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Hybrid composites manufactured by resin infusion with a fully recyclable bioepoxy resin

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ABSTRACT

Bioepoxy based monomers were formulated with a cure inhibitor and a cleavable amine to obtain a recyclable epoxy system suitable for resin infusion at room temperature. Hybrid flax/carbon fiber layup were used. Tensile, flexural and dynamo-mechanical properties for the composites were studied. The cured laminates were chemically recycled obtaining from the epoxy matrix a thermoplastic. The recycled was processed by fused deposition modelling (FDM) and injection molding after mixing with short kenaf fibers.

1. Introduction

The use of epoxy based composites is increasingly accepted in many fields. In the automotive sector, electric-mobility, CO_2 emission limits, gasoline and energy prices are some of the driving factors guiding the lightweight automotive design. The requirement for lightweight structures, combined with the need for high volume production rates, pushed the development of mass production techniques like High Pressure Resin Transfer Molding (HP-RTM) [1]. In the aerospace sector, liquid resin infusion of thermosets is increasingly accepted because of its low cost and suitability for producing of large structures [2–4]. Liquid resin infusion is well established in transportation and naval sectors too [4,5]. In the civil fields the use of epoxy composites is widely accepted too [6,7].

The widespread use of thermoset composites is raising environmental concerns about the recycling options and because of the use of petroleum based raw materials. To address the latter point, natural fibers as reinforcements [8–15] and bioepoxy resins are becoming a focal point of interest for industry [16,17]. In the last years a lot of attention has been drawn by the use of hybrid natural fiber layup to optimize composite's mechanical properties [18–20]. The use of hybrid fabric layup add complexity to the recycling operation if fiber recovery is desired because, in some cases, the high value of some natural fabrics oblige not to destroy them.

The status of the recycling techniques for fiber reinforced composites was recently reviewed by Oliveux et al. [21] and many differences compared to traditional plastic recycling of solid waste can be observed [22]. Rybicka et al. [23] analyzed the technology readiness level for many composite recycling techniques: incineration and landfilling were classified as TRL 9 while, pyrolysis for carbon fiber and mechanical grinding for glass fiber applications resulted on a TRL 8. Pyrolysis for glass fiber and mechanical grinding for carbon fiber achieved TRL 7. Finally, fluidized bed pyrolysis and solvolysis process achieved a median TRL of 4. The main limitations of thermal and mechanical recycling processes are fiber's properties degradation and that matrices are destroyed or only partially recovered in useful forms.

Chemical recycling is an interesting alternative approach because it allows to obtain clean reclaimed fibers and valuable monomers from the epoxy matrix [24]. Similar methods have been presented by several authors [25,26]. Researchers from Lamborghini showed their interest in the use of chemical recycled fibers [27]. However, most of the known chemical recycling approaches rely on the use of solvent mixtures which inhibit their application to natural fiber reinforced composites. A sustainable solution to

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overcome these limits is offered by the cleavable amines developed by Connora Technology. These amines allow to synthesize epoxy thermosets which can be recycled yielding thermoplastics and clean fibers in mild aqueous solutions at low temperatures (80–120 °C) [28].

In a previous paper, we discussed the environmental benefits of this approach showing the avoided environmental impacts associated with the use of recyclable epoxy resins [29]. We also presented some data about the development of a recyclable epoxy formulation for HP-RTM with some preliminary characterization of the recycled thermoplastic [30]. In the present paper, we extended the use of the Connora recycling approach by developing a recyclable biobased epoxy formulation suitable for resin infusion. Hybrid flax/carbon fibers layup were used and the effect of the stacking sequence evaluated. The composites panels obtained were then recycled and the potential uses of the recycled thermoplastic addressed.

2. Experimental

2.1. Materials and method

2.1.1. Materials

SuperSap epoxy monomers CLX(S) and the cure inhibitor INH by Entropy Resins were mixed with the Recyclamine® 301 by Connora Technologies. The inhibitor was added in the percentage of 25% to the epoxy monomer to have a pot life of 90 min at 25 °C. The CLX(S) monomer is composed of epoxidized pine oils, bisphenol A/F type epoxy resin, benzyl alcohol, and proprietary reactive epoxy diluents. Similar resin systems are reported as a green system for resin transfer molding [31]. The Recyclamine® 301 is a cleavable polyamine ether patented by Connora Technology.

The carbon fabric used was a twill fabric of T300 carbon fibers with 200 gsm (grams per square meter) areal weight purchased from Prochima, Italy. Flax fabrics (400 gsm, twill) were purchased by Composites Evolution (UK). Short kenaf fibers were supplied by Sachsenleinen, Germany.

2.1.2. Composite preparation

Composite panels were prepared by resin infusion. Different stacking sequences were tested as reported in Table 1. The dry fabrics were stacked on a steel plate. During mold layup of the natural fibers fabrics no relevant fabric deformation was observed with this type of woven fabrics in contrast to what reported for non-woven fabrics [32]. An adhesive silicone tape was placed around the perimeter of the layered stack to provide a proper seal and a flexible vacuum bag was placed on top. An inlet tube and an outlet tube were placed inside the vacuum bag. The inlet tube was connected by a valve to a pot filled with unmodified epoxy resin while the outlet tube was connected to a vacuum pump. The vacuum was applied while the inlet valve was closed in order to compact the layers and to remove excess air. The premixed epoxy resin was vacuum infused into the stacked layers, which was maintained at 25 °C under a constant vacuum (−75 cm Hg). The laminates were kept at 25 °C for 6 h before demolding them.

2.1.3. Composites recycling

A sample (200 gr) of composite was treated with 3 L of acetic solution (25 vol % of acetic acid) at 80 °C for 1.5 h. The mixture was then filtered and the fibers separated from the liquid phase. The reinforcing fibers were allowed to dry and weighed. The acetic solution was neutralized with a NaOH (pH = 10) until a solid precipitate appeared. The mixture was cooled and filtered. The solid was washed in distilled water at about 40 °C. The solid dissolved again. Few drops of NaOH solution were added and a white solid precipitated from the solution, an epoxy thermoplastic polymer.

2.1.4. Recycled thermoplastic processing

The recovered thermoplastic was blended with 5 wt% and 10 wt % of short kenaf fiber at 190 °C for 10 min with a speed of 30 rpm using a batch mixer (Brabender 50 EHT) controlled by a Lab-Station. The thermoplastic and the kenaf fibers were dried at 50 °C under vacuum for 48 h before mixing.

Tensile specimens with dimensions according to ASTM D638 were fabricated from the blends using a 12 cc microinjection molder (DSM Xplorer) at 190 °C melt temperature and 50 °C mold temperature with injection and holding pressure of 16 bar. The specimens were allowed to cool down in the mold for 5 min before extraction.

Thermoplastic filaments with 1.75 mm diameter were also produced from the recovered thermoplastic. Thermoplastic filaments were prepared in a single-screw extruder with screw diameter (D) of 20 mm and screw length of 25 × D (model E 20 TH; Collins). Thermoplastic pellets were dried before use at 50 °C under vacuum for 48 h; after that pellets were loaded in the extruder hood by using a volumetric feeder. The temperature pattern of the extruder was 55°C–160°C-170°C-190°C-190 °C from input to output zones, the screw speed was set at 30 rpm, and the melt pressure, checked during all of the extrusion process, was 40 bar. An extruder head with a circular die (diameter = 3 mm) was used. The melted thermoplastic was drawn, cooling it with an air knife before collecting it on a rotating spool. The melt extruded filament, due to the drawing action of a rotating spool, varied in its diameter from 3 mm, at the exit of the extrusion head, to 1.75 ± 0.05 mm on the spool. The extruded filaments were processed by Fused Deposition Modelling (FDM) using a prototypal FDM machine Roboze one 400+ (Roboze, Bari, Italy).

2.2. Characterization

2.2.1. Mechanical testing

Composite specimens were cut from the panel and tested in tensile and flexural mode accordingly to ASTM D3039 and ASTM D790. A universal testing machine Instron 5982 operating at a constant speed of 1 mm/min with a load cell of 100 kN was used for testing.

Differences in mechanical results, for the composites samples, were statistically analyzed by one-way analysis of variance (ANOVA) using Minitab 17 software. To identify which groups were significantly different from other groups, means comparison was done using the Tukey's test with a 95% confidence level.

Tensile properties of the injection molded specimens were measured by using an Instron 5982 universal testing machine, equipped with a load cell of 10 kN in accordance to ASTM D638 type 1.

2.2.2. Dynamic mechanical analysis (DMA)

Composite specimens (mm 15 × 10 × 2) were tested by dynamic mechanical analysis (DMA). Storage modulus and Tanδ were measured using a dynamic mechanical analyzer (Tritech by Triton Ltd, UK). Experiments were carried out in single cantilever mode by

Table 1
Designation of the non-hybrid and hybrid laminate composites.

Sample Code	Stacking sequence C: Carbon F: Flax
NF	FFFF
CF	CCCCCCCC
FCF	FCCCCCCF
CFC	CCCFFCCC