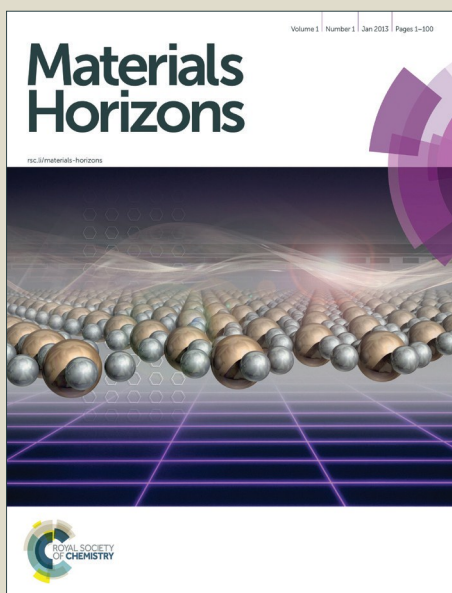


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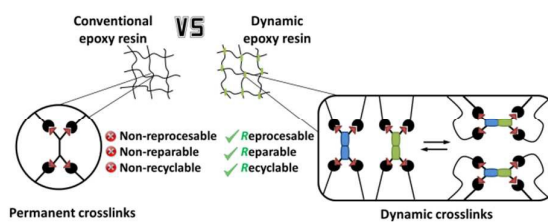
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## TOC



Thermoset fiber-reinforced polymer composites can now be reprocessed, recycled and repaired, thanks to a dynamic epoxy resin.



Journal Name

COMMUNICATION

## Epoxy Resin with Exchangeable Disulfide Crosslinks to Obtain Reprocessable, Repairable and Recyclable Fiber-Reinforced Thermoset Composites

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**Fiber-reinforced polymer composites (FRPCs) made of a “dynamic” epoxy resin possess good mechanical properties, while showing reprocessability, reparability and recyclability. The FRPCs are easily synthesized from readily available materials, and could therefore be easily implemented in transportation, energy or construction industries, among others.**

### 1. Introduction

It is foreseen that the use of FRPCs in lightweight structures will strongly increase energy efficiency and conservation of resources. In this sense, constant demands for fuel efficient vehicles and environmental regulations for low CO<sub>2</sub> emissions drive the growth of composite market. Among the different FRPCs, glass- or carbon-reinforced thermoset epoxy composites are usually preferred when structural performance is required. Epoxies generally out-perform most other resin types in terms of mechanical properties and resistance to environmental degradation, which leads to their almost exclusive use in aircraft components. Other advantages include good thermal properties, high water resistance, low cure shrinkage, etc. However, due to their thermosetting nature, epoxy composites also have some very important drawbacks: Once a thermoset composite is cured, it cannot be remolded, reshaped or dissolved, and therefore, their recycling or repairing is extremely difficult. Moreover, their associated component manufacturing processes are mostly focused on low-medium volume productions, due to the relatively long curing-times required to chemically form the polymer network.

Dynamic covalent chemistries<sup>1</sup> have been recently applied for the obtaining of unconventional polymer networks with intriguing properties. Thus, new concepts such as Dynamers,<sup>2,3</sup> Covalent Adaptable Networks (CANs)<sup>4-6</sup> or Vitrimers<sup>7</sup> have

emerged as a hot topic in polymer and materials science. The latter concept, pioneered by Leibler and co-workers, is an especially interesting approach which could potentially overcome some of the above mentioned limitations related to thermoset FRPCs. The idea underneath is to introduce exchangeable bonds in a polymer network, which can rearrange thermally (or under another stimulus), while keeping the network integrity. This enables unprecedented functionalities to such polymer networks, such as thermoforming, repairing, reprocessing or recycling. It is worth noticing that most of the state-of-art examples of dynamic thermosets are based on soft, non-structural materials,<sup>8,9</sup> with a few exceptions.<sup>7,10-12</sup>

In a very recent and comprehensive *minireview* from Du Prez and co-workers,<sup>13</sup> vitrimer materials developed so far are overviewed according to the nature of the dynamic exchange reaction. The most popular dynamic chemistries used for the design of vitrimer or vitrimer-like materials have been carboxylate transesterification,<sup>7,14</sup> transamination of vinilogenous urethanes,<sup>12</sup> transalkylation of triazolium salts,<sup>15</sup> transcarbamoylation,<sup>16</sup> siloxane silanol exchange,<sup>17</sup> olefin metathesis,<sup>18</sup> disulfide exchange<sup>19</sup> and imine amine exchange.<sup>20</sup> Despite the great scientific significance of all these systems, their use in real industrial applications, such as FRPCs, is far from being straightforward. This is due to different issues which are inherent to the chemical nature of each system: catalyst insolubility, aging or leaching; long-term instability towards oxidation or hydrolysis; thermal degradation during reprocessing; low mechanical properties; scalability and cost; etc. In this scenario, the development of new industry-friendly vitrimer systems is still necessary, in order to obtain innovative thermoset structural materials which can be easily (re)processed, repaired and recycled.

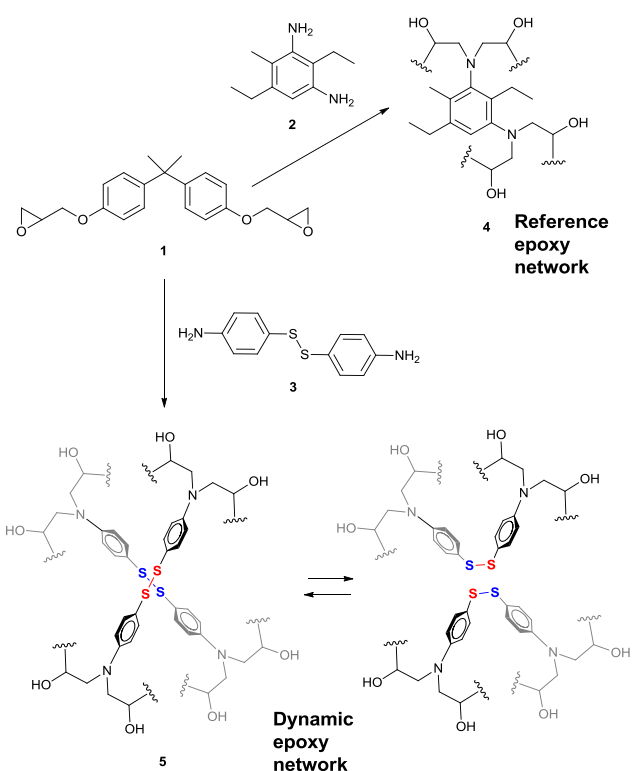
Reversible epoxy networks based on Diels-Alder chemistries have been previously reported.<sup>21-23</sup> However, even these systems are reprocessible and recyclable, they are not considered vitrimers due to the dissociative nature of the Diels-Alder moieties. In these systems there is a temporary loss of cross-links, which results in a sudden viscosity drop, as

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is normally observed for thermoplastic materials. Having all this in mind, here we report a new epoxy vitrimer system, whose uniqueness compared to other related vitrimers relies on several aspects, such as: i) ease of synthesis from readily available starting materials in a scalable manner, ii) fast stress relaxation at high temperature (vitrimer behavior) without the need of a catalyst, and iii) can be easily applied for the manufacturing of (re)processable, repairable and recyclable FRPCs. This dynamic epoxy system is based on the reversible exchange of aromatic disulfides, an approach that we have recently reported for the creation of self-healing<sup>19</sup> and reprocessable<sup>8</sup> poly(urea-urethane) elastomers. Such exchange reaction has been recently proposed to proceed via a radical-mediated [2+1] mechanism.<sup>24</sup>



**Scheme 1.** Synthesis and chemical structure of reference and dynamic epoxy networks here studied.

## 2. Results and discussion

### 2.1. Synthesis and characterization of reference and dynamic epoxy resins

A wide range of epoxy monomers with different functionalities are commercially available and widely used in the composites industry. Reaction of these monomers with different hardeners (typically having amine, anhydride or carboxylic acid functionalities) gives access to a wide choice of epoxy networks, which can be tuned according to the targeted material properties by varying the monomers, hardeners or the stoichiometry. In order to constitute a representative example of a material with good mechanical properties and high glass transition temperature ( $T_g$ ), diglycidyl ether of

bisphenol A (DGEBA, **1**) was chosen for being one of the most widely used epoxy monomers in the market. Diethyltoluenediamine (DETDA, **2**) was chosen as the reference hardener, whereas 4-aminophenyl disulfide (AFD, **3**) was chosen as the dynamic hardener (see Scheme 1).

The epoxy networks were prepared by mixing DGEBA with the corresponding hardener in bulk at 60–80 °C followed by a curing process at higher temperatures. The reaction was followed by Fourier transform infrared spectroscopy (FTIR), where the disappearance of bands corresponding to the epoxy group at 915  $\text{cm}^{-1}$  (C–O stretching of oxirane ring) and 3056  $\text{cm}^{-1}$  (C–H stretching of oxirane ring) was used as criteria to establish that the curing was complete (see Figure S1 in ESI).

No residual curing exothermic peak was observed by differential scanning calorimetry (DSC), confirming the complete curing of both epoxy networks (Figure S2 and Figure S3). From the DSC thermograms, comparable  $T_g$  values were determined for reference network **4** and dynamic network **5**, respectively (Table 1).

From the dynamic mechanical analysis (DMA),  $T_g$  and storage modulus ( $E'$ ) values showed to be comparable for both reference network **4** (Figure S4) and dynamic network **5** (Figure S5). A rubbery plateau of 20 MPa at 150 °C, typically attributed to chemically crosslinked polymer systems, confirmed the presence of a network (Table 1).

Thermogravimetric analysis (TGA) showed that both resins possess thermal stabilities up to 300 °C (Figure S7, Figure S8). The dynamic network **5** showed a slightly inferior degradation temperature ( $T_d$ ) (Table 1), which could be attributed to the presence of disulfide species, which are energetically less stable than carbon-carbon bonds.

Tensile tests were performed in order to characterize the mechanical properties of both reference and dynamic epoxy resins (Figure S9). Both materials showed similar stress and strain at break (Table 1), which means that the mechanical properties of both systems are similar at temperatures below  $T_g$ .

Thus, the thermal and mechanical properties of both reference and dynamic networks resulted to be comparable. This indicates that the use of AFD instead of a classical diamine hardener (DETDA) does not, in principle, alter the thermal or mechanical performances of the resulting epoxy thermosets. This is quite important for potential industrial applications, as the substitution of current resins for dynamic resins would not affect the performance of the final components.

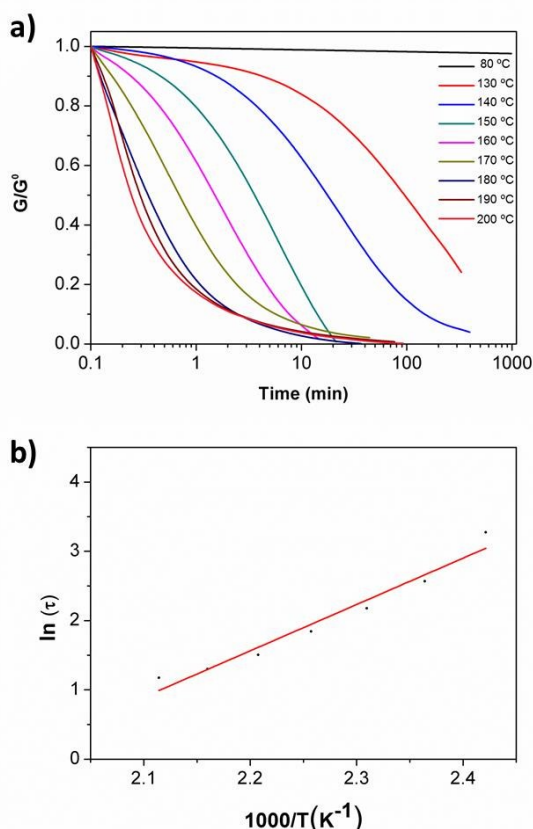
**Table 1.** Thermal and mechanical properties of reference and dynamic epoxy networks **4** and **5**.

	$T_g$ (DSC) [°C]	$T_g$ (DMA) [°C]	$T_d$ [°C]	$E'$ (25 °C) [GPa]	$E'$ (150 °C) [MPa]	Stress <sup>a)</sup> [MPa]	Strain <sup>a)</sup> [%]
Reference network <b>4</b>	127	130	350	2.5	20	81	7.3
Dynamic network <b>5</b>	130	130	300	2.6	20	88	7.1

<sup>a)</sup> Values at break.

## 2.2. Dynamic properties

As shown above, AFD could be used to obtain epoxy networks that are thermally and mechanically comparable to classical networks obtained with commercial diamine hardeners. However, for containing such reversible disulfide bridges, dynamic network **5** was expected to show vitrimer behavior and thus, some interesting features derived from it. As shown in the following subsections, stress relaxation was studied first, followed by reprocessing, repairing and recycling tests.



**Figure 1.** a) Normalized stress relaxation curves of dynamic epoxy network **5** at different temperatures. b) Fitting of the relaxation times to the Arrhenius' equation ( $R^2 = 0.946$ ).

### 2.2.1. Stress relaxation

The time and temperature dependent relaxation modulus of dynamic network **5** was tested by DMA in order to characterize its heat induced malleability. During the test, a specimen of  $12.5 \times 6 \times 1$  mm was first preloaded by applying  $10^{-3}$  N to assure straightness. After reaching the required temperature, 1% strain was applied and the relaxation modulus was monitored as a function of time. Figure 1a shows the normalized stress relaxation curves at different temperatures (namely, 80, 130, 140, 150, 160, 170, 180, 190 and 200 °C). The results showed that at temperatures above  $T_g$ , the epoxy network was able to completely relax stress and flow. Based on the Maxwell's model for viscoelastic fluids, relaxation times were determined as the time required to relax 63% of the initial stress. The obtained relaxation times ( $\tau^*$ ) ranged from 3

hours at 130 °C to 20 seconds at 200 °C. To the best of our knowledge, no other uncatalyzed vitrimer with  $T_g$  or  $T_v$  above 100 °C has been reported to have such rapid relaxation time. As shown in Figure 1b, the value of the relaxation time  $\tau^*$  as a function of the temperature follows the Arrhenius' law, which is given by Equation 1.<sup>25</sup> From this equation, an activation energy ( $E_a$ ) of  $55 \text{ kJ mol}^{-1}$  was calculated for the dynamic epoxy network **5**. Such activation energy is lower than other reported systems,<sup>7, 12, 15, 16, 18, 26</sup> in good agreement with the fact that aromatic disulfide metathesis does not require heat.<sup>19</sup>

$$\tau(T) = \tau_0 \exp\left(\frac{E_a}{RT}\right) \quad (\text{Equation 1})$$

A key characteristic for vitrimer materials is the topology freezing transition temperature ( $T_v$ ).  $T_v$  corresponds to the temperature in which transition from solid to liquid occurs as a result of bond exchange reactions in the network. Such transition is considered at the point at which the viscosity becomes higher than  $10^{12} \text{ Pa s}$ .<sup>27-29</sup> In our case,  $T_v$  could be determined by the extrapolation of the Arrhenius' fitted line (Figure 1b) when  $\tau^* = 3 \cdot 10^5 \text{ s}$ .† For our dynamic epoxy system **5**, the hypothetical  $T_v$  value obtained was  $-13 \text{ °C}$ , which is well below its  $T_g$  ( $127 \text{ °C}$  from DSC). This is indicative of a fast exchange reaction embedded in a rigid polymer matrix. In these cases,  $T_v$  is calculated via extrapolation of stress relaxation.<sup>13</sup> It is worth noticing this transition is hypothetical, since the network is not frozen from the reaction kinetics, but by the lack of segmental motions associated to the  $T_g$ . Thus, this would explain why at temperatures above  $T_g$  the relaxation of this system was very fast.

For comparison, the stress relaxation of reference epoxy network **4** was measured at 160 °C, where no significant relaxation was observed (Figure S11).

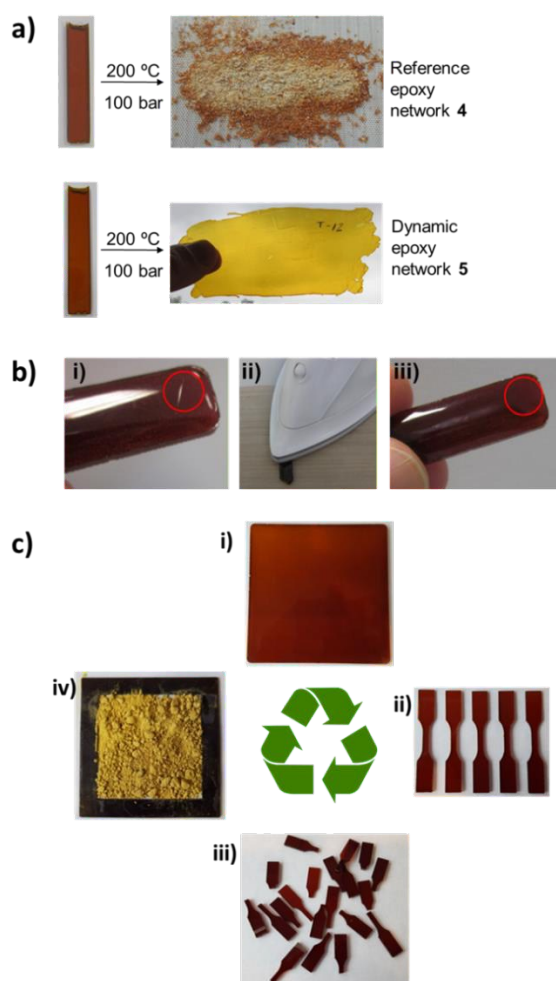
### 2.2.2. Reprocessing/reshaping

Thus, once the vitrimer behavior of the material was confirmed, the reprocessability of the dynamic epoxy network was studied. From these very short relaxation times (20 s at 200 °C), one could expect that this dynamic system, although presenting similar or equal mechanical properties than conventional epoxy resins, could be easily reprocessed at temperatures above  $T_g$ . The reprocessability of fully cured reference epoxy network **4** and dynamic epoxy network **5** was studied by hot pressing experiments. The corresponding specimens were processed in a hot press at 200 °C and 100 bar for 5 minutes. As shown in (Figure 2a), hot pressing of the reference epoxy **4** led to a broken material in the form of powder. In contrast, the dynamic epoxy network **5** gave a reshaped object in the form of a film. In this case, the reprocessed material showed the same mechanical properties as the pristine material, as confirmed by DMA measurements (Figure S6). This process could be theoretically repeated as many times as desired, although repeated processing may cause the aging of the material.

### 2.2.3. Repairing



Repairing of thermoset objects is a very difficult issue, since once the chemical network is disrupted by damage, the formation of new chemical connections would be necessary in order to recover the integrity of the material. In our everyday life, broken thermosets are usually repaired by applying glue. However, dynamic thermosets offer a new paradigm towards damage repair; recently, aromatic disulfide containing elastomers have been shown to have self-healing ability at room temperature.<sup>19</sup> However, in the present epoxy system disulfide reshuffling is frozen due to the high  $T_g$  of the material. Thus, repairing by disulfide bond reshuffling requires temperatures above  $T_g$ . In order to show the reparability of the dynamic epoxy resin **5**, a small scratch performed on a specimen was repaired just by applying heat and pressure with a household iron ( $\sim 200$  °C, Figure 2b). Attempts to repair reference epoxy resin **4** were unsuccessful.



**Figure 2.** a) Reprocessing experiments of reference and dynamic epoxy specimens in a hot press. b) A scratched dynamic epoxy specimen (i) was repaired by applying heat and pressure with a conventional iron (ii) obtaining a repaired specimen (iii). c) A pristine film of dynamic epoxy **5** (i) was used for obtaining dumbbell-shaped specimens (ii) which after being tested (iii) was grinded to powder (iv) and hot-pressed to obtain a recycled film.

#### 2.2.4. Recycling

The presence of dynamic chemical crosslinks in thermoset polymers also allows their recyclability. Depending on the

nature of the dynamic chemical bonds, such recycling can be achieved both chemically and mechanically. In the case of aromatic disulfide bonds, chemical degradation and dissolution of similar epoxy systems has been studied to a certain extent.<sup>30-33</sup>

In order to study the mechanical recycling of dynamic epoxy network **5**, the material was grinded to fine powder, which was then compacted into a mold by applying heat and pressure. Figure 2c shows photographs of the complete recycling sequence. Samples obtained after recycling showed perfect visual appearance. In addition, the mechanical properties of the mechanically recycled materials resulted to be comparable to the pristine materials (Figure S10), as tensile tests showed no changes in stress and strain at break after recycling. This could be explained by the fact that the less energetically stable disulfide bonds would preferentially break during the grinding process, and due to their reversible nature, the reshuffling of such bonds would lead to a full recovery of mechanical properties during the compacting process.

As can be concluded from Figure 2a, the reference epoxy resin **4** could not be recycled from powder.

#### 2.3. Application in fiber-reinforced polymer composites

As mentioned in the introduction, FRPCs based on thermoset epoxy resins are a class of high-performance structural materials with a great potential in a broad variety of industrial sectors. However, their difficulties for (re)processing, repairing or recycling, which are inherent to their thermoset nature, are limiting their fast growth in applications such as automotive. In the following sections, FRPCs made of dynamic epoxy system **5** and glass- or carbon-fiber reinforcements are studied.

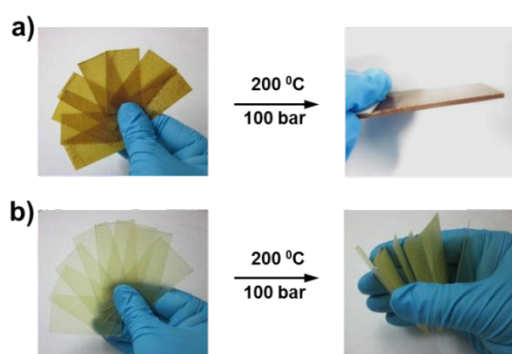
##### 2.3.1. Enduring preregs

Preregs, consisting of a reinforcement material impregnated with a resin matrix, are widely used as starting materials in the manufacturing of thermoset composite components. Usually, the matrix system used to impregnate a prepreg material is an epoxy-based resin. Once the reinforcement is impregnated, the epoxy matrix is partially cured (referred to as B-staged) and tacky, and in this form is supplied to the composite manufacturer, who can use it to lay-up the part. Such partial curing of the matrix prevents the epoxy resin from leaking from the reinforcement fibers, while still keeping enough epoxide and hardener functional groups to perform the curing and consolidation of the final thermoset component in a final manufacturing step. Although such prepreg systems are widely used in industry, they still have some limitations: a) Since the matrix is in a B-stage, the prepreg sheets need to be covered on both sides with a protective release film, which needs to be eliminated prior to use; b) the preregs need to be stored either refrigerated or frozen prior to use, having the material a limited shelf-life (the maximum storage life when stored continuously in a sealed moisture-proof bag, typically at  $-18$  °C) and out-life (the maximum accumulated time allowed at room-temperature during its manipulation). This is due to the fact that the epoxide groups of the resin slowly keep reacting with the hardener, and after a certain period of time (specified

by the manufacturer), such reactive functional groups will no longer be present in a sufficient amount for the final consolidation step; c) once the expiration date is past (shelf-life and out-life), the prepreg does no longer have the capacity to adhere to itself or to the tool, being impossible to use it to form a consolidated laminate or final component. In this case the expired prepregs are rejected, creating a non-reusable waste; and d) when the prepregs are extracted from the refrigerators prior to use, they need to be kept in a sealed bag until reaching room-temperature, in order to avoid the condensation of water droplets due to the difference of temperature. This process can take hours, if the prepreg rolls are large.

The dynamic character of the here described epoxy resin **5** would permit the manufacturing of a new class of “enduring prepregs”, as totally cured prepreg sheets could still be valid for the fabrication of multilayered composite parts. Thus, prepreg sheets made of dynamic epoxy resin **5** would no longer need to be stored in refrigerators, avoiding all the above mentioned drawbacks.

In order to demonstrate that, eight single enduring prepreg sheets made from totally cured dynamic epoxy resin **5** were laid-up and hot pressed. The result was a perfectly compacted multilayer composite (Figure 3a). When equivalent prepreg sheets made of reference epoxy resin **4** were submitted to the same process, no multilayered composite was obtained (Figure 3b).



**Figure 3.** a) Individual prepreg sheets of fully cured dynamic epoxy resin **5** with 50 v% of glass-fiber prior (left) and after being hot-pressed (right) to obtain a compact multilayered composite. b) Individual prepreg sheets of fully cured reference epoxy resin **4** with 50 v% of glass-fiber prior (left) and after being hot-pressed (right) to remain as single sheets.

In order to demonstrate the effectiveness of such manufacturing process, an equivalent multilayered composite laminate was made by manual lay-up (see section 3.7. in ESI). As shown in Table 2, the mechanical properties of the laminate made from enduring prepregs showed superior compression, interlaminar shear, flexural and impact strengths. This could be attributed to a better compacting of such laminate, due to the higher pressure used in the processing of enduring prepregs.

### 2.3.2. Reprocessable thermoset composites

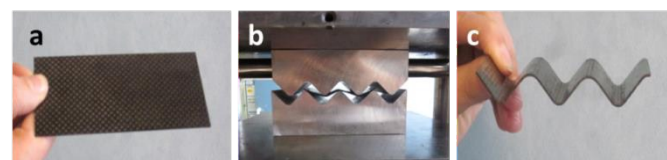
It was demonstrated above that dynamic network **5** could be easily reshaped by applying heat and pressure. Therefore,

composites based on such resin could be “thermoformed” even after curing. This could enable the fabrication of 3D thermoset FRPC parts from previously manufactured 2D laminates, which cannot be performed using conventional epoxy composites. Such thermoforming process could be very fast compared to actual manufacturing processes, thus having a tremendous impact for sectors such as automotive, where high volume productions are a must.

**Table 2.** Mechanical characterization of multi-layered laminates carried out by means of compression strength, flexural strength, impact strength and interlaminar shear strength (ILSS) measurements.

Composite preparation	Compression strength [MPa]	Interlaminar shear strength [MPa]	Flexural strength [MPa]	Impact strength [KJ m <sup>-2</sup> ]
Manual composite layup	242 ± 18	29 ± 1	557 ± 7	159 ± 18
Enduring prepregs	292 ± 16	37 ± 3	595 ± 39	194 ± 18

In order to demonstrate this, a 50 × 60 × 2 mm sheet of a multilayered dynamic carbon-fiber reinforced composite was manufactured by resin transfer molding (RTM). The sheet was then placed inside a preheated zig-zag mold and reprocessed in a hot press. After cooling to room-temperature, a zig-zag shaped 3D composite was obtained (Figure 4). An equivalent composite made from reference epoxy **4** could not be reprocessed, but the composite was broken instead when submitted to the same process.



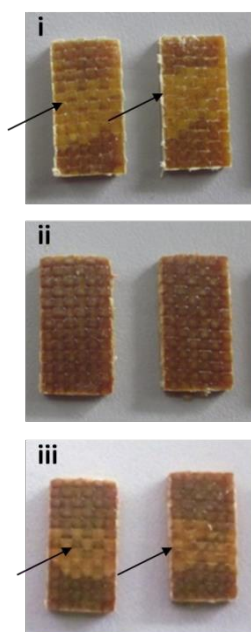
**Figure 4.** Thermoforming of cured composite laminate. A 2 mm thick carbon-fiber reinforced dynamic epoxy laminate (a) was compression-molded in a zig-zag shaped mold (b), rendering a thermoformed wavy 3D part (c).

### 2.3.3. Repairable thermoset epoxy composites

During service, high performance thermoset composites are susceptible to suffer different kinds of damage, such as (micro)cracks, delaminations, impacts, fractures, abrasion, etc. Current repair techniques for composites require special techniques and skilled workers, which makes them slow and expensive. In this sense, faster and more automated repairing methods are strongly required for composites in order to gain competitiveness against light metals. For instance, if the bodies of future ultra-light vehicles are going to be made from FRPCs, repairing of routine damage from events such as minor collisions will need to be feasible in a straightforward manner.

Delaminations are probably the most common failures in multilayered composite parts, which cannot be repaired in a straightforward manner. An approach to solve this problem could be the use of a dynamic epoxy resin, which could self-adhere by applying heat and pressure.

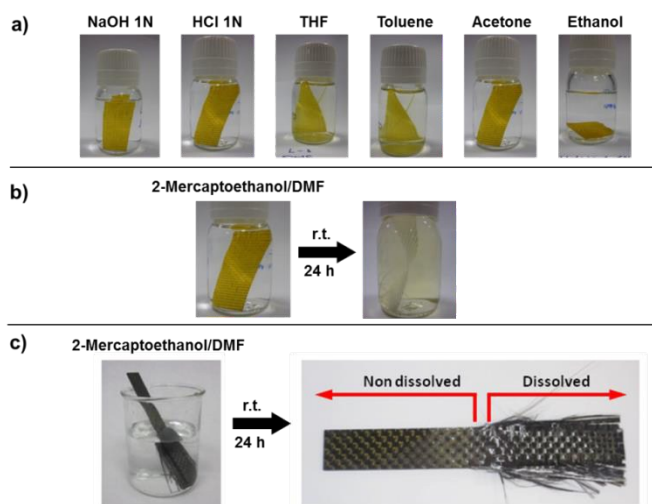
In order to investigate the repairing ability of FRPCs made of dynamic epoxy **5**, the following experiment was carried out. First,  $20 \times 10 \times 1.8$  mm specimens (ISO 14130) were cut from a FRPC sheet manufactured from enduring prepregs (see section 3.6. in ESI). Then, delamination was induced while performing interlaminar shear strength (ILSS) tests. ILSS tests are usually made to quantify the strength necessary to induce a delamination in the specimen. Thus, pristine specimens made of dynamic GFR epoxy composites gave an average strength value of  $37 \pm 3$  MPa, showing visual evidence of delamination (Figure 5i). The specimens were then submitted to 200 °C and 100 bar for 5 minutes in a hot press. After this, the reparation of the delamination was visible to the eye, as can be observed in Figure 5ii. Finally the samples were submitted again to ILSS tests, showing an average strength value of  $38 \pm 2$  MPa, which indicated a quantitative recovery of the damage.



**Figure 5.** i) Specimens of dynamic glass-fiber reinforced epoxy composites submitted to interlaminar shear strength (ILSS) test. ii) Repaired specimens after compression at 200 °C and 100 bar for 5 minutes. iii) Specimens after a subsequent ILSS test. The arrows indicate delaminated zones.

### 2.3.4. Recyclable thermoset composites

Thermoset composites cannot be easily recycled due to their permanent network structure. This is creating a strong barrier which limits their growth in the global market, especially in high volume applications such as automotive or wind energy. Current recycling methods are mostly based on high energy consuming processes such as pyrolysis, where the resin matrix cannot be recovered. FRPCs made of dynamic resin **5** offer the possibility for both chemical and mechanical recycling, as described below.



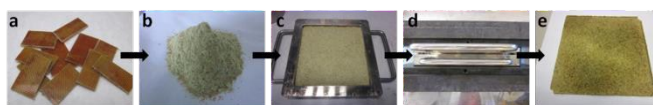
**Figure 6.** a) Sheets of dynamic epoxy composite remained unaltered after immersing in different chemical agents at room temperature for 72 h. b) Complete resin dissolution of a sheet of dynamic epoxy composite in a thiol-containing solution, whereas the glass-fiber reinforcement remained unaltered. c) Partial dissolution of CFR-epoxy composite in a thiol-containing solution, where the carbon-fiber in contact with the solution was recovered unaltered.

### Chemical Recycling

Similarly to conventional epoxy composites, dynamic epoxy composites showed good resistance to different chemical media such as THF, toluene, acetone, ethanol, NaOH or HCl (Figure 6a). However, due to the reversible nature of the disulfide crosslinks, the resin could be easily dissolved in the presence of a thiol, due to the thiol-disulfide exchange reaction which disrupts such crosslinks.<sup>33</sup> In order to proof that, a small fragment of the enduring epoxy prepreg was immersed in a solution of 2-mercaptoethanol in DMF. The system was magnetically stirred at room temperature for 24 hours, after which the epoxy matrix was completely dissolved (Figure 6b). The glass-fiber reinforcement was recovered undamaged by drying in an oven at 100 °C under vacuum for 24 hours. The same experiment was performed using a multilayered carbon-fiber composite made of epoxy resin **5**. As shown in Figure 6c, the carbon fibers were recovered undamaged after matrix dissolution.

### Mechanical Recycling

As another interesting approach, FRPCs made of dynamic epoxy resin **5** could also be recycled mechanically. This involved a two-step process, consisting of (i) grinding FRPC scraps into fine powder and (ii) compression molding of the powder to obtain “2<sup>nd</sup> generation” parts (Figure 7). It is worth noticing that in this case, the resulting short-fiber composite parts are not expected to have the mechanical performance of the initial continuous-fiber composite materials, and would therefore be used for other non-structural applications.



**Figure 7.** Mechanical recycling of dynamic epoxy composites. FRPC scraps (a) were ground to fine powder (b), which was then transferred to a square mold (c) and



submitted to 200 bars and 210 °C in a hot press (d) to obtain a 2nd generation composite sheet (e).

### 3. Conclusions

In the present paper we have shown that the combination of DGEBA and AFD leads to an epoxy vitrimer with very fast relaxation times and low activation energy. Unlike other reported vitrimer systems, here the starting materials are readily available and the synthetic process is easily scalable, which makes this system easily applicable for the manufacturing of FRPCs. The so-prepared FRPCs show equivalent mechanical properties as the reference epoxy counterparts, while showing new features such as (re)processability, reparability and recyclability, as demonstrated in the above examples. The FRPCs presented here are manufactured using standard manufacturing processes and equipment, by just substituting the conventional hardener by AFD, which is readily available in tonnes quantities at a competitive price. Thus, such system constitutes a step forward towards the implementation of vitrimers in industrial applications, and offers the possibility of obtaining a new generation of fiber-reinforced composite structures with enhanced functional properties.

### Acknowledgements

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### Notes and references

† We used the Maxwell relation:  $\eta = G \cdot \tau^*$ ,  $G$  being the shear modulus.  $G$  was calculated from the tensile modulus as measured by DMA from the relation:  $G = E' / (2(1 + \nu))$ , with  $\nu \approx 0.5$ , the Poisson's ratio usually used for rubbers, and  $E' \approx 10$  MPa.

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### Conceptual insights statements

Here we present a new epoxy vitrimer which has many advantages compared to the existing ones (simplicity, low cost, scalability and excellent properties) and we use such material for the fabrication of reprocessable, repairable and recyclable fiber-reinforced polymer composites. This is the first time that a vitrimer material is applied in the manufacturing of fiber-reinforced polymer composites. Someday, fiber-reinforced polymer composites might live up to its hype and make all of our cars and airplanes more lightweight and efficient. Today, though, parts made of the material are very expensive to manufacture, and are used mainly in race cars, high-end sports cars, and new jetliners. In addition, they cannot be reprocessed, repaired nor recycled. The new technology demonstrated in this paper will open the way towards high volume fabrication of fiber-reinforced polymer composites which, although being thermoset, can be reprocessed, repaired and recycled. The impact of this technology will be tremendous for the automotive, aeronautic, construction and wind energy sectors, and will be a revolution in the composite field.