Graphene nanoplatelets-biocomposites for advanced pultrusion profiles adapted to building envelope

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Abstract

Previous studies [1&2] have shown that biocomposites manufactured from natural materials such as fibres and bio-derived polymers; offer a sustainable alternative to traditional polymers and composites.

Graphene nanoplatelets have been regarded as one of the most promising reinforcements for next generation high performance composites since they can have a dramatic impact on mechanical and fire resistance properties [3]. Strong interfacial adhesion between the graphene platelet and the composite matrix is crucial to improve mechanical properties [4&5]. Interfacial adhesion can be greatly improved by chemically functionalization of graphene surface, which can also aid platelets dispersion in the matrix. By this way, radical chemistry [6] and a number of other chemistries [7] have been used for assuring an optimal compatibility degree.

Proper formulations of the bioresin / graphene and processing parameters have been established in order to achieve a suitable dispersion of graphene as a first processing step.

The adaptation of the existing processing pultrusion techniques to the specific characteristics of the new biomaterials and graphene has been also assessed.

As a result, demonstrators of pultrusion profiles with enhanced mechanical properties adapted to building envelopes have been carried out incorporating novel materials, graphene nanoplatelets and bio-based resin.

1 Introduction

An alternative composites answer in the envelope sector is the fabrication by pultrusion of narrow interlocking panel sections and profiles. These impact-resistant structural elements have the advantage of quicker, safer installation and their modular design equally answers many identical building and other applications [8].

An additional development in this area can be the obtaining of a sustainable alternative to current composite profiles. Previous studies [1&2] have shown that biocomposites manufactured from natural materials such as fibres and bio-derived polymers; offer a sustainable alternative to traditional polymers and composites.

The goal of this development is to replace the typical light gauge steel profile with a state of the art bio-composite integrated system. The finish profiles can also be used to finish existing masonry partition walls, cladding mechanical and extraction shafts and column cladding. The profiles have been designed using bio-polymers, reinforced with graphene where possible and necessary (figure 1).

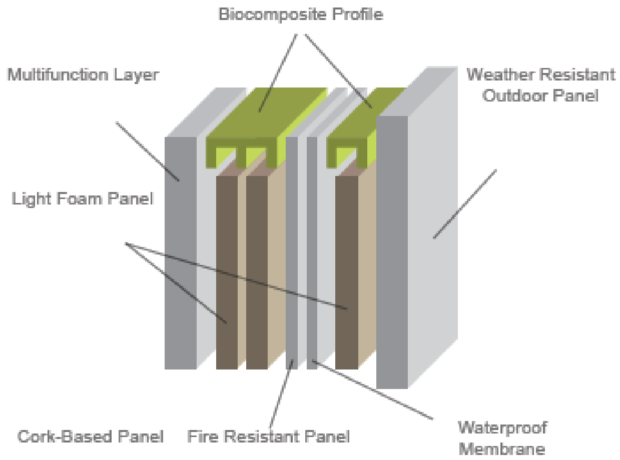

Figure 1. Assembled modular multi-layer envelope based on biocomposites in which is integrated developed biocomposite profile

The incorporation of additives to biopolymer is being studied in order to improve mechanical properties and adhesion between matrix and fiber. Graphene addition to polymers is offering a significant potential for the development of advanced materials in numerous and various applications due to its high surface area which can have a dramatic impact on mechanical and fire resistance properties [9]. Using graphene as an intumescent flame retardant in synthetic materials has attracted more and more interests in both, research and industry circles in recent years. During a fire network of graphene inside a material can act as a barrier for chemicals diffusion and thermal transport. Graphene have been regarded as one of the most promising reinforcements for next generation high performance composites. However carbonaceous nanoestructures outstanding properties have been restrained by technical challenges such as dispersion and interfacial bonding for load transfer to the resin. Although adding graphene can greatly improve properties such modulus, toughness and fatigue properties, strong interfacial adhesion between the graphene platelet and the composite matrix is crucial to achieving these gains [5]. Interfacial adhesion can be greatly improved by chemically functionalizing the graphene surface, which can also aid platelet dispersion in the matrix.

Proper formulations of the bioresin / graphene and processing parameters have been established in order to achieve a suitable dispersion of graphene as a first processing step. The adaptation of the existing processing pultrusion techniques to the specific characteristics of the new biomaterials and graphene has been also assessed. As a result, demonstrators of pultrusion profiles with enhanced mechanical properties adapted to building envelopes have been carried out incorporating novel materials, graphene nanoplatelets and bio-based resin.

2 Functionalization and dispersion study of graphene.

2.1 State of the art. Evaluation of graphene functionalization routes

Graphene is a two dimensional material, in the form of a monolayer, in which the carbon atoms are strongly bonded in a hexagonal plane. It is possible to find a unique carbon plane, graphene sheet, or structures based on stacked sheets with nanometric thickness, within the range of 3-100 nm called graphene nanoplatelets (figure 2).

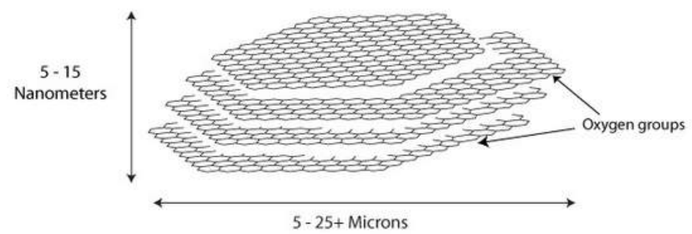

Figure 2. Typical scheme of configuration of graphene nanoplatelets.

A single graphene layer shows an excellent thermal and electrical conductivity , a Young modulus of 1TPa and a high strength, around 130 GPa that indicates - superior mechanical properties [10]. These exceptional properties coupled with the high specific surface of layers promoting their use as reinforcement in polymeric resins in order to improve thermal stability and mechanical or other thermophysical properties [11].

Resin composites with graphene usually are prepared by solution mixing, mechanical bending or in situ polymerization. However, the achievement of a homogeneous dispersion and efficient interfacial interactions are still the main challenges to develop a good quality composite [12] with optimal properties due to the strong tendency to aggregation of graphene sheets.

Different approaches for improving the dispersion of graphene are mainly related with the use of high energy mixing mechanisms and the functionalization or chemical modification of graphene surface.

2.2 Chemical modification of commercial graphene

Different strategies were performed in order to modify the chemistry of graphene and create a high number of interactions with bioepoxy resin that result in a good quality dispersion.

For that purpose, small batches of commercial graphene, 1-10 g, were functionalized at laboratory scale and subsequently characterized. The selected reactions are listed below:

- A non-covalent functionalization with Triton X-100.
- Covalent modification with glycidyl groups by a radical reaction by means of peroxides.
- Covalent modification with aminosilanes in a friendly medium (simple alcohol).

All the explained strategies have common phases that could be summarized as: a first stage for preparing all reactants (for graphene it was performed under a safety cabin), a second one during which the reaction was taking place, and post-process phases of filtering, washing and drying in an oven (Figure 3).

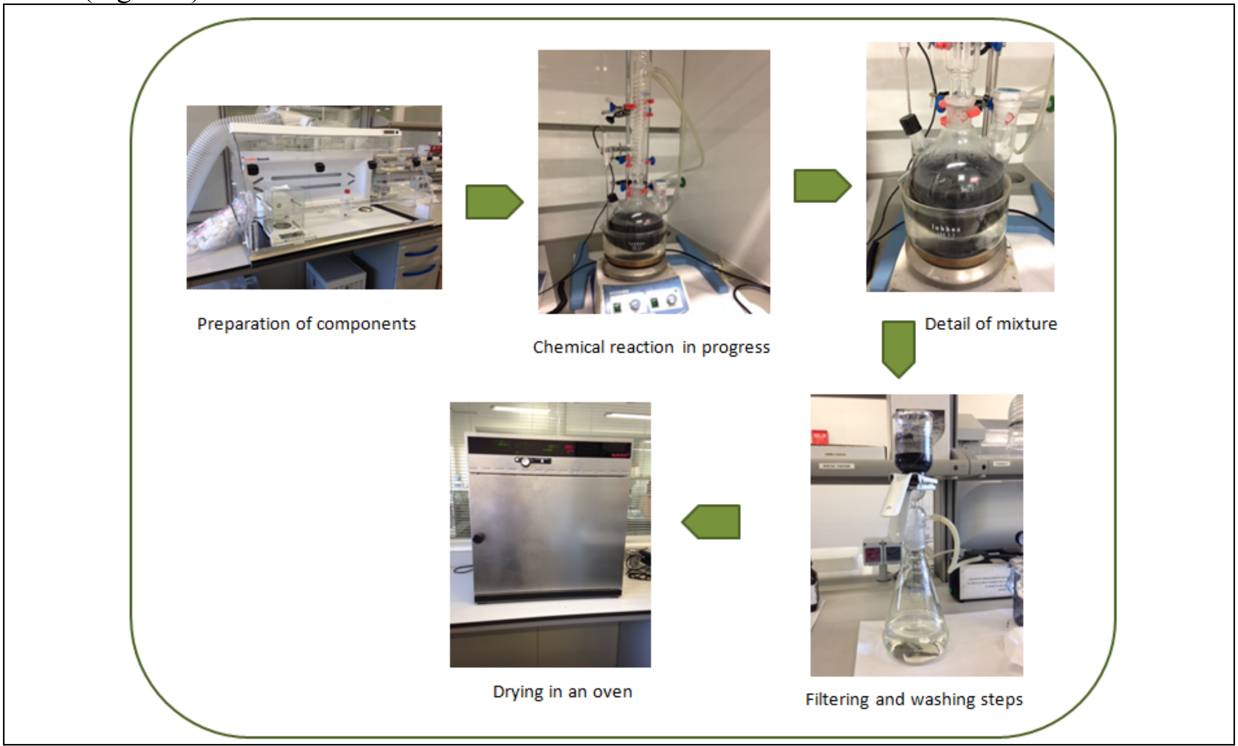

Figure 3. Phases of chemical modification reactions.

2.3 Dispersion of selected modified graphene into bioepoxy pultrusion resin at pilot plant level.

Main problem to incorporation of nanomaterials to polymeric matrices, in general, is their tendency to form agglomerates. From a technical point of view, processes needed to work with nanomaterials are based on the elimination of agglomerates, the dispersion of aggregates and stabilization of the medium. The equipments used to dispersion process depend on size of required final particle. From technical requirements of dispersion of bioepoxy resin and graphene (high viscosity, high shear stresses, among others), the 3-roll mill technique was selected as suitable equipment to dispersion trials at pilot plant.

Dispersion cycle of bioepoxy and graphene with 3 roll calender, as optimum technique, was optimized and established (Figure 4 and Table 1). Trials at pilot plan level have been carried out with selected modification and 0.5% of nanofiller.

Figure 4. Dispersion of graphene by 3-roll mill at pilot plant

Table 1. Dispersion Cycle.

Dispersion Cycle definition
Cycle 1: gap130/45 Cycle 2: gap 90/30 Cycle 3: gap 60/20 Cycle 4: gap 30/10 Cycle 5: gap15/5

2.4 Characterization of modified graphene.

2.4.1 Scanning electron microscopy (SEM).

An in-depth study of the microstructure and organization of pristine graphene sheets and modified was performed with the objective of determining the possible alteration after the different chemical processes. The characterization was conducted in a scanning electron microscopy Phenom World Pro X with backscattered electrons. The voltage was selected at 10 and 15 KeV and the magnification 300-2000x. Samples were previously coated with a gold layer by means of a sputtering equipment to achieve an optimal electrical conductivity during test. Results for modified graphene nanoplatelets with aminosilanes are shown in Figure 5.

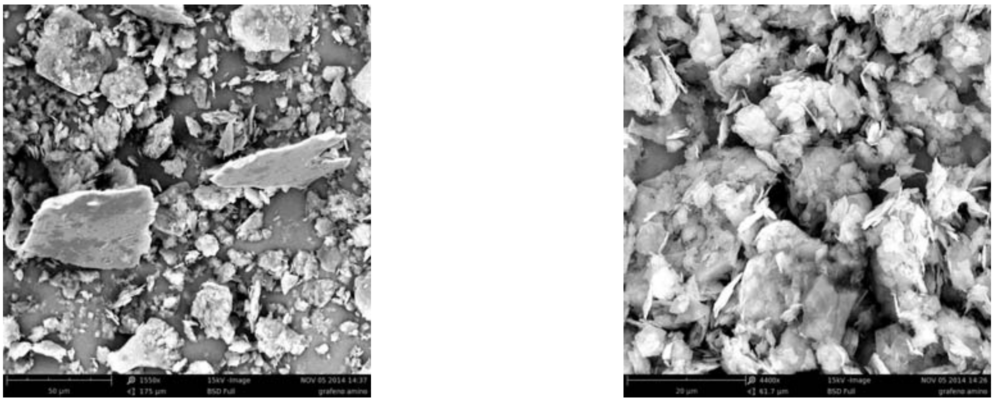

Figure 5. Graphene nanoplatelets modified with aminosilanes micrograph X1550, 4400.

Considering the obtained SEM images there is not a clear evidence of a graphene flakes breakage introduced by dispersion techniques because of the wide range of sizes that the original unmodified graphene presented.

2.4.2 Dynamomechanical Analyzer (DMA)

The prepared composites with different modifications were characterized by DMA to determine the effect of graphene in viscoelastic modulus, and subsequently in mechanical properties, and also in the glass transition temperature. This modulus gives information about the degree of dispersion and thus the effect of material quality in thermal stability (other important issue to accomplish) and mechanical properties. Tests were carried out in a DMA TA Instruments 2980 with a dual cantilever clamp by applying a sinusoidal deformation with 1 Hz of frequency and 20µm of deformation. A ramp temperature was programmed from 25ºC up to 200ºC in order to cover all possible thermal transitions of bioepoxy composite (Table 2).

Table 2. DMA results (modified and unmodified graphene)

Sample	Tg onset E' (ºC)	Tg peak E'' (ºC)	Tg tan delta (ºC)
Neat epoxy resin	76.82	78.16	93.86
0.5% unmodified graphene	74.25	75.02	92.22
0.5% graphene surfactant	72.27	71.30	93.07
0.5% graphene aminosilane	78.48	79.59	95.39
0.5% graphene glycidyl	74.65	76.29	91.30

It was observed that an increase in Tg values is registered for contents of 0.5 % of graphene aminosilane.

3 Pultrusion trials at pilot plant

In the first stage, pultrusion trials of neat bioepoxy composite profiles were carried out in order to evaluate the processability of the system and assess the curing cycle (Figure 6 and Figure 7).

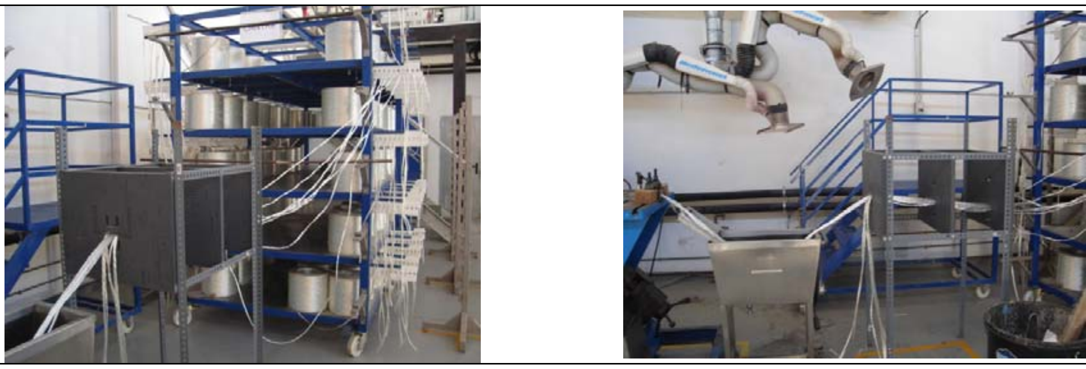

Figure 6. Different steps of the processing of bioepoxy composite profiles

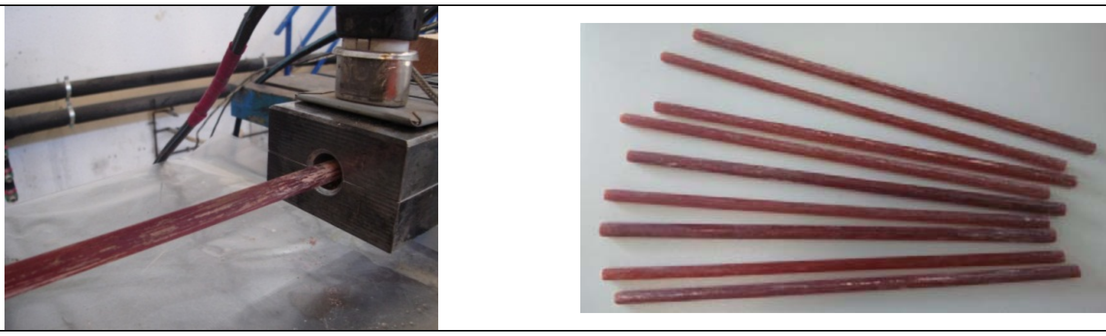

Figure 7. Optimised bioepoxy composite profiles obtained by pultrusion

Pultrusion trials with bioepoxy composite profiles and 0.5 % graphene (Figure 8) were performed in order to evaluate the processability of the system and assess the curing cycle (bioepoxy + graphene). Graphene was dispersed with bioepoxy system in 3-roll mill following the dispersion cycle defined in Table 2.

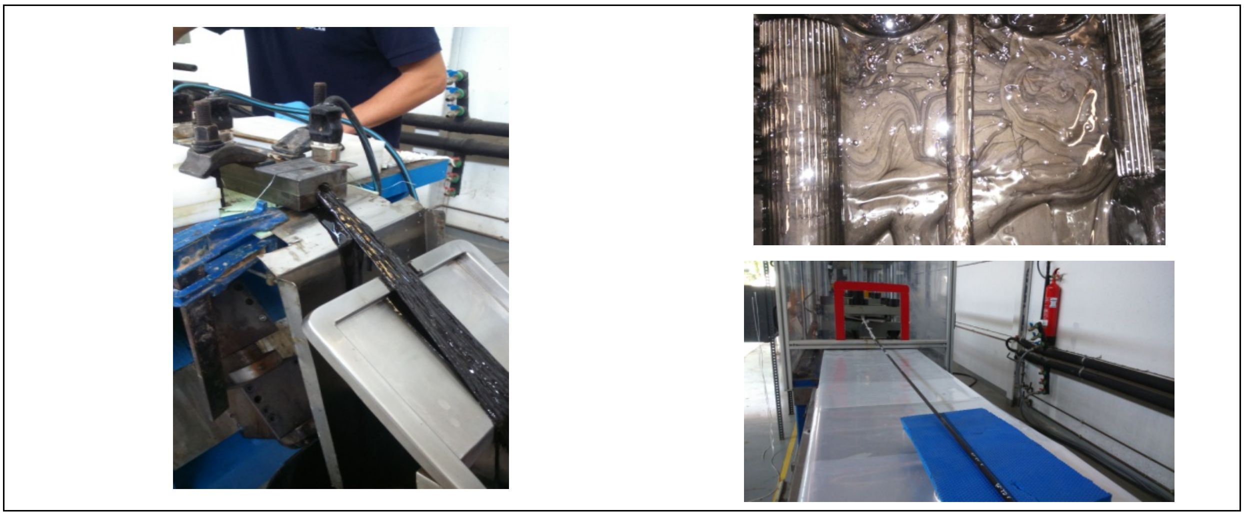

Figure 8. Pultrusion trials: Different steps of the manufacturing of bioepoxy and graphene composite profiles.

4 Conclusions

- Different strategies of chemical modification of graphene were performed in order to modify the chemistry of graphene and create a high number of interactions with bioepoxy resin that result in a good quality dispersion: a non-covalent functionalization with Triton X-100, covalent modification with glycidyl groups by a radical reaction using peroxides, covalent modification with aminosilanes in a friendly medium (simple alcohol).

- A procedure about phases of chemical modification reactions adapted to different strategies of different chemical modifications has been defined: a first stage for preparing all agents (under a safety cabin), a second one during which the reaction was taking place, and post-process phases of filtering, washing and drying in an oven (Figure 3).

- From technical requirements of dispersion of pultrusion bioepoxy resin and graphene (high viscosity, high shear stresses, among others), the 3-roll mill was selected as suitable equipment to dispersion trials at pilot plant. Dispersion cycle of pultrusion bioepoxy and graphene with 3 roll mill was optimized and established (Table 1).

- From DMA tests of different dispersed modifications, it can be concluded that graphene nanoplatelets functionalized with aminosilane presents higher values of storage modulus along all the temperature range pointing out a reinforcement effect of nanomaterials. Moreover, the glass transition temperature is slightly superior providing an improvement in the thermal stability. Therefore the modification of graphene with aminosilane was selected as the most suitable chemical functionalization for improving compatibility with matrix.

- Pultrusion trials with bioepoxy composite profiles with with 0.5 % graphene were carried out in order to evaluate the processability of the system and assess the curing cycle.

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