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Toward a constitutive model for cure-dependent modulus of a high temperature epoxy during the cure

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ABSTRACT

A constitutive model, based on Kohlrausch–Williams–Watts (KWW) equations, was developed to simulate the evolution of the dynamic relaxation modulus during the cure of a 'high temperature' epoxy. The basic assumption of the modelling methodology proposed is the equivalence of the mechanisms underlying the evolution of the glass transition temperature and the relaxation time shift during the cure, leading to the use of a common potential function. This assumption is verified by the comparison of normalized glass transition data and principal relaxation times, which have been found to follow a single master curve. Results show satisfactory agreement between experimental data and model prediction over the range of chemical conversion considered.

1. Background

During the polymerization of any synthetic thermosetting polymer the material undergoes chemical and physical transformations which lead to the hardening of the material, with a corresponding transition from a viscous liquid to an elastic solid. Under normal service conditions the material is usually far below its glass transition temperature and follows linear elastic behaviour. However, during the manufacturing process, the polymer matrix exhibits viscoelastic behaviour which affects the development of residual stresses. If the resin is used as the matrix in a continuous fibre reinforced composite, such residual stresses can lead to significant distortion in the final part. An accurate model for the development of residual stresses and the monitoring of deformations during the manufacturing stage requires a quantitative sub-model of the gradual evolution of the matrix mechanical properties. Overestimation of the residual stress induced during the process can be eliminated only by considering the actual value of viscoelastic modulus evaluated at intermediate degrees of chemical conversion (degree of cure). Modelling of the modulus evolution is necessary for the analysis of both mechanical and non-mechanical loads developed during the manufacturing process, due to interactions between the tooling and the often complex material arrangement. The dependence of the viscoelastic properties of thermosetting systems on the degree of cure has been the subject of only very few investigations, both in terms of experimental results and modelling approach. Suzuki et al. [1] presented relaxation data for epoxies cured following various cure cycles. The cure state of these samples was not determined and the relationship between mechanical properties and cure evolution could not be explored. In a work by Kim and Hahn [2], a fixed value is assumed for the elastic modulus of the uncured and the fully cured systems, while a linear relationship is assumed between the elastic modulus and the degree of conversion, in the entire region between gelled resin and its glassy state. White and Hahn [3] used a viscoelastic formulation to study warpage and residual stresses in asymmetric composite laminates during cure, assuming a time- and cure-dependent model to simulate transverse modulus.

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Investigations of the behaviour of neat resin at various post-gelation degrees of conversion under relaxation mode for various temperatures [4] have led to the development of a model of the relaxation modulus at lower degree of cure based on the Gibbs-Di Marzio [5] formulation for the volume relaxation in glasses. Yi et al. [6] included viscoelastic effects in the analysis of residual stress development in laminated plates using a chemo-thermo-viscoelastic constitutive equation and considering a discontinuous model for the mechanical properties with a step at the gel point. O'Brien et al. [7] have reported a series of experiments on the unreacted, partially reacted and post-gelled resin. Simon et al. [8] have presented a study on the cure-dependent storage modulus of a commercial toughened epoxy resin, giving a general methodology to model the time–temperature-conversion effects in viscoelastic of thermosets.

The present study focuses on modelling the evolution of resin viscoelastic modulus during the cure. Experimental results reported in a complementary study [9] are analysed in the context of KWW models which is modified to account for the dependence of mechanical properties on conversion. The considered model uses the concept of principal relaxation time for each degree of conversion with principal relaxation times normalized with respect to the value for the fully cured state in order to find a suitable correlation with structural changes. Assuming that the same mechanism of structural evolution governs both the development of the glass transition temperature and of the mechanical modulus, an identical "potential function" can be adopted. This assumption leads to an excellent agreement of the experimental data with the model predictions. These results are supported by dielectric relaxation measurements presented in the literature [10].

2. Materials and methods

The synthetic resin system used in the present work was a pre-commercial formulation based on a tetrafunctional epoxy, cured with an amine hardener and containing an aromatic thermoplastic component. Whilst the exact composition of the resin is unimportant, the blend can be considered to be representative of the class of resins known as 'high temperature aerospace grade toughened epoxies'. Partial curing of plaques of the resin was performed in a cavity formed by two glass plates and an aluminium spacer. Each of the plates was covered with a layer of PTFE/glass release film as well as liquid release agent (FREEKOTE 700). Five different plaques were prepared following isothermal curing schedules with a dwell temperature in the 160–180 °C range. The final degree of conversion of the five plates as calculated using cure kinetics information on the resin system [11] was 0.68, 0.80, 0.87, 0.90 and 0.96. Dynamical mechanical tests using a TA Instruments DMA, type 2940, were performed on rectangular strips taken from each of the partially cured plate. A three-point bending test mode configuration was employed. Each sample was equilibrated for about 5 min before a test segment starting at each temperature, to provide a uniform temperature distribution inside the material. Three specimens were tested for each degree of conversion. Stress relaxation data were captured during each segment. More details of standard experimental procedures and data treatment for DSC and DMA analysis can be found in Ref. [9].

Table 1
Values of fitting parameter for Eq. (1).

C_{E_∞}	D_{E_∞}	F_{E_∞}
−5.18 log(Pa)	4.10 log(Pa)	89.02×10^3

3. Modeling results

3.1. Cure-dependent ultimate relaxation modulus

The variations of ultimate modulus were found to be significant and an appropriate model is developed to express the dependence on the degree of cure. Within the gelation region, where the three-dimensional network starts to form, the modulus rises from a very low value of 1.38 MPa to a value of 60.9 MPa at temperature above the corresponding glass transition temperature.

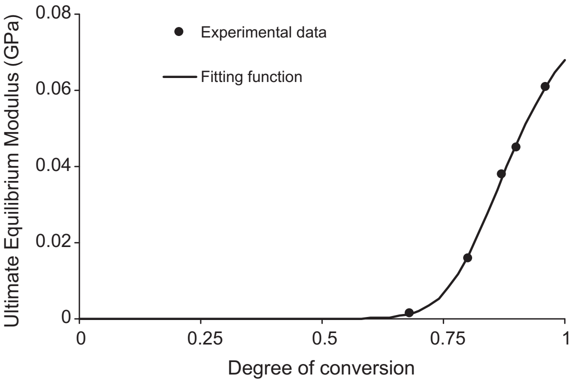

Fig. 1. Experimental points and fitting curve for ultimate relaxed modulus.

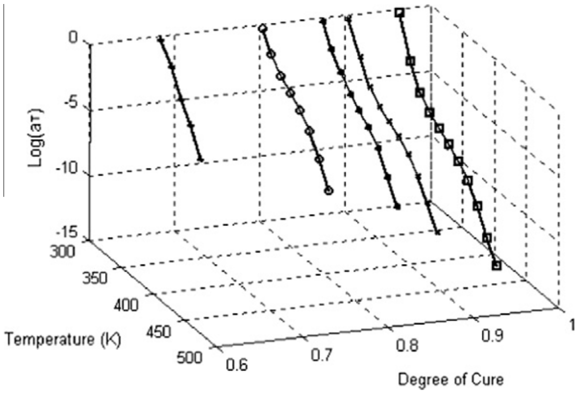

Fig. 2. 3D plot of experimental shift factors vs. temperature and degree of cure.

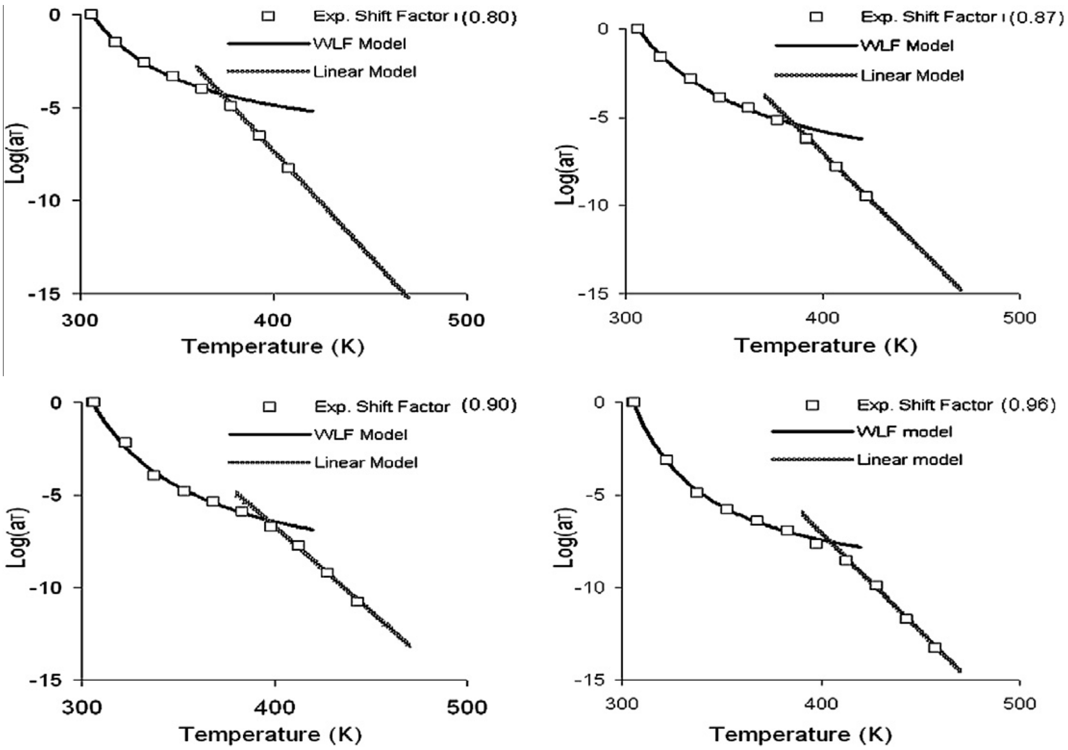

Fig. 3. Shift factors for partially cured samples (0.80–0.87–0.90–0.96) fitted with WLF and linear models.

The cure dependence of the equilibrium relaxation modulus is modelled using an empirical function proposed by O'Brien et al. [7], which expresses the value of relaxed modulus as a function of the degree of cure assuming a very low modulus value before gelation:

$$\log[E_\infty(\alpha)] = C_{E_\infty} + \frac{D_{E_\infty}}{1 + e^{\left(\frac{\alpha_{gel}-\alpha}{F_{E_\infty}}\right)}} \tag{1}$$

where C_{E_∞}, D_{E_∞} and F_{E_∞} are fitting parameters and α_{gel} is the conversion at gelation (0.66 for the resin system of this study). It should be noted that this model is valid for degrees of cure over the gelation conversion. The values of the parameters obtained from the fitting of the experimental results are reported in Table 1. Fig. 1 shows a comparison between fitting results and experimental data for the ultimate relaxation modulus indicating a close agreement.

3.2. Shift factor: results and phenomenological model

For viscoelastic materials, the mechanical response is history-dependent and involves the use of a reduced time which can be expressed using a temperature-cure-dependent shift factor as follows:

$$\xi = \frac{t}{a_T(\alpha, T)} \tag{2}$$

where ξ is the reduced time, t is the actual experimental time and $a_T(\alpha, T)$ is the degree of cure-dependent temperature-conversion shift factor.

For polymeric materials, shift factors are generally functions of temperature; in the case of a reactive system the dependence on fractional conversion needs to be taken into account in implementing the model. Fig. 2 shows the horizontal shift factors used to generate the master curves of stress relaxation modulus assuming as reference temperature the value of 302 K as indicated by the initial value of each shift factor curves in Figs. 2 and 3.

As in the works of O'Brien et al. [7] and Simon et al. [8], shift factor curves cannot be modelled using a WLF type equation. The Williams–Landel–Ferry model can be applied only to the first part of each curve; for the remaining part, a linear shift factor model shows better agreement with the experimental points.

The shift factor curves for degrees of cure equal to 0.80, 0.87, 0.90 and 0.96 are illustrated in Fig. 3, alongside a linear and a WLF model fit in the high and low temperature region respectively. Both parts of each curve show very good agreement. Comparisons of these curves with the $\tan\delta$ curves, obtained by torsional rheometry presented in [10] indicate that the intersection point of the WLF and the linear models corresponds to the onset of the post cure reaction.

Presenting experimental shift factors as a function of the difference T–T_g, where T is the test temperature and T_g the glass transition temperature for the corresponding level of conversion, allows the use of the following expression to model the shift factors upon the degree of cure and temperature:

$$\log(C_9 + a_\tau)\frac{C_3 \cdot \alpha}{1 + C_4 \cdot a_\tau^{C_5 \cdot \alpha + C_6}} = C_1 \cdot \alpha + C_2 + (C_7 \cdot \alpha + C_8)(T - T_g) \tag{3}$$

The fit of the model presented in Eq. (3) to experimental data, as obtained using the generalised reduced gradient non-linear optimisation method implemented in the solver of Microsoft Excel, is illustrated in Fig. 4a. The values of the nine parameters of the model are given in Table 2. The predictions of the model described by Eq. (3) over the whole degree of cure range are shown in Fig. 4b. It has to be noticed that at this stage, Eq. (3), was build without any physical meaning associated with the conversion dependent modulus.

3.3. Kohlrausch–Williams–Watts model (KWW)

The time-dependent properties (mechanical, dielectric, and thermal) of glass-forming materials (organic, mineral and metallic) follow the stretched exponential or so-called Kohlrausch–Williams–Watts [12–15] function (KWW). For a generic polymer system the modulus can be written as follows:

$$E(t) = E_\infty \cdot e^{-\left(\frac{t}{\tau_p}\right)^\beta} \qquad (4)$$

where β and τ_p, are two constants characteristic of the material and E_∞ is the fully relaxed modulus. The physical meaning of the two parameters can be identified by considering the characteristic bell shape of the relaxation time distribution associated with the curve of relaxation modulus. The value of τ_p (called the characteristic relaxation time) represents the central point of the time distribution function, whereas β (called the non-exponential parameter) is

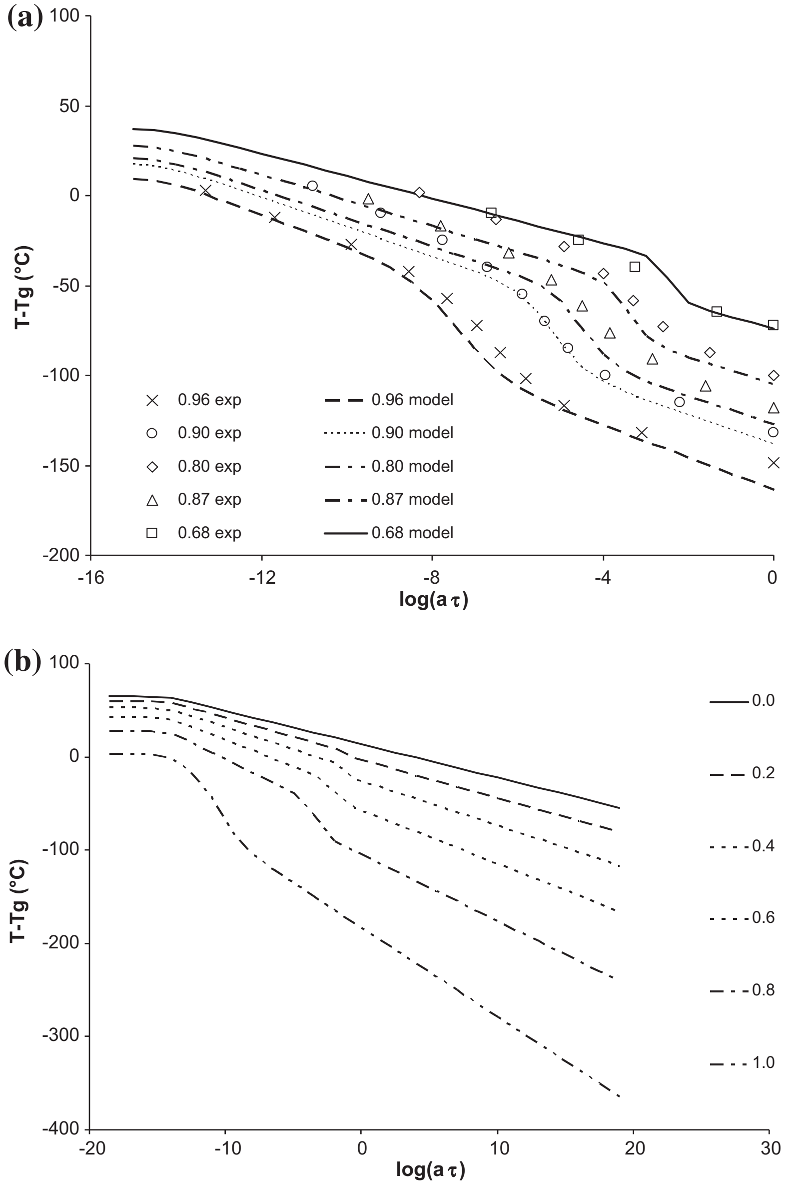

Fig. 4. (a) Experimental shift factors vs. (T–T_g) and model at each conversion and (b) model predictions over the full degree of cure range.

Table 2
Values of the coefficients of the shift factor model (Eq. (3)).

C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	Log(C_9)
−23.01	3.80	−5.28	4.73×10^3	−5.53	6.08	0.17	−0.28	−14.31

Table 3
Values of the KWW parameters at different degrees of cure.

Sample/conversion	0.68	0.80	0.87	0.90	0.96
E_∞ (GPa)	1.39×10^{-3}	1.61×10^{-3}	3.78×10^{-2}	4.49×10^{-2}	6.10×10^{-2}
β	2.74×10^{-1}	2.01×10^{-1}	1.98×10^{-1}	1.87×10^{-1}	1.57×10^{-1}
τ_p	2.53×10^4	3.05×10^5	1.32×10^7	3.78×10^7	7.25×10^8
E_0 (GPa)	3.43				

inversely related to the breadth of the relaxation time distribution. The non-exponential parameter, ranges from 0 to 1, with $\beta = 1$ corresponding to a single-relaxation time Debye response. Lower values of β typically reflect increased intermolecular co-operativity as influenced by the chemical structure of the polymer, as well as potential constraints owing to the presence of crystallinity or cross-links [16]. Fitting of the experimental master curves was carried out using the Levenberg–Marquardt non-linear least squares fitting algorithm implemented in Origin v6.0; the values of the KWW parameters for each degree of cure are reported in Table 3. A high correlation coefficient of about 0.999 has been obtained. Artificial points have been added in order to force the fitting within the glassy state, adopting an average value of 3.43 GPa for the glassy relaxation modulus.

Eq. (4) implies that different materials are characterised by distinct values of the parameters β and τ_p. The same assumption can be made for the resin during the cure: at each degree of cure a pair of KWW parameters (β, τ_p) can be evaluated. Consequently, a functional dependence for the values of these parameters on the degree of cure can be established. For a given reference temperature, T_{ref}, and by using different values of the parameters (β, τ_p) for each degree of cure, the following general form of degree a cure-dependent KWW model is obtained:

$$E(t,T,\alpha) = E_\infty(\alpha) \cdot e^{-\left(\frac{\xi(t,T,\alpha)}{\tau_p(\alpha)}\right)^{\beta(\alpha)}} \tag{5}$$

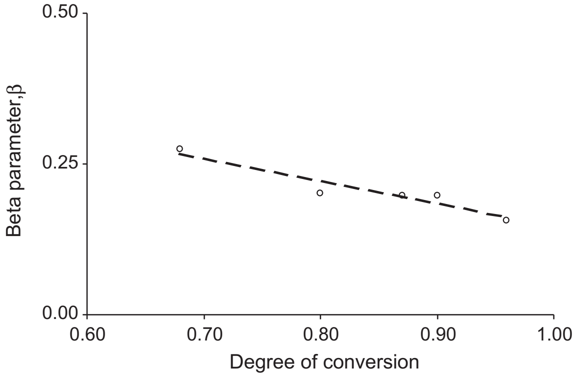

Fig. 5. Linear fitting of the beta parameter values.

The dependence of parameters β and τ_p on the degree of cure has not been investigated widely. However, Mijović et al. [10] have obtained satisfactory results using a simple linear model for the non-exponential parameter β, as follows:

$$\beta(\alpha) = c_{1\beta} \cdot \alpha + c_{2\beta} \tag{6}$$

where $c_{1\beta}$ and $c_{2\beta}$ are fitting parameters. Fig. 5 shows the linear fit for the values reported in Table 3, with parameters $c_{1\beta}$, $c_{2\beta}$ equal to −0.377 and 0.522 respectively. The increase in the breadth of the relaxation time distribution implied by this dependence is related to the increase in the complexity of the polymer network during cure which leads to a reduction in the mobility of the polymer molecules.

A direct consequence of the increased network complexity and presence of entanglements is a reduction in relaxation rate. For a generic polymer system, stress relaxation time decreases as the temperature increases, with a sharp reduction in the modulus value over its glass transition temperature. In the case of an epoxy resin under stress, relaxation times increase with increasing degree of cure. Assuming that the molecular mobility influences the glass transition through the same mechanism that controls the stress relaxation function, the behaviour of the glass transition temperature at a fixed degree of cure can

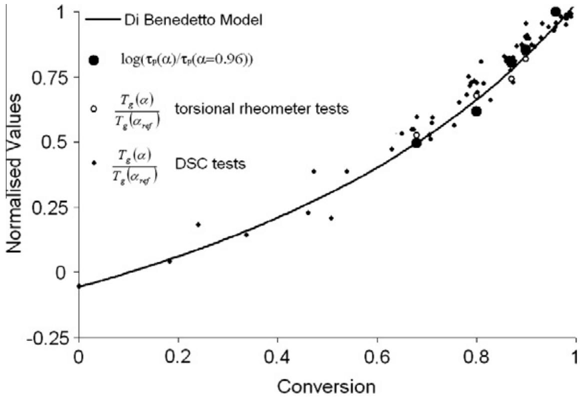

Fig. 6. Normalized values of single-relaxation time vs. conversion with normalized values of glass transition temperature obtained experimentally by thermal analysis and torsional rheometry alongside the DiBenedetto model (solid line).

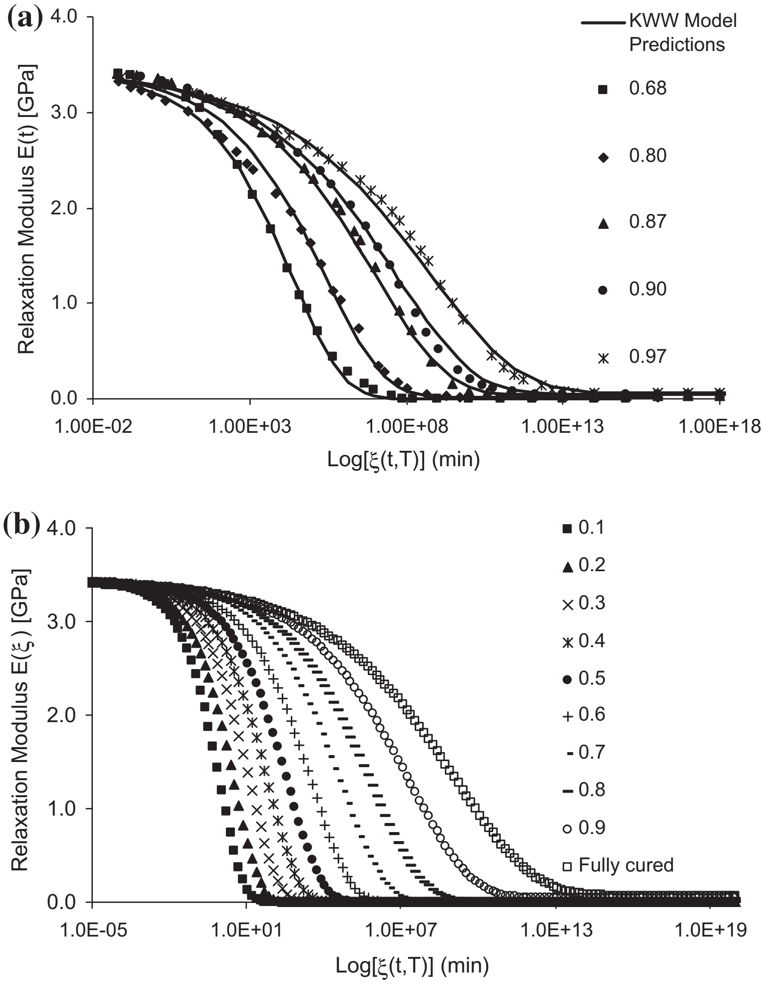

Fig. 7. (a) Model predictions and experimental stress relaxation modulus curves. (b) Prediction for the relaxation modulus over the full degree of cure range.

be normalized with respect to its value for a given reference conversion. This approach leads to the definition of a potential function, which is identical to that obtained by normalizing the characteristic relaxation times with respect to the relaxation time at the same conversion. Thus:

$$\frac{T_g(\alpha)}{T_g(\alpha_{ref})} = g_{T_g}(\alpha) \tag{7}$$

where $T_g(\alpha)$ is the glass transition temperature as a function of the degree of cure, and $T_g(\alpha_{ref})$ is the reference conversion. If the same mechanism drives the change in normalized relaxation time then:

$$\log\left(\frac{\tau_p(\alpha)}{\tau_p(\alpha_{ref})}\right) = g_{\tau_p}(\alpha) \tag{8}$$

with

$$g_{T_g}(\alpha) = g_{\tau_p}(\alpha) \tag{9}$$

where $\tau_p(\alpha)$ is the relaxation time expressed as a function of the degree of cure, and $\tau_p(\alpha_{ref})$ is its value at the reference conversion α_{ref}.

Fig. 6 reports the normalized values of the single-relaxation time τ_p and the glass transition temperature values taken from the DSC tests and tanδ curves; the best fitting obtained using the DiBenedetto [17,18] equation, commonly used to model the evolution of the glass transition temperature, is also superimposed. The mentioned DiBenedetto model is a single fitting parameter model already used by the author for the same material to model the evolutionary progression of glass transition temperature with degree of cure, and it can be suitable implemented in computational routine. The results show very good agreement for the two potential functions, thereby supporting the assumption that the assumption of a common effective mechanism that governs the change in glass transition temperature with the progress of the reaction and the change in stress relaxation times during cure. It is important to note that measurements of the glass transition temperature made using different experimental techniques will yield different results, due to the inherent time scales, relaxation mechanisms and specimen sizes associated with specific methods [19,20]. In order to apply correctly the assumptions underlying Eq. (9), comparisons need to be based on congru-

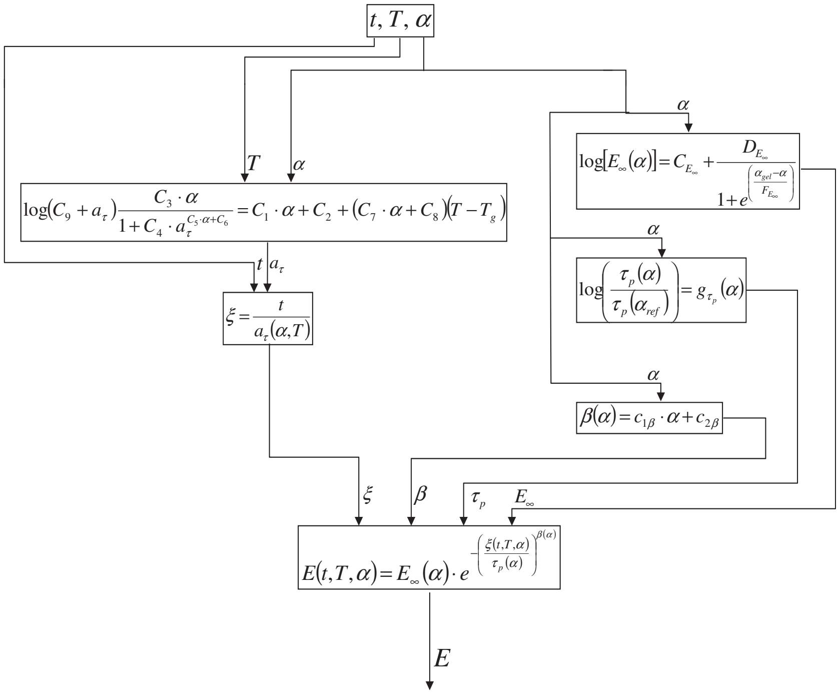

Fig. 8. Sub-model schematic.

ent measurements. For this reason, values of the glass transition temperature were taken as the temperature of the peak in tanδ obtained by solid torsional rheometry. The stress relaxation modulus has been evaluated for all the levels of conversion using the system of Eqs. (3), (5)–(7) (or (8), depending on the experimental data, glass transition temperature or principal relaxation times, used to compute the potential function). Fig. 7a compares master curves based on experimental stress relaxation data and on the predictions of the KWW model, indicating a very satisfactory agreement. The prediction over the whole range of conversions is reported in Fig. 7b; the curves show a gradual shift towards higher values of reduced time as expected and a constant value for the glassy modulus.

The computational procedure required for the implementation of this model as a sub-model of process simulations is illustrated in Fig. 8. The sub-model accepts a time, temperature, degree of cure point form the process simulation and returns a value for the cure and temperature dependent viscoelastic modulus of the thermosetting matrix.

4. Conclusions

The cure-dependent viscoelastic modulus of an epoxy system can be described by a modification of the general Kohlrausch–Williams–Watts equation. The KWW model has been implemented by introducing a potential function to account for the structural evolution of the system from a liquid polymer like to a solid vitrified material. The mechanism of relaxation is assumed directly related to the density of cross-links because of the inherent constraints imposed on molecular mobility as the network is formed. The potential function has been produced by normalizing the principal times with respect to the time of reference conversion, to account for the effect on the principal relaxation times of the polymer structural evolution. The model shows a very good agreement with experimental data for the conversion experimentally examined.

Acknowledgement

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