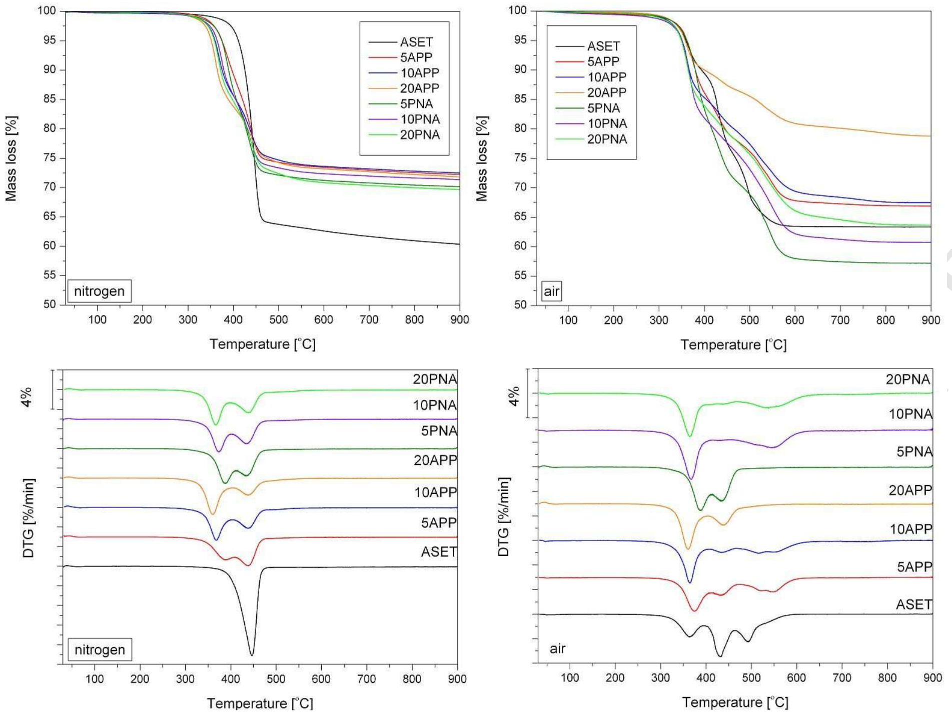

Fig. 2. TGA and DTGA curves investigated composites under nitrogen and air atmosphere.

Table 2. TGA and DTGA data of ASET composites investigated under nitrogen atmospheres.

	Sample	**5% Mass loss [°C]**	**Residual mass [%]**	**DTG**
NITROGEN	ASET	410.9	60.36	446.3°C; -9.11 %/min
	5APP	374.6	72.23	438.8°C; -3.00 %/min
	10APP	359.5	72.48	368.1°C; -3.34%/min
	20APP	351.3	71.83.	360.5°C; -3.95 %/min
	5PNA	374.8	70.15	387.4°C; -3.74 %/min
	10PNA	364.1	71.38	373.4°C; - 3.54 %/min
	20PNA	358.1	69.65	367.9°C; -3.85 %/min

Table 3. TGA and DTGA data of ASET composites investigated under air atmospheres.

	Sample	**5% Mass loss [°C]**	**Residual mass [%]**	**DTG**
AIR	ASET	359.3	63.35	429.7°C; -3.74 %/min
	5APP	361.5	66.89	373.6°C; -2.84 %/min
	10APP	350.9	67.48	362.9°C; -3.47 %/min
	20APP	357.6	78.78	368.2°C; -4.23 %/min
	5PNA	361.7	57.21	384.3°C; -3.66 %/min
	10PNA	350.5	60.73	362.9°C; -3.47 %/min
	20PNA	349.4	63.68	362.8°C; -3.71 %/min

UL-94 Horizontal Burning Test

The results of the UL-94 burning test are shown in Table 3. The addition of flame retardants decreased the burning rate (V) of composites, in comparison to the V of the neat sample. Sample with 20 wt.% PNA extinguished as quick as the burning process started. The presence of the ammonium polyphosphate and melamine polyphosphate as IFR in epoxy matrix led to a production of char layer to protect polymer and reduce burning. During burning at the samples' surface, significant amount of ash layer was observed. These results are presented in Figures 4. During heating, polymers containing intumescence compounds swell to form a porous carbonaceous foam which shield to prevent heat, air and pyrolysis products from entering the surface of the material [33].

Table 4. The flammability of epoxy composites with APP and PNA

	ASET	**5APP**	**10APP**	**20APP**	**5PNA**	**10PNA**	**20PNA**
V [mm/min]	16.0	9.8	7.5	5.5	7.5	7.0	self
Classification	HB40	HB40	HB40	HB40	HB40	HB40	HB40
Dripping drops	yes	yes	no	no	no	no	no
LOI	25.9	29.1	29.7	30,1	32.5	31.3	31.5

Limiting oxygen index

The differences between UL94 and LOI test results stem from in the two test geometries. LOI values for ASET composites without flame retardants was 25.9, introducing APP into epoxy matrix led to an increase of this value to 30.0. The fact that the LOI values for these composites were from 31.3 to 32.5 confirms a higher efficiency of PNA compound (Table 4).

Visual observation

In Figure 2.1., no significant char amount was observed for the reference sample.

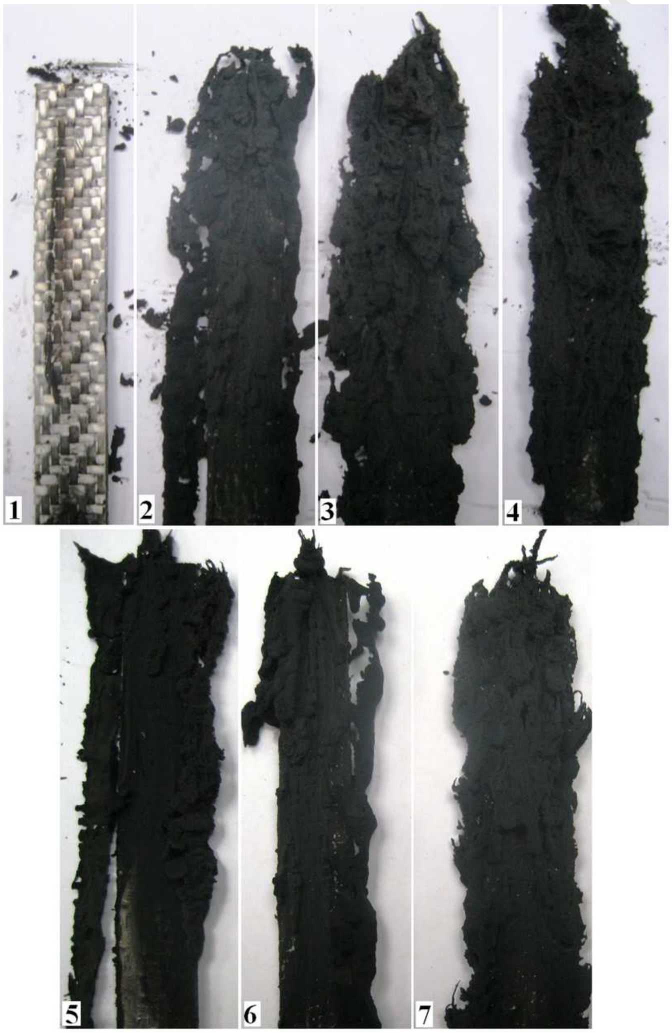

Fig. 3. Photographs of investigated composites after burrning process: 1- ASET, 2-5APP, 3-10APP, 4- 20APP, 5-5PNA, 6-10PNA, 7- 20PNA.

In case of APP samples, a considerable swell char layer was visible. However, on these surfaces, some holes, which may provoke defects of protective char layer, were observed [14]. For the PNA samples, char layer was more continuous and lamellar. Based on these pictures, it can be stated that the types of phosphorus-containing flame retardants strongly influence the structure of epoxy composites' char layer. Therefore, proper choice of these compounds is very important in view of their flame retardant performance.

FTIR analysis

The FTIR analysis was applied to assess the influence of the flame retardants on the chemical structure of char layer [34]. The FTIR spectra of the investigated composites' char after UL-94 test are presented in Figure 4. For all unburned composites (Fig. 5), a characteristic peak of epoxy resin was noticed: 800-850 cm^{-1} correspond to aromatic ring, 1000-1100 cm^{-1} are attributed to –C-O-C- stretching band, 1150-1300 cm^{-1} confirmed -C-C-O-C- stretching band, 1500-1600 cm^{-1} Ar -C=C-H stretching band and 2800-3000 cm^{-1} CH_2- , -CH_3- symmetric stretching band.

After the burning process, these characteristic peaks disappeared and on the spectra of burned samples a few peaks were observed. For the burned reference sample, the only broad peak at 1588 cm^{-1}, which confirmed the formation of polyaromatic carbons, was noticed [14]. For APP and PNA samples, a characteristic peak at 880 cm^{-1} and 1080 cm^{-1}, corresponding to symmetric and asymmetric stretching vibration of P-O-P, was noted. Moreover, between 1150-1300 cm^{-1} stretching vibration, attributed to the P-O-C band, was observed [24,35]. The intensity of these peaks, for samples with PNA, was significantly higher than for the samples with APP. This fact confirmed the above results, based on UL94, LOI and visible observation, where samples with PNA had higher value of char layer. It can be stated that PNA has better flame retardant properties for the investigated composites than APP.

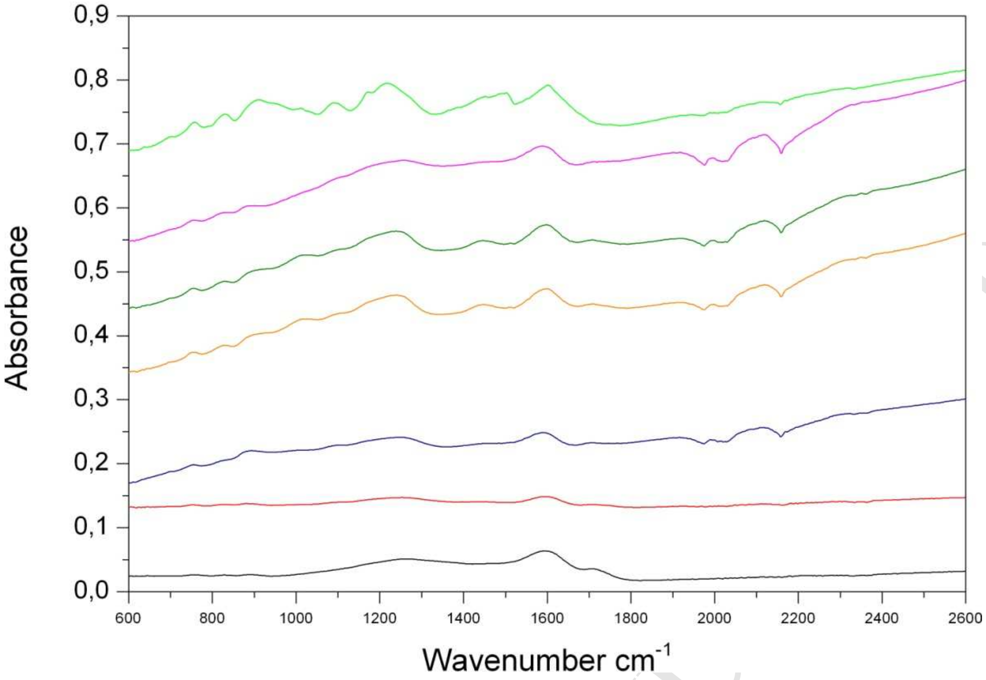

Fig. 4. FTIR spectra for burned composites a range from 600 to 3600 cm^{-1}, 1- ASET, 2-5APP, 3-10APP, 4-5PNA, 5-10PNA, 6- 20PNA

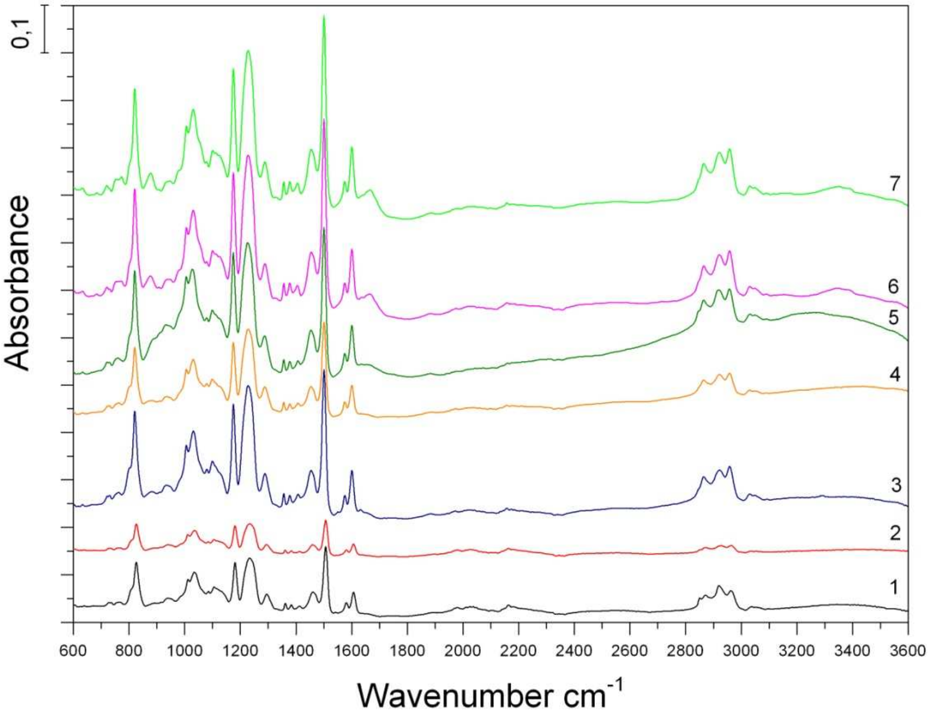

Fig. 5. FTIR spectra for unburned composites a range from 600 to 3600 cm^{-1}, 1- ASET, 2- 5APP, 3-10APP, 4-5PNA, 5-10PNA, 6- 20PNA.

Static Tensile Test:

To determine the effect of selected flame retardants on the strength properties of investigated GFRP the quasi-static tensile tests were carried out. The figure 6 shows selected samples after the test. Specimens were fractured at the center what confirms the correctness of performed investigation. The table 5 shows the averaged results of static tensile tests of investigated composites: tensile strength (σ), strain (ε) and the Young's modulus (E).

Fig. 6. Selected composite specimens after tensile test: 1-ASET, 2-5APP, 3-5PNA.

On the basis of the results obtained in the static tensile test can be stated that the addition of flame retardants does not affect significantly strength properties of investigated materials. In relation to the tensile strength it can be seen that in most cases addition of flame retardants increased strength of composites. Only in the case of adding 20% of melamine polyphosphate, 3% loss of strength in comparison to a reference sample has been observed. In the case of the sample containing 5% of this additive, 11% increase in strength was noticed. After analysis of the results of deformation it can be stated that the addition of flame retardants does not significantly affect the stiffness and deformation of tested materials. Such results are very promising in the context of future applications of the investigated materials. In most cases, the addition of flame retardants adversely affect the mechanical properties [36]. Here, no negative effects of selected flame retardants on the strength properties of GFRPs were observed.

Table 5. Results of static tensile tests

Sample	**σ [MPa]**	**ε [%]**	**E [GPa]**
ASET	351 ± 14	4 ± 0,2	12 ± 0,6
5APP	365 ± 28	4,4 ± 0,4	12 ± 1,2
10APP	352 ± 12	4,5 ± 0,2	10,9 ± 0,5
20APP	358 ± 13	4,6 ± 0,2	11,6 ± 0,9
5PNA	388 ± 13	4,6 ± 0,1	11,9 ± 1,4
10PNA	365 ± 12	4,6 ± 0,2	11,6 ± 0,5
20PNA	343 ± 5	4,7 ± 0,1	11,2 ± 0,7

Conclusion

The flame retardancy of modified composites was significantly improved with addition of ammonium polyphosphate and melamine polyphosphate, from 26 LOI to 32 LOI. Better flame retardancy properties were obtained for PNA composites and their surface during combustion was covered by thick protective char layer. Selected type of additives can replace the previously used halogen flame retardants, because they contain no toxic substances, and do not pollute the environment. The study confirms the possibility of distribution of 20 %wt. of additives in GFRPs without negatively affecting their structure and thus properties. There was no decrease in the quality of the samples with additives. In many cases, additives increased the tensile strength of the composites. The results obtained in this article are very promising and can be useful to improve fire resistant of fibre reinforced composites without affecting their strength properties. Thanks to modifications shown in this article, composites based on epoxy resins will be able to be applied in industries where previously it was not possible due to the high flammability, such as: civil engineering, railway industry or automotive. Modified material of the composites matrix in combination with a fast and highly efficient Resin Powder Molding manufacturing process may in future influence the market of composite materials.

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Figure Captions

Fig. 1. Sonograms of investigated composites manufactured in RPM process: 1- ASET, 2- 5APP, 3-10APP, 4- 20APP, 5-5PNA, 6-10PNA, 7- 20PNA.

Fig. 2. TGA and DTGA curves investigated composites under nitrogen and air atmosphere.

Fig. 3. Photographs of investigated composites after burrning process: 1- ASET, 2-5APP, 3-10APP, 4- 20APP, 5-5PNA, 6-10PNA, 7- 20PNA.

Fig. 4. FTIR spectra for burned composites a range from 600 to 3600 cm^{-1}, 1- ASET, 2-5APP, 3-10APP, 4-5PNA, 5-10PNA, 6- 20PNA.

Fig. 5. FTIR spectra for unburned composites a range from 600 to 3600 cm^{-1}, 1- ASET, 2- 5APP, 3-10APP, 4-5PNA, 5-10PNA, 6- 20PNA.

Fig. 6. Selected composite specimens after tensile test: 1-ASET, 2-5APP, 3-5PNA.

Table Captions

Table 1. The samples names.

Table 2. TGA and DTGA data of ASET composites investigated under nitrogen and air atmospheres.

Table 3. TGA and DTGA data of ASET composites investigated under air atmospheres.

Table 4. The flammability of epoxy composites with APP and PNA.