



# The role of $\beta$ relaxations in controlling compressive properties in hyperbranched polymer-modified epoxy networks

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## Abstract

In this work, a largely miscible second-generation aliphatic polyester hyperbranched polymer (HBP) is used as a modifier in a cured epoxy amine network to explore molecular mobility in the glassy state and its impact on compressive properties. The  $\beta$  relaxation determined by dynamic mechanical analysis is used as a measure of short-range motion in the glassy state and is related to the compressive modulus and yield properties. The parameters explored include an increased HBP concentration, enhanced HBP, and epoxy matrix interactions through pre-reaction via a rigid covalent linkage and a modified epoxy network of flexible butanediol diglycidyl ether (BDDGE) and highly crosslinkable tetraglycidyl diamino diphenyl methane (TGDDM). The  $\beta$  relaxation peaks are analyzed in terms of their area, FWHM, and position ( $T_{\beta}$ ) and are observed to correlate strongly with changes in the modulus, yield stress, and strain.

## Introduction

Epoxy resins are critical to the modern world because of an array of structural applications in the construction, automotive, oil and gas, and aerospace industries that take advantage of their superior mechanical and thermal properties and comparatively low cost and processability [1, 2]. However, as crosslinked polymer networks, they are inherently brittle, which has limited their even wider application. Multitudes of studies over the years have sought to improve the ductility of these materials, with various degrees of success [3, 4], but invariably, this has led to a reduction in other desirable properties, such as stiffness and processability. Hyperbranched polymers (HBPs) have a unique chemical structure, which has proven beneficial in enhancing ductility while often not reducing processability [5–7]. They have a three-dimensional spherical dendrimer-like structure with many surface functional groups. Their compact 3D structure generally allows them to flow easily past each other under applied stress, resulting in a low melt viscosity, even at

high molecular weights [5, 7, 8]. A low melt viscosity combined with a high density of surface functional groups therefore presents an opportunity to tailor HBPs as next-generation additives to simultaneously improve competing properties in epoxy resin formulations. However, the purpose of this study is not to add to the myriad of studies on toughening epoxy networks [8] but to use an HBP as a modifier for an epoxy network and further understand the role of  $\beta$  relaxation or short-range molecular mobility within glassy networks in controlling macroscopic mechanical properties, such as yield and modulus. Although there have been many systematic studies on structure–property relationships in epoxy networks to improve specific properties [9–12], understanding and increasing the yield stress and strain has not been a common focus, despite the importance of these properties. Mayr et al. calculated the size of the plastic deformation zone (i.e., short-range molecular mobility) and reported its relationship to the yield stress of the network polymer. Oleinik [13] also studied yield in epoxy networks and described the plastic deformation of an amorphous glassy polymer as repeated localized plastic shear transformations that store internal energy until a critical point is reached, after which they relax and yield.

Mobility in the glassy state has been widely characterized using a number of techniques, including solid-state <sup>13</sup>C NMR [14–16], dielectric spectroscopy [17], FTIR [18, 19] and, most commonly, dynamic mechanical analysis

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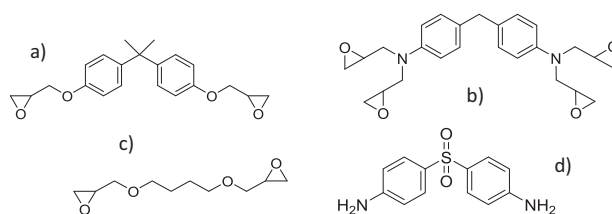
[20, 21]. Conveniently measured from the  $\tan \delta$  response using subambient dynamic mechanical analysis, the  $\beta$  relaxation is a broad low-intensity peak consisting of overlapping transitions attributed to different short-range motions within the epoxy amine network structure controlled by crosslink density [8, 17, 22], chemical architecture [23], and free volume [19].

With respect to HBP addition, whether miscible, covalently attached to an epoxy network or phase separated from the epoxy network,  $\beta$  relaxation is used here to gain new insights into mobility in the glassy state and to better understand its role in determining the compressive yield and modulus. To do this, a 2nd-generation commercially available polyester HBP that does not phase separate at lower concentrations during cure has been used as a modifier for a diglycidyl ether of bisphenol A (DGEBA)/diamino diphenyl sulfone (DDS) cured network. Their subambient  $\beta$  relaxations have been measured, and their relationship to macroscopic properties, such as compressive properties, has been discussed. The parameters explored in this work include HBP concentration and covalent bonding between HBP and the epoxy matrix. Finally, the 10-wt% HBP-modified system was modified using tetraglycidyl diphenyl diaminomethane (TGDDM) and butanediol diglycidyl ether (BDDGE) to further explore the effect of increased crosslink density and flexibility on network properties, respectively.

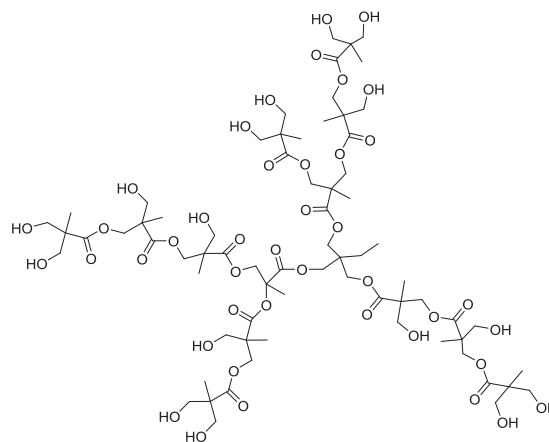
## Experimental

### Materials

The epoxy resins used were DGEBA (DER-331, Dow USA), EEW = 182–192 g/eq.; TGDDM, EEW = 117–134 g/eq. (MY720, Vantico, Australia); and BDDGE, EEW = 101 g/eq. (Sigma-Aldrich, Australia). The epoxy resins were dried in a vacuum oven at 80 °C overnight prior to use; otherwise, they were used as received. The aromatic amine used was 4,4 DDS, AEW = 62 g/eq. (Aradur 9664–1, Vantico, Australia), supplied in powder form. Prior to use, the DDS was ground into a fine powder using a mortar and pestle by rigorous grinding for 5 min and then stored in a dark and dry place prior to use. The chemical structures of the epoxy resins and DDS are shown in Fig. 1. Methylene diphenyl diisocyanate (MDI) was obtained from Sigma-Aldrich (Australia). The 2nd-generation polyester HBP used is based upon a polyalcohol core and 2,2-dimethylol propionic acid (Boltorn H20, Perstorp, Sweden). It consists of 16 surface hydroxyl groups and has a hydroxyl value between 490 and 520-mg KOH/g. Its theoretical molecular weight is 1749 g/mol, and it has a  $T_g$  of 30 °C. Boltorn H20 (HBP) was used as received, but care was taken to prevent moisture ingress of the samples during storage by placing



**Fig. 1** Chemical structures of the epoxy resins used in this work, including **a** diglycidyl ether of bisphenol A (DGEBA), **b** tetraglycidyl methylene dianiline (TGDDM), **c** butanediol diglycidyl ether (BDDGE), and **d** the aromatic amine hardener diamino diphenyl sulfone (DDS)



**Fig. 2** Idealized structure of Boltorn H20

the samples in a desiccator over dried silica. Its chemical structure is shown in Fig. 2.

### Sample preparation

#### Unmodified

To prepare the unmodified DGEBA/DDS formulation, DGEBA was placed in a round-bottom flask along with sufficient DDS to achieve a 1:1 epoxide:amino stoichiometry ratio. The blend was mixed using a rotary evaporator under vacuum at 110 °C for ~30 min until the DDS had completely dissolved and was free from bubbles.

#### Blending with HBP

The HBP-modified DGEBA/DDS samples were prepared by dissolving the HBP into DGEBA in the minimum quantity of acetone required through refluxing and stirring using a magnetic stirrer bar. When the sample was fully dissolved, the solvent was completely removed using a rotary evaporator, and DDS was added to ensure a 1:1 epoxide:amino stoichiometry. Mixing was then continued until the DDS had completely dissolved and was free of bubbles.

## Pre-reaction

Pre-reacted formulations containing HBP and DGEBA/DDS were prepared according to a method described elsewhere [24], but the general process was as follows. HBP (25 g, 223.2 mmol) was dissolved in dichloromethane and added dropwise over 2 h to a stirred solution of MDI (5.6 g, 224.1 mmol) at 40 °C under a blanket of nitrogen and then heated and stirred for an additional 2 h. The stoichiometric composition of HBP and MDI was intended to promote covalent attachment while not unnecessarily consuming the high concentration of OH groups from the HBP. After this time, the solvent was removed using a rotary evaporator, DGEBA was added, and DDS was blended with DGEBA/HPB in the same manner as for the blended systems.

## Dual epoxy modified resin systems

The 10-wt% HBP DGEBA/DDS resin systems were systematically modified using flexible bi-functional BDDGE epoxy resins and highly crosslinkable tetrafunctional TGDDM epoxy resin. The blended only 10-wt% HBP resin was prepared in the same way as above, with the only difference being that the BDDGE or TGDDM was first blended with the DGEBA prior to addition of the HBP. Care was taken to ensure that a 1:1 epoxide:amino stoichiometric ratio was maintained. The formulations prepared and the preparation strategies explored in this work are described in Table 1.

All of the prepared resin systems were poured into pre-heated molds, cured in an oven at 177 °C for 5 h and then allowed to cool to room temperature overnight. Figure 3 shows selected samples of the 2.5, 7.5, and 10-wt% HBP-modified DGEBA/DDS blends, highlighting the transition from miscible (and transparent) to phase separated (and translucent) at higher concentrations of HBP.

## Dynamic mechanical thermal analysis (DMTA)

DMTA was performed using a Rheometrics Scientific IV dynamic mechanical thermal analyzer. Samples with dimensions of 50 × 10 × 2 mm were placed in a dual cantilever configuration and heated at a rate of 2 °C/min while

applying a strain of 0.05% and a frequency of 1 Hz. For subambient analysis, samples were heated from −100 to 50 °C, and for the above ambient analysis, samples were heated from 50 to 300 °C. The glass transition ( $T_g$ ) and  $\beta$  relaxation ( $T_\beta$ ) temperatures were determined from peaks in the  $\tan \delta$  spectra above and below ambient conditions, respectively. The crosslink densities ( $\nu_e$ ) of the networks 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.

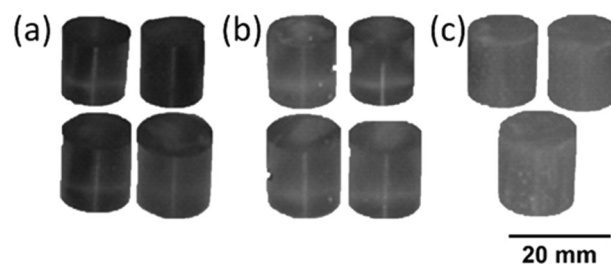
## Compressive properties

The compressive modulus, yield strain, and stress were determined using an Instron Universal Testing Machine 4468. Samples were placed between parallel plates and loaded in compression using a 50-kN load cell at a cross-head rate of 1 mm/min. The cylindrical samples had diameters and lengths of 12 mm.

## Results

### Dynamic mechanical analysis

Dynamic mechanical analysis of the cured HBP-modified DGEBA/DDS networks displays a consistent decrease in  $T_g$

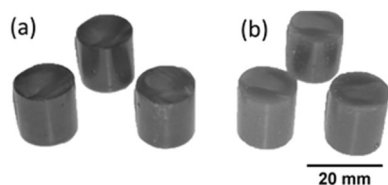
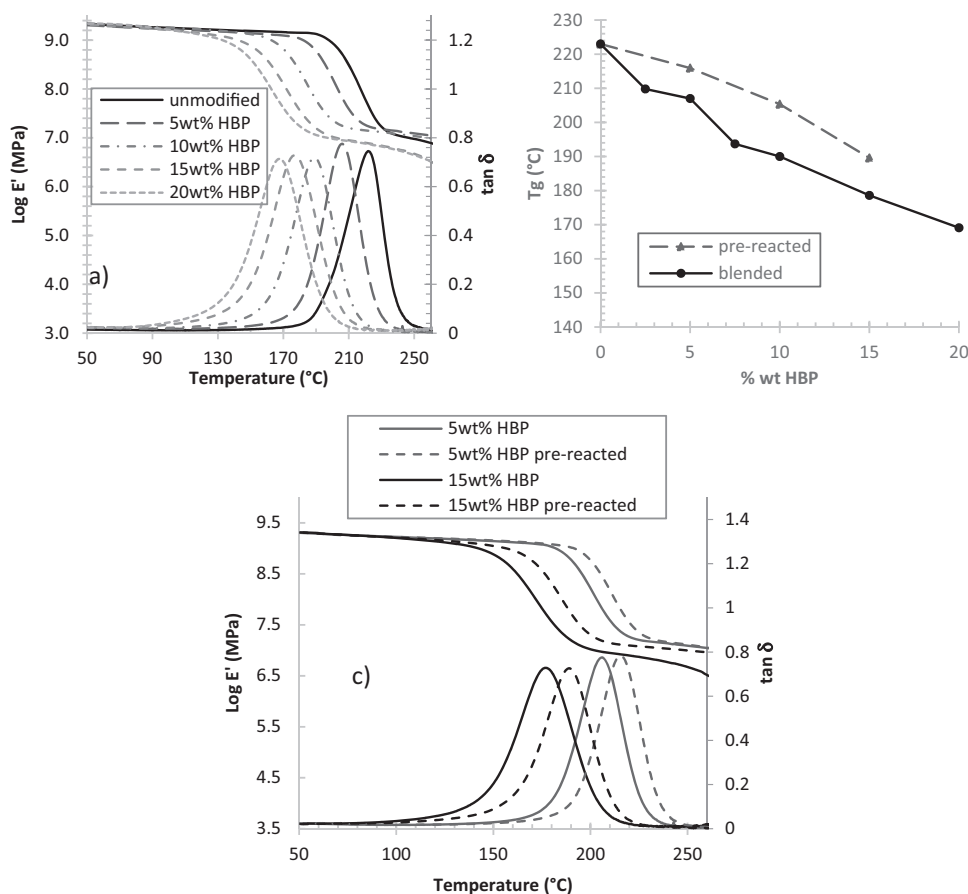


**Fig. 3** **a** 2.5 wt%, **b** 7.5 wt%, and **c** 10 wt% HBP-modified DGEBA/DDS blends

**Table 1** Description of the HBP-modified epoxy amine formulations prepared in this work

Epoxy #1 (mol%)	Epoxy #2 (mol %)	Preparation	%wt HBP					
			2.5	5.0	7.5	10.0	15.0	20.0
DGEBA (100)	–	Blended	2.5	5.0	7.5	10.0	15.0	20.0
DGEBA (100)	–	Pre-reacted (MDI)	–	5.0	–	10.0	15.0	–
DGEBA (90)	BDDGE (10)	Blended	–	–	–	10.0	–	–
DGEBA (80)	BDDGE (20)	Blended	–	–	–	10.0	–	–
DGEBA (70)	BDDGE (30)	Blended	–	–	–	10.0	–	–
DGEBA (70)	TGDDM (30)	Blended	–	–	–	10.0	–	–
DGEBA (50)	TGDDM (50)	Blended	–	–	–	10.0	–	–

**Fig. 4** **a** Storage moduli ( $E'$ ) and  $\tan \delta$  of the cured networks as a function of HBP concentration, **b** plot of the impact of blending and pre-reaction on  $T_g$ , including the calculated  $T_g$ , and **c** storage moduli ( $E'$ ) and  $\tan \delta$  of the 5 and 10-wt% HBP blended and pre-reacted networks



**Fig. 5** Examples of the cured 15 wt% HBP DGEBA/DDS samples after **a** pre-reaction and **b** blending only

with increasing HBP concentration, as measured by the peak in the  $\tan \delta$  and the exponential decrease in the storage modulus ( $E'$ ) shown in Fig. 4a. The unimodal nature of the  $\tan \delta$  peak suggests a homogeneous microstructure and is consistent with the HBP being miscible within the DGEBA/DDS network after curing. The large decrease in  $T_g$ , as shown in Fig. 4b, from 223 °C for the unmodified network to 169 °C for the 20-wt% HBP-modified epoxy network is consistent with plasticization due to high levels of miscibility but also from the steric hindrance of the HBP, which reduces the final  $T_g$  at higher concentrations.

The effect of isocyanate pre-reaction of the HBP on the  $T_g$  of the modified networks is also shown in Fig. 4b, which reveals higher  $T_g$ s than those of the simply blended samples, with values between ~9 and 15 °C depending

upon the concentration. The storage modulus and  $\tan \delta$  spectra are compared directly in Fig. 4c for the pre-reacted and blended networks at 5 and 15 wt% concentrations and clearly illustrate these consistently higher  $T_g$ s as well as higher rubbery moduli,  $E_r$ . Increased  $T_g$  and  $E_r$  likely arise because of the enhanced covalent bonding and increased rigidity of the rigid aromatic MDI structure. A qualitative assessment of the increased miscibility as a result of pre-reaction is shown in Fig. 5, which compares pre-reacted and blended only samples at 15 wt% HBP where the pre-reacted sample is less opaque than the corresponding blended only sample.

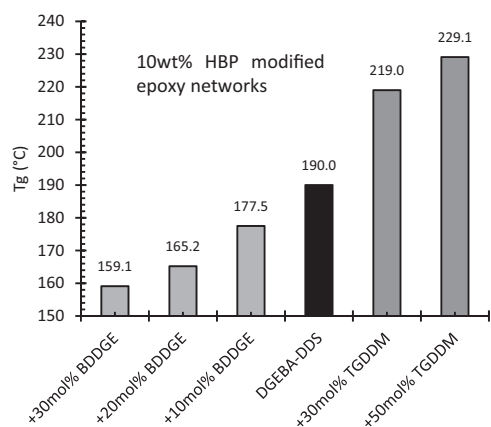
Despite the reductions in  $T_g$  shown in Table 2 (blended only) and Table 3 (pre-reacted), the glassy moduli ( $E_g$ ) at 60 °C were relatively unaffected by HBP addition. However, despite some scatter, the  $E_r$  and crosslink density  $\nu_e$  initially increase with increasing concentration up to 10 wt% HBP, after which they decrease, almost to the values of the unmodified network. This likely reflects the high level of HBP miscibility within the epoxy network at concentrations of up to 10-wt% HBP, but as phase separation becomes more important at higher HBP concentrations,  $E_r$  and  $\nu_e$  approach the values of the unmodified network. Finally, pre-reaction was also observed to increase  $E_r$  and  $\nu_e$ , providing support for

**Table 2** Dynamic mechanical analysis of the blended only HBP DGEBA/DDS networks

HBP (wt%)	$T_g$ (tan $\delta$ ) (°C)	$E_g$ (@60 °C) (GPa)	$E_r$ (@ $T_g + 30$ °C) (MPa)	$\nu_e$ (mol cm <sup>-3</sup> )	$T_\beta$ (°C)	FWHM (°C)	Peak area
0	222.1	2.06	9.23	704.8	-52.5	63.91	2.98
2.5	208.5	1.99	13.85	1085.5	-54.0	48.43	2.45
5	206.1	1.95	14.18	1116.7	-54.8	44.54	2.25
7.5	192.6	2.06	11.99	969.8	-55.0	44.36	2.21
10	188.9	2.12	14.34	1168.6	-54.9	43.90	1.95
15	176.5	2.00	9.28	775.2	n/a	n/a	n/a
20	167.4	2.17	9.97	849.0	-55.7	38.38	1.74

**Table 3** Dynamic mechanical analysis of the MDI pre-reacted HBP DGEBA/DDS networks

HBP (wt%)	$T_g$ (tan $\delta$ ) (°C)	$E_g$ (@60 °C) (GPa)	$E_r$ (@ $T_g + 30$ °C) (MPa)	$\nu_e$ (mol cm <sup>-3</sup> )	$T_\beta$ (°C)	FWHM (°C)	Peak area
0	222.1	2.06	9.23	704.8	-52.5	63.91	2.98
5	215.4	1.96	14.52	1134.1	-52.9	50.45	2.41
10	206.2	2.04 <sup>a</sup>	14.60	1140.6	-53.5	49.55	2.39
15	189.3	1.97	10.77	841.5	-54.4	46.56	2.21

<sup>a</sup>Measured at 80 °C**Fig. 6** Effect of a 2nd epoxy compound on the  $T_g$  of the cured 10-wt% blended only DGEBA/DDS network

the suggestion that pre-reaction increased miscibility between the HBP and the epoxy matrix.

To further explore the effect of HBP addition on the thermal properties of the DGEBA/DDS network, the tetrafunctional epoxy resin TGDDM was added at 30 mol% and 50 mol%, while the BDDGE epoxy resin was added at 10 mol%, 20 mol% and 30 mol%. As might be expected, Fig. 6 shows that the  $T_g$ s of the 10-wt% HBP epoxy networks increased consistently with TGDDM but decreased with BDDGE addition. Clearly, the changes in  $T_g$  are dominated by the increased crosslink density imparted by the TGDDM and the inherent flexibility of the BDDGE. These effects are also reflected in small increases and decreases in the glassy moduli at 60 °C ( $E_g$ ) shown in Table 4 for TGDDM and BDDGE addition, respectively. Table 4 shows that there is an initial increase in  $E_r$  and  $\nu_e$  with increasing BDDGE, followed by a somewhat unexpected decrease at higher concentrations given the lower

molecular weight of BDDGE. A similar decrease is also observed unexpectedly with increasing addition of the highly crosslinkable TGDDM. Both decreases in  $\nu_e$  can be attributed to the onset of network degradation, which dramatically reduces  $E_r$  at  $T_g + 30$  °C. The larger effect for the TGDDM-modified network likely reflects the greater degradation at higher temperatures due to the higher  $T_g$  of these networks than of the BDDGE networks.

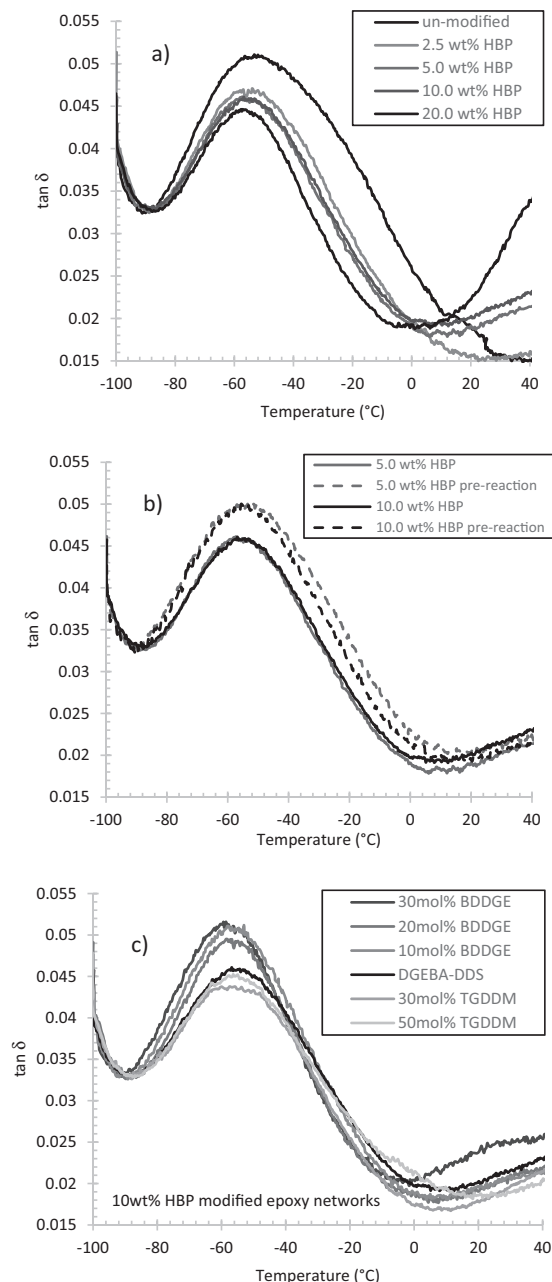
### Subambient $\beta$ relaxation

The subambient  $\beta$  relaxation reflects short-range molecular mobility, such as phenylene rotations of the epoxy (low temperature side of the peak) and amine (high temperature side of the peak) components of the network and motion of the aliphatic crosslinked unit and the hydroxyl propyl ether linkage (central region) [21, 23]. Figure 7a–c shows these  $\beta$  relaxations as a function of the tan  $\delta$  spectrum for the HBP blends, the pre-reacted blends, and the BDDGE- and TGDDM-modified blends, respectively. All of the relaxations appear as broad, low-intensity peaks across a temperature range from  $\sim -90$  °C to  $\sim 0$  °C. Importantly, at temperatures above 0 °C, tan  $\delta$ , particularly at higher HBP concentrations, trends upwards, likely from the onset of a peak reflecting increasing HBP phase separation from the DGEBA/DDS network, as discussed above.

Figure 7a illustrates the effect of increasing HBP concentration on the  $\beta$  relaxation peak, while Table 2 presents the calculated peak areas, the full width half maximum (FWHM), and the  $\beta$  relaxation peak temperature ( $T_\beta$ ). The overall size of the peak decreases (FWHM and area) with increasing concentration, while  $T_\beta$  decreases. The reduction in the peak area reflects the reduced short-range molecular motions of the epoxy network, while  $T_\beta$ , that is, the

**Table 4** Dynamic mechanical analysis of the 10-wt% HBP/DGEBA/DDS network with a 2nd epoxy compound

2nd Epoxy compound	$T_g$ (tan $\delta$ ) (°C)	$E_g$ (@60 °C) (GPa)	$E_r$ (@ $T_g + 30$ °C) (MPa)	$\nu_e$ (mol cm <sup>-3</sup> )	$T_\beta$ (°C)	FWHM (°C)	Peak area
+30 mol% BDDGE	158.2	1.98	11.33	984.8	-57.8	39.22	2.01
+20 mol% BDDGE	164.3	1.98	12.01	1030.2	-55.8	40.04	2.03
+10 mol% BDDGE	176.4	1.88	15.78	1318.9	-55.2	40.75	2.15
(100 mol% DGEBA)	188.9	2.12	14.34	1168.6	-54.9	43.90	1.95
+30 mol% TGDDM	218.3	2.17	8.10	622.4	-55.2	43.75	1.89
+50 mol% TGDDM	228.0	2.14	9.97	752.4	-54.9	40.53	1.90

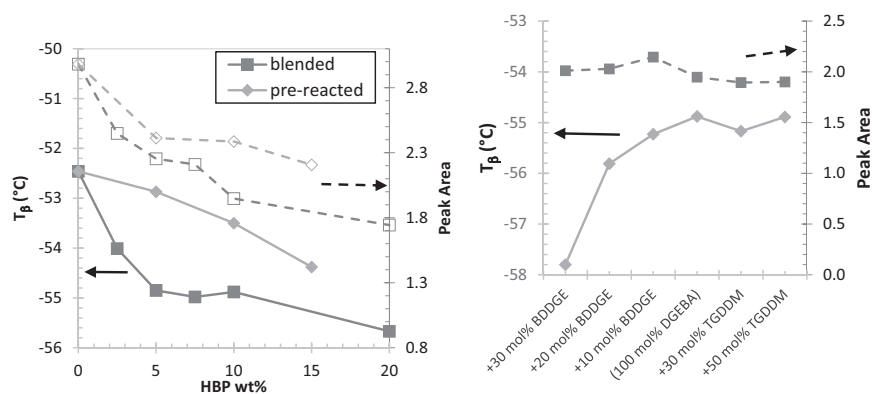
**Fig. 7** Dynamic mechanical analysis (tan  $\delta$ ) of the  $\beta$  relaxation of the a HBP blended only modified networks, b 5-wt% and 10-wt% pre-reacted networks and c 2nd epoxy compound to the 10-wt% HBP network

temperature where the network reaches a maximum mechanical activation, is also reduced or depressed. The changes in peak area and  $T_\beta$  are plotted as a function of HBP in Fig. 8a (see also Table 2) and emphasize that most of the decreases occur at concentrations of up to 10 wt%, where the HBP is still largely miscible in the network. As the HBP concentration increases and phase separation becomes more apparent, further reductions in  $T_\beta$ , peak area, and FWHM are far more modest.

Figure 7b illustrates the effect of MDI pre-reaction between the HBP and the epoxy network on the  $\beta$  relaxations, with Table 3 presenting the calculated  $T_\beta$ , peak area, and FWHM. A comparison between the 5 and 10 wt% pre-reacted and blended only HBP samples reveals increases in the FWHM and peak area for the pre-reacted samples, indicative of increases in short-range molecular mobility. It is proposed that the increased molecular mobility arises from an expected increase in free volume due to the rigid aromatic MDI linkage between the HBP and epoxy network. Despite this increase in mobility, similar reductions in the peak areas and  $T_\beta$ s with increasing HBP concentration compared to the blended only samples are also shown in Fig. 8a. Although modest, the reduced increase in tan  $\delta$ , considered to be evidence for phase separation, from  $\sim 0$  °C and above, shown in Fig. 7b also supports the hypothesis that covalently linking the HBP to the epoxy network enhances its miscibility.

The  $\beta$  relaxation for the 10-wt% HBP network modified with BDDGE and TGDDM is shown in Fig. 7c along with the analysis in Table 4. Figure 8b also plots the  $T_\beta$  and peak area as a function of additive, where the impact of BDDGE and TGDDM on molecular mobility and mechanical activation is more clearly compared. Compared to the 10-wt% HBP DGEBA/DDS network only, increasing the concentration of the flexible aliphatic BDDGE increases the peak areas very modestly but increases the peak height while reducing FWHM and decreasing  $T_\beta$ . The inherent flexibility of the BDDGE therefore appears to marginally increase mobility but over a narrow range at lower temperature. The effect of TGDDM addition is even less, displaying a small reduction in molecular mobility and similar mechanical activation temperatures. This is somewhat

**Fig. 8** Effect of  $T_{\beta}$  on the **a** blended and pre-reacted networks and **b** 2nd epoxy compound 10-wt% HBP networks

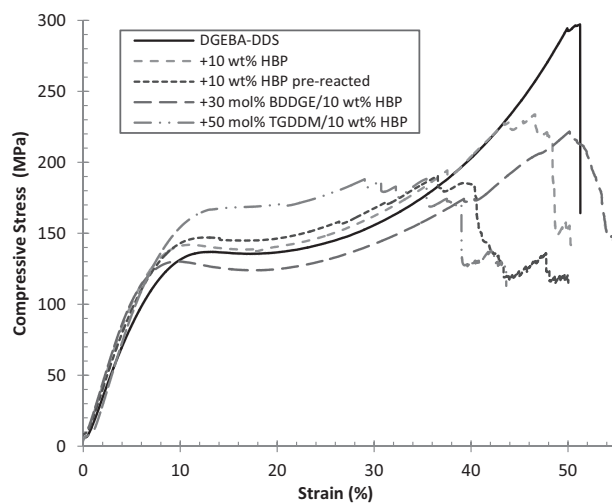


surprising given its rigid aromatic structure and capacity for increasing the crosslinking density.

### Compressive properties

The compressive stress versus strain plots for the unmodified and modified epoxy networks in Fig. 9 exhibit behavior typical of glassy epoxy amine networks, beginning with an elastic response followed by yield, strain hardening, and ultimately failure. Immediately apparent is the increase in modulus and yield stress as a result of HBP addition and a clear additional increase as a result of pre-reaction. The addition of the flexible BDDGE reduces the stress and yield strain while still increasing the modulus, while the addition of the highly crosslinkable TGDDM increased the modulus, stress, and yield strain.

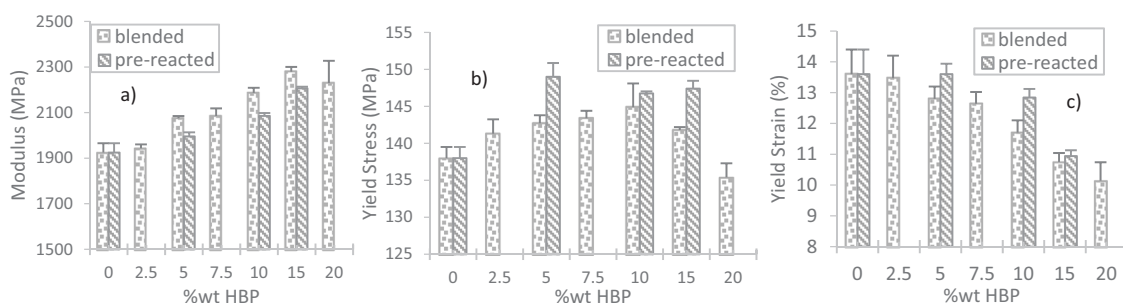
The overall compressive properties of the HBP blended and pre-reacted epoxy networks are shown in Fig. 10a–c for the modulus, yield stress, and yield strain, respectively. HBP addition increases the modulus (in Fig. 10a) regardless of the preparation method, but more so for the blended only samples than for the pre-reacted samples. Indeed, a maximum 18% increase in modulus is achieved for the 15-wt% HBP-modified samples, while an increase of 14% is achieved for the pre-reacted sample at the same concentration. Once the network is vitrified and completely cured, the modulus is dependent upon short-range molecular motions and free volume [7, 25, 26], so the increases observed here appear to correlate well with the reduced mobility observed from the measured  $\beta$  relaxations. Furthermore, the comparative decrease in modulus for the pre-reacted samples at the respective HBP concentrations can be attributed to the increased freedom of motion evident in the larger  $\beta$  relaxation peaks observed [4, 7, 21, 23]. Figure 10b similarly shows an increase in the yield stress with HBP addition, which increases up to 10 wt% and then decreases as the concentration increases. This result likely reflects the changing microstructure as phase separation becomes more evident. The HBP is a thermoplastic that would be expected to have a much lower stress than the DGEBA/DDS network, particularly for a



**Fig. 9** Representative compressive stress versus strain plots for the unmodified and modified polymer networks

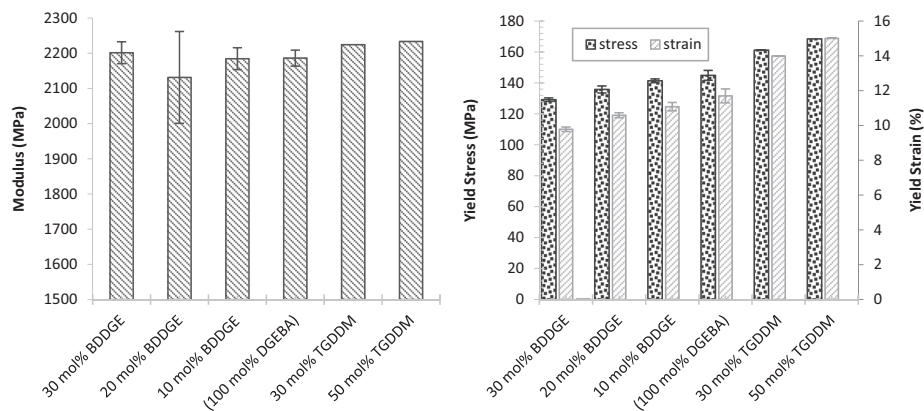
phase-separated microstructure. However, the pre-reacted systems at each concentration reveal a higher comparative yield stress due to the enhanced covalent interaction between the HBP and cured epoxy matrix. The yield strain in Fig. 10c decreases consistently with increasing HBP concentration, with no evidence of a difference between miscible and phase-separated systems. Again, this can be attributed to the reduction in short-range mobility and free volume increasing the yield point. Pre-reaction again reveals a higher comparative strain at each respective HBP concentration and can again be related to the higher free volume and enhanced mobility observed from the  $\beta$  relaxation traces.

The mechanical properties of the BDDGE- and TGDDM-modified epoxy networks are plotted against the addition of the second epoxy compound in Fig. 11. For these formulations, the 2nd epoxy compounds were entirely miscible in the DGEBA, and the changes in the  $\beta$  relaxations were more modest than those of the other systems. As a result, it is difficult to correlate mechanical properties with the observed  $\beta$  relaxations, particularly the peak areas and the FWHM. Despite this, Fig. 11a shows a relatively unchanging modulus



**Fig. 10** The **a** modulus, **b** yield stress, and **c** yield strain of the HBP-modified DGEBA/DDS networks comparing preparation methods

**Fig. 11 a** Modulus and **b** yield stress and strain of the 10-wt% HBP/DGEBA/DDS networks blended with a 2nd epoxy compound as a function of  $T_g$  (30 and 50 mol% TGDDM values from a single measurement)



regardless of epoxy modifier, while the corresponding  $\beta$  relaxations also show little change. The yield stress and strain plots in Fig. 11b reveal consistent changes with flexibility (BDDGE) and crosslink density (TGDDM), decreasing with increasing flexibility and increasing with increasing crosslink density. Although there is little relationship with the peak area or FWHM of the  $\beta$  relaxations, the changes do correlate well with the mechanical activation temperatures,  $T_{\beta}$ , in Fig. 8b.

## Conclusion

This study explored short-range molecular mobility within a glassy epoxy amine network using a HBP (HBP). Although the miscibility of the HBP within the DGEBA/DDS network decreased at higher HBP concentrations, useful insights were gained concerning the role of  $\beta$  relaxations in controlling the mechanical properties of the material. Increasing the HBP concentration decreased the short-range glassy mobility, as evidenced by a reduction in the peak size of the  $\beta$  relaxation transition, which correlated closely with an increase in the modulus and a decrease in the yield strain. Pre-reaction with MDI increased the size and area of the  $\beta$  relaxations, which also correlated with the observed further increase in modulus and the comparatively higher yield strain. This was attributed to the covalent aromatic MDI linkage between the HBP and epoxy network enabling

greater molecular mobility and likely increasing the free volume. The addition of the flexible BDDGE and the highly crosslinkable TGDDM had a modest impact on the  $\beta$  relaxations, although the yield stress and strain were strongly correlated with increased flexibility and crosslink density.

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## Compliance with ethical standards

**Conflict of interest** The authors declares that they have no conflict of interest.

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