Extension of Group Interaction Modelling to predict chemorheology of curing thermosets

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Abstract

This paper describes an extension of viscoelastic Group Interaction Modelling (GIM) to predict the relaxation response of linear, branched and cross-linked structures. This model is incorporated into a Monte Carlo percolation grid simulation used to generate the topological structure during the isothermal cure of a gel, so enabling the chemorheological response to be predicted at any point during the cure. The model results are compared to experimental data for an epoxy-amine systems and good agreement is observed. The viscoelastic model predicts the same exponent power-law behaviour of the loss and storage moduli as a function of frequency and predicts the cross-over in the loss tangent at the percolation condition for gelation. The model also predicts the peak in the loss tangent which occurs when the glass transition temperature surpasses the isothermal cure temperature and the system vitrifies.

Keywords: group interaction modelling, gelation, chemorheology

1. Introduction

The fabrication of thermoset materials involves the conversion of monomers into a three-dimensional network structure. The dramatic change in the molecular weight and polymeric architectures throughout curing results in a dramatic change in the material's rheological response. For reacting systems with functionality greater than two, the number of functional groups increases with the size of the molecules. This means that the larger the molecule, the more rapidly it reacts to become even larger (Dotson et al., 1996). The result is a power-law molecular weight distribution which extends to higher and higher molecular weights up to the gel point when a cluster that spans the entire reaction chamber is formed. This incipient gel is capable of sustaining mechanical deformation so that there is a shift in the rheological behaviour of the material from liquid-like to solid-like behaviour. A monomer functionality greater than two, however, also leads to the formation of self-similar, fractal structures. Winter and Chambon (1986) have shown that these are rheologically characterised by a power-law relaxation behaviour. This power-law relaxation behaviour has been modelled by a number of researchers (Martin et al., 1988, 1989; Adolf et al., 1990, 1998) who have assumed a power-law distribution of relaxation times for the gel cluster (due to the self-similar structure) as well as a power law distribution of relaxation times for the sol fraction (due to the power-law distribution of molecular weights).

More recently, Garcia-Franco et al. (2001) have highlighted the similarity in the rheological response of long chain branched polymers to that of chemical gels. Both gels and long chain branched polymers show a plateau in the loss tangent as a function of frequency. In gels, this plateau extends, at least in theory, to zero frequency. In branched polymers, the plateau extends to a lower frequency bound which decreases as the degree of branching increases. Garcia-Franco and co-workers suggested that the degree of branching in long-chain branched structures can be calculated from the width of the loss tangent plateau. This similarity in the response of long chain branched polymers to that of gels suggests that the similarities in the rheological response may be intimately related with similarities in the molecular structure.

Therefore this suggests that any model that can describe the behaviour of branched polymers should also be able to describe the behaviour of gels and vice-versa. Such a model must be able to describe the relaxation behaviour of polydisperse linear, star and branched polymers, ranging from unentangled to entangled molecular weights. One promising linear viscoelastic model which shows potential to describe the behaviour of a wide range of polymeric architectures, as it does not rely on the notion of entanglements to describe the behaviour of high molecular weight structures, is Group Interaction Modelling (GIM) for polymer properties developed by Porter (1995). In this model viscoelasticity is treated as resulting from the stor-
age and dissipation of mechanical energy. In this paper the model developed by Porter for monodisperse linear polymers is extended to polydisperse, branched and cross-linked polymers so that it can predict the linear viscoelastic response of thermosets throughout the entire cure process.

2. Viscoelastic Model

2.1. Engineering moduli

In the Group Interaction Model, Porter (1995) develops a method of predicting the properties of polymers by considering the storage and dissipation of potential energy in the polymer as the structure is deformed or an external field applied. He makes the assumption that the amount of energy that gets stored is that required to increase the separation distance between the molecules, as these are the weakest connections. This is given by an interaction energy between the molecules and summarised in a potential energy function.

The potential energy function follows a Lennard-Jones form given by

$$\phi = -\phi_0 + H_c + H_T + H_w = \phi_0 \left( \frac{r_0^12}{r^12} - 2 \frac{r_0^6}{r^6} \right)$$  \hspace{1cm} (1)

where \(r_0\) is the molecular separation at which the energy is lowest. \(\phi_0\) is the energy minimum and is proportional to the cohesive energy \(E_{coh}\) of the molecules, as obtained from group contribution tables. \(H_w\) is the mechanical energy.

\(H_c\) is the configurational energy resulting from bond deformations at zero temperature. For an amorphous polymer this is given by \(H_c = 0.107 \phi_0\) (Porter, 1995).

\(H_T\) is the thermal energy from cooperative skeletal mode oscillations of the polymer chain, which is given by the Tarasov Equation (Porter, 1995):

$$H_T = \frac{N_c k}{3} \left( T - \frac{\theta}{6.7} \arctan \left( \frac{6.7T}{\theta} \right) \right)$$  \hspace{1cm} (2)

where \(k\) is Boltzmann’s constant, \(N_c\) is the average number of degrees of freedom per mer unit in the backbone of the polymer, and \(\theta\) is a reference temperature which characterises the vibrations of the chain axis.

Thus three parameters can define the complete energy profile of a polymer \((E_{coh}, N_c, \text{ and } \theta)\). Two further parameters are needed to obtain absolute values for a particular property. These are the van der Waals volume, \(V_w\), and the length of a mer unit.

The main elastic property obtained is the bulk elastic modulus, \(B\), calculated as the ratio of pressure to volumetric strain. The pressure is related to the rate of change of potential energy with volumetric deformation and so the bulk modulus can be obtained from the second derivative of this potential energy with respect to volume. The local arrangement of polymer chains is assumed to be hexagonal, with each chain being surrounded by six neighbours, so the volume is proportional to the square of the average separation distance between chains. The shear modulus can then be calculated from the bulk modulus through the standard relationship involving the Poisson’s ratio, \(\nu\):

$$G = \frac{3(1-2\nu)B}{2(1+\nu)}$$  \hspace{1cm} (3)

2.2. Relaxation Modes and Linear Viscoelastic Moduli

In the more traditional entropy-based models, viscoelastic properties are explained in terms of the view of the motion of molecules inside a tube made of topological restrictions with the surrounding chains (de Gennes 1971; Doi and Edwards 1978). In Group Interaction Modelling, the restrictions for translational movement instead result from dielectric dissipation of energy between neighbouring polymer segments which implies the need for cooperative relaxation behaviour. The polymer is represented by a bead and spring model with each bead subject to a friction force with the surrounding molecules and to a spring force between neighbouring beads. When the beads in the chain move, they redistribute the stored energy and dissipate it to the surroundings due to the friction with other chains.

These motions can be divided into three main groups: localised vibration motion of atoms and short segments of the molecule, rotation about axes, and translational motion. The rubber-like plateau observed in thermoplastics arises from a large difference between the time scales for vibrational and translational motion. In thermoset materials translational motion is prevented by the existence of crosslink junction points and the plateau extends to infinite times. The rubbery-plateau modulus can be calculated by subtracting from the total shear modulus (in the elastic limit or at zero time) the energy dissipated through short relaxation time events. This is the amount of energy dissipated through the glass transition, \(\tan \Delta_\nu\), and leads to an approximate equation for the plateau modulus in terms of the defined parameters for the polymer (Porter, 1995):

$$G_N = \frac{10^6 E_{coh}}{(1+\tan \Delta_\nu)^2 V_w}$$  \hspace{1cm} (4)

The glass transition energy dissipated is given by
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\[ \tan \Delta_\phi = 0.0085 \frac{E_{\text{wib}}}{N_c} \]  

(5)

where \( N_c \) is the average number of degrees of freedom per mer unit in the backbone.

In the case of a curing thermostet as discussed later, this will change as the number of cross-links and chain ends vary during the cure. This variation can be evaluated using our Monte Carlo Percolation Grid Simulation (Altmann et al., 2007) and two additional parameters are required; \( N_{\text{end}} \), the additional number of degrees of freedom associated with a chain end and \( N_{\text{cross}} \), the number of degrees of freedom lost per cross-link. Thus \( N_c \) can be calculated as

\[ N_c = \frac{Z^{N+\text{merge}-\text{need}-\text{cross}}}{Z} \]  

(6)

where \( Z \) is the total number of mer units in the chain and \( N_{\text{end}} \) and \( N_{\text{cross}} \) are the numbers of dangling ends and cross-links respectively. \( N \) is the number of degrees of freedom per mer unit.

The way the beads move as the system relaxes can be obtained by applying the equation of motion to each of the beads in the chain. This results in a system of second order coupled differential equations. The solution to the set of equations gives a set of sinusoidal oscillations. The inverse of the frequency of these oscillations can be related to the relaxation time of the chain.

For a linear polymer, these relaxation times correspond to the well-known Rouse relaxation modes.

\[ \tau_i = \frac{\zeta_i}{Zs} \]  

(7)

where \( \zeta_i \) is the friction force coefficient, \( s \) is the spring force coefficient, \( Z \) is the number of mer units in the polymer, and \( i \) is the deformation mode (one for a period of deformation involving all mer unit segments, two for a period involving all but one segment, etc.).

One of the innovative features of Group Interaction Modelling is to consider both the friction force and the spring force a result of the deformation of the weak intermolecular forces between chain segments. In this manner, both the friction force and the spring force coefficients are intimately related to the potential energy function and Porter makes this link by associating them with the plateau modulus \( G_N \). The spring force coefficient \( s \) and friction force coefficient \( \zeta \) are given by

\[ s = 3G_Nr \]  

(8)

\[ \zeta = 3G_N\tau_c \]  

where \( r \) is the average separation distance between mer units and \( \tau_c \) is a characteristic relaxation time associated with the movement of all mer units. This characteristic relaxation time depends on the molecular weight and molecular topology environment. Group Interaction Modelling gives the expression for monodisperse linear polymers. In this paper we introduce an approximation for the value of this characteristic relaxation time for polydisperse and branched environments so that the chemorheological response of thermosets can be predicted. The following sections describe the friction force coefficient and the relaxation events that take place in monodisperse linear polymers, polydisperse linear polymers and branched and cross-link polymers.

### 2.2.1. Monodisperse Linear Polymers

For a linear chain, the relaxation time of all mer units in the chain is simply given by the sum of the individual relaxation times for each mer unit:

\[ \tau_m = Z\tau \]  

(9)

where \( Z \) is the number of mer units in the chain, and \( \tau \) is the mer unit relaxation time, which can be calculated using Matsuoka’s expression for the monomeric relaxation time (Matsuoka, 1992). This gives a theoretical interpretation for \( \tau \) in terms of an activation energy \( E_a \) and a cooperativity domain \( z \). The activation energy is ultimately related to the activation energy for C–C bond rotation and the cooperativity domain is dictated by the temperature difference from the glass transition temperature \( T_g \):

\[ \tau = \frac{h}{2\pi kT} \exp \left( \frac{E_a}{RT} \right) \]  

(10)

where \( h \) is Plank’s constant, \( k \) is Boltzmann’s constant, \( T \) is temperature, and \( z \), the cooperativity domain given by:

\[ z = \frac{T^*-T_{\theta}}{T^*-T_g} \]  

(11)

\( T^* \) is a high temperature limit which has been suggested to be universal for all polymers and to assume a value of 500°C, and \( T_{\theta} \) is the thermodynamic glass transition temperature.

An expression for the longest relaxation time \( (i=1) \) for a linear polymer \( \tau_c \) becomes

\[ \tau_p = \frac{\tau}{2\pi Z^z} \]  

(12)

Since \( \tau \) is also dependent on the molecular weight of the polymer through the dependence of the glass transition temperature on the molecular weight this leads to a 3.4 power dependence of \( \tau_c \) on \( Z \), in agreement with experimental data, actually results.

Although it is fairly easy to calculate the relaxation modes, difficulty arises in calculating the weight of each of the relaxation modes to the overall relaxation response of the polymer. Porter follows the work of Doi and Edwards (1978) and assumes the weight of each relaxation mode to be inversely proportional to the square of the mode number, counting odd modes only as these contribute to the dif-
fusion along the length of the chain and thus to relaxation. The over prediction of the decrease in moduli at frequencies higher than the inverse of the longest relaxation time which results from this is corrected by adding an overall energy dissipation factor. Matsuoka (1992) instead proposed that the weight should be inversely proportional to the mode number, again counting odd mode numbers only, but this gives a too high predicted value of the loss modulus at high frequencies.

In our approach we follow Matsuoka in assuming that the weight of each mode is proportional to the participation of the period of that mode in the overall size of the polymeric chain, but note that the size of each segment varies as the inverse square root of the mode number. Including this factor modifies Matsuoka’s result to give the weight as inversely proportional to the mode number to the power 1.5. This gives a good agreement between model results and experimental data. We also add rotational modes, contributing with a weight proportional to the square root of the mode number, and a segmental relaxation term relating to the internal oscillations of an individual mer unit.

An example is shown in Fig. 1 for linear polystyrene (PS) of molecular weights 290, 750 and 3000 kg/mol. The experimental data is for narrow molecular weight distribution polymers from the work of Schausberger et al. (1985). The viscoelastic model parameters used are given in Table 1.

By considering vibrational modes (whose characteristic relaxation time is only dependent on the molecular weight through the dependence on the mer unit relaxation time on the glass transition temperature), as well as rotational and translational modes (whose relaxation times are dependent on the molecular weight on a power-law exponent higher than three) the shift in the power-law exponent of the zero shear viscosity on the molecular weight can also be predicted as shown in Fig. 2. The experimental data is for polystyrene from the work of Majeste et al. (1998).

The model results for loss and storage moduli for Fig. 1 were predicted through the following equations:

![Fig. 1. Model results for storage ($G'$) and loss ($G''$) moduli for linear polystyrene of three different molecular weights compared with experimental data (Schausberger et al., 1985).](image)

**Table 1.** Viscoelastic model parameters for polystyrene (PS), polybutadiene (PB) and the cross-linking agent DGEBF/MDA

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PS</th>
<th>PB</th>
<th>DGEBF/MDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M$ (g/mol)</td>
<td>104</td>
<td>54</td>
<td>766</td>
</tr>
<tr>
<td>$E_{coh}$ (kJ/mol)</td>
<td>36</td>
<td>18</td>
<td>320.7</td>
</tr>
<tr>
<td>$V_w$ (cm$^3$/mol)</td>
<td>65.0</td>
<td>37.4</td>
<td>290.0</td>
</tr>
<tr>
<td>$\theta_1$ (K)</td>
<td>295.0</td>
<td>316.0</td>
<td>460</td>
</tr>
<tr>
<td>$E_a$ (kJ/mol)</td>
<td>21.7</td>
<td>12.3</td>
<td>23</td>
</tr>
<tr>
<td>$N_{ext}$</td>
<td>9</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>$N_{cross}$</td>
<td>-</td>
<td>-</td>
<td>21</td>
</tr>
</tbody>
</table>
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\[ G'(\omega) = G_s \sum_{i=1, odd} G_{r_i}^0 \frac{1}{(1 + \frac{\omega \tau_i}{2})^2} \]

\[ + G_s \sum_{i=1, odd} G_{r_i}^0 \frac{1}{(1 + \frac{\omega \tau_i}{2})^2} \]

\[ G''(\omega) = G_s \sum_{i=1, odd} G_{r_i}^0 \frac{1}{(1 + \frac{\omega \tau_i}{2})^2} \]

Here the first term in each expression corresponds to the contribution from translational motion, the second to rotational motion and the third to segmental relaxation events.

The pre-factors \( G_s \) and \( G_{r_i}^0 \) are calculated by assuming that the overall sum of all translational or rotational modes corresponds to the plateau modulus \( G_N \).

In the final segmental relaxation term, \( G_e \) is the elastic modulus and \( \tau_g \) is the segmental relaxation time which is assumed to be linearly proportional to the mer unit relaxation time. This term only contributes appreciably at high frequencies or at low temperatures. For polystyrene the proportionality factor that best fits the experimental data in Fig. 1 and Fig. 2 is ten.

### 2.2.2. Polydisperse Linear Polymers

In the case of a polydisperse polymer, the friction force coefficient is still correlated with the dissipation of energy as mer units slide past one another. However, polydispersity implies that the number of mer units in neighbouring chains may differ from that of the relaxing chain. Thus the friction force coefficient in polydisperse systems should be estimated based on the molecular size the average mer unit in the system “feels”. This corresponds to the weight average molecular weight so that the friction force coefficient in a polydisperse environment becomes:

\[ \zeta = 3 G_e Z_{\text{m}} \tau_r \]

where \( Z_{\text{m}} \) is the number of mer units in a chain whose molecular weight is equivalent to the weight average molecular weight.

Thus the longest relaxation time for a chain of \( Z \) mer units in a polydisperse environment is:

\[ \tau_P = \frac{\tau_r}{2\pi} Z_{\text{m}} Z \]

This reproduces well the experimentally observed effect that the presence of high molecular weight species increases the relaxation time of the lower molecular weight species and vice-versa (Ferry, 1980; Porter, 1995). Fig. 3 compares the prediction of the modified Group Interaction Model described here with experimental data for two polydisperse polystyrene samples (samples M1 and M2) prepared from a mixture of monodisperse linear polymers. The experimental data was from the work of Wasserman and Graessley (1992), where details of the molecular weight distributions can be found. The group interaction model parameters are the same as those which have been used to describe the data for the monodisperse samples in the above section.

### 2.2.3. Branched Polymers

In a branched polymer the friction force coefficient for the
average mer unit will be quite different to that of a mer unit in a linear chain. Experimental data for star polymers suggests an exponential dependence of the zero shear viscosity on the molecular weight of the arm (Raju et al., 1979; Graessley and Raju, 1984; Carella et al., 1986; Fetters et al., 1993; Hatzikiriakos et al., 2000). This exponential dependence is explained by the idea of primitive path fluctuations which require that a branch must diffuse to the branch point and then out again for cooperative motion of whole chain (Doi and Kuzuu, 1980). Thus, in a branched polymer, we suggest that the characteristic relaxation time \( \tau_{m} \) (which in turn affects the friction force coefficient) should be calculated by the sum of the individual relaxation times of each mer unit in the main backbone plus the sum of the relaxation times for each branch.

\[
\tau_m = Z_b \tau + \sum_{k=1}^{n} \tau_k
\]  

(16)

where \( Z_b \) is the number of mer units in the backbone, \( n \) is the number of branches in the chain, and \( \tau_k \) is the relaxation time of the branch \( k \). The relaxation time of a branch is not merely a sum of the relaxation times of each individual mer unit in the branch, as there is the requirement that all mer units relax in cooperation allowing the branch to diffuse towards the backbone. This notion of cooperativity is akin to the notion of cooperativity used by Matsuoaka in describing the mer unit relaxation time so the expression for the relaxation time of a branch must include both the cooperation domain, \( z_b \), for a linear chain, as defined above (Equation 10) and also an intra-chain cooperativity domain, \( z_b \), assumed to be a linear function of the number of mer units or molecular weight of the arm:

\[
\tau_b = \frac{h}{2kT} \exp\left( \frac{E_{b}}{kT} \right) \exp\left( \frac{z_b}{1 + z_b} \right)
\]  

(17)

where \( E_b \) is the energy barrier for the mer unit relaxation time.

The effects of branching, however, cannot be summarised only through the effect of branching on the friction force coefficient. Literature results suggest a widening of the distribution of relaxation times and the appearance of extra relaxation events in branched polymers in comparison to their linear counterparts (Fetters et al., 1993; Majeste et al., 1998; Hatzikiriakos et al., 2000; Pattamaprom et al., 2000; Wood-Adams et al., 2000; Robertson et al., 2001). The more successful models incorporate several different relaxation processes such as contour-length fluctuations, dynamic dilution, tube dilation, and constraint release Rouse motion (McLeish and Larson, 1998; McLeish and Milner, 1999). In terms of Group Interaction Modelling, the relaxation modes could in theory be calculated by solving the set of differential equations which results from applying Newton’s equation of motion to each bead on a three dimensional lattice, however, to a first approximation, they can be calculated as if the branches were linear segments (Sammler and Schrag, 1988b, a; Gurtovenko and Gotlib, 1998, 2000; Gurtovenko et al., 2000; Altmann, 2002). Thus, this work assumes that relaxation time for the branches is given by Equation 6, with \( Z \) replaced by \( Z_b \), the number of mer units in a branch, with the friction force constant, \( \zeta \), depending on the type of branch and type of motion.

Fig. 4 shows a representation of a branched polymer. The backbone is taken to be the longest path through the molecule, as indicated by the bold line in the figure. This dictates the molecular motion of the whole polymer and, therefore will present both translational and rotation diffusion. The global friction force coefficient for the backbone is given by:

\[
\zeta_{global} = 3G_z \left( Z_b \tau + \sum_{k=1}^{n} \tau_k \right)
\]  

(18)

The branches other than the backbone need to follow it when undergoing translational motion. Because the branches follow the backbone they are confined to their local ‘neighbourhood’ and therefore we assume that they only experience a local friction force coefficient. As the friction force coefficient is a measure of the dielectric dissipation of energy as atoms slide past one another (Porter 1987) we can assume this sliding action as only involving the mer units of the branch so that the local friction force is given by:

\[
\zeta_{local} = 3G_z Z_b \tau
\]  

(19)

where \( Z_b \) is the number of mer units in the branch for which the relaxation events are being calculated.

The dangling-end branches, that is, branches which have no branching points out of them such as the ones which appear in stars and combs, and the dotted branches in the structure shown in Fig. 4, can also perform rotational...
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motion. Since when undergoing rotational motion the branches do not necessarily need to follow the translational motion of the backbone, we have assumed that the friction force that best measures the dielectric dissipation of energy for rotational motion of the dangling ends is the global friction force coefficient, calculated through Equation 17.

The assumption of a local friction force coefficient for molecular motion of branches is in line with the results of the cooperative motion algorithm developed by Pakula and co-workers which shows that the relaxation of star arms is much faster than the translational relaxation of whole molecules (Pakula et al., 1996). Unfortunately, there are no experimental methods sensitive enough to directly quantify the nature of motion of polymer molecules so that it is impossible to test the correctness of the assumptions made here upon the relaxation times of branches in polymeric structures. Nevertheless, the model may prove useful if it fits experimental data well. One of the difficulties of validating the model, however, lies in the difficulties in predicting the molecular weight distribution of branched polymers accurately (Drott and Mendelson 1970a, b; Tackx and Tacx 1998). Star molecules, however, whose structures can be determined experimentally with a high degree of certainty (Fetters et al., 1993) provide one way to test the model. The model predictions using Group Interaction Modelling parameters and the relaxation times and friction force coefficients given above are compared to experimental data (Hatzikiriakos et al., 2000) for linear and star polybutadiene in Fig. 5. The activation energy for relaxation, the cooperativity domain for the branch relaxation, and the proportionality factor between the relaxation time that characterises the high frequency relaxation and the mer unit relaxation time were fitted to the experimental data but are the same for the three sets of data shown. Group Interaction Modelling parameters were obtained from group contribution tables and are given in Table 1.

In summary, the equation for the model calculations of the storage modulus for branched polymers is:

$$G_{branched} = G'_b(\omega) + \frac{1}{n} \sum_{i=1}^{n} G'_i(\omega)$$

where $n$ is the number of branches, both dangling ends (shown as dotted lines in Fig. 4) and internal branches (thin solid lines in Fig. 4). The expression for the loss modulus $G''_{branched}$ is similar. The contribution from the backbone, $G'_b$, is calculated using equation 12 using the appropriate relaxation modes relating to the number of mer units in the backbone and the global friction force coefficient from equation 17. The contribution of the dangling ends uses the local friction coefficient for the translational modes and the global friction coefficient for the rotational modes. The internal branches use the local friction coefficient for the translational modes and disallow rotational modes. Because this rotational motion is not allowed, the amount of energy that can be dissipated through segmental motion or the ‘glassy’ relaxation events also decreases so that the overall contribution of the internal branches amounts to the elastic modulus $G_e$. 

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**Fig. 5.** Model results for storage ($G'$) and loss ($G''$) moduli for linear and two different star polybutadienes compared with experimental data (Hatzikiriakos et al., 2000).
2.2.4. Cross-linked Polymers

The previous discussion introduced the expression for the dynamic moduli in hyper-branched structures. In curing thermostets, molecules can form loop structures. Once such loops are connected to other portions of the molecule and the molecule forms a network structure that spans the entire sample, elastic active junctions are formed. These elastic junctions mean that the global friction force coefficient is infinite, as their dislocation would involve the dislocation of every other segment in the network. Therefore, once cross-linked structures are formed, the global friction force coefficient loses its meaning and all relaxation events involve only local relaxation domains. Furthermore, the existence of these infinite relaxation times determines the existence of an equilibrium elastic modulus. The strength of the modulus is proportional to the weight percent of loop molecules in the overall mass of the chain times the plateau modulus of the chain. The equations for the storage and loss moduli for the gelled cluster are then given by:

\[
G'_\text{gel} = G'_\text{branched} \omega(w_l G_N)
\]

where \(w_l\) is the weight percentage of molecules in loops or cross-linked structures.

The size of each relaxation domain in cross-linked structures is calculated ignoring the existence of cross-link points, that is, each branch starts at a chain-end and finishes at another chain end or at a previously labelled branch (Altmann et al., 2007). The differences between cross-linked and simply branched structures in this model is accounted for through the ability of cross-link points to store energy \((w_l G_N)\) and the reduction of the characteristic friction force coefficient for all types of molecular motion as molecules no longer experience the average overall environment after gelation (Dotson et al., 1996).

3. Results and Discussion

The model for the linear viscoelastic behaviour of polymers was incorporated in the Monte Carlo Percolation Grid Simulation described in a previous paper (Altmann et al., 2007) which predicts structures throughout the entire isothermal cure process. Each structure has an array of internal branches, dangling-end branches and loop branches. The relaxation behaviour of each cluster is obtained from the sum of the relaxation events of each of the branches and then the relaxation behaviour of the whole system is obtained from the weighted average sum of the relaxation events of each cluster. In this manner, storage and loss moduli during isothermal cure and the storage and loss moduli as a function of frequency at various points in the isothermal cure can be calculated. The results for chemorheological response, gelation and vitrification are compared here to experimental data on an epoxy-amine system (DGEBF/MDA). Details of the materials and experimental procedure are in our previous paper (Altmann et al., 2007).

3.1. Chemorheology

Fig. 6 compares the model result with experimental data for the dynamic moduli for isothermal cure at 110°C and 120°C. The agreement between the features observed in the experimental data and model result is remarkable. The model describes well (i) the increase in loss and storage modulus with cure time; (ii) the decrease in the loss tangent with cure followed by a peak at vitrification; (iii) the crossover in moduli around the gelation transition; and (iv) the plateau in storage modulus after vitrification. The major difference corresponds to a secondary small peak in the damping tangent. This peak is related to a discontinuity in the molecular weight distribution of branch sizes. We believe the discontinuity arises from the limitations in the grid size (Altmann, 2002).

3.2. Gelation

The rheological condition for gelation is taken here as the
Winter-Chambon criterion of same exponent power-law dependency of the dynamic moduli on frequency. The simulation does give a power law behaviour of the dynamic moduli at the point of percolation as is shown in Fig. 7 for isothermal cure at 120°C. The power-law slope agrees well with the experimental result of 0.65 as is shown in Fig. 8 for gelation at 80°C.

It is sometimes difficult, however, to measure the power law behaviour at the exact point of gelation and gelation is usually determined by the point where the damping tangent is independent of frequency (self-similar behaviour). Again the model results are able to correctly describe the crossover in the damping tangent as is shown in Fig. 9.

3.3. Vitrication

Vitrication is rheologically characterised by (i) a step increase in the storage modulus, (ii) a peak in the loss modulus, and (iii) a peak in the damping tangent. As can be seen in Fig. 6, such characteristics are reproduced well by the chemorheological model developed here. Furthermore, the model reproduces well the frequency dependence of the vitrification process.
At the beginning of the reaction both storage and loss moduli are dependent on frequency. The dependency is shown in Fig. 12(a) and is typical of a Newtonian liquid.

At a certain point in the cure process the storage modulus increases sharply and assumes a plateau value which is independent on the frequency of observation.

At a later stage the storage modulus becomes again dependent on frequency and a step increase in its value is observed.

After the step increase, the storage modulus becomes again nearly independent on frequency but assumes a value which is three orders of magnitudes higher than the rubbery plateau.

Simultaneously with the step increase in the storage modulus, the loss modulus achieves a peak value. The peak occurs earlier for the higher frequencies. Before the peak, the loss modulus increases with frequency and after, it decreases.

Fig. 12 shows the model results for the frequency dependency of the dynamic moduli at (a) 10% conversion, (b) 46% conversion, (c) gelation, (d) 70% conversion, (e) 90% conversion, and (f) 94% conversion. The results are compared to experimental data obtained from the multiwave isothermal time sweeps for 1.6, 3.1 and 12.5 rad/s. Unfortunately, not enough torque signal was obtained before gelation for 3.1 and 12.5 rad/s. The simulation results show that up to gelation both storage and loss modulus increase with increasing frequency and as cure progresses the same exponent power-law region of loss and storage modulus broadens and shifts to lower and lower frequencies. This behaviour results from the broadening of the molecular weight distribution and distribution of branch sizes as reported in our previous paper (Altmann et al., 2007). After gelation, the storage modulus becomes independent of frequency for a broad frequency range due to the increase contribution to the overall moduli of cross-linking domains which possess infinite relaxation times. At high frequencies storage modulus again increases with frequency. This is a result of relaxation events which do not have time to occur within these high frequencies and therefore contribute to the storage of energy. As vitrification proceeds and the relaxation times increases further as the glass transition temperature of the material approaches the isothermal cure temperature, the glassy region shifts to lower and lower frequency. This is also captured through the experimental
data as seen in Fig. 12(e). After vitrification (Fig. 12(f)) all modes of relaxation have frozen in. The storage modulus is again independent on frequency and the loss modulus decreases as the frequency is decreased. The simulation overestimates the decrease in loss modulus after vitrification suggesting the existence of fast relaxation mechanisms not accounted for by the present model.

In summary, the linear viscoelastic model developed in this work is able to predict well:
(i) the behaviour of dynamic moduli during cure;
(ii) the power-law behaviour around gelation; and
(iii) the frequency dependent behaviour up to gelation, at gelation and through vitrification.

4. Conclusion

We have developed a useful viscoelastic model for thermoset polymers that is based on energetic interactions. The model is an extension of the Group Interaction Model previously developed by Porter (1995) for linear thermoplastics. The main changes required to the original model were the modification of the friction force coefficient for highly polydisperse and branched polymers, and the incorporation of extra relaxation modes due to branching. In our previous paper (Altmann et al., 2007) a Monte Carlo Percolation Grid algorithm was employed to predict the evolution of molecular structures during isothermal cure. Here this information was used as an input to the linear viscoelastic model and very good agreement between simulation and experimental data was obtained for the viscoelastic properties and key transitions (gelation and vitrification) during the cure of a model epoxy-amine thermoset. One of the main achievements of the model is to predict the power-law relaxation behaviour at gelation. As the viscoelastic model also correctly describes the linear viscoelastic behaviour of simpler polymeric structures such as linear, polydispersed and star thermoplastics, the origins of the peculiar rheological response of gels can be traced to relaxation events that happen in branches and in polydisperse structures. Further results, including the investigation of other thermosetting systems, are required to confirm some of the assumptions used in the model particularly with respect to the effects of polydispersity and branching on the friction force coefficient. Nevertheless, we hope that the results presented here will invoke much discussion into energetic approaches to describing viscoelastic behaviour as readily applicable systems (such as nanocomposites) are already benefiting from this approach (Vaia and Giannelis, 1997; Ginzburg et al., 2002; Lee et al., 2002; Lim et al., 2002).

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