

# Development of natural fibre reinforced flame retarded epoxy resin composites

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## Abstract

Natural hemp fabric reinforced epoxy resin composites were prepared in flame retarded form. Fabrics were treated in three ways: the first method involved the immersion of preheated fabric into cold phosphoric acid solution (allowing penetration into the capillaries of the fibres) and subsequent neutralization, the second way was a reactive modification carried out with an aminosilane-type coupling agent, while the third treatment combined the sol-gel surface coating with the first method. The introduction of P-content into the reinforcing fibres resulted in decreased flammability of not only the hemp fabrics, but also of the flame retardancy of epoxy composites, comprising it changed advantageously. By applying amine-type phosphorus-containing curing agent (TEDAP) in combination with the treated fabrics, V-0 UL-94 rating was achieved. Composites of unexpectedly improved static and dynamic mechanical properties could be prepared only when the simple phosphorous fibre treatment and reactive flame retardancy was combined.

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## **1 Introduction**

Automotive industry and more recently even the aircraft producers require composites of renewable and/or biodegradable structural materials; thus development in this field is urgently needed. The introduction of natural fabric reinforcement instead of man-made fibres in the thermosetting matrices, such as epoxy resins, results in lower weight, lower density and lower costs accompanied with the renewability and biodegradability (in bioepoxy matrix) [1]. These advantages make biofibres attractive substitutes of the commonly applied synthetic carbon, glass or aramid fibres [2]. However, a major drawback of natural fibre reinforced composites is the relatively poor interaction at the fibre–matrix interphase [3]. To improve adhesion, the natural fibres are usually surface treated [4]. With the alkali treatment of natural fibres [3,5], improvement in the mechanical properties of epoxy composites was reported indicating better adhesion between the matrix and the treated fibres. The alkali treatment can also be combined with different silanes [6]. The silanization with silanes having reactive functionalities (e.g. amine) can result in covalent bonds between the fibre and the matrix, which also lead to improved mechanical properties [7].

When the polymer composites are used to replace metallic structural units, their flammability is one of the main limits of their application. Biofibre reinforcements are flammable, thus the heat release of natural fibre-reinforced composites is even higher than that of the inorganic fibre (e.g. glass or carbon) reinforced ones [8]. To overcome this fact, an efficient flame retardant method has to be developed to extend the applicability of the natural fibre reinforced composites. For decreasing the flammability of these fibres, and thus reducing the so-called

candlewick effect, several inorganic phosphorous compounds have already been applied (phosphoric acid, ammonium phosphates [9,10,11]) in thermoplastic composites. Several papers deal with the flame retardancy of thermoplastic biocomposites by incorporating flame retardants (FRs) into the matrix [12,13,14]. Introduction of FR into the composites is mostly accompanied with the deterioration of the mechanical properties [15]. This problem can be solved or moderated by using flame retarded biofibres combined with matrix containing flame retardant additive, by which way the polymer concentration of the matrix and thus its strength can be maintained [16,17,18].

In this work the idea of flame retarded reinforcement was adapted to epoxy resin composites, by combining it with P-containing crosslinking agent as reactive flame retardant in the matrix. Hemp fabrics were selected for forming flame retarded reinforcement and a P-containing amine [19,20] was applied as curing agent in the FR matrix composites.

## **2 Materials and methods**

### *2.1 Materials*

The epoxy resin matrix consisted of epoxy component of IpoX MR 3016 (tetraglycidyl ether of pentaerythritol, epoxy equivalent: 156–170) type applied with IpoX MH 3122 curing agent (3,3'-dimethyl-4,4'-diamino-dicyclohexyl-methane, amine number 464–490 mg KOH/g) supplied by IPOX Chemicals Kft. (Hungary). A phosphorus-containing amine-type curing agent (TEDAP) was applied as flame retardant [19,20]. As reinforcement twill woven hemp fabrics (surface mass: 580 g/m<sup>2</sup>), received from the Institute of Natural Fibres and Medicinal Plants (Poznan, Poland), were used. Fabrics were treated with phosphoric acid (75%, Azúr Vegyszerbolt Kft., Hungary), ammonium hydroxide (25% solution) and Geniosil GF-9 (*N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane), provided by Wacker Chemie AG (Germany).

## 2.2 *Fabric treatment*

Twill woven hemp fabrics (HF) were washed with water to remove dust and impurities and then dried in oven at 70 °C for 12 h. The fibres were treated in three ways in order to render them flame retardant. In the first case, the so-called thermotex procedure [21] was applied. The high-temperature treatment of the fabrics allows better absorption of the treating solution to the capillaries of the fabric. For this purpose, the fabrics were preheated at 120 °C for 2 h, and then immersed in cold 17 mass% phosphoric acid solution for 5 min. The ratio of fabric to phosphoric acid solution was 1 g to 10 ml. As the acid may induce long-term degradation in cellulose fibre structure, it was neutralized by immersing the fabrics in 5% ammonium hydroxide solution. The excess of the treating and neutralizing solutions were removed by pressing the fabrics by a foulard. After treatment, the fabrics were dried in air. The amount of the absorbed phosphorus was determined by the mass increase of the treated fibres and by elemental analysis using energy-dispersive X-ray spectroscopy (see section 2.3.3). The mass increase of the THF fibres was 8 mass%, which means the absorption of 1.7 mass% of P (1.65 mass% by elemental analysis).

In the other case, sol-gel treatment of the fabrics was carried out using Geniosil GF-9 amine-type silane. The fabrics were immersed in 10 mass% toluene solution of aminosilane. The ratio of fabric to the aminosilane solution was 1 g to 10 ml. After the addition of the catalyst (3 droplets of dibutyl tin dilaurate to 100 ml solution), the fabrics were refluxed at 110 °C for 6 h. After cooling to room temperature, the excess was removed by foulard, and then the fabrics were dried in an oven at 130 °C, so that the formation of chemical bonds between the fabric and the silane can occur [17,22]. The amount of the adsorbed/chemically bound Si was determined by the mass increase, which arose to 63.6%, so the Si-content of the fabrics was set to 4.9 mass%.

The third treatment was the combination of the above-mentioned thermotex and sol-gel treatments. In this case, after the treatment with Geniosil GF-9, thermotex treatment with phosphoric acid solution was carried out. As only the fibres, and not the silane compounds can absorb the neutralized phosphoric acid, the mass increase after the thermotex treatment arose to further 4.8 mass%, which means that the silylation did not affect the effectiveness of the thermotex treatment. The P-content of the fibres/fabric was set to 1.3 mass% (1.35 mass% by elemental analysis) and the Si-content to 4.9 mass%.

## 2.3 *Methods*

### 2.3.1 *Preparation of samples*

The epoxy and curing agent amine components were mixed at room temperature in a glass beaker in order to obtain a homogenous mixture. Composites using twill woven hemp fabrics were prepared using the hand lay-up technique; the fibre content was kept at 30%. The fibre-reinforcement consisted of two plies of twill woven hemp fabric, resulting in 4 mm-thick sheets. The prepared composites were cured at room temperature for 24 h, followed by a post-curing at 80 °C for additional 4 h. The specimens were cut to appropriate dimensions with diamond disc.

### 2.3.2 *Thermal analysis*

Setaram Labsys TG DTA/DSC instrument was used for thermogravimetric analysis (TGA). TGA measurements of biofibres were carried out in the temperature range of 25–500 °C at a heating rate of 10 °C/min under nitrogen gas flow rate of 30 ml/min. About 15–20 mg of sample was used in each test.

### 2.3.3 *Scanning electron microscopy*

Scanning electron microscopic (SEM) images of the biofibres and the fracture surfaces of the composites were taken using a JEOL JSM-5500 LV type apparatus (JEOL Ltd., Akishima, Tokyo, Japan). The samples were coated with gold–palladium alloy before examination to prevent charge build-up on their surface. The used SEM apparatus is equipped with EDS (energy-dispersive X-ray spectroscopy) unit capable of performing elemental analysis of the samples.

#### 2.3.4 *Flame retardant characterization*

The fire resistance of the matrices and twill woven hemp fabric reinforced composites was characterized by *limiting oxygen index* measurements (LOI, according to ASTM D2863). The LOI value expresses the lowest oxygen to nitrogen ratio where specimen combustion is still self-supporting.

Standard UL-94 *flammability tests* (according to ASTM D3081 and ASTM D635, respectively) were also carried out. UL-94 classification is used to determine ignitability, dripping and flame spreading rates.

The modified fabrics were subjected to comparative *Mass Loss type (ML) cone calorimeter tests* in an instrument made by FTT Inc. One ply of the different treated and untreated fibres (approx. 6 g) was exposed to a constant heat flux of 50 kW/m<sup>2</sup> and ignited with a spark igniter. For the testing of the composites, *oxygen consumption cone calorimetric measurements* according to ISO standard 5660 were carried out, with the same conditions.

#### 2.3.5 *Mechanical characterization*

The tensile properties of the reinforcing fabrics were determined both at micro and macro scale. For the *micro-scale measurements*, 50 mm-long elemental fibres were prepared from

the different (treated and untreated fabrics) in order to determine their tensile strength. The measurements on at least 30 elemental fibres were carried out on a Zwick Z005 instrumented tester (25 mm grip distance and 2 mm/min cross-head speed). The prepared fibres were mounted in a paper frame. After placing to the tensile tester, the vertical parts of the paper frame were cut off, so that the fibres could be tested. For the determination of the cross-section (considered as a circle), the diameter of the prepared fibres was measured at 5 points on the whole length using Olympus BX 51M type optical microscope with 20x objective, equipped with C-5060 CAMEIDA type digital camera and AnalySIS image processing software.

In the case of *macro-scale measurement*, the fabrics were subjected to strip tensile tests using Zwick Z020 instrumented tensile tester with a grip distance of 100 mm and 50 mm width. At least 5 specimens were tested with a cross-head speed of 5 mm/min, according to the ISO 13934-1:2013 standard. The applied force was parallel to the chain direction of the fabrics.

Comparative static *tensile tests* were performed on rectangular specimens of 10 mm × 150 mm (width × length) using a Zwick Z020 universal testing machine with a cross-head speed of 2 mm/min (according to the ISO 527-4:1997 standard).

The *flexural strength* was determined according to ISO 178:2001, using rectangular specimens of 10 mm × 4 mm (width × thickness). The cross-head speed was set to 5 mm/min; the span was 64 mm (16 × thickness).

Instrumented *falling weight impact (IFWI) tests* were performed using a Fractovis 6785 instrument (Ceast, Pianezza, Italy) with the following settings: maximal energy: 228.64 J, diameter of the dart: 20 mm, diameter of the support rig: 40 mm, weight of the dart: 23.62 kg and drop height: 1 m (according to the ISO 6603-2:2001 standard). Square specimens with

dimensions of 70 mm × 70 mm were subjected to IFWI tests. From the IFWI tests the thickness related perforation energy ( $E_p$  [J/mm]) was determined.

### 2.3.6 Determination of the fibre-matrix adhesion

**Microbond tests** were carried out in the following way in order to determine the interfacial shear strength (IFSS) between the fibres and the matrices: matrix droplets were placed on the elemental fibres prepared as described above, and the shear strength was determined using Equation 1.

$$\tau = \frac{F_{max}}{d_f \cdot \pi \cdot L_0} \quad (1)$$

where  $F_{max}$  is the maximum force measured during the pull out of the fibre,  $d_f$  is the diameter of the elemental fibre and  $L_0$  is the length of the microbond area. The measurement was carried out using a microbond device fixed onto a Zwick Z005 instrumented tester [23], with a test speed of 2 mm/min.

**Contact angle measurement** of deionized water droplets on the surface of the matrices was carried out according to ASTM D5946. Droplets of 5  $\mu$ L were placed on the surface of the matrix specimens; and at least 10 angles were measured. The contact angles ( $\theta$ ) were determined using Equation 2.

$$\theta = 2 \tan^{-1} \frac{h}{r} \quad (2)$$

where  $h$  is the height of the droplet and  $r$  is the half of its width.

## 3 Results and discussion

### 3.1 Characterization of the treated fabrics

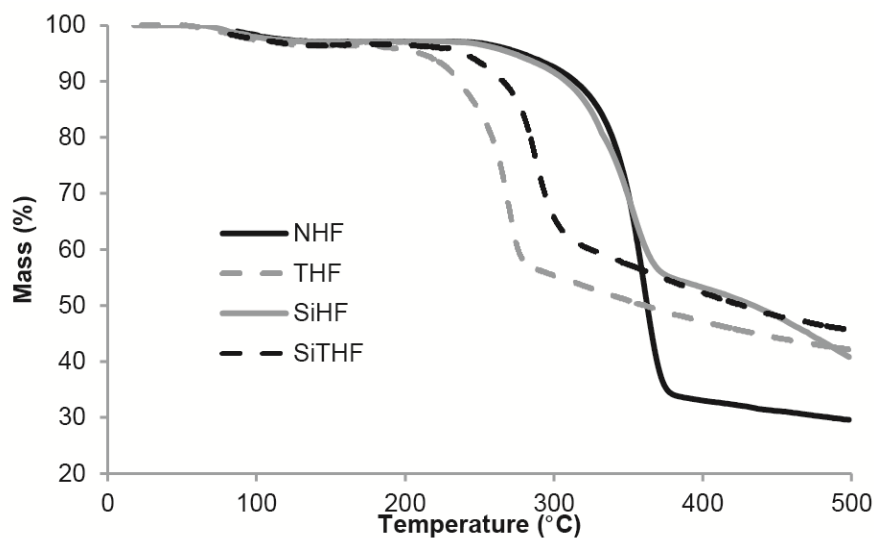
The applied twill woven hemp fabrics were treated in three ways (described in details in 2.2): thermotex treatment (THF: thermotex-treated hemp fabric) and sol–gel treatment with GF9 aminosilane (SiHF: silane treated hemp fabric), and sol–gel treatment followed by thermotex



treatment (SiTHF: silane and thermotex-treated hemp fabric). The effect of the applied modifications on the thermal stability and flammability of the fibres, compared to the unmodified fabric (NHF: non-modified hemp fabric), was tested by TGA and ML cone calorimetry.

### 3.1.1 TGA

TGA measurements were carried out under nitrogen atmosphere in order to determine the thermal stability of the treated fibres. Although thermal stability of the fibres is irrelevant during the composite formation at room temperature (see in 2.3.1), it is valuable information for the understanding of their mode of action on the flammability of the composites. The recorded TGA curves of the different fabrics are plotted in **Figure 1**, while additional data are summarized in **Table 1**.



**Figure 1** TGA curves of the different treated and untreated fabrics

(NHF: non-treated hemp fabric, THF: thermotex treated fabric, SiHF: sol-gel treated fabric, SiTHF: thermotex and sol-gel treated fabric)

The adsorbed water content, released at about 100 °C, was independent of the surface treatment of the fabrics, and was measured as 3% in each case, which is the first weight loss step on the curves. The thermal degradation of the different fabrics showed significant difference. The untreated (NHF) fabric and the sol–gel treated (SiHF) fabric were the most thermally stable, their degradation starts at about 270 °C, and is only slightly affected by the treatment [24]. The thermotex treatment (applying ammonium phosphate) decreased the initial degradation temperature by more than 60 °C, as expected [9,25]. The SiTHF fabric showed an intermediate range of decomposition, which can be ascribed to the protecting effect of the sol–gel treatment on the fabrics, partially avoiding the acidic hydrolysis of cellulose [16,26,27]. This way, the temperature corresponding to 5% mass loss increased by 30 °C, compared to THF (from 210 °C to almost 240 °C).

**Table 1** TGA data of the different fabrics

(NHF: non-treated hemp fabric, THF: thermotex treated fabric, SiHF: sol–gel treated fabric, SiTHF: thermotex and sol–gel treated fabric)

fibre	T <sub>-5%</sub> (°C)	T <sub>-50%</sub> (°C)	dTG <sub>max</sub> (%/°C)	T <sub>dTGmax</sub> (°C)	residue (%)
NHF	278.0	362.5	1.7	360.7	29.6
THF	210.0	361.3	1.4	269.6	42.2
SiHF	272.0	434.0	0.8	352.3	40.8
SiTHF	239.5	426.7	1.1	287.5	45.7

T<sub>-5%</sub>: temperature at 5% mass loss; T<sub>-50%</sub>: temperature at 50% mass loss, dTG<sub>max</sub>: maximum mass loss rate; T<sub>dTGmax</sub>: temperature belonging to dTG<sub>max</sub>

The temperatures belonging to the maximal mass loss rates of the fabrics (**Table 1**) showed similar tendency to the beginning of the degradation (T<sub>-5%</sub>). Owing to the thermotex treatment with neutralized phosphoric acid, the main degradation of the THF fabric occurred at a temperature 90 °C lower than in the case of the unmodified and sol–gel treated fabrics (NHF





and SiHF). The decomposition rate was significantly lowered when the fabrics were treated: from 1.7%/°C in the case of the untreated NHF to 1.1%/°C for the SiTHF and 0.8%/°C for the SiHF that can be ascribed to the protective effect of Si, which, by reacting with the superficial –OH groups of the fibre, encumbers the dehydration of the cellulose structure, so retarding the thermal degradation. The  $T_{-50\%}$  increased significantly, by about 70 °C when sol–gel treatment was applied, indicating prolonged degradation. The amount of the residue increased considerably, when the fabrics were treated, but no remarkable difference (only 3–4.5%) was detected between the three types of treatments.

### 3.1.2 *Mass loss cone calorimetry*

In order to determine the effect of the different surface treatments on the macroscopic flammability characteristics of the fabrics, ML cone calorimetric measurements were performed. One ply of the fabrics was placed in the sample holder and ignited. The data recorded during burning are summarized in **Table 2**. The time to ignition (TTI) of the treated and untreated natural fibres was extremely short: the fabrics caught fire after 3 sec. When the combined treatment was applied (SiTHF), TTI showed fivefold increase to 15 sec, due to the protecting effect of the sol–gel treatment. The peak of heat release rate decreased when P-containing treatments were performed. Compared to the untreated (NHF) fibres, a drop from 68 kW/m<sup>2</sup> to 18 and 9 kW/m<sup>2</sup> was reached in the case of THF and SiTHF, respectively. The sol–gel treatment, applied alone, did not influence the fire behaviour of the hemp fabric.

**Table 2** Mass loss type cone calorimetric data of the different fibres

fibres	TTI (sec)	pHRR (kW/m <sup>2</sup> )	pHRR time (sec)	THR (MJ/m <sup>2</sup> )	residue (%)	residue description	residue photo
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NHF	3	68.1	35	5.55	5	yellowish white, fluffy	
THF	4	17.6	14	1.95	2	fluffy, charred black	
SiHF	6	62.0	34	5.64	15	fluffy, white	
SiTHF	15	8.5	62	1.39	40	consistent, charred black	

Comparing the residues of the burnt fibres after the cone calorimetric measurements, it can be observed that the incorporation of P into the fibres promoted the charring of the samples: the residues of the THF and SiTHF were black, while the untreated and only sol–gel treated fabrics burnt to yellowish white or white fluffy ash. The beneficial effect of the sol–gel treatment and the P–Si synergism can be seen comparing the residues of the treated fabrics: comparing to the residue of the THF fabric, the SiTHF-treated one is much more consistent.

### 3.2 Flame retardancy of the composites

Composites with reference (ref) and flame retarded (FR) matrices were prepared using natural (NHF), thermotex treated (THF) and sol–gel and thermotex treated (SiTHF) twill woven hemp fabrics. The P-content of the flame retarded matrix was chosen to be 2.5 mass%, to reach V-0 rating in UL-94 tests, according to previous studies of the authors [19,28]

### 3.2.1 LOI and UL-94

The untreated NHF reinforcement of the reference matrix (NHF-ref) resulted in a somewhat decreased LOI value (**Table 3**), due to the well-known candle-wick effect of the natural fibres [29]. This phenomenon could be overcome by the application of flame-retardant-treated fabrics: the LOI increased by 4% compared to the untreated fabric reinforced composite in the case of the thermotex treated fabric, while when the fabric with combined treatment was applied even better LOI value of 28% was reached for the composite with reference matrix. In the case of the UL-94 tests, the application of NHF as reinforcement slowed down the horizontal burning of the samples from 32 mm/min of the reference matrix to 18.2 mm/min. When treated fabrics were used, no horizontal burning rates were detected; however, the samples did not reach the V-categories as the flame reached the brace during the vertical test.

**Table 3** LOI and UL-94 results of the composites

matrix	reinforcement	LOI	UL-94*	P-content (%)
reference	-	23	HB (32.0)	0
	NHF	22	HB (18.2)	0
	THF	26	HB	0.51
	SiTHF	28	HB	0.39+ 1.47% Si
FR	-	29	V-0	2.5
	NHF	32	V-1	1.75
	THF	32	V-0	2.26
	SiTHF	32	V-0	2.14+ 1.47% Si

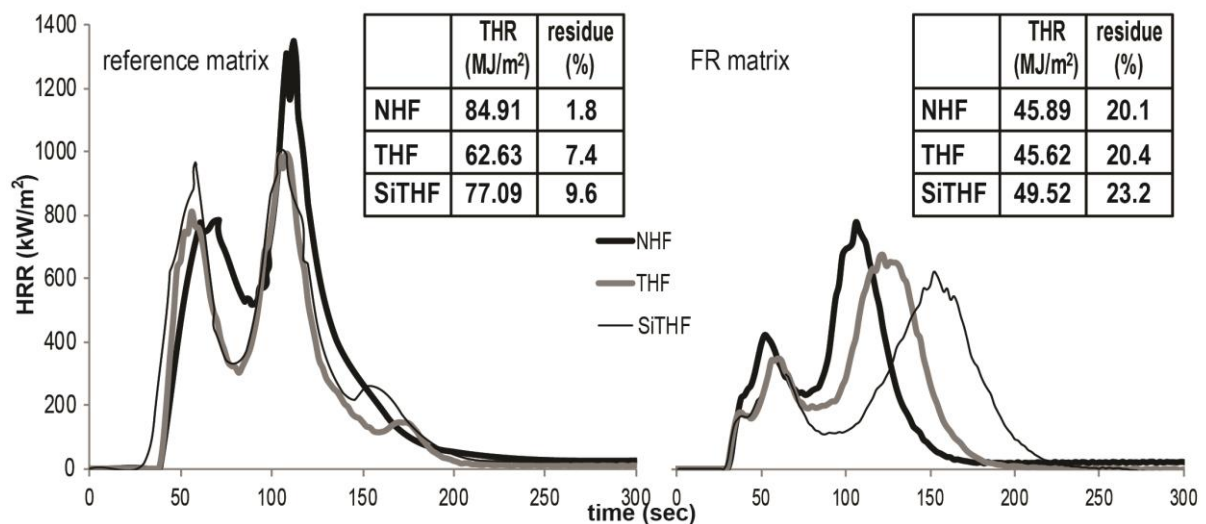
\* the horizontal burning rate is displayed in brackets, where it was measurable

When the matrix was flame-retarded (**Table 3**), the LOI value increased in all cases. With reinforcement an LOI of 32% was reached, independently of the treatment. The effect of the flame retardant curing agent covered the differences observed in the case of the composites

with reference matrix including the advantageous effect of Si. This can be attributed to the intense charring of the matrix, combined with the increased strength of the FR composites compared to the neat FR matrix, so that the charred residue was fixed at the top of the sample, further protecting the virgin polymer from the flame. The results confirm the earlier defined general rule of the necessity of at least 2% P to reach V-0 [30,31]. The application of 30 mass% untreated fabric as reinforcement decreased the overall P-content of the FR composite below 2 mass%, so the UL-94 rating was only V-1 in this case. When treated fabrics were applied with FR matrix, the P-content of the composite increased and V-0 rating was reached.

### 3.2.2 Cone calorimetric measurements of the composites

For modelling the macro-scale fire behaviour, the reference (ref) and flame retarded (FR) composites were investigated with oxygen consumption cone calorimeter applying external heat flux of  $50 \text{ kW/m}^2$ , equivalent to a trash-can-fire [32]. The HRR curves recorded during the measurements are plotted in **Figure 2**, separately for the reference and flame retarded matrices, for a better comparison.



**Figure 2** Cone calorimeter curves of the reference and flame retarded composites

Evaluating the heat release of the composites prepared with the reference matrix (left side of **Figure 2**), no significant difference could be determined between the effects of the treated fabrics. The first peak appeared 15 sec earlier, than in the case of the untreated fabric, as expected from the TGA measurements of the fabrics (see section 3.1.1). However, the maximal heat release was reached at about 110 sec for all the reference composites. The treated fabrics reduced the pHRR by about 25%, compared to the NHF-ref specimen, independently of the type of surface treatment.

The application of flame retardant (FR) matrix (right side of **Figure 2**) decreased the pHRR values by about 32–42%, compared to the reference matrix composites. The difference between the effect of the different fabric treatments (THF and SiTHF) is quite pronounced. In the case of THF-FR composite, the pHRR appeared 15 sec later than in the case of the NHF-FR composite, and its value decreased by 15%. With the application of the silylated-thermotex treated fabric (SiTHF-FR composite), further 10% decrease was observed in the peak of heat release, while the maximum was reached 45 sec later, compared to the reference fabric (NHF-FR composite). Considering the total heat release of the different flame retarded and reference composites (**Figure 2**), it can be seen that the modifications reduced the THR comparing to the reference (ref) matrix in different extent. This decrease was the most significant in the case of the THF-ref sample. The amount of the residues increased when the treated fabrics were applied with reference matrix. However, the increase of the amount of the charred residues with the application of flame retarded matrix was much more pronounced: the quantities in these cases were more than 10 times higher than in the case of NHF-ref composite, and almost the same for all FR composites. This phenomenon can be explained by the strongly charring character of the applied FR matrix [19], which overcomes the effect of the fabric treatments.

The smoke generation, CO and CO<sub>2</sub> emissions are important parameters of a fire, as the loss of visibility and toxic gas generation can hinder the escape from the fire. The average SEA (specific extinction area), CO and CO<sub>2</sub> emissions are summarized in **Table 4**.

**Table 4** Average SEA, CO and CO<sub>2</sub> emissions of the different composites

matrix	reinforcement	Average SEA (m <sup>2</sup> /kg)	Average CO (kg/kg)	Average CO <sub>2</sub> (kg/kg)
reference	NHF	457.19	0.0352	1.3534
	THF	432.02	0.0478	1.0508
	SiTHF	503.89	0.0501	1.2346
FR	NHF	224.70	0.0723	0.8948
	THF	282.19	0.0390	0.6530
	SiTHF	228.39	0.0309	0.6607

Considering the average CO production in the case of the reference matrix composites, the lowest value was measured for the NHF-ref sample, contrarily to the FR matrix composites, where the highest value corresponded to the NHF-reinforced composite. When both the matrix and the reinforcement are flame retarded (THF-FR and SiTHF-FR) the lowest average CO emission was measured, similarly to the CO<sub>2</sub> emission. Additionally, the CO<sub>2</sub> emissions of the FR matrix composites are significantly lower than those of the reference matrix composites.

The specific extinction area (SEA) describes the amount of smoke evolved per mass unit of volatile produced upon heating. From the data presented in **Table 4**, a significant drop of SEA can be observed comparing the reference and FR matrix composites. The FR composites show in average a 50% reduction of SEA, which allows longer time to escape in case of fire.

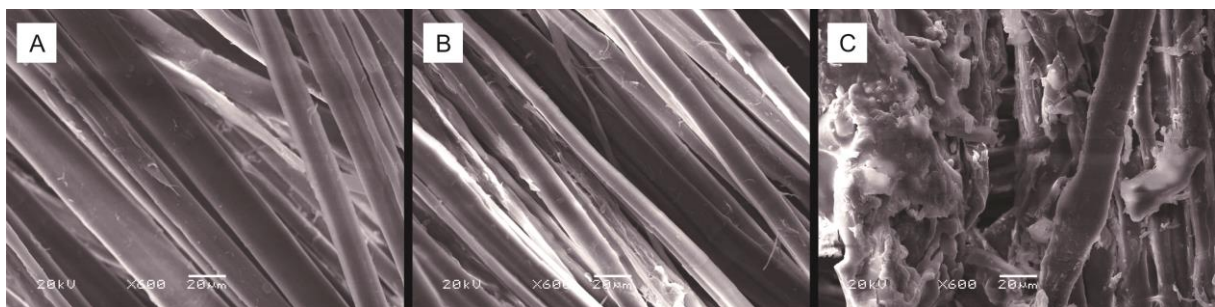
### 3.3 Mechanical characterization of the reinforcing fabrics



For the determination of the mechanical properties of the reference and flame retarded hemp fabric reinforced composites, the effect of the different treatments on the micro- and macroscale strength of the reinforcing fabrics was investigated as a first step.

### 3.3.1 Tensile strength of the elemental fibres

Elemental fibres were taken from the rowings composing the fabrics and mounted in a paper frame for the determination of the tensile properties. As it can be seen, the elemental fibres were easily separable in the case of the untreated (NHF) and THF treated fabrics (**Figure 3 A** and **B**). However, during the sol–gel treatment of the SiTHF fabrics, the forming silica not only covered the surface of the hemp fibres, but also attached them to each other (**Figure 3 C**); thus, elemental fibres could not be prepared for the tensile measurement.



**Figure 3** SEM micrographs of the fibres. A: NHF; B: THF; C: SiTHF (Magnification: 600x)

The results obtained after testing at least 30 elemental fibres of the non-modified (NHF) and the thermotex-treated (THF) fabrics, are summarized in **Table 5**.

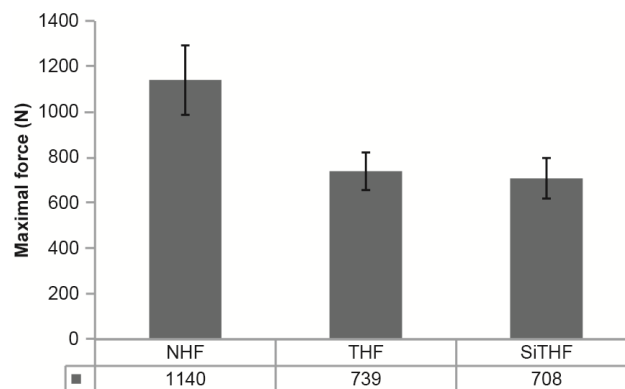
**Table 5** Tensile strengths of the elemental fibres

fibres	tensile strength (MPa)
NHF	$616.7 \pm 251.7$
THF	$449.6 \pm 213.2$

Because of the imperfectness of the natural fibres, and the big difference in the diameters of the single fibres, the deviation of the strengths is relatively high [23,33]. The decrease in the strength of the THF fibres was still significant. As the strength of the natural fibres strongly depends on the cellulose content [34], the hydrolysis caused by the acidic treatment of the fabric rendering it flame retardant resulted in decreased tensile strength. In order to avoid the hydrolysis, sol–gel treatment was applied; however, the effect of the treatment could not be determined due to the attachment of the elemental fibres.

### 3.3.2 Strip tensile properties of the fabrics

As single fibres could not be prepared from the sol–gel and thermotex-treated (SiTHF) fabric, strip tensile tests were performed in order to investigate the effect of this modification on the tensile properties of the fabrics. The specimens were cut to appropriate size containing the same number of rowings (22) in the direction of the loading. The measured maximal forces are plotted in **Figure 4**.



**Figure 4** Maximal forces measured for the different fabrics

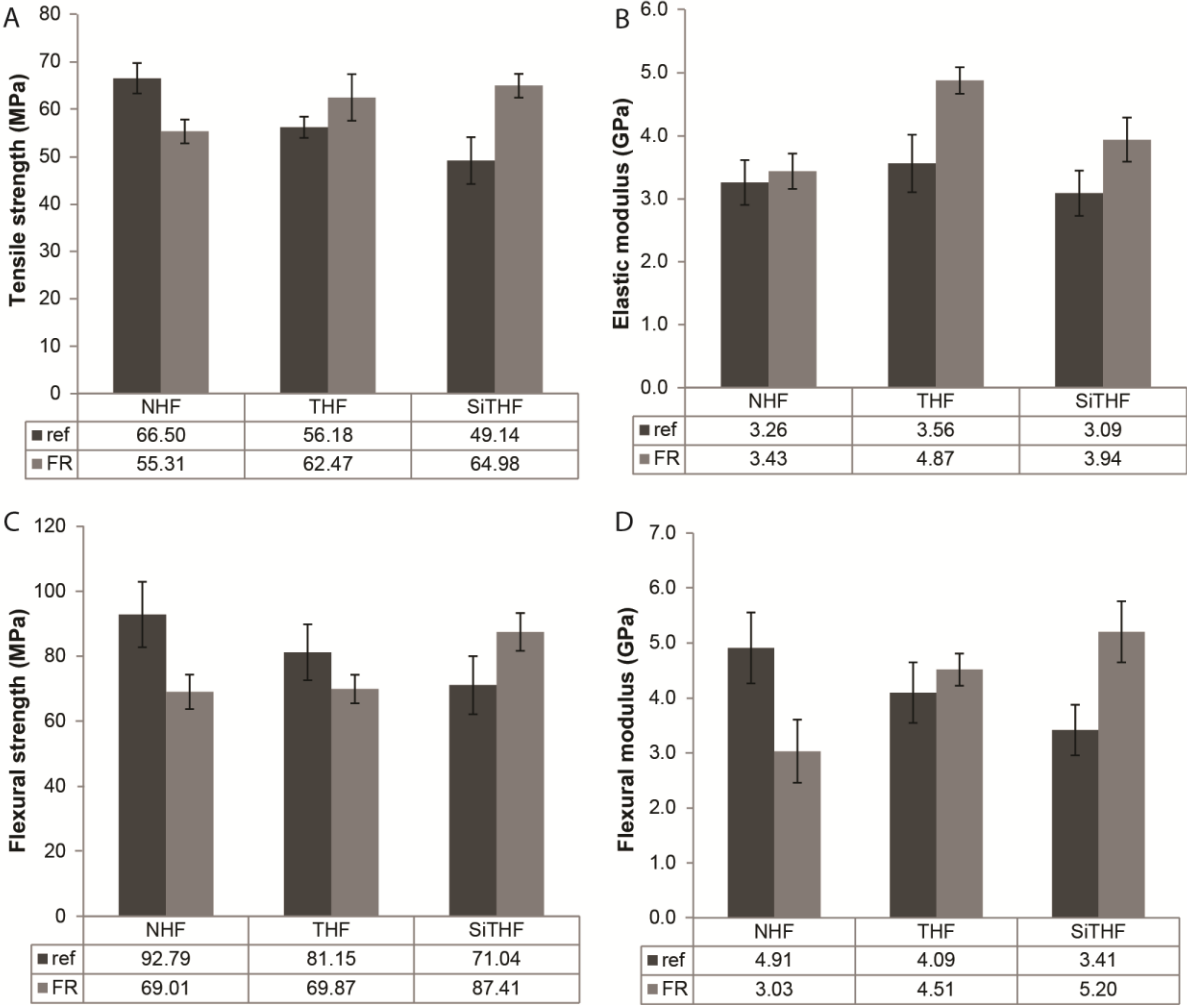
The macro-scale test shows a significant difference between the unmodified and treated fabrics. A drop of about 35% in the maximal force values was measured. The difference between the strength of the treated fabrics is negligible. These results also confirm the effect

of the acidic degradation of the cellulose on the tensile properties of the natural fabrics, which could not be avoided even by the sol–gel treatment.

### 3.4 Mechanical performance of the composites

#### 3.4.1 Static tensile and bending properties

Tensile and three-point bending tests were carried out in order to determine the static mechanical performance of the reference and flame retarded matrices reinforced with non-modified or treated hemp fabrics. The tensile and bending strengths as well as the moduli are given in **Figure 5**.

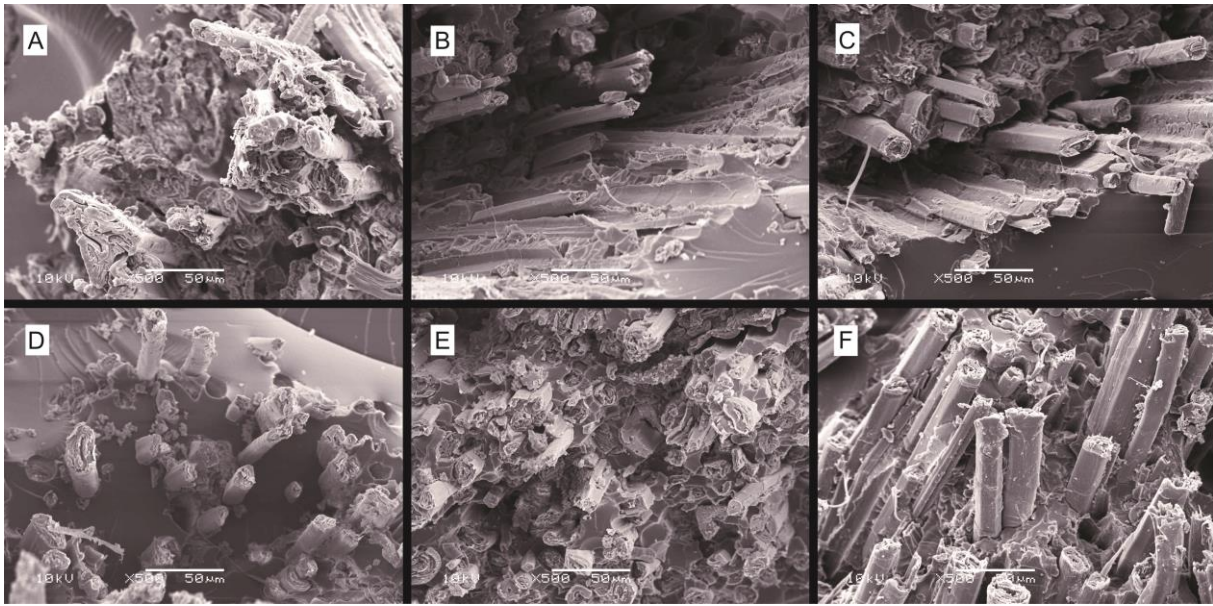


**Figure 5** Static tensile and bending properties of the reference and flame retarded composites

Considering the tensile strength of the composites with reference matrix (**Figure 5 A**), a decrease by the treatment of the reinforcing fabric can be seen as expected from the mechanical properties of these fabrics, described above. It is very surprising, based on these results and earlier findings (reporting decreased glass transition temperature and mechanical properties due to the FR modification of the matrix) [28], that the tensile strength of the FR-matrix composites showed just the opposite tendency: composites with treated fabrics exceeded the strength value of the NHF-FR sample. Similar trend can be observed comparing the flexural strengths of these composites (**Figure 5 C**). When applied with the FR matrix, the SiTHF treated fabric showed increased flexural strength. The results of the tensile and bending tests indicate increased fibre-matrix adhesion.

Comparing the moduli of the composites (**Figure 5 B and 5 D**), no significant difference can be seen between the reference matrix composites. When both the matrix and the reinforcing fabrics were flame retarded, somewhat higher values were measured. The highest modulus corresponds to the FR matrix reinforced with thermotex treated fabric (THF-FR) at the tensile test, and to SiTHF-FR at the three-point bending test, which indicates increased adhesion between the treated fibre and the FR matrix.

The SEM micrographs of the fracture surfaces of the different composites can be seen in **Figure 6**. The micrographs indicate good fibre-matrix adhesion in the case of THF-FR (**Figure 6 E**) and SiTHF-FR (**Figure 6 F**) composites: neither fibre-pull outs, nor delamination can be seen, the fibres are covered with the matrix. In the case of NHF-FR composite (**Figure 6 D**), mainly fibre-pull outs can be seen; while in the case of THF-ref (**Figure 6 B**) and SiTHF-ref (**Figure 6 C**) delamination can be observed.

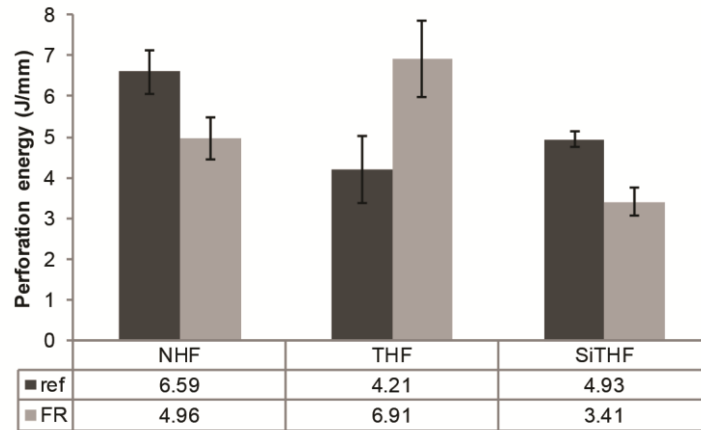


**Figure 6** SEM micrographs of the fracture surfaces. A: NHF-ref; B: THF-ref; C: SiTHF-ref, D: NHF-FR, E: THF-FR, F: SiTHF-FR (Magnification: 500x)

The phenomenon in tensile and flexural strengths and moduli implies a possible ‘hybrid’ effect when both the natural fibre reinforcement and the matrix contain phosphorus also confirmed by the micrographs of the fracture surfaces. Similar observations were drawn in the case of thermoplastic starch [9], and also in the case of PLA combined with TPS [17].

### 3.4.2 *Dynamic impact performance*

For the determination of the dynamic impact performance of the composites, instrumented falling weight impact (IFWI) tests were performed. The measured perforation energy values for the reference and flame retarded composites are shown in **Figure 7**.



**Figure 7** Perforation energies of the composites

In general, the perforation energy of the composites with treated fabrics, or with flame retarded matrix is lower than that for the reference sample. Only the THF-FR shows similar impact resistance. The very good adhesion between the sol-gel treated fabric and the FR matrix (SiTHF-FR), which was beneficial in the three-point bending strength, is disadvantageous in terms of the impact resistance, because in this case one of the most energy-absorbing micromechanical deformations, the separation of interphases, is missing. The decreasing energy absorption of the treated-fabric-reinforced reference composites can be explained by the decreased strength of the fabrics, while the high perforation energy of the THF-FR composite can also be explained by a possible synergistic effect between the phosphorus-containing fabric and FR matrix. In order to make it more clear, the fibre-matrix interaction was evaluated.

### *3.4.3 Determination of the fibre-matrix adhesion*

The fibre-matrix adhesion was determined by means of interfacial shear strength (IFSS) measurements applying microbond test. In the case of the SiTHF fabric, elemental fibres could not be prepared as the fibres were attached to each other as a consequence of the sol-gel

treatment. Thus the adhesion of NHF and THF fabrics to the reference and flame retarded matrices was determined. The measured values are summarized in **Table 6**.

**Table 6** Measured contact angles and interfacial shear strengths

	matrix	
	reference	FR
contact angle (°)	92 ± 6	82 ± 4
IFSS NHF (MPa)	13.2 ± 2	5.3 ± 2
IFSS THF (MPa)	6.8 ± 3	n.a.

Among the measurable interfacial shear strength values, the highest one was measured in the case of the untreated NHF fibres with reference matrix. In all other cases it decreased significantly. However, when both the fibre and the matrix was flame retarded, the method was not applicable because the droplets placed on the fibres were partially absorbed by the fibre therefore the diameter of the spread droplets became too small to catch by the blades of the microbond device. Thus no pull-outs could be detected at all. This phenomenon indicates significantly increased fibre–matrix adhesion, which explains the improved tensile, bending and impact properties of the composites.

The contact angles of deionized water and the matrices were investigated as well. The measured angles can be seen in **Table 6**. In the case of the FR matrix, the measured value (82°) was significantly lower than in the case of the reference matrix, indicating the more hydrophilic character of the FR matrix. The thermotex treatment (applying first phosphoric acid, followed by neutralization) of the natural fibres hydrolyses the cellulosic structure to some extent, increasing the size of the capillaries in the fibres. The more hydrophilic resin can easily enter these larger capillaries and better adhesion can be reached between the fibre and

matrix. These results are considered to be the first step towards understanding the surprising mechanical performance of the investigated FR epoxy composites.

#### **4 Conclusions**

In this work twill woven hemp fabric reinforced epoxy resin composites were prepared and flame retarded with a dual approach. On the one hand, the curing agent was replaced by a P-containing amine; on the other hand, the hemp fabrics were treated in order to decrease their flammability. The modification of the fabrics led to decreased flammability of the reference matrix composites characterized with increased LOI values and with a 25% reduction of heat release rate. The flame retardancy of both the matrix and fabrics was necessary to reach the V-0 rating in the UL-94 test. Regarding the mechanical properties of the composites, unexpected results were found when both the matrix and the fabrics contained phosphorus; despite the poorer mechanical performance of the FR matrix, and the decreased strength of the surface treated fabrics, the measured values for the flame retarded samples reached that of the reference composite in almost all cases. These surprising results can be explained by the increased fibre–matrix adhesion between the treated fabrics and FR matrix, and their easier wetting interaction in the case of the more polar P-containing matrix.

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