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ASSESSMENT OF MECHANICAL AND THERMOMECHANICAL PROPERTIES OF EPOXY-BASALT COMPOSITES MODIFIED WITH HALOGEN-FREE INTUMESCENT FLAME RETARDANTS

This study aims to examine the effect of flame retardants (FRs) on the mechanical and thermomechanical properties of epoxy composites reinforced with basalt fibers. To effectively modify fire behavior, it is usually necessary to introduce significant amounts of FRs, which raises many concerns due to the potential deterioration of other functional properties, including mechanical performance. In this work, 30 wt.% halogen-free FRs, including a two-component FR (ammonium polyphosphate with pentaerythritol) and melamine cyanurate, were introduced into the polymer matrix. The unmodified and intumescent FR-modified epoxy resin composites reinforced with basalt fibers were subjected to static flexural test and thermomechanical properties assessment. The research results were correlated with the analysis of changes in the chemical composition assessed using Fourier transform infrared spectroscopy. As a result, the saturation of the reinforcing fabrics by the modified epoxy resin was limited, which caused a different failure mechanism under static bending and impact test conditions. Both FR systems reduced the flammability of the modified epoxy laminates along with also acceptable deterioration of the mechanical properties. The most beneficial effects considering the combination of all the analyzed features were noted for the two-component FR system containing ammonium polyphosphate and pentaerythritol.

Keywords: epoxy, basalt, composite, laminate, intumescent flame retardants, mechanical properties

INTRODUCTION

Epoxy resins are successfully combined with various reinforcing materials such as glass, carbon, aramid, basalt fibers (BF), and fabrics [1, 2]. After hardening, they obtain favorable mechanical and thermal properties. Therefore, they are used as the matrix in layered composites in construction or automotive applications [3, 4]. The widespread use of such composites, especially those reinforced with continuous fibers, has changed the paradigm in the design of lightweight structures. The possibility of obtaining composites with low specific strength in technologies that do not require significant financial outlays related to equipment compared to metal materials results in the continuous development of composite technologies as well as new technological and material solutions [5, 6]. However, attempts to add new functional features to materials, such as increased fire resistance or improved thermal and electrical conductivity [7, 8], often require the introduction of additives and fillers. Also, owing to the safety requirements of epoxy materials, various types of

modifiers are introduced into them, such as flame retardants (FRs), UV stabilizers, nanofillers, and pigments [9-11]. The effectiveness of the additives depends on their structure, properties, and solubility, the method of introducing them into the resin, and the conditions of curing the finished product [12]. As a result, hybrid systems are created, the final mechanical performance of which may deteriorate compared to unmodified composites containing only fibers [8]. These changes may of course be beneficial, but the complexity and anisotropy, which are the main features of composite materials, create problems in predicting the final properties of materials without experimental validation. This is due to the possibility of changing the rheological properties of the matrix, affecting the limited miscibility of the system, the phenomenon of phase separation or problems with supersaturation, and the appearance of structure discontinuities in the form of pores [13], uncontrolled changes in the cross-linking density of thermosets [14] or the crystallinity in the case of ther-

moplastic polymers [15]. The introduction of intumescent flame retardants (IFR) into layered composites enables improvement of their fire resistance but may significantly affect their functional properties, in particular, mechanical performance [16]. It should be underlined that in most research, a description of the mechanical properties of composites affected by adding FRs is only a supplement to the flammability assessment of their properties and fire behavior.

In recent years, BF_s have become increasingly popular. The possibility of utilizing high-temperature-stable BF_s, created a sustainable solution competitive with glass fibers (GF) gaining ground in scientific and industrial fields [17, 18]. While for composites containing the much more commonly used GFs or carbon fibers (CF), the aspect of hybridization or the introduction of an additional increased amount of FRs [19, 20], in particular from the intumescent group, was described, detailed analysis of the impact of FRs on composites reinforced with continuous basalt fiber still needs to be supplemented. Despite the similar chemical composition of GF and BF, our previous work [21] showed differences in the fire behavior of epoxy composites. Similarly, the mechanical performance of those two inorganic fiber-reinforced composites significantly differ. In various studies, the use of simultaneous BF_s and IFRs was reported in the case of the production of coatings [22, 23], as in the case of using short fibers dosed in an amount of 2 wt.% to bisphenol A epoxy resin containing ammonium polyphosphate (APP) and expanded graphite (EG).

Another publication [23] again referred to using BF_s and IFR to produce steel fire protection coatings. An interesting approach was proposed by Attia et al. [24], who used a polyaniline (PANI) coating for BF_s as the reinforcement of rubber composites. The effect of FRs was not associated with an additional modifier that hybridized the composite in any way; nevertheless, favorable mechanical properties of the PANI-coated BF-reinforced rubber composites were recorded for composites subjected to gamma radiation. All of these studies emphasize the beneficial effect of the BF addition on the reduction in flammability of their epoxy-based composites. Nonetheless, the influence of functional additives, including FRs, on the mechanical properties is still insufficiently described.

This work involves a structurally correlated analysis of the mechanical properties of epoxy composites reinforced with continuous basalt nonwoven fabrics modified with halogen-free IFRs. Laminates containing a constant amount of FRs after determining the changes in the chemical composition using Fourier transform infrared spectroscopy (FTIR) were subjected to flexural tests, interlaminar shear strength (ILSS), and impact strength measurements. These analyses were supplemented with an assessment of the thermomechanical properties by means of dynamic thermomechanical analysis (DMTA), and the flammability was determined by the cone calorimetry test.

MATERIALS AND METHODS

Materials and sample preparation

An epoxy resin based on bisphenol A diglycidyl ether (DGEBA) Epidian 652 (CIECH Sarzyna, Poland) was used as the matrix of the composites. The liquid resin has a viscosity of 500–900 mPa·s at 25°C, a density of 1.1 g/cm³, and epoxy number 0.48–0.51 mol/100 g, according to the producer's data. The composition was cured with an isophorone diamine (IDA)-based hardener (CIECH Sarzyna, Poland), with a viscosity of 150–300 mPa·s, a density of 1.03 g/cm³, and amine number 200–350 mg KOH/g. Basalt fiber woven fabric (BF), plain weave, BAS 220.1270.P, weighing 210 g/m² (BASALTEX) was used to reinforce the laminates. Three types of commercial FRs were applied: APP Addforce FR APP 201, pentaerythritol (PER) Addforce FR Penta M40, and melamine cyanurate (MC) Addforce FR MC 8 from WTH (Germany). Commercially available FRs were selected for the analysis to enhance the potential impact of the obtained results and provide a basis for future research on their novel counterparts developed by the research team members.

The compositions of the epoxy monomer with two sets of IFR were prepared by mechanical mixing utilizing a ProLAB Disperlux stirrer equipped with a disc agitator at 3000 rpm for 10 min under subatmospheric pressure (0.2 bar). After degassing, the IDA curing agent was introduced, and the composition was stirred again at 1000 rpm for 3 minutes. The constant resin-to-curing agent ratio (100:50 by weight) was applied, while the amount of the IFRs was dosed in relation to the mass of the epoxy monomer in the concentration of 30 wt.%. Before manufacturing, the fabrics and IFRs were dried by means of a Chemland vacuum cabinet dryer for 48 h at 50°C. The twelve-layer laminates were prepared with 330 x 330 mm² sheets of fabric by the hand lay-up method, followed by vacuum bagging to minimize the void content and improve the saturation of the fibers by the epoxy matrix. After the forming process, without applying clamping pressure after the fiber saturation process, the samples were cured at ambient temperature for 168 h and post-cured for the next 24 h at 70°C using a Memmert ULE 500 cabinet dryer. The specimens for the mechanical tests were prepared by waterjet cutting.

The series of laminates reinforced with BF_s are related to the composition used as the matrix and designated as follows: EP – unmodified epoxy; FR – two-component composition containing APP and PER in a mass proportion of 3:1; MC – melamine cyanurate.

Characterization techniques

The viscosities of the epoxy compositions filled with IFRs were determined using an Anton Paar MCR 301 rotational rheometer operated with a 25-mm parallel plate measuring system with a gap of 0.5 mm. All the specimens were pre-sheared before testing for 180 s at

a shear rate of 1 s^{-1} and with a subsequent relaxation time of 120 s. The measurements were carried out in the constant shear mode implementing 10 and 100 s^{-1} shear rates at 30°C . The presented dynamic viscosity results are the mean values from the 300 s experiment.

FTIR spectroscopy was conducted with a Jasco FT/IR-4600 spectrometer at room temperature (23°C) in the attenuated total reflectance (ATR) mode. 64 scans at the resolution of 4 cm^{-1} were conducted.

The mechanical behavior of the composites was analyzed by means of static flexural tests performed following the ISO 178 standard with a Zwick/Roell Z020 testing machine at room temperature. The flexural strength measurements were realized with a 2 mm/min cross-head speed. The number of tested specimens was 10 for each series.

A Tescan MIRA3 (Brno, Czech Republic) scanning electron microscope (SEM) was employed to carry out fractographic analysis of the epoxy composites. The investigated samples were examined with an accelerating voltage of 12 kV and a working distance of 16 mm. A thin carbon coating of approximately 20 nm thickness was deposited on the specimens using a Jeol JEE 4B vacuum evaporator.

The impact strength of unnotched specimens was measured by the Charpy method (ISO 179) at 25°C . A Zwick/Roell HIT 25P impact tester with a 15-J hammer was utilized for the measurement. The number of tested specimens was 7 for each series.

Short beam shear tests were conducted to compare the ILSS of the prepared composites according to the ISO 14130 standard. The tests were performed on a universal testing machine, Zwick/Roell Z010. To meet the requirements of the standard, where the thickness/span length proportion should be 1:4, the three-point bending fixture was set to a 25-mm span distance. The cross-head speed was set to 1 mm/min.

DMTA analysis was conducted in the torsion mode using an Anton Paar MCR 301 rheometer with an SRF measuring system. The investigations were carried out at a constant frequency of 1 Hz and a strain of 0.01%. The measurements were performed in a 25 to 200°C temperature range with a $2^\circ\text{C}/\text{min}$ temperature ramp for 3 specimens from each series.

The burning behavior was assessed by cone calorimeter tests conducted on a Fire Testing Technology apparatus following the ISO 5660-1 and ISO 5660-2 procedures [25]. The horizontally oriented cuboid specimens, with the dimensions $100 \times 100 \times 4 \text{ mm}$, were irradiated at a heat flux of $50 \text{ kW}/\text{m}^2$. Spark ignition was used to ignite the pyrolysis products. An optical system with a silicon photodiode and a helium-neon laser provided a continuous survey of the smoke. The number of tested specimens was 4.

RESULTS AND DISCUSSION

The rheological properties of the epoxy compositions before incorporating the hardener were measured

by rotational rheometry. The average viscosity values obtained at constant shear rates (10 and 100 s^{-1}) for 300 s are presented in Figure 1. It can be observed that the compositions modified with IFRs have the characteristics of typical shear-thinning liquids. As the shear rate increased, their viscosity decreased significantly. The addition of the FR systems resulted in a significant increase in the relative viscosity of the unmodified epoxy resin, although in the case of the MC-modified series, this value was twice as high as for FR (10 s^{-1}) and higher by 42% in the case of the measurements made at 100 s^{-1} . It can be concluded that both of the used compositions will be characterized by a reduced ability to saturate the reinforcing fibers in comparison to the pure epoxy. More unfavorable rheological properties were recorded for the MC-modified epoxy.

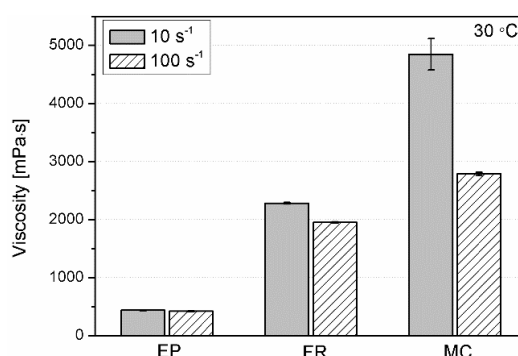


Fig. 1. Viscosity of compositions used as matrix for manufacturing composites

The changes in the chemical compositions of the cured laminates were investigated by means of FTIR spectra (Fig. 2). The spectrum of the epoxy resin before curing shows peaks from which the most important are that of the epoxide group at 915 cm^{-1} and that of the *p*-substituted aromatic ring at 833 cm^{-1} [26]. As a hardener, an IDA was applied, with high reactivity resulting from the high nucleophilicity of the nitrogen atom of the amino group, although its chemical structure conditioned it. Thus, one expects well-defined absorptions in the mid-infrared ranges, i.e. stretching and deformation of the N-H bonds, i.e. between 3500 and 3300 cm^{-1} , one single band reflecting symmetric stretching modes, and between 1650 – 1500 cm^{-1} N-H deformation bands [27].

In the FTIR spectra of the unmodified EP series, a broad peak at 3365 cm^{-1} can be observed, which can be assigned to N-H stretching. Moreover, absorption bands originating from symmetrical and asymmetrical C-H stretching at 2923 cm^{-1} and 2855 cm^{-1} , occur. In addition, at the EP spectrum, absorption bands arising from N-H bending (1605 cm^{-1}), a deformation vibration mode of CH_3 (1505 cm^{-1}), C-H in-plane bending (1241 and 1035 cm^{-1}), and C-H out-of-plane bending (825 cm^{-1}), occur. The incorporation of the two-component FR composition containing APP and PER in the mass proportion of 3:1 caused a slight shift of the absorption peak assigned to N-H stretching to

3315 cm^{-1} , while the absorption bands originating from symmetrical and asymmetrical C-H stretching (in the range of $3000\text{--}2700\text{ cm}^{-1}$) diminish. Nonetheless, for this system, the characteristic absorption band of the P-O-C-group at 1016 cm^{-1} [28] and 3326 cm^{-1} that can be attributed to absorptions of the C-OH group of PER, could be observed (Fig. 2b).

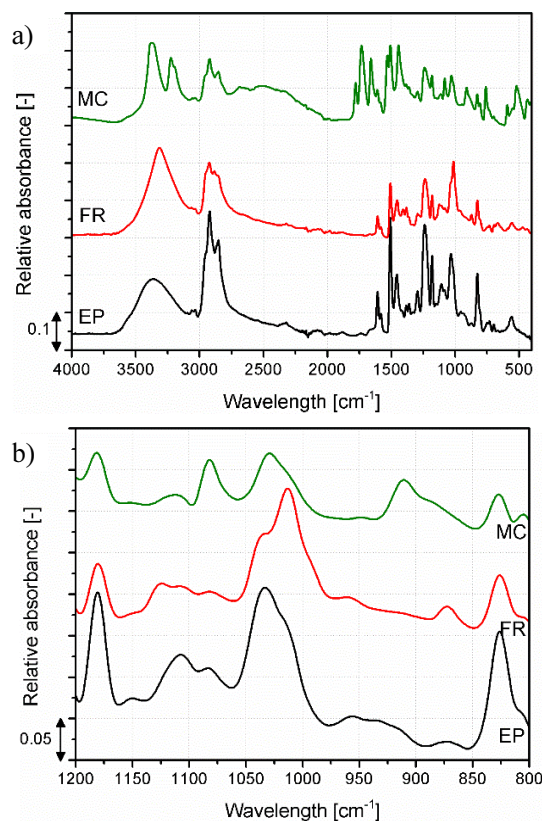


Fig. 2. FTIR spectra of cured epoxy laminates in wavelength range of $4000\text{--}400\text{ cm}^{-1}$ (a) and $1200\text{--}800\text{ cm}^{-1}$ (b)

The most significant differences in the FTIR spectra were observed for the system containing MC, mainly in the range of $3500\text{--}3000\text{ cm}^{-1}$, two absorption bands (instead of one, like for the EP system) at 3387 cm^{-1} corresponding to symmetric NH_2 stretching vibrations of the triazine group, and a band at 3321 cm^{-1} due to the symmetric NH_2 stretching vibrations in melamine crystal [29]. Moreover, the absorption band at 2916 cm^{-1} diminished, while a broad absorption band in the range of $2500\text{--}2000\text{ cm}^{-1}$ appeared. This one can be assigned to the asymmetric NH_2 stretching vibration [30]. There are also three new high-intensity absorption bands at 1783 cm^{-1} , 1736 cm^{-1} and 1664 cm^{-1} . The stretching vibration of the carbonyl group C=O at 1784 cm^{-1} is due to the cyanate anion [31]. The peak at 1736 cm^{-1} can be assigned to NH_2 scissoring [32], while the absorption band 1664 cm^{-1} corresponds to NH_2 bending vibration [32]. In turn, the absorption band at 1028 cm^{-1} is much less intense than for the unmodified EP system. Particularly noteworthy is the absorption band that appears at approximately 912 cm^{-1} , which could falsely indicate that the system is not cross-linked, and,

in fact originates from ring breathing vibration in this system [33].

Such changes in the chemical composition of epoxy-based systems containing halogen-free FRs are, among others, in agreement with the observation made by Chen et al. [28], who synthesized a series of epoxy resins containing melamine phosphate (MP) and investigated their thermal and flame retardation properties. Moreover, Chen and Wang [34] not only studied the influence of the molar ratio of MP and PER, but also investigated how this system (melamine salt of pentaerythritol phosphate (MPP) prepared from MP and PER) affected the flame retardation, thermal stability and mechanical properties of the polymer matrix.

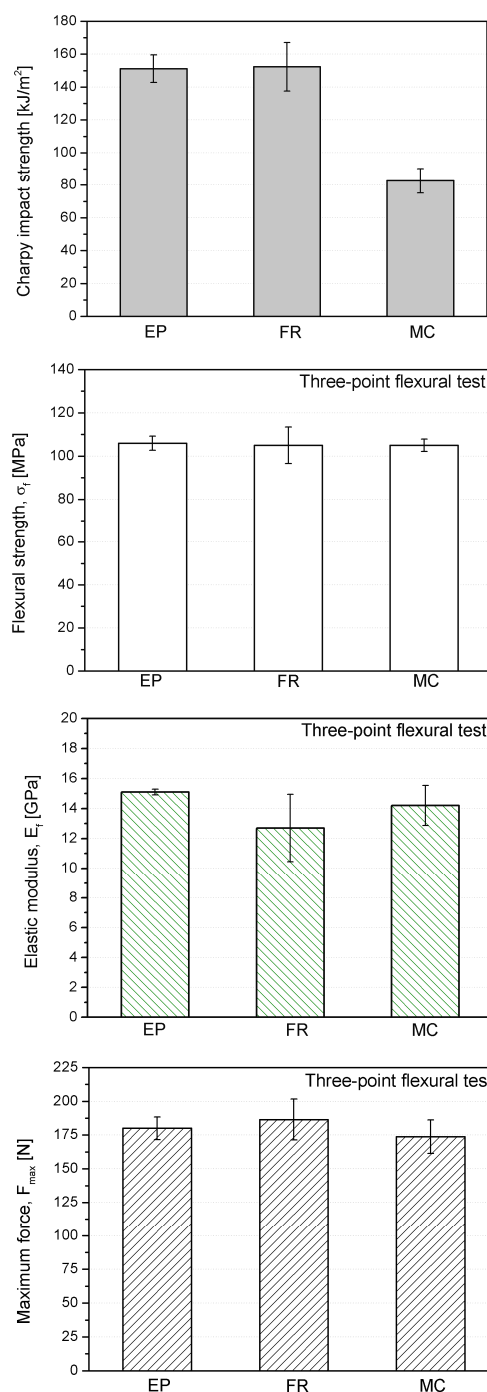


Fig. 3. Mechanical properties of epoxy-basalt laminates

Figure 3 shows the results of the mechanical tests for the unmodified epoxy-basalt composite and the FR-modified specimens. When a complex FR system miscible with an epoxy resin was used, the impact strength remained at a level comparable to that of the unmodified composite. However, introducing only MC resulted in a 50% reduction in the ability to withstand impact loads. The supplemented fractographic analysis is presented in the later part of the manuscript. In the case of the flexural tests, all the considered series of composites exhibited comparable properties. Nonetheless, the measured values of the modulus of elasticity during bending were different. The stiffness of the composite containing the three-component FR system was reduced to 12.7 GPa, compared to the unmodified EP series with 15.1 GPa. The incorporation of MC did not significantly affect the deterioration in stiffness, which was 14.2 GPa for this system, despite the mentioned deteriorated rheological behavior resulting in limited miscibility in the epoxy monomer. In the case reported by Patrick Lim et al. [16], epoxy-glass composites modified with MC, a different trend was noted; with the introduction of MC, the stiffness and strength of the composite samples slightly increased. Nevertheless, the authors used a lower modifier concentration, i.e. a maximum of 20 wt.%. Despite a slight deterioration in the elastic modulus, the modified composites retained excellent stiffness, acceptable from the point of view of use as a construction material.

The SEM micrographs taken from a side view of the selected specimens after the Charpy impact strength test are presented in Figure 4. The destruction processes of the structure of fiber-reinforced composite materials is a complex mechanism resulting from interlayer damage modes, which include the phenomenon of matrix and fiber cracking in addition to the occurrence of interlayer damage, mainly delamination [35]. The composites modified with FRs exhibited a different fractographic feature compared to the EP series. Much better interlayer adhesion of the EP composites can be observed in the SEM micrographs taken at higher magnification. The coherence failure mode was noted for the unmodi-

fied EP, with limited delamination compared to the IFR-containing series. Impact cracks are observed in the interlayer space, and the number of extensive longitudinal splits occurring outside the area of direct impact and resulting in secondary cracking behavior and delamination in the final fractured structure was seen [36]. In the case of the EP and FR composites, more distinct damage to the structure at the point of impact was observed. On the outer surface, a loss of cohesion of the external layers and the appearance of cracked fibers in the plane perpendicular to the direction of impact were observed. This effect was much smaller for the MC-modified series. The observed different fracture behavior of the MC specimens after impact loading may be related to the significantly lower impact strength values induced by visible agglomerated inclusions of the modifier [35]. Intense debonding in the deeper layers with simultaneous distinct failure at the point of impact for the FR series resulted in high energy dissipation of the impact energy and favorable dynamic properties. Thanks to the better miscibility of the FRs used in the FR-series compared to MC, the FR-modified laminates exhibited greater interlayer cohesion and adhesion. Moreover, the significantly higher viscosity of the MC-modified resin limited saturation by the epoxy composition of subsequent fabric layers, which resulted in an observable tendency of the laminates containing reinforcement to lose cohesion at the moment of impact.

The results of the short beam shear measurements (Fig. 5) revealed that interlaminar interactions for the prepared composites strongly align with the results of the standard flexural tests. The load peak position, as well as ILSS calculations, confirmed that for EP and the FR-modified specimens, the mechanical properties are very similar, with little benefit to the EP material. For the MC-based composites, the shear strength values are visibly lower, which confirms that the delamination phenomenon leads to deterioration of the mechanical properties of this type of material. It applies mainly to the impact resistance performance, where the delamination phenomenon causes significantly faster crack propagation and visibly lower impact strength.

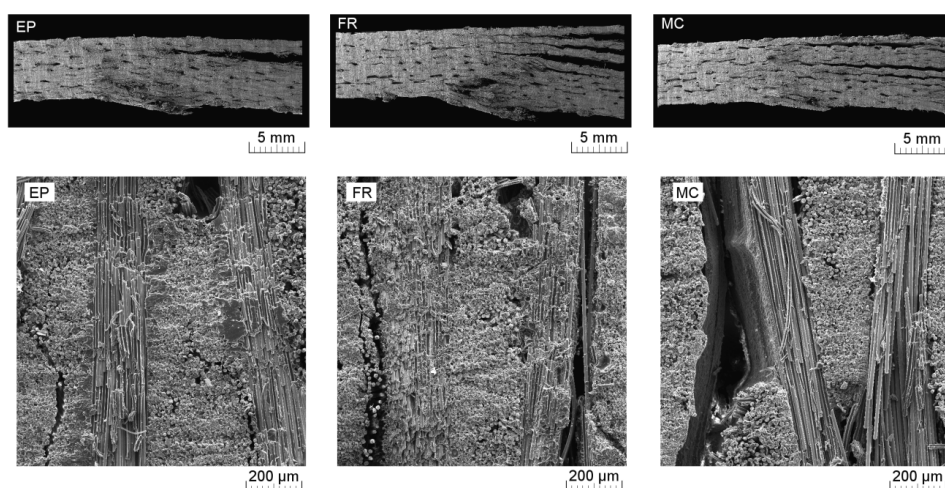


Fig. 4. Side view SEM micrographs of specimens after Charpy impact strength test

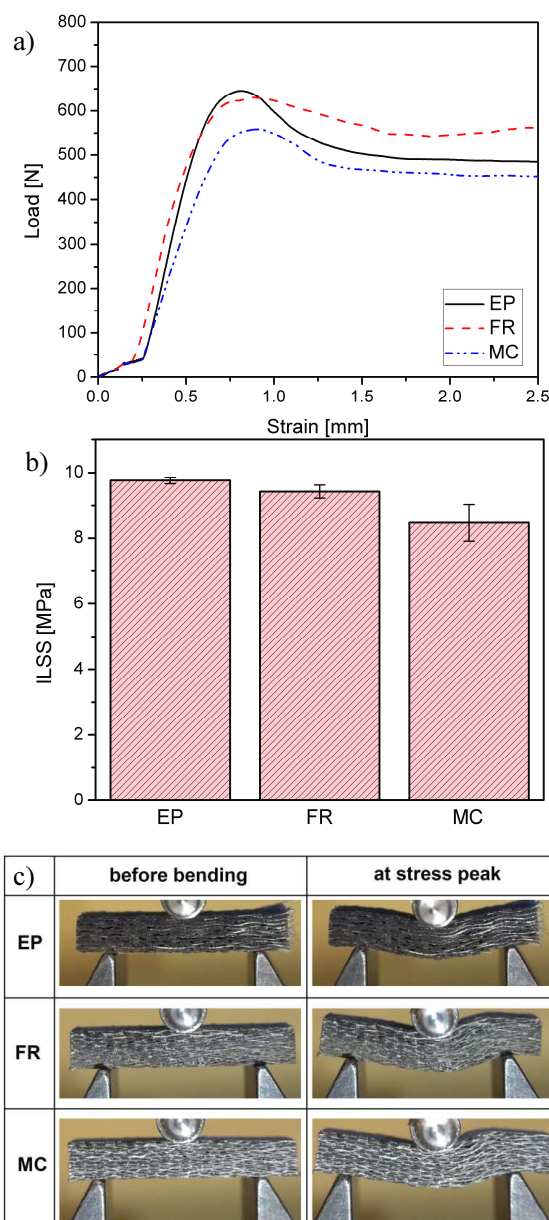


Fig. 5. Comparison of short beam shear test results: a) load/strain plots, b) ILSS values, c) appearance of specimens

Epoxy composites containing two different FRs systems were assessed regarding their thermomechanical properties by DMTA. The results pointing to changes in the storage modulus (G') and damping factor ($\tan \delta$) as a function of temperature are presented in Figure 6. In the case of the IFR-modified composites, no significant changes in the course of the G' curves were noted. This series exhibited increased stiffness above the α -relaxation temperature of the epoxy [37], which can be concluded based on the increased storage modulus. The location of the maximum at the $\tan \delta$ temperature curve, taken as the glass transition temperature (T_g), was 64.5°C (EP), 65.1°C (FR), and 62.0°C (MC), respectively. While the slightly increased T_g value in the case of the FR-series may result from the presence of a finely dispersed phase characterized by proper adhesion to the epoxy matrix, in the case of the reduced

value recorded for the MC series, this effect can be attributed not to limited adhesion, but to a change in the chemical structure of the matrix. The reduced $\tan \delta$ value in the α -relaxation area indicates reduced damping properties, resulting from the stiffening of the matrix structure containing insoluble, finely dispersed inclusions of the FR composition components. Similar effects attributed to the heterogeneity within the internal structure of the layered composites were described by Zulfli et al. [38] for epoxy/GF composites reinforced with nanometric calcium carbonate.

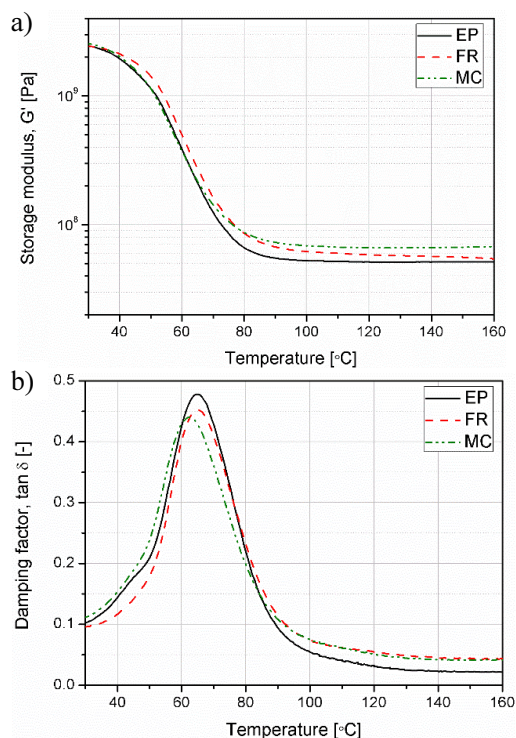


Fig. 6. DMTA curves of epoxy-basalt laminates: a) storage modulus, and b) $\tan \delta$ temperature plots

Investigations by the cone calorimeter, simulating a well-ventilated fire scenario, were carried out to define the burning behavior of the materials. Table 1 displays the average values of the fire hazard parameters, including the heat release rate (HRR), maximum average rate of heat emission (MARHE), total heat release (THR), effective heat of combustion (EHC), and total smoke release (TSR).

TABLE 1. Cone calorimeter results of EP composites

| Parameter | Unit | EP | FR | MC |
|-----------|--------------------------------|-------------|------------|------------|
| TTI | s | 31.7 ± 2.6 | 28.0 ± 5.3 | 45.0 ± 1.0 |
| pHRR | kW/m ² | 343 ± 26 | 189 ± 17 | 241 ± 1 |
| MARHE | kW/m ² | 210 ± 11 | 118 ± 10 | 152 ± 4 |
| THR | MJ/m ² | 68.9 ± 4.3 | 53.3 ± 3.3 | 55.9 ± 4.3 |
| EHC | MJ/kg | 23.7 ± 0.1 | 22.4 ± 0.5 | 19.9 ± 0.1 |
| TSR | m ³ /m ² | 2791 ± 498 | 2165 ± 67 | 2074 ± 142 |
| SEA | m ² /kg | 1030 ± 20.6 | 913 ± 34 | 740 ± 6 |
| Residue | % | 70.3 ± 1.2 | 76.3 ± 0.9 | 71.1 ± 1.5 |

The FR caused a shorter time to ignition (TTI), characteristic of IFRs, which form oxyacid, accelerating polymer decomposition. Subsequently, shorter chains cyclize and form char [39]. The maximum HRR (pHRR) values for EP reached 343 kW/m², while for the specimens with fire retardants they were notably reduced. The lowest results were received for FR, where pHRR was almost two times lower. Similarly, the greatest reduction in MARHE, used to assess the hazard of fire spread, was observed for the same specimen. The use of both fire retardants also led to a decrease in THR from 69 to 54 MJ/m². The noticeable EHC reduction in the MC specimen suggests that MC works by diluting the gas phase. On the other hand, the growing amount of residue for FR demonstrates that a decrease in the total heat release was mainly connected with action in the condensed phase.

Both FRs reduced the parameters determining the amount of smoke emitted: the specific extinction area (SEA) and TSR. The highest decrease, by 28% and 26%, respectively, was observed for MC, the decomposition of which generates non-flammable dilution gases, such as NH₃ and N₂. In turn, the reduction in smoke in the case of FR results from incorporating decomposition products into the forming char.

CONCLUSIONS

This study aimed to examine the effect of FRs on the mechanical and thermomechanical properties of epoxy composites reinforced with BFs. The research assessed the impact of additives on the chemical structure using FTIR spectroscopy, which excluded significant adverse effects resulting from a limited cross-linking process of the epoxy matrix caused by FRs. The employed halogen-free FRs, including a two-component co-composition (APP with PER) (FR) and MC, despite the 30% addition, did not cause an uncontrolled reduction in the mechanical properties. The used FRs differed in their uniformity of distribution in the polymer matrix; MC exhibited much less favorable miscibility, resulting in an increased composition viscosity. As a result, the saturation of the reinforcing fabrics by the modified epoxy resin was limited, causing a different failure mechanism under the static bending and impact test conditions. Both FR systems reduced the flammability of the modified epoxy laminates. The most beneficial effects were obtained by the two-component FR system containing APP and PER.

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Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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