The use of recyclable epoxy and hybrid lay up for biocomposites: technical and LCA evaluation

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ABSTRACT

Thermoset composites end of life is an increasing problem for many industrial sectors. The widespread and increasing use of thermoset-based composites in automotive applications poses increasing concerns about composite's end of life because of EU directives. Specifically, the Directive 2000/53/EC requires that about 85% of the weight of the vehicle must be re-used as end of life option by recycling or energy recovering process. The use of thermal-based recycling methods has two main limitations: it does impact the environment and it does damage the reinforcing fibers. To overcome such limitation recyclable amine technology patented by Connora Technology appears as a promising solution. In addition to that, most of the epoxy formulation used nowadays are still based on petroleum-derived epoxy monomers. This limits the green content of the composites used thus impairing their overall environmental impact.

In the present paper we discuss the use of green recyclable epoxy formulation based on the use of bioepoxy monomers cured with recyclamines by Connora. The final goal of the paper is to demonstrate the possibility to develop truly green recyclable composites based on thermoset matrices. The hybridization of carbon fiber fabrics with natural fiber fabrics is also addressed. The study focus both on technical and environmental aspects. On the technical side the processing and mechanical performances of the composites developed were analyzed. The use of recycled products obtained by the novel recycling approach were also studied. The environmental relevance of the composites and of the recycled products were addressed by the use of Life Cycle Analysis. LCA allowed to unveil the environmental burden connected with the use of recyclable amines and hybrid carbon/natural fiber composites.

1. INTRODUCTION

The use of vegetable oils as monomers for green thermoset was recently reviewed by Xia et al [1]. Different synthetic routes exist in literature which allows thermoset resins starting from renewable vegetable oil [2]. However, from the commercial point of view less options exist which are truly green. Since few years, the company named Entropy Resins expanded its market share by developing a green resin branded as Super Sap. This resin, which is based on the replacement of petroleum based carbon with renewable plant-based carbon,present a biocarbon content of about 48%. Di Landro and Janszen [3] discussed hemp reinforced composites obtained using the entropy resins as matrix. All composites were obtained by RTM. The grade used presented mechanical properties in the range of standard epoxy resin used for nautical applications. The glass transition for such bio-epoxy matrix was

between 55°C and 65°C even for samples subjected to post-curing at 180°C. Despite these limitations the properties of the entropy epoxy resins could be further improved by appropriate choice of the curing agents.

The major limitation of thermoset matrices is their limited recyclability options. Once reacted, thermosets form a network which renders them unprocessable. This limits the use of thermoset in those applications where recyclability is a must. In the automotive field, in EU nut also in USA, there is an increasing need for materials easy to recycle with lower impact on the environment. Pimenta and Pinho [4] discussed the different techniques for thermoset recycling providing some numbers on the process scale (Fig.1).

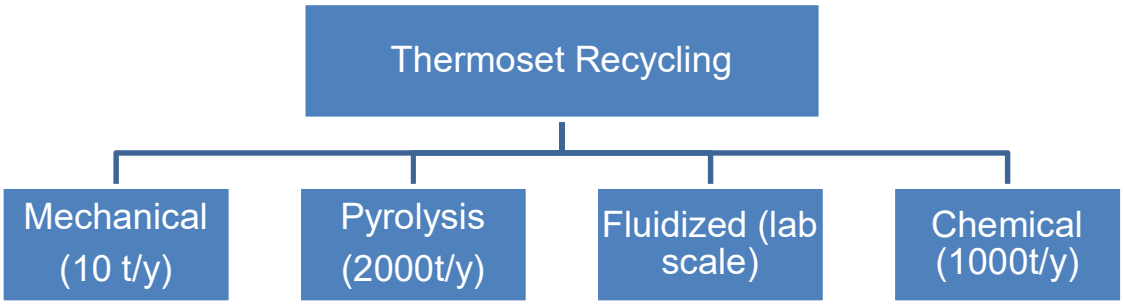

Figure 1 Thermoset Recycling techniques with production rates accordingly to Pimenta and Pinho

The higher production rates are, nowadays, reached by pyrolysis. ELG Carbon Fibre Ltd., in UK, is selling several products trademarked as Carbiso which are derived by an industrially scaled pyrolytic process. A major problem with thermal degradation of thermoset networks to recover carbon fibres is the deterioration of fiber properties and the lack of recovery of a reusable product from the matrix.

In order to overcome such limitation some companies tried to develop chemical routes for the recycling of composites. The company Adherent Technologies, for example, developed a wet-chemical treatment to break down the matrix resin of the composite in a liquid, producing a very clean fiber under much milder conditions than those found in pyrolysis processes. It is not clear, from information released, if decomposition products from the matrix can be reused.

Hitachi Chemical (http://www.hitachi-chem.co.jp/english/report/056/56_sou01.pdf) developed a recycling technology using depolymerization of cured epoxy resin under ordinary pressure. The process dissolves epoxy resin with tripotassium phosphate as a catalyst and benzyl alcohol as a

solvent at 200°C for 10 hr. The depolymerization of the epoxy network resulted in the formation of diesters and bis-diols as resulting monomers (Figure 4). The carbon fibers reclaimed with this process were claimed to be clean and with no degradation. This process was scaled up to production rate of 12 t/y and LCA (Life Cycle Analysis) showed that recovered carbon fibers can be produced with energy consumption of 63MJ/kg versus 286MJ/kg for virgin fibers.

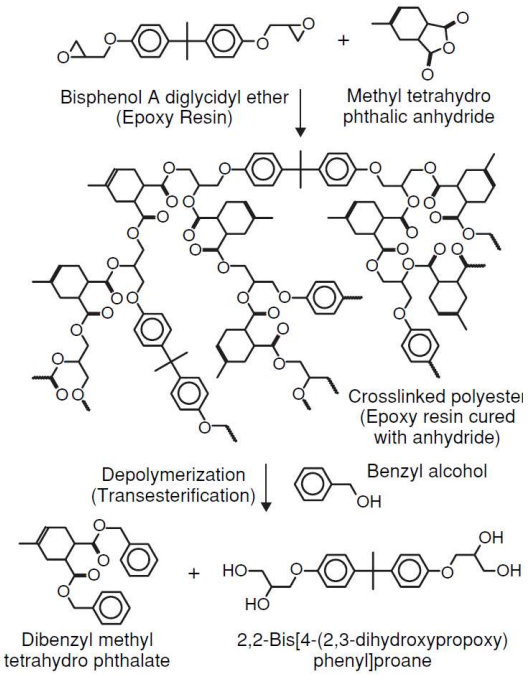

Figure 2 Depolymerization monomers obtaioned with Hitachi route

Li et al [5] recently presented a novel approach for chemical recycling thermoset composites by using a two steps process. The composites sheets were first treated in acetic acid at 120 °C for 30 min and then dissolved in hydrogen peroxide and acetone mixed solution at 50–120 °C for 30 min. The degraded products obtained from the matrix were analyzed showing the presence of bisphenol A and its derivatives, such as phenol derivatives.

Banatao et al [6] presented a much efficient recycling method based on the patented technology Recyclamine. In this paper, the main focus was on demonstrating the feasibility of recyclamine to obtain recyclable thermoset. The recycling method developed allowed to use very mild conditions to transform all the thermoset matrix in a thermoplastic resin. The carbon fibers obtained were proved to be very clean and with no sign of degradation. In the present paper, the use of recylamine is further studied by combining them with bioepoxy monomer and hybrid carbon/natural fibers lay up. In addition to technical analysis LCA was used to quantify the environmental benefits of the proposed approach.

2. EXPERIMENTAL

Epoxy monomer SuperSap300 by Entropy Resins was mixed with the Recyclamine®301 by Connora Technology. The SuperSap300 is composed of epoxidized pine oils, bisphenol A/F type epoxy resin, benzyl alcohol, and proprietary reactive epoxy diluents. The Recyclamine® 301 is cleavable polyamine ether. For the samples cured with VARTM at room temperature a curing inhibitor was added to the formulation. The carbon fabric use was a twill fabric of T300 carbon fibers purchased from Prochima, Italy. Natural fiber fabrics were outsourced from different producers: flax fabric (Composite Evolution,United Kingdom) were obtained by Composites Evolution (UK); hemp mat (uk) were purchased from Hemp Core Ltd, UK. The technical details of the materials used are reported in Table 1.

Table 1 Technical details of the reinforcements used for laminates preparation

Fabric Details			
Fabric Type	**Carbon**	**Flax**	**Mat**
Fabric textures	Twill	Twill	Random
Areal weight	190gsm	400gsm	600gsm
Fiber type	T300	Flax Yarn	Hemp Short fibers

Two different techniques were used to prepare composites laminates: HPRTM and VARTM. For the HPRTM samples the HPRTM cell of the Cannon-Afros laboratory in Saronno, Italy. The HP-RTM cell has a 1000ton press and an HP-RTM unit developed by Cannon-Afros. The mold used for the trials is an omega shaped mold with one central injection point (Fig.3). The reinforcements were cut manually and placed in the mold preheated at 120°C. No preconsolidation or binder was used for preforming. Once the mold was filled with the reinforcements the mold was automatically closed and vented. The resin was then injected in about 20sec and the injection stopped when the internal pressure in the mold reached 50bar. The curing times tested varied from 5 to 15min. The panels were postcured for 1hr at 120°C for comparison with precured samples.

Figure 3 Omega shaped mold used for HPRTM specimen manufaturing

The VARTM specimens were produced using a standard VARTM approach. 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 (Fig.4). 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 epoxy resin was vacuum infused into the stacked layers, which was maintained at room temperature under a constant vacuum (-75 cmHg). The temperature was kept at room temperature °C for 6 h and then the samples were postcured at 120°C for 1 h before testing.

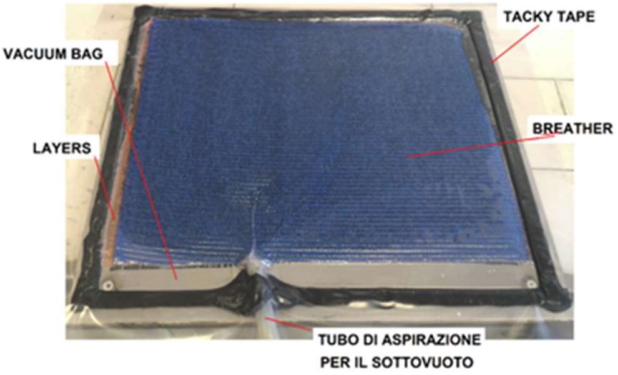

Figure 4 VARTM assembly to prepare hybrid lay up

For both VARTM and HPRTM the following hybrid lay up were tested.

Table 2 Hybrid lay up tested

SAMPLE CODE	Layers	Fabric
4NF	4	Flax Biotex
8CF	8	Carbon
1NF/6CF/1NF	1 + 6 + 1	Flax + Carbon + Flax
3CF/1NF/3CF	3 + 2 + 3	Carbon+ Flax + Carbon

Composite laminates were characterizied in tensile and flexural mode with an Instron 5092 ma-chine equipped with a 10kN load cell. Dynamic Mechanical Analysis was carried out in three point bending mode using a Triton DMA. Scanning electron microscopy (SEM) was carried out on gold sputtered samples with a SEM EVO from Zeiss. Life Cycle Analysis (LCA) was perfomed using SimaPro 8 software.

3. RESULTS

Fig.5 shows the results of tensile characterization for the hybrid samples produced with HPRTM and VARTM. The results for tensile strength showed a clear advantage when using HPRTM instead of VARTM. This result seems the consequence of better compaction achieved in the HPRTM cell. Fig.5 shows the SEM characterization of the HPRTM fractured specimen which confirmed the quality of the laminates. Young modulus measurement revealed similar behavior. Flexural testing was performed on the same samples. The results showed similar trends of tensile testing in terms of better mechanical properties of HPRTM samples over VARTM. The differences were however even higher. Moreover, the effect of hybridization was markedly different between 1NF/6CF/1NF and 3CF/1NF/3CF. The latter laminate configuration showed flexural modulus and strength of 25.58 GPa and 300.55 MPa respectively. These values were comparable to those of 8CF sample (i.e. E_f = 31.2 GPa, σ_f= 193.14 MPa) and higher than 1NF/6CF/1NF laminate (i.e. E_f = 6.76 GPa, σ_f= 90.2 MPa). Similar results were published by Zhang et al [7] in a study on the hybridization of glass fiber with flax fiber. In this case the findings were explained as the result of improved stress transfer efficiency due to the rough surface of flax fiber and the twisted flax yarn structure which played a bridging effect role.

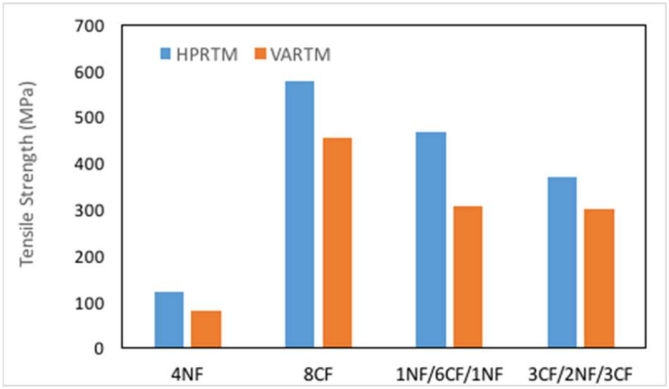

Figure 5 Tensile testing results on hybrid specimens

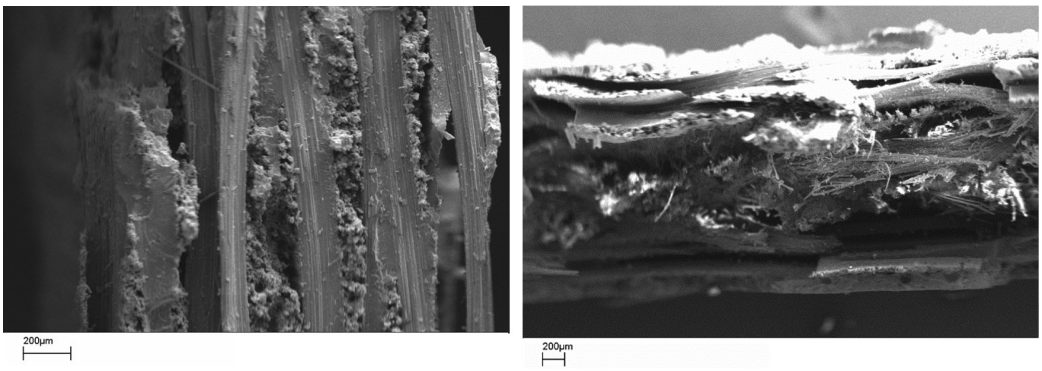

Figure 5 SEM micrograph of fractured specimens: sample 8CF (sx), sample3CF/1NF/3CF (dx)

Once completed the characterization of the laminates the recycling of the cured laminates was carried out in the laboratory using a water/acetic acid solution. The cured laminates were treated in the solution for 3 h at 80°C. After three hours the matrix was fully dissolved and the fibers were clean. In order to recover the thermoplastic matrix resulting from the cleaving action of the recyclamine washing and separation was carried out with the following procedure: the mixture (i.e. solution + dissolved matrix +fibers) was filtered and the fibers separated from the liquid phase. The fibers were allowed to dry and weighed. The acetic solution was neutralized with a NaOH (pH=10) until a brown solid precipitated appeared (Fig.5). When natural fiber reinforced samples were tested the natural fiber were recovered with no apparent degradation. The recycled carbon fibers were also analyzed in their virgin and recycled form (Fig.7) and no clear sign of degradation was observed.

The recovered brown powder was pelletized and further processed in a microinjection unit set with a barrel temperature of 180 °C and a mold temperature of 25 °C. Dog bone shaped specimens were obtained (Fig.8). These samples were tested accordingly to ASTM D790 in tensile mode and the results are showed in Fig.9. The recovered thermoplastic displayed a tensile strength of 42.29 MPa and a tensile modulus of 2.85 GPa. This value are fairly close to those reported in literature for the so called epoxy thermoplastic which are foreseen to present a chemical structures similar to those obtained by the chemical recycling of the epoxy network with our proposed approach.

Figure 6 Scheme of chemical recycling and resulting products

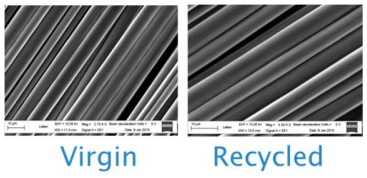

Figure 7 SEM micrograph of virgin carbon fibers compared to the carbon fibers recovered from chemical recycling of cured 8CF sample

Figure 8 Dog bone specimens produced by injection molding of the recovered thermoplastic obtained from the chemical recycling of the epoxy network of cured laminates

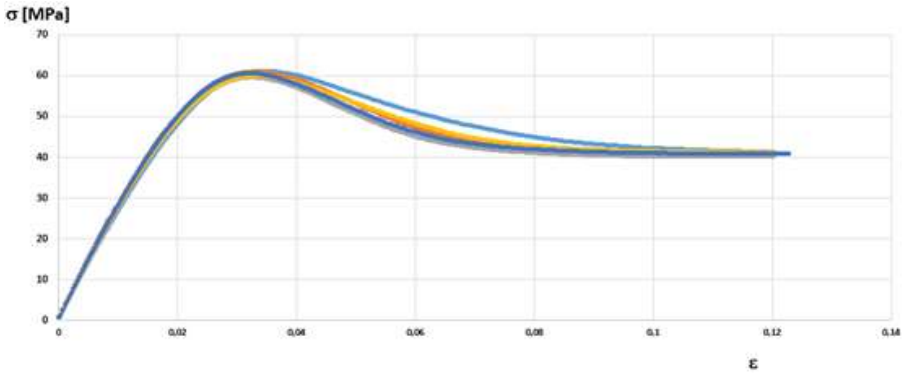

Figure 9 Tensile-strain curves for 8 Dog bone specimens produced by injection molding of the recovered thermoplastic

In the attempt to define the environmental impact of the hybrid lay up design combined with the use of the developed formulation LCA was performed. To obtain a better and more inclusive analysis the hybrid lay up simulated with LCA included the use of hemp mat as well. The results, for the global Warming Potential indicator, are summarized in Fig.10. The data obtained were comparable to previous models developed by our group [8-10]. The 8CF lay up is the most impacting due to the use of carbon fibers. The use of hybrid layup lowers the impact on GWP but is only for lay up using hemp mat only that substantial reduction were observed. This result is the consequence of the different cultivation methods for flax and hemp and the higher impact for the production of yarn in place of mat.

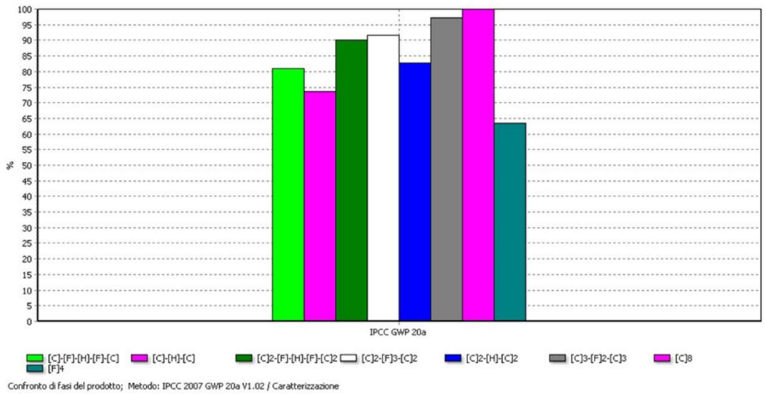

Figure 10 IPCC GWP indicator analysis for hybrid lay up composite laminates in the case of VARTM processing

LCA analysis were carried out to evaluate the environmental benefit of chemical recycling as well. In this case the impacts of different recycling methods were compared to landfill and incineration. The results (Fig.11) showed that, in terms of IPCC GWP, the chemical recycling developed allows to save more than 60%. These findings open new possibility in terms of reuse of recycled carbon fibers but, also, in the case of natural fibers.

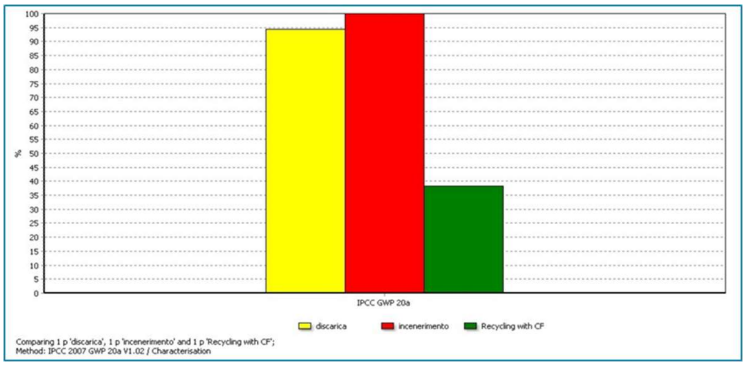

Figure 11 10 IPCC GWP indicatoranalysis for different end of life options for recycling of 8CF laminates

4.CONCLUSIONS

In the present paper the use of a novel bioepoxy formulation was discussed. The combination of bioepoxy monomers with cleavable ammine is the novelty of the approach. Hybridization of the carbon fibers with natural fibers. The novel formulation proved to be processable both with HPRTM and VARTM. However, the higher compaction used in HPRTM resulted in better mechanical properties. The hybridization approach was confirmed to be an efficient method to obtain high performances laminates with reduced environmental impact as showed by LCA analysis. However, LCA revealed that proper choice of natural fiber reinforcement could be relevant to get higher improvements in terms of environmental benefits. Finally, it was demonstrated the feasibility of the recycling method developed to lead to the recovery of clean reinforced fibers and usable thermoplastic matrix. LCA analysis of the recovered carbon fibers evidenced the potential benefits of this recycling approach to yield products with high impact in terms of resources savings.

5. REFERENCES

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