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Prediction of the glass transition temperatures for epoxy resins and blends using group interaction modelling

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Abstract

Application of modern simulation methods for the prediction of the engineering properties of polymeric materials may be a substitute for more time consuming experiments. The principles of molecular modelling have been combined with group interaction modelling (GIM) for the prediction of properties of thermoset resins. The glass transition temperature of the systems was predicted from the chemical structure of the resins and the effect of different hardeners on T_g was assessed. Different chemical reaction mechanisms which occur during resin cure were incorporated into the model for better predictions. A new set of expanded GIM equations include one for determination of model input parameters from the conventional modelling principles for the estimate of T_g. Differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) experimental values of degree of cure and glass transition temperature were used to provide comparative analysis for the computations. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Group interaction modelling; Epoxy resins; DDS

1. Introduction

Composite materials rely on a polymeric matrix to support the reinforcing fibers in a structural component. At angles other than 0° to the applied stresses, the matrix contributes significantly to the load-bearing capacity of the composite. Unfortunately, the service temperature is determined by the glass transition temperature of the resin, which can be reduced by moisture absorption [1]. Other relaxation events can also develop in the glassy matrix and reduce further the temperature at which the off-axis modulus of the composite is reduced. These β-transitions can also lead to a highly non-linear matrix expansion coefficient which enhances the constrained contraction on cooling and increases the magnitude of the thermal strain which develops in a laminate structure [2]. These residual strains are tensile in the plies which lead to first ply cracking and often dominate the damage accumulation mechanisms. It therefore becomes feasible to predict the performance of a composite laminate, especially under environmental conditions from the predicted matrix properties.

Detailed understanding of the chemical reactions which occur during the cure of an epoxy resin (e.g. glycidyl ether epoxies cured with aromatic diamines) network which determines its glass transition temperature can be studied using experimental techniques such as differential scanning calorimetry (DSC) [3–6], spectroscopy [7,8], nuclear magnetic resonance [9] and fluorescence [10].

Such methods provide a detailed knowledge of the cure mechanisms and the advisable temperature during the formation of three-dimensional network in the material. Among the many factors which influence the glass transition temperature of a polymer are the monomer functionality, average molecular weight of a network chain between cross-links, the amount of unreacted monomer and type of cross-linking agent employed [11]. Low temperature relaxations can be observed in thermoset resins and probably arise from cooperative bond rotation of components of the network chains. In a recent study [12], a number of empirical correlations between structure and shape of the secondary relaxation curves were proposed.

Group interaction modelling (GIM) [13] is one of the existing methods for property prediction in polymers derived from classical thermodynamics and atomistic modelling principles and is a generalized type of cell model. These models consider the Van der Waals interatomic interaction between neighbouring units in a

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Nomenclature

A_{ij}	short range repulsive forces
a_{H}	fraction of fully reacted hardener
a_{f}	fraction of fully reacted molecule
B_{ij}	long range attractive forces
b	fraction of unreacted hardener
C	degree of cure
C_{et}	fraction of etherification reactions
$C_{\mathrm{mon-H}}$	hardener-epoxy degree of cure
DSC	differential scanning calorimetry
E_{coh}	cohesive energy
$E_{\mathrm{coh}_{\mathrm{et}}}$	cohesive energy of a single ether group
$E_{\mathrm{coh}_{\mathrm{H}}}$	cohesive energy of hardener
$E_{\mathrm{coh}_{\mathrm{mon}}}$	cohesive energy of monomer
ΔE_{et}	loss in cohesive energy during etherification reaction
f	functionality of the polymer
$f_{\mathrm{H\,max}}$	maximum functionality of hardener
$f_{\mathrm{H}_i\mathrm{re}}$	functionality of reacted hardener in resin system
f_{mon}	functionality of the monomer
ϕ	total energy of interaction between polymer mer units
ϕ_0	total energy of interaction between polymer mer units for molecular conformations of lowest energy
h	Planck constant
H_{C}	configurational energy
H_{M}	mechanical energy
H_{T}	thermal energy
m_{cr}	number of cross-links per averdge repeat unit
M_{ep}	monomer molar mass
M_{H}	molar mass of hardener
N	number of degrees of freedom
N_{C}	number of degrees of freedom lost due to molecule cyclization
N_{f}	degrees of freedom for fully reacted molecule
N_{H}	number of degrees of freedom of hardener
N_{L}	number of degrees of freedom lost by each reacted chain end
N_{mon}	number of degrees of freedom for monomer
N_{R}	number of degrees of freedom lost by non-epoxy groups reactions
N_{un}	number of degrees of freedom for unreacted molecule
m	number of side chain epoxy groups in monomer
n_{a}	Avogadro number
n_{ep} and n_{H}	mole coefficients of epoxy monomer and curing agent
π	constant 3.141592654
R_{ij}	non-bonded distance between interacting atoms
T	temperature
T_{g}	glass transition temperature
ν	vibrational frequency of the chain
ω	cohesive energy conversion coefficient
w_{C}	the percentage of epoxy groups consumed by monomer cyclization reactions
w_{im}	the percentage of monomer impurities
$\chi_{\mathrm{st\,H}}$	stoichiometric coefficient of hardener

system consisting of a central mer unit and six surrounding mer units. These seven units form the hexagonal molecular chain packing of a cell, where thermodynamic principles can be used to describe the changes in cell geometry at temperatures below and above the glass transition. The key factors in the cell models are the strength of the interactions (described by a change in potential of the system), the number of contacts between molecules and the degrees of freedom per molecule.

Some of the most practical and less time consuming calculations in atomistic modelling are molecular mechanics and molecular dynamics methods. Molecular mechanics, considers the molecular geometry, bond energies and different conformational states while molecular dynamics simulates the interaction between a group of atoms in terms of the potential energy of the system as a function of time. Computer codes can be used for the calculation of the intermolecular interactions and packing geometry, whereas the thermodynamic approach of Gibbs and DiMarzio [14] can be used to estimate changes in conformational entropy.

The principles of the GIM model can be used together with connectivity indices [15] and atomistic modelling methods, to provide a practical approach for the prediction of thermo-mechanical properties of a highly cross-linked thermosetting resin.

2. Modelling methodology

2.1. GIM review

The basis of the GIM method is an energy balance of intermolecular forces calculated from the thermodynamic parameters for individual molecular segments. The Lennard-Jones function can be used to estimate the total energy of interaction, ϕ, which can be defined by the Van der Waals and other intermolecular forces. The Lennard-Jones potential is given by Eq. (1).

$$\phi = \Sigma\left(\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^{6}}\right), \tag{1}$$

where A and B are the short range repulsive and the long range attractive forces, respectively; and R_{ij} is the non-bonded distance between the interacting atoms.

The energy balance is made up from contributions from: configurational (H_C), thermal (H_T) and mechanical (H_m) energies

$$\phi = -\phi_0 + H_C + H_T + H_m, \tag{2}$$

where ϕ_0 is the energy of interaction for the molecular conformation of lowest energy.

In GIM, all of the input parameters were taken from reliable sources and are supported by experimental measurements. Depending on its structure, each chemical group has certain number of degrees of freedom which determine the ability to change the conformation. The most stable conformations are those with the lowest total energy, where the total energy is described as the sum of potential and kinetic energies of interaction between neighbouring molecular chains. The GIM cohesive energy sums all intermolecular forces of interaction between the neighbouring mer units and is proportional to the potential of the system ϕ_0 in the lowest state of total energy.

GIM cohesive energy E_{coh} can be obtained from group contribution tables, and is related to ϕ_0 [13]

$$E_{coh} = \frac{3}{4}\phi_0 n_a, \tag{3}$$

where n_a is Avogadro number.

Eq. (2) can be solved by including contributions for H_c, H_m and H_T. Furthermore, at the glass transition temperature

$$\phi = \phi_g = 0.787\phi_0, \tag{4}$$

$$H_C + H_T = 0.213\phi_0. \tag{5}$$

H_C is also related to ϕ_0 according to Eq. (6)

$$H_C = 0.107\phi_0. \tag{6}$$

The equation for mechanical energy can be written to compensate for the elastic responses of the polymer to an external force field, whereas the term H_m itself represents the amount of energy stored in polymer unit

$$H_m = \frac{N}{3}k\Delta T_m, \tag{7}$$

where N is the number of degrees of freedom, k the Boltzmann constant and ΔT_m is a hypothetical temperature increment.

Thermal energy (H_T) is expressed by the Tarasov approximation [16] of Debye theory for one-dimensional chain oscillation between two neighbouring mer units. Porter [13] suggests that only the skeletal vibrations of the chain contribute to thermal energy and a simplified form of the Tarasov approximation can be used for GIM

$$H_T = N\frac{k}{3}\left[T - \frac{\theta}{6.7}\tan^{-1}\left(\frac{6.7}{\theta}T\right)\right], \tag{8}$$

where θ is the Debye reference temperature, N the number of degrees of freedom and can be taken from GIM group contribution table and T is the temperature in K.

Eq. (8) can be further simplified by assuming the temperature to be T_g, expanding the $\tan^{-1}$ function and incorporating Eq. (5) for the thermal energy at the glass transition, where ϕ_0, is related to cohesive energy by Eq. (3). The result is a predictive formula for the glass transition temperature

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

where reference temperature θ is related to the vibrational frequency of the chain.

2.2. Glass transition temperature prediction

For the prediction of the glass transition temperature, GIM model-parameters can be assigned from the group contribution tables according to the chemical structure. The advantage of this model is in its flexibility. Based on GIM conventional principles, we can calculate the number of degrees of freedom of a linear polymer, and take into account the degrees of freedom which were lost due to formation of the cross-links. Thus Eq. (9) was modified accordingly and the concentration of each component was included in the formula by introducing the stoichiometric

Table 1
The cure schedules for DDS and DICY cured resins

Resin type	Hardener level (wt%)	Curing procedure
MY721-DDS	26	Degas for 2 h at 80°C, pour into mould, cure at 130°C for 1 h, heating 1°C/min up to 180°C, cure for 2 h; cooling at 3°C/min
MY0510-DDS	36	
924-epoxy	22 wt% DDS 8 wt% DICY	
MY721-DICY	14	Degas for 2 h at 80°C, pour into mould, cure at 160°C, heating at 1°C/min for 2 h; heating 1°C/min up to 175°C and cure for 1 h
MY0510-DICY	19	Degas for 2 h at 60°C, pour into mould, heat at 2°C/min to 110°C for 20 min, cooling to 90°C, at 5°C/min, dwell 30 min, to 110°C at 2°C/min, dwell for 30 min, cool to 100°C at 5°C/min, dwell 30 min, heating up to 122°C dwell for 3 h, cooling at 2°C

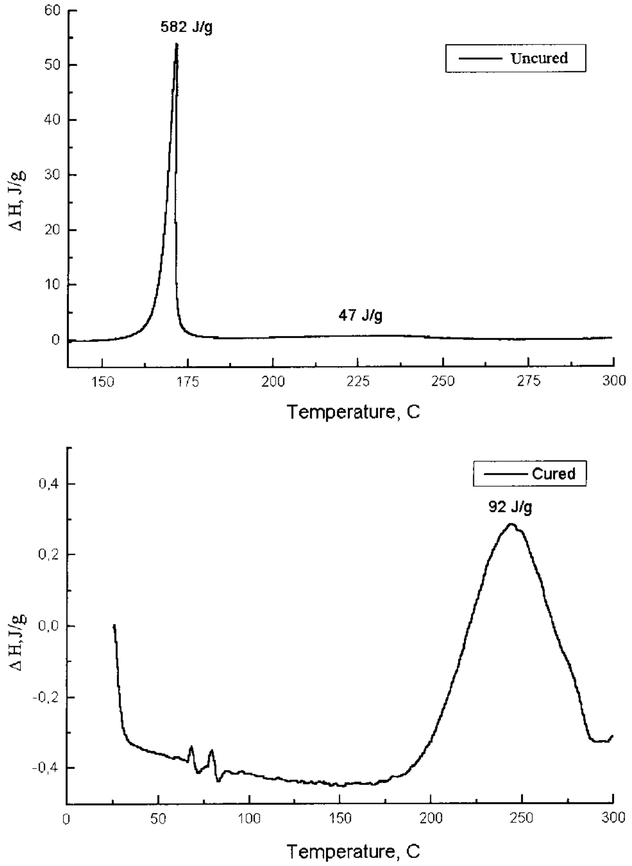


Fig. 1. DSC Curves for the MY721-DICY resin/hardener mixture and cured resin.

coefficient x_{st}

$$T_g = 0.224\theta + 0.0513\frac{E_{coh_{mon}} + x_{st\ H1}E_{coh_{H1}} + x_{st\ H2}E_{coh_{H2}} - \Delta E_{et} - \omega}{(N_{mon} - fN_L) + x_{st\ H1}N_{H1} + x_{st\ H2}N_{H2}}, \quad (10)$$

where subscript H1 and H2 define the type of hardeners used, N_{H1} and N_{H2} are the average number of degrees of freedom for the hardeners per single mer unit, N_L stands for the number of degrees of freedom lost by each epoxy group and ω the cohesive energy conversion coefficient describes the cohesive energy per epoxy groups which is lost during the formation of the cross-links. GIM tabulated values of cohesive energy assume that polymer has a linear chain. Therefore, for a network, this can be taken into account by calculating the loss in cohesive energy using the Eq. (11)

$$\omega = m_{cr} \times 33,000(C - 0.5), \quad (11)$$

where m_{cr} is the number of monomer cross-links per single average mer unit and $(C - 0.5)$ is the fraction of cure above the critical level. The critical level of 50% assumes the formation of a linear chain only.

In different epoxy systems, particularly those cured with aromatic amines, the etherification reactions play a significant role and should be included in the model. For instance, in TGDDM–DDS system the hydroxyl group reacts with an epoxy group in the formation of a bridging ether linkage [17,18]. Thus each reacted epoxy group loses its degree of freedom, whereas the reacted hydroxyl group has lost cohesive energy in the formation of an ether group. The estimate is given by Eq. (12)

$$\Delta E_{et} = f_{mon}C_{et}(E_{coh_{OH}} - E_{coh_{et}}), \quad (12)$$

where f_{mon} is the functionality of the monomer and C_{et} is the fraction of etherification reactions.

3. Experimental

To assess the accuracy of new GIM-based model, we considered different epoxy resin systems.

3.1. Investigated resin systems

924-epoy resin (Hexcel), a composite matrix, was chosen for the analysis since its approximate chemical recipe can be ascertained from safety data sheets. In commercial use, it is toughened by a thermoplastic polyether sulphone. But we have studied the base epoxy resin. It is believed to be a 50:50 blend of tetrafunctional glycidyl amine (MY721) and the triglycidyl aminophenol (MY0510) monomers. Diaminodiphenylsulphone (DDS) and dicyandiamide (DICY) are the hardeners.

Four simpler epoxy resins based on these components were prepared. Thus MY721 and MY0510 monomers were cured separately with DDS and DICY hardeners.

3.2. Resin cure

All resin mixtures were prepared according the chosen recipe and cured following the procedure described below. For DDS-based resins, a standard cure schedule was employed, whereas the resins cured with DICY required the optimization of the cure regime to avoid the exothermicity of the amino-epoxy reaction (Table 1). The cured resin plates were used for dynamic mechanical thermal analysis (DMTA) and DSC investigations while the pure resin mixtures were used for measuring the heat of cure by DSC.

3.3. Glass transition temperature measurement

The dynamic mechanical thermal analyser Mk3 (Rheometric Scientific) at 1 Hz was used to determine the glass transition temperature of a cured resin (sample

Table 2
The degree of cure for analyzed resin systems

Resin type	MY0510-DDS	MY0510-DICY	MY721-DDS	MY721-DICY	924-epoxy
ΔH_{cured} (J/g)	26	154	86	92	37
$\Delta H_{\text{uncured}}$ (J/g)	504	844	643	629	483
Conversion (%)	95	82	87	85	92
T_g (°C)	285	218	288	258	234

size $40 \times 10 \times 1.4$ mm^3). The samples were heated from ambient temperature to 310°C at the scanning rate of 2°C/min. To verify the validity of the data, a new resin mixture with the same composition was prepared, cured and analyzed by DMTA. The result was within 2°C.

3.4. Determination of the degree of cure

The DSC (Du Pont Instruments) was used to assess the degree of cure of the resins. The heating rate in case of 924-epoxy, MY721-DDS systems was 10°C/min for both cured and uncured samples. In the case of MY721-DICY and MY0510-DICY resins, low heating rates were employed such as 2 and 1°C/min, respectively. This was necessary to avoid the exothermic reaction during cure in DSC. The enthalpy of cured specimens was measured at a high rate of 10°C/min.

From the difference between the enthalpy of cured and uncured samples, the degree of cure for all systems was calculated. Our experimental set-up was calibrated to determine the overall heat of reaction at these defined heating rates.

Higher scanning rates are preferable because a shorter experiment time minimizes material decomposition that can contribute to the heat content. Such influences on the overall enthalpy can bring measurement errors.

In the case of DICY cured systems, initially, higher scanning rates such as 5°C/min were found to be complicated by the exotherm so that lower rates of 1 and 2°C/min were selected.

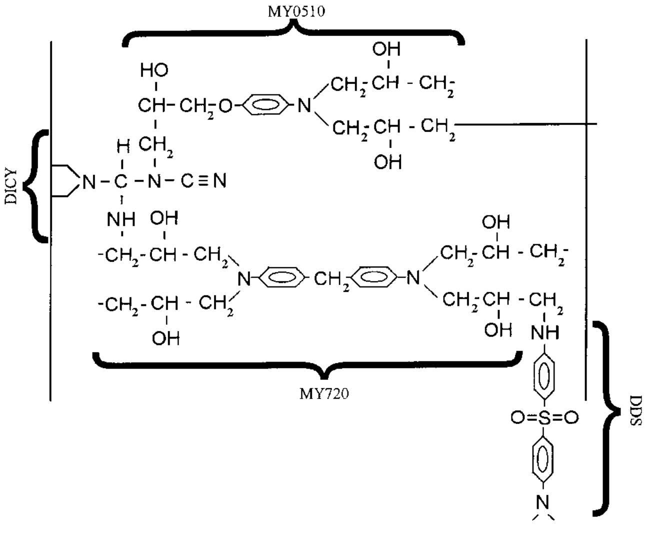


Fig. 2. Approximate Chemical structure of the cured 924-epoxy resin used for the calculations.

4. Experimental results

The degree of cure has been estimated from the residual exotherm of the resin plaque as given in Eq. (13). Typical DSC curves are given in Fig. 1. This can be attributed to the extent of reaction of the glycidyl or epoxy groups.

$$C = \frac{\Delta H_{\text{cured}}}{\Delta H_{\text{uncured}}} \text{ [J/g]}. \tag{13}$$

The estimated degrees of conversion of epoxy groups are given in Table 2 together with the glass transition temperatures obtained from the DMTA experiment.

4.1. Modelling results

For the calculation of the glass transition temperature, the resin chemistry has to be considered.

In 924-epoxy, the curing reactions are complex. Therefore for the model, we have made assumptions concerning the extent of primary and secondary amino epoxy a reactions. For example, the extent of primary amine–epoxy reaction in the beginning of the cure is known to be 2.3 times greater than the secondary amine–epoxy reaction, which occurs subsequently [19]. The overall rate of both reactions may differ and primarily depends on hardener level, cure temperature and purity of the monomer.

Therefore, the average structure (Fig. 2) accepted in the model assumes that under the recommended cure schedule the contribution from secondary β-hydroxy amine reaction in case of aromatic amines (such as DDS) to the glass transition temperature can be neglected in 924-epoxy. This is because these reactions are much slower and probably occur at a later stage. Thus the reactions of the second hardener — DICY will most probably complete the cure and chemically constrain the DDS secondary amine reactions.

The known DICY–epoxy reaction mechanism [20] shows that the DICY can be described as a polyamine and that the by-products of DICY–epoxy reaction play a insignificant role in determining the glass transition temperature. Therefore, the complexity of molecular architecture of the 3D thermosetting 924-epoxy resin has been simplified as shown in Fig. 2 to a combination of average molecular structures for the individual hardener–epoxy reaction.

For epoxy-based resins, the average reaction mechanism of the hardener was assumed. When the level of hardener is in stoichiometric amount, it is believed to react as a branched molecule. Higher hardener levels usually result in linear reactions. In this model, an average reaction mechanism of hardener was approximated by calculating the number of average degrees of freedom of hardener for a single repeat unit. The estimate was made from the standard measure of hardener and the degree of cure using simple chemical proportion (see Appendix A).

The degree of cure obtained from DSC indicates the total cure of the system which includes amino–epoxy reactions and etherification. The etherification in epoxy resins occurs in systems cured with aromatic amines such as DDS. It varies from 10 to 30% and mainly depends on the resin systems and level of hardener. For our DDS cured resin systems with excess of epoxy, we assume that 15% of epoxy groups form ether complexes, whereas in the 924 epoxy blended resin a higher amount of etherification is probable since the last one is catalyzed by presence of tertiary amines [19] which can be formed by DICY reactions. In DICY cured systems, there is no evidence of etherification as it is unlikely for such processes to occur without the presence of aromatic amines. In the 924-epoxy resin (having both hardeners DDS and DICY) DICY reactions lead to a higher tertiary amine concentration in the network and increase the degree of etherification. Thus in the model we have assigned an approximate value of 20%.

The glass transition temperature was estimated from Eqs. (10)–(12), taking the loss of six degrees of freedom of each reacted epoxy group Table 3. The values of cohesive energy for the monomer and hardener for use in formula (10) were taken from Table 4. The values of number of degrees of freedom for monomer and hardener were

Table 3
Calculated values of degrees of freedom (GIM) for main components of 924-epoxy Resin in accordance with their reaction mechanism

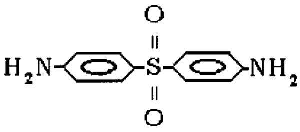
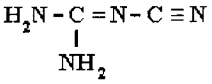
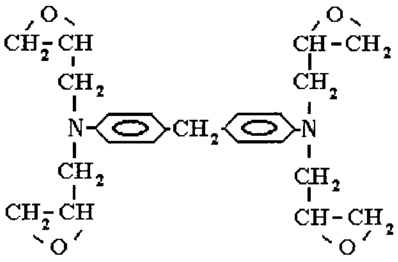
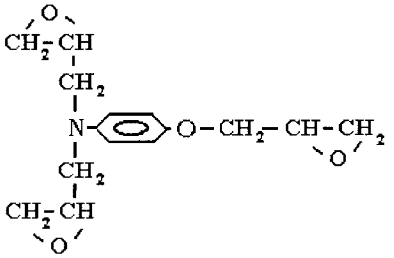
Chemical name	Chemical formula	Degrees of freedom (N)		
		Unreacted N_{un}	Single cross-link trifunctional	Two cross-links tetrafunctional N_f
Diamino diphenyl sulphone (DDS)		18	9	6
Dicyan diamine (DICY)	 $H_2N-\underset{\substack{\mid\\ NH_2}}{C}=N-C\equiv N$	9	4	3
Tetrafunctional glycidyl amine TGDDM (M720)		46	28	22
Trifunctional glycidyl amine (MY0510)		34	14	–

Table 4
Model input parameters

Chemical name	Van der Waals volume (cm^3/mol)	Molar volume (cm^3/mol)	GIM cohesive energy (J/mol)	Molecular weight (g/mol)
Diaminodiphen-ylsulphone (DDS)	121.5	176.8	113,000	246.5
Dicyandiamine	37.2	50.2	44,000	82.1
Tetrafunctional glycidylamine (M720)	243.4	367.5	204,000	436.5
Trifunctional glycidylamine (MY0510)	164.3	246.0	139,300	297.3

Table 5
Model parameters and glass transition temperature for MY0510-DICY system

Wt%	n_{DICY}	$x_{\mathrm{st\ DICY}}$	C	f_{mon}	$f_{\mathrm{DICY-max}}$	a_{f}	N_{DDS}	T_{g} (°C) calcd
19	0.85	0.68	0.82	3	4	0.72	4.65	213

calculated from GIM group contribution tables and are given in Table 3.

For the simple system MY0510-DICY, the degree of cure was taken from Table 2 assuming negligible amount of side-chain reactions. The model parameters and glass transition temperature were calculated and are given in Table 5.

For MY0510-DDS, two resin mixtures cured with different levels of hardener were considered (Table 6).

For MY721 resin, the presence of impurities in monomer plays a significant role in altering the curing chemistry thus influencing the T_g. The existing Eq. (10) neglects the influence of monomer cyclization reactions or reactions of non-epoxy groups from incomplete reaction during synthesis and may continue during or be involved in resin cure. Thus the use of Eq. (10) for MY721 resin resulted in predictive errors of 20–30° against the experimentally obtained values. Such errors were observed for both DICY and DDS cured resins. To improve the accuracy of the predictions the effect of TGDDM impurities was taken into account by expanding Eq. (10).

$$T_{\mathrm{g}} = 0.224\theta \quad + 0.0513\frac{E_{\mathrm{coh_{mon}}} + x_{\mathrm{st\ H1}}E_{\mathrm{coh_{H1}}} - \Delta E_{\mathrm{et}} - \omega}{(N_{\mathrm{mon}} - fN_{\mathrm{L}}) + x_{\mathrm{st\ H1}}N_{\mathrm{H1}} - w_{\mathrm{im}}N_{\mathrm{R}} - N_{\mathrm{C}}w_{\mathrm{C}}}, \quad (14)$$

where w_{im} is the percentage of TGDDM impurities, w_{C} the percentage of epoxy groups consumed by monomer cyclization reactions, N_{R} the number of degrees of freedom lost by non-epoxy group reactions and N_{C} is the number of degrees of freedom lost due to molecule cyclization.

A detailed discussion of the effect of impurities on T_g of MY721 resin will be presented in a subsequent manuscript [21]. The concentration of synthesis by-products in MY721 resin was obtained from the literature [19]. The average functionality of MY721 resin was lower than that of a pure TGDDM and was calculated to be 3.79. From Tables 3 and 4, a new estimate of cohesive energy and a number of degrees of freedom for MY721 resin was made.

Calculated model parameters and glass transition temperatures for these resins cured with DICY and DDS hardeners are given in Tables 7 and 8. For the complex 924-epoxy resin, the model requires estimates of cure which was done by modifying Eqs. (A6) and (A7) in Appendix A

$$C_{\mathrm{mon-H1}} = \frac{n_{\mathrm{H1}}f_{\mathrm{H1_{re}}}}{n_{\mathrm{H1}}f_{\mathrm{H1_{re}}} + n_{\mathrm{H2}}f_{\mathrm{H2_{re}}}}(C - C_{\mathrm{et}}), \quad (15)$$

$$C_{\mathrm{mon-H2}} = \frac{n_{\mathrm{H2}}f_{\mathrm{H2_{re}}}}{n_{\mathrm{H1}}f_{\mathrm{H1_{re}}} + n_{\mathrm{H2}}f_{\mathrm{H2_{re}}}}(C - C_{\mathrm{et}}), \quad (16)$$

where $f_{\mathrm{H_{re}}}$ is the functionality of reacted molecule and in case of DDS it is taken as 2.

For DICY and DDS, the values of $f_{\max}$ are taken as 4. The cohesive energy and a number of degrees of freedom for 924-epoxy were calculated as an average sum of both monomers

$$E_{\mathrm{coh_{924}}} = \frac{E_{\mathrm{MY721}} + E_{\mathrm{MY0510}}}{2}. \quad (17)$$

Table 6
Model parameters and glass transition temperature for MY0510-DDS system

Wt%	n_{DDS}	$x_{\mathrm{st\ DDS}}$	C	$C_{\mathrm{mon-DDS}}$	f_{mon}	$f_{\mathrm{DDS-max}}$	a_{f}	N_{DDS}	$\Delta E_{\mathrm{ether}}$ (J/mol)	T_{g} (°C) calcd
36	0.67	0.42	0.95	0.80	3	4	0.89	7.35	3015	283
45	0.98	0.54	0.97	0.82	3	4	0.61	10.65	3015	268

Table 7
Model parameters and glass transition temperature for MY721-DDS system

Wt%	n_{DDS}	$x_{st\ DDS}$	C	$C_{mon-DDS}$	f_{mon}	$f_{DDS-max}$	ΔE_{ether} (J/mol)	T_g (°C) calcd
26	0.62	0.46	0.87	0.65	3.79	4	3808	281

Table 8
Model parameters and glass transition temperature for MY721-DICY system

Wt%	n_{DICY}	$x_{st\ DICY}$	C	f_{mon}	$f_{DICY-max}$	a_f	N_{DDS}	T_g (°C) calcd
14	0.865	0.74	0.85	3.79	4	0.93	3.41	249

Assuming negligible monomer cyclization and taking $N_R/2 = 1.5$ with $w_i = 0.21$, the model parameters and the glass transition temperature were calculated (Table 9).

5. Discussion

A comparison of the computed and experimental values of glass transition temperature is given in Table 10. There is good agreement in each case, which demonstrated the value of GIM.

The accuracy of predictions from this GIM-based model depends on good knowledge of resin chemistry. The model shows good sensitivity to the influence of different hardeners as well as variable degree of cure on resin glass transition temperature. The comparison of the modelled and experimental values of glass transition temperature showed good agreement for all considered systems (Table 10).

The influence of cross-link density on glass transition temperature is confirmed by examining the data for MY0510 resin and MY721 cured with DDS, where the trifunctional MY0510 has a lower glass transition temperature, as a result of lower cross-link density. Curing with excess DDS leads to a more linear chain giving a reduced cross-link density and T_g. Modelling is shown to be highly effective in accounting for this respect.

In DSC experiments factors such as decomposition of the resin, may influence the exact value of enthalpy. For our resin systems, we assumed negligible degrees of decomposition. However, any contribution from this effect would not affect the determination of the degree of cure because a difference method was employed. The GIM technique has also been adapted effectively to a complex commercial blend of two epoxy resins, cured with two hardeners. The good agreement between the predictions and experimental values demonstrate that wider application is possible.

6. Conclusions

The GIM-based model has been shown to be effective at estimating the glass transition temperature of a number of epoxy resin and hardener combinations. Thus the GIM technique can be confidently employed to aid future resin design. Furthermore, the methodology can then be effectively employed to examine the contribution of individual components to the properties of a resin blend.

The model was shown to be sensitive to the various chemical reaction mechanisms and hardener concentration. In a future report, the effect of moisture absorption will be considered [21].

Table 9
Parameters used with the model to estimate glass transition temperature of 924-epoxy resin

n_{DDS}	n_{DICY}	$x_{st\ DDS}$	$x_{st\ DICY}$	$C_{mon-DICY}$	$C_{mon-DDS}$	C
0.46	0.51	0.327	0.357	0.4962	0.2237	0.92
f_{mon}	$f_{DICY-max}$	$f_{DDS-max}$	N_{DICY}	N_{DDS}	ΔE_{ether} (J/mol)	T_g (°C) calcd
3.39	4	4	4.04	13.04	4509	241

Table 10
Predicted and experimental glass transition temperature of investigated resin systems

Resin type	MY0510-DDS		MY0510-DICY	MY721-DDS	MY721-DICY	924-epoxy
	36 wt% DDS	45 wt% DDS				
$T_{g_{cal}}$ (°C)	283	268	213	281	249	241
$T_{g_{exp}}$ (°C)	285	276	218	288	258	234

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Appendix A

A set of equations given below was used to obtain necessary model parameters required for the computation of glass transition temperature in Eq. (10). These parameters are the functionality of polymer repeat unit, number of degrees of freedom for hardeners, the degree of cure and stoichiometric coefficient of hardener.

The stoichiometric coefficient of hardener in Eq. (10) can be found from the hardener weight fraction. It represents the amount of hardener per single mer unit and is calculated from the usual measure of hardener (Eq. (A1))

$$x_{\mathrm{st\ H}} = \frac{M_{\mathrm{ep}}}{M_{\mathrm{H}}} w_{\mathrm{H}}, \tag{A1}$$

where M_{ep} and M_{H} are relative molecular masses of the epoxy monomer and hardener, respectively, and w_{H} is the weight fraction of hardener taken in accordance with stoichiometry (Eq. (A2))

$$\frac{n_{\mathrm{ep}}}{n_{\mathrm{H}}} = 1:1, \tag{A2}$$

where n_{ep} and n_{H} are the number of moles of epoxy monomer and hardener calculated from the component weight

$$n_{\mathrm{ep}} = \frac{w_{\mathrm{ep}}}{M_{\mathrm{ep}}}, \qquad n_{\mathrm{H}} = \frac{w_{\mathrm{H}}}{M_{\mathrm{H}}}.$$

The concentration of hardener is selected to give a slight excess of either epoxy or hardener. For complex systems with two hardeners, Eq. (A2) can be written in the following form:

$$n_{\mathrm{ep}} = n_{\mathrm{H1}} + n_{\mathrm{H2}}. \tag{A3}$$

The loss in degree of freedom on reaction of the epoxy groups can be estimated from the average functionality of polymer repeat unit f

$$f = f_{\mathrm{mon}} C, \tag{A4}$$

where f_{mon} is the functionality of the monomer and C is the overall degree of cure and can be calculated from Eq. (A5)

$$C = C_{\mathrm{mon\text{–}H1}} + C_{\mathrm{mon\text{–}H2}} + C_{\mathrm{et}}, \tag{A5}$$

where $C_{\mathrm{mon\text{–}H1}}$ and $C_{\mathrm{mon\text{–}H2}}$ are the degrees of cure of the hardener 1 and hardener 2-epoxy, respectively, which can be estimated from the concentration and functionality of hardener ($f_{\mathrm{H\ max}}$) using Eqs. (A6) and (A7).

$$C_{\mathrm{mon\text{–}H1}} = \frac{n_{\mathrm{H1}} f_{\mathrm{H1\ max}}}{f_{\mathrm{H1\ max}} n_{\mathrm{H1}} + f_{\mathrm{H2\ max}} n_{\mathrm{H2}}} (C - C_{\mathrm{et}}), \tag{A6}$$

$$C_{\mathrm{mon\text{–}H2}} = \frac{n_{\mathrm{H2}} f_{\mathrm{H2\ max}}}{f_{\mathrm{H1\ max}} n_{\mathrm{H1}} + f_{\mathrm{H2\ max}} n_{\mathrm{H2}}} (C - C_{\mathrm{et}}). \tag{A7}$$

The hardener can be reacted into the network by different extents so that the degree of freedom is given by the average incorporation with the network

$$N_{\mathrm{H}} = a_{\mathrm{H}} N_{\mathrm{f}} + N_{\mathrm{un}}(1 - a_{\mathrm{H}}), \tag{A8}$$

where a_{H} is the fraction of fully reacted hardener, N_{f} and N_{un} are the degrees of freedom for the fully reacted and unreacted hardener, respectively.

Fraction of fully reacted hardener is estimated in Eq. (A9) from monomer–hardener functionality and hardener mole ratio given by relations (A1) and (A2).

$$a_{\mathrm{H}} = \frac{f_{\mathrm{mon}} C_{\mathrm{mon\text{–}H}}}{n_{\mathrm{H}} f_{\mathrm{H\ max}}}. \tag{A9}$$

The presence of unreacted hardener can be included by defining N_{H} according to Eq. (A10)

$$N_{\mathrm{H}} = N_{\mathrm{H}} + b N_{\mathrm{un}}, \tag{A10}$$

where b is the fraction of unreacted hardener.

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