

Effect of chain flexibility in the network structure on the viscoelasticity of epoxy thermosets

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Abstract In this paper a detailed study in investigating the effect of the chain flexibility in epoxy-amine crosslinked network is done. In order to introduce flexibility into the crosslinked network a homologous series of four aliphatic diamine curing agents varying only in the chain length and having a constant functionality ($f=4$) is taken and cured stoichiometrically with aromatic epoxy ($f=2$) resin. For each of the cured mixture the viscoelastic master curve and corresponding shift factors were determined. It is found the introduction of flexibility shifts the viscoelastic curves by 5 decades with respect to frequency scale. This shift in the viscoelastic curve is modeled with a parameterized Havriliak-Negami model for the master curve. The free volume contribution for the changes in the coefficient of thermal expansion at T_g is also determined.

Keywords Resin · Functionality · Thermosets · Crosslink density · Flexibility · Viscoelasticity · Rubber elasticity

Introduction

Thermosets are polymeric materials whose properties (mechanical, thermal, etc) depend on time and temperature. The dependence of the thermoset properties with time and temperature is termed as viscoelasticity and plays an vital role in the long term performance of thermosets. The position of the viscoelastic transition region is characteristic for the determining the thermo-mechanical properties of

these thermoset materials. The viscoelasticity (or viscoelastic response) of thermosets depends mainly on the network structure which is formed after the cure reaction between the resin and curing agent. The network structure formed depends on the properties of initial reacting resin-curing agent. The viscoelastic response of epoxy resins cured with various curing agents has been studied in the past by many researchers [1, 6, 19]. From our previous studies and also from other research work it was found that the viscoelastic response of the cured epoxies is sensitive to the variation of the reacting mixture (or group) functionalities, mixing ratios, conversion, curing conditions and the crosslink density of the network formed [9, 11, 14, 15].

Flexibility of the network structure is another important parameter which can effect the position of viscoelastic transition region and can be determined using DiMarzio's approach [2].

In this paper a model is proposed which relates the chemistry of the reacting resin-hardener mixtures to the final viscoelastic behavior. The proposed model can be achieved in two steps. First we assume that the governing factor to predict the viscoelastic properties of thermosets is the crosslink density. Since the crosslink density is a function of the reacting functional groups, mixing ratio and conversion, these inputs have to be determined. Theoretically, the crosslink density can be predicted by the Macosko and Miller theory [12] and experimentally it can be estimated from the rubbery modulus using the concept of rubber elasticity. In the second step we use the calculated crosslink density to predict the shape of the viscoelastic master curve.

In order to investigate the effect of network flexibility on the viscoelasticity, stoichiometric ratios of aromatic epoxy ($f=2$) and homologous series of amines having constant functionalities are cured such that full conversion of the

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epoxy groups are achieved. The fully cured products are then tested for their thermo-mechanical properties in tension mode in the Dynamic Mechanical Analyser (*DMA*). Time-temperature-superposition (TTS) is applied to the data obtained from the *DMA* tests. We then parameterize the shape changes of the relaxation master curves. This result in a attaining a set of parameters such as the glassy, rubbery modulus, the position (relaxation time constant) and the shape of the glass transition region. The obtained parameters are then related to the crosslink density. The Havriliak-Negami fit function is used to describe the viscoelastic behavior of these cured resin systems.

In our previous study [14] a model system is selected based on epoxy-amine system. The model system contains an epoxy (BADGE) and three different amines. The functionality (f_E) of the initial selected epoxy reactant has EEW of 175 and a functionality of 2 i.e., $f_E=2$. Three types of amines are selected in which the functionality of the amine is varied from $f_A=2$ to $f_A=4$. The BADGE is mixed with the three amines independently. The independent reactions of the epoxy with the three amines is done such that 100% epoxy reaction is achieved. Three types of solid epoxy samples are obtained after the three independent reactions. The epoxy samples are then characterized for their viscoelastic properties in the *DMA*. It was observed that the increase in the functionality of the amine from $f_A=2$ to $f_A=4$ has increased the rubbery modulus (E_r) (at T_g+30) from 9 MPa to 35 MPa. While the T_g increased from 93°C to 136°C (i.e., increase of 43°C). The change in the rubbery modulus and T_g is mainly due to the change in the crosslink density values from 1104 mol/m³ to 3270 mol/m³.

For the present study, our understanding is that by increasing the chain length in the amine reactant increases the flexibility within the crosslinked epoxy-amine network. Also, as the functionality of the epoxy and amine reactants does not change and therefore the the crosslink density of the epoxy-amine network formed is slightly affected.

Further, it is expected that the properties such as T_g , free volume, Coefficient of thermal expansion (*CTE*) etc will change. So, a systematic variation in the chain length of the amine reactant can be exploited to understand the changes in the physical properties i.e., T_g , free volume, *CTE* etc.

The aim of this paper is to understand the effect of the varying the chain length (or spacer length) of the initial resin chemistry on the final properties of their cured products. This understanding gives a firsthand estimate of the final properties and thereby saves time for the characterization of polymeric materials which is tedious. Moreover, if a good understanding of the relation between the resin chemistry and the final properties of the cured product is known then it would be possible to be able to predict the properties and furthermore to tailor the properties of the polymeric materials.

Experimental

Materials

Bisphenol A diglycidyl ether (DER 332, 97%) and four aliphatic amine curing agents EDA (1,2-Diamino ethane, 99% pure), BDA (1,4-Diamino butane, 98% pure), HDA (1,6-Diamino hexane, 98% pure), ODA (1, 8-Diamino hexane, 99% pure) were purchased from Sigma-Aldrich Logistik GmbH, Schnelldorf, Germany. These materials were not purified and used as received. The chemical structures of the epoxy and amines are shown in Fig. 1 and the curing reaction between them is shown Fig. 2. The amino curing agents consists of 2, 4, 6 & 8 respectively of methylene spacer groups.

Sample preparation

Neat resin castings for *DMA* studies were prepared in aluminum moulds. The aluminum mould consist of an

Fig. 1 Shows the compound name, structure, average functionality (f) of the epoxy and four aliphatic amines

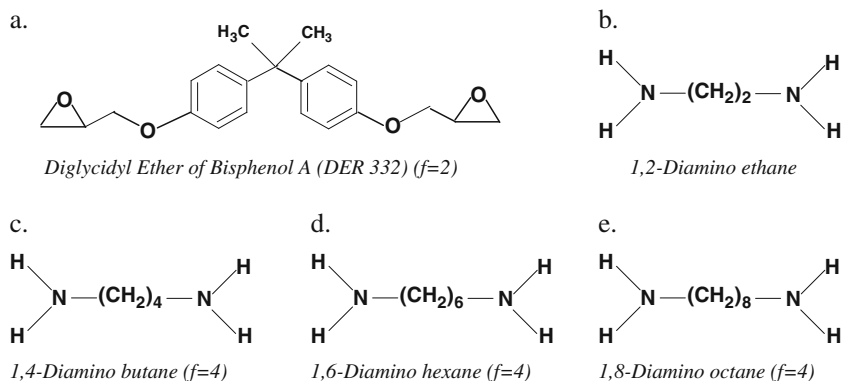
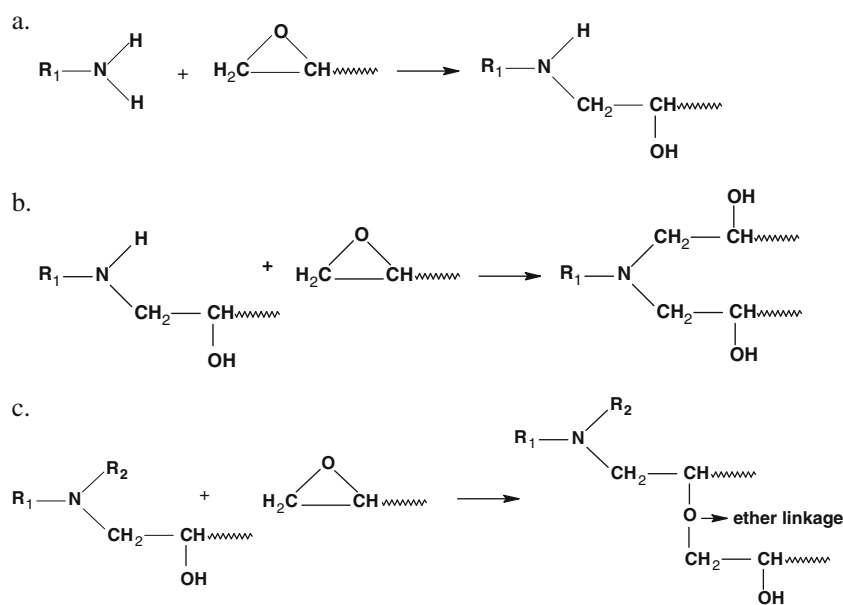


Fig. 2 a. Epoxide ring-opening reaction with primary amine b. Epoxide ring-opening reaction with secondary amine, c. Etherification reaction between hydroxyl group of reacted epoxy and unreacted epoxy groups (usually occurs at temperature above 100°C) (or) homo polymerisation of epoxy



aluminum insert with gaps of dimension $6.0 \times 1.5 \times 3$ mm and is fastened in between two aluminum plates into which the premixed resin is poured and cured at different curing schedules. High temperature mirror glaze wax, (Meguiar's Inc., Irvine, U.S.A) is used as mould releasing agent. Firstly, a known amount of epoxy resin (DER 332) is taken in a beaker. Since the epoxy partly crystallizes at room temperature it is heated at 80°C for half an hour so that the epoxy crystals melt and also the absorbed moisture is removed. To this a stoichiometric amount of amines is added and mixed thoroughly. The prepared mixture is then cast in the aluminium mould. Then they are cured and post cured at different temperatures to obtain full conversion of the epoxy. Cured samples of stoichiometrically mixed amines and epoxy are prepared with different mixing ratios and cure schedules. For all formulations containing different mixing ratios curing is done initially at 80°C for 3 h and 100°C for 1 h and then post cured. Table 1 shows the different stoichiometric mixing ratios and post curing temperatures. Preliminary measurements showed that too high post cure temperature for the lower functionality

resins resulted in the undesired etherification reaction shown in Fig. 2c. In order to avoid this etherification all the mixtures were post cured for 4 h at 150°C .

Viscoelastic measurement

A TA-Instruments Q800 model (Dynamic Mechanical Analyzer) was used. Viscoelastic study of cured resins was done on rectangular bars of cured specimen's in tension mode at different frequency sweeps (0.3–60 Hz) with a heating rate 1°C min^{-1} . Evolution of storage modulus (E') and energy dissipation ($\tan \delta$) with temperature was measured. The resulting viscoelastic data is then shifted along the frequency axis to obtain both a master curve and the corresponding shift factor curve.

Density

The densities of the cured resins are measured using the Archimedes principle that states that the volume is proportional to the difference in weight between a dry and submerged sample. The experimental set up consists of

Table 1 Shows the sample name, average functionality, composition, post cure schedule and the molecular weight between crosslinks for the post cured samples

Sample name	f	Stoichiometric mixing ratio	Post cure	M_C (g/mol)
CL2	4	1 DER332+1 EDA	4 h@ 150°C	307
CL4	4	1DER332+1 BDA	4 h@ 150°C	380
CL6	4	1 DER332+1 HDA	4 h@ 150°C	390
CL8	4	1DER332+1 ODA	4 h@ 150°C	410

weighing balance and glass filled with silicone oil (Type: M100, Dow Corning). The sample weight is determined both in air and oil. The density is calculated using Eq. 1.

$$Density(\rho) = \frac{\rho_{oil} \times Sample_{dry}}{Sample_{dry} - Sample_{wet}} \tag{1}$$

ρ_{oil} is the density of silicone oil (0.965 g/cm³), $Sample_{dry}$ is the weight in grams of the sample in air and $Sample_{wet}$ is the weight in grams of the sample in silicone oil. The test procedure was calibrated with polystyrene and polycarbonate samples of known density.

Coefficient of linear thermal expansion measurement (α_L)

The coefficient of linear thermal expansion, α , is determined using a thermo mechanical analyzer (TMA) and is shown by the Eq. 2. The temperature range was from RT-180°C and the heating rate 10°C /min. The measurement of α_L is always done in the second heat scan

$$\alpha_L = (1/L_0)(\Delta L/\Delta T) \tag{2}$$

Where $\Delta L/\Delta T$ is the slope of the dimensional change—temperature curve and L_0 is the initial length.

Calculation of the properties

Average functionality and stoichiometric ratio

Let us consider an arbitrary mixture of polydisperse monomers A_i with f_i functional groups and monomers B_j with g_j functional groups. The number average functionalities then become

$$\bar{f}_{n,A} = \frac{\sum n_{Ai0}f_i}{\sum n_{Ai0}}, \bar{g}_{n,B} = \frac{\sum n_{Bj0}g_j}{\sum n_{Bj0}} \tag{3}$$

in which n_{Ai0} and n_{Bj0} denote the initial number of moles of A_i and B_j monomers, respectively. For future use we also define the mole fractions of crosslinkable A and B groups a_i and b_j as

$$a_i = \frac{n_{Ai0}f_i}{\sum n_{Ai0}f_i}, b_j = \frac{n_{Bj0}g_j}{\sum n_{Bj0}g_j} \tag{4}$$

and the stoichiometric ratio as the initial ratio of all available A groups to those of all B groups

$$r_A = \frac{\text{initial no. A groups}}{\text{initial no. B groups}} = \frac{\sum n_{Ai0}f_i}{\sum n_{Bj0}g_j} \tag{5}$$

For equal numbers of A and B groups this ratio equals unity. Consider now the case that there are more B groups available ($r_A < 1$) and that the A groups have reacted to

extent p_A (defined as the number of reacted A groups divided by the initial number of A groups). Since the number of reacted B groups equals that of the reacted A groups the conversion of B, denoted as p_B , can then be expressed as

$$p_B = \frac{\text{no. reacted B groups}}{\text{initial no. B groups}} = \frac{\text{no. reacted A groups}}{\text{initial no. B groups}} = p_A r \tag{6}$$

Crosslink density

In order to relate the resin chemistry to viscoelastic behavior the crosslink density has to be determined. Calculated Cross-link density (v_c^{calc}), which is a function of conversion (p_A), mixing ratio (r_A) and functionality (f_i) can be determined from the Miller and Macosko theory [12, 13], and is given by the relation

$$v_c^{calc} = \frac{\sum_{m=3}^{f_k} \frac{m-2}{2} \sum_{f_i=m}^{f_k} n_{Ai0} P_{m,f_i}(x)}{V} \tag{7}$$

Where n_{Ai0} is the molar concentration of A_i , V is the network volume related to mass network (M_n) and density (ρ) of the fully cured epoxy material as shown in Eq. 8 [19]

$$V = \frac{M_n}{\rho} \tag{8}$$

and $P_{m, f_i}(x)$ and the probability that an A_f monomer has become an effective crosslink of degree m given by relations

$$P_{m,f_i}(x) = \binom{f_i}{m} x^{f_i-m} (1-x)^m \tag{9}$$

and x stands for the probability that a randomly picked A_f group is connected to a finite chain (dangling end). This quantity follows by solving

$$p_A \sum b_j \left[1 - r_A p_A (1 - \sum a_i x^{f_i-1}) \right]^{g_j-1} - x - p_A + 1 = 0 \tag{10}$$

Where $0 < x < 1$. A numerical solution for x is readily obtained with mathematical tools like MatLab. For the present model system B_{2+A_4} , the value of x is determined by solving the Eq. 11.

$$x^3 - (1/p^2)x - 1 + 1/p^2 = 0 \tag{11}$$

Where p is the conversion of epoxy. A detailed study for calculating the crosslink density is available in the literature [9].

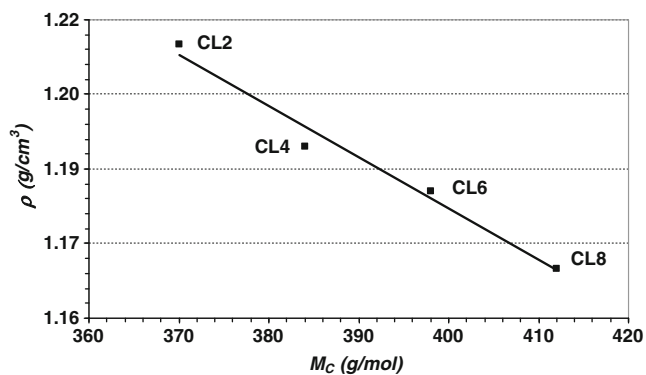


Fig. 3 Density versus Molecular weight between crosslinks (M_C). The filled symbols with thick line indicate the density values and its linear fit. The numbers CL2 to CL8 corresponds to the amount of methylene spacer groups

Molecular weight between crosslinks (M_C)

The molecular weight between crosslinks (M_C) can be calculated using Eq. 12 [4]

$$M_C = \frac{2 \left(M_e + \sum_{f=2}^{\infty} \frac{M_f}{f} \Phi_f \right)}{\sum_{f=3}^{\infty} \Phi_f} \quad (12)$$

Where M_e is the epoxide equivalent weight of the resin, f is the functionality of the amine, M_f is the molecular weight of the f -th functional amine, and Φ_f is the mol fraction of amine hydrogens provided by the f -th functional amine.

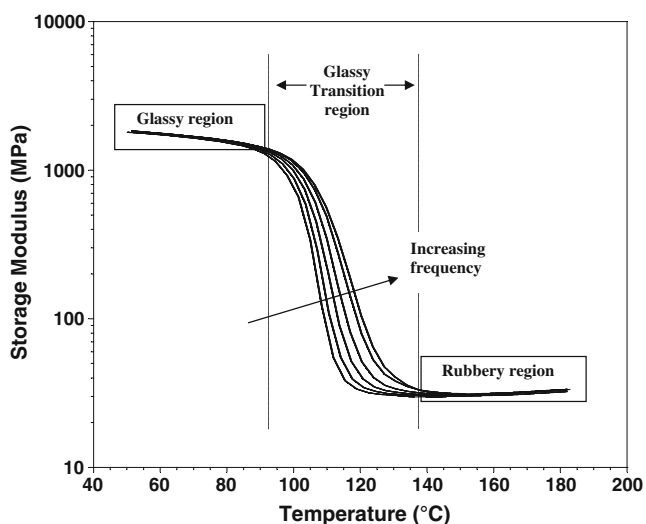


Fig. 4 Plot of storage modulus $E'(\omega)$ versus temperature for the CL2 sample. Each line corresponds to the modulus response with respect to temperature for different frequencies

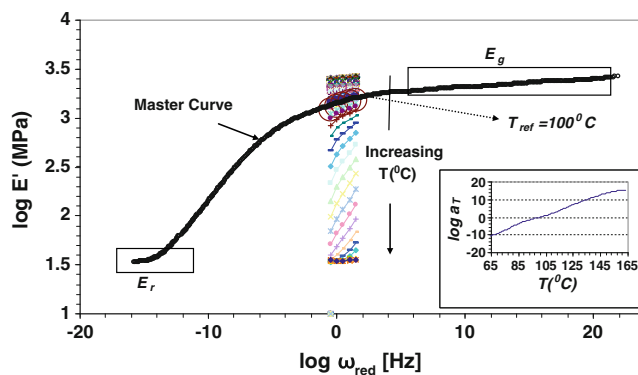


Fig. 5 Plot of storage modulus (E') with respect to reduced frequency (ω_{red}) for CL2 sample. E_g , E_r and T_{ref} are the glassy modulus, rubbery modulus and reference temperature (100°C [indicated by circles]). The lines with symbols are modulus values of all frequencies at different temperature. Master curve shown by *full line*. A plot of shift factor ($\log a_T$) versus temperature is shown as an insert

Glass transition temperature (T_g)

One way of defining the glass transition temperature is by determining the temperature at the peak maximum of the $Tan \delta$ curve for 1Hz and is denoted by $T_{g(DMA)}$ in this paper. Further, the glass transition temperature can also be predicted using DiMarzio equation and is denoted by T_g (*Dimarzio*) and is defined by Eq. 13.

$$T_{g(Dimarzio)} = \frac{T_{gl}}{(1 - K_{DM} F v_c^{calc})} \quad (13)$$

Where T_{gl} is the T_g of the uncrosslinked or linear polymer chain, K_{DM} is constant, F is the flexibility

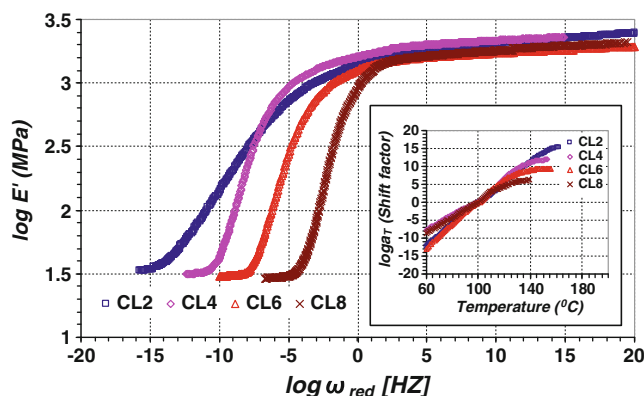


Fig. 6 Plot of master curves obtained after frequency-temperature superposition to a reference temperature ($T_{ref}=100^\circ\text{C}$) of the increasing network chain length with respect to the reduced frequency (ω_{red}). The shift factor ($\log a_T$) curves corresponding to the obtained master curves of varying chain length with respect to the temperature is shown as an insert

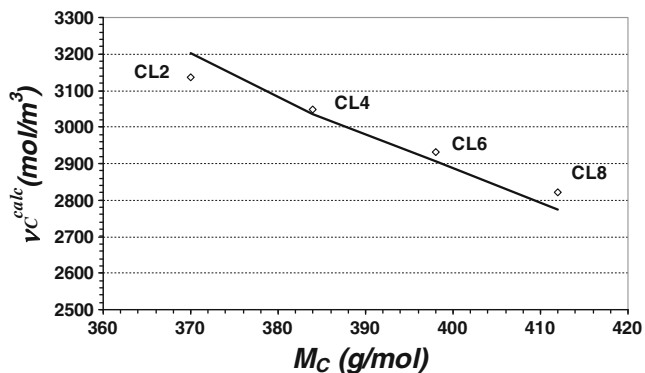


Fig. 7 Crosslink density versus Molecular weight between crosslinks (M_C). The unfilled symbols indicate the Measured crosslink density ($v_c^{Meas.}$) and the thick line indicates Calculated crosslink density (v_c^{calc})

parameter in g/mole and v_c^{calc} is the calculated crosslink density in mole/g. The eq. 13 can be written as

$$T_{g(Dimarzio)} = T_{gl} \left(1 + \frac{K_{DM} F v_c^{calc}}{1 - K_{DM} F v_c^{calc}} \right) \tag{14}$$

The Eq. 14 is similar to Fox-Losheak equation [5] as shown by Eq. 15

$$T_g = T_g^\infty \left(1 + K_{FL} \left[\frac{v_c^{calc}}{1 - v_c^{calc}} \right] \right) \tag{15}$$

Where K_{FL} is constant.

Results and discussion

Density studies

From Fig. 3 it can be seen the density decreases linearly with the increase in the molecular weight between cross-

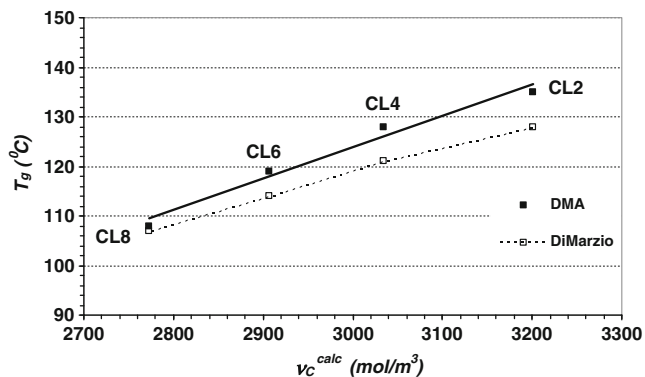


Fig. 8 T_g versus calculated crosslink density (v_c^{calc}). The filled symbols with thick line indicate the $T_{g(DMA)}$ values and its linear fit (shown by equation). Similarly, the empty symbols, dotted line indicate $T_{g(Dimarzio)}$ and its linear fit

links (M_C). This can be due to the increase in the chain length of the amine curing agent the hydrophobic nature increases. The increase in hydrophobic nature separates the polar amine groups and will therefore decrease the density of the cured epoxy network.

DMA studies

Figure 4 shows the experimental storage modulus data versus the temperature at different frequencies (0.32, 1, 3.2, 32 and 60 Hz). The experimental storage modulus contains three regions i.e., glassy plateau, rubbery plateau and transition region. The modulus in the glassy plateau is termed as glassy modulus and denoted by E_g . Rubbery modulus (E_r) is defined as the modulus in the rubbery region. The glass transition temperature T_g from DMA experiments can be determined from the storage modulus, Loss modulus and Tan δ curves. The glass transition temperature T_g in this paper is determined using the Tan δ curve and is denoted by $T_{g(DMA)}$. The $T_{g(DMA)}$ is the temperature at the peak maximum of the Tan δ curve for 1Hz. Since, epoxy thermoset materials are polymeric materials whose properties vary with temperature as well as time, the incorporation of time (or frequency) dependency on the viscoelasticity is very important. This can be done by constructing a viscoelastic master curve. Therefore, the storage modulus data at different temperatures from the DMA experiment is plotted with respect to frequency scale in as shown in Fig. 5. According to Time Temperature Superposition principle [10] the modulus data can be shifted along the frequency axis to generate a so-called master curve (included in Fig. 5). Figure 5 shows the storage modulus master curve plotted against reduced angular frequency (ω_{red}) for CL2 formulation obtained after shifting the modulus data on frequency to a reference temperature ($T_{ref}=100^\circ\text{C}$) [17]. Where ω_{red} is given by

$$\omega_{red} = \frac{\omega}{a_T} \tag{16}$$

And ω is the angular frequency (rad/s) and a_T is the shift factor. The corresponding shift factor is shown as an insert in Fig. 5. In order to understand the effect of chain length in the cured network the master curves for all the formulations are generated using Time Temperature Superposition principle. The storage modulus master curves and their corresponding shift factor curves for all our formulations are obtained by shifting modulus data towards a reference temperature ($T_{ref}=100^\circ\text{C}$) and shown in Fig. 6. We can see that the viscoelastic transition region has shifted to higher frequency scales with the increase in network chain length. Note that the glass transition shifts from -7 to -2 from CL2 to CL8 curve with respect to angular frequency. This means that there is a shift of 5 decades along frequency axis. Also

Table 2 Shows the sample name, Glassy modulus, Rubbery modulus, Measured crosslink density

Sample name	Glassy modulus E_g [MPa]	Rubbery modulus E_r [MPa]	v_c^{Meas} mol/m ³ Eq. 17	v_c^{Calc} mol/m ³ Eq. 7	Flexibility (g/mole)	Fractional free volume (f_g) at T_g
CL2	1898	35	3135	3201	22.11	0.04692
CL4	1891	33	3048	3034	22.73	0.04932
CL6	1770	31	2931	2907	23.00	0.05370
CL8	1789	29	2822	2773	23.15	0.05709

Calculated crosslink density, Flexibility parameter, Fractional free volume of varying chain length

Fig. 6 shows that the shift factor ($\log a_T$) curves shifts to lower temperatures with increase the network chain length.

From Fig. 6 it can be observed that the glassy modulus is independent of increase in the chain length of the network. This is because below the T_g the molecular motion is limited and hence the network chain length has no effect. From Fig. 6 it can be seen that the rubbery modulus slightly decreases with increasing chain length (around 5MPa) which is within experimental scatter and hence can be considered as constant. According to the theory of rubber elasticity, the rubbery modulus [9] is directly proportional to the crosslink density

$$E_r = 3Av_c^{meas} RT \tag{17}$$

Where A is the front factor often assumed to be unity, $R=8.314$ J/mol/K, T is the absolute temperature in K and v_c^{meas} is the measured crosslink density. Since some of the viscoelastic data of our DMA studies showed broad transition region, the modulus at $T_g+30^\circ\text{C}$ is taken as the rubbery modulus and is the measure of crosslink density. This will be the measured crosslink density. In order to compare the measured and calculated crosslink density results a graph (Fig. 7) is plotted between crosslink density versus M_C . From Fig. 7 it can be seen that calculated crosslink density agreed

relatively well with the measured crosslink density values. The calculated crosslink density (v_c^{calc}) and measured crosslink density (v_c^{meas}) are expressed in mol/m³. From Fig.7 it can be seen that there is a slight decrease in the cross-link density with the increase in M_C .

The DMA results are also used to determine the glass transition temperature (T_g). The glass transition temperature is the temperature for which the 1 Hz frequency $Tan \delta$ curve shows a maximum [16]. The T_g can also be calculated using Dimarzio’s approach (Eq. 13). In order to analyze the effect of calculated crosslink density (v_c^{calc}) on the T_g , v_c^{calc} is plotted against the T_g and is shown in Fig. 8. The calculated and measured crosslink density values can be compared with theoretical crosslink density of Halary’s work [8]. The filled symbols with full lines in Fig. 8 corresponds to the $T_{g(DMA)}$ and its linear fit which shows that the T_g has increased linearly from 108°C to 136°C [i.e., about 28°C] with the increase in the calculated crosslink density (v_c^{calc}) and this can be modeled by the Eq. 18 [5]

$$T_g = T_{gv0} + Bv_c^{calc} \tag{18}$$

Where B is the slope which is the order of 0.0713 C m³/mol and v_c^{calc} is the calculated crosslink density. T_{gv0} shows the

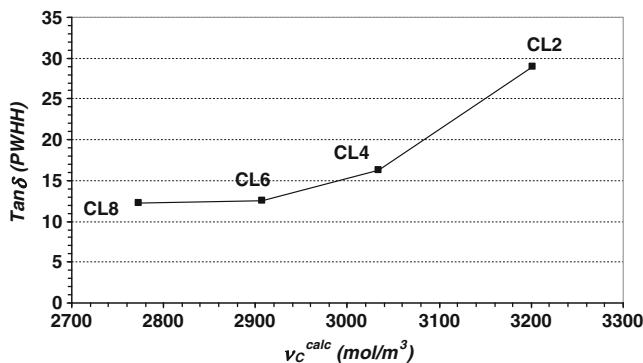


Fig. 9 Plot of Tan delta peak width at half height ($Tan \delta_{(PWHH)}$) for 1 Hz frequency versus calculated crosslink density (v_c^{calc}). The thick line with filled symbols indicates the line connecting the data points (indicated by sample name)

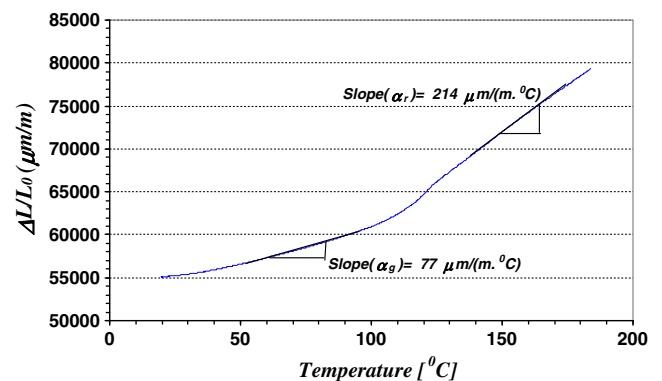


Fig. 10 Typical plot of Dimension change ($\Delta L/L_0$) versus Temperature for the sample name CL6. The slope below and above T_g gives the Coefficient of linear thermal expansion of glassy and rubbery regions

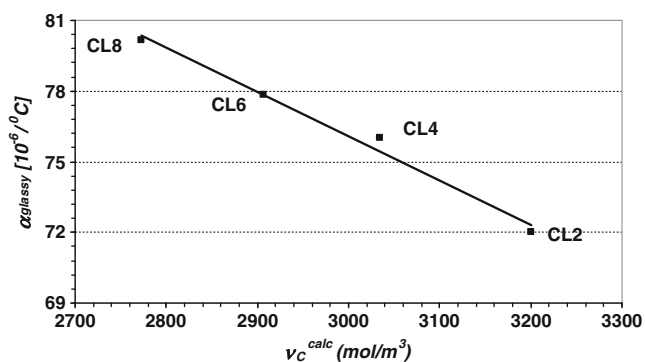


Fig. 11 Plot of Coefficient of thermal expansion in the glassy region (α_{glassy}) versus calculated crosslink density (v_c^{calc}). The filled symbols are experimental α_g values and the straight line indicates its linear fit

axis offset value, which represents the glass transition for the uncrosslinked linear polymer chains.

The T_g can also be predicted using DiMarzio's approach (Eq. 13). The unfilled symbols with dotted lines from Fig. 8 is the predicted T_g i.e., T_g (Dimarzio) also shows increasing trend in the T_g in comparison to T_g (DMA). The predicted T_g i.e., T_g (Dimarzio) are calculated based on the value of $K_{DM}=2.91$, v_c^{calc} and the T_{gl} determined by Bellenger [3]. In Bellengers [3] work the T_{gl} is determined using Differential Scanning Calorimetry (DSC). Therefore the difference in the T_g (DMA) and T_g (Dimarzio) values could be because of the determination of T_g in different experimental methods. Further, the T_g values determined by DSC are always 10–15°C lower than the T_g determined by DMA. Flexibility factor (F) in Dimarzio's equation is calculated using bellenger's approach [2, 3] and the values are shown in Table 2. According to DiMarzio hypothesis, the value of $(T_g - T_{gl}) / v_c T_g$ is proportional to F . The

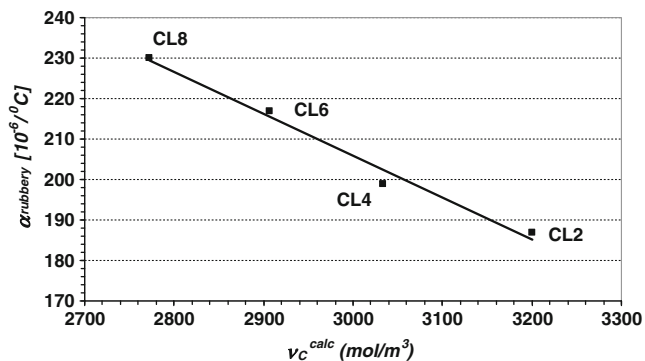


Fig. 12 Plot of Coefficient of thermal expansion in the rubbery region ($\alpha_{rubbery}$) versus calculated crosslink density (v_c^{calc}). The filled symbols are experimental α_r values and the straight line indicates its linear fit

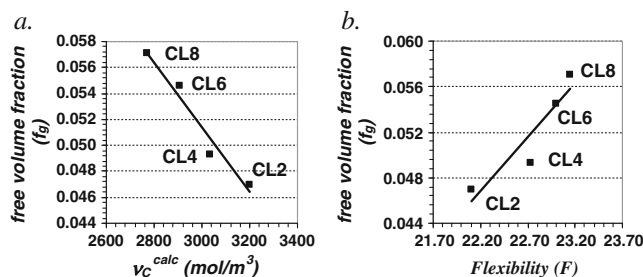


Fig. 13 a. Plot of free volume fraction (f_g) versus calculated crosslink density (v_c^{calc}). b. Plot of free volume fraction (f_g) versus Flexibility (F). Note: The filled symbols are experimental values and the straight line indicates their linear fit

flexibility F is calculated using (Eq. 19)

$$F = \frac{\sum N_i F_i}{\sum N_i} \quad (19)$$

Where N_i is the number of crosslink reactants of type i (whose flex param F_i) in the repeating unit of the network.

Figure 9 shows the $\tan\delta$ peak width at half height ($\tan\delta$ (PWHH)) for 1Hz frequency for all formulations versus calculated crosslink density (v_c^{calc}). The $\tan\delta$ (PWHH) is the measure of width [units:°C] of the $\tan\delta$ peak at its half height when plotted against temperature. It can be seen that from Fig. 9 that with small increase in the calculated crosslink density (v_c^{calc}) the peak width at half height of the $\tan\delta$ peak increases largely. In other words the sample CL8 shows lowest $\tan\delta$ (PWHH) and the sample CL2 shows the highest $\tan\delta$ (PWHH). This trend is mainly because in the CL8 sample the flexibility of network structure is high and hence can undergo relaxation fast with respect to temperature and hence shows lowest $\tan\delta$ (PWHH). Whereas for the

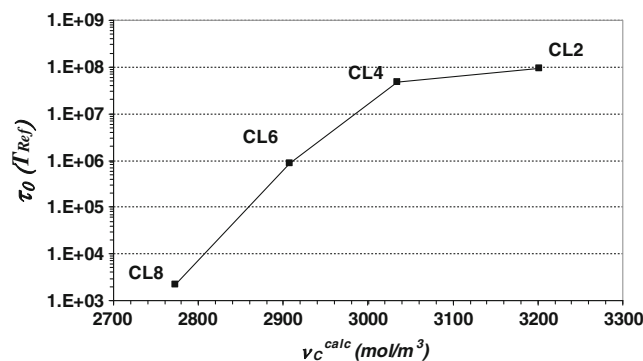


Fig. 14 Plot of relaxation time constant at reference temperature ($T_{ref} = 100^\circ\text{C}$) versus calculated crosslink density (v_c^{calc}). The filled symbols are experimental α_r values and the straight line indicates its linear fit

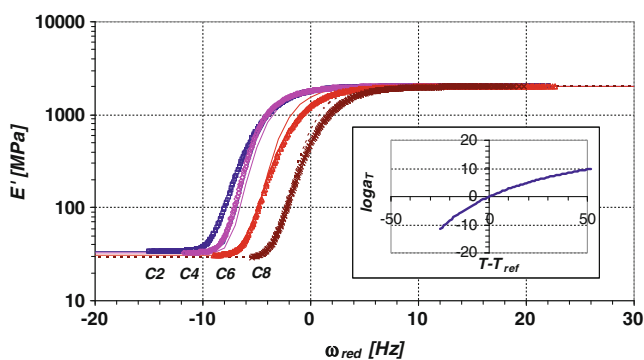


Fig. 15 Master curves for the four formulations obtained after using common shift factor in comparison to the globally fitted master curves (*full lines*) [taken $T_{ref}=100^{\circ}\text{C}$]. The shift factor ($\log a_T$) curve with respect to $T-T_{ref}$ is shown as insert

CL2 sample has lowest network flexibility in the sample series and hence has the highest $\tan\delta$ (P_{WHH}).

Coefficient of thermal expansion studies

Figure 10 shows the typical plot of dimensional change with respect to temperature for the CL6 sample. Since the length-temperature plots are composed of two linear regions below and above T_g , thermal expansion coefficients in the glassy state (α_{glassy}) and in the rubbery state ($\alpha_{rubbery}$) could be determined. From Fig. 11 it can be observed that the coefficient of linear thermal expansion in the glassy region (α_{glassy}) decreases with the slight increase in calculated crosslink density (v_c^{calc}). From Fig. 12 it can be observed that the coefficient of linear thermal expansion in the rubbery region ($\alpha_{rubbery}$) decreases from 230 to 187 [10^{-6} K^{-1}] with the slight increase in calculated crosslink density (v_c^{calc}). This is because the fractional free volume (f_g) for the different formulations decreases with the increase in the crosslink density (see Fig. 13a). The fractional free volume is calculated using Simha-Boyer approach [7] and is shown in Table 2. The Simha-Boyer free volume fraction (f_g) at T_g is related to the change in the coefficient of thermal expansion and is shown by Eq. 20.

$$f_g = (\alpha_r - \alpha_g)T_g \quad (20)$$

Further, from Fig. 13b it can be seen that the fractional free volume (f_g) increases linearly with the increase in the flexibility of the network.

Modeling of relaxation curves

In order to predict the generated relaxation master curve as discussed earlier the master curve has to be

parameterized with a well known fit-function. Therefore, the main features of all the master curves are fitted to Havriliak-Negami (HN) fit function as shown by Eq. 21 [18].

$$E' = E_r + \frac{E_g - E_r}{[1 + (\omega_{red}\tau_0)^{-m}]^n} \quad (21)$$

The HN-fit function is a simple analytical function to describe the measured relaxation master curves and contains five parameters, which are the glassy storage modulus (E_g) (MPa), rubbery modulus (E_r) (MPa), reduced angular frequency (ω_{red}) (rad/s), position of the transition region (τ_0) (s^{-1}) and power law parameters m and n (shape of transition region). The parameter n is the slope of the transition region and m is the slope at the end of the transition. In order to compare the different experimental master curves it is necessary to use a common shift factor curve. We can therefore choose T_g as the reference temperature and determine WLF (Williams-Landel-Ferry) fit parameters.

$$\log a_T = \frac{C_1^g(T - T_g)}{C_2^g + (T - T_g)} \quad (22)$$

This common shift factor parameters C_1^g , C_2^g are determined to be 25.7, 79.92. It is well known that the relaxation time constant τ_0 in Eq. 21 depends strongly on temperature. So, for thermorheological simple materials this temperature dependency can be taken into account with the so called shift function $a_T(T, T_{ref}) = t_0(T)/t_0(T_{ref})$. Where τ_0 is determined by taking the reference temperature at 100°C in the equation below

$$\tau_0 = \tau_{0g} a_T(T, T_g[v_c^{calc}]) \quad (23)$$

The determined τ_0 is plotted against the calculated crosslink density (v_c^{Calc}) to see the effect of crosslink density on the relaxation time constant. It can be seen from the Fig.14 that the relaxation time constant has increased by 5 decades with the increase in the calculated crosslink density (v_c^{Calc}). The CL2 sample which is having highest crosslink density shows highest relaxation time constant.

The common shift factors C_1^g , C_2^g are used for obtaining new master curves. Further, non-linear curve fitting using the Eq. 21 is done to the new master curves by taking fixed value for E_g and different values for E_r . The shape parameter i.e., m & n are determined. The values of m & n obtained for all the new master curves are different. Therefore fixing the value of $n=8$ and performing the non-linear curve fitting gives $m=0.25$. Therefore a set of single parameters $E_g=2000 \text{ MPa}$, $\tau_{0g} =$

1 [s], $m=0.25$, $n=8$ are obtained. With this set of parameters global or predicted master curves could be generated for each of the 4 formulations. In Fig. 15 these predictions (full lines) were compared with the experimental new master curve (symbols). We can see that the HN-fit function describes the measured curves relatively well.

Conclusions

In this paper a model is proposed in order to understand the effect of introduction of flexibility into the network structure by increasing the chain length of reacting mixtures. Bisphenol A epoxy and a homologous series of aliphatic amines varying in their chain length are taken as starting reacting compounds and cured and were tested in *DMA* for their viscoelastic behavior. It is observed that by systematically varying the chain length of the reacting compounds the crosslink density of cured network varied slightly. The measured and predicted crosslink density values were in agreement to each other. The T_g changed by 28°C and also the relaxation master curves shifted by 5 decades on the frequency scale within the sample series. This is mainly due to the flexibility of the network chain. The shift of the relaxation master curves was also predicted well using HN-fit function. A single set of 9 parameters (m , n , B , v_c^{calc} , C_1 , C_2 , E_n , E_g , τ_0) turned out to be sufficient to describe all viscoelastic data.

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