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RESEARCH ARTICLE

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Improving mechanical properties and processability of a very high T_g epoxy amine network via anti-plasticizer fortification

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Abstract

In this work, molecular fortifiers are added to a highly aromatic and rigid epoxy monomer bis(2,7 diglycidyl ether naphthalenediol) methane (NNE) possessing a very high glass transition temperature (T_{o}) when cured with 4,4'diaminodiphenyl sulfone (DDS) to explore their impact upon mechanical and thermal properties and reactivity. The molecular fortifiers used are the nonfunctional naphthalene (NAPH), the reactive diluent o-cresyl glycidyl ether (CGE) and an adduct of dihydroxy naphthalene and CGE (molecular fortifier naphthalene, MFN), a variant on the partially reacted substructures approach. The fortifiers are found to affect NNE/DDS reactivity and increase processability depending upon their propensity to attach to the network either through hydrogen bonding or pi-pi electron interactions. Thermal analysis shows that the fortifiers increased cure conversion although the T_{es} of the networks were generally unaffected until higher levels of addition. The fortifiers reduce moisture ingress and suppress glassy state β relaxations while increasing modulus significantly. Although there is little improvement in toughness overall, some evidence for higher fracture toughness is observed for the MFN and NAPH modified networks. This work highlights the effectiveness of different molecular level fortifiers on improving properties, in particular the rigidity of highly crosslinked networks.

KEYWORDS

mechanical properties, resins, structure-property relationships, viscosity and viscoelasticity

1 | INTRODUCTION

Highly crosslinked epoxy amine networks are well known for their excellent thermal and mechanical properties such as their high glass transition temperature, rigidity and strength. However, they are also characterized by a lack of ductility, and indeed a lack of toughenability due to the restricted molecular mobility and inhibition of toughening mechanisms such as shear banding and plastic deformation.^{1,2} The use of additives such as

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rubbers, thermoplastics, block co-polymers or inorganic and carbonaceous micro- and nano-scale particles to name some of the most common, have all been used extensively to improve fracture toughness with varying degrees of success.³⁻¹⁰ However, a common theme of this nonreactive additive approach is that they all have some deleterious effect upon mechanical performance^{11,12} and thermal properties.⁷ Furthermore, the resultant micro- or nano- scale morphology often creates processing challenges due to increased viscosity or particle filtration during composite fabrication.^{8,13} For these reasons, improving properties through control of the network structure, rather than by creating a micro- or nano- phase separated structure is of significant interest. Many studies have explored structure property relationships in epoxy amine networks,^{14–20} although the comprehensive assessment of the role of the crosslink density and chain flexibility by Halary²¹ is particularly noteworthy. These studies highlight that processability and final network properties can often be conveniently controlled via the addition of miscible bi- or higher functionality epoxy resin or amine hardener with a flexible or rigid backbone.

However, less conventional approaches have sought to avoid the inevitable trade off in properties by using mono-functional reactive diluents, partially reacted substructures, and molecular level modification or reinforcement of the epoxy amine networks. Espuche et al. added a cycloaliphatic mono-functional amine to a common epoxy amine resin and found that despite a reduction in glass transition temperature and a modest reduction in vield strength after cure, the modulus and fracture toughness both increased significantly. This was attributed to the enhanced chain flexibility initiating plastic deformation, rather than any reduction in crosslink density.²² A related study by Jing et al. explored the effect of a series of long chain aliphatic mono-amines on the mechanical properties of an epoxy amine network and reported an improvement in the tensile strain to failure, despite a reduction in tensile modulus and strength. The improvement in elongation to failure was attributed to the increased flexibility of the alkyl chains.²³ When using mono-functional epoxy resins, Marks et al. reported an improvement in the impact strength and fracture toughness using only 2.5% of phenyl glycidyl ether (PGE) added to an epoxy amine network where greater plastic deformation was observed during fracture.²⁴ Aside from improvements in fracture toughness, Reyes et al. have reported that mono-functional epoxy diluents significantly increase modulus, which was attributed to antiplasticization effects and the restriction of glassy state mobility.²²

The use of partially reacted substructures (PRS) is an emerging strategy seeking to develop a network topology

able to strain harden under tension while not significantly impacting T_{g} . This is supported by molecular dynamics simulations, which predicted that increased ductility arises from a combination of void formation under strain and lower crosslink density of the polymer network.^{25,26} The premise is that localized concentrations of noncovalently bound molecular surfaces will induce favorable void growth under strain and hence improved ductility. Sharif and Palmese showed that by pre-reacting a mono-amine and a tetra-functional epoxy resin to 60% and 80% conversion prior to addition to the uncured epoxy resin network,²⁷ a higher elongation to break was achieved despite a significant reduction in T_g . Gao et al. demonstrated that the degree of polymerization directly affected the ability of this strain-hardening behavior by comparing unreacted and 75% converted PRS structures to a difunctional and tetrafunctional epoxy-amine system.²⁸ More recently, Eaton et al. utilized a cycloaliphatic diamine and a low molecular weight mono-amine, to exhibit nano-scale domains that greatly enhanced the toughness of epoxies.²⁹

The use of nonreactive or noncovalently bound fortifiers which reinforce the network at a molecular scale is another approach to improve mechanical properties of a highly crosslinked network. Daly et al. used an antiplasticizer formed by the reaction between phenyl glycidyl ether and 2-(acetylamino)phenol to show that modulus and strength could be improved by suppressing the subambient β -transition within an epoxy network.³⁰ Notably, it was observed that under tension, the network exhibited increased ductility as well as higher overall strength. Additional work on these fortifiers by Garton et al. related the consumption of free volume by the additives to the higher strain at failure and tensile strength compared to the unmodified epoxy resin.³¹ Further work by Heux et al. studied the suppression of the β -transition and associated enhancement of modulus, noting that lower crosslink density corresponded to hindered segmental motions across multiple units, in contrast to the ring-flip of the monomer backbones.³² Sauvant and Halary studied three antiplasticizers that varied by molecular weight and flexibility, all of which successfully enhanced modulus, displayed suppressed β-transitions and reduced equilibrium moisture uptake.33

This study seeks to apply some of these concepts to a highly crosslinked epoxy amine network based upon bis (2,7 glycidyl ether naphthalenediol) methane (NNE) and diamino diphenyl sulphone (DDS). NNE is of particular interest for applications ranging from micro-electronics to aerospace composites due to its very high glass transition temperature (T_g). First synthesized by Ogura and Takahashi, the homopolymerised network exhibits a T_g above 325° C,³⁴ which is significantly higher than

commercially available high performance epoxy networks based upon tetraglycidyl diaminodiphenyl methane (TGDDM) and triglycidyl-p-amino phenol (TGAP). A disadvantage however, is the higher melt temperature, low strength and toughness,²⁰ and high viscosity of the epoxy when cured with an aromatic diamine,³⁵ which is often undesirable for composite manufacture.^{36–38} Recent studies from these authors have studied the evolution of cure, thermal performance, and mechanical properties of an amine-cured NNE network and compared it to aminecured TGDDM. The findings illustrated a faster gelation and vitrification, a higher T_{g} , improved thermal stability above 200°C but generally higher moisture ingress and lower mechanical properties, attributed in part, to the higher free volume of the network after cure.²⁰ Furthermore, the very high T_{g} and crosslink density renders the network extremely difficult to toughen via traditional approaches providing further impetus to explore alternative toughening strategies.^{39,40}

Fortification strategies like those mentioned above are investigated in this work, to explore their impact upon structure property processing relationships such as reaction rate, processability, moisture ingress, thermal and mechanical properties with an emphasis on antiplasticizing effects and fracture toughness. The first approach was to covalently incorporate the monofunctional epoxy resin o-cresyl glycidyl ether (CGE) into the network. The second was to use a modified PRS strategy consisting of a pre-reacted naphthalene oligomer end-capped with CGE (MFN) attached to the network via noncovalent hydrogen bonding. The third was to use naphthalene (NAPH) as a nonreactive and miscible molecular level reinforcement to the network. The concept here is that each of these modifiers regardless of how they may be attached to the network, would likely reside within the free volume of the network, acting as anti-plasticizers to suppress molecular mobility and enhance molecular level reinforcement. The differences between them relate to how they are attached to the network, either covalent, noncovalent hydrogen bonding or finally via pi-pi electronic interactions.

2 | MATERIALS AND EXPERIMENTAL METHODS

2.1 | Materials

The tetra functional epoxy resin used was bis(2,7 glycidyl ether naphthalenediol) methane (Epiclon 9470, NNE, EEW = 170 g/eq.) kindly provided by DIC Corp., Japan and the amine hardener used was 4,4' diaminodiphenyl sulfone (DDS, AEW = 248.30 g/eq.) obtained from TCI

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Chemicals, Inc., Japan. The mono-functional epoxy resin was *o*-cresyl glycidyl ether (CGE, EEW = 164.2 g/eq.) obtained from Hexion Corp., USA, analytical grade naphthalene (NAPH, MW = 128.17 g/mol, 99% purity) was purchased from Sigma-Aldrich, USA, and 2,7-dihydroxy naphthalene (27DHN, MW = 160.17 g/mol) was purchased from Acros Organics, USA. The triethylamine (MW = 101.19 g/mol, TEA) catalyst was purchased from Sigma-Aldrich, USA. Analytical grade dichloromethane (DCM), ethanol, and methyl ethyl ketone (MEK) were used without further purification. The structure of the NNE epoxy monomer, DDS amine hardener, monofunctional epoxy CGE, and NAPH are shown in Figure 1.

2.2 | Preparation of end-capped molecular fortifier naphthalene

The end-capped molecular fortifier naphthalene (MFN) fortifier was synthesized by reacting CGE with 27DHN using a 2:1 molar ratio in a round bottom flask after dissolving together in 100 ml of ethanol. After the addition of 1 wt% of TEA the solution was mechanical mixed at 80°C for 24 h. The tertiary amine was used to promote ring-opening of the unreacted epoxide with the available hydroxyls from the naphthalenediol. The ethanol was then removed under vacuum using a rotary evaporator at 120°C for 1 h then further heated at 150°C for 36 h in a convection oven. The synthesis and idealized chemical structure of the resulting molecular fortifier, MFN, is shown along with the midinfrared spectra in Figure 2a,b. Analysis of the mid-IR spectra demonstrated the epoxy-hydroxyl interactions of the MFN product. Present in the spectra of the o-cresyl glycidyl ether was a peak at 915 cm⁻¹ associated with unreacted epoxide groups that disappears from the MFN spectra.⁴¹ A shift in the hydroxyl peak at $3300-3600 \text{ cm}^{-1}$ and the formation of a shoulder at 3550 cm⁻¹ have been associated with intramolecular bonds as a result of ether bonds formed between the naphthalenediol and epoxide groups of the o-cresyl glycidyl ether.⁴²

2.3 | Sample preparation

The NNE was first melted and de-gassed under vacuum until no bubbles were visible using a rotary-evaporator at 120°C. The respective modifiers, referred to as fortifiers, MFN, NAPH and CGE were added and mixed for 30 min until completely dissolved. The DDS was then mixed under vacuum at 120°C until again fully dissolved and free of bubbles. Once prepared, the resins were quickly removed from the rotary-evaporator and poured into the pre-heated silicon molds, then cured in an oven at 150°C

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Wavenumber (cm⁻¹)

FIGURE 2 (a) Reaction sequence of the synthesis of the molecular fortifier naphthalene (MFN) fortifier from 2,7'- dihydroxynaphthalene and o-cresyl glycidyl ether in the presence of TEA and (b) mid-IR spectra of the MFN compound [Color figure can be viewed at wileyonlinelibrary.com]

for 4 h, 180°C for 4 h and finally 220°C for a further 2 h. For all formulations, the total epoxide to active amine hydrogen ratio used was 1:0.9. For the CGE containing formulations, CGE was added at 5, 10 15 and 20 mol% of the total epoxide moles, while the NAPH and MFN modifiers were added at 5, 10, 15 and 20 wt% of the total resin. Table 1 more clearly describes the composition of the resin systems prepared in this work.

2.4 | Experimental methods

I S I O

(d)

A Netzsch Polyma 214 DSC was used in dynamic and isothermal mode to understand rate of cure, the final glass transition temperature and determine the reaction kinetics using the Flynn Wall Ozawa (FWO) and autocatalytic kinetic models. Uncured samples of approximately 10 mg were placed in an aluminum crucible and heated from 50 to 300°C at heating rates of 2.5, 5, 10, 15, and $20^{\circ}C/$ min to determine the peak temperature (T_p) required for the FWO model. Uncured resin was similarly prepared and isothermally cured at 150°C for 8 h after which a dynamic rescan from 50 to 300°C was performed to determine the glass transition temperature (T_g) of the network and fractional cure conversion (α). The Flynn–Wall– Ozawa method⁴³ for dynamic DSC was utilized to determine activation energies (E_a) and autocatalytic kinetic modeling was performed as described elsewhere.⁴⁴

Oscillatory shear rheology measurements were performed on an Anton Parr MCR92 equipped with 40 mm diameter parallel plates. The solid resin samples were heated to 90°C and the top plate was quickly put into the measurement position of a 0.5 mm gap spacing. Then the apparatus and sample were quenched to room temperature. For dynamic rheology, samples were then heated at a constant 2°C/min heating rate from 25 to 200°C under a 10 Hz oscillating frequency and 1% strain rate. The gelation temperatures were taken as the intersection of storage modulus (*G*') and loss modulus (*G*") traces. A "processing window" was determined from dynamic scans and represented the width of the storage modulus (*G*') curve defined arbitrarily as the temperature range over which storage modulus was below to 0.1 MPa.

A Bruker Alpha FTIR was used in transmission mode to obtain near infrared spectra (NIR) in the range from 4200 to 7500 cm⁻¹ at a resolution of 2 cm⁻¹. Cured resin bars of 2.75 mm nominal thickness were placed in the

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Epoxy/amine	Fortifier	Stoichiometry	Concentration			
NNE/DDS	-	1:0.9	-	-	-	-
NNE/DDS	CGE	1:0.9	5 mol%	10 mol%	15 mol%	20 mol%
NNE/DDS	MFN	1:0.9	5 wt%	10 wt%	15 wt%	20 wt%
NNE/DDS	NAPH	1:0.9	5 wt%	10 wt%	15 wt%	20 wt%

TABLE 1 Composition of modified resins prepared for the CGE, MFN and NAPH fortifiers

Abbreviations: CGE, cresyl glycidyl ether; MFN, molecular fortifier naphthalene.



FIGURE 3 (a) Dynamic thermograms of the uncured resins for the unmodified NNE and the 10 (wt% or mol%) modified NNE resins, and (b) isothermal thermograms during cure at 150°C of the same resins followed by a dynamic rescan (inset) [Color figure can be viewed at wileyonlinelibrary.com]

beam. A total of 64 scans were used to generate the absorbance spectra of the specimens.

Dynamic thermal mechanical (DMTA) analysis was performed using a TA Instruments DMA Q800 to determine the glass transition temperature (T_g) and glassy state β relaxations (T_β). For each measurement, samples of approximately, 60 mm x 10 mm x 3 mm were placed in a dual cantilever beam fixture and heated from either -130 to 100°C at 3°C/min, or from 50 to 380°C at 5°C/ min. During heating, a frequency of 1 Hz was continuously applied while under a constant displacement of 10 µm. The glass transition temperature was determined from the peak in the tan δ spectra. The β relaxation transition was also characterized by its peak in the tan δ spectra while the area of the peak was also determined.

Mechanical properties of the resins were studied for their flexural properties and single-edge notch fracture toughness (SENB). Flexural properties were determined in accordance with ASTM D790 standard test methodology on rectangular coupons of nominal 2.75 x 60 x 13 mm dimensions. The SENB samples had dimensions of about 13 x 6 x 55 mm with a pre-wedge crack area of width to crack length ratio of 0.5 following ASTM D5045 standard test methodology. A fresh hardened steel razor blade was used each time to promote a single pre-crack tip in the sample before testing. An electromechanical load frame (Instron Corp., USA) using a load cell of 10 kN and a crosshead speed of 1 mm/min was used for the flexural properties and 10 mm/min for SENB evaluation. The span used for flexural testing was 48 mm and for SENB the span was 42 mm.

Moisture ingress was studied by immersing the cured resins in a sealed vial containing deionized water in a water bath at 80°C. Periodic measurements were made every 24 h for 14 days and the moisture ingress was averaged over the weight gain of three specimens.

3 | RESULTS AND DISCUSSION

3.1 | DSC thermal analysis and reaction kinetics

Representative dynamic and isothermal thermograms illustrating the effect of 10 (wt% or mol%) of each fortifier on the cure reaction are shown in Figure 3a,b, respectively. A summary of the thermal analysis results for all formulations including autocatalytic kinetic modeling is also provided in Table 2. Typical exothermic behavior

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TABLE 2 Peak exotherm temperature (T_p) , activation energies (E_a) , fractional conversion (α) , glass transition temperature (T_g) , and kinetic rate constants $(k_1 \text{ and } k_2)$ obtained from dynamic and isothermal DSC analysis

	Dynamic		150°C isothermal + dynamic rescan			
% Fortifier	<i>T</i> _p (10°C/min) (°C)	E _a (kJ/mol)	α	<i>T</i> _g (°C)	$k_1 (10^{-4}) \mathrm{s}^{-1}$	$k_2 \ (10^{-4)} \ \mathrm{s}^{-1}$
NNE						
0	203.9	65.8	0.79	195.9	3.62	15.69
CGE						
5 mol	205.4	65.8	0.84	199.1	4.57	20.03
10 mol	208.5	67.5	0.83	198.1	3.53	17.28
15 mol	210.4	67.7	0.86	195.1	3.79	14.14
20 mol	212.0	67.5	0.89	194.7	4.05	13.27
NAPH						
5 wt	208.7	68.4	0.84	194.9	3.72	18.98
10 wt	210.6	66.7	0.87	192.2	3.02	16.84
15 wt	211.7	66.1	0.83	192.1	3.93	11.84
20 wt	216.3	66.9	0.85	189.5	2.86	13.50
MFN						
5 wt	204.9	66.6	0.80	197.2	4.55	21.35
10 wt	208.6	66.5	0.83	198.2	4.49	18.78
15 wt	206.2	67.4	0.84	196.1	4.86	16.97
20 wt	206.7	65.4	0.86	196.0	5.04	16.17

Abbreviations: CGE, cresyl glycidyl ether; MFN, molecular fortifier naphthalene.

during cure is observed from both the dynamic and isothermal thermograms with each fortifier having a modest but systematic impact upon the cure reaction and glass transition temperature (T_{g} ; Figure 3b inset). The T_{p} measurements and the activation energies, $E_{\rm a}$, suggest that the fortifiers have a modest retardation effect in order of NAPH > CGE > MFN, despite the cure conversion (α) increasing with fortifier addition. The T_{gs} display a modest initial increase, followed by a decrease with increasing fortifier addition. Modeling of the autocatalytic kinetic rate constants k_1 and k_2 , with increasing fortifier concentration reveal competing influences, such as an initial acceleration from the increased hydrogen bonding available to a subsequent reduction in rate from the dilution of the reactive species. Increasing CGE and MFN concentration in particular, both exhibit an increase in k_1 , while NAPH appears to be relatively unaffected. This could be expected since k_1 measures the impact of proton donors present initially on the cure reaction, and the additional hydroxyl groups available from the CGE and MFN likely catalyze reaction via the stabilization of the intermediate terpolymer complex via hydrogen bonding.45,46 Conversely, the lack of available proton donors and functional groups from the NAPH, equally supports the observation of no discernible impact caused by the NAPH. The k_2 , a reflection of proton donors formed

during cure, similarly increases initially for all systems, albeit more so for CGE and MFN, but then all systems display a decrease in k_2 with increasing fortifier concentration. The initial increase again likely reflects the role of proton donors within the fortifiers but as their concentration increases, the dilution or steric hindrances arising during the later stages of cure, likely contributes to a reduction in the reaction rate. In seeking to compare the impact of different modifiers on the reaction kinetics, despite the modest changes, the NAPH modifier, with no available proton donors has the largest dilution effect compared to MFN and CGE, exhibiting the largest increase in T_p and decreases in k_1 and k_2 . Similarly, the MFN with the greatest propensity for hydrogen bonding due to its higher concentration of hydroxyl groups displays the smallest increase in $T_{\rm p}$, the largest initial increase in k_1 and the least deceleration in k_2 with increased MFN concentration.

3.2 | Rheology

The high melting point of NNE creates additional challenges during processing, so the low viscosity of the fortifiers used here, provide an opportunity to improve processability. Representative dynamic rheological

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FIGURE 4 Evolution of the (a) complex viscosities and the (b) storage (dash) and loss (solid) modulus during cure for the NNE/DDS and the 10 (wt% or mol%) modified NNE/DDS resins [Color figure can be viewed at wileyonlinelibrary.com]

% Additive	Min. Viscosity (Pa s)	Viscosity at $T = 100^{\circ}$ C (Pa s)	Gel. temp. (°C)	G' at T _{gel} log (Pa)	$G' = 0.1 \text{ MPa}$ range (Δ° C)
NNE					
0	28.6	1880.0	175.25	5.82	78.0
CGE					
5 mol	12.87	382.5	176.4	5.58	79.3
10 mol	1.39	20.5	182.3	5.05	113.5
15 mol	0.73	6.9	184.9	4.79	126
20 mol	0.51	3.7	184.9	4.61	132.9
NAPH					
5 wt	3.28	104.2	182.5	5.28	101.3
10 wt	1.09	20.3	185.8	4.94	116.3
15 wt	1.04	6.0	191.0	4.49	131.6
20 wt	0.38	3.0	188.4	4.51	136.5
MFN					
5 wt	25.46	944.4	173.7	5.63	80.4
10 wt	52.18	2380.0	171.2	5.43	73.6
15 wt	13.71	581.3	175.3	5.03	87.8
20 wt	24.40	836.8	172.0	5.02	83.2

TABLE 3 Rheological analysis of the unmodified and modified NNE/DDS resins

Abbreviations: CGE, cresyl glycidyl ether; MFN, molecular fortifier naphthalene.

measurements of the uncured resins during cure illustrating the complex viscosity and loss and storage shear moduli (G' and G'') are in Figure 4a,b, respectively. Rheological analysis including the minimum viscosities and viscosities at 100°C, gelation temperature and a proposed processing window across all concentrations is shown in Table 3. Figure 4a clearly highlights the significant reduction in viscosity across a wider temperature range caused by the addition of CGE and NAPH. Indeed, the minimum viscosities and the viscosities at 100°C shown in Table 3 suggest that these modified resins would be far more readily processable than the unmodified NNE/DDS resin. The lack of any significant improvement in processability by the MFN is likely a result of its oligomeric nature and thus higher viscosity compared to the monomeric CGE and NAPH fortifiers. The

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FIGURE 5 Near infrared spectra of the unmodified and 10% modified NNE/DDS networks [Color figure can be viewed at wileyonlinelibrary.com]

temperature at gelation also increases somewhat for the CGE and NAPH samples highlighting their greater diluting effect, particularly for the nonfunctional NAPH as discussed above. The MFN conversely, displays a modest acceleration, due to the increased concentration of hydroxyl groups and hence available hydrogen bonding, also supporting the DSC results presented above. Further to this, the CGE and NAPH display similar levels of reduction in storage modulus (G') at gelation down from 5.82 MPa for the unmodified network, to 4.61 to 4.51 MPa, respectively. The MFN however, only reduced to 5.02 MPa, which again can be attributed to its higher molecular weight and greater propensity for hydrogen bonding to the covalent network. A processing window, between the melt and gelation, was defined by a temperature range where the G' remained below an arbitrary value of 0.1 MPa. As can be seen from Figure 4a and Table 3, this processing window expands greatly with increasing CGE and NAPH concentration. In contrast, the MFN fortifier displayed no improvement in processability, in fact appeared to be slightly less processable. The significant reduction in viscosity for the CGE and NAPH fortifiers clearly their advantageous impact upon processability, with only minor deleterious impacts upon rate of reaction.

3.3 | NIR spectroscopy of networks

Near-infrared spectroscopy of the cured networks was used to understand any changes in the network structure as a result of fortifier addition. Spectra of the unmodified and 10% modified networks shown in Figure 5 are typical of a highly crosslinked epoxy amine network illustrating a

residual epoxide peak at 4521 cm^{-1} , a large hydroxyl peak at about 7000 cm^{-1} and a significant secondary amine peak at about 6600 cm^{-1} . The strong secondary amine peak after cure relates directly to the topologically constrained environment of the reactive functional groups within the highly crosslinked networks. The first clear difference between the unmodified and modified networks is the intensity of the epoxide peak. Although only qualitative, a reduction in intensity of the epoxide peak at 4521 cm⁻¹ for NAPH, CGE and MFN compared to the unmodified NNE/DDS suggests that the modifiers increase the epoxide conversion, providing support to the isothermal DSC measurements. The lack of any obvious or significant differences between the secondary amine and hydroxyl peaks (\sim 6600–6800 cm⁻¹ and \sim 6800–7200 cm⁻¹. respectively) further suggests that this increased epoxide conversion occurs via homopolymerization of the epoxy resins rather than epoxy amine addition. A clear difference however is the peak at $5220-5240 \text{ cm}^{-1}$, which directly relates to the stretching and bending combination of hydroxyl groups⁴⁷ commonly associated with hydrogen bonding.⁴⁸⁻⁵⁰ Both CGE and MFN display strong peaks, larger than the unmodified network, while NAPH displays a complete absence. This is entirely expected given the lack of any available proton donors in NAPH, but equally provides strong evidence again for the role of hydrogen bonding and/or available proton donors in enhancing cure reaction for CGE and MFN and any role it may play in network properties to be discussed later.

3.4 | Dynamic mechanical thermal analysis

3.4.1 | Glass transition temperature

The storage modulus and tan δ spectra of the 10% modified and unmodified NNE networks after cure are presented in Figure 6a. As presented previously,^{20,35} the unmodified NNE network after post-cure exhibits two peaks, the $T_{\rm g}$ and $T_{\rm g\infty}$, attributed to the partially reacted and fully reacted network structure respectively. This twophase structure arises from the topological constraints imposed by the combination of the rigid backbone and the highly crosslinked network structure. Indeed, despite being post-cured at 220°C, NIR spectroscopy confirmed here and elsewhere³⁵ that unreacted epoxide functional groups remained after post-cure creating the lower temperature T_{g} . Despite different degrees of noncovalent and covalent interactions, the introduction of the modifiers do not ease the topological constraints to create a more homogenous network. Dynamic mechanical analysis suggests that the modifiers maintain the two phase network

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FIGURE 6 (a) Storage modulus and $\tan(\delta)$ spectra of the unmodified and 10% modified NNE/DDS networks and (b) the overall effect of fortifier concentration on T_g and $T_{g\infty}$ [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 7 Sub-ambient dynamic mechanical spectra showing the storage modulus (E') and tan(δ) as a function of temperature for the unmodified and 10% modified NNE/DDS networks (annotations refer to peak areas) [Color figure can be viewed at wileyonlinelibrary.com]

structure, indeed they accentuate the two phase behavior, particularly so for NAPH at higher concentration. Figure 6b highlights the reduction in $T_{g\infty}$ as a function of fortifier concentration, but also that the T_{gs} remain comparatively stable, apart from a marked decrease in T_{g} for the NAPH at higher 20 wt% reflecting a higher level hindrance of the cure reaction.

3.4.2 | Sub-ambient β relaxations

Sub-ambient dynamic mechanical analysis of the unmodified and 10% modified NNE networks are shown in Figure 7 which reveal broad diffuse tan δ peaks described as β transitions elsewhere and attributed to short range molecular motions such as aromatic ring flips and crankshaft rotation of hydroxy ether segments.^{48–50} Addition of the fortifiers shifts the peak temperature in the tan δ spectra lower from about -25°C to approximately -50° C, while diminishing the peak intensity while the peak areas are annotated on Figure 7. This represents a suppression of short-range molecular mobility, or restriction of the β transition, resulting in an antiplasticization effect which has been studied extensively by sub-ambient DMTA.^{32,33,51,52} This effect also increased the storage moduli (E') for the modified networks, which are significantly higher than the unmodified NNE/DDS network across the entire temperature of measurement as shown in Figure 7.

The tan δ peaks observed from between 75 and 100°C for the modified samples are also interesting to contrast against the unmodified NNE network which does not exhibit any peak in this region. This transition, referred to as the T_{Ω} , has been associated with larger segmental motions and hydrogen bonding^{53,54} in the glassy state. It is proposed in this work therefore that the T_{Ω} transition associated with the MFN and CGE modified networks is due to the hydrogen bonding associated with increased hydroxyl groups present from these modifiers. It is proposed that the much larger T_{Ω} transition arising from the NAPH modified network is more likely due to its 80°C melting point, rather than hydrogen bonding. The complete lack of a T_{Ω} in the unmodified NNE/DDS network strengthens the suggestion that these peaks are directly related to the modifiers.



FIGURE 8 (a) Moisture ingress of the unmodified and 10% fortifier modified NNE/DDS networks and (b) and the overall effect of the equilibrium moisture uptake at 5%–20% fortifier concentrations [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 9 (a) Flexural modulus, (b) the average notched SENB fracture toughness values for the unmodified and modified NNE/DDS networks, and (c) representative stress-strain curves at 10% modifier addition [Color figure can be viewed at wileyonlinelibrary.com]

% Fortifier	Strain to failure (mm/mm)	Flexural strength (MPa)
NNE		
0	0.0241 ± 0.0036	68.5 ± 11.3
CGE		
5 mol	0.0194 ± 0.0033	57.1 ± 9.1
10 mol	0.0149 ± 0.0028	49.3 ± 10.9
15 mol	0.0212 ± 0.0035	70.4 ± 14.1
20 mol	0.0218 ± 0.0033	71.4 ± 13.8
NAPH		
5 wt	0.0170 ± 0.0006	52.9 ± 1.8
10 wt	0.0145 ± 0.0051	53.4 ± 9.0
15 wt	0.0212 ± 0.0029	67.2 ± 6.3
20 wt	0.0199 ± 0.0042	67.4 ± 5.6
MFN		
5 wt	0.0204 ± 0.0034	56.3 ± 10.7
10 wt	0.0186 ± 0.0020	57.3 ± 6.0
15 wt	0.0184 ± 0.0036	58.1 ± 10.5
20 wt	0.0200 ± 0.0028	66.8 ± 10.9

TABLE 4 Flexural strain to failure and flexural strength for the unmodified and modified NNE/DDS networks

Abbreviation: CGE, cresyl glycidyl ether; MFN, molecular fortifier naphthalene.

3.5 | Moisture ingress

The rate and magnitude of moisture ingress for the 10% modified and unmodified NNE networks are compared in Figure 8a, while the final values are plotted in Figure 8b as a function of fortifier concentration. As can be seen, with increasing fortifier concentration, the moisture ingress is reduced, proposed to be a direct result of the anti-plasticization effect filling the interstitial voids within the previously unoccupied free volume and excluding moisture. Overall, the extent of reduction in moisture ingress, appears to be similar regardless of fortifier used.

3.6 | Flexural properties and fracture toughness

The flexural modulus, fracture toughness, and some representative stress-strain curves of the modified and unmodified NNE networks are shown in Figure 9a-c, respectively, while Table 4 lists the flexural strength and strain to failure. As can be seen, large improvements in modulus are evident with increasing fortifier concentration, up to a maximum improvement of 46.7% (CGE),

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50.1% (MFN) and 46.5% (NAPH). These results clearly highlight the impact of anti-plasticization and molecular level reinforcement of the NNE network by these fortigiers. Marks et al studied mono-functional epoxides incorporated into a DGEBA-based network and noted that a critical value of mono-epoxide behaved as a mild anti-plasticizer and termed as nonelastically active pendant chains.²⁴ It is notable that the modulus shown for CGE, NAPH, and MFN modified NNE now approaches the value of the TGDDM formulation reported in a corollary study.²⁰ It is of course important to state that the fortifier addition had a negative effect on flexural strength and strain to failure as shown in Table 4. The reduction in strain to failure and hence strength, is presumably a direct result of the suppression of glassy state mobility and the anti-plasticization effect.

In terms of the fracture toughness, the NAPH modified networks displayed some improvements, while the MFN modified networks were relatively similar to the NNE/DDS while the CGE network displayed a significant reduction. It has previously been reported that antiplasticization decreases the fracture toughness, as the network is less able to absorb and dissipate energy partly due to the increased modulus.²¹ The mostly lack of an improvement to fracture toughness from CGE more closely mirrors the results of Grishchuc et al. where increased modulus by a reactive diluent decreased fracture toughness.⁵⁵ It is interesting, then, that the NAPH and the noncovalently bound MFN modifiers show some improvement to the fracture toughness as well as enhanced modulus providing some promise, particularly for the NAPH modified networks.

4 | CONCLUSIONS

Three molecular fortifiers each providing molecular level reinforcement to the highly crosslinked NNE/DDS network in different ways have been studied for their impact upon the cure reaction and mechanical and thermal properties. Increased hydrogen bonding for the CGE and MFN networks was identified from NIR spectroscopy and proposed to play a role in an initial acceleration of cure as measured by k_1 for the CGE and MFN fortifiers. Dilution of reactive species however, played an increasingly important role in reducing the rate of reaction during the later stages of cure, for all fortifiers. Suppression of glassy state mobility was also observed in the β relaxations of the network for all fortifiers, with the NAPH modified network displaying the largest restriction. These effects combined to produce a large improvement in flexural modulus and reduced moisture ingress. Some improved toughening was presented in the case of NAPH, the

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NAPH and CGE modified networks significantly improved processability as evident from a lower viscosity and a wider processing window.

AUTHOR CONTRIBUTIONS

Russell J. Varley: Conceptualization (equal); writing – review and editing (equal). Samuel R. Swan: Conceptualization (lead); data curation (lead); formal analysis (lead); investigation (lead); writing – original draft (lead); writing – review and editing (lead). Houlei Gan: Formal analysis (supporting); investigation (supporting); methodology (supporting). Claudia Creighton: Supervision (equal); writing – review and editing (equal). James M. Griffin: Funding acquisition (equal); supervision (equal); writing – review and editing (supporting). Bekim V. Gashi: Supervision (equal); writing – review and editing (supporting).

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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