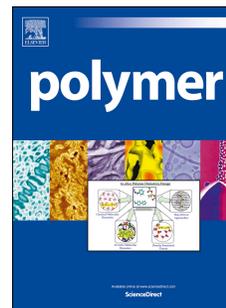


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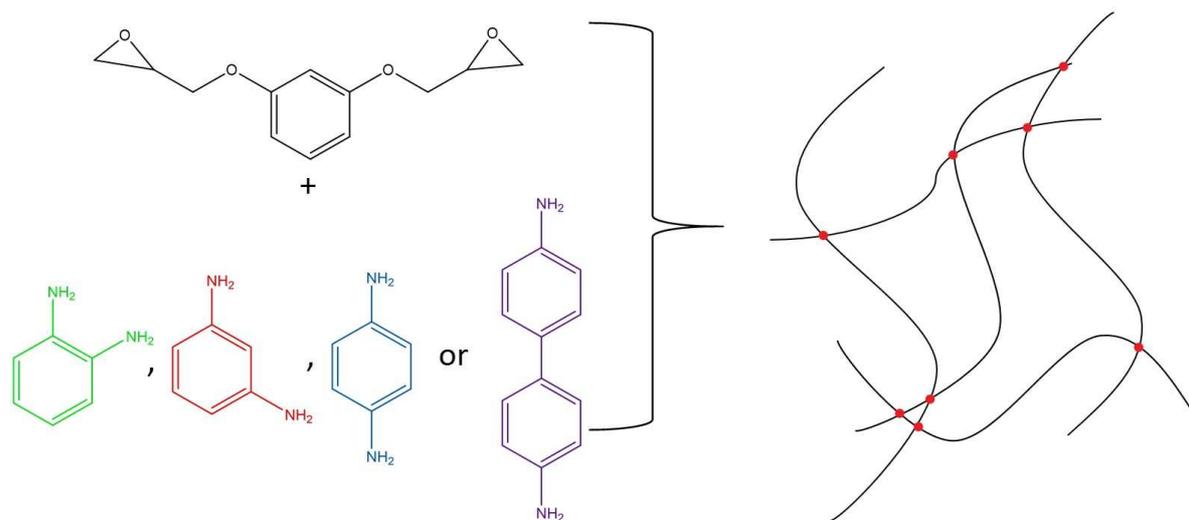
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ACCEPTED MANUSCRIPT

Characterizing the structural formation of epoxy-amine networks: the effect of monomer geometry

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Abstract

We develop an approach for quantifying cure that applies thermodynamic modelling to interpret DSC data that is consistent with solid state NMR. The effect of elements of monomer geometry, such as the angle between functional groups and the distance between them, on curing of epoxy-amine thermosets is explored experimentally using this new technique. The effect of the angle between functional groups on the glass transition temperature of the final cured network is significant. The effect of spacing between functional groups is masked by the rigidity of the spacer. Our approach to interpreting DSC data allows us to detect processes that would have been missed otherwise. This is exemplified by the observation of slow exothermic deterioration reaction. Our NMR results indicate that significant etherification occurs at 140°C, unlike the commonly held belief that it is insignificant at such low temperatures.

1. Introduction

Epoxy-related applications are widespread and include adhesives^{1,2}, composites³ and stereo-lithography 3D printing⁴. However, epoxy systems are particularly difficult to characterise due to their complex network structures resulting from gelation⁵, cross-linking and side reactions⁶, and the variation of reactivity, mobility⁷ and steric hindrance⁸ as the structure evolves. The effect of structure on glass transition are described by the free volume theory using factors such as cross-linking density and chain stiffness.⁹ Navigating this complexity by, for example, separating gelation from vitrification¹⁰, is of great research interest.

Monomer geometry acts as an architectural precursor⁷ for network topology. The evolving network eventually prevents unreacted functional groups from meeting, at a state called the “topological limit”⁷. Two theoretical approaches to describing epoxy systems are consistent with experiments: the lattice simulations reviewed by Oleinik⁸ and the tree-like approach of Dušek⁷ (inspired by Flory^{5,11}). The lattice simulations relate topological parameters to T_g and yield stress⁸, emphasizing the importance of monomer geometry on curing and final network properties.

The literature exploring effects of monomer architecture is rich but still incomplete. Dušek reviews many architectures, including star-like and hyperbranched⁷ molecules. Kim et al.¹² show that bulkier curing agents increase conversion rates. Studies applying theoretical and experimental analysis show that increasing the length of the curing agent molecule between functional groups decreases T_g ¹³. These works consider monomers with multiple geometric differences, including the angle, and length between functional groups and the degrees of freedom of the molecule. Studying each of these geometric differences separately could enrich our understanding of these systems but this work brings challenges: the structure of cured epoxy cannot be simply defined and is only indirectly

measurable and the monomer geometry is so much smaller in scale than the cured network that its effect could be obscured. We believe however that understanding in detail the effect of the monomer geometry is important because it is the basis upon which the overall network structure is built. Here, we study two elements: the angle and the length between functional groups varied without changing the degrees of freedom of the molecule. This is a starting point to understanding those elements of monomer geometry.

The cure of epoxy systems can be characterised by techniques such as titration¹⁴, NIR¹⁵, sol-gel analysis¹⁶ and differential scanning calorimetry (DSC). With DSC data we typically infer percentage of cure via the heat emitted during the exothermic curing⁶. The measured heats are routinely referenced to the maximum experimentally observed heat which is assumed to represent 100% cure^{4,11}. This reference implies that all functional groups have reacted when the experimental maximum heat is achieved. However, it is very likely that unreacted functional groups will remain in the network after reaching the topological limit. We develop an approach to calculate a more accurate percentage of cure referenced to the theoretical maximum heat that would be released if all functional groups were to react.

2. Experimental

2.1 Materials

Resorcinol diglycidyl ether (>96%), *o*-phenylene diamine (99.5%), *m*-phenylene diamine (99.9%) and *p*-phenylene diamine (99%) from Sigma Aldrich; Benzidine (95%) from Toronto Research Chemicals Inc. and dichloromethane (DCM) (99.5%) from Caledon are used without further purification. Resorcinol diglycidyl ether, initially semi-crystalline, is melted at 50°C and cooled to room temperature prior to use. Diamines are manually ground into fine powder using a mortar and pestle. Figure 1 shows the chemical structures of the reagents.

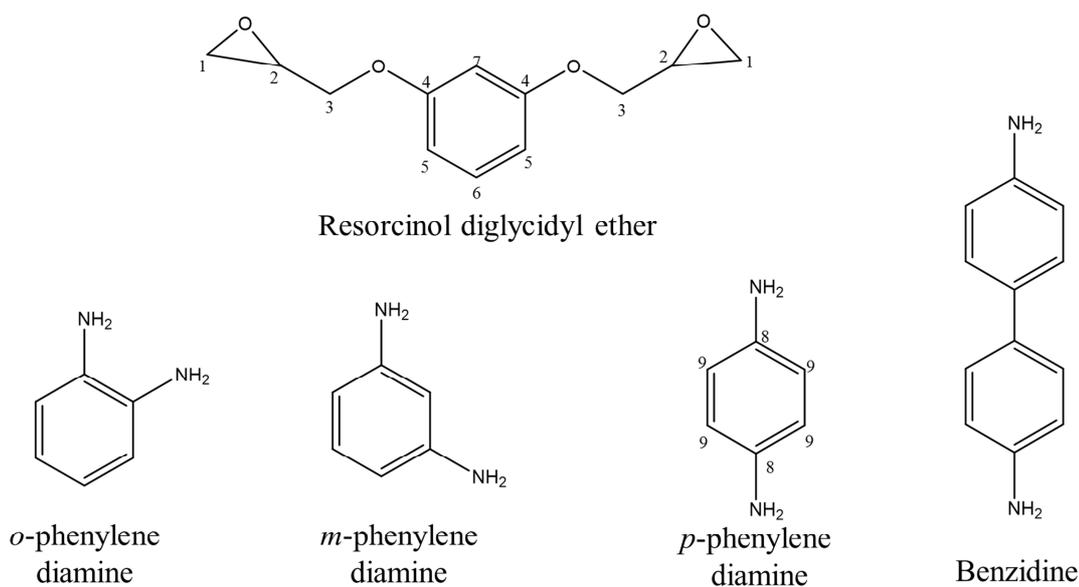


Figure 1. Reagents

2.2 Mixture preparation

Each mixture weighs 1.5 grams in total with a 1:1 molar ratio of epoxide to NH. The epoxy and amine monomers are dissolved separately in DCM (0.5 mL and 4 mL of DCM respectively) in 20 mL vials. The two solutions are combined and stirred for 10 minutes. The mixture is transferred to a 250 mL beaker and placed under 600 mmHg vacuum for 30 minutes to evaporate the DCM.

2.3 DSC observation of curing

DSC experiments are performed on 5-10 mg samples in hermetically sealed pans using a TA Q10 DSC referenced to an empty pan and repeated a minimum of 3 times. Isothermal curing at 140°C is performed followed in some instances by isothermal post curing at a higher temperature. The DSC is heated to 140°C and then the sample cell is loaded and allowed to cure for 2 hours. The T_g is then measured by ramping at 5°C/min between 100°C and 200°C. For experiments with post curing, the 140°C curing procedure is first executed without T_g measurement and then the sample is removed. The DSC is then heated to $T_{g140^\circ\text{C}} + 100^\circ\text{C}$. Here, $T_{g140^\circ\text{C}}$ is the T_g of another sample of the same mixture previously measured after the curing process at 140°C. Finally, the cell is returned to the DSC and post cured for 10 hours. The final T_g is measured by ramping at 5°C/min between 100°C and the post curing temperature.

2.4 Thermogravimetric Analysis (TGA)

TGA experiments are conducted to ensure that post cure temperatures are lower than those for thermal degradation. The TGA samples, 20 mg each, are cured isothermally for 2 hours in an open platinum pan at 140°C and under nitrogen inside a TA Q50 TGA. The temperature is then ramped at 20°C/min up to 1000°C to determine the thermal degradation temperature at which weight loss occurs. The lowest degradation temperature among all systems is 300°C, well above the highest post curing temperature.

2.5 Nuclear magnetic resonance (NMR) experiments

NMR samples are prepared using an epoxy/p-phenylene diamine mixture. About 0.5 g of the mixture is transferred to an open platinum pan and then cured isothermally at 140°C for 2 hours under nitrogen in TA Q50 TGA. The resulting solid film is manually ground using a mortar and submitted to solid-state NMR analysis. After analysis, the same sample is post cured at 223°C for 10 hours and once again submitted to NMR analysis.

All spectra are recorded on a Bruker Avance III HD operating at a frequency of 400.03 MHz for ^1H and 100.60 MHz for ^{13}C using a double resonance 4 mm magic-angle spinning (MAS) probe and a spinning frequency of 12.5 kHz. In order to make peak integration more quantitative, cross-polarization was avoided and all spectra were recorded using a single 3.33 μs long 90° pulse with 85 kHz TPPM ^1H decoupling during acquisition. The recycle delay is set to 30 s and the acquisition time to 15 ms. Spectra were externally referenced with respect to TMS at 0 ppm by setting the downfield peak of adamantane to 38.23 ppm. The spectra were processed using MNova (Mestrelab Research S.L., Santiago de Compostela, Spain).

2.6 Data reporting

Significance is judged using 90% confidence two tailed t-tests except for NMR data as they were not repeated.

3. Methodology

To explore the effects of angle between functional groups, three epoxy-amine systems are studied where the curing agent is either *o*-phenylene diamine, *m*-phenylene diamine or *p*-phenylene diamine. The angle between functional groups in these diamines is 60°, 120° and 180°, respectively. In addition to the geometric difference, there are other differences between the systems including nucleophilicity¹⁷ and solvent effects¹⁸. We separate the two classes of factors using a two-step experiment: curing at a low temperature (incomplete cure) and post curing at a higher temperature (approaching the topological limit and full cure). Molecular structures affect the free volume available presenting as steric hindrance which could be significant enough to be observed in the initial curing step. We assume that factors such as nucleophilicity and solvent have similar effects on the reaction during cure and post cure. The network topology is expected to affect final properties such as T_g only during post curing when the topological limit or full cure is approached giving the ultimate glass transition temperature, $T_{g,\infty}$. One should note that the measured T_g is a single number used to describe a transition that occurs over a range of temperatures.¹⁹

We post cure at $T_{g,140^\circ\text{C}} + 100^\circ\text{C}$ to minimize the difference of the initial molecular mobilities in the systems^{20,21} stemming from the variation in the free volume available due to differences in molecular structures. This ensures that all systems start under the same mobility conditions and have approximately the same rates of polymeric configurational rearrangements and monomer diffusion²², as described by the WLF equation²³. The WLF equation is only valid within a specific temperature range^{23,24}. Therefore, any observed differences in T_g between post cured systems can be attributed to the different angles between amine groups.

We studied an additional benzidine system to observe the effect of the monomer length. This system is compared to that with *p*-phenylene diamine. Benzidine is longer than *p*-phenylene diamine. The overall monomer rigidity is the similar because they have a similar number of degrees of freedom. In this way, we study the effect of length without changing the rigidity of the curing agent.

3.1 Calculation of percentage cure

An approach based on the molar heat of the amine-epoxy reaction at a given curing temperature is introduced to obtain accurate measurements of percent of cure. The molar heat of reaction, h_T , is calculated from the standard heat of formation, h_0 , at 25°C (-120.3 kJ/mol) and the molar heat capacity, C_p , (0.01513 kJ/mol K)²⁵ as shown in Equation 1.

$$h_T = h_0 + C_p \Delta T \quad (1)$$

The theoretical total heat, $H_{max,T_{cure}}$, that would be emitted per gram of mixture if all functional groups were to react at the curing temperature, T_{cure} is calculated using Equation 2:

$$H_{max,T_{cure}} = n_i h_{T_{cure}} \quad (2)$$

where n_i is the initial number of moles of the limiting functional group per gram of mixture. The percent of cure, $\alpha_{T_{cure}}$, can then be estimated using Equation 3:

$$\alpha_{T_{cure}} = \frac{H_{m,T_{cure}}}{H_{max,T_{cure}}} \quad (3)$$

Here, $H_{m,T_{cure}}$, is the total heat measured by the DSC per gram of mixture during cure. This is also used to calculate the number of moles of the limiting functional group that have reacted per gram of mixture, $n_{r,T_{cure}}$, according to Equation 4:

$$n_{r,T_{cure}} = n_i \times \alpha_{T_{cure}} \quad (4)$$

Similarly, Equations 5,6 and 7 are used to calculate the theoretical total heat, $H_{max,T_{post\ cure}}$, that would be emitted per gram mixture if all remaining functional groups were to react at the post curing temperature, $T_{post\ cure}$, the percent of cure due to post curing, $\alpha_{T_{post\ cure}}$, and the number of moles of the limiting functional groups that have reacted during post cure per gram mixture, $n_{r,T_{post\ cure}}$ respectively:

$$H_{max,T_{post\ cure}} = (n_i - n_{r,T_{cure}}) h_{T_{post\ cure}} \quad (5)$$

$$\alpha_{T_{post\ cure}} = \frac{H_{m,T_{post\ cure}}}{H_{max,T_{post\ cure}}} \quad (6)$$

$$n_{r,T_{post\ cure}} = (n_i - n_{r,T_{cure}}) \alpha_{T_{post\ cure}} \quad (7)$$

Here, $H_{m,T_{post\ cure}}$ is the total heat measured by the DSC per gram of mixture during post curing at $T_{post\ cure}$ and $(n_i - n_{r,T_{cure}})$ is the number of moles of the limiting functional group that are left unreacted after the first curing process per gram of mixture.

Finally, the ultimate percent of cure, α_u , is calculated using Equation 8:

$$\alpha_u = \frac{n_{r,T_{cure}} + n_{r,T_{post\ cure}}}{n_i} \quad (8)$$

Each amine-epoxy reaction leads to an epoxy molecule bonded to an N-H group as shown in Figure 2 for resorcinol diglycidyl ether reacting with *p*-phenylene diamine. In this analysis we assume that no etherification occurs, which was previously believed to be reasonable for a curing temperature of 140°C^{25,26}. C_p is dependent on temperature. However, the change of C_p over a range of 100°C is only 10 J/mol K so that effect has been neglected and C_p is assumed to be constant at its value at 25°C.²⁵

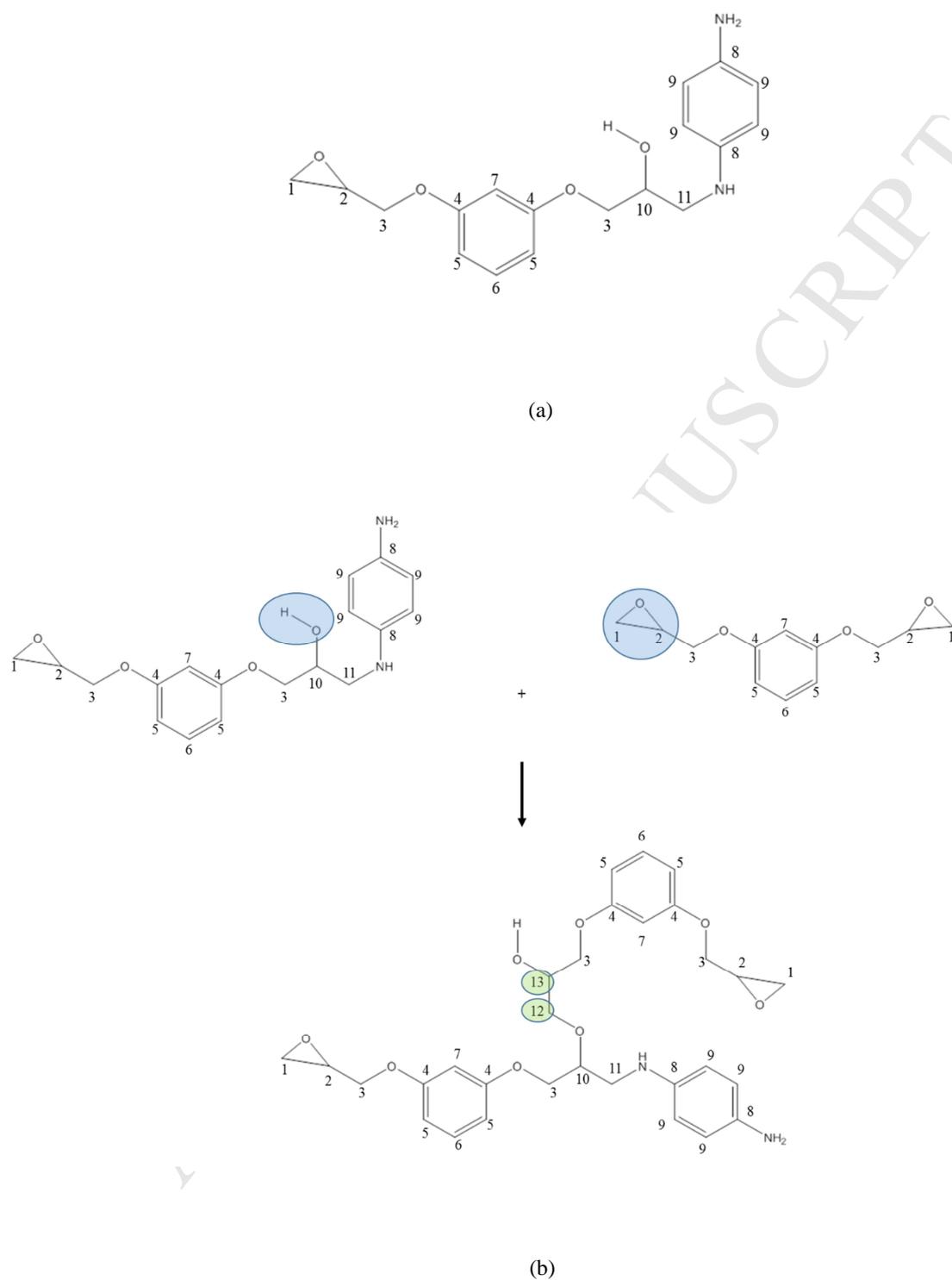


Figure 2. (a) The product of epoxy reacting with *p*-phenylene diamine. (b) Etherification

4. Results and Discussion

Examples of the DSC traces for cure and post cure are shown in Figure 3 a and b respectively. As explained previously the areas under these curves are used in the calculations of percent of cure (Equations 3 and 6).

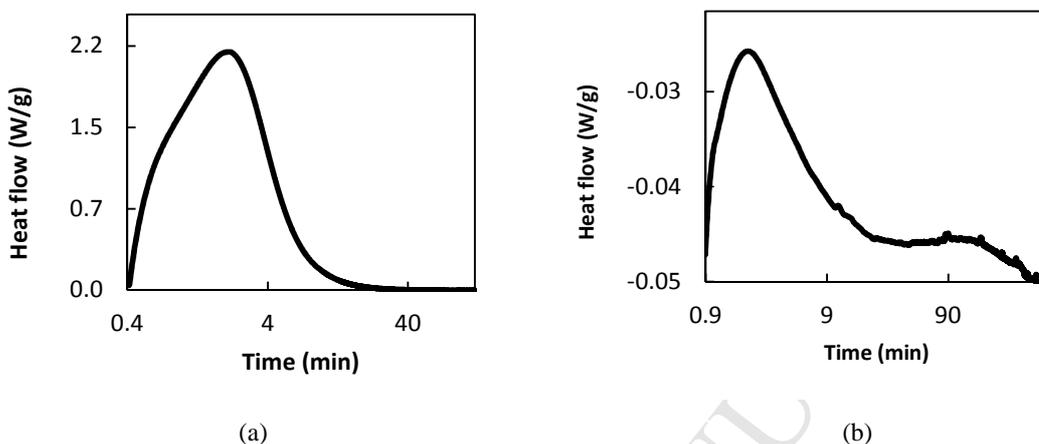


Figure 3. Example DSC traces of: (a) curing at 140°C and (b) post curing of the same sample, resorcinol diglycidyl ether and *o*-phenylene diamine at 229°C. The total heat is the area between the curve and the baseline.

4.1 DSC results

Table 1 summarizes the results of all DSC experiments. The maximum curing rate at 140°C increases with the angle between the amine functional groups. This makes sense because free volume is lowest and steric hindrance is highest when functional groups are closest to each other as in *o*-phenylene diamine and vice versa when they are furthest apart as in *p*-phenylene diamine. After curing, the *o*, *m* and *p*-phenylene diamine systems all have a percent of cure of ~70% and a T_g of ~125°C. We assume that steric hindrance and nucleophilicity affect the curing rate most significantly during post cure as well.

The maximum obtained T_g , where the systems are closest to their topological limits, are 129, 131 and 148°C for *o*, *m*, and *p*-phenylene diamine respectively which occurs after the curing step in the case of *o*-phenylene diamine and after post curing for the other two systems. The differences between their ultimate T_g values are much more significant than those differences between the same systems after only cure. This indicates that the angle between functional groups has a significant effect on the network properties close to the topological limit. A spot check using MDSC (Table S-1) validates the T_g data reported in Table 1 for all three systems.

Table 1: Summary of study of geometric factors, angle and distance between amine functional groups*

		Cure at 140°C				Post cure at T _g 140°C +100°C		
Material and angle between amine groups (°)		α_T	$n_{r,T_{cure}}$	Max. curing rate	T _g	α_U	$n_{r,T_{post\ cure}}$	T _g
		(%)	(mole/g mixture)	(mol/g· min)	(°C)	(%)	(mol/g mixture)	(°C)
		[6]	[6]	[6]	[3]	[3]	[3]	[3]
<i>o</i> -phenylene diamine	60	71 (2)	0.0051 (0.0002)	0.0010 (0.0002)	129 (7)	82 (1)	0.0009 (0.0003)	113 (5)
<i>m</i> -phenylene diamine	120	73 (4)	0.0052 (0.0002)	0.0022 (0.0002)	125 (2)	97 (7)	0.0019 (0.0003)	131 (6)
<i>p</i> -phenylene diamine	180	67 (7)	0.0048 (0.0005)	0.0070 (0.002)	123 (3)	106 (8)	0.0025 (0.0004)	148 (7)
Benzidine	180	76 (3)	0.0048 (0.0002)	0.0011 (0.0001)	154 (3)	110 (7)	0.0025 (0.0006)	175 (10)

*Values inside square brackets are sample size. Values in round brackets are standard deviations.

The *p*-phenylene diamine and benzidine systems illustrate the effect of monomer length. Percentage of cure on a mass basis is not useful for comparing these two systems as the two curing agents have different molecular weights. Therefore, we make the comparison on a molar basis using the η_r parameters. Both systems have the same number of moles of amine-epoxy reaction per gram of sample after curing and after post curing. Here, a mole of reaction is where one mole of epoxide groups reacts with one mole of NH groups. Note that the monomer molecular weight also affects T_g. The T_g of the benzidine system is higher than the *p*-phenylene diamine system after curing and after post curing. The conclusions of previous studies¹³ may indicate that systems with the shorter monomer, *p*-phenylene diamine would have a higher T_g, if those conclusions are generalized.

Note that there are two types of components in the networked systems: rigid benzene rings and flexible chains. There are more benzene rings in the benzidine system compared to that in the *p*-phenylene diamine system. This means that the benzidine system has a larger rigid fraction leading to a higher T_g than that of the *p*-phenylene

diamine system. Also, the packing density in the benzidine system is likely lower than in the *p*-phenylene diamine system due to the increase in length. Thus, there are two competing effects on T_g as the monomer length increases in this case: the increased rigid fraction and the decreased packing density. Soni et al¹³ increased monomer length by increasing flexible chain length. In that case, the increased flexible fraction lead to the observed decrease in T_g . Considering both the observations of the current study and those of Soni et al¹³ we can conclude that length certainly affects packing in an unambiguous way, but its effect on T_g may be primarily determined by the rigidity of the units.

Further, we compare T_g after cure and after post cure in Table 1. T_g increases after post curing for all systems with the exception of that of the *o*-phenylene diamine system which decreases from 129°C to 113°C during post curing. This indicates that the network is deteriorating in the post curing process. The apparent percent of cure of the *p*-phenylene diamine, *m*-phenylene diamine and benzidine systems are higher than 100% after post curing, implying that more heat is emitted than can be accounted for by the curing reaction. Including etherification in our analysis does not explain the excess heat since one mole of etherification emits less heat than one mole of amine-epoxy reaction.²⁴ That is to say that if all epoxide groups left react with alcohol groups instead of amine groups, less heat will be emitted contrary to the excess heat observed. To explore further, a benzidine system is post cured for a much longer time showing a decrease in T_g from 175 (10)°C after 10 hours of post cure to 158°C after post cure for only 34h. Also, the “apparent” percent of cure increases from 110 (7)% after 10 hours of post cure to 136% after post cure for only 34h. These results indicate that an exothermic network deterioration process occurs during post curing leading to erroneously high values for percent of cure and unexpectedly low values of T_g .

For the benzidine system, post curing results in a higher T_g than only curing, meaning that on the face of it one might expect nothing unusual to be happening. In other DSC approaches to determine percent of cure, the measured heat is referenced to the maximum heat obtained. Our approach, which references the theoretical heat of reaction, allows us to unambiguously capture the network deterioration process.

Table S-2 summarizes additional spot check experiments looking at T_g after post curing at $T_{g140^\circ\text{C}} + 100^\circ\text{C}$ for shorter times (10, 30, and 60 minutes) as well as after post curing at $T_{g140^\circ\text{C}} + 50^\circ\text{C}$ for 10 hours. These results indicate that the high post curing temperatures used here are necessary to reach the topological limits. Additionally, they show that both the *m*-phenylene diamine and *p*-phenylene diamine systems continue curing over time, further in the case of the *p*-phenylene diamine system. However, the *o*-phenylene diamine system degrades as soon as 30 minutes into post curing.

The thermal degradation reaction may involve bonds breaking and weaker ones being created, and/or chain rearrangements²⁷. Dyakonov et al²⁸ have found that systems consisting of DGEBA and *p*-phenylene diamine are less thermally stable than those consisting of DGEBA and *m*-phenylene diamine. Here, we see that systems with *o*-phenylene diamine is the least stable of all three isomeric curing agents.

4.2 Solid state NMR results

NMR analysis investigates which reactions are occurring during cure and post cure and verifies our DSC method for determining percent of cure. NMR measurements are conducted on the epoxy monomer, the *p*-phenylene diamine, and the cured and post cured samples. Table 2 shows the resulting chemical shifts and corresponding assignments.

	Chemical shift Epoxy (ppm)	Chemical shift <i>p</i>-phenylene diamine (ppm)	Chemical shift 140°C cured sample (ppm)	Area* 140°C cured sample	Chemical shift 223°C post cured sample (ppm)
C ₁	44.6	-	Missing	-	Missing
C ₂	50.2	-	47.8	0.09	48.7
C ₃	68.9	-	69.4	1	69.4
C ₄	159.8	-	159.7	0.18	159.6
C ₅	107.4	-	111	0.34	111
C ₆	130.1	-	130	0.19	129.7
C ₇	101.9	-	103.8	0.27	104.4
C ₈	-	138.5	140.3	0.18	140.9
C ₉	-	116.6	117	0.41	119.7
C ₁₀	-	-	69.4	1	69.4
C ₁₁	-	-	54.5	0.15	54.7
C ₁₂	-	-	69.4	1	69.4
C ₁₃	-	-	69.4	1	69.4
X ₁	-	-	-	-	146.7
X ₂	-	-	-	-	12.0

* Values are normalized with respect to the value for C₃.

The carbons are numbered in Figures 1 and 2 and assigned according to the literature^{29,30,31} for resorcinol diglycidyl ether, *p*-phenylene diamine and their reaction products. We assume that the C₁ and C₂ chemical shifts are merged somewhere in the middle of their respective chemical shifts in the cured and post cured samples. Two unassigned shifts, X₁ and X₂, that cannot be associated with the curing reactions, appear only in the post cured samples. These shifts fall in the regions of aromatics and aliphatics respectively supporting the hypothesis that another reaction is occurring during post curing as indicated by our DSC calculations and the bimodal DSC trace (Figure 3b). This

degradation reaction may differ from the thermal degradation observed with TGA at 300°C (well above post curing temperatures) or it could be the early stages of such thermal degradation that is yet to produce a significant amount of volatile fragments. It would not likely have been associated with a degradation reaction in DSC studies using the conventional approach to calculating percent of cure.

Percent of cure is calculated from NMR spectra using peak areas which depend on the concentration of the carbons corresponding to those shifts. Below, C_i is the area associated with carbon i.

$$\text{Initial epoxide concentration} \propto C_4 = C_5 = 2C_6 = 2C_7 \quad (9)$$

$$\text{Initial N - H amine concentration} \propto C_9 = 2C_8 \quad (10)$$

$$\text{Unreacted epoxide concentration} \propto \text{Peak}_{47.8}/2 \quad (11)$$

$$C - N \text{ formed due to amine - epoxy reaction concentration} \propto C_{11} \quad (12)$$

$$\% \text{epoxy cure} = \left(1 - \frac{\text{unreacted epoxy}}{\text{initial epoxide}}\right) \times 100\% \quad (13)$$

$$\% \text{amine - epoxy reaction} = \left(\frac{C-N \text{ formed due to amine-epoxy reaction}}{\text{initial N-H concentration}}\right) \times 100\% \quad (14)$$

$$\% \text{Etherification} = \% \text{epoxy cure} - \% \text{amine - epoxy reaction} \quad (15)$$

Percent of cure (Table 3) is calculated with reference to each separate shift in Equations 9 and 10 to obtain the average and standard deviation. Note that the unreacted epoxy concentration is proportional to half of the area of the shift at 47.8 because the area of C_1 equals that of C_2 .

Table 3: NMR calculations of percentages of cure*				
Average area corresponding to epoxide concentration	Average area corresponding to N-H concentration	Epoxy percentage of cure (%)	Amine percentage of cure (%)	Etherification (%)
0.36 (0.15)	0.34 (0.09)	85 (7)	45 (13)	39 (11)

*Values inside round brackets are standard deviations

Based on the data in Table 3 we observe that the average areas representing epoxide concentration and N-H concentration are similar within experimental uncertainty, consistent with the 1:1 molar ratio of the mixtures. The NMR-calculated percent of cure, 85 (7)%, is not far from the DSC-calculated percent of cure, 67 (6)% considering

the uncertainty. However, the DSC value is lower because of the inherent assumption that etherification is insignificant while clearly, 39 (11)% of etherification is significant. Since this result differs from the literature^{25,26}, an additional analysis of the NMR data is performed using the shift at 69.4 ppm. This shift includes carbons 3, 10, 12 and 13. The etherification percentage can be derived from C_{12} which also equals to C_{13} and calculated as follows:

$$OH - epoxy \text{ reaction concentration} \propto \frac{Area_{69} - C_3 - C_{10}}{2} \quad (16)$$

$$C_3 = \text{Average initial epoxide concentration} \quad (17)$$

$$C_{10} = C_{11} \quad (18)$$

$$\%etherification = \left(\frac{OH - epoxy \text{ reaction}}{\text{initial epoxide}} \right) \times 100\% \quad (19)$$

Accordingly, etherification is 68 (27)% which does not contradict the data in Table 3 considering uncertainty.

Further, the heat of reaction approach is used to back-calculate how much heat would be emitted due to the amine-epoxy reaction and etherification, if they occur according to the NMR-calculated percentages in Table 3. Table 4 compares the calculated heats with that measured by DSC. The NMR-back-calculated-heat does not contradict the raw heat data measured with DSC.

Table 4: Comparison between heat emitted according to NMR and DSC Analyses*			
NMR			DSC
Heat emitted from amine (J/g sample)	Heat emitted from etherification (J/g sample)	Total heat emitted (J/g sample)	Average Heat (J/g sample)
391 (109)	290 (84)	681 (138)	573 (59)

*Values inside round brackets are standard deviations

4. Conclusions

Several challenges in the studying of the effects of monomer geometry on thermosetting experimentally are addressed here. The complexity of the system is simplified by separating the geometric or topological factors from the other effects using a two-step experiment: curing and post curing. Steric hindrance, nucleophilicity and solvent effects affect the curing rate much more significantly than T_g and the percent of cure after the first step. They are assumed to have the same effects during post curing. Geometric effects are only expected to be measurable close to

the topological limit during post curing. A WLF approach is used to influence available free volume and keep initial mobility effects similar in all systems during post curing. The maximum obtained T_g , where the systems are closest to their topological limits, are 129, 131 and 148°C for *o*, *m*, and *p*-phenylene diamine respectively. Additionally, the systems differ in thermal stability as the *o*-phenylene diamine is the least stable and degrades after only 30 minutes at the post curing temperature. We conclude that the observed differences between the three systems in their network properties close to the topological limit are due to the angle between functional groups.

It is more difficult to study the effect of length as a geometric variable because the rigid and flexible fractions of the monomers have a critical role. Increasing the length either comes with an increase in the rigid fraction, increasing T_g , or an increase in the flexible fraction, decreasing T_g . Increasing the length also reduces the packing density which decreases T_g . It appears to be difficult to separate all other effects to explore this experimentally. Studies of the networks at the topological limit will provide a more detailed understanding of the effect of monomer geometry on the final network properties and a useful model for the design of epoxy-based materials.

The approach used to calculate the percent of cure based on the theoretical heat of reaction leads to the association of the observed extra processes to a degradation reaction that might have otherwise been missed or not associated with a degradation reaction. Eventually, this work may lead to an understanding of the nature of the degradation as well as allowing the exact determination of curing conditions under which such networks could reach the topological limit. More significantly, the proposed approach of using heats of reaction is consistent with NMR analysis. Finally, we show that there is significant etherification in our systems even at temperature as low as 140°C. We hope that this finding invites future work to determine more accurately the enthalpy and heat capacity of the amine-epoxy reactions as most previous work does not account for etherification. We have shown that NMR characterisation is required to verify if etherification is occurring.

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Highlights

- Effect of basic monomer geometry on T_g and degradation is explored.
- DSC technique accurately measures cure and detects other exothermic processes.
- Unexpected large amount of etherification observed at low curing temperatures.