



## 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 phosphorus into the reinforcing fibres decreased the flammability not only of the hemp fabrics, but also of the epoxy composites made thereof. 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 bio-epoxy 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 [9–11]) in thermoplastic composites. Several papers deal with the flame retardancy of thermoplastic biocomposites by incorporating flame retardants (FRs) into the matrix [12–14]. 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

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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 [16–18].

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–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–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 homogeneous 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

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