



Article

Enhanced Fire Resistance and Mechanical Properties of Epoxy and Epoxy-Based Fiber-Reinforced Composites with Hexachlorocyclotriphosphazene Modification

Tatjana Glaskova-Kuzmina ^{1,*}, Sergejs Vidinejevs ¹, Olegs Volodins ¹, Jevgenijs Sevcenko ¹, Andrey Aniskevich ¹, Vladimir Špaček ², Dalius Raškinis ³ and Gediminas Vagonis ³

¹ Institute for Mechanics of Materials, University of Latvia, Jelgavas 3, LV-1004 Riga, Latvia; sergejs.vidinejevs@lu.lv (S.V.); olegs.volodins@lu.lv (O.V.); jevgenijs.sevcenko@lu.lv (J.S.); andrey.aniskevich@pmi.lu.lv (A.A.)

² SYNPO, S. K. Neumann 1316, 530 02 Pardubice, Czech Republic; vladimir.spacek@synpo.cz

³ Composite Aviation, K. Donelaičio Str. 79-1, LT-44249 Kaunas, Lithuania; dalius.raskinis@etkc.lt (D.R.); vagonis@gmail.com (G.V.)

* Correspondence: tatjana.glaskova-kuzmina@lu.lv

Abstract: This research aims to develop fiber-reinforced composites (FRC) with enhanced fire resistance, which can be particularly useful for the transport industry (e.g., aviation, automotive, and train production). The fire retardation was achieved through epoxy matrix modification with hexachlorocyclotriphosphazene (HCTP). First, the fire-resistant and mechanical properties of the epoxy matrix filled with different HCTP contents (4.8, 7.2, and 9.5 wt.%) were studied to select the most effective HCTP content for the impregnation of FRC. Then, glass, basalt, and carbon fiber fabrics were impregnated with epoxy filled with 7.2 wt.% of HCTP, and the fire resistance, flexural, and interlaminar fracture properties were studied to select the most effective HCTP-modified type of fiber reinforcement based on the test results. It was concluded that basalt fiber impregnated with epoxy filled with HCTP could be selected as the most effective reinforcement type, allowing excellent mechanical and flame-retardant properties.

Keywords: fiber-reinforced composites; glass fibers; basalt fibers; carbon fibers; epoxy; hexachlorocyclotriphosphazene; fire resistance; mechanical performance



Citation: Glaskova-Kuzmina, T.; Vidinejevs, S.; Volodins, O.; Sevcenko, J.; Aniskevich, A.; Špaček, V.; Raškinis, D.; Vagonis, G. Enhanced Fire Resistance and Mechanical Properties of Epoxy and Epoxy-Based Fiber-Reinforced Composites with Hexachlorocyclotriphosphazene Modification. *J. Compos. Sci.* **2024**, *8*, 290. <https://doi.org/10.3390/jcs8080290>

Academic Editor: Francesco Tornabene

Received: 3 July 2024

Revised: 18 July 2024

Accepted: 26 July 2024

Published: 29 July 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The presence of fire in a confined space containing polymeric components rich in hydrocarbons can result in catastrophic outcomes. Therefore, it is crucial to use flame-retardant polymers in critical applications, such as in aircraft, automobiles, and building interior designs [1,2]. Traditional flame-retardant methods depend on adding halogens or non-halogens like N-, P-, or metal-hydroxide-based chemicals to achieve the required performance. However, the range of intrinsically flame-retardant polymers is relatively small, considering other aspects such as eco-friendliness, mechanical or chemical properties, and processing difficulties [3].

The FRC structures currently applied in the transport industry (e.g., aviation, automotive, and train production) mainly use carbon and glass textiles (fabrics) impregnated with epoxy binders. These combinations provide excellent mechanical performance and reliability. However, since most of the polymers and natural fiber textiles are organic, they are susceptible to a fire hazard that threatens the safety of human beings and property [4]. Therefore, significant social and legislative pressure and interest in FRC flame retardance exists.

Epoxyes are a standard matrix in advanced structural composites. Crosslinked epoxy matrices are combustible and can undergo self-sustaining combustion. Thus, they require

flame retardants to ensure fire safety in the industry [5]. However, this comes mainly at the expense of their mechanical properties. Thus, it is a challenge to find a balance between the mechanical and fire performances of the composites [6].

For epoxy matrices, flame retardants of the reactive type or additive retardants are most important due to the inherent flammability of epoxies [6]. Compounds containing halogens or nitrogen and phosphorus group atoms, as well as non-halogenated flame retardants (FRs)—e.g., metal hydroxides, such as aluminium trihydrate (ATH) and magnesium hydroxide (MDH)—are widely used to reduce flammability [7,8]. The commercially available hexachlorocyclotriphosphazene (HCTP) is well known to be an effective flame retardant for the epoxy matrix [9,10]. HCTP is an important starting material for synthesizing cyclotriphosphazene-based retardants because many different substituents (e.g., N and P atoms in cyclic rings) can replace its active chlorine atoms via nucleophilic substitution reactions [11]. Yang et al. [12] introduced the cyclotriphosphazene group into the epoxy matrix and improved its flame-retardant performance (a high char yield, excellent thermal stability, and combustion retardation).

In FRCs, the fiber reinforcement type may also influence the composite's flame-retardant performance. Carbon fibers (CFs) are generally non-flammable, do not easily ignite, and tend to resist combustion due to their high thermal stability [13]. Glass fibers (GFs) are made from silica and other oxides, which are inherently non-combustible materials. Moreover, GFs can withstand high temperatures encountered in most fire scenarios without decomposing or burning [14]. In addition to conventional GFs and CFs, basalt fibers (BFs) have recently become of interest in FRC design. BFs have a high strength and modulus; low elongation at break and chemical and thermal stability (in the range of -200 to 600 – 800 °C); good thermal insulation; and resistance to most weather conditions. According to the material cost analysis in [15], polymers reinforced with CF are approximately 10.1 and 7.5 times more expensive than those reinforced with BF and GF, respectively. BF's easy processability, eco-friendliness, and economical cost make them an attractive alternative to conventional fibers, enabling the potential development of sustainable and lighter FRC [16–20]. Different types of fiber reinforcement (BFs and GFs) were impregnated with commercial polymer matrices and experimentally investigated for use as novel passive fire protection by thermal shields/panels [21]. The heat release rate and fire retardance of thermoset matrix composites reinforced with combustible fibers (aramid and polyethylene) or non-combustible fibers (glass and carbon) were also analyzed [22]. Additionally, basalt fibers are an excellent choice for enhancing the fire resistance of composite materials due to their non-combustible nature and high thermal stability [23,24].

No direct comparison for the fire-retardant properties of carbon, glass, and basalt fiber-reinforced was found in the literature motivating developing the FRC enhanced fire-resistant properties that maintain high mechanical performance. Therefore, developing a technology for fire-resistant modification of a composite material without a noticeable increase in weight while maintaining mechanical properties employed is a scientific and technological problem for which the knowledge is not publicly available and is not yet applied in the transportation industry.

The work was intended to improve the flame-retardant and mechanical properties of different epoxy-based fiber-reinforced composites (FRC) through epoxy matrix modification with hexachlorocyclotriphosphazene (HCTP). First, the fire resistance, mechanical, and thermophysical properties of the epoxy matrix filled with different contents of HCTP (4.8, 7.2, and 9.5 wt.%) were studied to select the most effective HCTP content for the impregnation of FRC. Then, glass, basalt, and carbon fiber fabrics were impregnated with epoxy filled with 7.2 wt.% of HCTP, and the fire resistance, flexural, and interlaminar fracture properties were studied to select the most effective HCTP-modified type of fiber reinforcement-based on the test results.

2. Materials and Methods

2.1. Materials

The materials used to manufacture the test samples include epoxy matrix, additive, and fiber reinforcements. The epoxy resin was Epikote LR 285 (Hexion, Columbus, OH, USA) [25], which was mixed with a hardener Epikure LH 285 (Hexion, Columbus, OH, USA) [26] at a resin-to-hardener ratio of 100:40 by weight. The FR-additive was a trimer of cyclic phosphonitrile chloride or hexachlorocyclotriphosphazene (HCTP) with a chemical formula $(\text{NPCl}_2)_3$, which was provided by SYNPO (Pardubice, Czech Republic). Four samples were developed: pure epoxy and epoxy filled with 4.8, 7.2, and 9.5 wt.% of HCTP. The fiber reinforcement was unidirectional basalt fiber fabric BAS UNI 350 provided by Basaltex (Wevelgem, Belgium) with an area density of 416 g/m^2 [27], aero glass 2/2 Twill (6×6) glass fiber fabric (Havel Composites, Páslavice, Czech Republic) with an area density of 390 g/m^2 [28], and twill weave 2/2 (3 k), style 442 carbon fiber fabric (Engineered Cramer Composites, Heek, Germany) with an area density of 160 g/m^2 [29]. Altogether, for each material composition (pure epoxy and each of additive content), five dumbbell-shaped samples were produced for the quasistatic tensile tests, and five were produced for the vertical burn tests.

For the production of the epoxy matrix filled with HCTP with the epoxy matrix, the following steps were performed: (1) add the needed amount of HCTP additive to the pre-calculated amount of hardener LH 285 and mix manually for 5 min; (2) degas the mixture with the additive at 0.1 atm pressure for 5 min to reduce the air bubbles in the mixture; (3) add the needed amount of LR 285 epoxy resin to the mixture and mix manually for 5 min. This sequence of steps eliminated a rapid acceleration of the exothermic polymerization of the epoxy resin by admixing HCTP to the initial stoichiometric mixture of resin and hardener. To obtain similar thickness (approx. 3 mm) and weight fraction of fiber reinforcement, different numbers of plies were used: basalt FRC—12 layers, glass FRC—12 layers, and carbon FRC—16 layers. The weight fraction of fiber reinforcement was 75.5%, 78.5%, and 79.3% for carbon, basalt, and glass FRC, respectively. The fiber fabrics were cut into pieces of $320 \times 200 \text{ mm}$, and epoxy resin was mixed with the hardener at a resin-to-hardener ratio of 100:40 by weight. Based on the results for tensile, thermomechanical, and vertical burn tests, the most effective content of HCTP in the epoxy matrix was 7.2 wt.%, which was used to prepare flame-retardant/epoxy FRC samples reinforced with glass, carbon, and basalt fibers.

2.2. Methods

2.2.1. Tensile Tests of the Epoxy Filled with HCTP

The tensile tests were performed according to [30] using a Zwick 2.5 testing machine (Zwick Roell Group, Ulm, Germany) with a 2 mm/min crosshead speed at room temperature until failure. Tensile strength was defined as the maximum stress achieved in the specimen, and elastic modulus was calculated from the slope of a secant line between 0.05 and 0.25% strain on a stress–strain plot. Five dumbbell-shaped samples per material type were used, and the values provided corresponded to their arithmetic mean value.

2.2.2. Vertical Burn Tests of the Epoxy and Epoxy-Based FRC Filled with HCTP

The tests were performed according to [31] using test samples of $3 \times 13 \times 125 \text{ mm}$ and a gas burner. Five test samples per material type were used, and the values provided corresponded to their arithmetic mean value. The burner was positioned under the test sample at an angle of 45° because the molten material was dripping down the epoxy samples. The flame was applied to the test sample at a distance of 10 mm from the burner with a flame height of 20 mm. The flame was applied to the test sample for 10 s and then removed. The after-flame time was recorded and analyzed.

2.2.3. Three-Point Bending Tests of FRC

The mechanical properties of all FRC samples were tested in three-point bending according to [32]. A support span of 70 mm and a strain rate of 1.5 mm/min were chosen and applied to the test samples using the Zwick 2.5 machine (Zwick Roell Group, Ulm, Germany). From the stress–strain curves, the elastic modulus, flexural strength, and maximal strain were evaluated by a standard procedure described in detail in [33,34].

2.2.4. Interlaminar Fracture Toughness Tests of FRC

The test method applied in the current work meets the basic standard ASTM D5528 requirements [35]. The thickness of the samples was measured with a micrometer of precision of 0.001 mm and the width with a caliper of precision of 0.01 mm. The measurements were carried out in three places along the length of the expected crack growth (the average value is taken as the result). The crack length was measured on one side of the specimen.

DCB samples (as shown in Figure 1) were clamped and centered in the grips of the testing machine. The free part of the specimen was controlled to maintain a horizontal position. The loading was carried out with constant speed control. All samples were tested using a Zwick universal testing machine with a load cell of 2.5 kN at a constant crosshead speed of 2 mm/min. The load and the grips' displacement were automatically recorded during the test. The crack propagation was estimated by observing the crack propagation and marking the specific points with an interval of 1 mm for the first 10 points and 2 mm for the following 10 points in the Zwick built-in program for the interlaminar fracture toughness tests. Thus, 20 data points were obtained for each test and used in calculating the interlaminar fracture toughness for all FRCs, as described in [36].

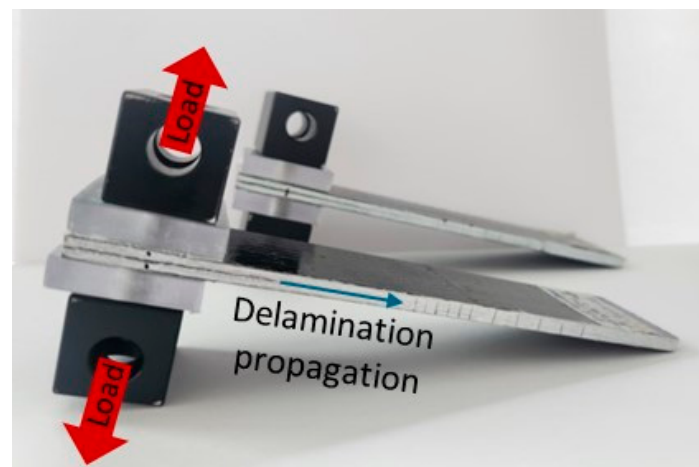


Figure 1. DCB samples of BFRC for Mode I interlaminar fracture toughness with the indication of test loading scheme and delamination propagation.

3. Results

3.1. Tensile Properties

The dumbbell-shaped samples produced for the tensile tests are shown in Figure 2a. The samples were produced using silicone molds and were polished to get flat surfaces, which initially were slightly curved due to the polymerization shrinkage. The representative stress–strain curves of the epoxy and epoxy filled with different additive content are shown in Figure 2b. The additive led to material brittleness, significantly decreasing their deformability and tensile strength. Thus, despite the seemingly uniform distribution over the resin, the by-product (ammonium salt) of the HCTP dispersion procedure did not ensure uniform intercalation of the precipitate particles in the polymer matrix, leading to decreased mechanical properties.

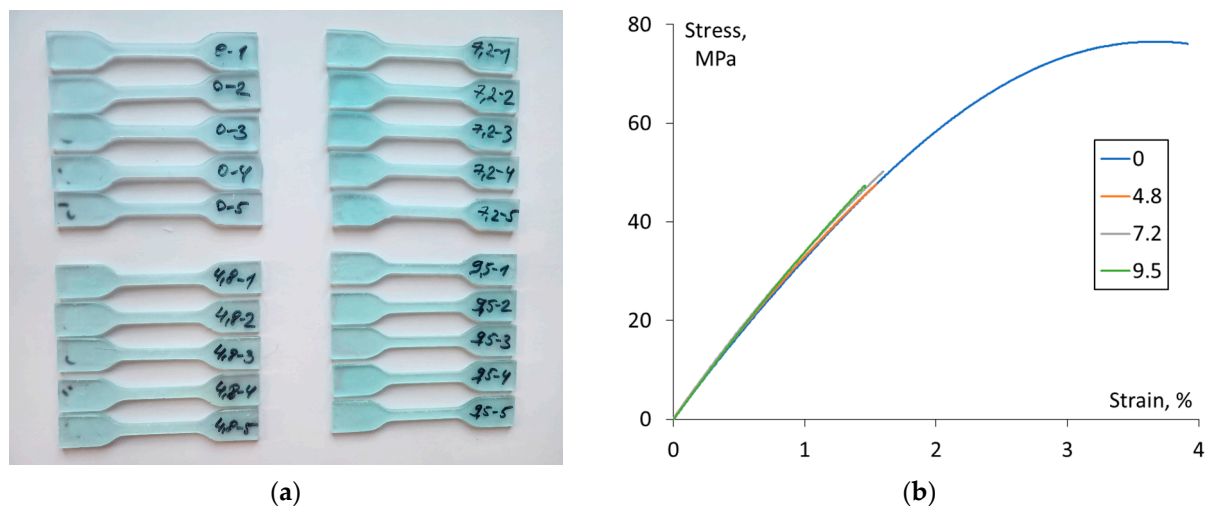


Figure 2. (a) Dumbbell-shaped samples and (b) representative stress–strain curves of the epoxy filled with 0, 4.8, 7.2, and 9.5 wt.% of HCTP.

The resulting stress–strain curves were used to evaluate and compare the elastic modulus, tensile strength, and maximal deformation for all materials tested. The elastic modulus of the samples tested is shown in Figure 3, revealing that the results obtained for the samples having different HCTP content were very close (3.5 ± 0.1 GPa). Nevertheless, the results for the tensile strength and maximal deformation provided in Figure 3 revealed a significant reduction caused by the additive, resulting in almost twice the lower results for the tensile strength and almost threefold reduction for the maximal deformation of the epoxy with all contents of the additive studied.

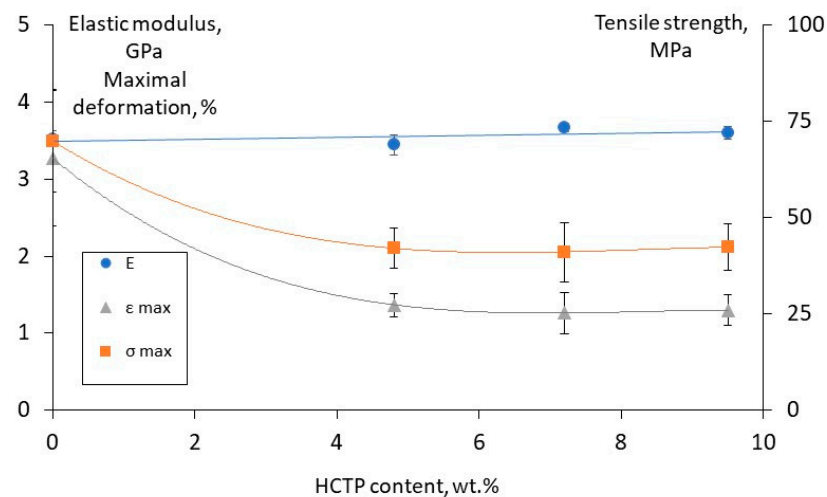


Figure 3. Elastic modulus (E), tensile strength (σ_{max}), and maximal deformation (ϵ_{max}) vs. HCTP content by weight (dots—experimental results, lines—approximation).

According to these results, manual mixing resulting in the presence of sedimented additive particles led to a decrease in the strength and maximal deformation. Therefore, it could be concluded that the resulting lower mechanical performance of the epoxy composite was possibly due to the sedimentation of by-products that accomplished the modification of the epoxy resin by HCTP. A similar reduction in the tensile properties of the epoxy filled with phosphorus flame-retardant additive (diethyl (hydroxymethyl) phosphonate) was revealed, which was attributed to significantly reduced crosslinking density followed by the decrease in the glass transition temperature [37]. Additionally, a decrease in the mechanical properties due to the addition of flame retardants to the poly-

mer can be a consequence of their poor compatibility, which can be improved by chemical modification (e.g., functionalization or grafting) and surface treatment of flame retardants, using compatibilizers to reduce the interfacial tension and improve adhesion or optimizing processing conditions [38,39].

3.2. Vertical Burn Tests for the Epoxy and Epoxy-Based FRCs

The flame was applied to the test samples for 10 s and removed. The after-flame time t_1 was recorded and is provided in Figure 4a. For the FRC samples, after the after-flame finishing, the flame was applied to the test specimen again for 10 s and then removed. The after-flame time t_2 of this final stage was recorded and is provided in Figure 4b. Figure 4c demonstrates the samples of glass/epoxy FRC and glass FRC impregnated with the epoxy filled with 7.2 wt.% of HCTP after vertical burn tests.

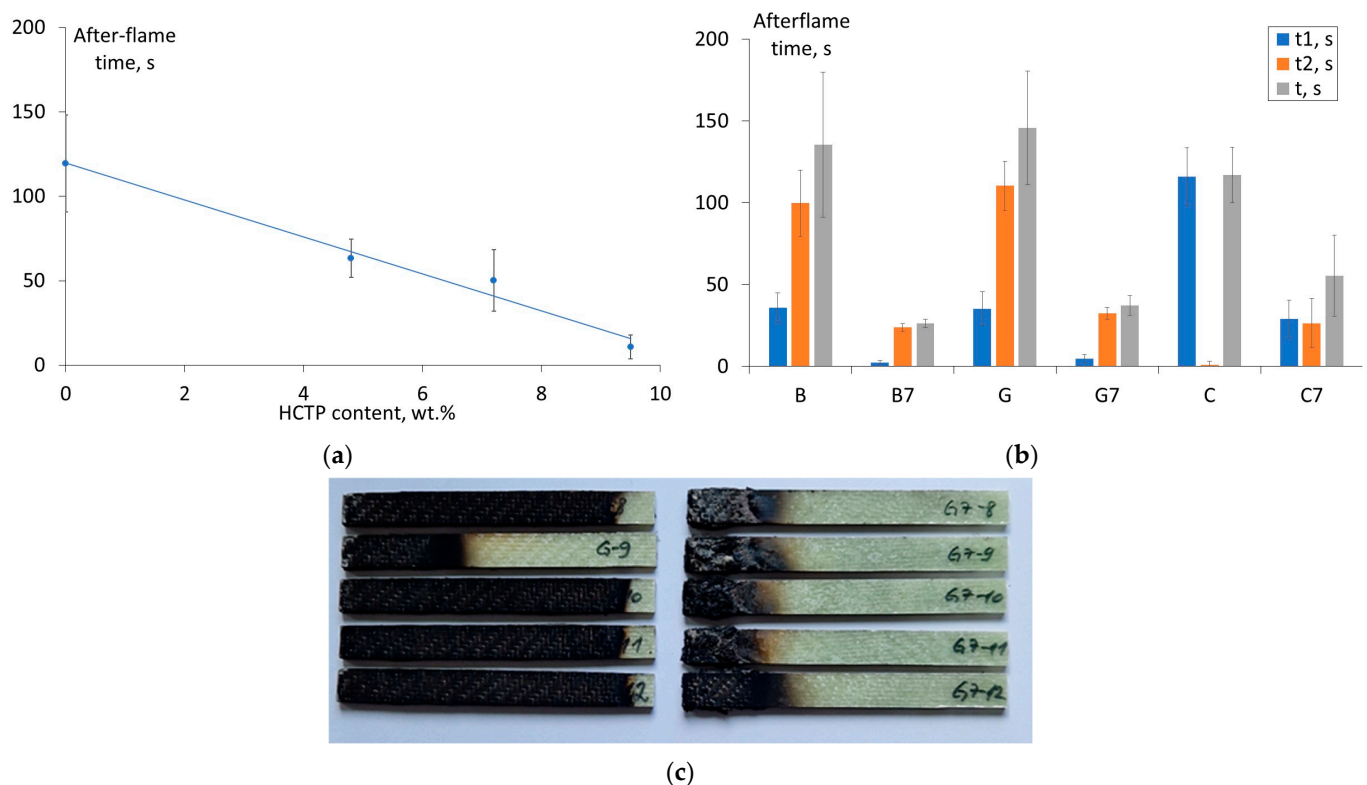


Figure 4. After-flame time for the epoxy and epoxy filled with HCTP (a), after flame time for the neat and HCTP-modified (7.2 wt.% in the epoxy matrix) glass (G and G7), basalt (B and B7) and carbon (C and C7) FRC samples (b), and glass/epoxy FRC samples (left), and glass FRC impregnated with epoxy filled with 7.2 wt.% of HCTP samples after vertical burning tests (c).

According to Figure 4a, adding HCTP has positively influenced the after-flame time. It should be noted that the epoxy samples were entirely burned during this after-flame period. In contrast, the epoxy samples containing HCTP had a flame that stopped after the after-flame period, keeping the total length of material samples around 6–9 cm. The higher the amount of HCTP, the more negligible the after-flame time was. Therefore, based on the results obtained, it can be concluded that the filler content of 9.5 wt.% was the most effective for improving the fire-resistant properties.

A comparison of the burning time of various composites (Figure 4b) allowed to conclude that the after-flame times t_1 and t of FRC samples containing 7.2 wt.% of HCTP were significantly smaller than that of the corresponding ordinary FRCs. The second after-flame times t_2 values, except for carbon FRC, demonstrated the same trend. At the same time, the ordinary FRC demonstrated $t_1 > t_2$ when the flammable FRC matrix mostly burned out already during t_1 . Accordingly, at the second stage, there was nothing left to

burn. In any case, the flame-retardant properties were significantly improved by adding 7.2 wt.% HCTP to the epoxy matrix of all three types of FRC, which was obvious.

The photos of the samples for glass/epoxy FRC and glass FRC impregnated with the epoxy filled with 7.2 wt.% of HCTP after vertical burning tests given in Figure 4 provide an illustrative positive result of adding HCTP. Similar photos were also taken for basalt and carbon FRC, but since they are dark in color, the consequence of the burning process is not as obvious for them as for glass FRC. Therefore, the flame-retardant properties analysis showed that basalt and glass FRCs had better results than carbon FRC, for which after-flame time was characterized by similar values, revealing significant improvement. Additionally, comparing surface flame propagation for basalt and glass FRC panels demonstrated better results for basalt FRC panels maintaining structural integrity after applying flame [21]. However, when exposed to the same radiant heat flux, the BF composite heated up more rapidly and reached higher temperatures than the GF laminate due to its higher thermal emissivity [23].

3.3. Flexural Properties of Neat and HCTP-Modified FRCs

The representative stress–strain curves for all neat and HCTP-modified glass, basalt, and carbon FRC samples are provided in Figure 5. Rather significant data scattering was obtained, which is typical for FRC mechanical testing. Still, all results from five samples for each material composition were considered to evaluate average flexural strength, elastic modulus, and strain at the flexural strength to show their actual distribution.

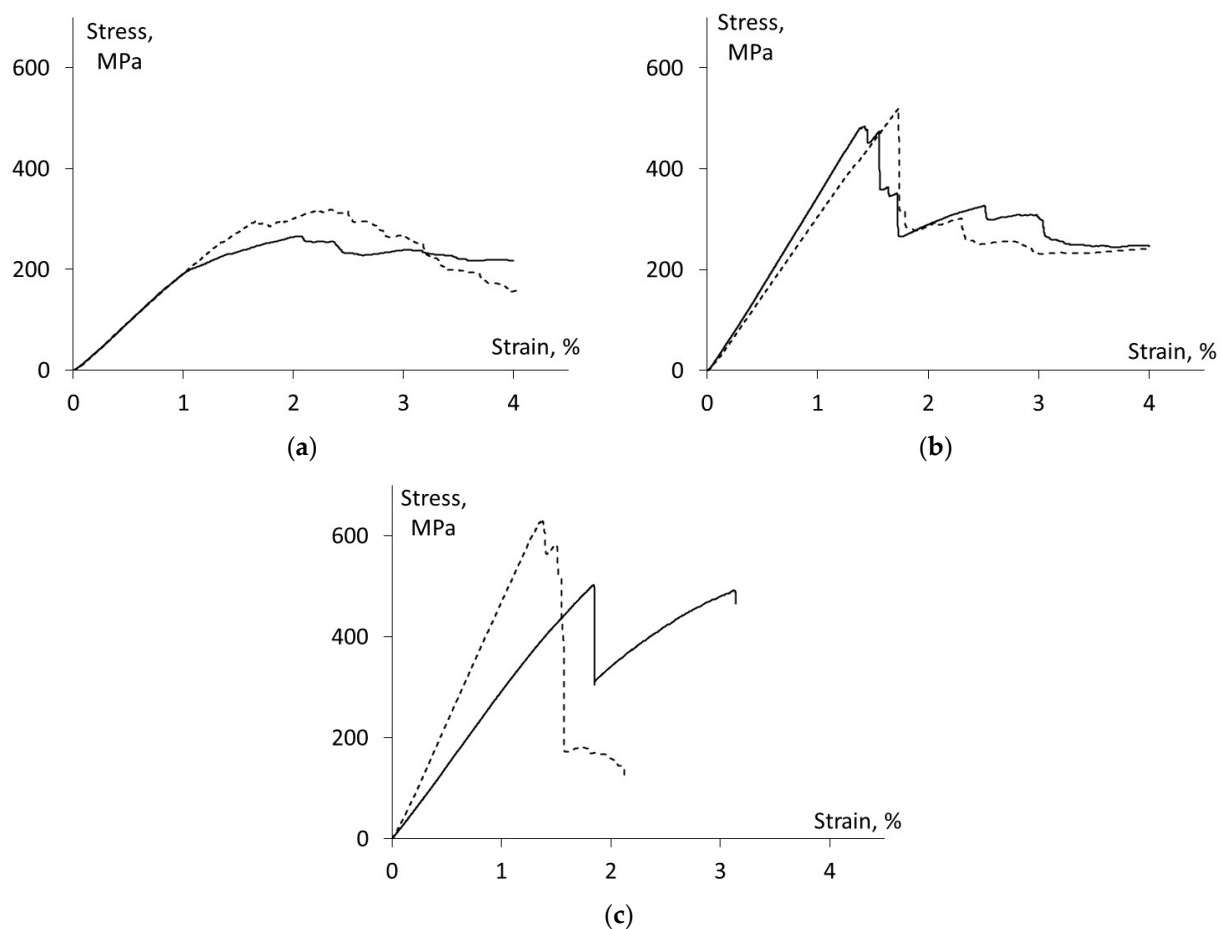


Figure 5. The representative stress–strain curves of the neat (solid line) and HCTP-modified (dotted line) glass (a), basalt (b), and carbon (c) FRC samples.

According to Figure 5, a positive effect of adding HCTP was observed for all materials except a slight reduction for basalt FRC. The length of the axes for all graphs was kept the same for comparative purposes. Notably, the addition of 7.2 wt.% to the epoxy matrix, which was used for the impregnation of FRCs, improved the mechanical performance for all FRCs, meaning that it had both the reinforcement effect and no existence of the defects, which may potentially be introduced during the manufacturing process.

The results for the flexural strength, elastic modulus, and strain at the flexural strength obtained for all FRC systems are summarized in Figure 6. According to the results provided in Figure 6a, the effect of HCTP on the flexural strength of glass, carbon, and basalt FRCs was 37%, −12%, and 30%, respectively. Moreover, adding HCTP to glass, basalt, and carbon FRCs led to a relative change of the elastic modulus of these composites by 14%, −17%, and 105%, respectively (see Figure 6b). Lastly, the strain at the flexural strength of glass, basalt, and carbon FRC changed by −0.2%, 0.1%, and −1.0%, respectively, due to the addition of HCTP (Figure 6c).

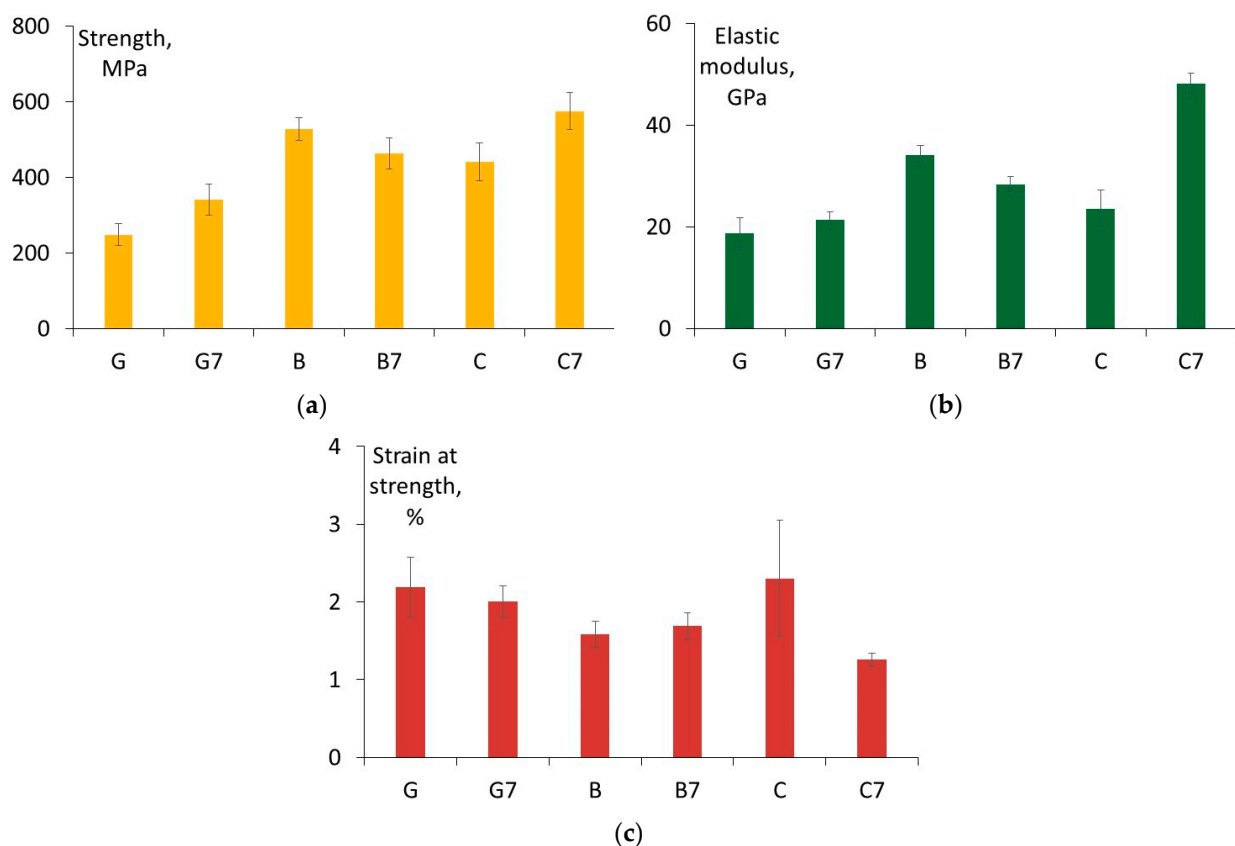


Figure 6. The flexural strength (a), elastic modulus (b), and strain at the flexural strength (c) for the neat and HCTP-modified (7.2 wt.% in the epoxy matrix) glass (G and G7), basalt (B and B7) and carbon (C and C7) FRC samples.

Analyzing the most effective flexural properties of tested FRC requires a complex approach. The effect of HCTP addition decreased basalt FRC's flexural strength and elastic modulus. Nevertheless, these characteristics are higher than those for the glass FRC after adding HCTP. For the carbon FRC, the flexural strength and elastic modulus are the highest when adding HCTP, but the strain at the flexural strength was significantly reduced. Therefore, the most effective composite reinforcement should be selected by considering the rest of the properties (flame resistance and interlaminar fracture toughness). The flexural and interlaminar fracture properties of CFRP due to the addition of flame retardant (a phosphorus-containing reactive amine, TEDAP) was reported, which was explained by the higher polarity of the flame-retardant component, which does not match

the sizing of the reinforcing fiber designed for unmodified epoxy resin [40]. Therefore, for composite materials in aircraft applications, it is usually crucial to find a balance between fire resistance and mechanical properties [41].

3.4. Mode I Interlaminar Fracture Toughness Tests of the Neat and HCTP-Modified FRCs

To estimate Mode I interlaminar fracture toughness, the modified beam theory Equation (1) was used to correct for the rotation at the delamination front by treating the DCB as if it contained slightly longer delamination, $a + \Delta$ where Δ may be determined experimentally by generating a least-squares plot of the cube root of compliance, $C^{1/3}$, as a function of delamination length:

$$G_I = \frac{3P\delta}{2b(a+|\Delta|)} \quad (1)$$

where P is the load, δ is the load point displacement, b is the specimen width, and a is the delamination length of the specimen.

The representative load-crack opening displacement (COD) curves obtained for glass, basalt, and carbon FRCs impregnated with the neat and HCTP-modified epoxy are provided in Figure 7. A rather significant deviation among the data could be observed, which is typical for such tests.

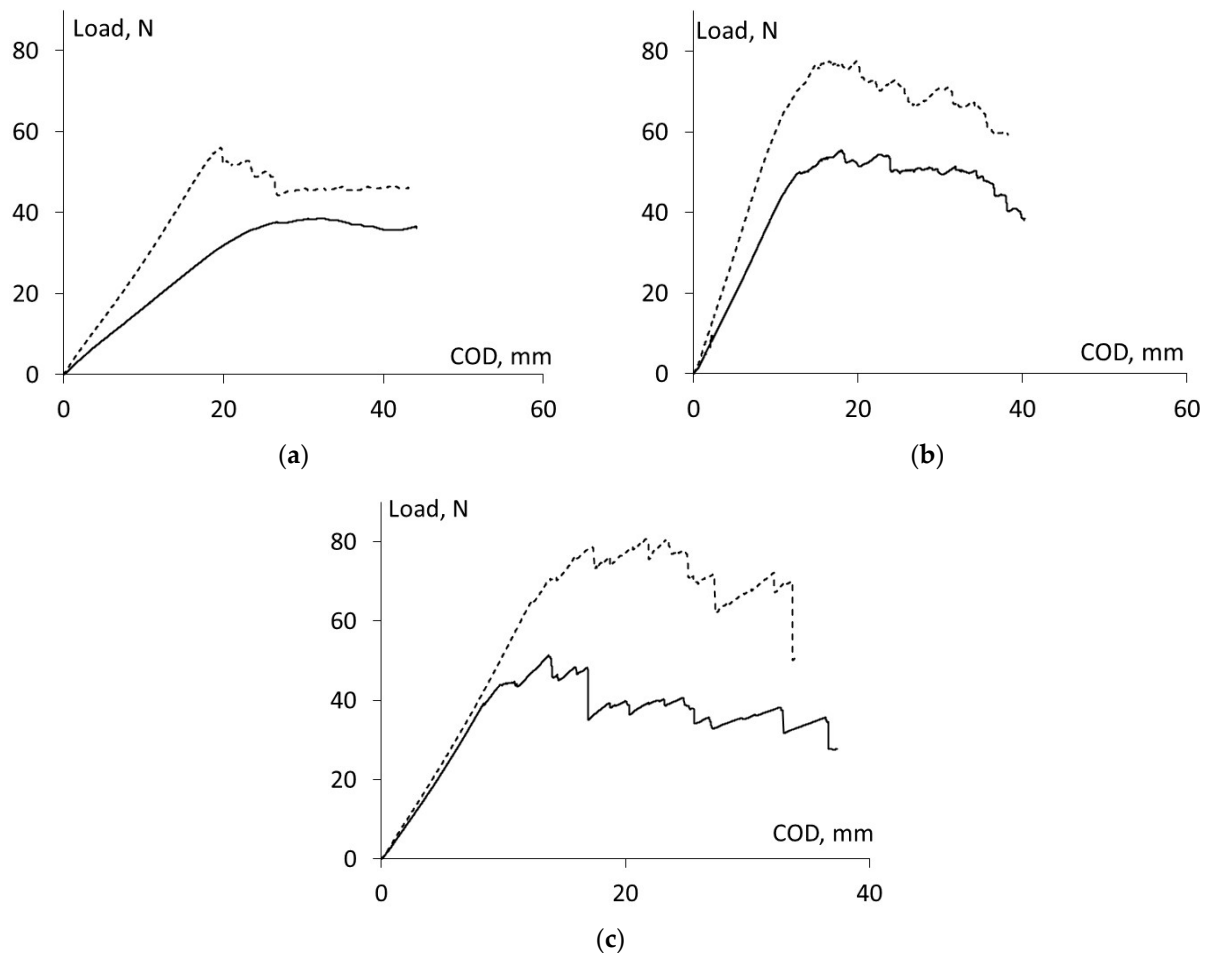


Figure 7. The representative load-COD curves from the DCB test of the neat (solid line) and HCTP-modified (dotted line) of glass (a), basalt (b), and carbon (c) FRC samples.

The critical loads P_c in load–COD curves of the above laminates are summarized in Figure 8a. The results for the fracture toughness evaluated by Equation (1) for all FRCs impregnated with the neat and HCTP-modified epoxy are shown in Figure 8b. According

to the results provided in Figure 8a, the effect of HCTP on the critical load of glass, carbon, and basalt FRCs was 38, 27, and 57%, respectively. Moreover, adding HCTP to glass, basalt, and carbon FRCs led to relative changes in the interlaminar fracture toughness of these composites by 8, 8, and 66%, respectively (see Figure 8b). It should be noted that adding HCTP improved the interlaminar properties of all FRCs studied, which can be explained by the matrix toughening and improved fiber–matrix interface, leading to enhanced mechanical performance and reliability in various applications.

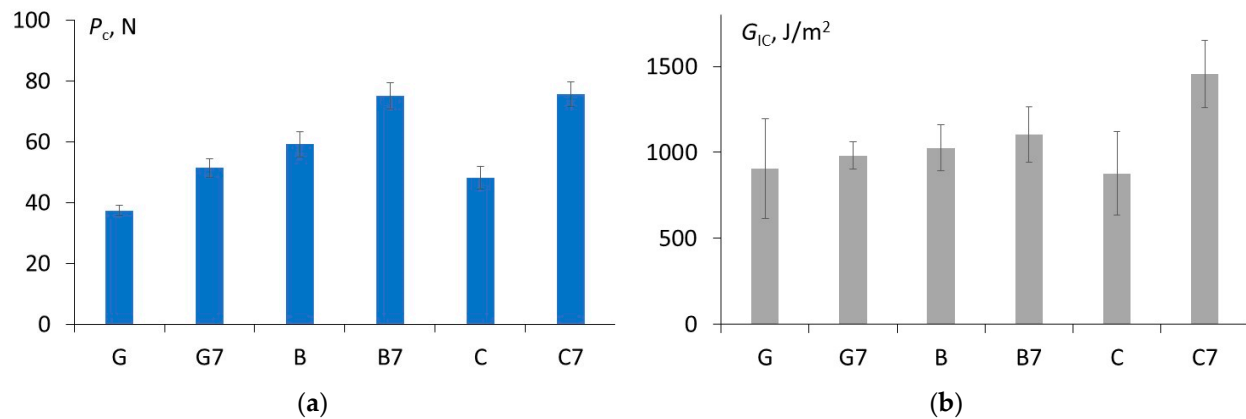


Figure 8. The critical load (a) and interlaminar fracture toughness (b) for the neat and HCTP-modified (7.2 wt.% in the epoxy matrix) glass (G and G7), basalt (B and B7), and carbon (C and C7) FRC samples.

In this case, selecting the most optimal fiber reinforcement for HCTP-modified composites is difficult. According to Figure 8, basalt and carbon FRC demonstrate excellent mechanical properties and can be chosen for applications requiring specific fire-retardant and mechanical properties.

4. Conclusions

The results of tensile tests showed that the mechanical properties (tensile strength and maximal deformation) significantly decreased with adding HCTP. At the same time, the elastic modulus was almost the same.

The after-flame time was significantly reduced at 9.5 wt.% of HCTP. The epoxy samples were entirely burned during this after-flame period, while the epoxy samples containing HCTP had a flame that stopped after the after-flame period, keeping the total length of material samples around 6–9 cm.

The most effective HCTP content, estimated based on tensile and fire-resistant properties tested, was 7.2 wt.% and was used to impregnate FRCs. By comparison of all HCTP-modified FRC (glass, basalt, and carbon), carbon FRC demonstrated the highest mechanical properties for the flexural and interlaminar fracture toughness tests. Nevertheless, basalt FRC was close to carbon FRC with approx. 20–30% lower mechanical characteristics for the case of HCTP-modified composites. The lowest mechanical properties were obtained for glass FRC. The effect of HCTP addition on the flame-retardant properties of basalt and glass FRCs was higher than that of carbon FRC.

The test results proved that basalt FRC with HCTP modification is a valuable alternative to composites with conventional fiber reinforcement, allowing excellent mechanical and flame-retardant properties.

Author Contributions: Conceptualization, T.G.-K.; methodology, T.G.-K. and S.V.; validation, T.G.-K., S.V. and A.A.; formal analysis, T.G.-K., J.S., O.V. and S.V.; investigation, T.G.-K., S.V., O.V. and J.S.; resources, A.A., V.Š., D.R. and G.V.; data curation, T.G.-K., S.V., O.V. and J.S.; writing—original draft preparation, T.G.-K., S.V., V.Š. and A.A.; writing—review and editing, T.G.-K., S.V. and A.A.; visualization, T.G.-K.; supervision, T.G.-K.; project administration, T.G.-K., D.R. and G.V.;

funding acquisition, D.R. and G.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the ERDF project “Development of fire resistant composite materials and their production technology in plan”, grant No. S-02-014-K-0093 (Lithuania).

Data Availability Statement: Data are available on request.

Conflicts of Interest: Vladimir Špaček was employed by the company SYNPO. Dalius Raškinis and Gediminas Vogonis were employed by the company Composite Aviation. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Lv, Y.F.; Thomas, W.; Chalk, R.; Singamneni, S. Flame retardant polymeric materials for additive manufacturing. *Mater. Today Proc.* **2020**, *33*, 5720–5724. [\[CrossRef\]](#)
2. Glaskova-Kuzmina, T.; Dejus, D.; Jātnieks, J.; Kruuv, P.-P.; Lancere, L.; Kobenko, S.; Sarakovskis, A.; Zolotarjovs, A. Flame-retardant and tensile properties of the polyamide-12 processed by selective laser sintering. *J. Compos. Sci.* **2022**, *6*, 185. [\[CrossRef\]](#)
3. Seraji, S.M.; Gan, H.; Swan, S.R.; Varley, R.J. Phosphazene as an effective flame retardant for rapid curing epoxy resins. *React. Funct. Polym.* **2021**, *164*, 104910. [\[CrossRef\]](#)
4. Chai, M. Flammability Performance of Bio-Derived COMPOSITE Materials for Aircraft Interiors. Ph.D. Thesis, The University of Auckland, Auckland, New Zealand, 2014.
5. Kim, N.K.; Dutta, S.; Bhattacharyya, D. A review of flammability of natural fibre reinforced polymeric composites. *Compos. Sci. Technol.* **2018**, *162*, 64–78. [\[CrossRef\]](#)
6. Shi, X.-H.; Li, X.-L.; Li, Y.-M.; Li, Z.; Wang, D.Y. Flame-retardant strategy and mechanism of fiber reinforced polymeric composite: A review. *Compos. B Eng.* **2022**, *233*, 109663. [\[CrossRef\]](#)
7. Dasari, A.; Yu, Z.-Z.; Cai, G.-P.; Mai, Y.-W. Recent developments in the fire retardancy of polymeric materials. *Prog. Polym. Sci.* **2013**, *38*, 1357–1387. [\[CrossRef\]](#)
8. Suihkonen, R.; Nevalainen, K.; Orell, O.; Honkanen, M.; Tang, L.; Zhang, H.; Zhang, Z.; Vuorinen, J. Performance of epoxy filled with nano- and micro-sized magnesium hydroxide. *J. Mater. Sci.* **2012**, *47*, 1480–1488. [\[CrossRef\]](#)
9. Tarasov, I.V.; Oboishchikova, A.V.; Borisov, R.S.; Kireev, V.V.; Sirotnin, I.S. Phosphazene-containing epoxy resins based on bisphenol F with enhanced heat resistance and mechanical properties: Synthesis and properties. *Polymers* **2022**, *14*, 4547. [\[CrossRef\]](#)
10. Yang, G.; Wu, W.-H.; Wang, Y.-H.; Jiao, Y.-H.; Lu, L.-Y.; Qu, H.-Q.; Qin, X.-Y. Synthesis of a novel phosphazene-based flame retardant with active amine groups and its application in reducing the fire hazard of epoxy resin. *J. Hazard. Mater.* **2019**, *366*, 78–87. [\[CrossRef\]](#)
11. Huo, S.; Song, P.; Yu, B.; Ran, S.; Chevali, V.S.; Liu, L. Phosphorus-containing flame retardant epoxy thermosets: Recent advances and future perspectives. *Prog. Polym. Sci.* **2021**, *114*, 101366. [\[CrossRef\]](#)
12. Yang, S.; Wang, J.; Huo, S.; Wang, J.; Tang, Y. Synthesis of a phosphorus/nitrogen-containing compound based on maleimide and cyclotriphosphazene and its flame-retardant mechanism on epoxy resin. *Polym. Degrad. Stab.* **2016**, *126*, 9–16. [\[CrossRef\]](#)
13. Gaifutdinov, A.M.; Andrianova, K.A.; Amirova, L.M.; Milyukov, V.A.; Zagidullin, A.A.; Amirov, R.R. Low-flammability carbon fiber reinforced composites based on low-viscosity phosphorus-containing epoxy binders for transfer molding methods. *Mater. Today Commun.* **2024**, *40*, 109340. [\[CrossRef\]](#)
14. Patel, P.; Hull, T.R.; Lyon, R.E.; Stoliarov, S.I.; Walters, R.N.; Crowley, S.; Safronava, N. Investigation of the thermal decomposition and flammability of PEEK and its carbon and glass-fibre composites. *Polym. Degrad. Stab.* **2011**, *96*, 12–22. [\[CrossRef\]](#)
15. Chen, D.; Sun, G.; Meng, M.; Jin, X.; Li, Q. Flexural performance and cost efficiency of carbon/basalt/glass hybrid FRP composite laminates. *Thin. Wall. Struct.* **2019**, *142*, 516–531. [\[CrossRef\]](#)
16. Asadi, A.; Baaij, F.; Mainka, H.; Rademacher, M.; Thompson, J.; Kalaitzidou, K. Basalt fibers as a sustainable and cost-effective alternative to glass fibers in sheet molding compound (SMC). *Compos. B Eng.* **2017**, *123*, 210–218. [\[CrossRef\]](#)
17. López de Vergara, U.; Sarrionandia, M.; Gondra, K.; Aurkekoetxea, J. Impact behaviour of basalt fibre reinforced furan composites cured under microwave and thermal conditions. *Compos. B Eng.* **2014**, *66*, 156–161. [\[CrossRef\]](#)
18. Diniță, A.; Ripeanu, R.G.; Ilincă, C.N.; Cursaru, D.; Matei, D.; Naim, R.I.; Tănase, M.; Portoacă, A.I. Advancements in Fiber-Reinforced Polymer Composites: A Comprehensive Analysis. *Polymers* **2024**, *16*, 2. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Lopresto, V.; Leone, C.; De Iorio, I. Mechanical characterization of basalt fibre reinforced plastic. *Compos. B Eng.* **2011**, *42*, 717–723. [\[CrossRef\]](#)
20. Balaji, K.V.; Shirvanimoghaddam, K.; Rajan, G.S.; Ellis, A.V.; Naebe, M. Surface treatment of basalt fiber for use in automotive composites. *Mater. Today Chem.* **2020**, *17*, 100334. [\[CrossRef\]](#)
21. Landucci, G.; Rossi, F.; Nicolella, C.; Zanelli, S. Design and testing of innovative materials for passive fire protection. *Fire Safety J.* **2009**, *44*, 1103–1109. [\[CrossRef\]](#)
22. Mouritz, A.P.; Mathys, Z.; Gibson, A.G. Heat release of polymer composites in fire. *Compos. A Appl. Sci. Manuf.* **2006**, *37*, 1040–1054. [\[CrossRef\]](#)

23. Bhat, T.; Chevali, V.; Liu, X.; Feih, S.; Mouritz, A. Fire structural resistance of basalt fibre composite. *Compos. A Appl. Sci. Manuf.* **2015**, *71*, 107–115. [[CrossRef](#)]
24. Dhand, V.; Mittal, G.; Rhee, K.Y.; Park, S.-J.; Hui, D. A short review on basalt fiber reinforced polymer composites. *Compos. B Eng.* **2015**, *73*, 166–180. [[CrossRef](#)]
25. Epoxy Resin EpikoteMGS LR 285, Hexion. Available online: <https://www.havel-composites.com/en/products/epoxy-resin-l-285-mgs-7-2575> (accessed on 17 June 2024).
26. Hardener Epikure MGS LH 285, Hexion. Available online: <https://www.r-g.de/en/art/110119> (accessed on 17 June 2024).
27. BAS UNI 350. Basaltex. Available online: <https://www.basaltex.com/products/multi-axial-fabrics> (accessed on 17 June 2024).
28. Glass Fabric AEROGLOSS 390 g/m² Twill 2/2, Havel. Available online: <https://www.havel-composites.com/en/products/glass-fabric-aeroglass-390g-m2-twill-2-2-2508-9478> (accessed on 17 June 2024).
29. ECC. Carbon Fabric (Style 442-5 Aero, Twill Weave). Available online: <https://www.r-g.de/en/art/190225> (accessed on 17 June 2024).
30. ISO 527-1:2019; Plastics—Determination of Tensile Properties. Part 1: General Principles. International Organization for Standardization: Geneva, Switzerland, 2019. Available online: <https://www.iso.org/standard/75824.html> (accessed on 18 June 2024).
31. ASTM D3801; Standard Test Method for Measuring the Comparative Burning Characteristics of Solid Plastics in a Vertical Position. ASTM International: West Conshohocken, PA, USA, 2020. Available online: <https://www.astm.org/d3801-20a.html> (accessed on 17 June 2024).
32. ASTM D790; Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials. ASTM International: West Conshohocken, PA, USA, 2017. Available online: <https://www.astm.org/d0790-17.html> (accessed on 17 June 2024).
33. Glaskova-Kuzmina, T.; Aniskevich, A.; Papanicolaou, G.; Portan, D.; Zotti, A.; Borriello, A.; Zarrelli, M. Hydrothermal aging of an epoxy resin filled with carbon nanofillers. *Polymers* **2020**, *12*, 1153. [[CrossRef](#)] [[PubMed](#)]
34. Glaskova-Kuzmina, T.; Zotti, A.; Borriello, A.; Zarrelli, M.; Aniskevich, A. Basalt fibre composite with carbon nanomodified epoxy matrix under hydrothermal ageing. *Polymers* **2021**, *13*, 532. [[CrossRef](#)] [[PubMed](#)]
35. ASTM D5528; Standard Test Method for Mode I Interlaminar Fracture Toughness of Unidirectional Fiber-Reinforced Polymer Matrix Composites. ASTM International: West Conshohocken, PA, USA, 2022. Available online: <https://www.astm.org/d5528-13.html> (accessed on 17 June 2024).
36. Glaskova-Kuzmina, T.; Stankevics, L.; Tarasovs, S.; Sevcenko, J.; Špaček, V.; Sarakovskis, A.; Zolotarjovs, A.; Shmits, K.; Aniskevich, A. Effect of core-shell rubber nanoparticles on the mechanical properties of epoxy and epoxy-based CFR. *Materials* **2022**, *15*, 7502. [[CrossRef](#)] [[PubMed](#)]
37. Kim, Y.-H.; Baek, J.J.; Chang, K.C.; Lim, H.S.; Choi, M.-S.; Koh, W.-G.; Shin, G. Influence of Thiol-Functionalized Polysilsesquioxane/Phosphorus Flame-Retardant Blends on the Flammability and Thermal, Mechanical, and Volatile Organic Compound (VOC) Emission Properties of Epoxy Resins. *Polymers* **2024**, *16*, 842. [[CrossRef](#)] [[PubMed](#)]
38. Niu, M.; Zhang, Z.; Wei, Z.; Wang, W. Effect of a Novel Flame Retardant on the Mechanical, Thermal and Combustion Properties of Poly(Lactic Acid). *Polymers* **2020**, *12*, 2407. [[CrossRef](#)]
39. Liu, Q.; Wang, D.; Li, Z.; Li, Z.; Peng, X.; Liu, C.; Zhang, Y.; Zheng, P. Recent Developments in the Flame-Retardant System of Epoxy Resin. *Materials* **2020**, *13*, 2145. [[CrossRef](#)]
40. Toldy, A.; Szolnoki, B.; Marosi, G. Flame retardancy of fibre-reinforced epoxy resin composites for aerospace applications. *Polym. Degrad. Stab.* **2011**, *96*, 371–376. [[CrossRef](#)]
41. Parveez, B.; Kittur, M.I.; Badruddin, I.A.; Kamangar, S.; Hussien, M.; Umarfarooq, M.A. Scientific Advancements in Composite Materials for Aircraft Applications: A Review. *Polymers* **2022**, *14*, 5007. [[CrossRef](#)] [[PubMed](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.