Effects of epoxy/hardener stoichiometry on structures and properties of a diethanolamine-cured epoxy encapsulant

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Abstract. For the epoxy encapsulant cured by diethanolamine, optimal epoxy/hardener stoichiometry could hardly be predicted due to the complex curing mechanisms. In this paper, the influences of stoichiometry were investigated by FTIR, DMA and tensile testing. The results showed that stoichiometry has a dominating effect on both $T_g$ and tensile properties of the cured epoxy. The largest $T_g$, highest crosslink density as well as excellent ductility appeared in epoxy encapsulant cured with 14 wt% diethanolamine. When the content of diethanolamine was lower than 14 wt%, epoxy encapsulants showed smaller glycidyl conversion even with long-duration post-cure. Larger tensile strength and modulus were also observed in the glycidyl-rich epoxies, which could be explained by anti-plasticization effect. The amine-rich epoxy, however, had extremely high glycidyl conversion and presented brittle tensile behavior. A diethanolamine content of 12-14 wt% for the epoxy encapsulant is suggested to obtain optimal thermal and tensile properties.

1. Introduction

Epoxy resins have broad applications in the impregnations, potting and encapsulations of high-voltage electronics, primarily due to their facile preparation, excellent thermal/mechanical properties and remarkable electrical insulation [1]. The resin/hardener ratio, also named stoichiometry, is the basis of an epoxy encapsulant formulation, which plays a dominating role in determining the properties of the cured resin [2, 3]. Particularly, stoichiometry in the interfacial area tends to deviate from bulk epoxy [4], affecting distinctly the interfacial performance of the epoxy encapsulants.

For typical epoxy hardeners, such as amines and anhydrides, a stoichiometric formulation could be readily predicted from the amount of reactive hydrogen of the hardener, which usually presents maximum $T_g$ [5,6]. However, stoichiometric formulations do not necessarily guarantee optimal mechanical properties. Meyer et al associated improved fracture toughness and higher modulus of epoxy with a stoichiometric offset with excess glycidyl, taking 4,4’-diaminodiphenyl sulfone as the curing agent [5]. More ductile tensile behavior and enhanced impact strength have been reported in the amine-rich epoxy resins cured by triethylene tetramine [7].

Diethanolamine (DEA) has been widely used as epoxy hardener, which has the merits of long induction period, low curing exotherm and small curing stress [8]. The multiple hydroxyls in DEA also enhance the adhesion of epoxy to other materials. Unlike typical amine-based hardeners, DEA cures epoxy with complex mechanisms that mainly rely on self-catalyzed condensations and homopolymerizations, making direct prediction of stoichiometry impossible. Thus there is a demand to
experimentally acquire the stoichiometric formulation of DEA-cured epoxy encapsulants and establish the stoichiometry-structure-property correlations.

In this paper, stoichiometry effect upon DEA-cured epoxy encapsulant was studied through analyzing structural, thermal and tensile properties. The epoxy resin that yielded the highest $T_g$ and crosslink density was considered to be the stoichiometric formulation. The abundance of glycidyl content was found to be essential in obtaining epoxy resins with optimized thermal and tensile properties. A proper range of DEA content for epoxy encapsulant was suggested according to the stoichiometry effect.

2. Experimental

2.1. Materials and sample processing
A diglycidyl ether bisphenol-A (DGEBA) based epoxy precursor (WSR 618) was purchased from Nantong Xingchen Synthetic Material. DEA was purchased from Aladdin. The chemical structures of DGEBA and DEA are shown in figure 1. To prepare epoxy encapsulants, DEA was mixed with DGEBA at fixed ratios shown in table 1, and the mixture was then degassed, casted into aluminum molds and cured.

2.2. Instruments and characterizations
Attenuated total reflectance Fourier transform infrared (ATR-FTIR) analysis was performed on a FTIR spectrometer (Nicolet 6700) equipped with a SMART ITR accessory.

Dynamic mechanical analysis (DMA) was performed on a DMA Q800 (TA Instrument) using three point bending clamp. Measurements were conducted over a temperature ranging from -100 °C to 150 °C at a heating rate of 3° C min$^{-1}$ and a frequency of 1.0 Hz.

Bulk density was measured at 25°C using a Mettler-Toledo XS204 balance adapted with a density determination kit.

Tensile tests were performed using dumbbell-shaped samples according to ASTM D638-96 on a MTS 800 instrument equipped with a 10 kN load cell. A crosshead speed of 5 mm min$^{-1}$ was used for all measurements.

3. Results and discussion

3.1. Reaction mechanism and ATR-FTIR analysis
It is known that both secondary amines and hydroxyls in DEA are reactive to glycidyls, while the reactivity of amine is much higher than that of hydroxyl [8]. As a result, reactions between DGEBA and DEA virtually occurred in a two-step manner. As shown in figure 1, Amine-glycidyl condensations takes place soon after mixing DEA with DGEBA, wherein adducts are generated

| Sample | DEA content (wt%) $^a$ | Molar ratio of DEA/DGEBA | Cure schedule         |
|--------|-----------------------|--------------------------|-----------------------|
| D08    | 8                     | 0.15:1                   | 65 °C (10 h) + 90 °C (32 h) |
| D10    | 10                    | 0.18:1                   | 65 °C (10 h) + 90 °C (16h) |
| D12    | 12                    | 0.22:1                   | 65 °C (10 h) + 90 °C (16h) |
| D14    | 14                    | 0.26:1                   | 65 °C (10 h) + 90 °C (16h) |
| D16    | 16                    | 0.30:1                   | 65 °C (10 h) + 90 °C (16h) |
| D18    | 18                    | 0.33:1                   | 65 °C (10 h) + 90 °C (16h) |
| D20    | 20                    | 0.37:1                   | 65 °C (10 h) + 90 °C (16h) |

$^a$Based on the weight of DGEBA.
containing tertiary amines with glycidyl ends (namely DEA-endcapped DGEBA). Crosslinked networks could only be formed through etherifications, including tertiary-amine-catalyzed hydroxide-glycidyl condensations and epoxy homo-polymerizations.

![Schematics of DEA/DGEBA curing reactions.](image)

**Figure 1.** Schematics of DEA/DGEBA curing reactions.

![ATR-FTIR spectra of DEA/DGEBA before/after cure (a) and with varying stoichiometry (b).](image)

**Figure 2.** ATR-FTIR spectra of DEA/DGEBA before/after cure (a) and with varying stoichiometry (b).

**Table 2.** Normalized absorptions at 3400 cm\(^{-1}\) \(A_{3400}\) and 1109 cm\(^{-1}\) \(A_{1109}\) in ATR-FTIR.

| Sample | \(A_{3400}/A_{1509}\) | \(A_{1109}/A_{1509}\) |
|--------|-----------------------|-----------------------|
| D08    | 1.27                  | 0.39                  |
| D10    | 1.36                  | 0.40                  |
| D12    | 1.63                  | 0.42                  |
| D14    | 1.67                  | 0.47                  |
| D16    | 2.24                  | 0.43                  |
| D18    | 2.47                  | 0.41                  |
| D20    | 2.65                  | 0.42                  |

ATR-FTIR spectra taken before and after cure in figure 2(a) showed three major absorption changes at 3400 cm\(^{-1}\), 1109 cm\(^{-1}\) and 913 cm\(^{-1}\), which denoted the accumulation of hydroxyls in hydrogen-bonding states, generation of aliphatic ethers, and depletion of glycidyls. These absorption signals also changed when adjusting DEA content as shown in figure 2(b). All the characteristic absorption peak areas were normalized to the peak area of the aromatic ring at 1509 cm\(^{-1}\) \(A_{1509}\) to make quantitative comparisons. As listed in table 2, the normalized absorption around 3400 cm\(^{-1}\)
enhanced with increasing DEA content, indicating an increment of hydroxyl pendants with DEA/DGEBA stoichiometry. The normalized absorption at 1109 cm$^{-1}$ reached maximum in D14, implying a most abundance of ether linkage in the formulation. Glycidyl conversion derived from the absorption peak at 913 cm$^{-1}$ was taken as a measure for the cure degree of each epoxy formulation (table 3). Both D08 and D10 had a relatively-low glycidyl conversion around 90%. It should be noted that D08 epoxy underwent a long-duration post-cure treatment, otherwise the resin would be extremely brittle and could hardly be detached from the casting mold. Apparently, the deficient amount of DEA in D08 hindered the efficient construction of the epoxy network. Under the same curing schedule, increasing DEA content led to much higher glycidyl conversion in the cured epoxy resin. In the case of D18 and D20, no glycidyl signals could be detected from ATR-FTIR, indicating a complete cure.

| Sample | $T_g$ (°C) | $E_{T_g,50}$ (MPa) | $M_c$ (g·mol$^{-1}$) | $n$ (mol·m$^{-3}$) | $A_{beta}$ (min)$^a$ | Glycidyl conversion (%) | Density (g·cm$^{-3}$) |
|--------|-----------|---------------------|----------------------|---------------------|-----------------|------------------------|------------------|
| D08    | 80        | 17.4                | 693                  | 1730                | 0.1996          | 89.2                   | 1.195            |
| D10    | 79        | 16.3                | 738                  | 1625                | 0.3026          | 90.6                   | 1.195            |
| D12    | 91        | 22.8                | 544                  | 2207                | 0.4803          | 97.2                   | 1.195            |
| D14    | 93        | 24.8                | 502                  | 2389                | 0.5614          | 98.6                   | 1.195            |
| D16    | 90        | 21.2                | 583                  | 2057                | 0.6773          | 99.8                   | 1.196            |
| D18    | 77        | 19.1                | 627                  | 1913                | 0.7553          | 100                    | 1.197            |
| D20    | 72        | 13.8                | 857                  | 1400                | 0.6711          | 100                    | 1.198            |

$^a$ Area of beta-relaxation peak obtained from tanδ curve of DMA.

### 3.2. DMA study

![Figure 3](image_url)

**Figure 3.** Storage modulus (a) and tanδ (b) curves for stoichiometric and off-stoichiometric DEA/DGEBA epoxies.

For the stoichiometric and off-stoichiometric epoxies, evolutions of storage modulus and tanδ as a function of temperature were studied by DMA, as shown in figure 3. It appears that $T_g$ was significantly affected by stoichiometry, as shown in table 3. The maximum $T_g$ appeared in D14, and the $T_g$s of D12 and D16 were only slightly lower than that of D14. However, $T_g$ dropped sharply when the DEA content decreased to below 12 wt% or increased to above 16 wt%. The smaller $T_g$ in D08 and D10 should be due to the lower glycidyl conversion and subsequent inefficient construction of crosslink...
network. The smaller $T_g$ in D18 and D20, which had extremely high glycidyl conversion, might be related to complex reaction mechanisms as discussed later.

In figure 3(a), no matter under $T_g$ or in the rubbery state, the storage modulus varied with DEA/DGEBA stoichiometry. According to previous reports [2, 9], the apparent crosslink densities ($n$) and the molecular weight between crosslinks ($M_c$) of epoxies could be estimated from the rubbery modulus at $T_g + 50 \, ^\circ\text{C}$ ($E'_{T_g + 50}$) using the following equation:

$$E'_{T_g + 50} = 3nRT = 3q\rho RT / M_c$$

(1)

Where $q$ is front factor and is usually taken as 1 when crosslinks of the networks are mobile, $\rho$ is density, and $R$ is gas constant. It should be emphasized that equation (1) is an empirical equation and only provide an approximate trend for comparative evaluation [5].

The estimation results of $M_c$ and $n$ are also listed in table 3. As the DEA content increased from 8 wt% to 20 wt%, $M_c$ changed in a reverse manner to $T_g$. The highest crosslink density as well as the lowest $M_c$ also occurred in D14 epoxy. Therefore, D14 should represent the stoichiometric formulation for DEA/DGEBA encapsulant.

Broad beta-relaxations were observed for all formulations (insert in figure 3(b)), typically in the temperature range between -80 °C and 20 °C. Particularly, both width and height of the beta-relaxation peak increased monotonously with the DEA content. The origins of beta-relaxation in epoxy are complex, potentially involving motions of hydroxylether, flips of diphenolpropane ring and even motions of crosslinks [10].

3.3. Interpretation of crosslink structures

Based on the above analysis, the network structure evolution of epoxies with varying DEA/DGEBA stoichiometry was depicted in figure 4.

![Figure 4](image-url)

**Figure 4.** Schematic illustration of network structures in stoichiometric and off-stoichiometric states.

At low DEA content, the formulation has less amount of DEA-endcapped DGEBA adducts and more remnant glycidyl pendants. According to literatures [11], both tertiary amines and secondary hydroxyls formed in DEA-endcapped DGEBA have acceleration effects on epoxy etherifications. Etherification reactions are thus less favorable at low DEA content, wherein an epoxy network with smaller glycidyl conversion and lower crosslink density is generated, as has been proved by DMA and ATR-FTIR.

As the DEA content increases, increment of crosslink density is expected due to the abundant tertiary amines and hydroxyls. Maximum $T_g$ appeared in D14, the stoichiometric DEA/DGEBA formulation, where the molar ratio between DEA-endcapped DGEBA and intact DGEBA was about 1. Under this condition, the number of hydroxyls (including the primary hydroxyls from DEA and the
secondary hydroxyls in endcapped DGEBA) approximates the number of residual glycidyls (including intact DGEBA and endcapped DGEBA).

At high DEA content, the amine-glycidyl condensation consumes more glycidyls to form DEA-endcapped DGEBA adducts. The crosslinking reaction rate is increased due to the further increased concentrations of tertiary amines and hydroxyls. The crosslink density is decreased, however, primarily due to the lack of abundant glycidyls for chain growth. Another possible reason is that undesirable chain transfers and chain terminations in epoxy homo-polymerization become more favorable in the presence of high amount of tertiary amines [12], which also hinders chain propagations.

3.4. Analysis of tensile properties

![Stress-strain curves (a), tensile strength (b), Young’s modulus (c) and strain at break (d) of DEA/DGEBA as a function of DEA content.](image)

Figure 5. Stress-strain curves (a), tensile strength (b), Young’s modulus (c) and strain at break (d) of DEA/DGEBA as a function of DEA content.

The stress-strain curve shapes of DEA/DGEBA epoxies also changed with stoichiometry, as shown in figure 5(a). The glycidyl-excess formulations exhibited yielding under large tension, resulting in higher elongation at break. Both maximum tensile strength and maximum Young’s modulus appeared in the DEA-deficient D08, as shown in figure 5. The high modulus in epoxies with lower $T_g$/crosslink density has been explained by the concept of free volume [5]. The bulk densities of DEA/DGEBA epoxies were herein measured as a coarse measure of room temperature free volume [4], which only showed slightly variations among different formulations (table 3). It seemed that the tiny density variations in epoxies were too small to take charge of such a distinct difference in mechanical behavior. The so-called anti-plasticization effect reported by Won et al in amine-cured epoxy [13,14] provides a reasonable explanation. Anti-plasticization effect appears as a simultaneous decrease of modulus and increase of $T_g$, and had been associated with the local mobility of crosslinked chains [13]. In the case of D08 and D10, epoxy conversions were only around 90%. The pendant glycidyl chain ends could have played the role of internal plasticizer by reducing crosslink density. Similar to the results of Won [13], smaller beta-relaxation intensity occurred in the glycidyl-excess epoxy, as shown in figure 3(b). The lower intensity of high temperature part in beta-relaxation peak in D08 and D10 suggested a suppressed short-range molecular motion by the antiplasticizer. We therefore ascribe the ductile
tensile behavior and higher Young’s modulus of the glycidyl-rich resins to the anti-plasticization effect.

Epoxies with DEA-excess formulations, on the contrary, fractured in a brittle manner under tension. As a result, lower tensile strength and ultra-small elongation at break were obtained for all the DEA-excess epoxies (Figure 5). Previous studies on aromatic amine-cured epoxies have suggested that extremely-high glycidyl conversion in the fully-cured epoxy leads to decrease of epoxy toughness [15]. In addition, faster crosslinking reaction rate and undesirable chain transfer/terminations in amine-rich formulations were reported to induce local stress buildup [5], inhomogeneity [12] and micro-defects, which could also cause reduction of the ductility and toughness. As a matter of fact, notable defects in DEA-excess epoxies were observed when applying epoxy resin of large quantity to potting applications. Thus both the high glycidyl conversion, as well as network inhomogeneity in DEA-rich epoxies could contribute to the decreasing tensile strength and brittle tensile fractures.

4. Conclusions
This paper demonstrates that DEA/DGEBA stoichiometry has profound influence on both the structures and the thermal/mechanical properties of epoxy encapsulants. The epoxy possessed highest $T_g$ and largest crosslink density when DEA content reached 14 wt%, while either increasing or decreasing DEA content resulted in reducing of $T_g$. All the DEA-deficient formulations showed smaller glycidyl conversion in FTIR, weaker beta-relaxation in DMA, and larger strength and modulus in tensile testing, which was in support of an anti-plasticization effect of glycidyl pendants in epoxy network. Brittle tensile behavior was observed in the DEA-rich formulations, which was ascribed to the ultra-high glycidyl conversion and network inhomogeneity caused by the complex curing mechanism. The present results suggested an optimal DEA content of 12~14 wt% for higher $T_g$ and better tensile properties of the epoxy encapsulant.

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