

The Effect of Steric Hindrance on Physical Properties in an Amine-Cured Epoxy

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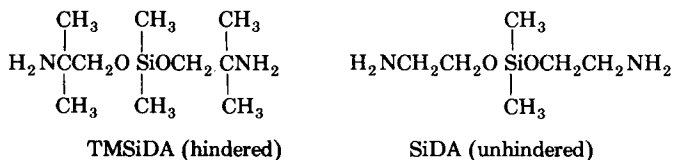
Synopsis

A pair of aliphatic amines were synthesized in order to study the effect steric hindrance has on the physical properties of an amine-cured epoxy resin. The hindered amine (TMSiDA) has NH_2 groups that are obstructed by the presence of adjacent methyl groups while the unhindered amine (SiDA) does not contain any NH_2 steric hindrance. DGEBA cured with TMSiDA is less dense, absorbs less moisture, and has a higher T_g than does SiDA/DGEBA. Torsional pendulum results show that TMSiDA/DGEBA has a slightly higher rubbery modulus and a secondary transition at a lower temperature than DGEBA cured with SiDA. Activation energies for the secondary transition were determined for TMSiDA/DGEBA and SiDA/DGEBA and are 19 and 14 kcal/mol, respectively.

INTRODUCTION

Epoxy resins cured with amines are widely used in composites, adhesives, and coatings. Charlesworth¹ found that the reaction rate of polymerization (k_1) and crosslinking (k_2) in an aliphatic amine/epoxy resin system are about the same. However, in the case of sterically hindered amines,^{2,3} the reaction rate of polymerization is many times faster than crosslinking, which allows relatively complete separation of these two reactions. Thus, a stable linear epoxy polymer can be prepared and then crosslinked at a later time. The physical properties and morphologies of epoxies cured with hindered and unhindered amines may be different because of their inherent reactivity differences. Rinde et al.² for example, reported that both the impact strength and glass transition temperature of an epoxy resin cured with the sterically hindered aliphatic amine 2,5-dimethyl-2,5-hexane diamine (DMHDA) increased markedly. However, a more recent study by Mijovic et al.⁴ has shown that the impact strength is about the same for both hindered (DMHDA) and unhindered amine (diethylene triamine) cured epoxies.

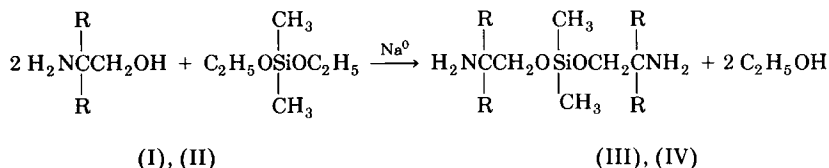
Previously, we reported⁵ on the reaction kinetics of phenylglycidyl ether with a hindered/unhindered amine pair based on the following structures:



In this paper we will report on the effect that structural differences between SiDA and TMSiDA have on the density, moisture absorption, glass transition temperature, and dynamic mechanical properties of a cured epoxy.

MATERIALS

SiDA and TMSiDA were synthesized for this work according to the procedure of Larsson.⁶ The generalized reaction scheme can be written as follows:



When R = H, then (I), (III = SiDA), and, when R = CH₃, then (II), (IV = TMSiDA).

The amines were fractionated through a 24-in. spinning band distillation column that had a 200 theoretical plate rating. The collected fractions were analyzed by gas chromatography using a thermal conductivity detector and were refractionated until a purity of 96–98% was obtained. The infrared spectra of TMSiDA and SiDA contained absorption peaks which were consistent with the indicated structures. Mass spectral analysis gave molecular weight values of 178 (theory SiDA 178.3) and 234 (theory TMSiDA 234.4). Elemental analysis gave the following results:

ANAL. SiDA—C₆H₁₈N₂SiO₂: Theory: C, 40.42%; H, 9.95%; N, 15.71%; Si, 15.75%. Found: C, 40.45%; H, 9.95%; N, 15.57%; Si, 15.89%; C, 40.77%; H, 9.88%; N, 15.62%; Si, 15.62%. TMSiDA—C₁₀H₂₆N₂SiO₂: Theory: C, 51.24%; H, 11.18%; N, 11.95%; Si, 11.98%. Found: C, 51.13%; H, 10.94%; N, 11.83%; Si, 11.77%; C, 51.30%; H, 10.81%; N, 11.86%; Si, 11.84%.

The diglycidyl ether of bisphenol A used in this study was DER 332 which had an epoxy equivalent weight of 174. Specimens were cured by heating at 50°C overnight followed by 100°C for 3 h.

EXPERIMENTAL

Density

Density measurements were made on samples which nominally measured 1.3 cm H × 1.9 cm D according to ASTM method D792.

Moisture Absorption

Bar samples which nominally measured 3.5 × 1.2 × 0.3 cm were placed in a sealed desiccator over a saturated Na₂Cr₂O₇ · H₂O at ambient temperature. The relative humidity obtained from this bath was 50–55%. The samples were weighed immediately after final cure at 100°C and placed in the desiccator. Periodically the samples were removed and reweighed, and the percent moisture gain was determined.

Glass Transition Temperature by DSC

Glass transition temperature measurements were made using a DuPont 9900 thermal analyzer in conjunction with the 910 differential scanning calorimeter (DSC) module. The programmed heating rate was 10°C/min, and the samples were scanned from 0 to 150°C in an argon atmosphere.

Dynamic Mechanical Properties

Dynamic mechanical measurements were made using a torsional pendulum following the design of Nielsen.⁷ For this measurement, the test specimens which were approximately $5 \times 1.2 \times 0.06$ cm in size, are manually excited into free oscillations, where the frequency of oscillation varies from 0.8 Hz at 70°C to 1.1 Hz at -160°C. These oscillations are digitized and stored by a waveform recorder (Hewlett-Packard 7090A) as digitized damped sine waves. Logarithmic decrement can be calculated from the relationship:

$$\Delta = (1/n)\ln[A(r)/A(r + n)] \quad (1)$$

where $A(r)$ is the amplitude of a reference peak and $A(r + n)$ is the peak amplitude n cycles later. Shear modulus (Pa) is calculated from the relation

$$G = 0.235 LI/CD^3\mu P^2 \quad (2)$$

where L is the length (cm) of the specimen between the clamps, C is the width (cm) of the specimen, D is the thickness (cm) of the specimen, I is the moment of inertia (g cm^2) of the oscillating system, μ is a shape factor, and P is the period (s) of the oscillations.

An automated data analysis was used to determine loss factor and shear modulus. A nonlinear least-squares method⁸ was used to determine a six-parameter equation which is assumed to represent the digitized data. The equation is of the form:

$$\theta = \theta_0 \exp(-\alpha t) \cos(\omega t - \phi) + Dt + B \quad (3)$$

where θ_0 is the amplitude at $t = 0$, α is the damping coefficient, ω is the angular frequency (rad/s), ϕ is the phase angle, D is the drift coefficient, and B is the DC offset voltage. D is related to the drift in the output voltage of the linear voltage differential transformer used in converting the mechanical motion of the pendulum to an electric signal. B is the charging voltage, approximately 7-8 V across the linear voltage differential transformer. Then the loss factor is determined from the damping coefficient as follows:

$$\Delta = \alpha P \quad (4)$$

where $P = 2\pi/\omega$.

Measurements were from -160 to 80°C. Samples were maintained at equilibrium temperature for a period of 20 min prior to collection of data.

RESULTS AND DISCUSSION

Density

The results of density determinations for TMSiDA/DGEBA, SiDA/DGEBA, and three equivalent weight fraction mixtures of TMSiDA/SiDA with DGEBA are presented in Figure 1. The SiDA cured epoxy resin (1.183 g/cm^3) is denser than the TMSiDA/DGEBA epoxy (1.152 g/cm^3). This 2.6% difference in density can be explained by the fact that TMSiDA, which contains bulky methyl groups, creates more internal free volume than does the

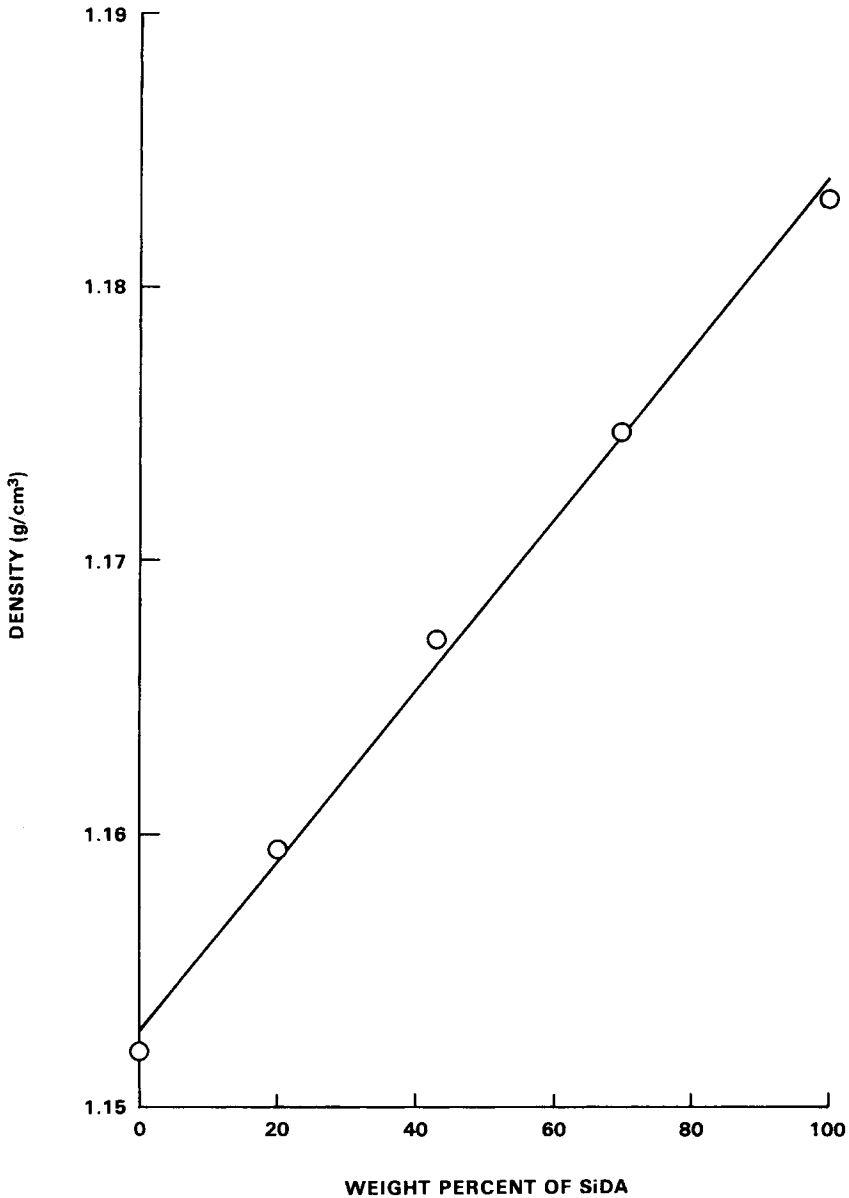


Fig. 1. Density of DGEBA cured with SiDA and TMSiDA.

unhindered SiDA curing agent. Consequently, the SiDA curative permits closer packing of the polymer chains which produces a denser resin system. The densities of DGEBA cured by mixtures of TMSiDA/SiDA fall on a straight line plot as predicted by the rule of mixtures.

Moisture Absorption

Augl⁹ has shown that epoxies absorb varying amounts of moisture depending on their structure and that the absorbed moisture produces a reversible

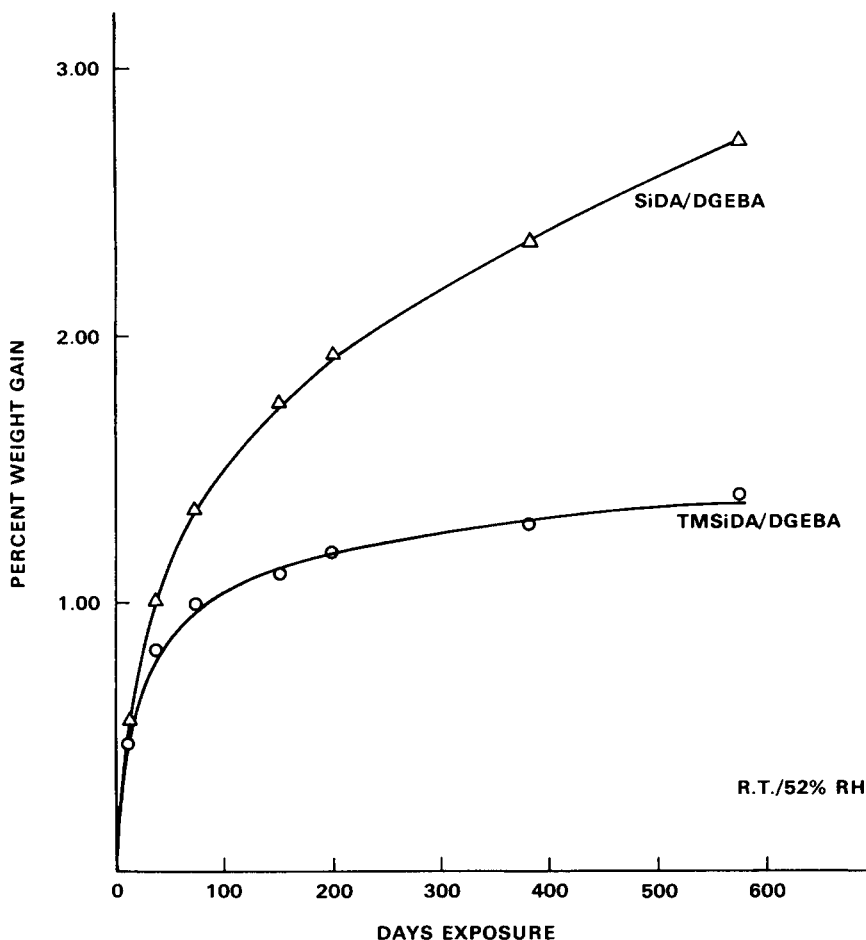


Fig. 2. Moisture absorption by TMSiDA/DGEBA and SiDA/DGEBA.

change in the mechanical properties. It was therefore of interest to determine the effect steric hindrance has on the moisture absorption properties of epoxy resins. Testing was done at ambient temperature in 50–55% RH and the results are shown in Figure 2. It was found that the SiDA/DGEBA system absorbed moisture at a faster rate initially and after 575 days of continuous exposure has absorbed twice as much moisture as TMSiDA/DGEBA (2.7 and 1.4%, respectively). The rate of moisture absorbed after 575 days is still high for SiDA/DGEBA while the TMSiDA cured epoxy appears to be approaching an equilibrium moisture level.

It has been already demonstrated by density measurements that the TMSiDA/DGEBA has more internal free volume than SiDA/DGEBA due to the presence of the bulky methyl groups. One might, therefore, expect a higher rate of moisture diffusion and absorption by the TMSiDA cured resin. Since this does not occur, it appears that some other mechanism is involved. A possible explanation is that steric hindrance in TMSiDA makes the tertiary amine nitrogen less accessible for hydrogen bonding with water and thus reduces the driving force for the absorption process.

Glass Transition Temperature by DSC

Charlesworth¹⁰ reported the presence of two T_g 's in an episulfide epoxy/glycidyl epoxy system cured by an aliphatic amine. Such a two-phase system is a direct result of differences in the reactivity between the epoxides. Since TMSiDA and SiDA react at different rates due to steric hindrance, there is a possibility that a two-phased epoxy would form, each with its own transition. Thus, the glass transition temperature of TMSiDA/DGEBA, SiDA/DGEBA, and several mixed amine cured epoxies were determined by DSC. The results from the composite plot (Fig. 3) show a gradual rise in T_g from the value of 74°C for SiDA(100%)/DGEBA to 84°C for TMSiDA(100%)/DGEBA. In the case of the TMSiDA/SiDA mixed amine cures, there is no evidence of two separate T_g 's. It should be noted that only 10°C separates the T_g 's of the homopolymers, and this may not be enough of a difference to detect dual transitions if indeed they are present. The results

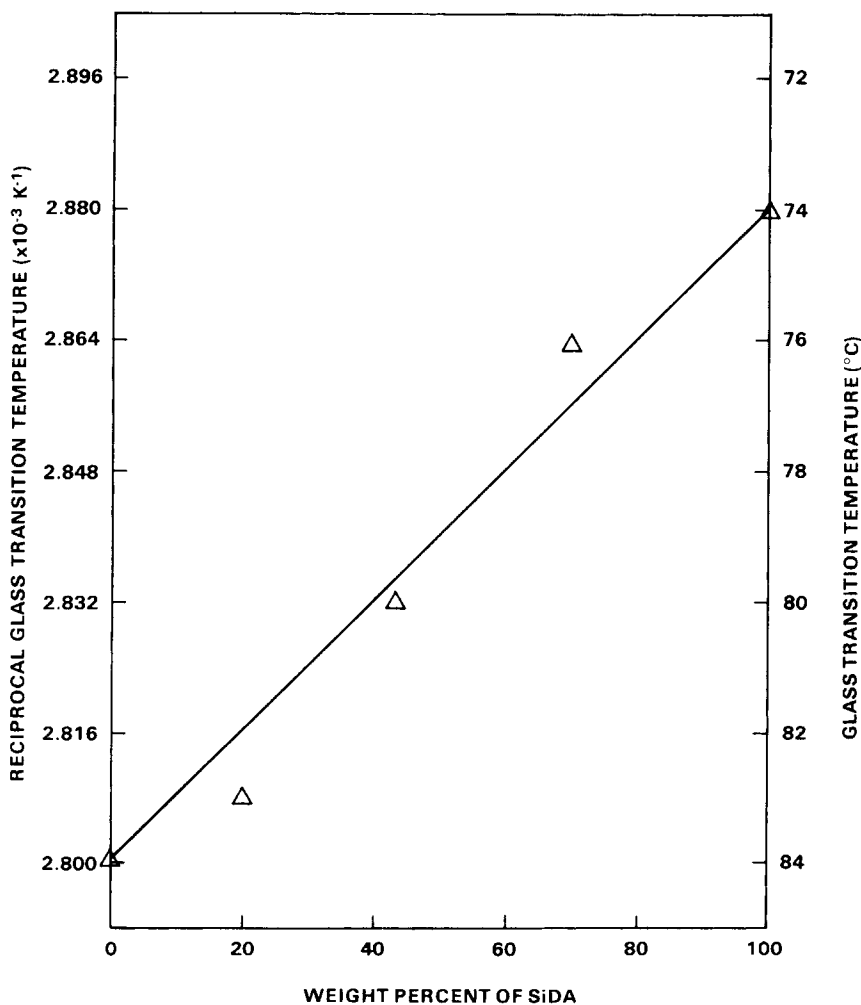


Fig. 3. Glass transition temperature of DGEBA cured with SiDA and TMSiDA.

obtained (Fig. 3) are in good agreement with the T_g values calculated from the copolymer equation¹¹:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (5)$$

where T_{g1} and T_{g2} are the glass transition temperatures for TMSiDA/DGEBA and SiDA/DGEBA, respectively, w_1 and w_2 are the corresponding amine weight fractions, and T_g is the glass transition temperature of the mixed amine-cured epoxy resin. It is also apparent that, over this narrow range of glass transition temperatures, a linear relationship for T_g would also fit the data.

Dynamic Mechanical Properties

Logarithmic decrement versus temperature results for TMSiDA/DGEBA and SiDA/DGEBA are presented in Figure 4. The data indicate two transitions in the temperature range covered. The higher temperature transition, the glass transition, is observed at 106°C for TMSiDA/DGEBA and 85°C for SiDA/DGEBA. These transition temperatures are both higher than those found by DSC measurement. This difference is due to the fact that the frequency of the DSC measurement (10°C/min = 0.2 Hz) is lower than that of the torsional pendulum (1 Hz). Lee and Hartmann¹² have measured 5–15°C differences in glass transition temperature when using these two methods. This result indicates that the substituted methyl groups sterically hinder the motion of the polymer chains, thus raising the glass transition temperature as also reported by Nielson.¹³

A secondary transition T_{sec} is also observed, which involves the crank shaft motion of the glyceryl group $[-OCH_2-CH(OH)-CH_2-]$ as shown by Pogany.¹⁴ The secondary transition of TMSiDA/DGEBA (-69°C) occurs at lower temperature than SiDA/DGEBA (-50°C) while the logarithmic decre-

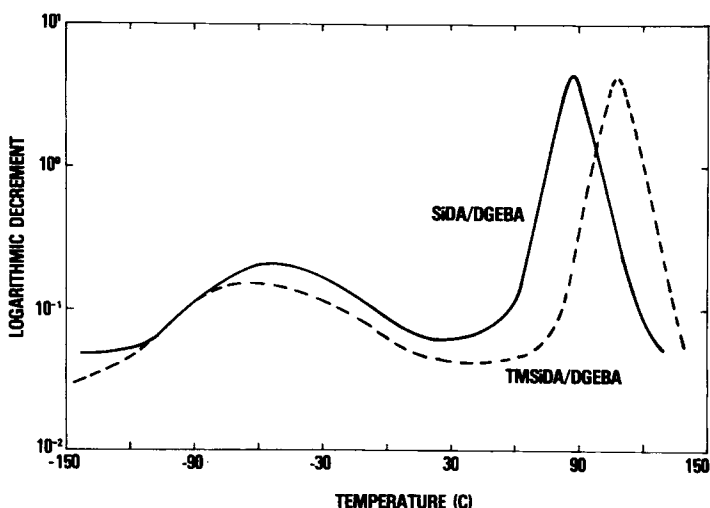


Fig. 4. Logarithmic decrement vs. temperature of TMSiDA/DGEBA and SiDA/DGEBA.

ment peak height which is a measure of the internal friction is slightly lower for the TMSiDA/DGEBA system. This lower internal friction is caused by the methyl groups in TMSiDA which create internal free volume, making it easier for the crankshaft motion to occur at lower temperature. Thus, steric hindrance in the form of pendant methyl group raises the T_g while at the same time lowering the secondary transition.

Activation energies of the secondary transitions were determined using the method of Read and Williams.¹⁵ They showed that the area under a logarithmic decrement curve in the vicinity of a transition is directly related to the activation energy ΔH for that transition. Their result can be expressed in the form

$$\Delta H = (G_U - G_R)R\pi \left[2 \int_0^\infty G'' d(1/T) \right]^{-1}$$

where R is the gas constant, T is absolute temperature, G_U is unrelaxed modulus, and G_R is relaxed modulus. The activation energy for TMSiDA/DGEBA is 19 kcal/mol and for SiDA/DGEBA is 14 kcal/mol, with an error of ± 2 kcal/mol. The activation energies calculated here are in reasonable agreement with the values obtained by Arridge and Speake,¹⁶ who found values that varied from 16 to 25 kcal/mol, depending on the cure temperature and the amount of curing agent. Thus, the transition with the higher activation energy is the one with the lower transition temperature, contrary to the suggestion of Boyer.¹⁷ This data, however, is within the scatter of the results presented by Boyer.

Shear modulus versus temperature for TMSiDA/DGEBA and SiDA/DGEBA are shown in Figure 5. The shear moduli below room temperature for both TMSiDA/DGEBA and SiDA/DGEBA are about the same. However, at temperatures above the glass transition temperature, the rubbery moduli of TMSiDA/DGEBA is slightly higher than SiDA/DGEBA (3.9 and 3.3 MPa, respectively.) The modulus difference can be explained by the presence of

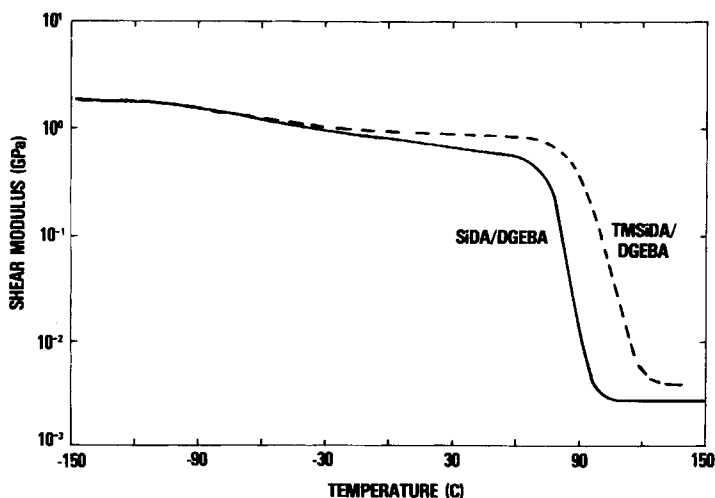


Fig. 5. Shear modulus vs. temperature for TMSiDA/DGEBA and SiDA/DGEBA.

pendant methyl groups in TMSiDA which increase the resistance of the chain segments to viscoelastic flow, thus raising the modulus. This is the same mechanism that is responsible for the glass transition temperature of TMSiDA/DGEBA being higher than SiDA/DGEBA.

CONCLUSIONS

Steric hindrance in an amine-cured epoxy has been shown to lower the density, reduce moisture absorption, and raise the glass transition temperature of the resin. Dynamic mechanical measurements show that the secondary transition for TMSiDA/DGEBA occurs at lower temperature than SiDA/DGEBA while the shear modulus of TMSiDA/DGEBA is higher than SiDA/DGEBA in the rubbery region. Activation energies for the secondary transition are 19 and 14 kcal/mol for TMSiDA/DGEBA and SiDA/DGEBA, respectively. These results are in agreement with reported values.

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