CHARACTERISATION AND CURE KINETICS OF MULTI-AROMATIC TETRA-FUNCTIONAL EPOXY RESINS

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ABSTRACT

A systemic study of the impact of aromatic substitution on the reaction rate and network performance of isomers of tri-phenyl epoxy resins cured with two different anhydride hardeners is presented here. The epoxy resins are based upon the structure N,N,N,N-tetraglycidyl bis (aminophenoxy) benzene (TGAPB) with substitution varying from all meta (133 TGAPB), to meta and para (134 TGAPB), and finally to an all para substituted (144 TGAPB) structure. The hardeners used to cure resins were methyl nadic anhydride (MNA) and methyl hexahydropthhalic anhydride (MTHPA) catalysed with imidazole. Increasing para substitution increased reaction rate, promoted the onset of vitrification and increased epoxide conversion. Thermal properties such as Tg and CTE both increased consistently with increasing para substitution, although thermal stability as measured via thermogravimetric analysis decreased. The flexural strength increased, modulus decreased while ductility almost doubled after post-cure as measured by the work of fracture and displacement at failure. Increased rigidity of a tri-aromatic all para substituted epoxy resin, was demonstrated to be extremely beneficial towards improved ductility, while either improving or maintaining important physical, thermal and mechanical properties apart from thermal stability.

1 INTRODUCTION

Epoxy resins are widely used in high performance composites due to their superior properties and processability compared with other polymer matrices in a wide variety of industries. While the cost of manufacturing has reduced dramatically over the years, the demand for improvements in processability, structural performance, durability and functionality have continued apace [1, 2]. There are many advantageous properties of epoxy networks, but their inherent lack of ductility and low delamination resistance to crack propagation remains [3-5]. Thus there is a need for new resins that are easier and more cost effective to process but also meet improved performance specifications, particularly for resin transfer moulding applications. This study reports on the synthesis of a family of new resin systems that are robust and easy to process and hold the potential for improved fracture properties, without compromising other advantageous properties via their inherent chemical structure rather than the use of an additive [6].

The approach taken here was to synthesise multi aromatic tetra functional epoxy resins (TGAPB) which have 3 aromatic rings linked together via an ether group. The epoxy resins synthesised were N,N,N,N-tetraglycidyl 1,4-bis (4-aminophenoxy) benzene (144 TGAPB), N,N,N,N-tetraglycidyl 1,3-bis (4-aminophenoxy) benzene (134 TGAPB) and N,N,N,N-tetraglycidyl 1,3-bis (3-aminophenoxy) benzene (133 TGAPB), and were each cured with two different anhydride hardeners catalysed with 1 methyl imidazole. It is proposed that these additional linkages afford enhanced ductility to the matrix via additional energy dissipation

mechanisms through increased molecular mobility. As isomers of each other, differing only in their aromatic substitution patterns, variations could be attributed directly to the substitution pattern of the epoxy resin. Great importance also was attached to the quality of the synthesis given the limited information available in the literature on these types of epoxy resins. It is believed that studies in the literature do not address this sufficiently, so this represents the first of its kind where the confidence in the composition of the epoxy resin is very high. The structures of the epoxy resins are shown in Figure 1.
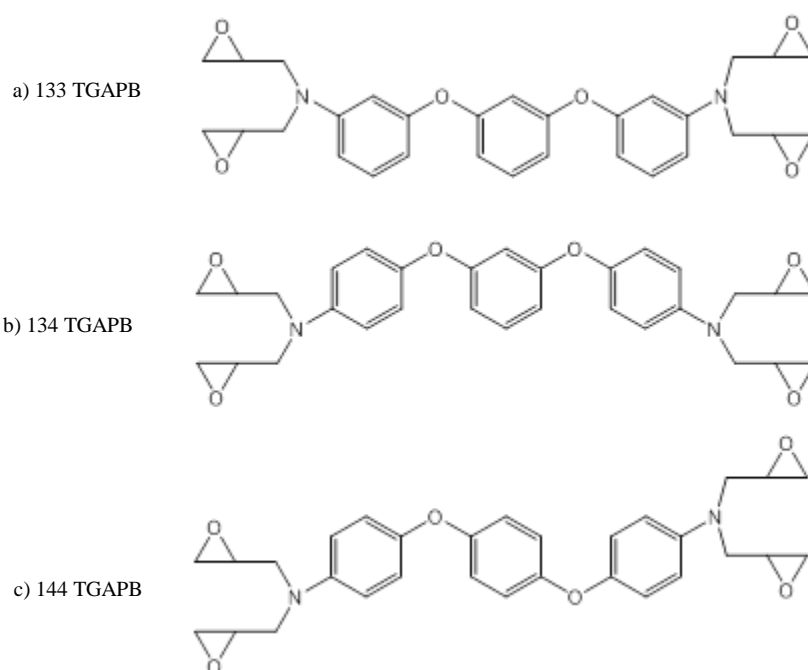

Figure 1 Chemical structures of the epoxy resins used.

2 EXPERIMENTAL

2.1 Materials

Methyl nadic anhydride (MNA), methyl tetrahydrophthalic anhydride (MTHPA), 1 methyl imidazole and epichlorohydrin were obtained from Sigma Aldrich (Japan). The cyclo aliphatic amine bis(4-amino-3-methylcyclohexyl)methane (BMCHA) was obtained from TCI chemicals (Japan). The 1,4-Bis(4-aminophenoxy)Benzene, 1,3-Bis(4-aminophenoxy)Benzene and 1,3-Bis(3-aminophenoxy)Benzene were obtained from Chriskev (USA). The dichloroethane and sodium hydroxide (NaOH) were purchased from Fluka (Japan). All chemicals were used as received. The tetra functional epoxy resins used in this work were synthesised according to the general method described below.

2.2 Synthesis of Epoxy Resins

Bis (aminophenoxy) benzene (5.84g 0.02mole), epichlorohydrin (27.75g, 0.3mole), dichloroethane (50 ml) and lanthanum nitrate (55 mg in 2ml of isopropanol) were placed in a 250ml three neck round bottom flask and refluxed in an oil bath for 90 minutes, then cooled to ~ 70-75°C. NaOH (4.0g, 0.1 mol) was ground into a coarse powder, suspended in iso-propanol and then slowly added to the solution in small portions over 30 minutes. After this, the mixture was stirred at 70-75°C for a further 15 minutes then allowed to cool to room temperature. The salt was removed via filtration, and the solvents and excess epichlorohydrin were removed using a rotary evaporator at ~50°C for 1 – 2 hours. The epoxy resins were analysed using NMR (1H and 13C), HPLC (Altima C18; mobile phase: 55% acetonitrile/water), MS (ESI) and DSC.

2.3 Sample Preparation

Each of the TGABP epoxy resins were cured with either MNA or MTHPA and catalysed using 1-methylimidazole. The composition consisted of 100 phr epoxy, 87 phr anhydride and 0.8 wt% 1 methyl imidazole and mixed at 70°C until fully dissolved. A reference blend of 134 TGAPB cured with 44 BMCHA was also prepared as well as a single highly catalysed formulation of 133 TGAPB and MTHPA catalysed with 8 wt% imidazole. The resin was poured into silicon moulds preheated at 110°C for a minimum of 1 hr then placed in an air circulating oven and cured for 4 hrs at 100°C, followed by 5 hrs at 160°C for the MTHPA formulations and 5 hrs at 190°C for MNA formulations as shown in Table 1.

2.4 Characterisation

Differential Scanning Calorimetry (DSC) was performed using a Rigaku Thermoplus EVO2 in the dynamic and isothermal modes to determine the rates of cure, glass transition temperatures and enthalpies during cure, after cure and after post-cure. Approximately 5-10 mg of sample was placed in an aluminium crucible under a blanket of nitrogen purging at a rate of 20 ml/min. Isothermal curing was performed according to the cure schedules described in Table 1 followed by a re-scan from 50 °C to 300 °C at a rate of 10 °C/min.

Near infrared (NIR) spectra were determined using a Perkin Elmer Spectrometer FTIR in transmission mode. Samples were placed in the beam and measurements were made between 4000 and 7000 cm-1 using an average of 32 scans.

Dynamic Mechanical Thermal Analysis (DMTA) was performed using a Perkin-Elmer SEIKO DMA Diamond II Series. Samples of approximate dimensions 12 mm x 50 mm x 2.8 mm were placed in a dual cantilever fixture and a force amplitude of 20 μm was applied at a frequency of 1Hz. The glass transition temperature of the network was measured by performing a temperature ramp from 50°C to 250°C a rate of 2°C/min

The flexural properties were measured using an Instron 3880 Universal Testing Machine fitted with a 1 kN load cell configured in the three point bending mode. The crosshead rate used was 1 mm/min and testing continued until the sample failed. The span to depth ratio was kept constant at 16:1.

3   RESULTS

3.1 Reaction Mechanism

DSC thermograms during isothermal cure of the epoxy resins with MTHPA and MNA in Figure 2a) and b) respectively, both display autocatalytic behaviour as evidenced by a peak in the heat output followed by a rapid decrease. Comparison of the two hardeners confirms that the MTHPA is more exothermic and faster curing than MNA. The slower cure of MNA is caused by a broad shoulder immediately after the peak, not present in the MTHPA thermograms and likely due to increased competition from the slower etherification reaction [26]. Although the variations between the individual thermograms are modest, reaction rates do exhibit systematic changes controlled by the substitution patterns on the aromatic groups. As can be seen, the 144 TGAPB reacts the fastest, followed by 134 TGAPB and then 133 TGAPB regardless of hardener as is supported by dynamic DSC traces.

Table 1 Description of the resin formulations prepared in this work and their cure profile.

| ID	Epoxy	Hardener	Catalyst	Cure and PC Profile
133-MNA	133TGAPB	MNA	0.8wt% imidazole	4 hrs 100°C/5 hrs 190°C
134-MNA	134TGAPB	MNA	0.8wt% imidazole	4 hrs 100°C/5 hrs 190°C
144-MNA	144TGAPB	MNA	0.8wt% imidazole	4 hrs 100°C/5 hrs 190°C
133-MTHPA	133TGAPB	MTHPA	0.8wt% imidazole	4 hrs 100°C/5 hrs 160°C
134-MTHPA	134TGAPB	MTHPA	0.8wt% imidazole	4 hrs 100°C/5 hrs 160°C
144-MTHPA	144TGAPB	MTHPA	0.8wt% imidazole	4 hrs 100°C/5 hrs 160°C
134-BMCHA	134TGAPB	44BMCHA	-	4 hrs 100°C/5 hrs 190°C
133-MTHPA-8.0	133TGAPB	MTHPA	8.0wt% imidazole	4 hrs 100°C
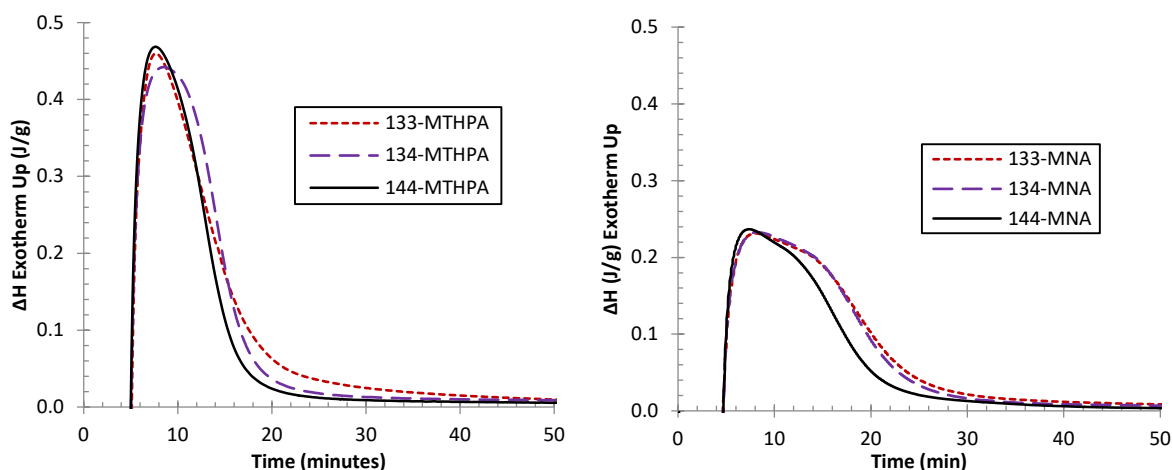
Figure 2. Isothermal thermograms of the TGAPB epoxy resins cured with a) MTHPA and b) MNA cured at 100°C

Representative NIR spectra of the 144-MNA and 144-MTPHA resins, prior to, after cure and post-cure are shown in Figure 5a) and b) respectively. The spectra illustrate the reduction in the size of the epoxide peak at 4550cm^{-1} but also the lack of any of significant changes to the spectra with increasing cure. The only other observation of chemical processes occurring during cure are the removal of hydrogen bonded water groups from the network at 4850 cm^{-1} [1] and the growth of hydroxyl groups at the far end of the spectra at 7000 cm^{-1} arising from epoxide ring opening [2]. The strong and distinct epoxide peak at 4550cm^{-1} therefore, makes it ideal from which to determine the rate of cure using the cure profiles in Table 1.
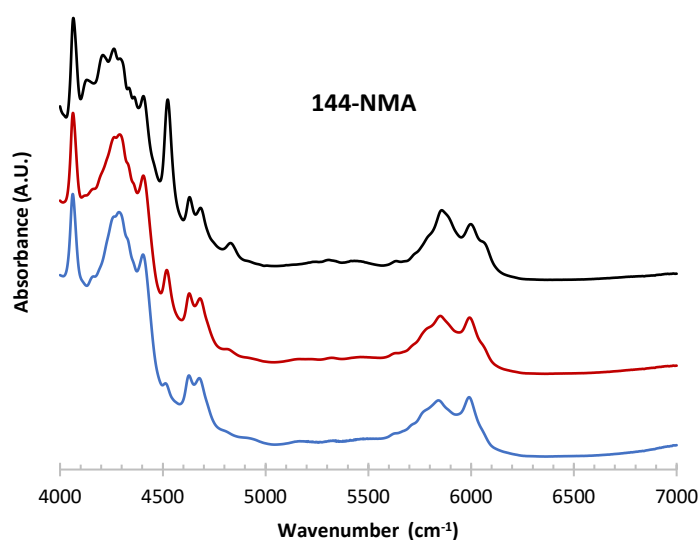

Figure 3. NIR spectra prior to cure, after cure and after post-cure for 144-MNA.

3.2 Network Properties

The Tg of any structural material is a critical parameter as it determines the maximum use temperature. Representative dynamic mechanical spectra of two TGAPB networks are shown in Figure 4 and clearly illustrate the effect of cure and post-cure. The tan δ and storage modulus spectra for 133-MTHPA and 144-MNA reveal a two phase micro-structure consisting of an incomplete network containing unreacted functional groups (low temperature) and a second fully reacted phase exhibiting the ultimate glass transition temperature of the network (high temperature). The tan δ spectra, manifests as two peaks, one smaller the other larger, while in the storage modulus spectra there are two sequential drops in modulus [3-5]. Post-curing removes these smaller transitions to produce a homogenous network, which practically results in a large increase in Tg of the network. In the example shown, the Tg of the as cured 133-MTHPA increased from around 128°C to 181°C after post-cure, while the 144-NMA went from 130°C to 220°C. Given the higher molecular weight between crosslinks, these Tgs compare well with TGDDM Tgs cured with 44 DDS at 254°C [6].
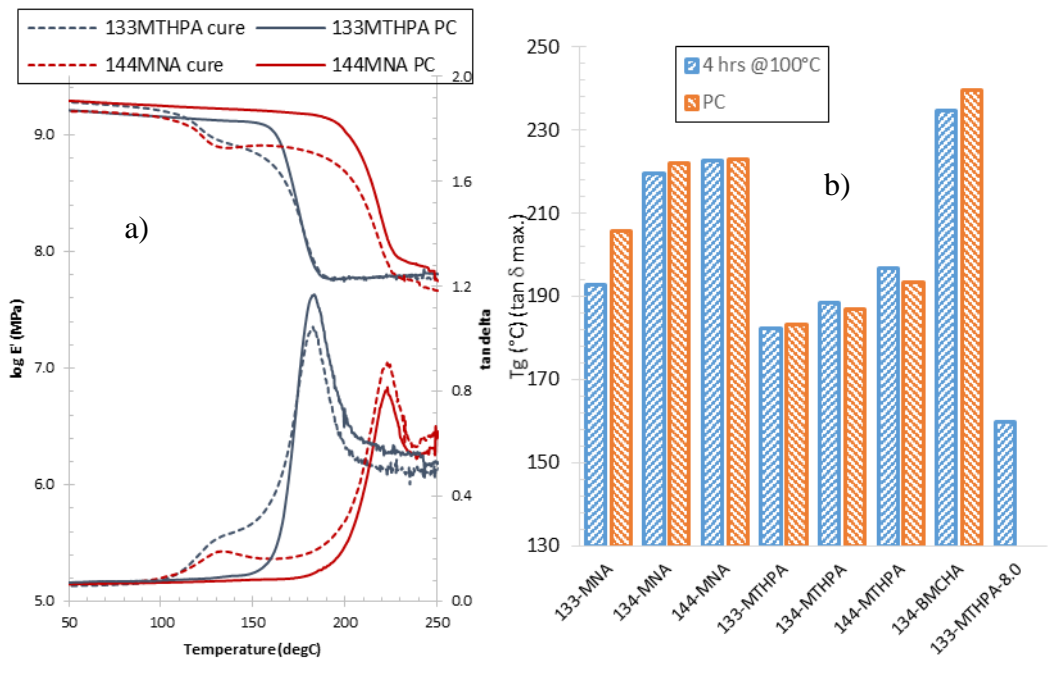

Figure 4 a) DMTA tan δ and storage moduli spectra of TGAPB networks after cure and post-cure. b) Glass transition temperatures as determined by the peak in the tan δ spectra

The flexural properties for the cured and post-cured networks in Table 2 highlight the role of increasing para substitution on the properties of the cured TGAPB networks. The flexural strength increases with increasing para substitution and increasingly so for the MNA networks after post-cure compared with MTHPA. It appears that increasing rigidity increases strength to the overall network. Given its higher molecular weight between crosslinks the flexural strength of the TGAPB networks varies from 93 to 146 MPa, which compares well with TGDDM cured with 4 4 diamino diphenyl sulphone at 138 MPa [6] or with a related cyclic anhydride at 122 MPa [7]. The flexural moduli in contrast, reduces with increasing para substitution and is attributed to the same increasingly rigid backbone creating more free volume reducing packing efficiency of the network allowing increased short range molecular motion, which in turn reduces modulus [8]. Post-curing further reduces the modulus reflecting a self-anti-plasticisation effect as the unreacted functional groups in free volume space are consumed, further increasing free volume, and further reducing modulus [9, 10].

Table 2. Flexural Strength and Modulus of samples after cure and post-cure

ID	Flex. Strength (MPa)		Flex. Modulus (MPa)	
	cure	**PC**	**cure**	**PC**
133-MNA	93.2 (13.8)	114.2 (12.2)	3681.7 (441.9)	3538.6 (209.3)
134-MNA	117.9 (34)	124.6 (15.6)	3496.6 (200.0)	2982.1 (122.1)
144-MNA	101.7 (11.1)	121.9 (11.6)	3389.9 (199.6)	2867.2 (314.8)
133-MTHPA	128.5 (15.4)	127.7 (5.7)	3851.6 (388.8)	3556.2 (89.6)
134-MTHPA	118.5 (5.9)	127.4 (5.4)	3035.7 (145.2)	3035.7 (145.2)
144-MTHPA	146.5 (19.8)	128.3 (7.0)	3421.6 (160.8)	3106.3 (201.1)
134-BMCHA	-	111.4 (3.0)	-	3521.5 (269.9)
133-MTHPA-8.0	109.2 (26.0)	-	3471.0 (210.7)	-

Large increases in the work of fracture in Figure 5 are observed with increasing para substitution and particularly so after post-cure for both the MTHPA and MNA networks. The continued increase provides the first indication that these tri-aromatic epoxy resins may have superior ductility compared with their bi-aromatic analogues. As proposed, their higher molecular weight between crosslinks in addition to an increasing stiffness or para substituted phenyl groups translate into a more ductile polymer without the need for additional modifiers. Importantly, the poorly formed 133-MTHPA-8.0 network and the 133-BMCHA network both appear to be particularly brittle when compared to the 144-MNA and 144-MTHPA networks.
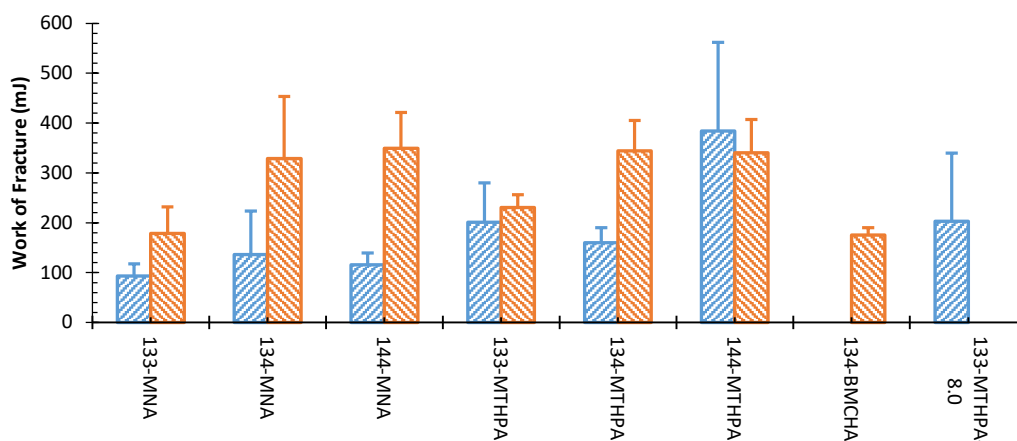
Figure 5 Flexural work of fracture for the TGAPB epoxy networks.

4. CONCLUSIONS

A systemic study of the impact of varying aromatic substitution on the reaction rate and network performance of 3 isomers of a tri-aromatic epoxy resin cured with different anhydride hardeners has been presented here. As the TGABP epoxy resins become more para substituted, from the all meta substituted 133 TGAPB, the meta, para substituted 134 TGAPB and finally to the all para substituted, 144 TGABP the reaction rate and cure conversion increased modestly. This was attributed to the increasing competition from the slower etherification reaction as the network vitrified and the kinetics became diffusion controlled. Increasing para substitution systematically increased the rigidity of the network which increased Tg, strength and ductility. A more rigid, all para substituted network structure within a multi-aromatic highly crosslinked epoxy network therefore shows much promise to either improve or maintain all other thermal and mechanical properties.

5. REFERENCES

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6. ACKNOWLEDGEMENTS