

Evaluation of healable epoxy matrices as covalent adaptive networks in uniaxial compression

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ABSTRACT

Vitrimers provide dynamic bonding that can allow a degree of self-healing capability in cross-linked resins. A commercial amine-cured epoxy resin, Prime 27, showed a compressive yield stress, measured in compression, of 88 ± 2 MPa and a compression modulus of 3.41 ± 0.03 GPa. This base resin was modified by incorporating various proportions of two commercial vitrimers, either Thioplast EPS35 (an aliphatic epoxy-terminated polysulfide) or Vitrimax T130 (an imine-cured DGEBA epoxy resin). The addition of increasing amounts of Thioplast EPS35 into the resin led to a rapid drop in the glass transition temperature of the matrices and also a reduction in compressive performance. After an initial test in quasi-static, uniaxial compression, samples containing vitrimers were heated for 1 h at 100 °C and then subjected to a second compression test; all of the matrices loaded with Thioplast EPS35 were able to recover their full initial compression performance. Addition of increasing amounts of Vitrimax T130 to the same commercial epoxy resin did not cause any change in its glass transition temperature. However, after initial compression testing, followed by heating (1 h at 100 °C), only the formulation containing 40 wt% Vitrimax T130-loaded matrix regained its full initial compressive performance. Optimal results in terms of healing capability, measured as the recovery of the initial compression performance during a second identical test, following a heating step, were achieved by incorporating 10 wt% of EPS35 or 40 wt% Vitrimax T130, with little to no drop in glass transition temperature. For these selected formulations, the incorporation of 10% Thioplast EPS35 in Prime 27 gave a yield stress of 83 ± 2 MPa and a compression modulus of 3.13 ± 0.02 GPa, while the addition of 40% Vitrimax T130 gave a yield stress of 79 ± 2 MPa and a compression modulus of 3.30 ± 0.02 GPa.

1. Introduction

Thermosets, such as amine-cured epoxy resins, are useful materials for high-performance applications, in wind energy, automotive and aerospace, due to their high dimensional stability and chemical resistance to most organic solvents, especially when compared to their thermoplastic counterparts. However, their highly-crosslinked chemical structure, based on irreversible covalent bonds, usually leads to increased brittleness, while preventing their ability to be reprocessed (e.g. through reshaping repairing or recycling); the opposite is true for thermoplastics [1,2]. To introduce plasticity in crosslinked polymer networks, dynamic crosslinks can be considered. Polymers containing such exchangeable bonds are also known as covalent adaptable networks (CANs) [3–5], which are usually classified into two groups

depending on their exchange mechanism [6].

The first group of CANs makes use of a dissociative crosslink exchange mechanism, where chemical bonds are first broken and then formed again in a different place within the polymer network. The second group uses associative bond exchanges between nearby polymer chains, where an original crosslink is only broken when a new covalent bond is formed [7]. An example of dissociative CANs relies on the reversible Diels–Alder reactions between furans and maleimides in organic polymer networks. Upon heating, the Diels–Alder crosslinking reaction becomes reversible, leading to an increased rate of bond breaking/reforming and also to a net bond dissociation, with this temporary loss of crosslinks typically resulting in a sudden drop in viscosity. Upon cooling, the crosslinks are re-formed, usually to the same extent as initially present in the starting material, thus preserving or reinstating

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the thermosets properties, such as stiffness and insolubility [8].

In contrast, associative CANs do not depolymerise upon heating and are thus characterised by a constant crosslinked density. The first reported associative CANs were based on photo-mediated free radical chain transfer reactions using moieties such as allyl sulphides [9,10]. In 2011, Leibler and co-workers developed associative CANs based on the addition of a transesterification catalyst to epoxy/acid and epoxy/anhydride polyester networks [11]. The thermally-triggered transesterification reaction resulted in crosslinked polyester/polyol networks that exhibited gradual decrease in viscosity upon heating, which is a distinctive feature of vitreous silica [12], thus leading to the more colloquial name “vitrimers”. The latter are characterised by a unique combination of malleability and reparability at high temperatures, while remaining insoluble in commonly used organic solvents [13]. More recent research endeavours have led to the development of commercial vitrimers, such as polysulfide-based materials [14], as well as imine-based polymers, which exhibit 90% polymer network relaxation after heating for 30 min at 80 °C [15]. We have selected commercial examples of both types of vitrimer for the present study.

When considering the mechanical properties of neat vitrimer-epoxy matrices, prior art has focussed solely on the tensile performance of commercial polysulfide-based vitrimers blended with diglycidyl ether of bisphenol A (DGEBA) formulations [16,17]. The earlier published work in tension on Thioplast EPS25 (an oligomer that is chemically related to Thioplast EPS35) produced flexible test specimens that were tested until they cleaved under tension and were then re-attached or re-shaped into tensile test specimens *via* thermal treatment. This approach was equivalent to re-moulding the tensile specimens, rather than evaluating the healing process at the molecular level within an intact test specimen. The tetrathiol-crosslinked matrix deliberately contained a very high disulfide bonds content (29 wt%) [16] and samples were subjected to two repair regimes: 20 min at 90 °C or 1 h at 60 °C, which promoted the intramolecular exchange of the disulfide (S—S) bonds between adjacent polysulfide polymer chains within the matrix. The reformed tensile test specimens were re-tested in tension, resulting in near complete recovery of the initial tensile performance of these materials; with a tensile modulus of approximately 1 GPa, a tensile stress at failure estimated at approximately 0.5 MPa, and an elongation at break of about 65% in the repaired specimens, all of which were similar to that of the original tensile specimens.

To date, there has been no published study on the mechanical properties of healable vitrimer-loaded epoxy matrices in compression. Thus, the present investigation focusses on evaluating, for the first time, the compression performance a simple commercial epoxy resin (Prime 27), and of its mixtures with various mass loadings of different types of

commercial vitrimers: one is an amine-cured polysulfide vitrimer and the other an imine-based vitrimer. The choice of Prime 27 as a candidate base resin was made on the basis that the formulation is comparatively ‘clean’ allowing inferences to be drawn from the mechanical properties and their relationship to chemical structure.

2. Materials and methods

2.1. Materials

All tested formulations were based on a commercial resin, Prime 27, supplied by Gurit, UK. Prime 27 is a proprietary diamine-cured aromatic DGEBA (or BADGE) diepoxy resin (epoxy equivalent weight of 180 g/eq). At room temperature, the epoxy groups from the resin react with the amine groups from the curative (Prime slow hardener), as represented in Fig. 1(a). Prime 27 was then mixed with an epoxy resin to amine hardener ratio of 100:28, which correspond to respective loadings of 78 wt% for the epoxy resin and 22 wt% for the amine hardener.

Two types of vitrimers were investigated in this study. Thioplast EPS35 (supplied by Nouryon, Sweden) is an aliphatic epoxy-terminated polysulfide polymer, as represented in Fig. 1(b), with an average epoxy equivalent weight of 700 g/eq. Vitrimax T130 (supplied by Mallinda, Inc., USA) is a proprietary imine-cured di-glycidyl ether of bisphenol A (DGEBA). This vitrimer is thus made from two parts (an imine hardener and a DGEBA epoxy resin) that are mixed in an imine to epoxy ratio of 2:1. Its vitrimeric properties are the result of reversible imine metathesis reactions in the matrix, as depicted in Fig. 1(c). These two vitrimers were added individually to Prime 27, at loading of 10, 20, and 40 wt%, respectively, as described in Table 1.

Formulations incorporating Thioplast EPS35 were simply mixed at room temperature, while mixes incorporating Vitrimax T130 required a

Table 1
Formulations of Prime 27 with various loadings of two different vitrimers.

Formulations	Mass (%)				
	Prime 27 resin	Prime 27 slow hardener	Thioplast EPS35	Vitrimax T130 resin	Vitrimax T130 hardener
Prime 27	78	22			
10% EPS35	70	20	10		
20% EPS35	61	19	20		
40% EPS35	45	15	40		
10% T130	70	20		3.3	6.7
20% T130	62	18		6.7	13.3
40% T130	47	13		13.3	26.7

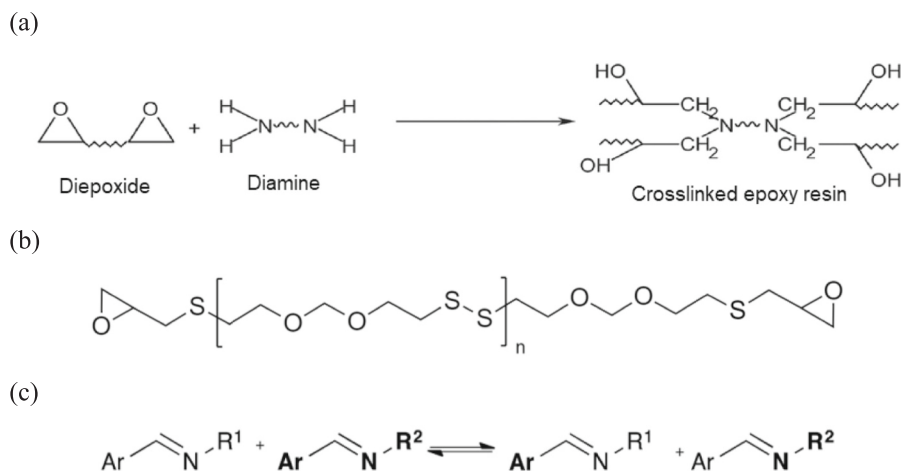


Fig. 1. Schematic showing (a) typical reaction between a diepoxide and a diamine, (b) Chemical structure of polysulfide vitrimer (typically $n = 7$), (c) Schematic showing reversible imine metathesis reaction.

more detailed procedure. The imine hardener (solid at room temperature) was first heated first at 80 °C for two hours, before being mixed at 60 °C with the Vitrimax T130 epoxy resin and the Prime 27 resin. The temperature of the blend was then allowed to decrease to 50 °C before adding the Prime slow hardener, which was mixed with the rest of the resin. All formulations were then degassed at 50 °C in a vacuum oven for 5 min before being poured into a silicone mould, featuring cylindrical cavities with a height of 10 cm and a diameter of 1 cm. All the formulations were left to gel at room temperature for 24 h before being post-cured at 80 °C for 16 h, after which all the cured epoxy cylinders were extracted from the silicone mould and machined on a lathe into cylindrical compression test specimens described in Section 2.4.

2.2. Thermogravimetric analysis

Thermogravimetric analysis was performed on the various cured materials using a STA (Simultaneous Thermal Analysis) 449 F3 Jupiter (Netzsch, Germany), using cured resin samples (10 ± 1 mg) placed in alumina crucibles. The furnace was heated from 50 to 800 °C, at a rate of 10 K/min, under a constant stream of dry nitrogen gas, flowing through the furnace at a rate of 50 mL/min. The degradation temperature (T_{dec}) and mass losses for the various matrices were measured. The decomposition temperature (T_{dec}) was determined at the intersection of tangents at the onset of mass loss, while total mass loss was determined as the overall difference in sample mass between 50 and 800 °C (see Fig. S1, supplementary information).

2.3. Dynamic scanning calorimetry

Dynamic scanning calorimetry (DSC) were performed on a Netzsch DSC 204 F1 Phoenix. Cured epoxy specimens (4 ± 1 mg) were loaded in aluminium pans that were further sealed with a pierced aluminium lid. DSC experiments were carried out from 0 °C to 150 °C at 10 K/min, under a constant flow of dry nitrogen gas set at a constant 20 mL/min. Glass transition temperatures (T_g) of the post-cured epoxy matrices were determined from the mid-point values of the discontinuity in the DSC response (see Fig. S2, supplementary information).

2.4. Preparation of specimens for compression testing

Each cured neat epoxy rod was machined on a lathe into individual cylindrical compression test specimens using a precise 1:1 (L/D) aspect ratio [18], hence with a diameter of 6.0 ± 0.1 mm and a height of 6.0 ± 0.1 mm (Fig. 2). The specimens were dried in an air-vented oven at 50 °C for 2 days, according to the procedure recommended in ASTM D618 [19]. After conditioning, the specimens were stored inside a sealed desiccator, prior to being spray-painted and speckled. The cylindrical compression specimens were then spray-painted individually using an acrylic matt white primer. After the paint dried, randomly scattered, black speckles (50 to 100 μ m in size) were applied over the entire surface of the test specimens, using an air brush, pre-loaded with India carbon-black colloidal ink. The speckled specimens were left to dry for 1 h.

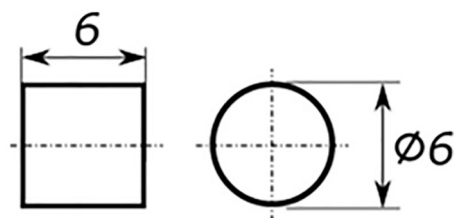


Fig. 2. Dimensions of the compression specimens (mm).

2.5. Quasi-static uni axial compression testing

Uniaxial quasi-static compression tests were performed at room temperature (23 ± 1 °C), with a constant vertical displacement rate of 0.36 mm/min, which corresponded to an initial strain rate in compression of 0.001 s^{-1} , as recommended in ASTM D695 [20]. All compression tests were performed on a Shimadzu universal mechanical test frame, AGS-10kNXD, fitted with a 10 kN load cell and a pair of stainless-steel cylindrical compression plates, each with diameter of 30 mm and a height of 60 mm. For each material, one specimen was tested to the maximum allowable load of 10 kN, to determine the yield point for each epoxy material. Then, the other six specimens, all taken from the same cured rod, were tested just past that yield point, as determined earlier for each of the materials to be investigated. Three of these tested specimens were re-tested under the same exact conditions, again just past the compressive yield point, while the remaining three specimens were placed for 1 h in an air-vented oven, pre-heated at 100 °C, above the glass transition of these materials. These specimens were left to cool in a desiccator before being re-tested in compression using the same test conditions. The top and bottom stainless steel compression plates were covered with a PTFE adhesive film (3 M PTFE film tape 5490, with a film thickness of 90 μ m) to eliminate friction and to avoid barrelling of the specimens.

2.6. Digital image correlation

Greyscale images of the speckled specimens were captured, at a frequency of 1 Hz, by a pair of DaVis LaVision 16MP CMOS Digital Image Correlation (DIC) cameras, positioned symmetrically at an angle of 12° to the test specimen, as shown in Fig. 3. After calibration and acquisition, images were analysed via the DaVis10 LaVision DIC software and synchronised with the load (F , in Newtons) analogue ± 5 V output of the Shimadzu universal test frame. The compression test specimens were illuminated by a pair of LED light arrays, throughout the entire duration of the tests.

For each test specimen, engineering radial and axial strains, e_{xx} and e_{yy} , respectively, were determined across the entire set of recorded correlated images, using the 'sum of differential' correlation mode, a subset size of 21 pixels and a step size of 7 pixels. The use of a virtual strain gauge (6 pixels \times 6 pixels), placed at the centre of the generated strain map, provided the values for instantaneous engineering radial and axial strain values, these values being correlated to instantaneous load values, acquired from the calibrated Shimadzu 10 kN load cell. For each set of correlated recorded images, true axial strain (e^r) values were calculated using Eq. (1).

$$e^r = \ln(\epsilon_{xx} + 1) \quad (1)$$

True axial stress (s) values were calculated using Eq. (2), where F is the value of the load and A_0 is the initial transverse cross-sectional area of the tested specimen.

$$\sigma = \frac{F}{A_0(1 + \epsilon_{xx})^2} \quad (2)$$

The values for true axial stress were plotted against the true axial strain values. The resulting stress-strain curves were used to determine the compression modulus (E) as the slope from the linear portion of the elastic region of the curve. The yield point is defined in ASTM D695 as the point on the stress-strain curve where stress values stop increasing with increasing strain values. At that point, the yield stress, s_y , was determined and reported for each of the four tested epoxy matrices. This behaviour has been depicted by Morelle et al. [21], indicating that the true stress-true strain response for all materials follows five distinct stages, as depicted in Fig. 4: (I) an initial, linear stage corresponding to the material's elastic behaviour; (II) a nonlinear stage corresponding to the yielding of the material, which reaches a maximum value at the peak

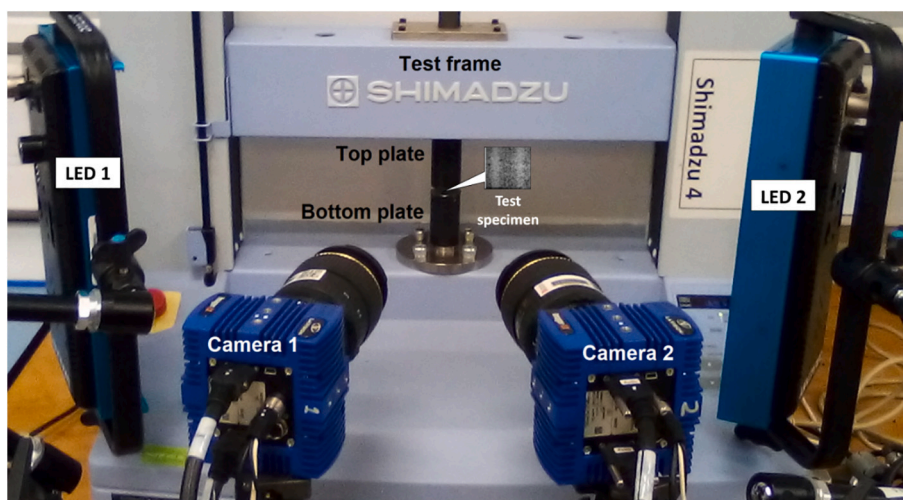


Fig. 3. Compression test rig and digital image correlation experimental set-up.

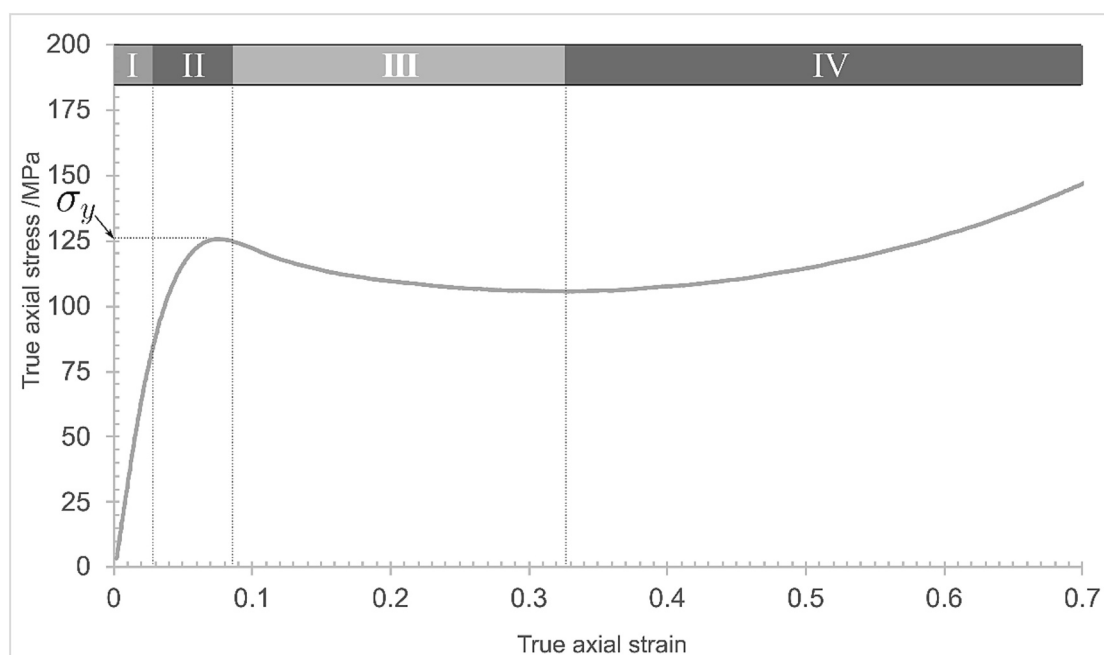


Fig. 4. Schematic showing the typical true stress – true strain curve of cured RTM6 epoxy resin in quasi-static uniaxial compression, as described by Morelle et al. [21]

yield point; (III) a strain softening stage following the yielding and (IV) further strain hardening. The fifth stage, not depicted here, is either fracture for the quasi-static strain rates, or unloading for the high strain rates.

In all instances, the work of compression (WoC) was determined for each resin formulation blend by integrating the plot of true stress vs. true strain up to a strain of 60%.

3. Results and discussion

3.1. Thermogravimetric analysis

The initial characterisation of the physical properties of the newly-produced resin formulations was undertaken to determine whether the introduction of the vitrimeric (healable) component would compromise the other properties of the base resin system (Prime 27). Consequently, a thermal analysis study was undertaken. Fig. 5 shows the full dataset,

while the baseline cured Prime 27 resin, indicating how the onset of degradation and the total mass loss (TML) were determined, is given in supplementary information, S1. The thermogravimetric data for all the epoxy matrices examined in this study are summarised in Table 2.

Key: T_{dec} = temperature of onset of mass loss determined from tangents, TML = total mass lost.

These data show a gradual decrease in decomposition temperature (T_{dec}) as the mass loading of Thioplast EPS35 increases, with an approximate 20 °C decrease in decomposition temperature for every incremental 20% increase in Thioplast EPS35. This effect could be explained by the increased amount of aliphatic polysulfide chains within the highly crosslinked aromatic DGEBA epoxy network, a decrease in decomposition temperature with increased amount of less thermally stable sigma (C–C, C–O, C–S, and S–S) bonds within the crosslinked chemical network is to be expected. Incremental additions of Vitrimax T130, which is similar in chemical structure to DGEBA crosslinked epoxy resins, led to no change in the decomposition temperature of

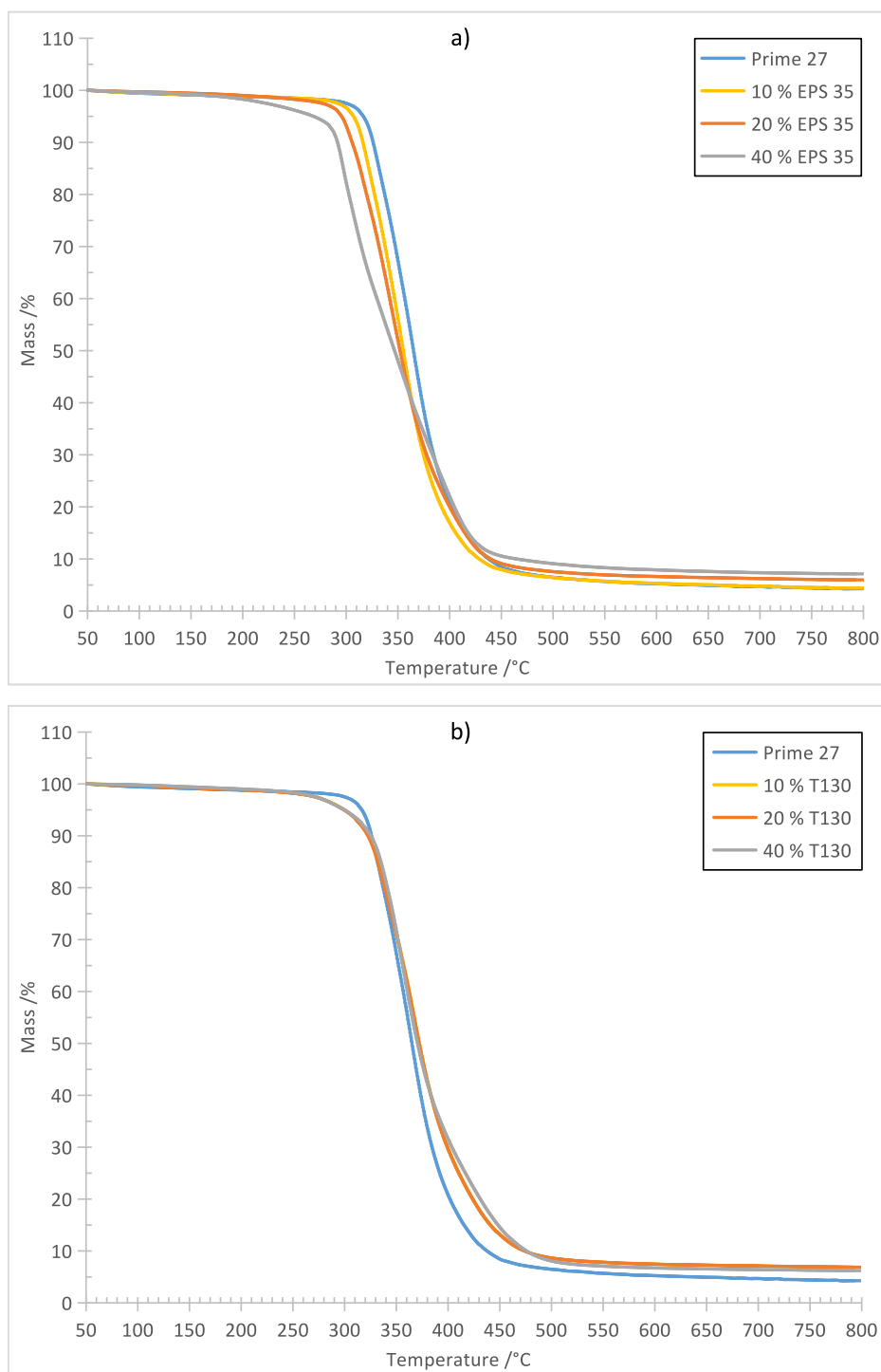


Fig. 5. Representative thermogravimetric analysis (TGA) of cured Prime 27 versus a) Prime 27 with Thioplast EPS35 and b) Prime 27 with Vitrimax T130.

Table 2
Thermogravimetric data for vitrimer-loaded Prime 27 formulations.

	Prime 27	Vitrimax T130			Thioplast EPS35		
		10 wt %	20 wt %	40 wt %	10 wt %	20 wt %	40 wt %
T_{dec} , °C	327	327	325	326	317	305	285
TML, %	96	93	93	94	96	94	93

Prime 27, with values remaining in the range of 326 °C. No measurable change in the TML was observed with an average mass loss of 94%, which is typical of DGEBA epoxy matrices that are cured using aliphatic amine hardeners [22].

3.2. Dynamic scanning calorimetry

The addition of the vitrimer component reduced the glass transition temperature (T_g) as shown by differential scanning calorimetry (DSC). Fig. 6 shows the DSC traces for the complete data set, while the data for cured Prime 27 resin (showing how the T_g was determined) is presented

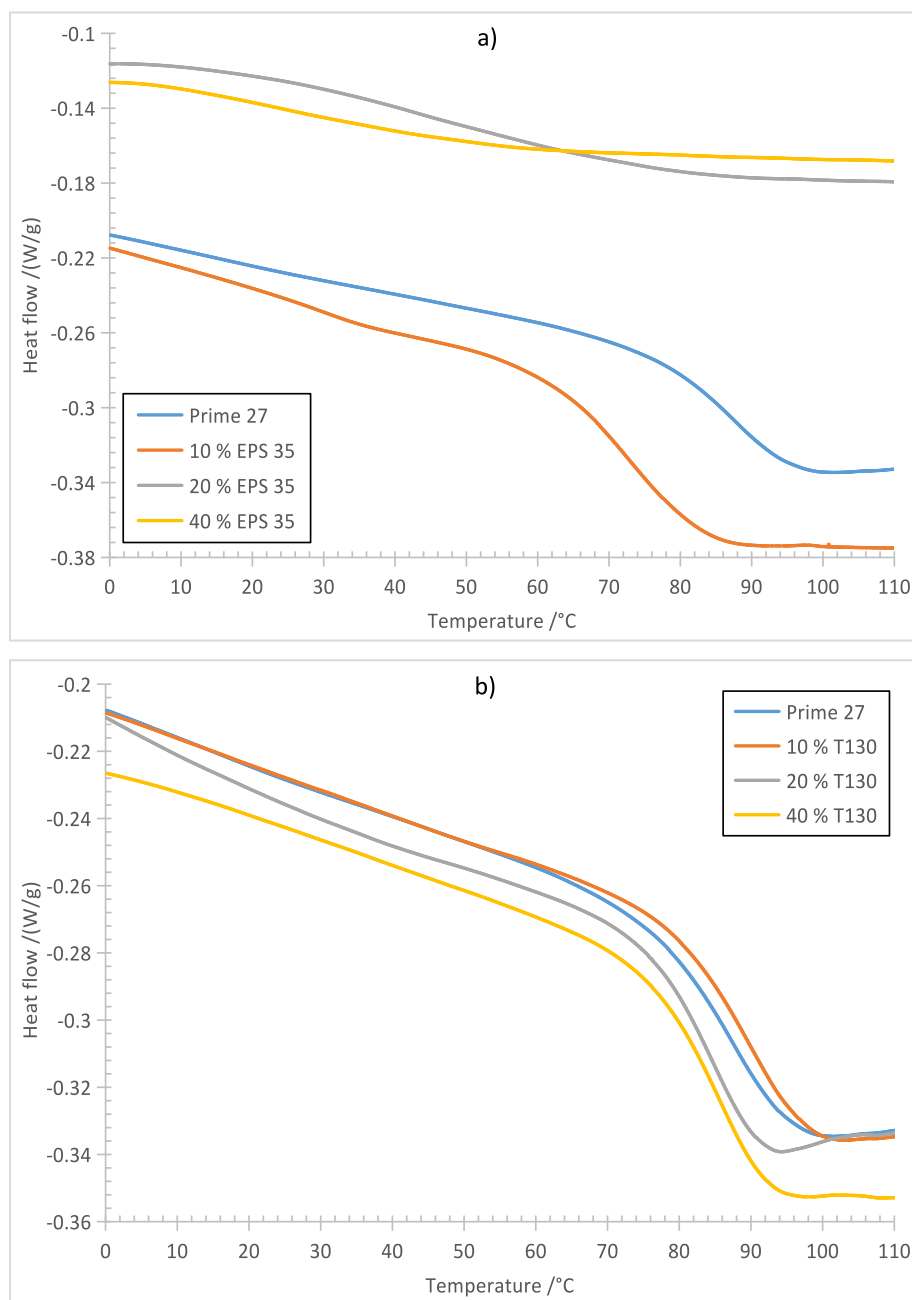


Fig. 6. Representative differential scanning calorimetry (DSC) of Prime 27 versus a) Prime 27 with Thioplast EPS35 and b) Prime 27 with Vitrimax T130.

in supplementary information, S2. The values for the tested matrices are compiled in Table 3.

The DSC results show that increasing the mass loading of Thioplast EPS35 into Prime 27 led to increasingly larger drops in cured T_g values, due to the increasing addition of linear segments inside an otherwise mostly aromatic crosslinked epoxy network. These DSC data suggest that while formulations containing between 10 and 20 wt% EPS35 merit

further attention in subsequent composite studies using more highly formulated resins, the impact on T_g of adding 20–40 wt% of EPS35 mean that the higher vitrimer loadings are probably excessive for general engineering applications. In contrast, the addition of increasing amounts of Vitrimax T130 did not cause any change to the cured T_g of Prime 27, due to the crosslinked aromatic nature of Vitrimax T130, which is similar to that of the unmodified cured Prime 27 cured DGEBA epoxy matrix.

The sensitivity of the T_g of cured epoxy resins to moisture uptake is well known, having been established by Wright in his seminal study which established an empirical relationship of a drop of 20 K in T_g for each 1% of sorbed water [23], and maintaining a high dry cured T_g is of paramount importance for engineering applications. The DSC results suggest that the formulator can explore a wider range of compositions using Vitrimax T130, without fear of compromising the dry T_g (although the presence of increasing amounts of imine, containing labile hydrogen

Table 3
Glass transition temperatures of cured specimens loaded with vitrimers.

	Vitrimax T130			Thioplast EPS35			
	Prime 27	10 wt %	20 wt %	40 wt %	10 wt %	20 wt %	40 wt %
T_g , °C	87	89	88	86	72	57	30

atoms would merit further examination of the moisture absorption behaviour and hot/wet properties of the cured resins).

3.3. Digital image correlation analysis of quasi-static uniaxial compression tests

The same range of resin formulations were tested for their mechanical properties in compression, as post-cured. Fig. 7 shows a classic response, qualitatively similar to that shown in Fig. 3. The sensitivity of each formulation to the concentration of the individual vitrimers is immediately apparent (*i.e.* measured by the reduction in s_y as the vitrimer concentration increases) and mirrors the T_g data acquired using DSC. Fig. 7a shows that the closest compression performance to Prime 27 was obtained with the addition of 10 wt% EPS35, while further increases in EPS35 mass loadings led to large reductions in overall uniaxial compression performance. Fig. 7b shows that the formulations incorporating 10, 20, and 40 wt% Vitrimax T130, respectively, performed similarly to each other and only moderately lower than unmodified Prime 27. The extracted mechanical parameters (compressive yield stress and modulus values) for Prime 27 with Thioplast EPS35 (Fig. 8) and Prime 27 with Vitrimax T130 (Fig. 9) quantify these trends. Comparison within each formulated system shows similar trends for both

stress and modulus (*i.e.* the profile of the bar graphs appears similar) and there is a degree of similarity between the profiles of the two vitrimer systems. The addition of increasing amounts of Thioplast EPS35 into the formulation of Prime 27 progressively degraded the mechanical performance of Prime 27 resin in uniaxial compression, due to the increased addition of high molecular weight, aliphatic chains to the crosslinked molecular network of the cured matrix.

Each plot of true stress vs. true strain measured in compression was integrated from the origin to a strain of 60% to obtain the work of compression (WoC) and the data for selected formulations containing Prime 27 and the two different vitrimers are contained in Table 4. Full-stress strain curves were measured only once for each resin system (these data were only used to determine the yield point for healing experiments, as highlighted in Section 2.5 of the manuscript). Therefore, these values do not have standard deviations attached to them.

The WoC of the Prime 27 is systematically reduced by the addition of increasing amounts of EPS 35 as the crosslink density falls rapidly, demonstrating that the practical benefit of adding more than *e.g.* 20% of the vitrimer is questionable in this application. In contrast, the WoC undergoes very little reduction over a very wide range of Vitrimax T130 loadings, losing only 7% of the initial value for Prime 27 at the highest level of incorporation tested. This result reflects the higher

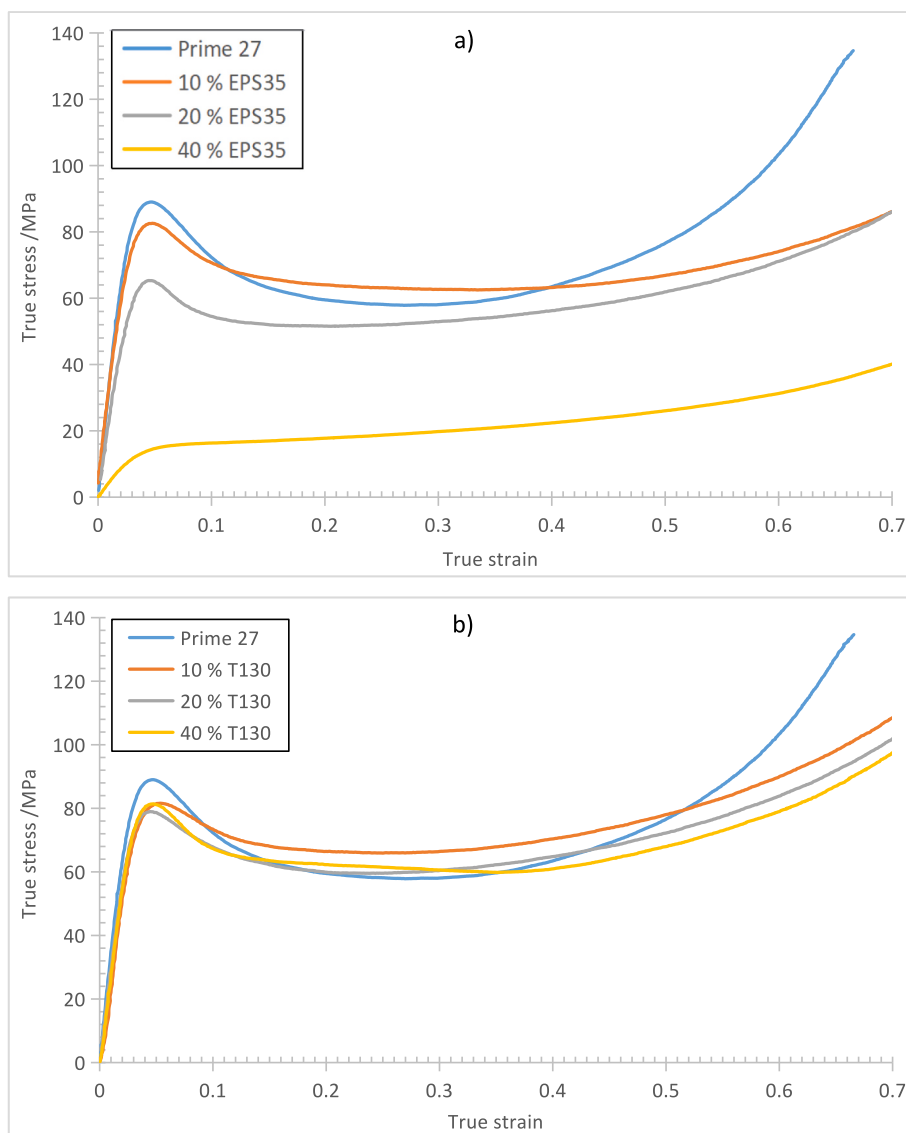


Fig. 7. Representative compression stress-strain curves for Prime 27 versus a) Prime 27 with Thioplast EPS35 and b) Prime 27 with Vitrimax T130.

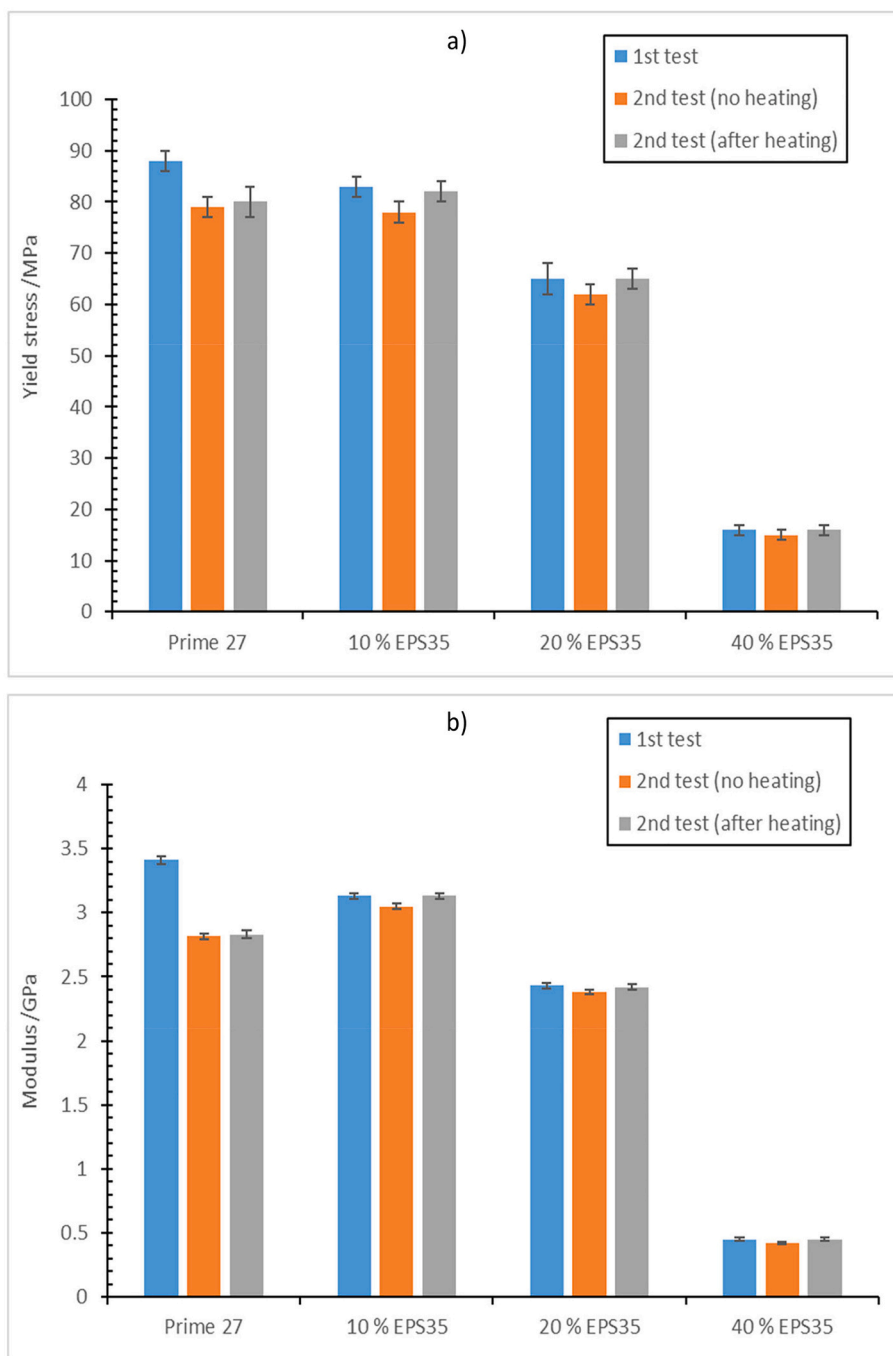


Fig. 8. Representative compression properties, with and without heating, of Prime 27 with and without various amounts of Thioplast EPS35, namely: a) compression yield stress and b) compression modulus.

crosslink density and of this network structure. For context, in a previous study within the programme [24], a series of high performance, fully formulate, commercial aromatic epoxy resins (supplied by Solvay) were tested under similar conditions to determine the WoC and typically developed values of between 65.3 and 80.3 MJ/m³ depending on the level of toughening.

The ability to heal damage within these resins was tested by a two-stage mechanical testing protocol. In the first instance, compression tests were carried out as-prepared specimens up to the yield point for each matrix system, at around 5% strain (Fig. 7a and b). Half of these tested specimens were then re-tested directly after standing in ambient conditions, while the other half of these specimens were first heated for 1 h at 100 °C; both sets were re-tested under identical compression test

conditions (all compression numerical test data were compiled in supplementary material, S3).

In all cases, without heating, the second compression tests showed lower yield stress and modulus values than the first tests, indicating damage to the molecular networks during yielding. The baseline, unmodified Prime 27 epoxy showed the same degree of degradation with and without heating, showing that no healing or recovery occurred with or without heating. In contrast, all the matrices loaded with various amounts of Thioplast EPS35 recovered nearly 100% of their initial compression performance, after heating, as shown in Figs. 8 and 10). It is also evident that the incorporation of Thioplast EPS35 into the formulation seems to reduce the damage caused during yielding of the matrices. To date, most of the research undertaken into the mechanical

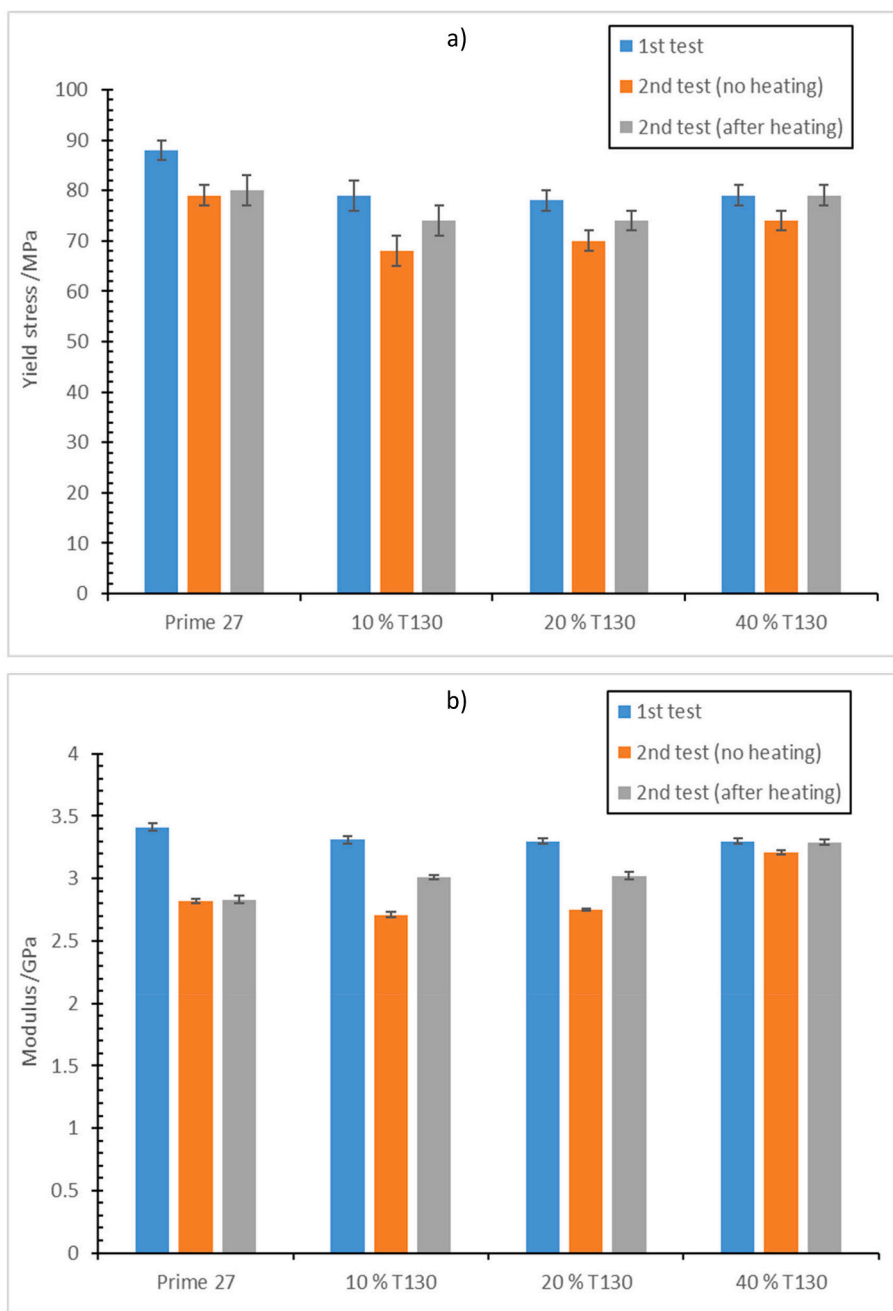


Fig. 9. Representative compression properties, with and without heating, of Prime 27 epoxy resin with and without various amounts of Vitrimax T130, namely: a) compression yield stress and b) compression modulus.

Table 4
Work of compression up to strain of 60% for vitrimer-loaded Prime 27 formulations.

	Prime 27	Thioplast EPS35			Vitrimax T130		
		10 wt %	20 wt %	40 wt %	10 wt %	20 wt %	40 wt %
WoC, 10 ⁶ J.m ⁻³	41.2	39.5	33.6	12.2	42.6	39.5	38.2

Key: WoC = work of compression.

properties of vitrimers has concentrated on their behaviour in tension and often in the form of homopolymers, whereas we have examined different levels of vitrimer components principally in the minority as

additives. Nevertheless, there are similarities observed in the behaviour in compression. Direct comparison with previous research on Thioplast EPS25 is difficult as in our studies we stopped the tests just past the yield points in compression, to avoid strain softening and subsequent strain hardening. If the latter were to occur, then the shape of the material would be changed irreversibly, which in turn would necessitate full remoulding and machining of the specimens prior to re-test. However, we almost fully recover the full compressive performance, under similar conditions, which is evidence that healing was achieved at the macro-molecular level. The result is in sharp contrast to the molecular network damage accumulated in the native Prime 27 specimens, after yielding, with or without heating.

The Vitrimax T130 also showed evidence of full recovery of the initial compressive properties, after heating, but only with 40 wt%

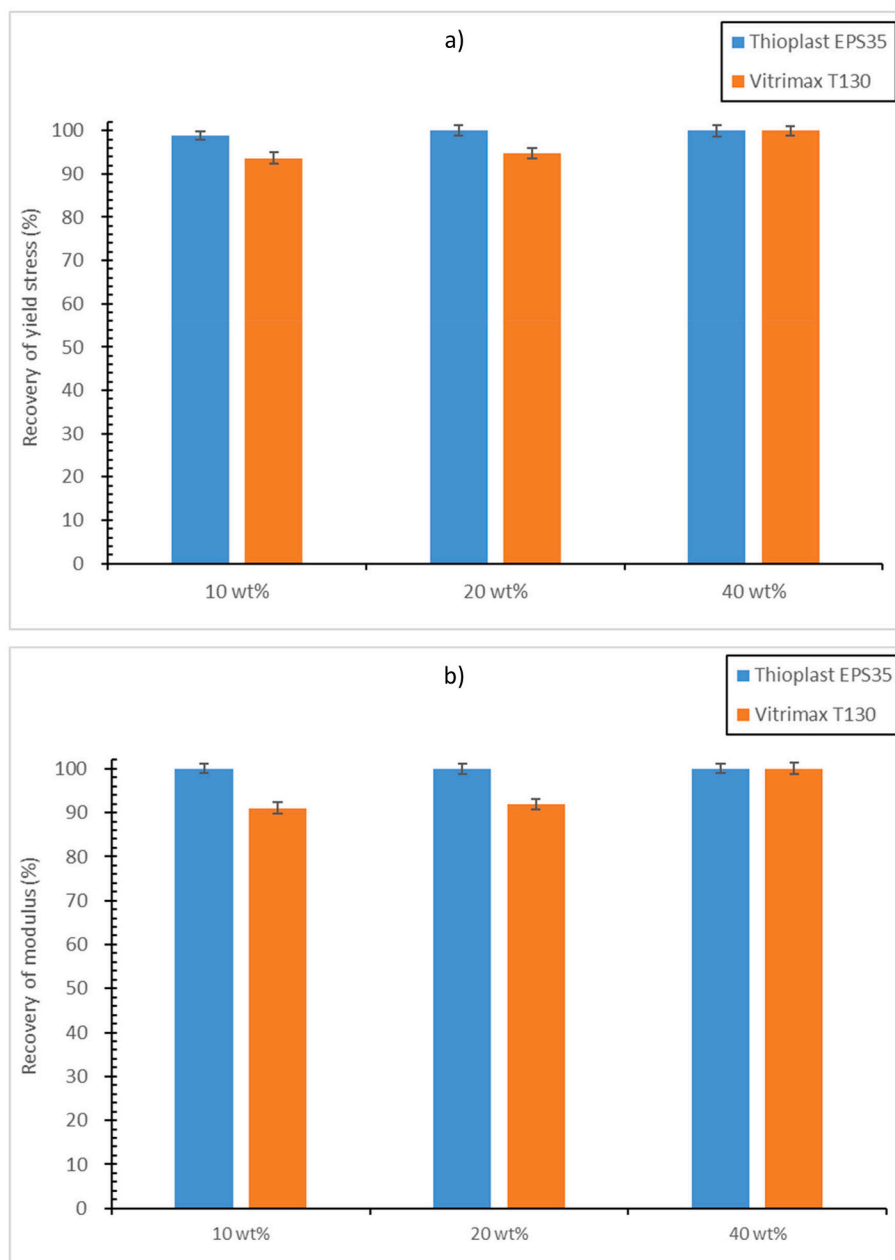


Fig. 10. Representative recovery (in %), after heating, of the compression properties of modified Prime 27 epoxy resin with various amounts of Thioplast EPS35 and Vitrimax T130, namely: a) compression yield stress and b) compression modulus.

Vitrimax T130 in Prime 27, as shown in Figs. 9 and 10. The observation that a higher mass loading is needed to achieve the full recovery of the compressive performance, compared to Thioplast EPS35, may reflect the reduced mobility of the imine bonds within the crosslinked aromatic network, compared to that of the higher molecular weight, polysulfide aliphatic chains of Thioplast EPS35. Whilst adding large proportions of Vitrimax T130 does not seem to affect the original compressive properties of Prime 27, the increased viscosity [25], and the potential impact of moisture absorption could prove to be important limitations, which remain to be determined in further studies.

4. Conclusion

The incorporation of two separate commercial vitrimers (one operating *via* a dissociative crosslink exchange mechanism; the other *via* associative bond exchanges) into a model commercial amine-cured

epoxy resin, Prime 27 have been demonstrated to effect a degree of self-healing capability. When exposed to a compressive strain of 5%, the Prime 27 yields and undergoes irreversible damage, losing 10% of its yield strength and over 17% of its modulus; further strain would have led to significantly greater damage. The base epoxy resin was first modified by incorporating a minimum of 10 wt% Thioplast EPS35 which led to reductions of 15 °C in the cured T_g , 1.7 MJ/m³, in the work of compression, and 10 °C in the onset of thermal degradation. The epoxy blend containing a minimum of 10% EPS35 was again exposed to 5% strain but regained full initial compressive performance after a period of 1 h at 100 °C. The base epoxy resin was secondly modified by incorporating up to 40 wt% Vitrimax T130 which led to reductions of 1 °C in the cured T_g , 3 MJ/m³, in the work of compression, and 1 °C in the onset of thermal degradation. The epoxy blend containing 40% Vitrimax T130 regained full initial compressive performance after a period of 1 h at 100 °C. These healable epoxy matrices could be usefully applied in fibre

composite materials, in compression, providing a means to recover their full compressive performance after the onset of matrix damage, which might occur during the manufacturing process or in service. These types of healable matrix could be combined with a variety of structural health monitoring strategies [26,27] to identify when a recovery treatment should be implemented.

CRedit authorship contribution statement

Joseph F. Gargiuli: Investigation, Writing – original draft, Methodology, Visualization. **Rachel G. Board:** Data curation, Visualization. **Milo S.P. Shaffer:** Funding acquisition, Supervision, Writing – review & editing. **Ian Hamerton:** Funding acquisition, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.reactfunctpolym.2023.105725>.

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