# RESHAPEABLE, REPAIRABLE AND RECYCLABLE HIGH PERFORMANCE EPOXY THERMOSET COMPOSITES

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## Abstract

Fiber-reinforced polymer composites (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 reprocessing, repairing or recycling, which are inherent to their thermoset nature, are limiting their fast growth in applications such as automotive. In an approach to solve such limitations, a novel "dynamic" epoxy network based on reversible chemical crosslinks has been developed. FRPCs made of such dynamic resin possess mechanical properties equivalent to reference epoxy composites, while showing: i) good reprocessability of postcured composites by thermoforming; ii) reparability of delaminations and microcracks by applying heat and pressure in the damaged part; iii) recyclability by matrix dissolution or by grinding and reprocessing. In addition, the new FRPCs are easily synthesized from readily available materials, and could therefore be easily implemented in transportation, energy or construction industries, among others.

## 1. Introduction

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 $CO_2$ emissions drive the growth of composite market. With increasing production of FRPCs, the environmental impact of these materials and manufacturing cost are big concern. Among the different FRPCs, glass- or carbon-reinforced thermoset epoxy composites are usually preferred when structural performance is required. Epoxies generally are better than most of the 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. The recycling of FRPCs has been an important topic over the last two decades in order to make them more sustainable materials. Moreover, manufacturing processes of composite materials are mostly focused on low-medium volume productions, due to the relatively long curing-times required to form the network.

The dynamic chemical bonds present in such resins gives them a series of "smart" properties that could overcome all the above limitations associated to fiber-reinforced thermoset composites. In attempt to obtain sustainable thermoset materials we have recently developed an epoxy resin based on a new family of crosslinking systems containing reversible chemical moieties [1].

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The developed dynamic epoxy resin will provide new functionalities to high performance FRPCs, e.g., the intrinsic ability to be reprocessed, repaired and recycled, features not currently possible with current thermoset composites. This will permit to create a more sustainable composite industry, since most of the manufacturing and end of life (EoL) waste will be re-used or recycled. At the same time, recovering waste as a raw material for manufacturing new composite parts will increase the competitiveness of composite manufacturers and end users, due to savings in virgin raw materials (both fiber and resin).

Dynamic covalent chemistry has been demonstrated as a very promising route to obtain recyclable thermoset materials. The most popular dynamic chemistries used for the design of dynamic thermoset materials have been carboxylate transesterification [2,3], transamination of vinilogous urethanes [4], transalkylation of triazolium salts [5], transcarbamoylation [6], siloxane silanol exchange [7], olefin metathesis [8], disulfide exchange [9] and imine amine exchange [10]. In the present study we described the preparation of a novel dynamic epoxy system based on the reversible exchange of aromatic disulfides. Thus, the aim of the present study is to apply such smart resins to the composite industry, to create a new era of reprocessable, repairable and recyclable components.

## 2. Results and discussion

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 reprocessing, repairing or recycling, which are inherent to their thermoset nature, are limiting their fast growth in applications such as automotive. The developed dynamic high-performance fiber-reinforced thermoset composites can be manufactured by traditional methods such as: infusion, resin transfer molding (RTM), prepreging, etc. Herein, we describe the manufacturing of reshapeable, repairable and recyclable high performance epoxy thermoset composites from woven glass and carbon fiber and dynamic epoxy network.

### 2.1. Synthesis and characterization of dynamic composites

### Enduring prepregs

Both reference and dynamic “enduring prepregs” were synthesized by manual impregnation, using the following procedure: A sealant tape was placed on a 400 x 400 mm square glass mold. Then, a releasing agent (Frekote 770-NC) was sprayed evenly onto the surface of the mold. A 250 × 250 mm layer of glass- or carbon-fiber reinforcement was then placed on the mold. This was then manually impregnated with a previously obtained mixture of DGEBA (100 g) and Araldite XB3473 (34 g) or 4,4’-aminophenyl disulfide (AFD, 43.8 g), with the help of a brush. Once the fiber reinforcement was homogeneously impregnated, it was covered with a release film and then a layer of breather cloth was placed on the top, to soak up excess resin and ensure an adequate path for the vacuum pressure. Finally, the system was sealed with a vacuum bagging film and a hose connected to a vacuum pump was attached to the sealed part. Vacuum was then applied to the enclosed part, to promote compacting. Once the air was evacuated, curing was carried out in an oven at 120 ºC for 2.5 hours and at 150 ºC for additional 2 hours, to obtain a monolayer epoxy composite film.

### Synthesis of composites from “enduring prepregs”

As the dynamic nature of disulfide bonds in the epoxy network enables the reprocessability of these composites, here we describe the synthesis of multilayered composites by simply pressing totally cured multiple single layer sheets together.

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As a proof of concept hot-pressing of “enduring prepregs” was carried out as follows: 8 single laminate sheets previously manufactured as described before were laid-up and processed in a hot press at 200 ºC and 100 bar for 5 minutes. Then, the material was cooled down below $T_g$ and demolded. A compact multilayered composite was obtained only for the case of dynamic epoxy resin. In the case of reference epoxy resin, the sheets did not adhere.

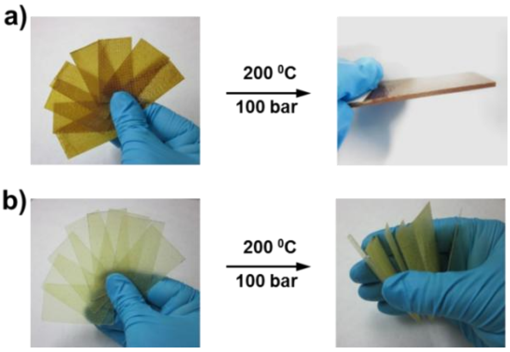

**Figure 1**. a) Individual prepreg sheets of fully cured dynamic epoxy resin with 50 v% of glass-fiber prior (left) and after being hot-pressed (right) to obtain a compact multilayered composite. b) Individual prepreg sheets of fully cured reference epoxy resin with 50 v% of glass-fiber prior (left) and after being hot-pressed (right) to remain as single sheets. Reproduced from Ref. 1 with permission from the Royal Society of Chemistry.

The mechanical properties of the multi-layered laminated were measured and as can be seen in Table 1, laminates made from enduring prepregs showed superior compression, interlaminar shear strength (ILSS), flexural and impact strengths.

**Table 1**. Mechanical characterization of multi-layered laminates carried out by means of compression strength, flexural strength, impact strength and ILSS measurements.

| Composite preparation | Compression strength (MPa) | Interlaminar shear strength (MPa) | Flexural strength (MPa) | Impact strength (KJ $m^{-2}$) |
|---|---|---|---|---|
| Manual composite layup | 242 ± 18 | 29 ± 1 | 557 ± 7 | 159 ± 18 |
| Enduring prepregs | 292 ± 16 | 37 ± 3 | 595 ± 39 | 194 ± 18 |

## Synthesis of dynamic composites by resin transfer molding (RTM)

The synthesis of dynamic composites was carried out by resin transfer molding (RTM). The reinforcement used was high-strength carbon-fiber (HexForce 43199) with plain wave architecture (basis weight 200 g $m^{-2}$). Eight reinforcement layers were placed in a flat square mold and this was then closed into a press at 130 ºC. The mold closure leads to compaction of the preform to the final part thickness, thereby leading to reduction in the preform permeability. The reactive resin mixture [premixed DGEBA (100 g) and AFD (43.8 g)] was then injected into the cavity with a pressure o 1.5 bar using a RTM equipment. Once all the reinforcement was wet out, the resin inlets were closed and compacted under 2.5 bar for 30 min, and finally the laminate was allowed to cure at 130 ºC for 1 h at the same pressure. After cooling down to room temperature, the resulting dynamic composite was demolded.

## 2.2. Reparability, reshapability and recyclability of high performance epoxy composites

### 2.2.1. Repairing

During service, high performance thermoset composites are susceptible to suffer different kinds of damage, such as (micro)cracks, delaminations, impacts, fractures, abrasion, etc. Due to the chemical nature of the thermoset materials is it a challenge to repair them and often damaged parts have to be completely replaced.

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 dynamic FRPCs, a delamination was induced into a GFR composite. We found that by applying heat and pressure to the broken sample a total repairing could be achieved (Figure 2). In order to quantify the recovery the following experiment was carried out. First, 20 × 10 × 1.8 mm specimens (ISO 14130) were cut from previously described FRPC sheets manufactured from enduring prepregs. Then, delamination was induced while performing interlaminar shear strength (ILSS) tests. Pristine GFR specimens gave an average strength value of 37 ± 3 MPa, showing visual evidence of delamination (Figure 3). The specimens were then submitted to 200 ºC 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 ± 2 MPa, which indicated a quantitative recovery of the damage.

**Figure 2.** (Top) Sideway view of delaminated specimen of dynamic glass-fiber reinforced epoxy composites. (Bottom) In the left hand side picture the delamination can be seen before repairing. The right hand side picture shows that half of the delamination was repaired after applying heat and pressure.

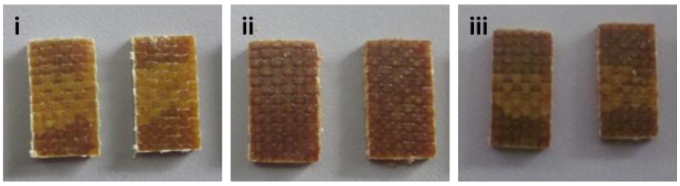

**Figure 3.** Specimens of dynamic glass-fiber reinforced epoxy composites submitted to interlaminar shear strength (ILSS) test. ii) Repaired specimens after compression at 200 ºC and 100 bar for 5 minutes. iii) Specimens after a subsequent ILSS test. Adapted from Ref. 1 with permission from the Royal Society of Chemistry.

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### 2.2.1. Reshaping

The dynamic character of the present epoxy resin can also enable reshaping of FRPCs. Cured composites based on such resin could be thermoformed by applying heat and pressure. To demonstrate that, a 50 × 60 × 2 mm dynamic CFRP composite manufactured by RTM was preheated at 200 ºC for 10 min. Then, it was placed into a steel zig-zag mold and hot pressed at 200 ºC and 100 bar for 5 min. After cooling down below $T_g$, a wavy 3D composite was obtained (Figure 4).

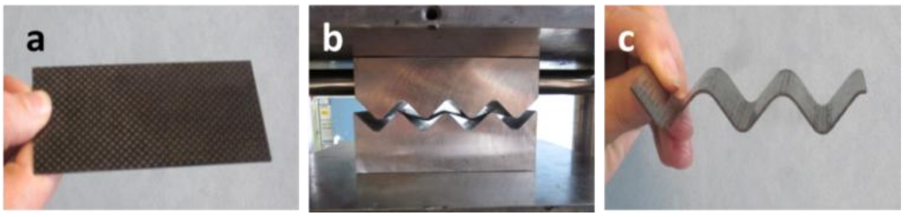

**Figure 4.** Thermoforming of cured composite laminate. A 2 mm thick carbon-fiber reinforced dynamic epoxy laminate (a) was compression-molded in a *zig-zag* shaped mold (b), rendering a thermoformed wavy 3D part (c). Reproduced from Ref. 1 with permission from the Royal Society of Chemistry.

### 2.2.1. Recycling

It is worth noticing that once a classical thermoset composite is cured, it cannot be remolded, reshaped or dissolved. Hence, the recycling of thermoset composites is extremely difficult. At present, there are very limited commercial recycling solutions for mainstream composite materials, due to this technological constraint. 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 offer the possibility for both chemical and mechanical recycling.

*Chemical Recycling*

The 3D polymer network made of dynamic epoxy resin can be completely disrupted by the addition of a thiol, due to the thiol-disulfide exchange reaction and thus, the resin can be totally dissolved without affecting the reinforcement. In order to demonstrate the chemical recycling of FRPCs made from the dynamic epoxy, a sample of the CFRP composite manufactured by RTM was immersed in a solution of 2-mercaptoethanol (0.2 mL) in DMF (20 mL) (
Figure 5). As can be seen in
Figure 5, the carbon fibers were recovered undamaged after matrix dissolution.

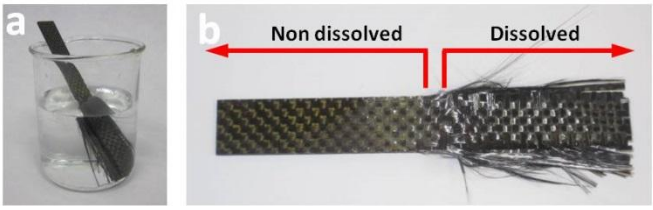

**Figure 5.** a) Partial dissolution of CFR-epoxy composite in a special reagent solution. (b) The fiber is recovered undamaged. Adapted from Ref. 1 with permission from the Royal Society of Chemistry.

Without the addition of the thiol, the resin is not soluble in traditional chemicals such as NaOH, HCl, TFH, toluene, acetone or ethanol (Figure 6). In this way, it will be possible to recover pristine fiber and the matrix in the form of a thermoplastic resin.

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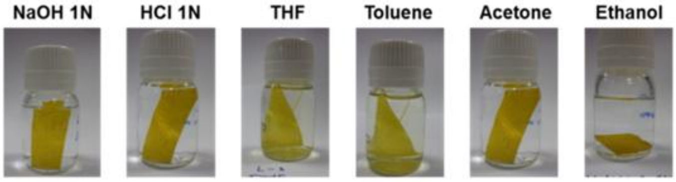

**Figure 6.** Sheets of dynamic epoxy composite remained unaltered after immersing in different chemical agents at room temperature for 72 h. Adapted from Ref. 1 with permission from the Royal Society of Chemistry.

*Mechanical Recycling*

FRPCs made of dynamic epoxy resin could also be recycled mechanically. This involved a two-step process, consisting of grinding FRPC scraps into fine powder and compression molding of the powder to obtain "2nd generation" parts. In order to demonstrate the mechanical recycling of FRPCs a dynamic composite made from enduring prepreg was chopped and ground to fine powder in a cutting mill. Then, the powder was introduced into a steel mold (150 × 150 × 1 mm) and hot pressed at 200 ºC and 100 bar for 5 min. After cooling down below $T_g$, a defect-free short-fiber reinforced composite sheet was obtained.

**Figure 7.** Mechanical recycling of dynamic epoxy composites. Reproduced from Ref. 1 with permission from the Royal Society of Chemistry.

## 3. Conclusions

In summary, in the present study we have demonstrated the use of newly developed dynamic epoxy resin as the matrix component for the manufacturing of FRPCs. The so-prepared FRPCs show equivalent mechanical properties as the reference epoxy counterparts, while showing new features such as reshapability, reparability and recyclability. The FRPCs presented here are manufactured using standard manufacturing processes and equipment, by just substituting the conventional hardener by a dynamic hardener. We have demonstrated that fully cured FRPC laminates can be remolded to a 3D shape by just applying heat and pressure. Delaminations present in FRPCs can be also easily repair by just applying heat and pressure. Finally we have demonstrated the complete recycling of FRPCs by mechanical or chemical methods. Thus, such system constitutes a step forward towards the implementation of dynamic epoxy resins in industrial applications, and offers the possibility of obtaining a new generation of fiber-reinforced composite structures with enhanced functional properties.

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## References

A. Ruiz de Luzuriaga, A. Rekondo, R. Martin, N. Markaide, , G. Cabanero, H.-J. Grande and I. Odriozola.

*Excerpt from ISBN 978-3-00-053387-7*

[1] A. Ruiz de Luzuriaga, R. Martin, N. Markaide, A. Rekondo, G. Cabanero, J. Rodriguez, and I. Odriozola. Epoxy resin with exchangeable disulfide crosslinks to obtain reprocessable, repairable and recyclable fiber-reinforced thermoset composites. *Materials Horizons*. 2016 (DOI: 10.1039/c6mh00029k)

[2] D. Montarnal, M. Capelot, F. Tournilhac, and L. Leibler. Silica-Like Malleable Materials from Permanent Organic Networks. *Science,* 334:965-968, 2011.

[3] K. Yu, P. Taynton, W. Zhang, M. L. Dunn, and H. J. Qi. Reprocessing and recycling of thermosetting polymers based on bond exchange reactions. *RSC Advances.* 4:10108-10117, 2014.

[4] W. Denissen, J. M. Winne, and F. E. Du Prez. Vitrimers: permanent organic networks with glass-like fluidity. *Chemical Science.* **7**:30-38, 2016.

[5] M. M. Obadia, B. P. Mudraboyina, A. Serghei, D. Montarnal, and E. Drockenmuller. Reprocessing and Recycling of Highly Cross-Linked Ion-Conducting Networks through Transalkylation Exchanges of C–N Bonds. *Journal of the American Chemical Society.* 137:6078-6083, 2015.

[6] D. J. Fortman, J. P. Brutman, C. J. Cramer, M. A. Hillmyer, and W. R. Dichtel. Mechanically Activated, Catalyst-Free Polyhydroxyurethane Vitrimers. *Journal of the American Chemical Society.* 137:14019-14022, 2015.

[7] P. Zheng, and T. J. McCarthy. A Surprise from 1954: Siloxane Equilibration Is a Simple, Robust, and Obvious Polymer Self-Healing Mechanism. *Journal of the American Chemical Society.* 134:2024-2027, 2012.

[8] Y.-X. Lu, F. Tournilhac, L. Leibler, and Z. Guan. Making Insoluble Polymer Networks Malleable via Olefin Metathesis. *Journal of the American Chemical Society.* 134:8424-8427, 2012.

[9] A. Rekondo, R. Martin, A. Ruiz de Luzuriaga, G. Cabanero, H. J. Grande, and I. Odriozola. Catalyst-free room-temperature self-healing elastomers based on aromatic disulfide metathesis. *Materials Horizons*. 1:237-240, 2014.

[10] P. Taynton, K. Yu, R. K. Shoemaker, Y. Jin, H. J. Qi, and W. Zhang. Heat- or Water-Driven Malleability in a Highly Recyclable Covalent Network Polymer. *Advanced Materials*. 26:3938-3942, 2014.

*Excerpt from ISBN 978-3-00-053387-7*