

# The role of $\beta$ relaxations in determining the compressive properties of an epoxy amine network modified with POSS and mono-functional epoxy resins

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## ABSTRACT

Presented here is an investigation into the glassy state molecular mobility of modified epoxy amine networks using sub-ambient  $\beta$  relaxations measured from dynamic mechanical relaxations and their relationship to compressive properties. Two classes of additives are used to modify the epoxy amine network, the first are bulky inorganic siloxane caged epoxy functional polysilsesquioxanes (POSS) and the second are mono-functional epoxy diluents. Different pre-reaction methods between the POSS and amine were used to maximise dispersion or improved covalent attachment within the epoxy amine network while the mono-functional epoxy diluents easily react into the network via simple blending. Despite the wide structural variations in modifier and result effects upon final structure, microstructure and properties, the glassy state molecular mobility as measured by sub-ambient  $\beta$  relaxations correlates strongly with changes in modulus and yield strain.

## 1. Introduction

The global composites industry faces many ongoing challenges, one of which is the need for new resin systems with improved mechanical and thermal properties that can be integrated seamlessly with advanced fabrication technologies such as pultrusion, automatic tape and fibre placement [1–3]. Although many resin formulations already exist, new blends and reactive monomers for the next generation of composite applications, require a more finely tuned and nuanced understanding of structure property relationships in crosslinked networks [4,5]. And despite being a mature research field consisting of multitudes of papers already expounding on the role of crosslink density [6–8], monomer structure [9–11], cure profile ([12,13], stoichiometry [7,14,15] reaction mechanism [16–18] and microstructure [19–21] in determining modulus, yield, strength and toughness in epoxy networks, understanding their molecular origin remains an ongoing challenge [22].

The ability of a glassy polymer network to dissipate or store energy is determined by its short range molecular mobility and surrounding free volume [23] which is controlled by crosslink density and network architecture. As an example, yielding in amorphous network polymers in simple terms occurs through molecular segments sliding past each other

under stress, despite being brittle and constrained by crosslinking. The ability of a network to withstand large plastic deformations has been described effectively using the Eyring model of viscous flow, where yield consists of stress activated jumps of molecular segments of a specific volume [24–26]. Oleinik et al. [27] reported that yield in glassy amorphous polymers occurs through a series of localised plastic shear transformations which store internal energy until a critical point is reached after which they relax and yield. Mayr et al. [28] calculated the volume of these molecular segments by systematically varying crosslink density in an epoxy network and found it to be equivalent to the volume of an epoxy monomer and two linked amino groups. Espuche et al. [29] also varied the crosslink density of an epoxy amine resin systematically using a mono aromatic amine as a chain extender and reported an increase in modulus via antiplasticisation. This correlated with reduced molecular mobility in the glassy state measured by the  $\beta$  relaxation. A similar study by Espuche et al. [30] introduced aliphatic chains into a rigid epoxy network at the same time as increasing crosslink density and reported that flexibility was more important in determining properties such as modulus and toughness. Molecular mobility in the glassy state, was found to increase with aliphatic (flexible) groups, reported to be governed by defect nucleation and propagation (pre-yield and yield) and

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modulus. A more recent study by Heinz et al. [31] studied yield and sub  $T_g$  dynamic relaxations using an epoxy resin cured with isomers of diamino diphenyl sulphone (DDS), namely 44 and 33 DDS. In this work the 44 DDS cured network exhibited greater pre-yield anelastic strain sooner than 33 DDS, attributed partially to increased short range molecular motions and higher free volume. These motions were a direct measure of the larger amplitude of the sub  $T_g$  relaxations of the 44 DDS network, clearly indicating a relationship between the macroscopic property of yield.

The molecular origin of the sub  $T_g$  dynamic mechanical relaxations has been widely studied using a number of techniques including solid state  $^{13}\text{C}$  NMR [32–34], dielectric spectroscopy and FTIR [23,35] but most commonly dynamic mechanical analysis [36–38]. Sub-ambient dynamic mechanical analysis generally reveals two distinct peaks referred to as  $\beta$  and  $\gamma$  relaxations, at times used interchangeably. To be clear, in this study the broad and diffuse peak commonly observed between  $-80^\circ\text{C}$  and  $-50^\circ\text{C}$  will be referred to as the  $\beta$  relaxation. The understanding of the molecular origin of this peak has evolved over time [39,40] originally being attributed to crankshaft rotations of the hydroxy ether segments and rotations of the isopropyl groups in diglycidyl ether epoxy resins. Important contributions to this topic have been made by several research groups using  $^{13}\text{C}$  NMR [32–34,41], dielectric spectroscopy [42,43], creep rate spectroscopy [44], dynamic mechanical analysis [38] and molecular modelling [37]; and the reader is referred to these studies. However, it is the view of these authors that the current understanding of the  $\beta$  relaxation peak is that it consists of three transitions. The first is phenylene rotations or “ring flips” within the epoxy resin part of the network on low temperature side of peak, the second related to crankshaft rotations of hydroxy propyl ether linkages around the peak and finally, the phenylene motion of the diamine part of the network on the high temperature side of the peak. A schematic representation of the molecular motions and their position on the  $\beta$  relaxation peak are shown in Fig. 1.

In this work, the  $\beta$  relaxation has been explored in modified epoxy amine networks to further understand its contribution to mechanical properties such as modulus, strength and yield. To do this, two different approaches to modify a diglycidyl ether of bisphenol A (DGEBA) epoxide and diethyl toluene diamine (DETDA) cured network have been undertaken. The first, used two different epoxy functionalised polysilsesquioxane (POSS) modifiers, mono- and octa-functional epoxide to incorporate the POSS either into the backbone of the network (octa) or pendant (mono) to the network. The second was to incorporate mono-functional epoxy diluents of varying chemical architecture into the network such as isopropyl glycidyl ether (IPGE), dodecyl glycidyl ether (DDGE) and tert-butyl phenyl glycidyl ether (tBuPGE). These different modification methods, the incorporation of bulky siloxane cages and mono-functional epoxy diluents of varying aliphatic and aromatic structure were chosen to ensure a wide variation in the resultant network properties. The modified DGEBA/DETDA networks were characterised using near infra-red spectroscopy (NIR), dynamic

mechanical thermal analysis (DMTA) and compression.

## 2. Experimental

### 2.1. Materials

The epoxy resins used were di-glycidyl ether of bisphenol A (DGEBA) obtained from Dow Australia under the trade name DER-331 (5.81 mmol epoxide/g), iso-propyl glycidyl ether (IPGE) (Sigma-Aldrich, Australia), dodecyl glycidyl ether (DDGE) (Heloxy modifier 8, Hexion Chemicals, Texas, USA) and tert-butyl phenyl glycidyl ether (tBuPGE) (Heloxy modifier 65, Hexion Chemicals, Texas, USA). The amine used was diethyl toluene diamine (DETDA, Ethyl Corporation, USA). Two polysilsesquioxane polymers (POSS) were obtained from Hybrid Plastics (GS, USA); iso-octyl mono-glycidyl POSS (EPO419) (m-POSS), and glycidyl POSS (EP0409) (g-POSS). The m-POSS has a single propyl glycidyl ether group and 7 aliphatic iso-octyl groups attached to the POSS cage. The g-POSS is a mixture of caged POSS structures but consists primarily of eight propyl glycidyl ether groups to the POSS cage. All of the epoxy resins and diluents were degassed in a vacuum oven at  $80^\circ\text{C}$  for 8 h prior to use. Apart from this, all chemicals were used as received and stored in a refrigerator when not in use. The structures of all the chemicals used in this work are shown in Fig. 2.

### 2.2. Sample preparation

The POSS modifiers, m-POSS and g-POSS were incorporated into the networks using different pre-reaction methods and simple blending. Without pre-reaction, a uniform dispersion of the m-POSS in the epoxy amine could not be achieved. To pre-react the m-POSS a 10 times molar excess of DETDA was added to m-POSS and placed in a glass beaker in an oven at  $120^\circ\text{C}$  and  $150^\circ\text{C}$ , each for 17 h. After this time, DGEBA was added and blended into the mixture to achieve overall concentrations of 2.5 wt%, 5.0 wt% and 10 wt% of the m-POSS and an overall DGEBA/DETDA epoxide amine stoichiometry of 1:0.9. In contrast to the m-POSS, g-POSS was completely miscible in the DGEBA/DETDA prior to cure, so pre-reacted and blended formulations were prepared as follows. Pre-reaction of g-POSS was performed by adding a 10 times molar excess of the DETDA to g-POSS and placed in an oven at  $100^\circ\text{C}$  for 2 h. After this time, varying amounts of DGEBA were similarly added to achieve an overall concentration of 2.5 wt%, 5.0 wt% and 10 wt% of the g-POSS in a DGEBA/DETDA network. For the blended only formulations, all of the components were mixed together manually at room temperature until the mixture were transparent.

The mono-functional epoxy diluents, iso-propyl glycidyl ether (IPGE), dodecyl glycidyl ether (DDGE) and tert-butyl phenyl glycidyl ether (tBuPGE) were added to the DGEBA/DETDA resin systems at 5 wt % and 10 wt% by simply blending the different components at room temperature until the mixtures were transparent.

The uncured resin systems were placed in pre-heated Teflon<sup>TM</sup> coated moulds and cured in an air circulating oven at  $130^\circ\text{C}$  for 2 h, followed by  $177^\circ\text{C}$  for a further 5 h. The cured resins were allowed to cool down overnight prior to removal. Table 1 lists the samples prepared in this work, noting in particular the overall epoxide amine stoichiometry of the overall blends once the POSS or mono-functional epoxy resins had been added.

### 2.3. Characterization

Near Infra-red spectroscopy (NIR) was performed on a Nicolet 6700 Spectrometer FTIR in transmission mode at a resolution of  $4\text{ cm}^{-1}$  and an average of 64 scans between  $4500\text{ cm}^{-1}$  and  $7500\text{ cm}^{-1}$ . Qualitative characterization of the extent of cure and network structure was determined using the relative magnitude of the epoxide peak at  $4530\text{ cm}^{-1}$ , the secondary amine peak at  $6500\text{ cm}^{-1}$  and the hydroxyl peak at  $7000\text{ cm}^{-1}$ .

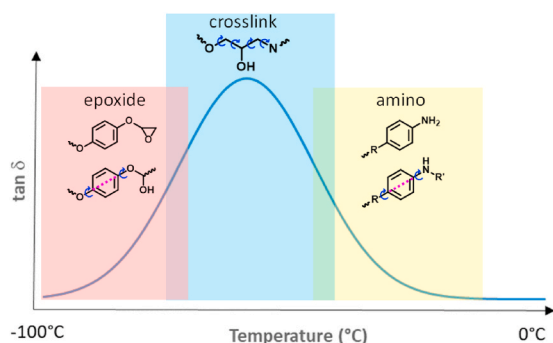


Fig. 1. Schematic representation of the  $\beta$  relaxation curve and the associated molecular rotations.

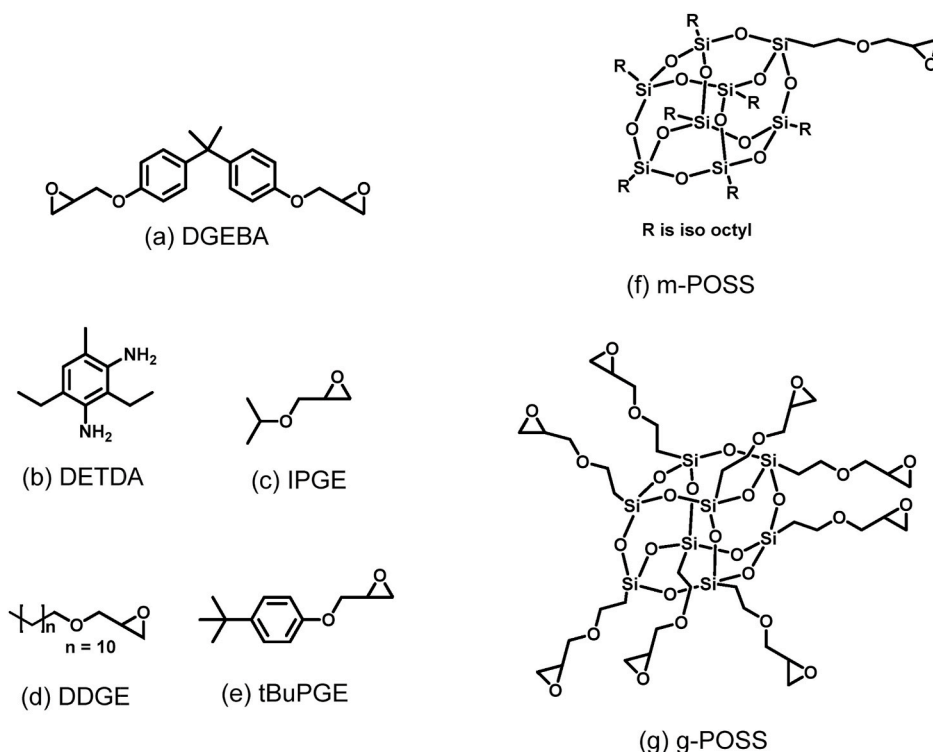


Fig. 2. Chemical structures of the compounds used in this work. a) DGEBA, b) DETDA, c) IPGE, d) DDGE; e) tBuPGE; f) m-POSS g) g-POSS.

Table 1

POSS and mono-functional epoxy additives, including epoxide amino stoichiometry and the preparation method.

Additive	Epoxide: amino stoich.	Preparation Method
–	1:0.92	Blended at RT
2.5 wt% m-POSS	1:0.91	pre-reaction at 120 °C and 150 °C for 17 h
5.0 wt% m-POSS	1:0.91	pre-reaction at 120 °C and 150 °C for 17 h
10.0 wt% m-POSS	1:0.90	pre-reaction at 120 °C and 150 °C for 17 h
2.5 wt% g-POSS	1:0.89	blended at RT and pre-reaction at 100 °C for 2 h
5.0 wt% g-POSS	1:0.86	blended at RT and pre-reaction at 100 °C for 2 h
10.0 wt% g-POSS	1:0.80	blended at RT and pre-reaction at 100 °C for 2 h
5 wt% IPGE	1:0.84	blended at RT
10 wt% IPGE	1:0.76	blended at RT
5 wt% DDGE	1:0.88	blended at RT
10 wt% DDGE	1:0.84	blended at RT
5 wt% tBuPGE	1:0.87	blended at RT
10 wt% tBuPGE	1:0.82	blended at RT

Dynamic Mechanical Thermal Analysis (DMTA) was performed using a PerkinElmer SEIKO DMA Diamond II Series. Samples of dimensions 12 mm × 50 mm × 2.8 mm were placed in a dual cantilever fixture and force amplitude of 20 μm was applied at a frequency of 1 Hz. The glass transition temperature ( $T_g$ ) of the network was determined from the peak in the  $\tan \delta$  plot as the temperature was increased from 50 °C to 250 °C at a rate of 2 °C/min. To investigate the sub-ambient glassy state molecular motions, the  $\beta$  relaxation, the same method was used except that the temperature was increased from –100 °C to 50 °C at a rate of 2 °C/min. The  $\beta$  relaxation transition was characterised by the peak temperature,  $T_\beta$  and its area. The crosslink densities ( $\nu_e$ ) of the network were calculated using the following equation:

$$\nu_e = \frac{E_r}{3RT_r}$$

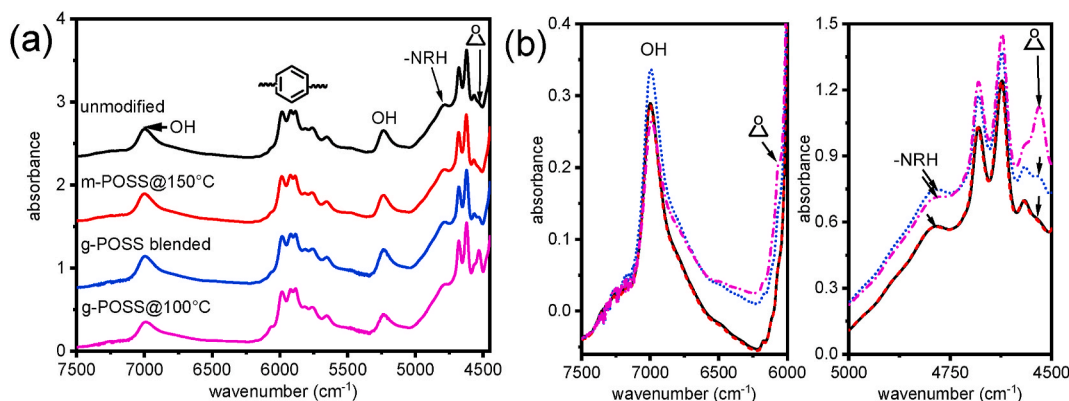
where  $E_r$  is the rubbery modulus at  $T_r$  ( $T_g + 30$  °C) and  $R$  is the real gas constant.

Compressive properties were determined using an Instron 3880 Universal Testing Machine fitted with a 100 kN load cell and flat platens. Cylindrical samples of dimensions 12 mm in height and a diameter of 12 mm were placed between the parallel platens and compressed using a crosshead displacement of 1 mm/min. The compressive properties such as moduli, stress and strain at yield and failure were determined using the proprietary Merlin Software.

### 3. Results

#### 3.1. Network structure

The NIR spectra of the cured unmodified and 10 wt% POSS modified networks are shown in Fig. 3a) and are typical of what is observed for highly cured epoxy networks [45]. Each spectrum displays large hydroxyl peaks at about 7000  $\text{cm}^{-1}$  and the lack of any distinct secondary amine peak at about 6500  $\text{cm}^{-1}$  is indicative of a high degree of secondary amine consumption regardless of modifier. The epoxide peak as determined from the overtone of the methylene of the glycidyl group at 4530  $\text{cm}^{-1}$  is very small for the DGEBA/DETDA cured network and combined with the lack of any secondary amine peak, suggests a high degree of network formation. As emphasised in the expanded view in Fig. 3b), the pre-reacted m-POSS and blended only g-POSS networks have relatively similar degrees of epoxide consumption compared with the unmodified network, suggesting that the additional epoxide groups are successfully incorporated into the network. For the pre-reacted g-POSS however, a larger epoxide peak (4530  $\text{cm}^{-1}$ ) is evident as well as a hint of lower secondary amine consumption (~6500  $\text{cm}^{-1}$ ) suggesting incomplete cure of the network. Preferential attachment of DETDA to g-POSS would be expected to promote formation of a g-POSS-DETDA oligomer and a more heterogeneous network via



**Fig. 3.** a) NIR spectra of the unmodified and 10 wt% POSS modified DGEBA/DETDA networks; and b) including an expanded view of the hydroxyl and epoxide regions.

deactivation of the amine, inhibiting further reaction with DGEBA to reduce final epoxide conversion.

The NIR of the mono-functional epoxy modified networks in Fig. 4a) are very similar after cure, even when observed more closely in Fig. 4b), despite the wide variation in epoxide amino stoichiometry. The large hydroxyl peaks (7000 cm<sup>-1</sup>) and the small epoxide peaks (~4530 cm<sup>-1</sup>) and lack of any distinct secondary amine peak (~6500 cm<sup>-1</sup>) suggested that the increased epoxide functional groups were easily accommodated into the network. Clearly, given the excess epoxide to amino groups in the formulation, increased etherification must be occurring during cure of these networks [46–48].

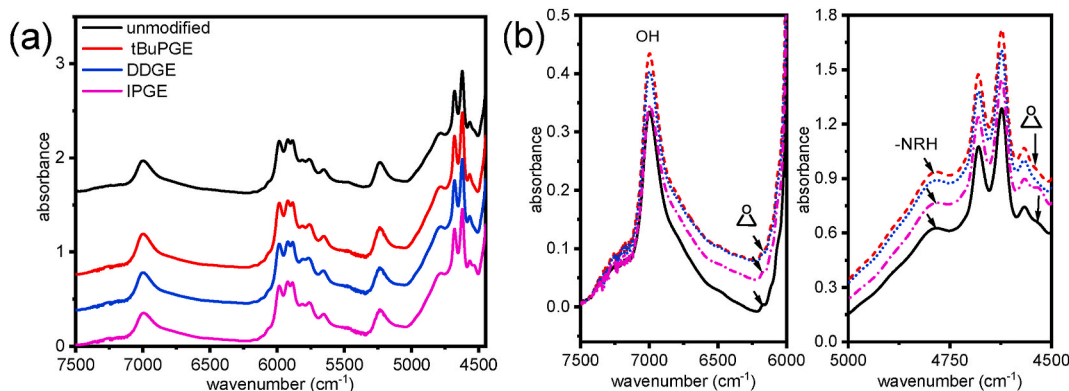
### 3.2. Thermal analysis

The dynamic mechanical spectra of the POSS modified networks, specifically the storage modulus and tan  $\delta$  in Fig. 5a) display a large decrease in the storage modulus and a peak in the tan  $\delta$  as the network goes through the glass transition ( $T_g$ ), typical of fully cured epoxy/amine networks. The tan  $\delta$  peaks for the m-POSS modified networks are quite unimodal and symmetric consistent with a homogenous micro-structure [49–53]. The g-POSS blended only tan  $\delta$  peak is quite symmetric and mostly unimodal apart from a very small shoulder on the low temperature side of the peak. The pre-reacted g-POSS modified network tan  $\delta$  peak, however, is significantly less unimodal and less symmetric compared with the other peaks, indicative of a more heterogeneous network and supportive of the above NIR spectral interpretations.

The  $T_g$ s (tan  $\delta$  peak) are plotted as a function of POSS concentration for each of the different preparation methods in Fig. 5b). As can be seen, the m-POSS pre-reaction produces modest decreases in  $T_g$ , going from 184 °C for the unmodified network to 176 °C for the 120 °C pre-reaction

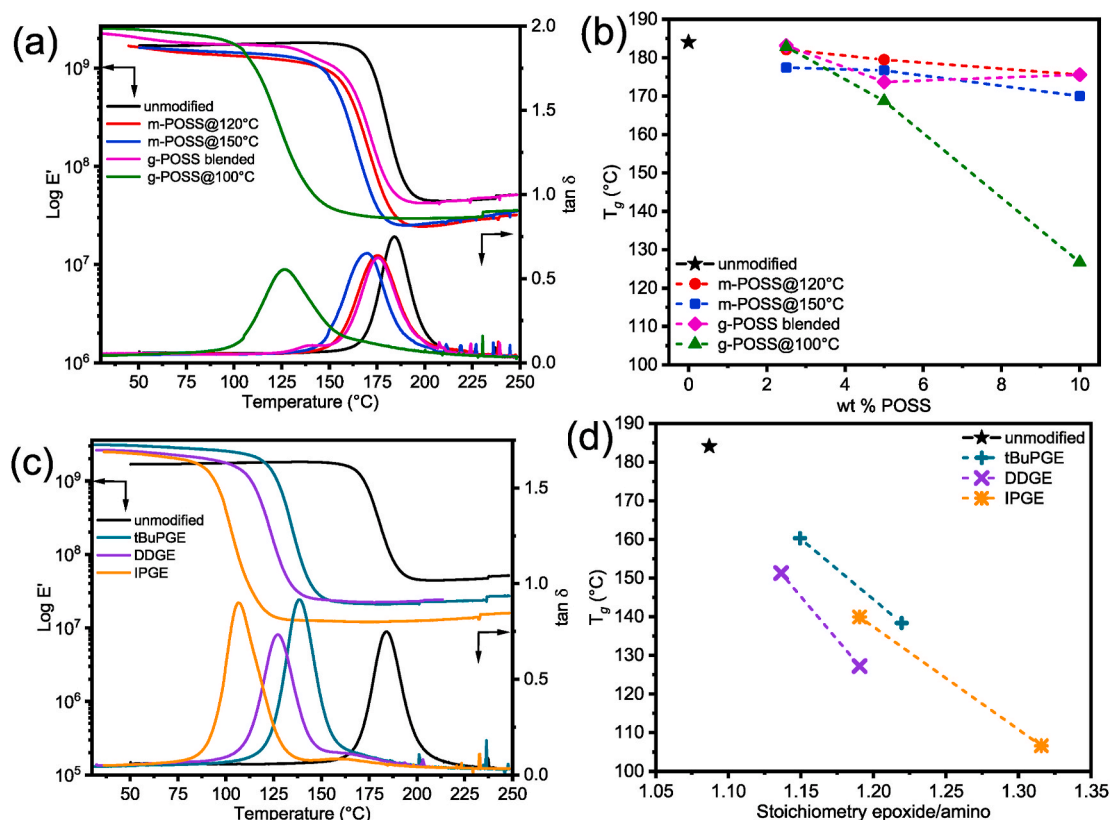
at 10 wt% m-POSS. The 150 °C pre-reaction, however, displays a consistently lower  $T_g$  of between 3 and 6 °C when compared to the 120 °C pre-reaction. These differences can be considered in terms of the incompatibility between the inorganic POSS structures and the organic DGEBA/DETDA network and the ability of the POSS structures to self-assemble into nanoscale and micro-scale domains [54,55]. The mono epoxide functional m-POSS also has seven iso-octyl groups extending from the corners of the siloxane cage to aid thermodynamic compatibility, but their successful incorporation or dispersion into DGEBA/DETDA requires pre-reaction at elevated temperatures. The lower  $T_g$ s are clearly indicative of improved dispersion or incorporation and support similar results observed elsewhere [56]. Sharma et al. [57] furthermore, compared a more uniform dispersion created using higher pre-reaction temperatures to the more restricted molecular motion evident when there is increased phase separation of bulky POSS units at lower pre-reaction temperatures.

The  $T_g$ s of the blended only g-POSS modified network in Fig. 5b) also display a similarly modest decrease with increasing g-POSS concentration compared with the m-POSS modified networks, reducing by approximately 8.5 °C at 10 wt% of g-POSS. The pre-reacted g-POSS modified network however, has the largest effect, decreasing by 57.4 °C–126.7 °C at 10 wt% of g-POSS. The g-POSS is composed of eight epoxide groups connected to the siloxane cage via propyl ether linkages which greatly enhance miscibility with the DGEBA/DETDA. The impact on  $T_g$  due to POSS addition to an epoxy network, can vary widely and has been reported to both increase [53,58] and decrease [53,59] being attributed to reinforcement from the self-assembled POSS structures or plasticisation respectively. It is proposed here, that the modest reduction for the blended only g-POSS networks is due to plasticisation arising from reduced the crosslink density (Tables 2 and 3) and incorporation of



**Fig. 4.** a) NIR spectra of the unmodified and 10 wt% mono-functional epoxide modified DGEBA/DETDA networks; and b) including an expanded view of the hydroxyl and epoxide regions.





**Fig. 5.** a) Dynamic mechanical analysis ( $E'$  and  $\tan \delta$ ) of the unmodified and POSS modified DGEBA/DETDA networks; b) effect of  $T_g$  as a function of POSS; c) dynamic mechanical analysis ( $E'$  and  $\tan \delta$ ) of the unmodified and 10 wt% mono-functional epoxy modified DGEBA/DETDA networks; and finally d) the effect of  $T_g$  as a function of mono-functional epoxy at 5 wt% and 10 wt%.

**Table 2**

Dynamic mechanical analysis of m-POSS additives on the DGEBA/DETDA network.

Additive	$T_g$ (°C)	$E_{rubbery}$ (MPa)	$\nu_e$ (mol. cm <sup>-3</sup> )	$T_\beta$ (°C)	Area $\beta$ relaxation	FWHM (°C)
Un-modified	184.1	44.9	3692.9	-59.8	4.8	116.6
2.5 wt% m-POSS-120	182.2	42.1	3479.2	-58.5	4.6	116.1
5 wt% m-POSS-120	179.5	27.5	2283.5	-56.8	5.0	131.5
10 wt% m-POSS-120	175.6	24.8	2080.4	-64.7	5.1	135.5
2.5 wt% m-POSS-150	177.4	33.0	2754.2	-63.2	4.9	129.4
5 wt% m-POSS-150	176.7	35.2	2942.3	-57.0	5.3	125.8
10 wt% m-POSS-150	170.0	26.0	2202.4	-66.1	4.5	116.5

the flexible aliphatic chains surrounding the POSS structure into the polymer network. The large reduction in  $T_g$  for the pre-reacted g-POSS is likely due to the preferential reaction with the amine as proposed above, through oligomer formation, increased heterogeneity and deactivation of the amine towards further reaction with DGEBA.

Fig. 5c) shows the dynamic mechanical spectra of some of the mono-functional epoxy modified networks for the storage modulus and  $\tan \delta$

**Table 3**

Dynamic mechanical analysis of g-POSS additives on the DGEBA/DETDA network.

Additive	$T_g$ (°C)	$E_{rubbery}$ (MPa)	$\nu_e$ (mol. cm <sup>-3</sup> )	$T_\beta$ (°C)	Area $\beta$ relaxation	FWHM (°C)
Un-modified	184.1	44.9	3692.9	-59.8	4.8	116.6
2.5 wt% g-POSS-B	183.2	34.6	2850.8	-57.1	4.9	124.9
5 wt% g-POSS-B	173.7	47.8	4016.9	-63.4	4.8	133.5
10 wt% g-POSS-B	175.6	42.4	3554.2	-62.2	4.4	119.9
2.5 wt% g-POSS-100	182.8	34.3	2827.3	-53.4	5.1	137.0
5 wt% g-POSS-100	168.7	34.30	2915.33	-62.8	4.4	107.2
10 wt% g-POSS-100	126.7	34.51	3220.09	-70.9	2.6	71.3

spectra which all show significant reductions in  $T_g$  as plotted in Fig. 5d). The unmodified and modified resins all exhibit a unimodal  $\tan \delta$  peak suggesting the absence of any micro-phase separation regardless of the modifier. The  $T_g$ s of the cured resins all decrease monotonically as does the crosslink density (Table 4) with increasing modifier content, as might be expected with the addition of a mono-functional epoxy diluent. The reduced  $T_g$  can be understood in terms of the increased mobility of the chain elements from the more flexible modifiers either aliphatic or aromatic and aliphatic combined. The reduction in  $T_g$  when taking

**Table 4**

Dynamic mechanical analysis of the mono-functional epoxy additives on the DGEBA/DETDA network.

Sample ID	T <sub>g</sub> (°C)	E <sub>r</sub> (MPa)	ν <sub>e</sub> (mol.cm <sup>-3</sup> )	T <sub>β</sub> (°C)	Area β relaxation	FWHM (°C)
Un-modified	184.1	44.9	3692.9	-59.8	4.8	116.6
5 wt% IPGE	160.3	29.5	2555.3	-65.0	4.6	121.5
10 wt% IPGE	138.4	21.5	1951.7	-66.7	4.0	107.1
5 wt% DDGE	151.3	25.9	2288.2	-66.4	4.0	104.2
10 wt% DDGE	127.2	23.5	2189.6	-72.9	3.3	87.8
5 wt% tBuPGE	139.4	18.3	1655.7	-55.7	3.3	87.8
10 wt% tBuPGE	106.6	12.7	1243.4	-66.7	3.6	107.1

stoichiometry into account in increasing order is tBuPGE < IPGE < DDGE. The tBuPGE modifier exhibited the least reduction due to its rigid aromatic structure while the progressively more aliphatic and flexible IPGE (short but flexible) and DDGE (long flexible) show consistently larger reductions.

The rubbery modulus, E<sub>r</sub> and the resultant crosslink densities are reported in Tables 2–4. Which also illustrate the effect upon network properties. The results are somewhat variable, but provide useful information on the molecular mobility in the rubbery state.

The β relaxations as measured by the tan δ plot are shown in Fig. 6a) and b) for the 10 wt% m-POSS and g-POSS modified networks respectively. The important observation from each trace is that the POSS additive, regardless of whether it is mono or octa functional, reduces molecular mobility in the glassy state compared with the unmodified network as evidenced by the reduced area of the peak. In the case of the m-POSS modified network, the peak area is smaller after pre-reaction at 150 °C compared with 120 °C, indicative of a further reduction in molecular mobility and a higher degree of molecular level dispersion or covalent attachment to the epoxy network. Also of note in the m-POSS β relaxation traces is the observation of separate peaks at around 0 °C. More pronounced for the 120 °C than the 150 °C pre-reaction method, this peak likely reflects micro-phase separation of clusters of self-assembled POSS molecules not covalently attached to the network. A larger peak for the 120 °C pre-reaction therefore represents increased phase separation and or less covalent attachment, supporting the above discussion [36,52,56] and correlates well with the observed less transparent network compared to the 150 °C pre-reaction. For the g-POSS modified networks in Fig. 6b), the effect is similar, but more pronounced for the g-POSS pre-reacted network which has a much lower peak area. Clearly, the effect of g-POSS pre-reaction further reduces molecular mobility, while the small peak at 0 °C similar to that of the m-POSS modified network again highlights the increased heterogeneity of the network. Furthermore, the reduction in T<sub>β</sub> for both plots with increasing POSS attachment reflects the lower mechanical activation temperatures of the silicon compounds.

A similar trend is observed for the mono-functional epoxide modified networks as shown in Fig. 7a) and b) which compare the different

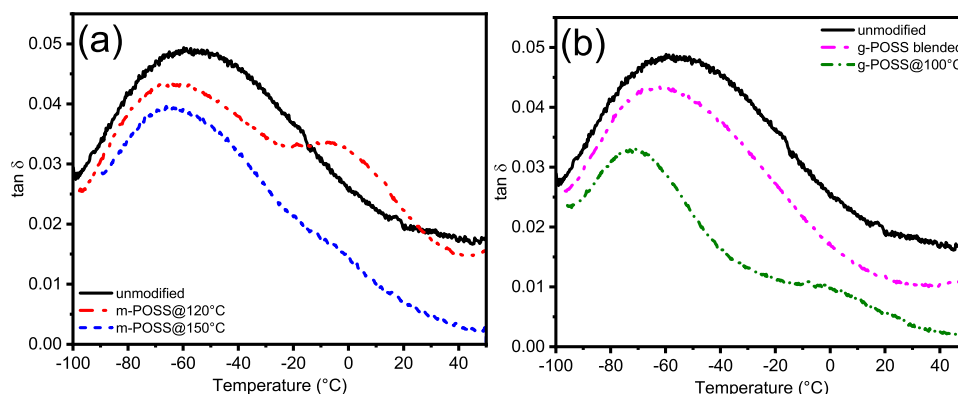
modifiers and the impact of increasing concentration of mono-functional epoxy diluent respectively, using IPGE as a representative example. It is important to note that this reduction in local mobility is evident, despite the reduced crosslink density of the networks, but indicative of a kind of self-reinforcement known as anti-plasticisation [29] where the short-range molecular motions are restricted through filling the free volume and increasing secondary molecular interactions. Another point of difference between the POSS modified networks is the lack of any other sub ambient transition, emphasising network homogeneity and full incorporation of the mono-functional epoxy diluents into the network.

All of the T<sub>β</sub>s are plotted as a function of POSS additive concentration and stoichiometry for the mono-functional epoxy diluent in Fig. 8a) and b) respectively and further illustrate the abovementioned trends. Clearly, reduced phase separation and or covalent attachment of POSS reduces T<sub>β</sub>, which reduces the temperature at which the network is mechanically active. For the mono-functional epoxy diluents, after considering stoichiometry in order of lowest T<sub>β</sub>, DDGE is followed by IPGE then tBuPGE, meaning that DDGE is the modifier that remains mechanical active at the lowest temperature. A summary of the dynamic mechanical analysis results from both sub-ambient and above ambient are shown in Table 4.

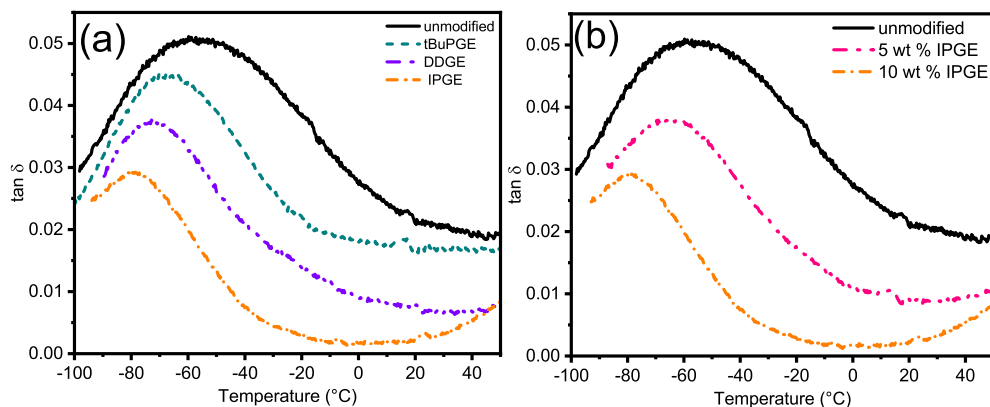
### 3.3. Compressive properties

The stress versus strain compressive properties are shown in Fig. 9a) and b), for the POSS and mono-functional epoxy modified systems, respectively. From the raw data, the effect on the DGEBA/DETDA network of the POSS modifiers appear relatively modest while the mono-functional epoxide modified networks display larger increases in modulus while reducing yield strain.

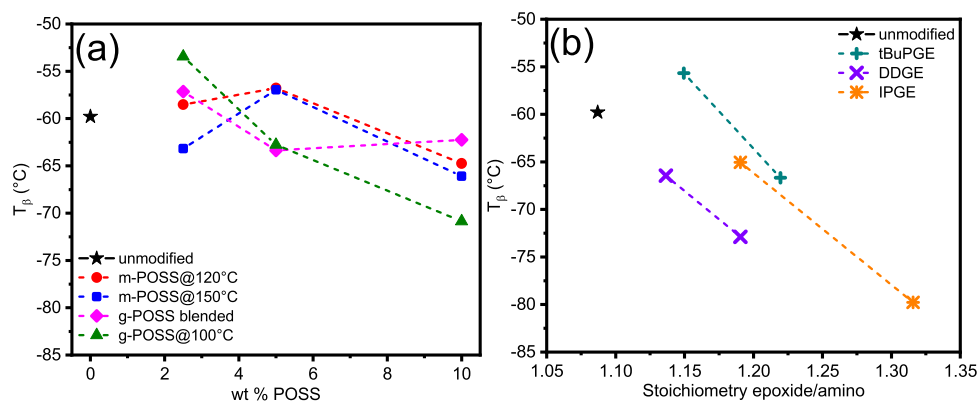
The measured modulus, yield strength and strain for the POSS modified networks are shown in Fig. 10a) and b) and c) respectively. The modulus can indeed be seen to increase modestly for most systems, but significantly so for the g-POSS pre-reacted network. This correlates well with the β relaxation of the POSS systems which shows that the pre-reacted g-POSS has the largest reduction in peak temperature and area



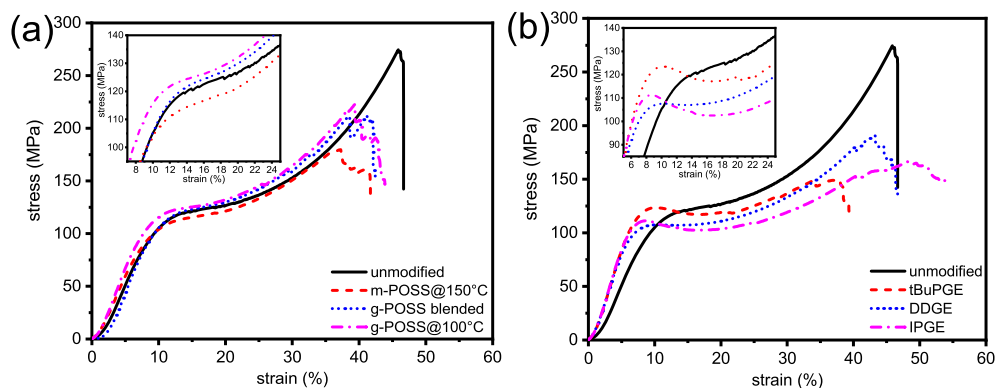
**Fig. 6.** β relaxation peaks for the unmodified DGEBA/DETDA networks a) 10 wt% m-POSS and b) 10 wt% g-POSS networks.



**Fig. 7.**  $\beta$  relaxation peaks for the unmodified DGEBA/DETDA networks a) and the 10 wt% IPGE, DDGE and tBuPGE modified networks; b) the 5 wt% and 10 wt% IPGE modified networks.



**Fig. 8.** a)  $T_\beta$  plotted as a function of wt% POSS concentration; and b)  $T_\beta$  plotted as a function of epoxide amino stoichiometry for the 10 wt% mono-functional epoxide additives.



**Fig. 9.** Stress versus strain data for the a) POSS modified and b) mono-functional epoxy resin DGEBA/DETDA networks.

(Table 3). Comparison of the pre-reacted m-POSS networks reveals that increasing pre-reaction temperature modestly increase modulus and yield strength while not affecting yield strain. This can be attributed to enhanced dispersion or chemical incorporation of the m-POSS into the polymer network. For the g-POSS networks, pre-reaction significantly increased modulus, modestly increased strength, while greatly reducing strain at yield. These results can be understood in terms of the oligomeric formation and increased heterogeneity enhancing self-assembly of the POSS micro-structure. This would also restrict mobility in the glassy state and promote anti-plasticisation which increases modulus and reduces yield strain. This effect is also observed for the m-POSS pre-reaction but is far more modest.

The modulus, yield strength and strain for the mono-functional epoxide modified networks are shown in Fig. 11a) and b) and c) respectively. Each of the epoxide additives increase the modulus significantly and decrease strain due to anti-plasticisation. When taking stoichiometry into account the effect of each different modifier increases modulus in increasing order of IPGE, DDGE and finally tBuPGE. The effect of different modifiers is more apparent for the yield strength, which shows a large reduction for the DDGE modified network, followed by the IPGE network and then tBuPGE, which has little impact. For the yield strain in Fig. 10c) all three additives produce a large reduction in yield strain, and after adjusting for stoichiometry, the DDGE has the largest impact, while IPGE and tBuPGE appear to cause a similar

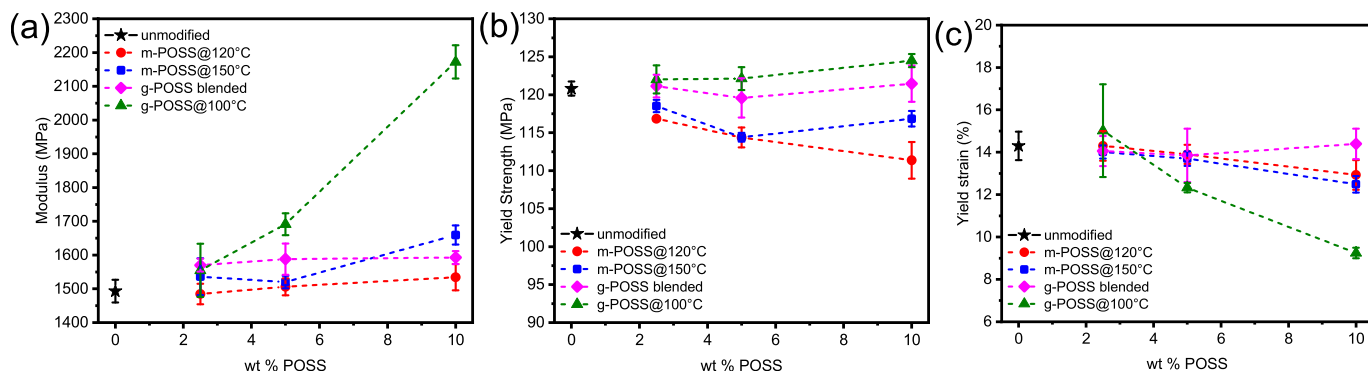


Fig. 10. Effect of POSS modification on the a) modulus, b) yield strength and c) yield strain of the DGEBA/DETDA networks.

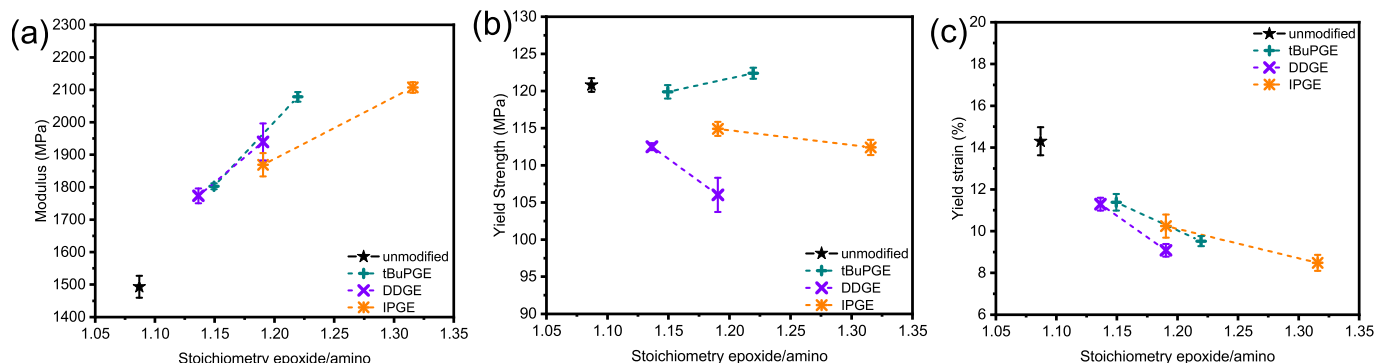


Fig. 11. Effect of mono-functional epoxide addition on the a) modulus, b) yield strength and c) yield strain of the DGEBA/DETDA networks.

reduction in yield strain.

#### 4. Discussion

The results presented in this work describe the use of two quite disparate additives to modify a DGEBA/DETDA network. The first were the largely inorganic siloxane POSS molecules that required careful processing to maximise incorporation or dispersion with the epoxy network. The second were the mono-functional epoxy additives that were more easily accommodated due to their inherent miscibility. For each set of modified networks, mechanical and thermal properties were determined including  $\beta$  relaxations and compressive properties. The  $\beta$  relaxations are discussed with respect to molecular mobility in the glassy state, but it is known that mechanical properties such as yield and modulus in particular, are also dependent upon molecular mobility and free volume. To explore this further, the areas of the  $\beta$  relaxation peaks were plotted against the compressive properties, (a) modulus, (b) yield

strain and (c) strength in Fig. 12. Despite being complex, a relationship between molecular mobility (area of  $\beta$  relaxation) and modulus and yield strain is evident. While dependency of mechanical properties on  $\beta$  relaxations has been reported previously [50–52], a relationship of this kind, that attempts to provide semi-quantitative support has not. Indeed, the fact that a master curve of any kind exists, particularly for such disparate additives is striking. Indeed, as expected the plots emphasise that as modulus increases, the molecular mobility reduces and as yield strain increases the molecular mobility increases. Finally, no relationship between yield stress and molecular mobility was observed which supports the understanding that yield stress is more related to longer scale molecular motions.

#### 5. Summary

Using additives ranging from bulky inorganic/organic hybrid siloxane cages through to mono-functional epoxide diluents, this work

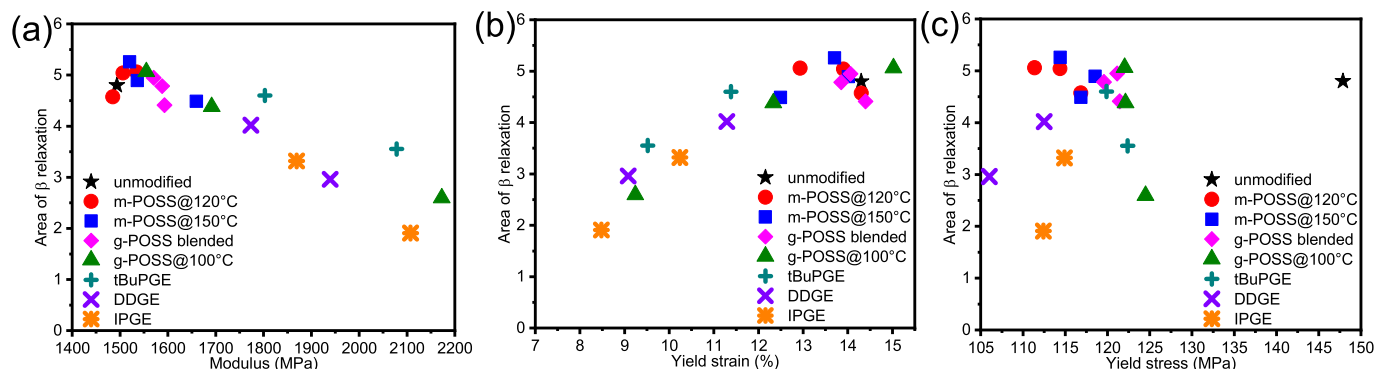


Fig. 12. Plot of a) modulus; b) yield strain; and c) yield stress and the area of the  $\beta$  relaxation peak.



has described new insights into the effect of short-range local mobility of epoxy amine networks on the final macroscopic properties such as glass transition temperature and compressive properties. The use of POSS cages, either attached covalently or dispersed effectively throughout the network has been investigated systematically and shown to reduce local mobility of the DGEBA/DETDA network which increases modulus and reduced yield strain modestly or otherwise, depending on the preparation method. The yield strength increased for g-POSS but decreased for m-POSS. The addition of mono-functional epoxy diluents also reduced molecular mobility which had somewhat clearer effects, reducing  $T_g$ , yield strain and yield stress, apart from tBuPGE which remained relatively unchanged, while significantly increasing modulus.

### Author statement

RV conceived and designed the overall study. LR, SS, JZ and RV all contributed to the construction of the ideas put forward in this work. The manuscript was written by LR and RV, with input from SS, JG, SMS and JZ. The manuscript was critically reviewed by all authors.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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