

Electronic Supplementary Information

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

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1. Materials

DGEBA-based epoxy resin (ARALDITE LY1564) and DETDA hardener (ARALDITE XB3473) were purchased from Huntsman Advanced Materials. DMF > 99%, 2-mercaptoethanol 99% and AFD 98% were purchased from Sigma-Aldrich and used as received. Carbon-fiber HexForce 43199 plain wave (basis weight 200 g m⁻²), glass-fiber HexForce 1103 PLAIN (basis weight 290 g m⁻²), release film and breather cloth were purchased from Gazechim. Frekote 770-NC release agent was purchased from Loctite.

2. Methods

FTIR spectra were recorded on a JASCO-4100 spectrometer with a diamond ATR probe. TGA were performed on a TA Instruments Q500 equipment under nitrogen atmosphere at a heating rate of 20 °C min⁻¹ from 25 to 600 °C. DSC measurements were performed using a Perkin Elmer Pyris Diamond DSC over a temperature range from 25 to 220 °C under nitrogen. Glass transition temperatures (T_g) were obtained as the inflection point of the heat flow step recorded at a scan rate of 20 °C min⁻¹. DMA experiments were performed using a TA Instruments DMA Q800 equipment. The mode of deformation applied was the single cantilever beam, and the mean dimensions of sample plaques were 12.5 × 2 × 17.5 mm. The temperature range varied from 25 to 250 °C. The temperature dependent behavior was studied by monitoring changes in force and phase angle, keeping the amplitude of oscillation constant (1 Hz) at a 3 °C min⁻¹ heating rate. Stress-relaxation experiments were also performed on a DMA Q800 instrument. Samples were initially preloaded at a force of 1 × 10⁻³ N to maintain straightness. After reaching the testing temperature, samples were allowed 30 extra minutes to reach the thermal equilibrium. The specimens were stretched by 1% and the deformation was maintained during the test. The decrease of stress was recorded and the stress relaxation modulus was calculated. Mechanical testing of epoxy resins was performed using an INSTRON 3365 Long travel Elastomeric Extensometer controlled by Bluehill Lite software.

Tensile strength measurements were carried out according to UNE-EN-ISO 527 standard, using dumbbell-type test specimens at an elongation rate of 1 mm min⁻¹. Mechanical testing of FRPCs was performed using an INSTRON 5985 controlled by Bluehill 3 software. Compression strength (ASTM 3410), flexural strength (ISO14125) and interlaminar shear strength (ILSS) (ISO 14130) measurements were carried out using the same equipment and according to international standards. Impact strength was measured using a CEAST 9050 impact pendulum (Instron, monitorized model) according to ISO 179. RTM fabrication of fiber-reinforced epoxy composites was performed on an Isojet DPE COMPACT injection machine.

3. Synthesis

3.1. Synthesis of epoxy networks

Synthesis of reference epoxy network 4: DGEBA (Araldite LY1564, 100 g) and DETDA (Araldite XB3473, 34 g) were mixed by heating at 60 °C and degassed under vacuum. Then, the resulting viscous homogeneous liquid was poured into a metallic mold and cured in an oven at 120 °C for 2.5 h and postcured at 150 °C for 2 h. The reaction was followed by Fourier transform infrared spectroscopy (FTIR), where a complete curing was confirmed by the disappearance of the epoxide bands at 3056 and 915 cm⁻¹.

Synthesis of dynamic epoxy network 5: DGEBA (Araldite LY1564, 100 g) and AFD (43.8 g) were mixed by heating at 80 °C and degassed under vacuum. Then, the resulting viscous homogeneous liquid was poured into a metallic mold and cured in an oven at 120 °C for 2.5 h and postcured at 150 °C for 2 h. The reaction was followed by FTIR, where a complete curing was confirmed by the disappearance of the epoxide bands at 3056 and 915 cm⁻¹ (see Figure S1).

3.2. Reprocessing/reshaping

The reprocessability of cured resins **4** and **5** was studied using 60 × 10 × 2 mm specimens obtained as described in section 3.1. Prior to hot pressing, the specimens were preheated at 200 °C for 10 min. The preheated specimens were then placed between two Teflon coated metal plates and hot pressed at 200 °C and 100 bar for 5 min. After cooling down below T_g , the samples were unmolded. As can be observed in Figure 2a, a broken material in the form of powder was obtained in the case of **4** and a defect free film in the case of **5** (see Figure 2a).

3.3. Repairing of dynamic epoxy network 5

The repairing of dynamic epoxy network **5** was studied using $60 \times 10 \times 2$ mm specimens obtained as described in section 3.1. First, a small scratch was induced with a sharp blade. Then, the repairing of the scratch was performed by ironing with a household iron for 5 min at ~ 200 °C.

3.4. Recycling of dynamic epoxy network 5

Scraps of dynamic epoxy network **5** were ground to fine powder in a cutting mill (Fritsch Pulverisette 19). The resulting powder was then introduced into a $90 \times 90 \times 2$ mm Teflon coated steel mold and hot pressed at 200 °C and 100 bar for 5 min. After cooling down below T_g , a defect free sheet was obtained (Figure 2c). Dumbbell shape specimens were cut in order to determine the mechanical properties of the recycled material by tensile test experiments.

3.5. Synthesis of “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 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 °C for 2.5 hours and at 150 °C for additional 2 hours, to obtain a monolayer epoxy composite film.

3.6. Synthesis of composites from “enduring prepregs”

Hot-pressing of “enduring prepregs” was carried out as follows: 8 single laminate sheets previously manufactured as described in section 3.5. were laid-up and processed in a hot press at 200 °C 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 **5**. In the case of reference resin **4**, the sheets did not adhere.

3.7. Preparation of dynamic multilayered composites by manual impregnation

A sealant tape was placed on a 400×400 mm square glass mold and a releasing agent (Frekote 770-NC) was sprayed evenly onto its surface. Then a 250×250 mm sheet of glass-fiber was placed on the mold. This was then manually impregnated with a mixture of DGEBA and AFD (9.65 g, in the ratio described in section 3.1.), using a brush. Then, another 250×250 mm layer of glass fiber was placed and the same operation was repeated until a total of 8 impregnated layers were completed. After, a release film was placed onto the part and then a layer of breather cloth was placed 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. The enclosed part was then compacted by applying vacuum. Once air was evacuated, curing was carried out in an oven at 120°C for 2.5 hours and at 150°C for additional 2 hours. After cooling to room temperature, a multilayered dynamic epoxy composite was obtained.

3.8. Synthesis of dynamic composites 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°C . 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 of 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°C for 1 h at the same pressure. After cooling down to room temperature, the resulting dynamic composite was demolded.

3.9. Reprocessing of dynamic composites

A $50 \times 60 \times 2$ mm dynamic CFRP composite as described in section 3.8. was preheated at 200°C for 10 min. Then, it was placed into a steel zig-zag mold and hot pressed at 200°C and 100 bar for 5 min. After cooling down below T_g , a wavy 3D composite was obtained.

3.10. Repairing of dynamic composites

$20 \times 10 \times 1.8$ mm dynamic composite specimens as described in section 3.6. were delaminated by ILSS tests. Then, the delaminated specimens were submitted to 200°C and 100 bar for 5 minutes in a hot press. After cooling down below T_g , totally repaired specimens were obtained.

3.11. Chemical recycling of dynamic composites

A sample of the dynamic enduring prepreg as described in section 3.5. was immersed in a solution of 2-mercaptoethanol (0.2 mL) in DMF (20 mL). The system was magnetically stirred at room temperature for 24 hours, after which the epoxy matrix was completely dissolved. The glass fiber reinforcement was recovered after drying in an oven at 100 °C under vacuum for 24 hours.

The same experiment was performed using a CFR dynamic composite as described in section 3.7. Half of the specimen was immersed in 2-mercaptoethanol/DMF mixture and stirred at room temperature for 24 h. After that time, the resin of the immersed part was completely dissolved to give clean carbon fibers.

3.12. Mechanical recycling of dynamic composites

A dynamic composite as described in section 3.6. was chopped and ground to fine powder in a cutting mill. Then, the powder was introduced into a steel mold ($150 \times 150 \times 1$ mm) and hot pressed at 200 °C and 100 bar for 5 min. After cooling down below T_g , a defect-free short-fiber reinforced composite sheet was obtained.

4. Fourier-Transform Infrared (FTIR)

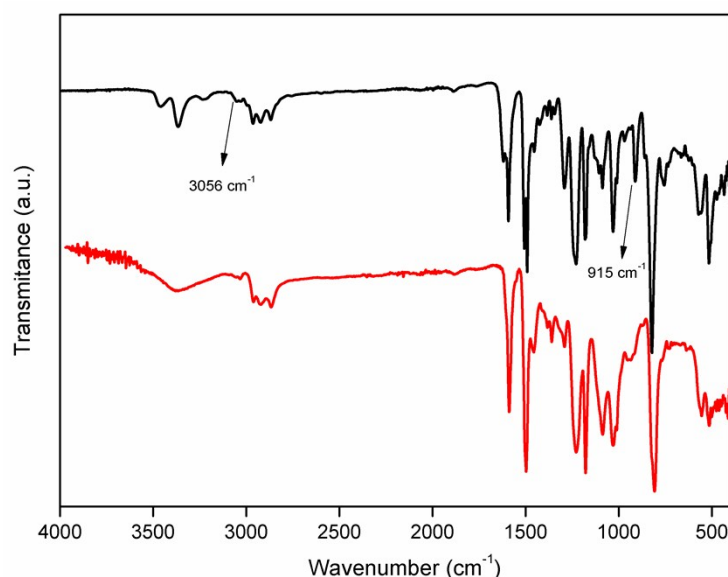


Figure S1. FTIR spectra of uncured (black trace) and cured (red trace) dynamic epoxy resin **5**, where the disappearance of bands corresponding to the epoxy group at 915 cm⁻¹ (C–O stretching of oxirane ring) and 3056 cm⁻¹ (C–H stretching of oxirane ring) was used as criteria to establish that the curing was complete.

5. Differential Scanning Calorimetry (DSC)

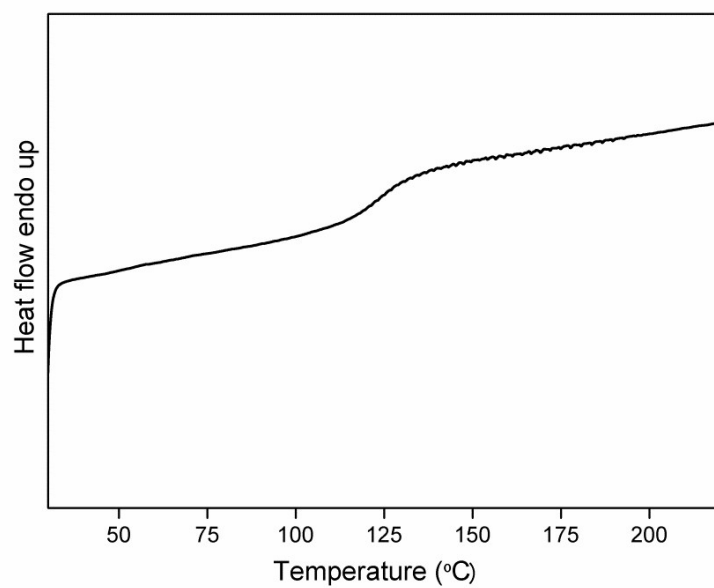


Figure S2. DSC thermogram for reference epoxy network **4**, from where a T_g value of 127 °C was determined.

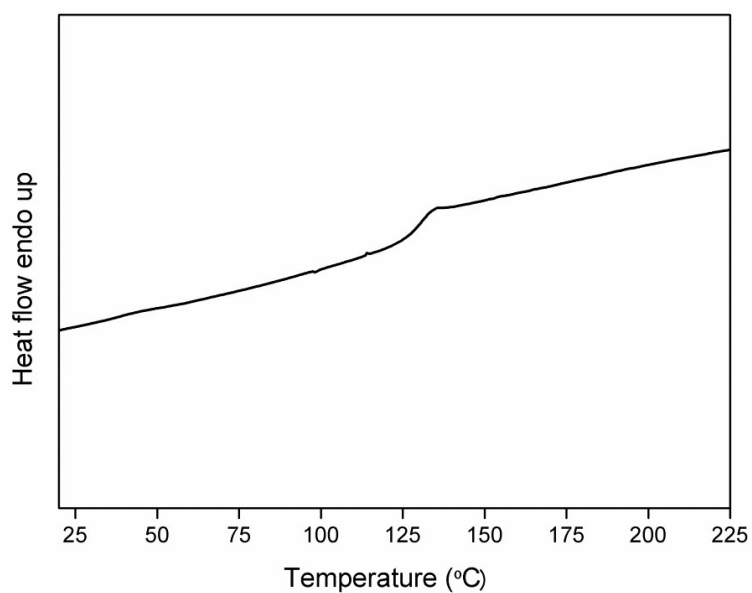


Figure S3. DSC thermogram for dynamic epoxy network **5**, from where a T_g value of 130 °C was determined.

6. Dynamic mechanical analysis (DMA)

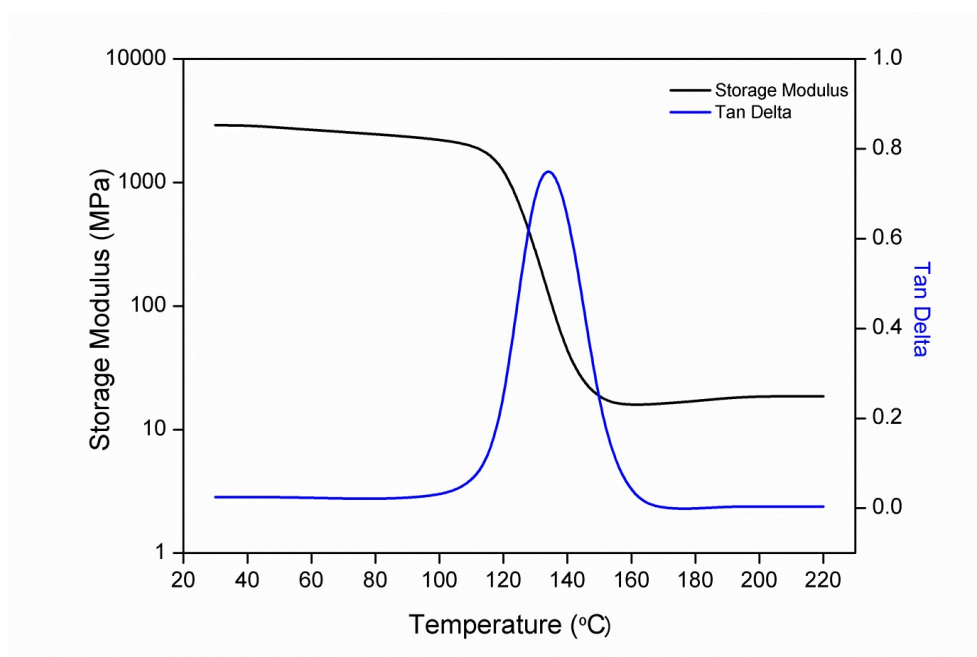


Figure S4. DMA curve obtained for reference epoxy network 4, representing storage modulus and tan delta versus temperature. $T_g = 130$ °C was determined from the maximum of tan delta.

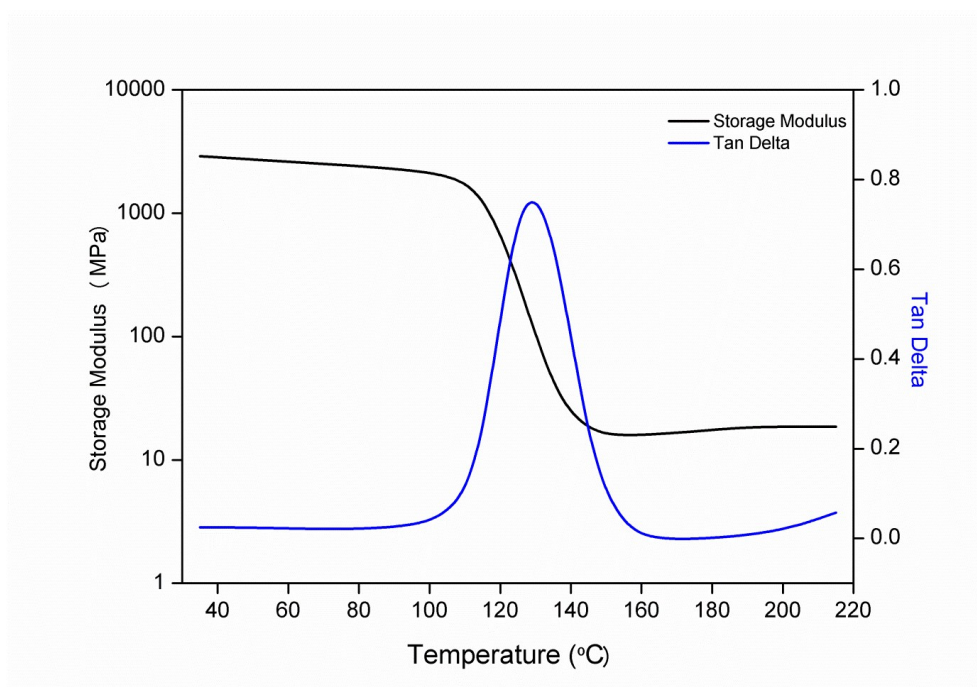


Figure S5. DMA curve obtained for dynamic epoxy network 5, representing storage modulus and tan delta versus temperature. $T_g = 130$ °C was determined from the maximum of tan delta.

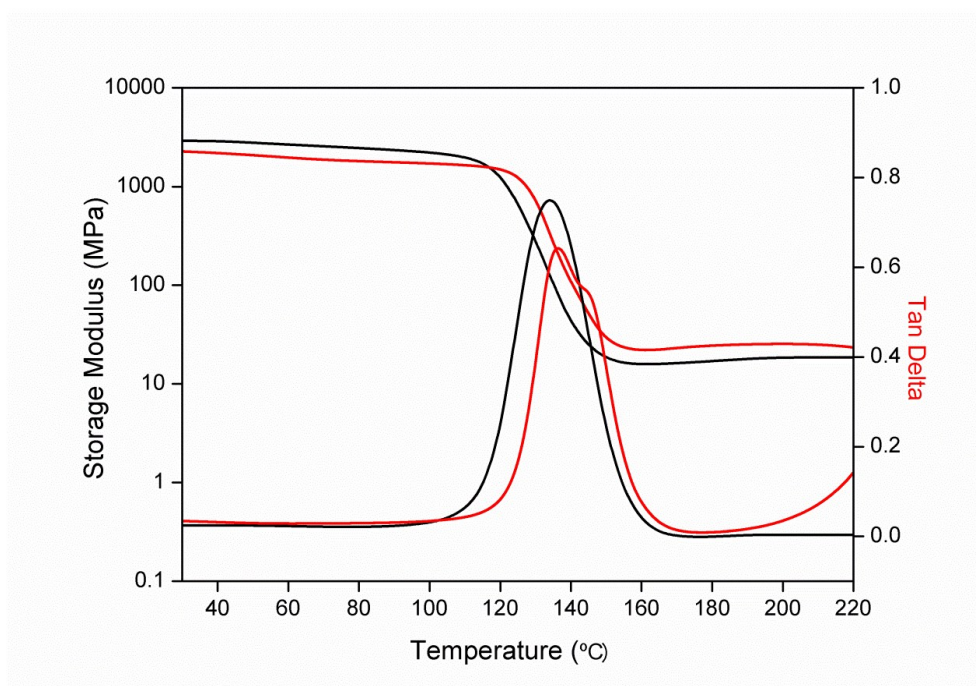


Figure S6. Thermomechanical characterization of pristine epoxy resin **5** (black trace) and reprocessed epoxy resin **5** (red trace).

7. Thermogravimetric analysis (TGA)

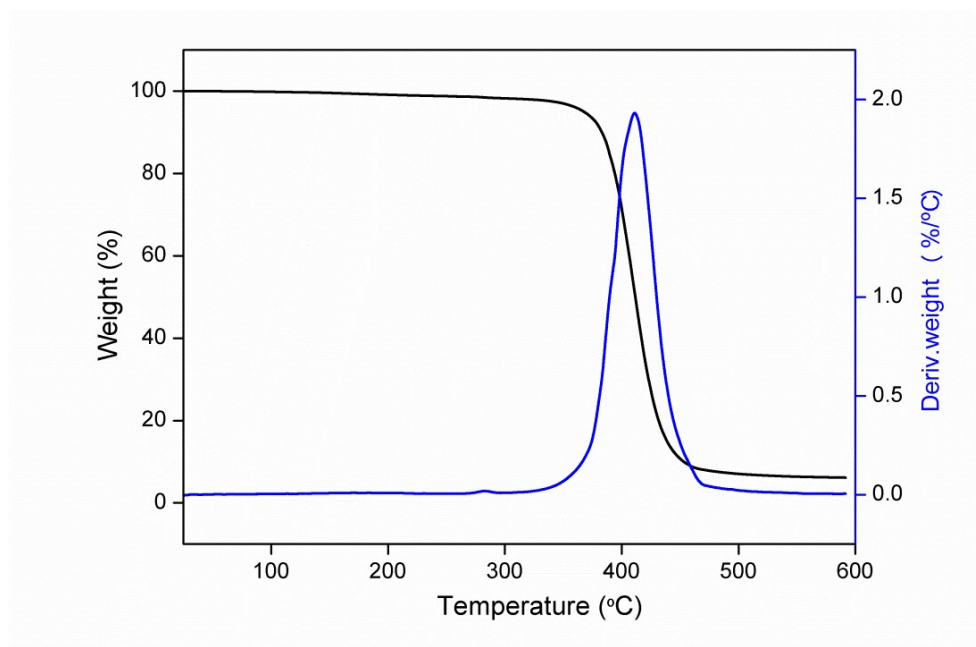


Figure S7. TGA thermogram of reference epoxy network **4**, representing weight loss (black trace) and derivative weight loss (blue trace) versus temperature.

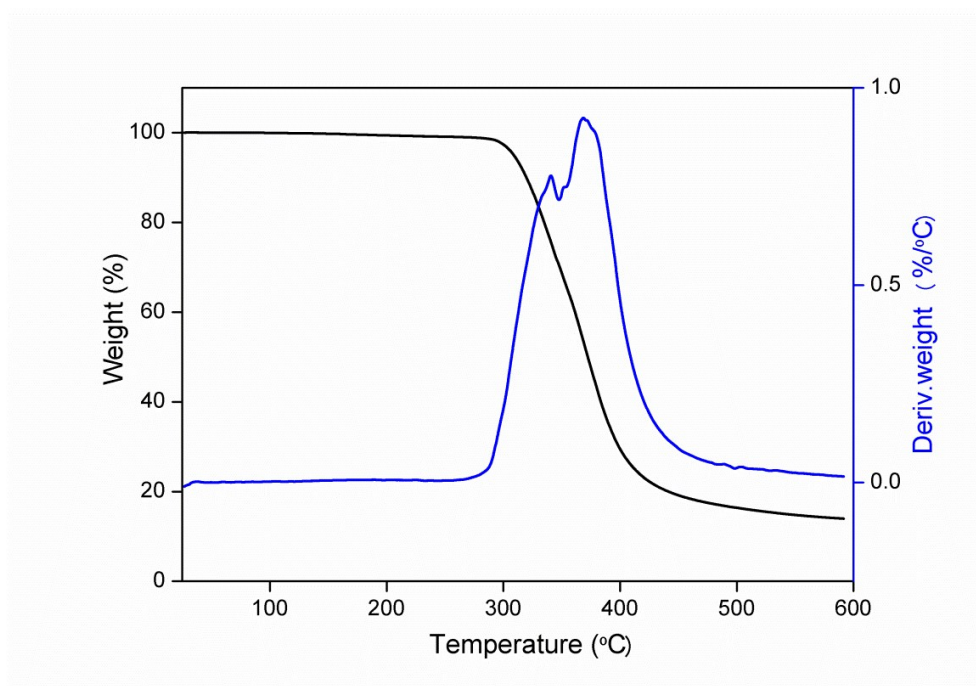


Figure S8. TGA thermogram of dynamic epoxy network **5**, representing weight loss (black trace) and derivative weight loss (blue trace) versus temperature.

8. Mechanical tests

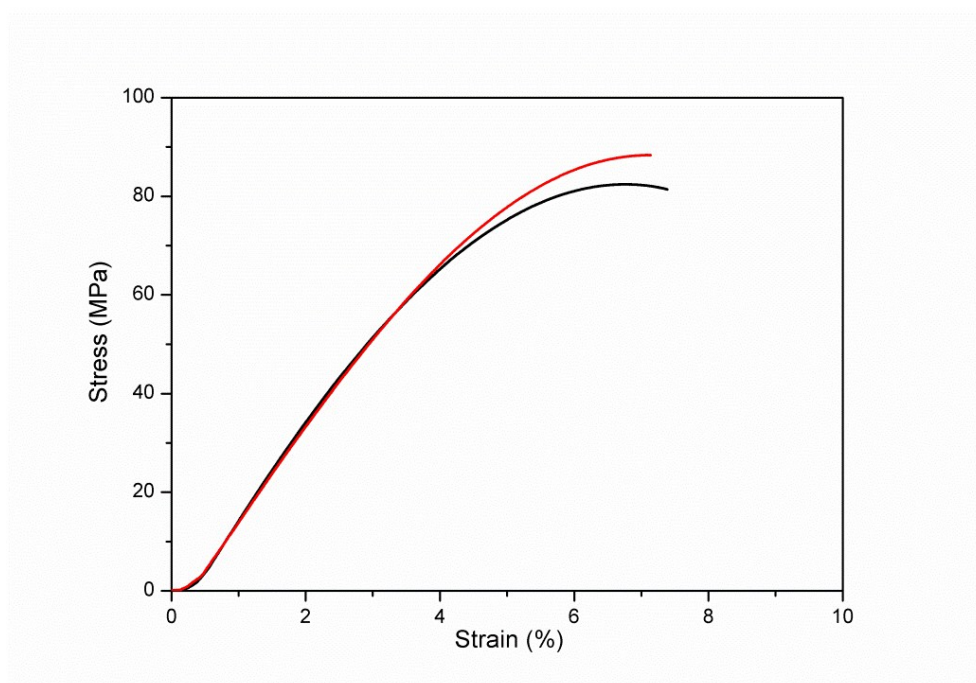


Figure S9. Stress-strain curves for reference epoxy network **4** (black trace) and dynamic epoxy network **5** (red trace).

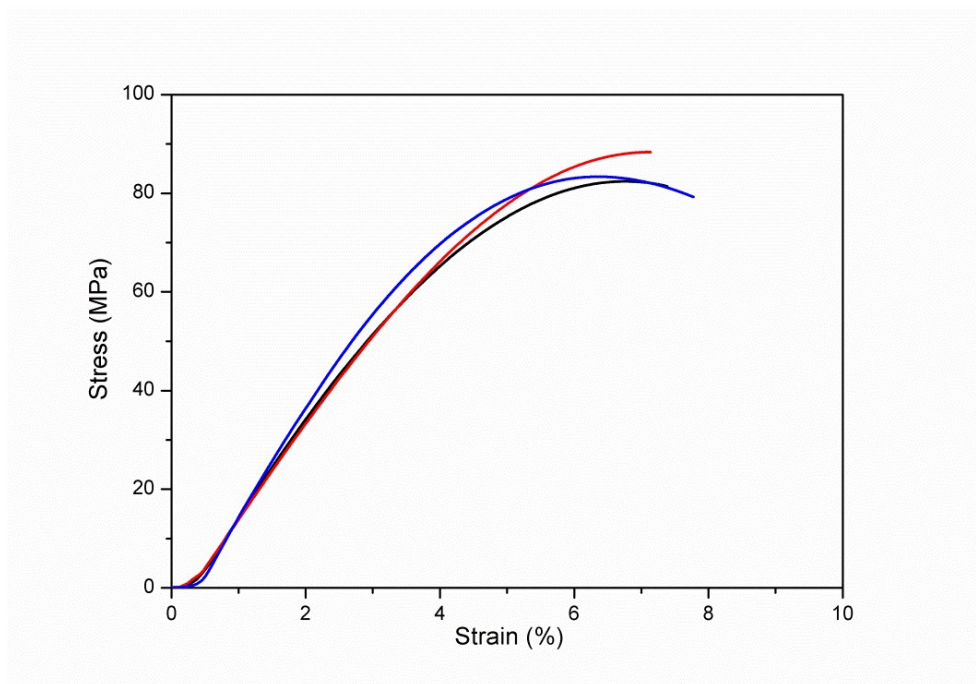


Figure S10. Stress vs. strain curves of reference epoxy network **4** (black trace), dynamic epoxy network **5** (red trace) and recycled dynamic epoxy network (blue trace).

9. Stress relaxation

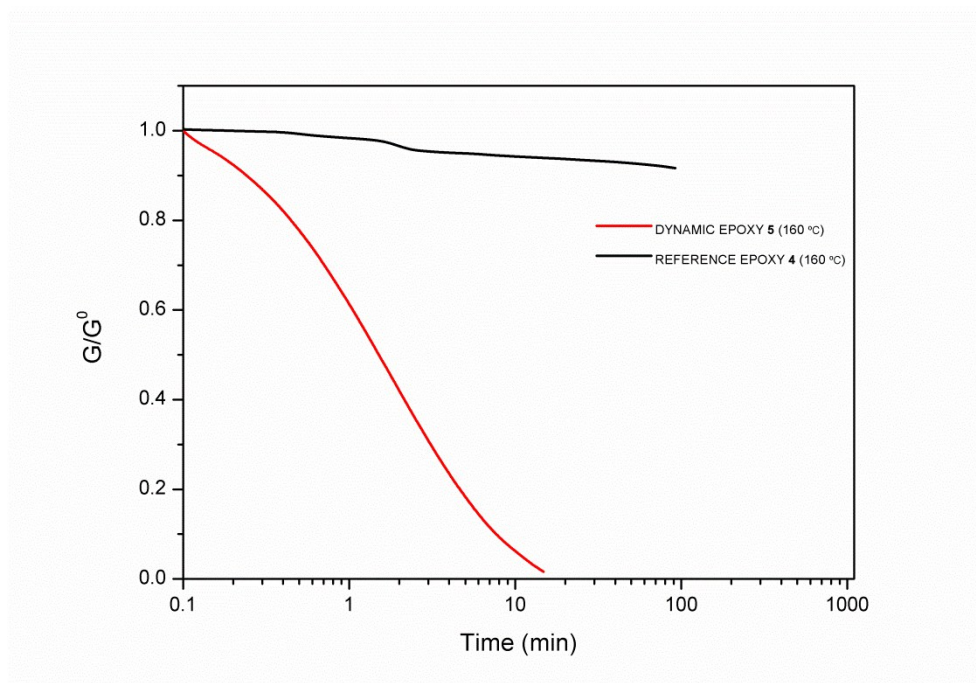


Figure S11. Comparison of normalized stress relaxation curves of dynamic epoxy network **5** (red trace) and reference epoxy network **4** (black trace) at 160 °C.