

FIRE RETARDANCY OF BIOFIBRE-, GLASSFIBRE- AND SELF-REINFORCED POLYMER COMPOSITES

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Abstract

Combined application of reinforcement and fire retardancy using fabrics of renewable resources or recyclable polymer and was applied in epoxy and recycled polyolefin matrices. The interfaces of natural fibres were modified with phosphorous and silicone compounds. Use of recycled waste polymer components combined with PP fiber reinforcements proved to be feasible way for economic production of fully recyclable fire retarded engineering material.

Introduction

The preferred use of renewable resources and recycled polymers provides real alternative to the current extended use of fossil resources. The predicted growth of such systems is larger than that of other materials but their fire resistance (FR) and mechanical characteristics require significant improvement in order to meet the expectations [1]. Reinforcement combined with fire retardancy is most relevant in transportation where safety is one of the most important issues. More recently the improvement of the environmental image of cars, buses tracks, trains, ships and airplanes, such as low fuel consumption and recyclability (coupled with high strength, good processability and low cost) is required too. The currently available engineering polymer composites are non- biodegradable, hardly recyclable (glass fibre is abrasive), expensive (carbon fibre reinforced epoxy costs 40x compared to steel) and still not fire retarded. Combined application of reinforcement and fire retardancy can be achieved using additives of waste origin [2]. Understanding of the relationship between the complex phase-structure and performance of such systems required the use of special analytical methods, such LP-FTIR [3].

In order to develop environmental and fire-safe alternative of the currently used polymer composites we considered several approaches including the modification of biofibre- and self-reinforced polymer composites application of reactive fire retardancy (FR) methods, while glass-fibre reinforced composites were used as reference. Green chemistry approach for synthesis of flame retardants has been applied for addressing the high challenges. The role of modified interfaces/interphases (IP) in governing the structure-property relationship also needed to be taken into account. Use of recycled polymer components combined with self-

reinforcements, proved to be a feasible way for economic and environmental production of functional polymer system.

Materials and testing methods

Epoxy matrix was ER type Eporezit AH-16 (non-modified, resin like reactive dilutant, epoxy equivalent: 160–175; viscosity at 25°C: 800–1800 mPa.s; density at 25 °C: 1.24 g/cm³) applied with Eporezit T-58 curing agent (amine number: 460–480 mg KOH/g; viscosity at 20°C: 100–200 mPa.s; density at 20°C: 0.944 g/cm³; curing time: 2 days at 25°C) supplied by P+M Polimer Kémia Kft., Hungary. A newly synthesized phosphorus-containing reactive amine, TEDAP (amine number: 510–530 mg KOH/g; viscosity at 20 °C: 400 mPa.s; curing time: 7 days at 25°C, 4 hr. at 80°C) was applied as flame retardant. Woven natural fabrics made of 100% hemp fabric; surface mass: ~580 g/m², twill weave (Institute of Natural Fibres, Poland) were used. Before embedding into the composites some bio-fabrics were also treated with ammonium dihydrogen phosphate (ADF) and/or with tetraethoxy silane according to the thermotex procedure [4]. The natural fabric containing composites consisted of 3 layers of natural fabrics and 4 layer of epoxy resin.

In the case of the recycled glass fabric (GF-REC) reinforced and self-reinforced (SR-REC) composites density-separated polyolefin fraction ($\rho < 0.92$ g/cm³) of automotive shredder waste, obtained from Alcufer Ltd. (Hungary), was used as matrix material. Intumescent flame retardant (IFR) additive was Exolit AP766 (produced by Clariant Ltd., Germany) based on ammonium polyphosphate (APP). In the case of thermoplastic multilayered composites at first IFR additive was blended with the matrix (PP or REC), then from the obtained compounds in the case of SR and GF composites 180 μ m thick matrix layers were compression moulded at 190°C in a Schwabenthan Polystat 300 S laboratory hot press. These multilayered composites were manufactured by lamination of 11 matrix layers and 10 woven glass or PP fabrics. The packages were hot-pressed to composites in the same hot press at 162°C with a pressure of 6 MPa, for 2 min. The thickness of the prepared self-reinforced (SR) composites was 3.78 mm, while that of the GFCs was 2.78 mm. For the sake of better comparison between the recycled GF and SR composites, the composition (number of layers) and the nominal reinforcement content (i.e. glass or PP fabric) of ca. 48 m/m% were also kept constant for each reinforced composites.

The fire resistance of the prepared composites and references were characterized by Mass Loss type Cone Calorimeter (ISO 13927 standard), UL-94 tests (ANSI//ASTM D-635/77) and Limiting Oxygen Index (ASTMD 2863 standard) measurements.

Results and discussion





The scope of the present work has been extended to both thermosetting and thermoplastic polymer systems. Both of them are considered as models for demonstrating different environmental approaches for fire retardancy of composites.

Epoxy composites reinforced with fibres from renewable resources

The development of new FR additives of low molecular mass is limited because of the restrictions of REACH regulations. Therefore the interest turns nowadays towards the physically and reactively bonded FR systems because these provide chance to meet the green requirements. Both types have been included in the concept of modification for ensuring V0 level for natural fibre-reinforced epoxy resin.

Formation of FR-active bio-fibers was the first task. For this purpose the interfacial structure of the flammable cellulosic natural fibres were modified by active substances according to the so called thermotex principl [4]. In this process P and Si containing compounds were used for saturation of the pores of natural fibres. The results of biofibre modification can be seen in Table 1.

Table 1 Results of combustion of the non-treated and treated natural fibres under Cone heating of 50 kW/m², sample codes: NF – non treated, TF – P-treated using thermotex method, SiF – Si treated, SiTF – Si + P (thermotex) treatment

Sample	TTI (sec)	pHRR (kW/m ²)	pHRR time (sec)	THR (MJ/m ²)	Residue (%)	Photo
NF	8	68,116	35	5,55	negligible	
TF	6	17,56	14	1,95	negligible	
SiF	6	62,02	34	5,64	negligible	
SiTF	-	8,52	62	1,39	19%	

It is clear from Table 1 that the combined treatment is the most effective for protecting the fibres therefore this modification was applied on the fabrics used for reinforcing the composites.

Epoxy-bio-fabric systems were prepared as model composites for evaluating the effect of natural fabrics, their treatment and FR crosslinking agent. The results indicating the FR levels are given in Table 2.

Table 2 Results of FR tests of epoxy resins reinforced with the non-treated and treated natural fabrics under Cone heating of 50 kW/m², sample codes: NHF_ref – Neat Hemp Fabric in reference matrix, SiTHF_ref – Si + P (thermotex) treated fabric in reference matrix, NHF_80FR – Neat Hemp Fabric in matrix cured with 80% TEDAP crosslinker, SiTHF_80FR – Si + P (thermotex) treated fabric in matrix cured with 80% TEDAP

Sample	UL-94	LOI	TTI (sec)	pHRR (kW/m ²)	pHRR time (sec)	THR (MJ/m ²)
NHF_ref	HB	22	27	571,72	253	174,16
NHF_80FR	V-1	32,5	30	426,28	195	94,61
SiTHF_ref	HB	28	37	434,49	215	129,1
SiTHF_80FR	V-0	32	30	369,35	231	121,66

On the basis of UL-94 results the reference matrices reached only the HB ranking, although these could not burn horizontally until even the first sign excepting the sample containing non-treated fabric (vflame = 18,2 mm/min). The effect of (Si and P containing) modified interlayer was especially important when matrix cured with 80% P containing (TEDAP) crosslinker. With this treatment the V-0 ranking could be achieved, while the reference sample reached only the V-1 level. The LOI values reflect the influence of surface treatment only in the case of reference samples in which the treatment of the reinforcing fabric increased the LOI from 22 to 28. When the matrix was fire retarded its effect prevailed over the influence of surface treatment.

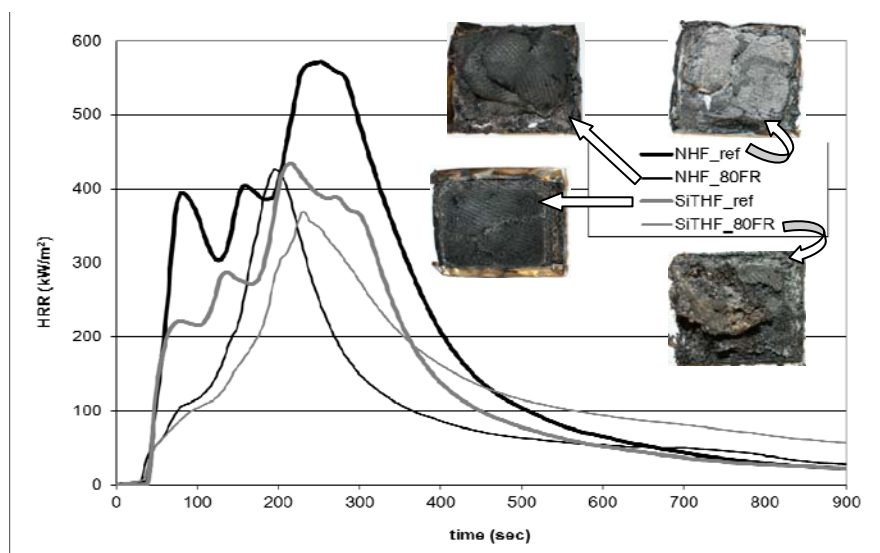


Figure 1 Results of combustion of epoxy resins reinforced with the non-treated and treated natural fabrics under Cone heating of 50 kW/m², sample codes: NHFref – Neat Hemp Fabric in reference matrix, SiTHFref – Si + P (thermotex) treated fabric in reference matrix, NHF80FR – Neat Hemp Fabric in matrix cured with 80%TEDAP crosslinker, SiTHF_80FR – Si + P (thermotex) treated fabric in matrix cured with 80%TEDAP crosslinker

The heat release curves in Figure 1 show waves according to the 3 fabric layers in case of the reference samples in which the modified interlayer reduced the pHRR with ~25%. The intensive foaming in presence of 80% TEDAP, however, suppressed these waves while the effect of the treatment of the fabric is visible in the reduction of the pHRR.

Self-reinforced PP systems of waste origin

Besides the preferred use of renewable resources the recycling of thermoplastic systems is also essential in order to meet the current environmental requirements. In industrial applications reduced flammability combined with reinforcement and recyclability are essential requirements. Therefore fully recyclable flame retarded composites were also prepared using secondary polyolefins. In order to reduce the flammability of the fabric reinforced composites, the recycled matrix layers have been modified by adding 34 wt% IFR additive i.e. 18 wt% considering the mass of the entire composites. Polypropylene reinforcing fabrics were used for forming self-reinforced composites that were prepared by lamination and hot-pressing (in accordance with the film-stacking [5]) method. The properties of these easily recyclable self-reinforced composites (SR-REC) were compared to glass fabric reinforced composites (GF-REC) (prepared by the same technological parameters) and to reference samples without reinforcement (REC).

The results of the performed LOI and UL-94 flammability tests are summarized in Table 3. With the IFR content of 18 wt% V-1 rating could be achieved in the case of REC-FR18 compound, which is in accordance with the fact that at least 20-22 m/m% IFR is required to achieve V-0 classification in PP [6].

Table 3. LOI values and UL-94 ratings of the recycled composites reinforced with glass fabric (GF-REC) and PP-fabric (SR-REC). FR18 = flame retardant content of 18 wt%

Sample	UL-94 Classification*	LOI (vol%)
REC	HB (31.5)	20
GF-REC	HB (19.9)	21
SR-REC	HB (34.6)	19
REC-FR18	V-1	26
GF-REC-FR18	V-0	33
SR-REC-FR18	V-0	30

*in parenthesis the horizontal burning rates (mm/min), if measurable, are indicated

Unexpectedly, the 18 wt% IFR content proved to be sufficient for the V-0 rating when incorporated into multilayered composites (GF-REC-FR18 and SR-REC-FR18). It is also shown, that in spite of the same IFR content 7 and 4 vol% higher LOI could be reached by preparing fabric reinforced composites. The lower flammability of GF-REC-FR18 can be explained by its high (ca. 48 m/m%) incombustible material (glass) content, which is also manifested by the low burning rate (19.9 mm/min) and relatively high LOI (21 vol%) of the additive-free GF reference composite (GF-REC). Nevertheless, the favourable behaviour of the self-reinforced composite (SR-REC-FR18), which is entirely composed of combustible materials, is much more surprising and remarkable.

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