Modelling the Effect of Moisture Absorption on the Thermomechanical Relaxation Spectra for Thermoset/Thermoplastic Resin Blends

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Summary: The principles of molecular modelling have been combined with Group Interaction Modelling (GIM) for the prediction of properties of thermoset/thermoplastic resins. The glass transition temperature of the systems was modelled and thermomechanical properties of epoxy resin polyether sulphone blends were discussed. As a result a full envelope of Dynamic Mechanical Thermal Analysis Relaxation (DMTA) curve for wet and dry material was predicted. Differential Scanning Calorimetry (DSC) and DMTA experimental methods were used to validate the modelling results.

Introduction

Advanced polymer matrixes such as epoxy resins are used in composite materials. The service temperature of a composite is determined by the glass transition temperature of the resin, which can be reduced by moisture absorption[1]. Therefore it is important to predict the properties of the composite from the predicted matrix properties based on resin molecular structure. For this purpose a good knowledge of resin chemistry is required.

Detailed understanding of the chemical reactions which occur during the cure of an epoxy resin (eg. glycidyl ether epoxies cured with aromatic diamines) network which determine the glass transition temperature can be studied using experimental techniques such as differential scanning calorimetry DSC[2–5], spectroscopy[6,7], nuclear magnetic resonance[8] and fluorescence[9].

Molecular mechanics is one of the most practical and least time consuming of the atomistic models. Molecular mechanics considers the molecular geometry, bond energies and different conformational states while molecular dynamics simulates the interaction between a group of

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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[10] can be used to estimate changes in conformational entropy.

The effect of moisture absorption on the glass transition temperature in single component resins and multifunctional blends can be studied by DMTA. Another method such as Thermally Stimulated Depolarization Current can be applied to the study of the influence of water on segment relaxation in polymers[11]. A theoretical description of such a process can be obtained from Rotational Isometric State Models[12,13] and Group Interaction Modelling principles[14].

In this work Group Interaction Modelling (GIM) was chosen. Such an approach 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 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.

In this work we used group interaction modelling and related models to predict the T_g of the resins and the broadening of glass-rubber transition in the dry state on moisture absorption.

The equilibrium moisture content is a thermodynamic property which is dependant on the relative humidity and is effectively independent of temperature. However the rate of diffusion can be increased according to the Arrhenius law. Any variations with temperature can be attributed to the lack of equilibrium or to the hydrolysis of the resin.

The absorbed moisture can exist in free and mobile form[15]. Since there is no clear evidence for the differing effects of bound and non-bound water on the glass transition temperature, it is appropriate to examine the glass transition temperature as a function of moisture content.

GIM Review

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

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

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

The energy balance is made up from the contributions of 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 where careful experiments were used to obtain data for GIM group contribution tables[14]. Depending on its structure, each chemical group has certain number of degrees of freedom which determines its ability to change 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.

One of the most powerful parameters in GIM is the cohesive energy. E_{coh} can be obtained from group contribution tables. It sums all intermolecular forces of interaction between the neighbouring mer units and is related to the total energy of interaction of the system ϕ_0 in the state of minimum energy[14].

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

where n_a is Avogadro number.

Equation 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 equation 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 is the Boltzman constant, ΔT_m is a hypothetical temperature increment.

Thermal energy (H_T) is expressed by the Tarasov approximation of Debye theory for one-dimensional chain oscillation. In GIM a simplified from of equation for thermal energy was derived:

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

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

By incorporating the empirical relation 5 into equation 8 and expanding the $\tan^{-1}$ function an equation for glass transition temperature estimate was obtained in GIM.

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

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

Modelling

Because of the complexity of these resin structures it was important to incorporate into the model chemical aspects such as the degree of resin cure, crosslink density, hardener concentration, side reactions and monomer purity. For this reason equation 9 was expanded:

$$T_g = 0.224\theta + 0.0513\frac{E_{coh\,mon} + x_{st\,H1}E_{coh\,H1} + x_{st\,H2}E_{coh\,H2} - \Delta E_{et} - \omega}{(N_{mon} - f\ N_L) + x_{st\,H1}N_{H1} + x_{st\,H2}N_{H2}} \tag{10}$$

The new parameters are the stoichiometric coefficient x_{st}, the average number of degrees of freedom for the hardeners per single mer unit N_{H1} and N_{H2}, where the subscripts H1 and H2 define the type of hardeners used. N_L stands for the number of degrees of freedom lost by each epoxy group, f – is the functionality of the polymer. ΔE_{et} - represents the cohesive energy lost due to the formation of the ether groups and is estimated from the fraction of etherification reactions. ω, the cohesive energy conversion coefficient, describes the cohesive energy per epoxy group, which is lost during the formation of the crosslinks.

The effect of moisture absorption on T_g can also be predicted by GIM. The method considers the absorbed water as a small molecule which adds cohesive energy and degrees of freedom to the system. These parameters can be estimated from the weight fraction of absorbed water and included into equations 9, 10. For complex systems such as a commercial epoxy with more than one hardener and monomer, the role of each component on moisture absorption can be analyzed by considering the hydrogen bonding density of the resin polar groups.

Results

The resin system under study was based on the 924-epoxy resin blend (Hexcel Ltd.) (Fig 1) which is believed to be 50:50 blend of tetrafunctional glycidyldiphenylmethane (TGDDM) and trifunctional glycidylaminophenolether cured with diaminodiphenylsulphone (DDS) and dicyandiamine (DICY)[16].

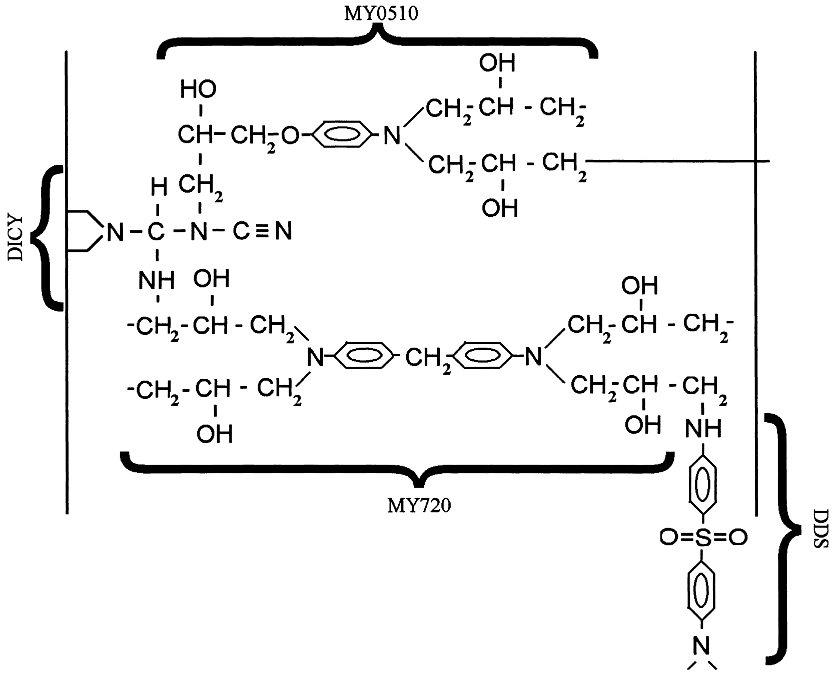

Figure 1: A schematic representation of the cured epoxy resin showing the individual components

To provide confidence in the modelling, we have studied the T_g of the individual component epoxy resins, experimentally and theoretically.

From equation 10 the glass transition temperatures of the 924-epoxy network and the individual components were estimated. The input parameters for the model were calculated from the chemical structure given in Fig. 1 and given in Table 1. The degrees of cure were determined by DSC /Table 2/.

Dynamic thermal analysis was used for the determination of experimental values of the glass transition temperatures, as given in /Table 3/.

Table 1 Model Input Parameters

Chemical Name	Number of degrees of freedom for unreacted molecules, N_{un}	Van der Waals Volume, cm^3/mol	GIM Cohesive Energy, J/mol	Molecular Weight, g/mol
Diaminodiphenylsulphone (DDS)	18	121.5	113000	246.5
Dicyandiamine (DICY)	9	37.2	44000	82.1
Tetrafunctional glycidylamine (M720)	46	243.4	204000	436.5
Trifunctional glycidylamine (MY0510)	34	164.3	139300	297.3

Table 2 The Degrees of Cure for the Various Combinations of Epoxy Resins and Hardeners

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

Table 3 Predicted and Experimental Glass Transition Temperatures of the Epoxy Resin Systems

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

Assuming that the T_g of the 924-epoxy resin is an average of its base resin components such as MY0510, MY720 resins and the toughening modifier polyether sulphone (PES) the DMTA relaxation spectra for dry 924-epoxy resin can be modelled by assessing the contribution of these components. This can be done by modelling the glass transition temperatures of dry component resins taking the degree of cure as a variable. Experimental findings showed a significant difference in T_g because of differing in chemical structures.

The envelope for a relaxation curve can be predicted using a Gaussian distribution[17].

Fig.2 shows a comparison of the experimental relaxation curve for the commercial blended epoxy with the predicted curves for the individual combinations of resin and hardener. A comparison of the predicted estimate for the network and its components demonstrated that averaging and scaling of the individual contributions was effective [18].

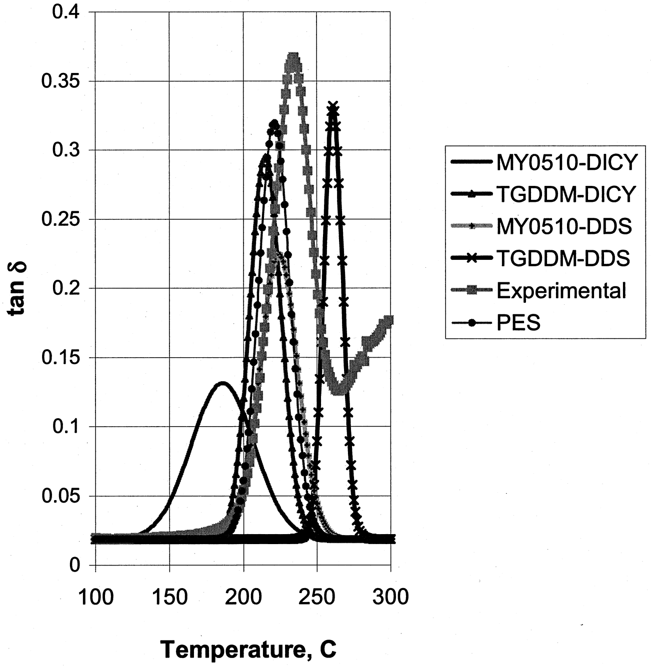

Figure 2. Comparisons of the Predicted DMTA Curves for the Individual Component Resins with the Experimental Data for the Dry 924-epoxy Thermoplastic Resin

It is now practical to examine the effect of plasticisation on the individual components.

For the wet 924 resin blend the DMTA relaxation curve can be predicted by assessing the effect of moisture absorption on T_g of the individual components of 924-resin.

It was hypothesised that the difference in moisture sensitivity of certain segments of a macromolecular network would account for the appearance of several sub-peaks in the DMTA curve for the wet resin Fig. 3. The GIM model was used to predict the curves for reacted hardener/epoxy combination in the presence of water. The height of the peak was calculated by SciPolymer software package which is based on Bicerano method[19]. The full envelop is given in Fig. 3.

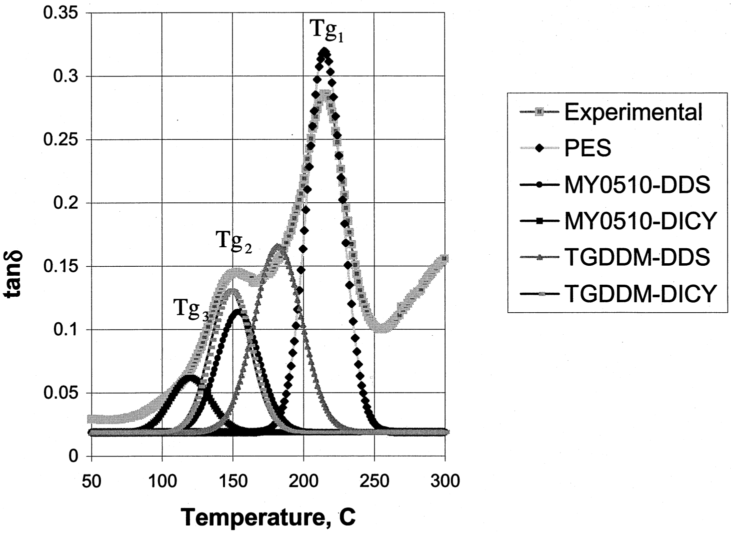

Figure 3. Comparisons of the Predicted DMTA Curves for the Individual Segments with Experimental Data Points of 924-epoxy Resin in the Presence of 3% Moisture.

Discussion

From the model it can be concluded that for the thermoplastic PES transition temperature appearing at 221 °C when dry and 215 °C when wet (3%) was less affected by water.

The appearance of a low temperature relaxation region (below 100°C) in the experimental data for the wet resin can be attributed to the plasticisation of MY0510/DICY structure ($T_{g\,3}$).

It is confirmed that a second transition ($T_{g\,2}$) appears in the experimental trace for the commercial resin when plasticised with 3% moisture. This can be assigned to the sensitivity of the trifunctional epoxy resin (MY0510) cured with DDS and the tetrafunctional epoxy (TGDDM) cured with DICY.

Conclusion

The GIM based model is effective at estimating the glass transition temperature of a number of epoxy resins. Furthermore, the methodology can then be employed to examine the contribution of individual components to the thermomechanical properties of a resin blend.

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