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Thermodynamic and mechanical properties of amine-cured epoxy resins using group interaction modelling

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Abstract The prediction of thermal and mechanical properties of amine-cured epoxy resins by group interaction modelling is presented. The derivation of the group interaction based approach to the prediction of macroscopic engineering properties of both linear and crosslinked epoxy resins is described with specific application to MY721 resin. The glass transition temperature, bulk and tensile modulus and linear thermal expansion coefficient of tetraglycidyl 4,4′-diaminodiphenylmethane (TGDDM) cured with 4,4′-diaminodiphenyl sulphone (DDS) are estimated using the model and compared with results from dynamic mechanical experiments. The glass transition of TGDDM/DDS is calculated to occur at approximately 248 °C and the reasons for a secondary peak in the spectrum cured to 180 °C are given. The bulk and tensile modulus of TGDDM/DDS are calculated to be 7.54 GPa and 5.34 GPa, respectively.

Introduction

Fibre composite materials consist of an array of fibres often in a polymeric thermosetting matrix. Without support from the resin, the fibres cannot be utilised to their full. In the process of making a composite material, uncured resin is impregnated into the fibres which are maintained in a defined orientation. After manufacture into a structure, the resin is cured usually in a high temperature stage. The resin chosen as the matrix of a composite material depends on its application and the manufacturing route of the artifact. In fibre reinforced plastics it is common to use unsaturated polyester resins for applications less demanding in mechanical and thermal environments. In advanced composite materials based on high performance fibres such as carbon most matrices rely heavily on the use of epoxy resins. For high temperature use other thermosetting resins are in use to a limited degree (including cyanate esters, bismaleimides and phenolics). In general, the high performance matrices bring cure issues with them. As a result, epoxy resins in various guises are used extensively for the manufacture of carbon fibre and glass fibre reinforced plastics. These epoxy resins consist of blends of differing functional epoxies with rubber or thermoplastic toughening agents. A thermoplastic modifier also acts as a flow control additive and a variety of hardeners or curing agents are available.

With epoxy resins the curing reaction is often a copolymerisation with the curing agent or a ring opening polymerisation is initiated. This means that the chemical structure of the cured resin varies with the chosen blend of epoxy resins, the relevant curing agent(s) and the thermoplastic or other toughening agent. As a result the structure of the cured resin can vary significantly from material to material. Furthermore, the detailed curing mechanisms are quite complicated leading to uncertainty over the actual structure of the resin. This means that modelling procedures to determine the properties of the resin need to take into account a number of factors which are rather uncertain. Any modelling requirement for a thermosetting resin used in this application is determined by the complexity of the chemistry involved. Models which use simplified average structures are therefore preferred if some predictive capability can be achieved.

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For angle ply laminates the micromechanics of failure of each individual lamina is constrained so that the composite material would normally fail by damage accumulation mechanisms. In order to achieve quasi isotropic properties it is normal to use 45°, 90° and 0° plies in dispersed array to form a structural laminate. Therefore, another factor determining the mechanical properties of a laminate will be the transverse fracture of a 90° ply. The transfer strength of an isolated 90° ply will be determined by the failure strain of the matrix as well as the strength of the interfacial bond between the fibres and the resin. Apart from the failure strain of the resin matrix the other factor which determines the transfer cracking strain within a laminate, is the residual thermal stress inbuilt during the manufacturing process. The residual strain which is present in an angle ply laminate results from the constrained shrinkage of the resin during cure and on cooling from the post-cure temperature. Much of the shrinkage due to cure does not contribute to the residual strain because it occurs before a polymer glass is formed. It is therefore the linear thermal expansion coefficient of the resin and the cooling interval which is responsible for the magnitude of the residual thermal strain and in need of predictive modelling.

The other factor which contributes is the strain free temperature. The strain free temperature is the temperature at which the thermal strains are induced into the material as a result of the solidification of the polymer glass. The appropriate thermal mechanical property of the matrix which determines the strain free temperature is the glass transition temperature. The glass transition temperature is therefore a major property in need of modelling [1]. The glass transition temperature also determines the service temperature of the structure. It is also well known that during the service life, polymeric matrix composites will absorb moisture from the environment. This will lead to a reduction in the glass transition temperature and the strain free temperature. This paper explores the possibility of predicting relevant matrix properties which can be incorporated into predictive codes for fibre laminates. The most important matrix properties worthy of consideration are the glass transition temperature (T_g), the stress or strain free temperature (T_1), the linear expansion coefficient (α) and the yield stress of matrix (τ_y). Where possible the prediction of a stress strain curve for the resin is ideally needed for incorporation in finite element modelling.

Group interaction modelling (GIM)

Porter [2] has developed the group interaction approach to the prediction of macroscopic polymer properties from molecular structure. This is a simplified approach which can be applied to a range of linear polymeric structures and has been recently extended to three-dimensional network polymers [3]. Traditional modelling techniques study either the repeat or ''mer'' units within the polymer chain or the complete macromolecule. In the latter, the statistical arrangement of the atoms is utilised whereas in the former the interactions between groups of elements are studied. Examples of the differing models described in the literature are: Molecular Mechanics [4, 5], Monte Carlo methods [6], Rotational Isomeric State Theory [7, 8], Group Contributions of van Krevelen [9], and the Connectivity Indices of Bicerano [10].

GIM relies on additivity principles of the properties of a group of elements and therefore lends itself to the prediction of the properties of the complex resin networks used in composite materials. It is an example of a generalised cell model which employs five molecular parameters which determine the thermodynamic properties of a polymer [11, 12]. These are the strength and range of the intermolecular interaction potential and the number of point centres, intermolecular contacts and external degrees of freedom per molecule. The strength of GIM is in the simple manner in which these aspects are quantified. In GIM, the van der Waals interactions between groups of elements within a cell consisting of a central unit and six surrounding units in hexagonal structure form the basis of the analysis. It was developed with the aim of calculating many relevant engineering properties of polymers. These properties arise from the exchange of energy between the material and its environment that occurs on a molecular level. For polymers, it is the intermolecular bonding between segments in the chain and the conformational energy associated with skeletal rotations, which determine their viscoelastic behaviour.

Porter [2] has suggested that these energies can be used to reduce the variables to a common reference frame using the following energy scaling tools. Firstly, ''A potential function which relates the separation scale between two adjacent, but non-chemically bonded, molecules to the total energy which participates in that intermolecular interaction'' and secondly ''A thermodynamic energy balance equation, which relates all the different energy contributions to the total energy in an assemble of molecular units.'' These two alternatives are combined to produce an effective equation of state for polymers which represents a potential function for the characteristic interaction between adjacent mer units within the cell.

The three most important energy components which can be calculated from first principles using quantum mechanics are the Cohesive Energy (from the polarisability and dipole moments within the molecular structure), the Thermal Energy (from vibrational frequencies within the groups of atoms) and the Configurational Energy (from chemical bond deformations). Quantum mechanics [13] and in particular ab initio calculations are highly computer intensive limiting the number of atoms which can be included in the molecule under study. Therefore the role of

GIM is to use a site interaction model which allows much larger groups of fused atoms to be studied rather than the detailed atomistic level calculations.

The second part of this paper describes the results of attempts to predict the thermal and mechanical properties of an amine-cured epoxy resin, namely Araldite MY721. The results are compared with experimental DMTA data in the normal fashion and such data is the driving force behind the derivation of the current models. The results are effectively a report on the current state of using GIM to model thermosetting amine-cured resins and represent a simplification of the method as a whole whilst extensions are made to its applicability. The major component of MY721 epoxy resin is tetraglycidyl 4,4′-diaminodiphenylmethane (TGDDM) which is cured with 26% (by weight) 4,4′-diaminodiphenyl sulphone (DDS) [14].

(i) Geometry of the model and the potential function

A hexagonal cell is chosen which consists of a central polymer chain surrounded by 6 equidistant polymer chains. The energy of interaction between the chains is considered to be mainly due to near neighbours and has a value of ϕ per interaction. The total interaction energy in a model hexagonal group is 3ϕ because the six interactions occur between 2 ''mer'' units.

The interaction energy, ϕ, can be described as a sum of the following contributions:

$$\phi = -\phi_o + H_C + H_T + H_M \tag{1}$$

where ϕ_o is the depth of the potential energy well at a separation distance r_o, which is the equilibrium position of a pair of interacting molecules at absolute zero. ϕ_o is therefore the energy of interaction for the molecular conformation of lowest energy. H_C is the configuration energy, H_T the thermal energy and H_M the mechanical energy. ϕ can also be estimated using a Lennard–Jones potential which describes the decrease in energy resulting from attraction forces as the segments are brought together. At a separation distance r_o, the segments tend to repel each other giving rise to an increase in energy.

$$\phi = \phi_o\left[\left(\frac{r_o}{r}\right)^{12} - 2\left(\frac{r_o}{r}\right)^{6}\right] \tag{2}$$

(ii) Cohesive energy

ϕ_o is the energy which holds the molecules together and against which the mechanical and thermal energies act. ϕ_o can be related to the cohesive energy (E_{coh}) which can be estimated from measurements of solubility parameter (δ_o) as shown below

$$\delta_o = \sqrt{\frac{E_{coh}}{V_o}} \tag{3}$$

where V_o is the molar volume of mer units. From the hexagonal geometry, the total interaction energy is $3\phi_o$

$$\delta_o = \sqrt{\frac{3\phi_o}{4V_{mo}}} \tag{4}$$

where V_{mo} is the volume of one mer unit. By comparison of Eqs. (3) and (4) and scaling using the Avogadro number the following relationship is obtained

$$E_{coh} = \frac{3\phi_o n_a}{4}. \tag{5}$$

This provides an expression for the potential energy well of the interaction function in terms of the cohesive energy which is a bulk material property. Cohesive energy is an advantageous input parameter because it has been considered extensively [9, 10]. Furthermore, to a first approximation, it is a molar additive property for segmental groups so that values can be obtained from group contribution methods such as GIM.

(iii) The number of skeletal modes of vibration (*N*)

The other parameter which influences the thermal energy is the number of skeletal modes of vibration (or degrees of freedom) which exist in the structure. In GIM, the number of active skeletal vibrations has to be identified carefully and may not equal the traditionally defined total number as only modes normal to the main polymer chain axis are included. Porter [2] has defined N as the number of skeletal modes which are active in dictating the glass transition temperature, T_g. As a result the T_g can be used as an empirical tool for the estimation of *N*. In addition, the Debye reference temperature, θ_1, is required for each polymer investigated.

(iv) GIM parameterisation

The relevant variables can be estimated using the group contribution approach, where the parameters for each group in the mer unit are summed to give a value for the mer unit as a whole [9]. E_{coh} and N are described above and are joined by V_w, the van der Waals volume of a mer unit. Additionally, the molecular weight of a mer unit, *M* and the length of a mer unit, *L* are required.

In the case of MY721 cured with 26% (by weight) DDS, the fundamental variables required for modelling the thermal and mechanical properties of the resin are explained below. The chemical structures of TGDDM (the main component of MY721) and DDS are shown in Fig. 1 with each functional group shown. In a two component system such as TGDDM/DDS where the mass fraction of hardener (m_{DDS}) is 26%, the molar fraction of DDS (x_{DDS}) is calculated using the molecular weights of the components (244 g/mol and 422 g/mol for DDS and TGDDM, respectively). So, $x_{\mathrm{DDS}} = \frac{m_{\mathrm{DDS}}/\mathrm{MW}_{\mathrm{DDS}}}{m_{\mathrm{DDS}}/\mathrm{MW}_{\mathrm{DDS}}+m_{\mathrm{TGDDM}}/\mathrm{MW}_{\mathrm{TGDDM}}} = 0.38$ and therefore $x_{\mathrm{TGDDM}} = 1 - x_{\mathrm{DDS}} = 0.62$.

Each chemical group in the two components of the resin makes a contribution to the total number of degrees of freedom. In GIM, only the skeletal modes normal to the main polymer chain axis are considered and the contribution each group makes is shown in Table 1. By summing each chemical group's contribution to the total degrees of freedom the totals for TGDDM and DDS are 36 and 12, respectively, though these values are for linear versions of these polymers. To include crosslinking, N is reduced by 3 for each three-way branched crosslinking site on each molecule, decreasing the values to 30 and 6, respectively. With stoichiometry included, the value of N for the TGDDM/DDS mer unit is (0.62 × 30) + (0.38 × 6) = 20.9.

Similarly, each chemical group makes a contribution to the total cohesive energy as indicated in Table 1. Therefore, the total summed cohesive energy for TGDDM and DDS are 151,700 J/mol and 113,000 J/mol, respectively. The net effect of the epoxy ring opening as part of the polymerisation is an increase in E_{coh} of 10,000 J/mol per epoxy group. Hence, the total cohesive energy for TGDDM and DDS are 191,700 J/mol and 113,000 J/mol, respectively. With stoichiometry included, the value of E_{coh} for the TGDDM/DDS mer unit is (0.62 × 191,700) + (0.38 × 113,000) = 161,794 J/mol.

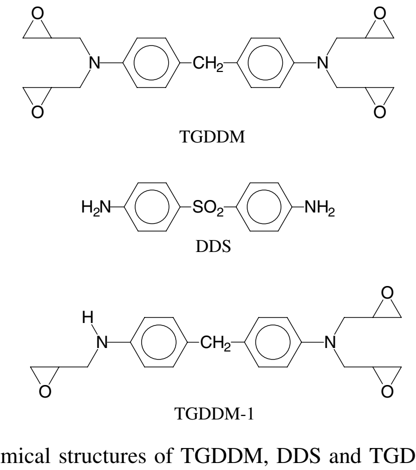
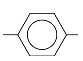
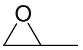


Fig. 1 Chemical structures of TGDDM, DDS and TGDDM-1

Table 1 GIM parameters

	E_{coh} (J/mol)	N	V_{w} (cm^3/mol)	M (g/mol)
CH_2	4500	2	10.25	14
	25,000	3	43.3	76
SO_2	45,000	2	20.3	64
N	9000	2	4	14
CHOH	20,800	2	11.5	30
	15,300	4	22	44

The van der Waal's volume and molecular weight group contributions are shown in Table 1 and are summed and averaged by the same method used for N and E_{coh}. The reference temperature, θ_1, for TGDDM/DDS is 550 K as is common to all phenyl ring containing polymers [2].

Thermal properties of polymers using GIM

Porter [2] has derived a number of expressions for the thermal properties of polymers. A summary of the important aspects of the derivation of a general glass transition temperature equation are presented below. Initially, expressions for H_{C}, H_{M} and H_{T} are substituted into Eq. (1). At the glass transition temperature, the interaction energy and thermal energy can be defined as ϕ_{g} and H_{g}, respectively. Now, $\phi_{\mathrm{g}}=0.787\phi_{\mathrm{o}}=\phi_{\mathrm{o}} - H_{\mathrm{g}} - H_{\mathrm{C}}$. Hence

$$H_{\mathrm{C}} + H_{\mathrm{T}} = 0.213\phi_{\mathrm{o}} \tag{6}$$

H_{M} represents the mechanical energy stored in the polymer unit and is given by

$$H_{\mathrm{M}} = \frac{N}{3}k\Delta T_{\mathrm{m}} \tag{7}$$

where k is the Boltzmann constant and ΔT_{m} is a hypothetical temperature increment used to give the mechanical energy an equivalent thermal energy per interaction. H_{T} can be given by the Tarasov approximation of the Debye theory for a one-dimensional chain oscillation between two mer units [15]. Porter [2] has provided a simplified form of the Tarasov approximation by considering only the skeletal vibrations.

$$H_{\mathrm{g}} = 0.11\phi_{\mathrm{o}} = N\frac{k}{3}\left[T_{\mathrm{g}} - \frac{\theta_1}{6.7}\tan^{-1}\left(\frac{6.7}{\theta_1}T_{\mathrm{g}}\right)\right] \tag{8}$$

Equation (8) can be solved by incorporating Eq. (6) and noting that $H_{\mathrm{C}} = 0.107\phi_{\mathrm{o}}$. From the relationship between E_{coh} and ϕ_{o} in Eq. (5) a predictive equation for T_{g} can be obtained.

$$T_g = 0.224\theta_1 + 0.0513\frac{E_{coh}}{N} \tag{9}$$

The excellent correlation between T_g values predicted by Eq. (9) and those from experiment for a range of linear polymers is presented in reference 2.

The specific example chosen to highlight the use of the GIM model is the amine-cured epoxy resin, MY721. Figure 2 shows two experimental DMTA tanδ plots for MY721 cured with DDS at 180 °C and 200 °C. There are two main points to make about these plots. Firstly, the major peak gives the glass transition temperature for the resin, which in both spectra is approximately 290 °C. This value compares well previously reported temperatures [3, 17], though other reported values vary significantly. It is important to emphasise at this stage that the absolute values of T_g is a function of the exact hardener composition and the degree of cure achieved. Furthermore, it can also differ with the measuring technique because it is a kinetically controlled transition. For the purposes of this work, the major features of the tanδ plot and the changes observed on increasing the cure temperature are of interest. The second point to observe from Fig. 2 is that, when cured to 180 °C, a secondary peak is seen at approximately 235 °C, 55 °C less than the observed T_g. This peak disappears when the resin is cured to 200 °C. The following analysis uses GIM to predict the T_g of MY721/DDS and explain the origin of the secondary peak.

The main difference between simple linear polymers and cured epoxy resins is the introduction of crosslinking between the polymers chains to form a network. The current method of dealing with the effect of crosslinking in GIM is to modify the degrees of freedom to account for changes at the molecular level. As mentioned earlier, this is done by reducing the number of degrees of freedom of each component by 3 for each three-way branched crosslink site. In addition, as a consequence of the epoxy ring being opened E_{coh} increases by 10,000 J/mol per epoxy group. These changes are intentionally simple in order to facilitate the calculation of properties of thermosetting polymers. In the case of TGDDM cured with DDS, Eq. (9) is modified to include stoichiometrically correct amounts of the epoxy and hardener as shown below

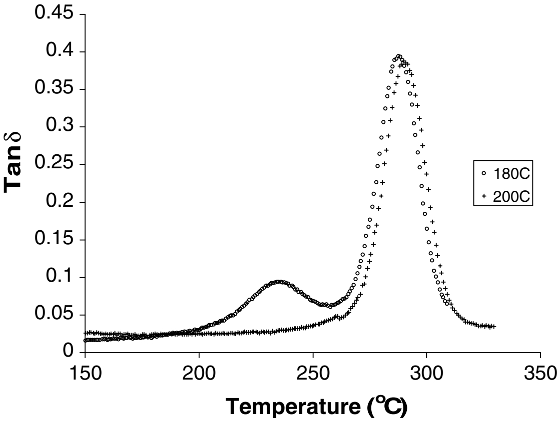


Fig. 2 DMTA plot of TGDDM cured with 26% by weight DDS to 180 °C and 200 °C

Table 2 Thermal and mechanical properties of TGDDM/DDS

	GIM	Experiment
Glass transition temperature, T_g (°C)	248	260–290
Density, ρ (g/cm^3)	1.26	1.29
Bulk modulus, B (GPa)	7.54	6.99
Tensile modulus, E (GPa)	5.34	5.03
Thermal expansion coefficient, α ($\times 10^{-6}$ K^{-1})	55	≈50

$$T_g = 123.2 + \left[\frac{0.0513(x_{DDS}E_{cohDDS} + x_{TGDDM}E_{cohTGDDM})}{x_{DDS}N_{DDS} + x_{TGDDM}N_{TGDDM}}\right] \tag{10}$$

where x_a is the molar fraction of component a and θ_1 = 550 K has been substituted in. Hence, the T_g for TGDDM/DDS is calculated by GIM to be 248 °C. Further refinement of the GIM prediction of thermal properties and increased accuracy in the absolute values of the glass transition temperature will be addressed in the future. A summary of the GIM calculated properties of TGDDM cured with DDS compared to the experimental values is presented in Table 2.

The complicated nature of the chemistry of the TGDDM/DDS system means the secondary peak in the tanδ spectrum at 235 °C could be caused by a variety of species. One of the strengths of GIM is the direct link between molecular architecture and observable properties and this can be exploited here. Two hypotheses regarding the cause of the extra peak arise. Firstly, the peak may be due to one of the impurities in MY721. The most abundant of these, ''TGDDM-1,'' has one of the four glycidyl groups replaced with a hydrogen [3, 16] (see Fig. 1). A reactive secondary amine group is therefore present in the monomer and this can be incorporated directly into the GIM model as shown below. $E_{cohTGDDM}$ is reduced by 10,000 for losing a hydrogen bond site and further reduced by 15,300 for having one less epoxy group, so $E_{cohTGDDM-1}$ = 166,400 J/mol. N_{TGDDM} is reduced by 6 for having one less epoxy group and increased by 3 for losing a three-way branched crosslink site, so $N_{TGDDM-1}$=27. Putting these modified values into Eq. (10) gives a T_g for TGDDM-1/DDS of 244 °C. This value is only 4 °C different to the previously calculated value for pure TGDDM/DDS, therefore the presence of TGDDM-1 in MY721 is unlikely to be the cause of the secondary peak.

Secondly, the extra peak may be a result of unreacted epoxy groups in the mix. Again, this situation can be modelled in GIM by changing the parameters to account for the altered chemistry. E_{cohTGDDM} is reduced by 10,000–181,700 for losing a hydrogen bond site and N_{TGDDM} is increased by 3 to 33 for losing a branched crosslink site. These modified values give a T_g for DDS cured TGDDM with an unreacted epoxy group of 201 °C. The difference between this value and the fully reacted TGDDM is 47 °C, a change which correlates nicely with the experimental gap between the peaks (55 °C). However, this is also not likely to be the cause of the secondary peak. A resin based on a stoichiometric ratio of DDS and MY721 is highly exothermic and practically it is difficult to cast resin coupons or composite materials which are void free and have a homogenous molecular structure. Further, the cure chemistry is rather complex because of the different reactivity of primary and secondary amines to epoxy groups. Therefore, DDS will have a functionality which ranges from 2 to 4. The probability of any secondary amines formed during the initial reaction between DDS and MY721, reacting further increases with cure temperature. Therefore, the crosslink density will be higher in the 200 °C resin compared to the 180 °C resin. In other words, the functionality of DDS could be ≈2 at 180 °C but as much as 20% larger at 200 °C [3].

In a similar manner, the functionality of the TGDDM epoxy may range from 4 to 8 because hydroxyl groups which form during the initial reaction can take place in etherification reactions. Hydroxyl–hydroxyl reactions are highly unlikely but hydroxyl–epoxy reactions can become significant in high temperature cures. Thus with a molar excess of epoxy, the network chains will be more linear and epoxy group terminated. On post-curing, secondary reactions will occur leading to a reduction in the average network chain length and the number of unreacted epoxy groups. Figure 3 illustrates the nature of the crosslinking phenomena. In particular, at the onset of secondary amine incorporation, the linearity of the network chains is changed significantly. The secondary relaxation which occurs in the 180 °C cured resin must reflect this high linearity of the network chains and can be attributed to the additional conformational freedom introduced with the ‘‘partially reacted epoxy’’ illustrated in Fig. 3. The secondary relaxation peak cannot be associated with pendant free epoxy groups otherwise most cured epoxy resins would exhibit similar relaxation events. For example, DMTA plots for DDS cured MY0510 (which has three epoxy groups rather than four) do not show a secondary peak [17].

Mechanical properties of polymers using GIM

To predict the stiffness properties of a composite material we use the Halpin–Tsai equations. These incorporate the

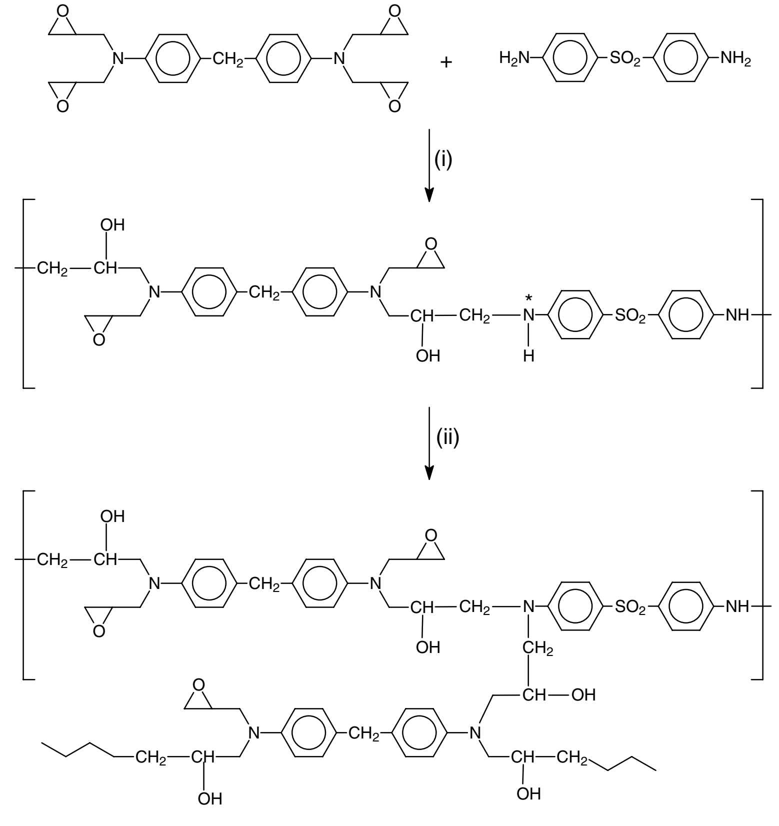


Fig. 3 Typical crosslinking process in TGDDM cured with DDS. In reaction (i), TGDDM reacts with DDS to form a linear chain in an initiation step. In reaction (ii), a second linear chain reacts with the first at a secondary amine site (N*) to form a crosslinked network

law of mixtures estimate for the longitudinal modulus of a unidirectional ply with Halpin–Tsai equation for the transverse modulus. The principle property of the matrix included in these estimates is the resin modulus. For the amorphous glassy polymers used as matrices in most composite laminates it has been established that the intermolecular forces between the macromolecular segments are responsible for the deformation under load. For example, it can be shown using Eq. (2) that the tensile or compression modulus of a glassy polymer is essentially the same as a rapidly quenched gas such as methane, at liquid nitrogen temperatures. In this case the gas was not allowed to crystallise and an amorphous glass formed which could be tested under compression. The bulk modulus B can be defined as equal to $V\frac{\mathrm{d}P}{\mathrm{d}V}$ and from this the following expression is derived

$$B = 1.7\frac{E_{\mathrm{coh}}}{V_{\mathrm{w}}}\frac{\left[2\left(\frac{r_{\mathrm{o}}}{r}\right)^{6}-\left(\frac{r_{\mathrm{o}}}{r}\right)^{12}\right]}{\left(\frac{r}{r_{\mathrm{o}}}\right)^{2}-1}. \tag{11}$$

Using appropriate values for the separation distance between segments in an amorphous glass the following generic expression is obtained for linear polymers

$$B = 6.4\frac{E_{\mathrm{coh}}}{V_{\mathrm{w}}}. \tag{12}$$

Again, Eq. (12) is plotted for a wide range of polymers in reference 2 and this illustrates the validity of the GIM approach for predicting the engineering moduli of linear polymers.

Equation (12), which represents the lower theoretical limit of B, has recently been reworked to account for the mechanical properties of spider silk [18, 19] as shown below

$$B_{\mathrm{o}} = 18\frac{E_{\mathrm{tot}}}{V}. \tag{13}$$

Now, the total energy, E_{tot}, and volume of the mer unit, V, are related to the bulk modulus and this represents the upper theoretical limit to B for a perfect 1:1 resin. In order to evaluate Eq. (13) it is therefore necessary to derive values for E_{tot} and V.

Combining Eqs. (1) and (2) and noting that to a first approximation, $V \propto r^2$ gives

$$E_{\mathrm{tot}} = E_{\mathrm{coh}}\left[\left(\frac{V_{\mathrm{o}}}{V}\right)^{6}-2\left(\frac{V_{\mathrm{o}}}{V}\right)^{3}\right] = -E_{\mathrm{coh}} + H_{\mathrm{T}} + H_{\mathrm{C}} \tag{14}$$

where H_{C}, the configurational energy, is equal to $0.107E_{\mathrm{coh}}$ and H_{T}, the thermal energy, is equal to $\frac{NR[T_1]}{4}$. [T_1] represents a term equal to $T - \frac{\theta_1}{6.7}\tan^{-1}\left(\frac{6.7T}{\theta_1}\right)$, a simplification of the Tarasov one-dimensional Debye functions. For TGDDM/DDS at 300 K, $[T_1]$ = 193 K. N is the degrees of freedom of the system and R the gas constant. By substituting the expressions for H_{T} and H_{C} and dividing through by E_{coh}, a quadratic expression in terms of $\left(\frac{V_{\mathrm{o}}}{V}\right)^3$ can be obtained. For TGDDM/DDS, this solves to give $\left(\frac{V_{\mathrm{o}}}{V}\right) = 0.844$ and as $V_{\mathrm{o}} = 1.26V_{\mathrm{w}}$ the volume of the mer unit, $V = 1.493V_{\mathrm{w}}$. As the van der Waal's volume of the mer unit is 188.65 cm^3/mol, V = 281.6 cm^3/mol and this value can be used in calculating the various moduli. As a simple experimental validation, the densities of four samples of MY721 cured with DDS to 180 °C were measured using water displacement giving an average value of 1.29 g/cm^3. The samples were immersed in distilled water for a maximum of 1 min to avoid the possibility of moisture absorption by the resin. The average molecular weight of the mer unit is 354.4 g/mol giving a GIM calculated density of 1.26 g/cm^3, a value which is in good agreement with experiment. With the variables in Eqs. (12) and (13) accounted for, the lower and upper limits for the bulk modulus of TGDDM/DDS are 5.5 GPa and 8.7 GPa, respectively.

The bulk modulus in Eq. (13) is referred to as B_{o} represents an overestimation due to the presence of a peak in the DMTA plot caused by a beta relaxation event. The peak, observed at ≈ –50 °C, is attributed to relaxations from glyceryl or diphenylpropane groups [20]. In order to account for this effect, a correction factor needs to be derived. From reference 2,

$$\tan\delta = A\frac{\mathrm{d}B}{\mathrm{d}T} \quad \text{where}\, A = \frac{150{,}000L}{\theta_1 M}. \tag{15}$$

Integration gives

$$B = B_{\mathrm{o}} - \frac{\int \tan\delta \mathrm{d}T}{A} \tag{16}$$

The molecular geometry parameter, A, is estimated using the total mer unit geometry and not the mean for convenience. In the case of TGDDM/DDS, the length of a mer unit, L, is 0.3 nm (estimated using a simple molecular modelling routine) and the total molecular weight, M, is 666. A is therefore approximately 1.29× 10^{-9}. The background cumulative loss tangent, $\int \tan\delta \mathrm{d}T$, is fairly constant for many polymers [2] and can be estimated to be approximately 2.25. The total cumulative value of tanδ between T = 0 K and 300 K as estimated from a typical DMTA spectrum [21] is 3.68. Hence, the cumulative loss tangent due solely to the beta transition is approximately

3.68 – 2.25 = 1.43. Now, the corrected value of the bulk modulus from Eq. (17), is 8.7–(1.43/1.23) or B = 7.54 GPa.

The following equation is used in the GIM estimation of the tensile modulus, E

$$E = B \exp\left[\frac{-\int_0^T \tan \delta \mathrm{d}T}{A \times B_{\mathrm{o}}}\right] \tag{17}$$

Using both the upper limit of the bulk modulus, B_{o}, and the corrected, real value, B, Eq. (16) gives a tensile modulus of 5.34 GPa. Standard mechanics equations relating the engineering moduli give a Poisson's ratio, v = 0.38. The experimental compressive modulus of TGDDM/DDS cured to 200 °C is 5.03 GPa at 22 °C [14]. In the elastic region, the compressive and tensile moduli are equal so the GIM calculated value is in good agreement with experiment. Using the Poisson's ratio of 0.38, the experimental bulk modulus is approximately 6.99 GPa. A summary of the GIM calculated properties of DDS cured TGDDM is presented in Table 2.

Briefly, the GIM estimation of the linear thermal expansion coefficient, α, can be included here. The calculation of α using the group interaction method is derived in Porter's text [2] and can be simplified as shown below

$$\alpha = \frac{1.38}{3} \cdot \frac{N}{E_{\mathrm{coh}}} \cdot [T_2] \quad \mathrm{where}[T_2] = \frac{\left(\frac{6.7T}{\theta_1}\right)^2}{1 + \left(\frac{6.7T}{\theta_1}\right)^2} \tag{18}$$

The term $[T_2]$ is approximately 0.93 at 300 K for TGDDM/DDS. Using the stoichiometrically correct values of N and E_{coh} estimated earlier gives $\alpha = 55 \times 10^{-6}\ \mathrm{K}^{-1}$ which compares well with experimental values of α obtained locally at $\approx 50 \times 10^{-6}\ \mathrm{K}^{-1}$ [15].

Conclusions

The use of group interaction modelling to predict macroscopic engineering properties of thermosetting amine-cured epoxy resins from molecular parameters has been addressed. Emphasis has been placed on the simplification of existing group interaction methods of assessing the thermal and mechanical properties of polymers whilst extending their applicability to include thermosets. Crucially, the effect of crosslinking has been incorporated into the model and the associated fundamental changes in the engineering properties are accounted for. The thermal and mechanical properties of a typical amine-cured epoxy resin (MY721/DDS) were calculated using the latest group interaction models and comparison to experiment is encouraging.

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