polymer reports

On the analysis of mechanical relaxation at the glass transition in thermoset polymers

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(Received 22 July 1991; revised 16 December 1991)

Measurements are presented of mechanical absorption in a commercial thermoset polymer at temperatures close to the glass transition. The data are shown to be accurately fitted by means of non-Arrhenian expressions for the temperature dependence of relaxation time and by allowing for non-exponential relaxation behaviour.

(Keywords: mechanical relaxation; glass transition; thermoset polymers)

Dynamic mechanical and thermal analysis (d.m.t.a.) has become a widely used technique for the characterization and investigation of polymeric materials. The analysis is based on the determination of the temperature dependences of the dynamic moduli and internal friction, measurements being made whilst the sample is vibrated at a particular frequency (usually in the range 1–100 Hz). It has been found that many polymers exhibit characteristic modulus changes and absorption peaks at specific temperatures which are employed as a means of 'fingerprinting' polymer types and for identifying important properties, such as the glass and other transitions. In recent years sophisticated computer-controlled commercial instruments have appeared that seem to have great potential for quantitative data analysis and feature enhancement. However, it is apparent that there is little guidance in the literature as to how to proceed with the data analysis of even the most commonly observed feature, namely the mechanical absorption peak (usually the α peak) associated with the glass transition. The purpose of this report is to attempt to rectify this situation by demonstrating that data obtained in the vicinity of the glass transition can be fitted by a pair of particularly simple analytical expressions, well suited to automated computer analysis.

The dynamic mechanical effects observed in polymers are similar to the phenomena, found in many other materials, that are attributed to anelasticity. The response of an anelastic material to a mechanical stress is not instantaneous but develops by relaxation processes that are characterized by a relaxation time, τ. Where the applied stress is periodic, as in a d.m.t.a. system, the elastic properties become a function of the ratio of the angular frequency of the applied stress to the material's relaxation rate, $\omega\tau$. When $\omega\tau$ is much less than unity, the frequency of the applied stress is low in comparison with the material's relaxation rate, τ^{-1}, and its elastic response is able to remain in phase with the stress throughout the applied cycle. By contrast, when $\omega\tau$ is much greater than unity the applied frequency is much greater than the natural relaxation rate and the anelastic component of strain is unable to respond to the rapidly changing applied stress. Consequently, as $\omega\tau$ is raised the material appears to stiffen. The analysis has much in common with the classical Debye theory of dielectrics and there is often a close, if not one to one, relationship between mechanical and dielectric relaxation phenomena. Both effects in polymers have been discussed at length by McCrum *et al.*[1].

In addition to changes in elastic moduli, anelasticity leads to the occurrence of mechanical absorption peaks. These are usually presented as peaks in $\tan\delta$ which is the ratio of the imaginary and real components of the complex elastic modulus. An expression for $\tan\delta$ is[1]:

$$\tan\delta = B\frac{\omega\tau_G}{(1+\omega^2\tau_G^2)} \tag{1a}$$

with

$$B = \frac{(G_U - G_R)}{(G_U G_R)^{1/2}} \tag{1b}$$

in which G_R and G_U are the relaxed and unrelaxed moduli of the material and τ_G is an effective relaxation time $\tau_G = (\tau_\sigma \tau_\gamma)^{1/2}$ where τ_σ and τ_γ are the true relaxation times associated with a constant stress or constant strain experiment. The function for $\tan\delta$ peaks when $\omega\tau_G = 1$. The relaxation time often falls with temperature in the thermally activated Arrhenius fashion:

$$\tau_G = \tau_0 \exp(E_a/kT) \tag{2}$$

in which E_a is the activation energy, τ_0^{-1} is an attempt frequency and k is the Boltzmann constant. Thus a mechanical absorption peak may be generated by sweeping temperature, the peak occurring at the temperature for which the relaxation time satisfies the condition $\omega\tau_G = 1$.

A set of mechanical absorption peaks obtained from a sample of Ciba Geigy LY1927 epoxy resin by means of a Polymer Laboratories DMTA, at a temperature scan rate of 2°C min^{-1}, are shown in *Figure 1*. This is a phenolic novolac resin containing ~7 epoxy equivalents kg^{-1} which is cured by 36 wt% of a formulated aliphatic polyamine hardener to a density of 1.17 g cm^{-3}. After mixing, the resin was degassed under vacuum, gelled at room temperature overnight, and then cured for 2 h at 60°C, followed by 2 h at 80°C and then 24 h at 100°C. It is evident that the peak temperature increases with measurement frequency as predicted by the expressions

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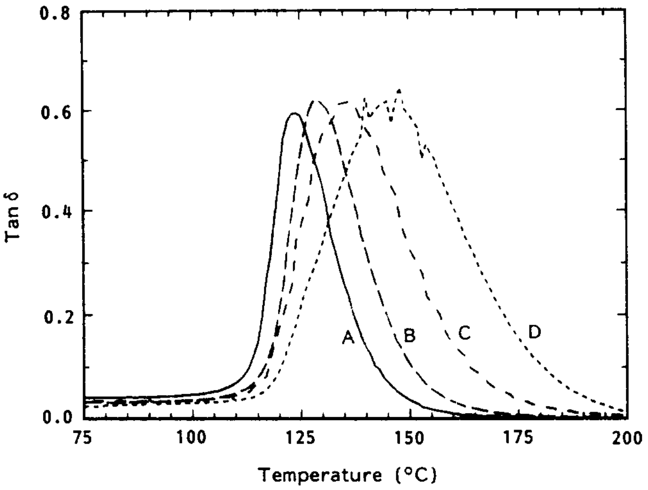

Figure 1 Experimental d.m.t.a. plots of tan δ as a function of temperature for Ciba-Geigy LY1927 resin at four frequencies: (A) 0.1; (B) 1; (C) 10; (D) 100 Hz

above. This temperature dependence can be employed, making the assumption $\omega\tau_G = 1$ at each peak, to determine the parameters E_a and τ_0 in equation (2). However, when the temperature dependence of the relaxation time deduced in this way is inserted into the Debye expression for mechanical absorption, equation (1a), the result is a very poor fit to the experimental data (see later).

In a polymer in the vicinity of the glass transition the applicability of the above expressions is questionable. The reason the mechanical loss peak is observed at a temperature a little above the glass transition temperature (T_g) is that in this temperature range elastically coupled entities within the polymer 'slow down' to a natural relaxation rate matching the low applied frequencies. This 'slowing down' is not correctly described by the simple Arrhenius expression above. Also, in this temperature range polymer components become strongly interacting and it is known^2 that relaxation processes become non-exponential—a simple exponential decay process was assumed in the derivation of the Debye expression [equation (1a)].

Although the conventional Arrhenius expression, equation (2), is often invoked to characterize d.m.t.a. data for polymers, the activation energies and attempt frequencies are in many quoted cases unphysically large. The data presented here provide a typical example: the apparent activation energy being 4.4 eV and the attempt frequency 1.7×10^{38} Hz. The latter is ridiculously large considering that the highest frequency possible in the material is the atomic vibrational frequency which is in the range of 10^{12}–10^{14} Hz. In addition, it is well known that the temperature dependence of viscosity, and consequently the relaxation time, in a polymer are not accurately represented by an Arrhenius relationship. The Vogel–Fulcher law, a simple modification of the Arrhenius relationship, provides a much improved fit to experimental data. The corresponding expression for relaxation time is:

$$\tau = \tau_0 \exp[E_a/k(T - T_0)] \qquad (3)$$

in which T_0 is a reference temperature which is obtained by fitting data. T_0 is usually only a few tens of degrees below T_g and as a consequence both E_a and τ_0^{-1} adopt much smaller and more realistic values than necessary for the Arrhenius expression.

Williams, Landel and Ferry (WLF)^3 showed from an analysis of a wide range of polymers that the temperature dependence of the ratios of mechanical relaxation times conformed to a universal empirical function:

$$\log_{10}(\alpha_T) = -8.86(T - T_s)/(101.6 + T - T_s) \qquad (4)$$

in which α_T is the ratio of the relaxation time at T to that at a reference temperature T_s, recommended to be ~ 50 K above T_g.

A more recent alternative, investigated by Souletie and Thoulence^4 for the paramagnetic susceptibility of spin glasses, is to treat the slowing down in the same way as the critical slowing down that occurs in the vicinity of a true phase transition. Phase transition theory has received an enormous amount of attention in recent years and the value of scaling relationships is widely accepted. The dynamic scaling near a transition at T^* should ideally follow a power law^5:

$$\tau = \tau_0[(T - T^*)/T]^{-\alpha} \quad \text{where } \alpha = z\nu \qquad (5)$$

in which ν is the critical exponent of the correlation length and z is the dynamic exponent.

In *Figure 2* we have fitted each of the above expressions to our estimates of relaxation time, assuming $\omega\tau_G = 1$ at each of the peaks shown in *Figure 1*. The Arrhenius fit was achieved by a standard linear regression procedure and the WLF line by choosing T_s to fit the highest and

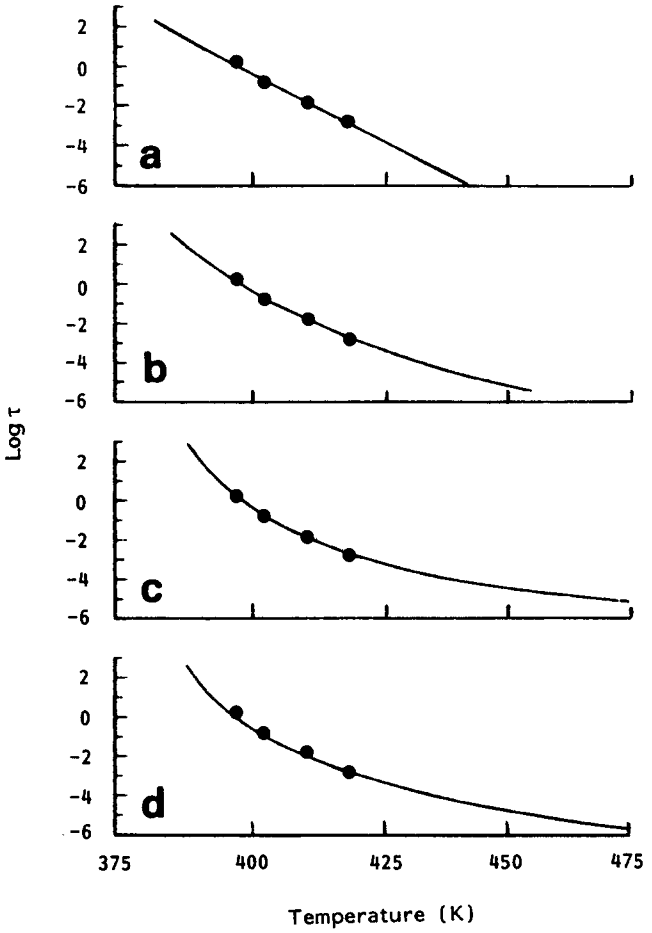

Figure 2 Comparison of the four theoretical relationships for the experimental data on temperature dependence of the tan δ peak frequency: (a) Arrhenius; (b) WLF; (c) Fulcher law; (d) power law

Table 1 Fitting parameters for the curves shown in *Figure 2*

Relationship	Equation	Parameters	
Arrhenius	2	τ_0	1.7×10^{-38} s
	(linear regression)	E_a/k	51.044 K
WLF	4	T_s	426.4 K
		τ_0	3.2×10^{-4} s
Fulcher law	3	T_0	362 K
		τ_0	2.76×10^{-8} s
		E_a/k	625 K
Power law	5	T^*	380 K
		τ_0	2.85×10^{-12} s
		α	8.4

lowest frequency data points. The parameters for the Fulcher and power laws were obtained by using the same objective criteria as those introduced by Souletie and Thoulence[4]. The change in peak temperature (T_p) with frequency (f) was measured and graphs of $(\mathrm{d}T_p/\mathrm{d}\ln f)^{1/2}$ and $\mathrm{d}\ln T_p/\mathrm{d}\ln f$ *versus* T were plotted. It was shown[4] that the intercepts and slopes of these graphs yield the fitting parameters τ_0, T^*, E_a and α. The various fitting parameters for the curves shown in *Figure 2* are tabulated in *Table 1*.

Whilst all four expressions provide equally good fits across the range of the data, we must clearly reject the Arrhenius expression because of the unphysical nature of its parameters, as mentioned above. The experimental data certainly provide no basis for choice between the other three and we cannot envisage any d.m.t.a. experiment for which the available 'experimental window' could provide such discrimination. Souletie and Thoulence[4] had similar difficulties but decided in favour of the power law on the basis of one data set covering many more decades of relaxation time than are available here.

We turn now to the problem of the mechanical relaxation response function [equation (1)]. The discrepancy between the prediction of the classical Debye expression and experimental data (*Figure 3*) is typical of both the mechanical and dielectric responses of polymers and a wide range of other materials. Traditionally[1], this was dealt with by postulating a distribution of relaxation times, each contributing a relaxation peak and thus accounting for the much broader peak than that attributable to a single relaxation time process. However, there is now considerable doubt about the validity of this procedure because it implicitly assumes each relaxation process to be exponential. As mentioned above, non-exponential relaxation characterizes the dynamics of polymers, particularly near T_g. There is an extensive body of theoretical work[2] that accounts for these non-exponential relaxations. Much of this arrives at the experimentally derived 'stretched exponential' sometimes called the Kohlrausch or Williams–Watts function:

$$f(t) = \exp[-(t/\tau)^n] \qquad (6)$$

where the exponent n has a value between 0 and 1. Jonscher[6,7] has developed a somewhat more adaptable function for fitting to the dielectric loss data of polymers. The function may be adapted to provide an expression for tan δ of the form:

$$\tan\delta = A[(\omega\tau)^{-m} + (\omega\tau)^{1-n}]^{-1} \qquad (7)$$

with two exponents n and m which enable the high and low $\omega\tau$ slopes of an absorption peak to be fitted separately. The function reverts to the Debye function on setting $n = 0$ and $m = 1$.

We have used the Jonscher expression and the temperature dependence of relaxation time provided by the power law, the Fulcher law and the WLF expression to generate curves to fit the data in *Figure 1*. It can be seen that the upper and lower extremities of the actual tan δ peaks are at slightly different levels, and to facilitate the curve fitting procedure the curves have been adjusted to bring both wings to a common (zero) base line by a linear subtraction. This makes no significant difference to the shapes of the curves or the heights of the peaks. The parameters shown in *Table 1* and intermediate values for n and m of 0.5 were used as starting parameters for an automatic non-linear regression computer fitting routine. *Figure 3* shows the set of fitted curves for the power law, and the final optimized parameters for all three relationships are shown in *Table 2*. Also shown are the mean deviations of the data from the fitted curves expressed as a percentage of peak height. It is clear that the use of the chosen functions results in very good fits to each of the four data sets. As expected, the fits employing the Fulcher, the power law or WLF are equally good for the most part. By contrast, the classical Debye expression [equation (1a)] for the 1 Hz curve in *Figure 3* gives a very poor fit, as mentioned earlier.

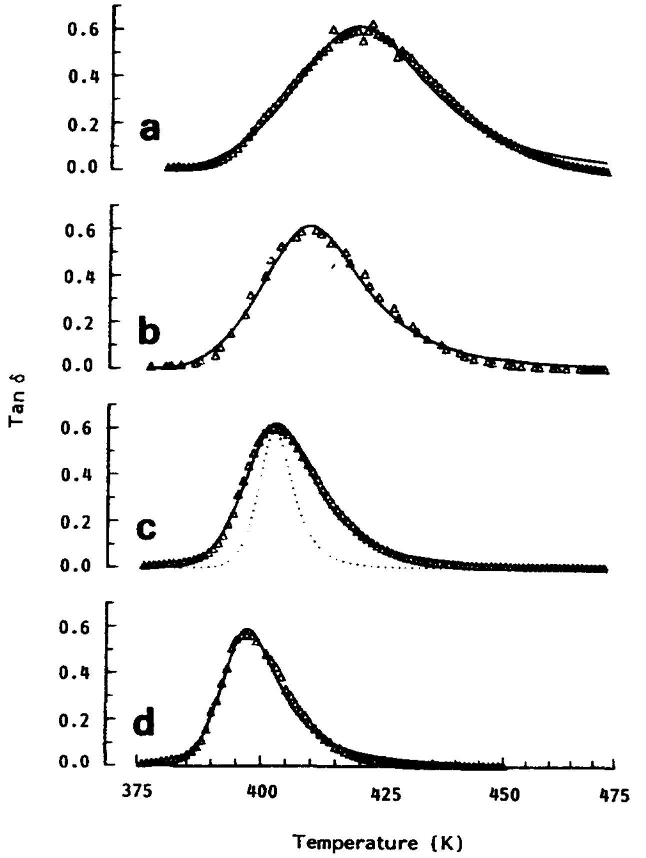

Figure 3 Power law expression of equation (5) fitted to the four tan δ peaks of *Figure 1*. The fitting parameters are $T_0 = 375$ K, $\tau_0 = 3 \times 10^{-12}$ s and $\alpha = 10$. The dotted curve represents an attempt to fit a classical Debye function to 1 Hz data. △, Experimental data; —, fitted power law. (a) 100 Hz, $m = 0.55$, $n = 0.71$, $A = 1.18$; (b) 10 Hz, $m = 0.53$, $n = 0.69$, $A = 1.14$; (c) 1 Hz, $m = 0.52$, $n = 0.58$, $A = 1.23$; (d) 0.1 Hz, $m = 0.46$, $n = 0.56$, $A = 1.18$

Table 2 Curve fit parameters for the three tan δ *versus* temperature relationships

Relationship	Frequency (Hz)	A	T_0[a] (K)	τ_0 (s)	α	E_a/k (K)	n	m	Error[b] (%)
WLF	0.1	1.15	431	3.2×10^{-4}	NA[c]	NA	0.56	0.39	2.38
	1.0	1.15	431	3.2×10^{-4}	NA	NA	0.61	0.38	2.67
	10	1.15	431	3.2×10^{-4}	NA	NA	0.70	0.35	4.35
	100	1.15	431	3.2×10^{-4}	NA	NA	0.71	0.31	5.20
Fulcher law	0.1	1.13	362	5.5×10^{-7}	NA	626	0.52	0.72	2.6
	1.0	1.17	362	5.5×10^{-7}	NA	626	0.60	0.70	2.2
	10	1.11	362	5.5×10^{-7}	NA	626	0.65	0.76	3.4
	100	1.06	362	5.5×10^{-7}	NA	626	0.78	0.77	3.5
Power law	0.1	1.18	375	3×10^{-12}	10	NA	0.46	0.56	2.7
	1.0	1.23	375	3×10^{-12}	10	NA	0.52	0.58	1.9
	10	1.14	375	3×10^{-12}	10	NA	0.53	0.69	3.0
	100	1.18	375	3×10^{-12}	10	NA	0.55	0.71	3.5

[a] The symbol T_0 represents different characteristic temperatures for the three laws, namely T_s for WLF, T_0 for Fulcher and T^* for the power law
[b] The errors are root mean square deviations of the curve from data points as a percentage of peak height
[c] NA, not applicable

We believe that the fitting routine we have demonstrated here should find general application in dealing with α peak data. The qualities of the fits are sufficiently good to facilitate the often needed detailed comparison of data obtained from samples of the same polymer processed in different ways or to distinguish subtle changes that might be attributable to the inclusion of secondary phases or strengthening fibres.

Of the three adopted expressions for the temperature dependence of relaxation time, the WLF expression has the attractions of having the smallest number of parameters and of proven universality for amorphous polymers. An attraction of the power law, however, is that the fitting process generates a physically useful parameter in the form of the apparent underlying phase transition temperature T^* which might be identified[8] with the T_g. The determination of T_g from equilibrium measurements is highly dependent on experimental conditions, in particular cooling rate. The applicability of the power law (dynamic scaling) suggests a method for the determination of T_g from measurements taken well above T_g where cooling rate effects are far less restrictive. We have found the power exponent $\alpha = 8.4$ accurately to reproduce the universal WLF expression at temperatures to within about 10 K of T_g. The Vogel–Fulcher law, although originally an empirical law, has now been obtained in numerous theoretical treatments of the glass transition. Its parameters, however, are not universal which is a disadvantage for use in an efficient curve fitting procedure.

It can be seen from *Table 2* that the fitting exponents m and n vary from curve to curve. These values characterize the relaxation process of the polymer in the temperature range covered by the relaxation peak. It is clear from *Figure 1* that the 100 Hz data are spread across a far wider range of temperatures than the 0.1 Hz data and therefore it is not surprising that the exponents differ for these two data sets. It is also clear that the quality of the fits deteriorates with increasing frequency. This may be a consequence of having to use a single exponent to represent the response across a wide range of temperatures, whereas ideally temperature-dependent exponents should be employed.

ACKNOWLEDGEMENT

This study is part of a wider programme on surface treatment of carbon fibres for composite materials carried out in collaboration with Professor J. Verbist and Dr C. Lefebvre of the Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium and funded by the EEC.

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