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Aromatic tetra-glycidyl ether versus tetra-glycidyl amine epoxy networks: influence of monomer structure and epoxide conversion 3

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Abstract

In this work, two epoxy resins, bis(2,7 glycidyl ether naphthalenediol) methane (NNE), tetraglycidyl 13 14 diaminodiphenylmethane (TGDDM) and a miscible blend of the two are cured with 4,4'-15 diaminodiphenylsulfone (DDS) to investigate the differences between glycidyl ether and glycidyl 16 amine crosslinked networks. This work explores in depth, and directly compares for the first time, the 17 structure/property relationships of a highly aromatic and thermally stable glycidyl ether epoxy network with a well-known highly aromatic and thermally stable glycidyl amine epoxy network. The 18 19 highly aromatic naphthalene motif of NNE imparts improved thermal stability and a significantly 20 higher glass transition temperature, above 340°C depending on the measurement technique. 21 However, it also produces comparatively lower epoxide conversion, higher moisture ingress and lower 22 flexural properties. These properties are attributed to the NNE having higher free volume and glassy 23 state mobility as suggested by the sub-ambient β relaxations. The glycidyl ether groups react primarily 24 via epoxide amino addition displaying only very minor evidence of homopolymerisation or other side 25 reactions even at 240 °C. This contrasts with the glycidyl amine groups of TGDDM which exhibit a much higher degree of non-epoxy amine addition. Increasing cure conversion also increases the glass 26 27 transition temperature, fracture toughness and reduced coefficient of thermal expansion. Overall, the results show that despite some reduced mechanical and thermal properties the NNE epoxy resin 28 29 system is a very thermally stable high temperature epoxy resin based upon glycidyl ether functional 30 groups suitable for a wide range of new applications.

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33 Keywords: Epoxy Resins, Structure-Property Relations, Thermal Stability, Moisture Ingress

34 1 Introduction

35 Polymer resins for hot zones are increasingly in demand as fibre reinforced plastics and new 36 applications for composites continue to emerge in the aerospace and space industries, the automotive 37 [1] and oil & gas industries [2]. Some examples include, near engine components in aircraft, structural 38 components in supersonic aircraft and space vehicles, high pressure pipelines and deep well drilling 39 for hydraulic fracturing. The microencapsulation of printed circuit boards, where thermal, 40 dimensional, and mechanical stability over wide temperatures ranges, particularly for short periods of 41 time is another increasingly important application [3]. As demand for even higher service temperatures has grown, monomers and polymers based upon more inherently thermally stable 42 43 structures have been developed, including cyanate esters ($T_g \sim 200-350 \text{ °C}$) [4], addition cured polyimides (T_g \sim 250-370 °C) [5], advanced phenolic resins (T_g >300 °C) [6,7], benzoxazines (T_g \sim 320-44 45 370 °C) [8], and high-Tg thermoplastics (Tg ~ 280 °C) [9]. Compared to epoxy resins, their high cost, 46 often challenging processing requirements along with health and toxicity concerns have ensured that 47 these materials remain mostly confined to niche applications. In contrast, epoxy resins have remained attractive polymer matrices and research dedicated to maximising their glass transition and service 48 49 temperature continues. Indeed, epoxy-based composites currently make up about 80% of the global 50 composite market [10].

51 The glass transition temperature of epoxy resins is typically well below 200°C but can be up to 250°C 52 for multi-functional epoxy resins [11]. Despite the importance of glass transition temperature (T_g) in 53 determining durability at elevated temperature; crosslink density, free volume, moisture ingress and 54 residual stress, will all impact performance [12]. The tetraglycidyl diaminodiphenyl methane (TGDDM) and triglycidyl-p-amino phenol (TGAP) epoxy resins, for example, both have Tgs of the order of 250°C 55 56 but also contain glycidyl amine motifs which can enable side reactions and undergo internal 57 cyclisation, to form mechanically inactive structures that prevent the network from achieving its 58 ultimate properties [13–16]. More recently, research into multifunctional highly aromatic glycidyl 59 ether epoxy resins has shown promising thermal performance due to the absence of this internal 60 cyclization. Liu et al. described the synthesis and characterisation of a tetrafunctional, nitrogen-free 61 epoxy resin and showed that a blend of the monomer with diglycidyl ether of bisphenol A (DGEBA) had a T_g similar to TGDDM [17]. Further work by Xing et al. showed similar results using a nitrogen-62 63 free tetrafunctional epoxy when blended with up to 60 wt% DGEBA [18].

Another notable development in novel high-T_g epoxy resin is the synthesis of the monomer bis(2,7
glycidyl ether naphthalenediol) methane (NNE), an epoxy resin with a dimeric naphthalene designed
to achieve a rigid backbone in the main polymer chain and a very high crosslink density. Ogura and

67 Takahashi showed that when homo-polymerised using an imidazole catalyst, NNE exhibited a T_g above 68 $320^{\circ}C$ [19] also suggesting that this was the highest T_g ever achieved by an epoxy resin. Additionally, 69 they compared the dimeric naphthalene epoxies to a commercial epoxy cresyl novolac and noted 70 consistently higher T_g at lower crosslink density, a characteristic they attributed to the rigid bis-71 naphthalene structure. To the authors knowledge it remains the highest published value at the time 72 of this paper. This epoxy resin is promoted for micro-electronics encapsulation applications where 73 with high heat and solder resistance is required [20]. While the very high T_g makes this resin attractive 74 for high temperature applications, there is a lack of fundamental knowledge regarding its 75 structure/property relationships, particularly when compared with the much more widely studied 76 DGEBA, TGDDM, and TGAP-based networks. Recent work by Vukovic et al. utilised molecular dynamics 77 simulations to study the structural origin of T_g and concluded that restricted segmental motions across 78 cross-linked domains by the rigid dimeric naphthalene backbone of NNE, contributed to a markedly 79 higher glass transition temperature compared with TGDDM [21]. More recently, our group investigated the cure reactions of the diamine-cured NNE resin and compared with TGDDM. It was 80 81 shown that NNE underwent gelation and vitrification more rapidly than TGDDM and as a consequence 82 formed a topologically constrained network with diffusion-controlled mechanisms ultimately limiting 83 the final degree of cure [22].

84 In light of the vastly different phase transition behaviour during the early stages of cure, this work 85 builds on the previous investigation and presents the detailed structure/property relations of the 86 glycidyl ether-based NNE epoxy resin cured with 4,4'-diaminodiphenyl sulphone (DDS), compared 87 against a glycidyl amine based TGDDM also cured with DDS. A third formulation consisting of a 70/30 88 molar blend of NNE and TGDDM respectively, cured with DDS was also investigated. The purpose of 89 the work is to better understand the role of the highly aromatic naphthalene structure and the glycidyl 90 ether functionality in determining the thermal properties including durability at elevated temperature, and mechanical properties of the resultant network. Although glycidyl amine and ether 91 92 chemistries are generally well understood, in the context of thermally stable and highly aromatic 93 network polymers, the impact of structural differences upon mechanical, thermal and physical 94 properties have not previously been directly compared. To do this, the chemical structures of the 95 networks were investigated using near infrared spectroscopy (NIR) and the thermal properties were 96 explored using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMTA), 97 thermomechanical analysis (TMA) and thermogravimetric analysis (TGA). Moreover, the physical 98 properties such as density and water absorption were studied and fracture toughness and the flexural 99 properties of the networks were also determined. The underlying motivation of the work is to

investigate an emerging and understudied high-temperature epoxy resin with potential forapplications in a wide range of demanding composite applications.

102 2 Experimental

103 2.1 Materials

The tetrafunctional epoxy resin bis(2,7 glycidyl ether naphthalenediol) methane (EEW = 170 g/eq., Epiclon HP4710, NNE) was supplied by DIC Corporation, Japan. Tetraglycidyl diaminodiphenyl methane (EEW = 124 g/eq., Araldite M721, TGDDM) was obtained from Huntsman Corporation, USA. The aromatic amine hardener 4,4'-diaminodiphenyl sulphone (AEW = 62 g/eq., DDS) was purchased from TCI Chemicals, Japan. The chemical structures of the monomers are shown in Figure 1.



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Figure 1 – Chemical structures of the (a) NNE, (b) TGDDM, and (c) DDS monomers

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112 2.2 Sample Preparation

The monomers were placed in a round-bottom flask and degassed under vacuum at 125 °C using a 113 114 rotary evaporator to melt and mix the resins. Upon sufficient degassing to remove any bubbles, DDS 115 was added to produce a 1:0.95 stoichiometric ratio of epoxide: amino and mixing continued until the 116 DDS had completely dissolved and the mixture was free of bubbles. Silicon moulds were placed in a 117 convection oven and pre-heated to 150 °C. The molten polymer mixture was quickly transferred from the rotary evaporator to the silicon moulds for casting of resin specimens. From this point forward 118 119 the NNE/DDS, TGDDM/DDS and [70 mol% NNE/30 mol% TGDDM]/DDS formulations are referred to 120 as NNE, TGDDM and NTG respectively. The cure profiles used for each resin systems are described in 121 Table 1.

Composition Sample ID Cure profile **Post Cure** NNE/DDS NNE-150 8 hrs at 150 °C 4 hrs at 150 °C - 4 hrs at 180 °C NNE-180 NNE-200 4 hrs at 150 °C - 4 hrs at 180 °C 2 hrs at 200 °C NNE-210 4 hrs at 150 °C - 4 hrs at 180 °C 2 hrs at 210 °C 4 hrs at 150 °C - 4 hrs at 180 °C NNE-220 2 hrs at 220 °C NNE-240 4 hrs at 150 °C - 4 hrs at 180 °C 2 hrs at 240 °C (70 mol% NNE-30 mol%)/DDS 4 hrs at 150 °C - 4 hrs at 180 °C 2 hrs at 220 °C NTG TGDDM/DDS TGDDM 4 hrs at 150 °C - 4 hrs at 180 °C 2 hrs at 200 °C

125 Table 1 – Resin composition, notations, cure profiles, and applied post-cure conditions

126

127 2.3 Characterisation

128 2.3.1 <u>Near Infra-red Spectroscopy</u>

A Bruker Alpha FTIR was used in transmission mode to obtain near infra-red spectra (NIR) from 4200 cm⁻¹ to 7500 cm⁻¹ at a resolution of 2 cm⁻¹. Each spectrum is an average from 64 scans. Semiquantitative epoxide conversion was determined according to the following equation:

132
$$\alpha_{EP} = \frac{A_0 - A_{cure}}{A_0 - A_F} = 1 - \frac{A_{cure}}{A_0}$$

133 where α_{EP} is the fractional conversion of the epoxide group, and the areas A_{cure} and A_0 represent the 134 area of the epoxide peak after curing and of the uncured polymer, respectively. The assumption made 135 is that when the network is fully cured, the peak area, A_F , is non-existent.

136 2.3.2 <u>Differential Scanning Calorimetry</u>

137 A Netzsch 214 Polyma DSC was used to determine the cure conversion, α , by heating approximately 138 10 mg of the uncured and cured resin samples from 25 °C to 350 °C at a rate of 10 °C/min under a 139 nitrogen atmosphere. The experiments were performed in triplicate from which an average 140 conversion was calculated. The equation for determining the epoxide cure conversion is given as:

141
$$\alpha = \frac{\Delta H_{residual}}{\Delta H_{total}}$$

where $\Delta H_{residual}$ and ΔH_{total} represent the average exotherm from thermograms of the cured resin and the average exotherm from five scans of the uncured resin at heating rates of 2.5, 5, 10, 15, and 20 °C/min.

145 2.3.3 Dynamic Mechanical Thermal Analysis

146 Dynamic mechanical analysis (DMTA) was performed using a TA Instruments Q800 instrument using 147 a dual-cantilever fixture with a span of 60 mm. Samples of dimensions 3 mm x 10 mm x 60 mm were 148 placed in the fixture and heated while applying a frequency of 1 Hz and an oscillating amplitude of 50 149 μ m. Low temperature measurements were heated from -130°C to 100°C at a rate of 3°C/min, while 150 high temperature measurements were heated from 50°C to 365°C at a 5°C/min. The glass transition 151 temperatures (Tg) were determined from the peak in the tan δ spectra and the extrapolated onset of 152 the storage modulus (E').

153 2.3.4 Thermomechanical Analysis (TMA)

The linear coefficient of thermal expansion (CTE), α_g in the glassy state was measured using a Netzsch Hyperion TMA in the expansion mode. Measurements were conducted on cubic resin blocks of 3 x 3 x 3 mm dimensions. Samples were placed between alumina plates and an external 0.05 N force was applied from the quartz crystal column. The samples were conditioned at 35°C and gradually heated at 3°C/min to 225°C with the mean CTE being determined between 50 - 150°C. The measurements were performed in triplicate.

160 2.3.5 <u>Thermogravimetric Analysis (TGA)</u>

Thermogravimetric analysis was performed using a Netzsch TGA 209 Libra in both isothermal and dynamic modes to determine mass loss over time, degradation temperatures for the mass loss at 95% (T_{95%}) and 90% (T_{90%}) and the maximum rate of mass loss (T_{max}) and char yields. Samples were heated at ramp rates of 2.5, 5, 10, 15, and 20°C/min from 30 to 800 °C and for selected samples, and the differential Friedman model was applied to determine the activation energy barrier to degradation [23,24]. Isothermal degradation at 225, 250, 275, and 300°C was conducted for 10 hours to determine mass loss.

168 2.3.6 <u>Physical Density and Moisture Ingress Measurements</u>

The density of the cured resins was determined by helium gas pycnometry using a Quantachrome Ultrapyc 1200e. Nominally, 2 g of cured resin was placed inside the chamber and the density was averaged over 7 scans. Moisture ingress was determined by immersing the cured resin bars (performed in triplicate) in deionised water held at 80 °C for 14 days. Samples were periodically dried using lint-free wipes and weighed on an analytical balance. The diffusion coefficient, D, was determined from an approximation based on Fick's Law for one-dimensional diffusion that takes the following form:

176
$$\frac{C_t}{C_s} = D^{1/2} \frac{4\sqrt{t_s}}{h\sqrt{\pi}}$$

where C_t represents the intermediate moisture content, C_s the moisture content at saturation, t is the length of time the sample has been submerged, and h is sample thickness. The slope of the linear portion of a plot of $\frac{C_t}{C_s}$ versus $\frac{4\sqrt{t_2}}{h\sqrt{\pi}}$ is then used to calculate the value of D.

180 2.3.7 <u>Mechanical Properties</u>

Flexural properties were measured using samples of nominal dimensions 60 x 12 x 2.75 mm using a three-point bend apparatus with a span of 48 mm. Testing was carried out on an Instron 5593 servoelectromechanical load frame equipped with a 10 kN load cell in accordance with ASTM Standard D790 [25]. The load frame crosshead speed was 1.3 mm/min. Sample properties were averaged over a minimum of 5 specimens.

Single end notched beam (SENB) fracture toughness tests were performed on specimens of nominal 50 x 12 x 6 mm cast resin bars using a mould with a pre-cast 6 mm notch in the centre of the span in accordance with ASTM Standard D5045 [26]. A crosshead speed of 10 mm/min and 42 mm span was utilised for fracture toughness testing. A fresh razor was used to score the pre-notch in one motion to ensure a single stress riser and prevent multiple crack tips. Sample properties were averaged over a minimum of 5 specimens. The fracture toughness notch factor was determined by the equation:

192
$$f(x) = 6x^{1/2} \frac{[1.99 - x(1 - x)(2.15 - 3.93x + 2.7x^2)]}{(1 + 2x)(1 - x)^{3/2}}$$

where x is the ratio of the specimen pre-crack notch to the total depth of the sample and f(x) is the resulting notch factor. The fracture toughness is then taken as:

195
$$K_{1C} = f(x) \frac{P_{MAX}}{BW^{1/2}}$$

where K_{1C} is plane-strain fracture toughness, P_{MAX} is the maximum load (complete linearity in load v
 displacement curve) and the specimen depth and thickness are B and W, respectively.

198 **3** Results and Discussions

199 3.1 Network Structure

The mechanical and thermal properties of crosslinked networks after cure are defined primarily by the polymer architecture and epoxide conversion. The NNE used here is based upon a tetraglycidyl ether and a bis naphthalene motif, which if fully cured should produce a highly crosslinked and thermally stable network. To explore the effect of the rigid structure and presence of glycidyl ether groups on the cure conversion and formation of the network, DSC analysis was performed. Figure 2(a) illustrates the residual exotherm, (indicative of incomplete cure), as a function of cure and post-cure temperature, gradually decreasing in size with increasing cure temperature as commonly observed. Less commonly observed however, is a much smaller and broad exotherm above 300°C, which can be attributed to the further curing of unreacted species. None of the cured networks exhibit a clear T_g due to the crosslink density and rigid structure inhibiting any endothermic relaxation. The corresponding cure conversions in Figure 2(b) reveal a steady increase from 85 % to essentially 100% conversion as the residual enthalpy diminished into the baseline. Comparison with the NTG and TGDDM networks exhibit a slightly lower conversion for NTG (95%) after post-cure at 220°C, and slightly higher conversion for the TGDDM (98%) at 200 °C post-cure.



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Figure 2 – (a) Offset DSC traces of the cured NNE resins at 10°C/min and (b) fractional conversion of the cured resin
 formulations relative to final cure temperature

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218 Determining epoxide conversion from DSC analysis assumes a close relationship between enthalpy and the epoxide amino

reaction and that remaining reactive functional groups eventually react. In a highly crosslinked network containing a rigid
 backbone, this is not necessarily the case, so the cure conversion measured via DSC should be treated with caution. In

221 contrast, NIR spectroscopy directly probes the chemical functionality of the overall network, and despite also having

222 challenges in quantitation from overlapping peaks, provides a more complete understanding of the network structure and

223 functional group conversion. For example, the NIR spectra of the uncured NNE resin and cured NNE networks as a function



225 Figure 3(a) and (b) and clearly highlight the increasing conversion of epoxide as the peak associated 226 with the oxirane ring (4525 cm⁻¹) decreases in intensity. The epoxide conversion determined from NIR, 227 inserted adjacent to each spectrum, is significantly lower than determined by DSC, increasing from 78.9% after NNE-150 to 90.7% after NNE-240. Other chemical changes observed with increasing cure 228 229 and post-cure temperature include the entire consumption of primary amine groups (5091 cm⁻¹), the 230 consistent reduction in secondary amine groups (6630-6800 cm⁻¹) and the growth of hydroxyl groups 231 (6800-7100 cm⁻¹). Figure 3(b) compares the effect of post-cure on reactions in the glassy state for the 232 NNE-220, NTG (220°C) and TGDDM (200°C) networks, highlighting important differences. In respect 233 to the epoxide conversion, lower epoxide conversions (larger epoxide peaks) for the NNE and NTG 234 systems compared with TGDDM after cure and post-cure are self-evident. This is attributed to the rigid 235 nature of the bulky naphthalene groups within the backbone inhibiting chemical mobility particularly 236 during the final stages of cure. Furthermore, after post-cure, NNE and NTG both display increases in 237 the hydroxyl groups and decreases in secondary amine groups, indicative of continued epoxy amine 238 addition. In contrast, TGDDM does not show any change in the size of either the hydroxyl or secondary 239 amine peaks after post-cure, illustrating the greater propensity for side reactions such as cyclisation 240 and etherification rather than epoxide amino addition. For NNE therefore, these results emphasise that despite the higher concentration of epoxide groups available after cure, the glycidyl ether epoxide 241 242 groups continue to preferentially react via amine addition rather than react via side reactions in the 243 glassy state.



Figure 3 – (a) Near-infrared spectra for NNE in the uncured and cured states with final epoxide conversion displayed 246 adjacent to the spectra and (b) comparison of the epoxide, secondary amine, and hydroxyl peaks of the NNE, NTG, and 247 TGDDM resins from final cure to post-cure

249 3.2 **Thermal Analysis**

Dynamic Mechanical Thermal Analysis 250 3.2.1

The dynamic mechanical spectra of the storage modulus and $tan(\delta)$ of the NNE networks at different 251 252 cure and post-cure temperatures are shown in Figure 4(a) and the summary of the measured T_gs are

253 provided in

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254 Table 2. Both the storage modulus and tan(δ) spectra display two transitions, a lower temperature T_g, 255 indicative of the incompletely cured network, and a $T_{g\infty}$ reflecting the highest possible T_g after 256 complete cure. As cure and post-cure temperatures increase, the lower T_g peak reduces in intensity 257 and moves to a higher temperature, such that at 220 °C and 240 °C post-cure, the peaks become barely 258 discernible shoulders on the $T_{g\infty}$ tan(δ) peak and small inflections on each storage modulus spectrum. Varley et al. observed similar behaviour for the tri-functional aromatic epoxy, tri-glycidyl p-amino 259 260 phenol (TGAP), and considered this to reflect the progressive decrease in molecular mobility as 261 crosslink density and conversion increased [27]. Similarly, Jiawu et al. investigating a TGDDM/DDS network, related the progressive disappearance to increased conversion of reactive species within the 262 network [28]. Nonetheless, a simple interpretation suggests that given an appropriate post-cure 263 264 temperature of about 210 °C or 220 °C, the NNE network can exhibit a T_g of between 340 and 350 °C 265 depending upon the measurement used in the DMTA spectrum. It is important to note however, that 266 at these high temperatures, there will be increasing competition with degradation, as evidenced by the lack of any measurable rubbery state in the cured networks. 267

268 Comparison of the NNE-220 and NNE-240, NTG and TGDDM networks in Figure 4(b) highlight the higher $T_{g\infty}$ of the NNE networks compared with the TGDDM. The $T_{g\infty}s$ (tan(δ) max) of the TGDDM and 269 270 NTG networks were 297.4 °C and 320.3 °C respectively, but increased to 349.9 °C and 352.7 °C for the 271 NNE networks after post-cure at 220 °C and 240 °C. All of the networks still displayed two transitions, 272 similar to those described above, the first T_g, appearing as a low intensity peak or shoulder on the lower temperature side of the much larger, second transition, the $T_{g\infty}$. The higher T_g and $T_{g\infty}$ of the 273 274 NNE networks compared with the TGDDM is again attributed to the highly rigid and thermally stable 275 aromatic naphthalene structures.



278Figure 4 – a) DMTA traces for storage modulus and $tan(\delta)$ of the NNE resin for the different final cure and post-cure279temperatures and b) DMTA traces for storage modulus and $tan(\delta)$ of the NNE (220°C and 240°C post-cures), NTG, and280TGDDM resin systems

281

282 Table 2 – Temperature of onset and $tan(\delta)$ from DMTA spectra

Samala ID	Tg (ext. onset E')	T _g (tan(δ) max)	$T_{g\infty}$ (tan(δ) max)				
Sample ID	(°C)	(°C)	(°C)				

NNE-150	201.9	213.5	355.3	
NNE-180	338.9	230.5	348.3	
NNE-200	335.6	245.8	347.9	
NNE-210	333.8	250.5	343.6	
NNE-220	341.5	292.8	349.9	
NNE-240	346.5	-	352.7	
NTG	318.0	-	320.3	
TGDDM	278.7	-	297.4	

284 The sub-ambient β relaxation, appears as a broad low intensity peak typically between -20 to -80°C 285 for crosslinked epoxy networks, and is used here to explore short range molecular mobility. The low 286 temperature side of the peak is associated with the motion of the phenylene rings of the epoxy 287 backbone, the mid-region with the crank-shaft rotation of reacted epoxide species, and the higher 288 temperature side of the peak with the motion of the amino backbone [16,29]. The tan (δ) spectra for 289 the NNE as a function of cure and post-cure are shown in Figure 5(a) while the peak temperatures and 290 areas are shown in Table 3. As the cure and post-cure temperature increases, the peak temperature 291 consistently increases from -38.5 °C to -23.8 °C, emphasising that higher energy is required to initiate 292 short range motions such as phenylene ring flips. The peak area reaches a maximum at NNE-220, 293 primarily because of the increasing influence of an overlapping higher temperature peak for the NNE-294 240 spectrum. Despite this, the greater peak areas suggest that as crosslink density and cure 295 conversion increase, glassy state mobility of the network actually increases. This is in accord with 296 Morel et al. who reported the strong influence of hydrogen bonding on dynamic moduli in the glassy 297 state noting that the ultimate T_g appeared independent of network rigidity, both for glycidyl ether and 298 glycidyl amine resins [30].

299 Comparison of the sub-ambient β relaxations of the NNE-220, NNE-240, NTG and TGDDM networks 300 after post-cure in Figure 5(b), again illustrate modest but important differences between the network 301 structures. The β relaxations of the TGDDM and NTG have lower peak temperatures, are less intense 302 but broader, producing larger peak areas, again indicative of even greater mobility in the glassy state 303 compared to the rigid dimeric naphthalene structure of NNE. Indeed, compared to the para 304 substituted TGDDM networks, the NNE is restricted in the glassy state due to the 2,7' aromatic 305 substitution pattern which does not possess a rotational axis about which ring flips can activate 306 [21,29,31,32].

The networks in Figure 5(a) and (b) both display additional peaks between 50-100°C, referred to here as the omega transition (T_{Ω}). In Figure 5(a) the T_{Ω} peak increases with cure and post-cure temperature, but is much larger for the NTG and TGDDM networks in Figure 5b. The origin of this peak is less well defined, although Ramsdale-Capper & Foreman related it to cooperative motion between the phenyl 311 ring of the epoxy monomer and a reacted epoxide group [16]. Ochi et al. related the peak to the 312 hydrogen bonded epoxide species indicative of etherification [33,34]. The systematic emergence of 313 this transition at increasing cure and post-cure temperature, particularly for NNE-240, and its larger 314 presence for the TGDDM and NTG networks would tend to support the proposition that side reactions 315 or etherification play an important role in determining this transition.

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Figure 5 – Traces of the sub-ambient beta transition a) relative to cure temperature of the NNE resin and b) traces of the sub-ambient beta transition relative to crosslink density of the NNE (220 °C and 240 °C post-cures), NTG, and TGDDM
 formulations

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able 3 - Peak temperature and dreas of the tan(o) peak								
Sample ID	T _β (°C) at Peak tan(δ)	Total Area	Area Left of Peak	Area Right of Peak				
NNE-150	-38.5	5.25	2.65	2.60				
NNE-180	-31.9	5.50	2.87	2.63				
NNE-200	-29.0	5.83	3.07	2.76				
NNE-210	-26.5	5.82	3.07	2.75				
NNE-220	-24.8	6.28	3.36	2.92				
NNE-240	-23.8	5.85	3.02	2.83				
NTG	-38.4	6.59	2.70	3.89				
TGDDM	-35.9	6.64	2.64	4.00				

322 Table 3 - Peak temperature and areas of the $tan(\delta)$ peak

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324 3.2.2 Coefficient of Thermal Expansion

The thermal expansion of crosslinked epoxy networks in the glassy state (α_g) is determined by various interrelated parameters such as cure conversion, physical ageing, crosslink density, free volume and molecular mobility [35,36]. For systematically varying glassy epoxy networks, increases in α_g have been discussed in terms of increasing free volume facilitating movement of chain segments [37] and reduced cure conversion [17], while decreases have been attributed to increases in the crosslink density and density of the aromatic structure of the network. Zhou et al. studied several highly 331 aromatic glycidyl ether networks and reported lower α_g for a bis-naphthalene epoxy resin when compared with other epoxy resins due to the restriction of movement of the planar structure leading 332 333 to enhanced interactions and a stacked network structure [38]. All of these competing trends are 334 apparent in the thermal expansion measurements obtained here, from the increasing cure 335 temperature and post-cured NNE, NTG and TGDDM networks. Examples of the raw TMA thermograms 336 of the networks are shown in Figure 6(a), noting that the very high T_g of the NNE networks and the 337 onset of degradation above Tg [39,40] prevented measurement of $\Delta \alpha$ and thus gaining further insight into the role of free volume. Figure 6(b), shows that the α_g of NNE-150 is the highest at 64x10⁻⁶ K⁻¹, 338 while having the lowest degree of cure and crosslink density. In contrast, the lowest α_g of 52.5x10⁻⁶ K⁻ 339 340 ¹ is observed for NNE-180 where crosslink density and cure conversion are significantly increased. Subsequent post-cure however, then caused α_{g} of NNE-200 to increase to $63 x 10^{\text{-6}} \mbox{ K}^{\text{-1}}$ despite 341 decreasing with increasing post-cure temperature to 59x10⁻⁶ K⁻¹. Larger free volume and greater short 342 range segmental motions (as suggested from the sub-ambient DMTA results) likely counteracts the 343 restriction from the increased crosslink density to result in higher α_g . This is likely a result of the rigid 344 345 and planar naphthalene structures becoming effectively frozen into a less optimum molecular packing configuration, thereby growing in free volume after cooling down from the high post-cure 346 temperatures. In contrast, the TGDDM and NTG networks have correspondingly lower α_g due to the 347 less rigid structure of TGDDM and hence better equilibrium packing as temperature decreases to 348 349 ambient conditions.



Figure 6 – (a) TMA traces of NNE (220 °C), NTG (220 °C), and TGDDM (200 °C) post-cure conditions and (b) thermal

coefficient of expansion relative to cure temperature and resin system

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- 351 352

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355 3.2.3 <u>Thermogravimetric Analysis</u>

356 Representative thermograms of the mass loss and rate of mass loss for the NNE-220, NTG and TGDDM

357 networks are shown in Figure 7 while a summary of the results is in

359 Table 4. Overall, the impact of cure and post-cure upon the thermal stability ($T_{95\%}$, $T_{90\%}$ and T_{max}) and 360 char yield does not exhibit strongly systematic changes, suggesting that thermal stability is controlled 361 more by the cohesive forces between molecules rather than epoxide conversion and network formation. Compared with the NTG and TGDDM networks however, the NNE networks have 362 significantly higher initial decomposition temperatures. Using NNE-220, the decomposition 363 364 temperatures are about 8°C > NTG; 26 °C > TGDDM and higher char yields of about 4 % > NTG; 8 % > 365 TGDDM, reflecting the higher thermal stability of the naphthalene backbone. The NNE-220 showed 366 significantly higher thermal stability compared to TGDDM prior to the onset of degradation as shown 367 by higher initial activation energies at T_{95%} and T_{90%}. At T_{max} however, the glycidyl ether networks 368 displayed the opposite trend, with the E_a of TGDDM being higher than both NNE-220 and NTG. This reflects a more rapid degradation of the glycidyl ether groups compared to glycidyl amine once 369 370 degradation accelerates. Combined with higher char yields, it is clear therefore that NNE networks 371 have greater thermal stability due to the naphthalene structure but accelerate rapidly once initiated.

372 It is notable that the onset of degradation is virtually the same as the onset temperature of E' and 373 value of the peak in the tan(δ) from DMTA for the NNE-220 further emphasising the competition 374 between degradation and T_g for the NNE networks. In contrast, TGDDM has an onset within 25°C of 375 NNE but the glass transition temperature is nearly 100°C lower. To explore this further, isothermal 376 ageing of the different networks, NNE-220, NTG and TGDDM below their T_gs was performed.



377

380

Figure 7 – Dynamic TGA traces of weight loss (solid) and derivative of weight loss (dashed) for the three resins at 10°C/min
 heating rate

Sample ID	T _{95%} (°C)*	T _{90%} (°C)*	T _{max} (°C)*	Char Yield (wt%)	
NNE-150	370.8	380.8	380.3	32.8	
NNE-180	368.3	378.3	380.8	31.0	
NNE-200	365.8	373.3	375.3	32.8	
NNE-210	363.3	373.3	375.8	32.3	
NNE-220	373.3 (235.7)	383.3 (192.4)	387.3 (175.4)	34.9	
NNE-240	363.3	373.3	378.3	32.1	
NTG	354.9 (216.1)	374.9 (173.3)	387.4 (173.1)	30.9	
TGDDM	324.9 (194.7)	357.4 (181.1)	392.4 (209.3)	25.4	

381 Table 4 - Summary of degradation performance from dynamic TGA scan

values in () brackets represent the activation energy barrier to degradation, E_a (kJ/mol)

383 The mass loss during isothermal ageing at 250°C in Figure 8a compares the same mass loss over a 384 wider temperature range in Figure 8b. Despite the isothermal temperatures being well below their 385 respective $T_{g\infty}$, all networks displayed about a 5 wt% decrease within the first hour. After this time, 386 the NNE-220 exhibited much greater thermal stability compared to the NTG and TGDDM networks. 387 After 10 hrs at 250°C the NNE-220 lost about 3 wt%, compared with 5 wt% for the NTG and TGDDM. 388 Liu et al. noted similar dynamic behaviour and that the multiple degradation routes facilitated by the 389 glycidyl amine TGDDM were absent in a tetra-functional glycidyl ether nitrogen-free epoxy monomer 390 [17]. Stutz noted similar degradation routes for TGDDM but highlighted only the dehydration reaction 391 for DGEBA [41]. Despite this, the lifetime assessment concluded virtually no difference between in-392 service temperature (extrapolated) and glass transition temperature. It is clear from these results that 393 using dynamic and isothermal TGA, both thermal shock (short time scale) and thermal stability (long 394 time scale) are improved for NNE. The superior thermal stability of the NNE-220 network compared 395 with NTG and TGDDM is evident across a wider thermal ageing range thereby reinforcing the role of 396 the thermally stable naphthalene backbone and the glycidyl ether crosslinks.



397

Figure 8 - Isothermal TGA of the three resin formulations, NNE-220, NTG and TGDDM for (a) 10 hours at 250°C and (b) final
 mass of the samples after long-term exposure to 225-300°C isotherms held for 10 hours (per cent difference from NNE
 shown above bars)

402 3.3 Moisture Ingress

403 The extent and rate of water ingress is also dependent upon a number of interrelated parameters, 404 including free volume, polarity, crosslink density and network topology [42] [43]. Plotted as a function 405 of cure profile and resin type in Figure 9a) and b) respectively, the calculated diffusion coefficients of 406 the three resins, the final moisture ingress and physical densities for each system are shown in Table 407 5Error! Reference source not found.. Moisture ingress in Figure 9a displays Fickian behaviour over 408 time, and a distinct increase in the final equilibrium water uptake with increasing cure temperature, 409 epoxide conversion and crosslink density. The mass gain for NNE-150 was 3.6%, steadily increasing to 410 5.9% for NNE-240, entirely supporting the hypothesis of increasing free volume with increasing 411 crosslink density and/or cure conversion. Recent work by Frank et al. similarly observed a concomitant 412 increase in moisture ingress with increased crosslink density of epoxy networks attributing it to an 413 increase in the fractional free volume, as opposed to the size of the free volume holes within the 414 network. In addition, the higher concentration of hydroxyl groups for more highly crosslinked 415 networks was also reported to be a factor, contributing to increased hydrogen bonding and hence 416 higher moisture absolution. Indeed, Soles and Yee [44] suggest that the higher free volume provides 417 access to polar sites effectively enhancing moisture ingress. The equilibrium water uptake of about 418 5.9% for the corresponding NNE-220 and NNE-240 networks, as shown in Figure 9b are also 419 significantly higher than both the NTG and TGDDM networks which both exhibit just below 5% mass 420 gain. While the NNE networks exhibit the highest moisture update, NTG and TGDDM networks are also high compared with di-functional networks. DGEBA/DDS networks are commonly reported to be 421 422 between 2.5% and 4% [45–48]. The higher value of NNE can be attributed to the inherently rigid nature 423 of the bis-naphthalene backbone preventing better packing of the molecular chains and ensuring a 424 higher fractional free volume due to the rapid vitrification of the network. Frank et al. also studied the 425 effects of stoichiometry on epoxy-amine blends, noting that moisture ingress reduced with an excess 426 of epoxy and lower crosslink density attributing this to more efficient chain packing [45].



Figure 9 - Moisture ingress of (a) the NNE resin with increasing cure and post-cure and (b) between the NNE (220°C and 240°C post-cures), NTG (220°C), and TGDDM (200°C) resin formulations

431

432Table 5 - Values of physical density, equilibrium wt%, and diffusion coefficients determined from moisture ingress for the433NNE resins of increased cure and post-cure condition and for the NTG and TGDDM resin formulations

	NNE					NTG	TGDDM	
Cure Temp. (°C)	150	180	200	210	220	240	220	200
ρ (g/cm³)	1.315	1.32	1.313	1.316	1.315	1.327	1.299	1.279
Eq. Wt. %	3.56	4.76	4.97	5.41	5.85	5.94	4.89	5.02
D (10 ⁻¹² m²/s)	1.387	1.279	1.269	1.247	1.221	1.162	1.164	1.101

434

DMTA and NIR was performed on the moisture-aged specimens to determine the effect on thermal 435 436 properties and the cured network as shown in Figure 10(a-c) and tabulated in Table 6. Although ingress 437 of water into polymer networks can both plasticise and provide opportunity for further crosslinking, 438 in this case, the networks appear plasticised and exhibit reduced storage modulus and lower T_{es} . 439 Interestingly, the wet tan(δ) trace for TGDDM shows heterogeneity with a secondary peak emerging below 220°C. Clearly the T_{gs} are much more impacted than $T_{g\infty}$, presumably a result of the higher 440 441 polarity and opportunities for hydrogen bonding with those parts of the networks associated with 442 unreacted functional groups. The NIR spectra of the peak around 5240cm⁻¹ commonly associated with hydrogen-bound water molecules [49] in Figure 10(b-c) clearly shows increases in the peak intensity 443 444 with respect to cure conversion for NNE and is again highest compared with the three resins. The peak intensity clearly implies a higher amount of hydrogen-bonded water in the glycidyl ether network after 445 446 post-curing. Overall, however, it is difficult to conclude that the increased hydrogen-bound water has 447 a larger effect upon plasticisation based upon the small differences in the wet and dry DMTA spectra. 448 The likely higher free volume of the NNE combined with the increased water ingress from hydrogen 449 bonding likely both contribute significantly to the observed higher moisture ingress.



⁴⁵⁰ 451 452

Figure 10 – a) DMTA traces of NNE (220°C) , NTG (220°C), and TGDDM (200°C) of storage modulus and the tan(δ) behaviour before (solid) and after (dashed) moisture ingress, b) OH peak from NIR of NNE relative to cure and post-cure temperatures, and c) OH peak from NIR of NNE(220-240°C), NTG (220°C), and TGDDM (200°C) resins

Table 6 - Temperature at peak of $tan(\delta)$ from DMTA of the samples after moisture ageing

		NNE							TGDDM
Tcure	• (°C)	150	180	200	210	220	240	220	200
T _g (°C)**	'C)**	188.7	200.6	206.7	206.9	255.8	272.4	-	216.4
	C)	(-13.1%)	(-14.5%)	(-19.6%)	(-21.0%)	(-14.5)	272.4		
Τ _{g∞} (°C)**	°C**	335.8	332.1	338.6	339.4	335.5	332.7	320.1	285.9
	CJ	(-5.8%)	(-3.2%)	(-2.9%)	(-2.5%)	(-4.3%)	(-6.0%)	(-0.8%)	(-4.0%)

⁴⁵⁵ ******(%) represents the % decrease from the dry specimens

456

457 3.4 Mechanical Properties

The flexural strain to failure, stress, and modulus for all the networks prepared here are shown in Figure 11. With increasing cure and post-cure temperature, and hence cure conversion, the strain to failure and strength rise consistently to a maximum at NNE-210, but then decrease. The initially low mechanical properties are caused by unreacted functional groups in the network that behave as defects and result in a lower effective crosslink density, steadily reducing with increasing cure temperature. The modulus mostly decreases with increasing temperature (apart from a modest 464 increase for NNE-240) corresponding to the higher free volume and greater short range molecular 465 motions indicated by the moisture ingress and β relaxation measurements respectively. Comparison 466 of the NNE-220 against NTG and TGDDM, shows that mechanical properties for the NNE networks are 467 lower. The indirect nature of β relaxation measurements in determining modulus is also highlighted in that TGDDM and NTG exhibit higher modulus despite the larger sub-ambient peak area compared 468 469 with the NNE networks.

470 Despite not being able to be directly attributed to increased cure conversion, a modest improvement 471 in K_{1C} of NNE is observed with increasing cure and post-cure. An initial reduction in toughness is 472 observed followed by an increase and eventual plateau at 220°C and 240°C post-cures. Ultimately, 473 the maximum values at NNE-220 and NNE-240 achieve similar levels as NTG and TGDDM.



475 476

Figure 11 - Mechanical properties determined from flexural three-point-bend testing showing (a) strain to failure, (b) the ultimate strength, (c) modulus, and (d) fracture toughness of the three resins

479 **4** Conclusions

This paper presents for the first time, a detailed structure property relationship study of a DDS cured 480 481 bis(2,7-dihydroxy-1-naphthalenediol) methane (NNE) epoxy resin to establishing the role of the rigid naphthalene motif and glycidyl ether conversion and compare it to a similarly cured glycidyl amine 482 TGDDM and TGDDM/NNE blend, NTG. The rigid nature of the naphthalene, whilst imparting higher 483 484 thermal stability and glass transition temperatures, also produced lower epoxide conversion, higher 485 coefficient of thermal expansion, lower flexural properties, and higher moisture ingress. All of these 486 properties can be attributed to a higher free volume as evidenced by greater short range molecular 487 mobility arising from poorer packing of the network. Despite the lower cure conversion, the glycidyl 488 ether groups were far less likely to react via homopolymerisation or other side reactions even at 240 489 °C, in contrast to the glycidyl amine groups of TGDDM which exhibited clear evidence of non-epoxyamine reactions. Increasing cure conversion, increased T_g and T_g, fracture toughness and reduced α_{g} , 490 491 of which the change can be attributed to an increased crosslink density, while the higher moisture 492 uptake and lower flexural modulus relate to the higher free volume arising from the network topology 493 of the rigid naphthalene structure. Finally, the NNE epoxy resin system is part of a family of emerging 494 glycidyl ether epoxy resins with very high glass transition temperatures and are thermally stable, and suitable for a broad range of applications, particularly for structural composites exposed to elevated 495 496 temperatures.

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