Journal of Alloys and Compounds, 211/212 (1994) 381–384
JALCOM 026

Dynamical mechanical analysis of glass-transition peaks in polymers and composites*

D.P. Almond, B. Harris, R.G. Hallett and O.G. Braddell
School of Materials Science, University of Bath, Bath BA2 7AY (UK)

Abstract

In an earlier paper, the mechanical loss peaks of an epoxy thermoset resin were shown to be fitted by a non-Arrhenius power-law expression for the temperature dependence of the relaxation time with allowance for non-exponential relaxation behaviour. We have now extended this type of analysis to characterize the loss peaks in two non-crystalline thermoplastic polymers, poly(methyl methacrylate) and polycarbonate, and we provide an example of how the analysis may be used to demonstrate subtle differences in the behaviour of composite systems, in particular, the way in which interphase coatings on carbon fibres may affect the loss behaviour.

1. Introduction

In earlier papers [1, 2] we presented a new method of analysing the internal friction at the glass transition and showed how well it fitted data obtained by dynamical mechanical analysis (DMA) of samples of a thermoset epoxy resin. In this new approach, it was suggested that it was more realistic to represent the temperature dependence of the relaxation time, above the glass transition temperature, T_g, by a phase transition power-law expression such as is widely used to model critical slowing down, rather than by a simple Arrhenius relationship. In addition, the internal friction peaks were shown to be fitted by a Jonscher [3] double power-law expression in place of the conventional distribution of Debye functions. In this paper we analyse data obtained from two quite different polymers, *viz.*, the non-crystalline thermoplastics poly(methyl methacrylate) (PMMA) and polycarbonate, in order to demonstrate the range of applicability of the new analytical method. An example is also given of the way the method may be used to detect subtle differences in data sets.

2. Experimental details

The system used in this work was the Polymer Laboratories DMTA Mark II equipment which has the capability of analysing samples over the temperature range −150 to +300 °C at frequencies from 0.1 to 200 Hz. Its temperature resolution is ±0.1 °C and it is equipped with a high-duty bending head which provides information about the flexural properties of samples with typical dimensions 30 mm × 10 mm × 2 mm, depending on the sample stiffness. The above temperature and frequency ranges encompass the important primary and secondary molecular processes in most of the commercially significant polymers. The present work concentrates on effects near the glass transition temperature and consequently on measurements taken at the upper end of the above temperature range.

3. The analytical technique

In the vicinity of the glass transition, it has been assumed that the internal friction reaches a maximum value at the condition $\omega\tau = 1$, where ω is the angular frequency of the applied mechanical vibration and τ is the internal relaxation time of the polymer test-piece. As a sample is cooled down from a temperature above T_g, this relaxation time increases in a fashion similar to that of the critical slowing down associated with many conventional phase transitions [4]. Phase transition studies show the temperature dependence of τ to be represented by the power law [4]:

$$\tau = \tau_0[(T - T^*)/T]^{-\alpha} \qquad (1)$$

in which α is a critical exponent and T^* is the critical temperature. The internal friction peaks that are recorded above T_g are considerably broader than would be predicted by the classical Debye expression, and it was shown [1, 2] that their shape could be accurately represented by the function:

$$\tan\delta = A[(\omega\tau)^{-m} + (\omega\tau)^{1-n}]^{-1} \qquad (2)$$

---

*Invited paper.

SSDI 0925-8388(93)00026-U

which was proposed by Jonscher [3] to account for dielectric loss characteristics of polymers. The exponents m and n are obtained by curve-fitting and attain values between 0 and 1. The first step in the analytical procedure is to establish reasonable values of the parameters τ_0, α and T^* by fitting eqn. (1) to the temperature dependence of the relaxation time. This may be obtained in the usual way by making measurements across a range of frequencies, determining the loss-peak temperatures, and assuming that $\omega\tau=1$ at each peak. An expression for the full temperature dependence of internal friction is then obtained by inserting the temperature-dependent expression for τ, eqn. (1), into eqn. (2), so that:

$$\tan\delta=\frac{A}{[\omega\tau_0(1-T^*/T)^{-\alpha}]^{-m}+[\omega\tau_0(1-T^*/T)^{-\alpha}]^{1-n}} \tag{3}$$

The amplitude parameter A may be obtained by fitting the function to the amplitude at the peak, and the exponents n and m are adjusted to the high and low temperature slopes of the curve. The method lends itself to computer-fitting techniques and has been shown [1, 2] to produce fits with overall errors of only a few percent. The resulting set of parameters τ_0, α, T^*, n and m provide a detailed characterization of the data that can be used to investigate quantitatively subtle changes produced by variations in the commercial manufacturing process or by additives.

4. Results for PMMA

Internal friction data for a commercial injection-moulded sample of PMMA obtained at 0.1, 1, 10 and 100 Hz are shown in Fig. 1. The curves were fitted to the data by using the parameters shown in Table 1 after preliminary evaluation had given the values $T^*=368$ K, $\tau_0=5\times10^{-12}$ s^{-1} and $\alpha=9.8$. These parameters, and the general appearance of the data, are remarkably similar to those used in the earlier work to fit the epoxy resin data. A falls slightly with increasing frequency, while m increases markedly. n also increases with frequency, but only to a limited extent. It is clear that the analysis provides a good representation of the internal friction above the glass transition in PMMA. The fitted parameters are given with an indication of the standard errors of the mean, as reported by the curve-fitting program (Fig. P, by Biosoft of Cambridge), and the overall non-linear regression correlation coefficient, r, for the stated number of degrees of freedom, also reported by Fig. P.

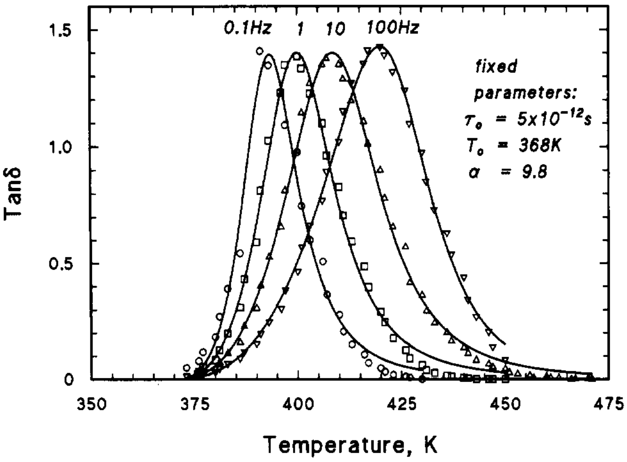

Fig. 1. Comparison of experimental tanδ data and fitted power-law curves for PMMA at four frequencies.

TABLE 1. Curve-fit parameters for PMMA. Fixed parameters are $T^*=368$ K; $\tau_0=5\times10^{-12}$ s^{-1}; $\alpha=9.8$

Fitting parameters	0.1 Hz	1 Hz	10 Hz	100 Hz
A	2.73(0.07)	2.69(0.04)	2.62(0.03)	2.48(0.02)
m	0.57(0.02)	0.61(0.01)	0.68(0.01)	0.96(0.02)
n	0.62(0.02)	0.66(0.01)	0.68(0.01)	0.70(0.01)
r (degrees of freedom)	0.991(24)	0.996(35)	0.997(46)	0.998(36)
error, % (see note)	3.27	2.55	1.92	1.74

Figures in parentheses for A, m and n are standard errors of the mean as reported by the graphing program. Error is reported as mean asbolute deviation as a percentage of peak height.

5. Results for polycarbonate (PC)

The samples used in these experiments were cut from a commercial sample of PC sheet. The glass transition temperature of polycarbonate is higher than that of PMMA and is also closer to the melting temperature than for PMMA. As a result, the internal friction above T_g, as shown in Fig. 2, has two components. The rising background internal friction associated with this melting must be extracted from the data containing the expected internal friction peak before proceeding with the analysis. An example showing a simple polynomial fitted to the background in the vicinity of the loss peak, together with the resulting corrected loss peak data, are given in the figure. The preliminary analysis gave the values $T^*=412$ K, $\tau_0=1\times10^{-13}$ s^{-1} and $\alpha=8$. Unlike the case of PMMA, however, good fits to the curves for all three test frequencies could not be obtained with this starting value of τ_0 and an optimum value of 1.8×10^{-13} s^{-1} had to be used instead. This is probably because (a) data sets for only three frequencies were obtained, instead of the four used for PMMA, and (b) the deconvolution process illustrated in Fig. 2 depends on somewhat arbitrary assumptions.

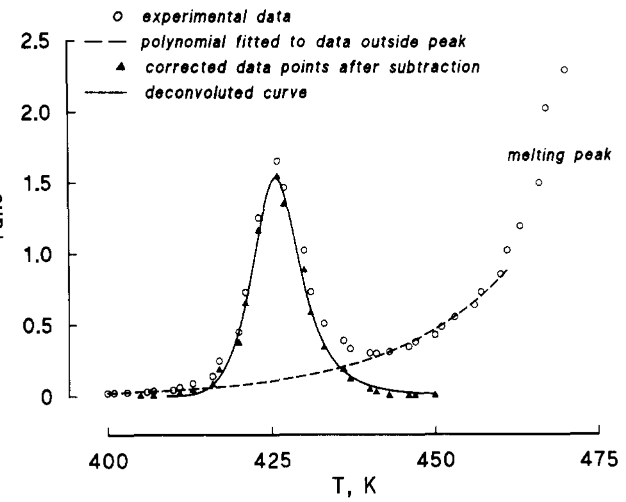

Fig. 2. Deconvolution of the tanδ peak for polycarbonate at 1 Hz.

TABLE 2. Fitting parameters for polycarbonate. Fixed parameters are $T^*=412$ K; $\tau_0=1.8\times10^{-13}$ s^{-1}; $\alpha=8$

Fitting parameters	1 Hz	10 Hz	100 Hz
A	3.13(0.09)	2.86(0.05)	2.86(0.08)
m	0.64(0.02)	0.75(0.02)	0.87(0.05)
n	0.51(0.02)	0.55(0.01)	0.49(0.04)
r (degrees of freedom)	0.994(17)	0.995(31)	0.995(24)
error, % (see note)	2.48	1.75	2.31

Figures in parentheses for A, m and n are standard errors of the mean as reported by graphing program. Error is reported as mean absolute deviation as a percentage of peak height.

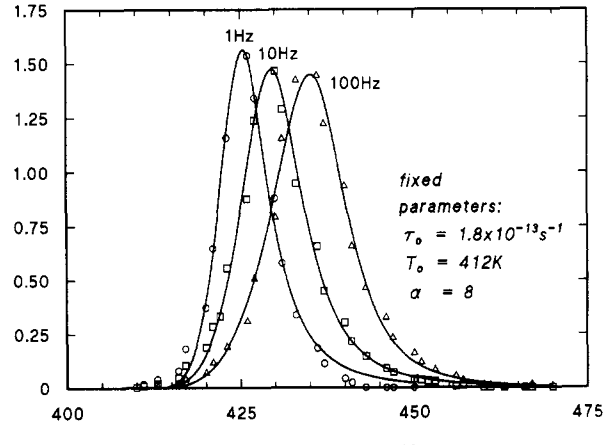

Fig. 3. Comparison of experimental tanδ data and fitted power-law curves for polycarbonate at three frequencies.

The polycarbonate data obtained at 1, 10 and 100 Hz, corrected for background and curve-fitted by using the parameters given in Table 2, are shown in Fig. 3. It can be seen that the peaks are considerably narrower than those for PMMA and epoxy resin. Again the data are fitted well by eqn. (3) with a similar precision to that attained for epoxy resin and PMMA. As in the case of PMMA, A falls slightly with increasing frequency and m increases markedly, while n is not very sensitive to ω.

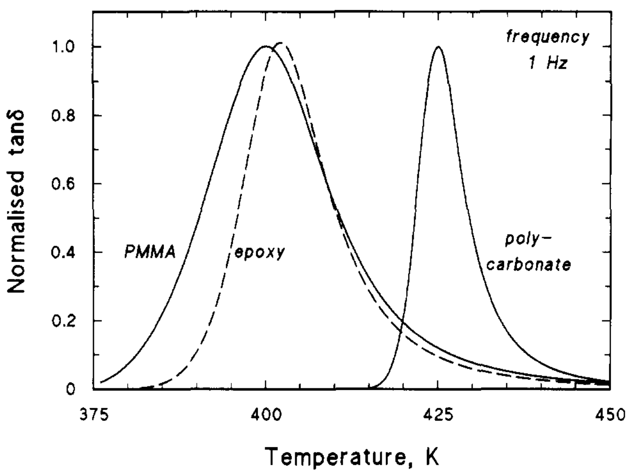

Fig. 4. Comparison of the fitted tanδ peaks for epoxy resin, PMMA and polycarbonate. The data are normalized to make the peak heights the same to facilitate comparison.

A comparison between the three polymers, epoxy resin, PMMA and PC is made in Fig. 4, where the fitted tan δ peaks for the three materials at 1 Hz are shown. The curves have been normalized with respect to peak height in order to emphasize the similarity in the shapes of the curves. The fact that the two curves for the thermoset epoxy resin and the thermoplastic PMMA are so closely similar is unexpected and suggests that despite their structural differences, the relaxation processes responsible for the main α peaks are the same.

6. Application to the study of fibre composite interphases

The purpose of developing an analytical function that would provide an accurate representation of internal friction in polymers was to facilitate detailed quantitative comparisons of samples of materials prepared in different ways or containing subtly different additives. There have been many reports of internal friction data being suitable to act as an indicator of compositional or structural properties. For example, the addition of fibres surface-treated in different ways has been reported [5–7] to alter internal friction characteristics. A review of the field may be found in a recent paper [2] by the authors.

An investigation of these effects was performed on model composite samples containing carbon fibres dip-coated with polymer interphases. This was accomplished

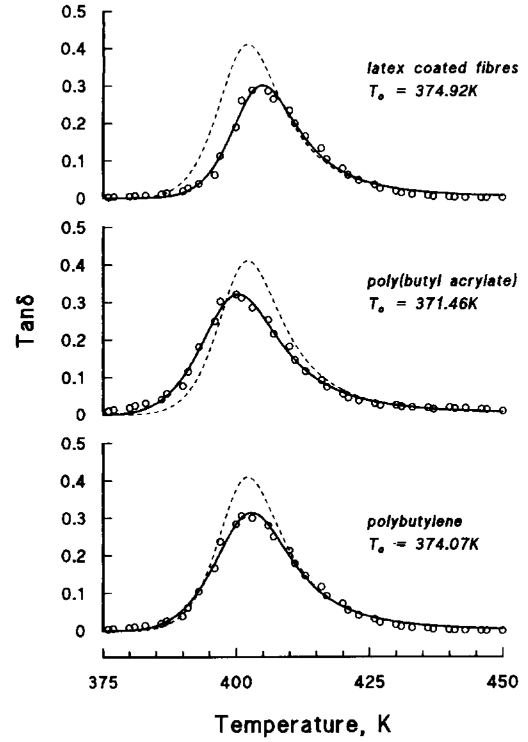

Fig. 5. Power-law model fitted to experimental tanδ *vs.* temperature curves for model composites containing carbon fibres coated with polybutylene, poly(butyl acrylate) and latex. Fibre orientation = 0°: fixed parameters are $\alpha = 9$, $\tau_0 = 1.1 \times 10^{-11}$ s^{-1}. The dashed curves represent the fitted curve for a composite containing fibres with no surface treatment.

TABLE 3. Curve-fit parameters for epoxy resin composites containing carbon fibres with different surface treatments. The fixed parameters were to $\tau_0 = 1.1 \times 10^{-11}$ s^{-1}, $\alpha = 9$

Sample	Power law parameters					
	T^*, K	A	m	n	error, %	r (deg of f)
plain resin	373.75	1.22	0.63	0.52	2.2	0.997(72)
untreated fibre	373.12	0.81	0.70	0.43	2.3	0.995(34)
PB coating	374.07	0.62	0.65	0.55	2.2	0.996(34)
PBA coating	371.46	0.64	0.60	0.54	1.9	0.996(34)
latex coating	374.92	0.60	0.64	0.37	2.7	0.994(32)

by dipping tows of Courtauld Grafil untreated (HMU) carbon fibres into a water-based emulsion of polyisoprene (latex), or into polybutadiene (PB) dissolved in cyclohexane, or into poly(butyl acrylate) (PBA) dissolved in acetone. These solutions were selected for convenience of handling by simple dipping methods: further details can be found in ref. 2. Sufficient tows to fill a mould were dipped into the solutions and spread as much as possible to facilitate penetration and the bundles were subsequently dried and laminated into model composites with a low-temperature curing epoxy resin, Ciba-Geigy LY1927. The approximate thicknesses of the coatings applied were estimated to be 0.2 μm for the latex, and about 0.04 μm for the PB and PBA. The fibres were oriented at 0° with respect to the sample long axis.

DMA tanδ data obtained at 1 Hz are shown in Fig. 5, curve-fitted and compared with the fitted curve established for untreated fibres. It is evident that the differences produced by dipping are small but distinguishable and quantifiable. An examination of the fitting parameters in Table 3 shows that the peak shape parameters m and n vary a little with coating type as well as the rather more obvious change in effective glass transition temperature, T_g. Because the effects are small, it is essential to have a well-characterized, untreated-fibre sample with which to make a comparison. The polybutylene curve is not displaced from that of the untreated sample, but the other two treatments appear to cause effects of an opposite nature. The PBA treatment shifts the curve to the left, whereas the effect of the latex coating is to shift the curve substantially to the right. Only the composite with the thicker latex dip-coated fibres showed a clear indication of a raised loss peak temperature, indicating a difference in character between this interphase and that present in composites with the other surface treatments.

7. Conclusions

This work has demonstrated that a simple analytical expression for internal friction at the glass transition can be successfully applied to a number of important varieties of polymer. It facilitates detailed and accurate parameterization of data and it is suitable for computer curve fitting and parameter refinement techniques.

References

1 D.P. Almond, O.G. Bradell and B. Harris, *Polymer, 33* (1992) 2234–2237.
2 B. Harris, O.G. Braddell, D.P. Almond, C. Lefebvre and J. Verbist, Study of carbon fibre surface treatments by dynamical mechanical analysis, *J. Mater. Sci., 28* (1993) 3353.
3 A.K. Jonscher, *Coll. Polym. Sci., 253* (1975) 231.
4 J. Souletie and J.L. Thoulence, *Phys. Rev., B32* (1985) 516.
5 P.S. Theocaris and G.C. Papanicolaou, *Coll. Polym. Sci., 258* (1980) 1044.
6 J.F. Gérard, *Polym. Eng. Sci., 28* (1988) 568.
7 J.L. Thomason, *Polym. Compos., 11* (1990) 105.