Journal of Thermal Analysis, Vol. 24 (1982) 223–232

CRITICAL PARAMETERS AFFECTING DYNAMIC MECHANICAL ANALYSIS USING A DU PONT 981 ANALYSER

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(Received January 4, 1982)

The parameters affecting Young's modulus and the glass transition temperature have been investigated. Sample dimensions as well as the sample clamping have been shown to be critical. For analysis at non-ambient temperatures the gas flow rate as well as the position of the sample thermocouple, are also important.

Polymers are viscoelastic solids and as such their mechanical properties are both time and temperature dependent. For instance, when a polymeric body is subjected to a constant stress, the strain will increase slowly with time, i.e. the polymer will creep. Similarly if the polymer is stressed and held at a constant strain, then the stress will slowly decay with time, i.e. stress relaxation will occur. One of the best ways of investigating the viscoelastic properties of polymers is by means of dynamic mechanical analysis (DMA) in which the sample is subjected to a sinusoidal stress. This gives rise to a sinusoidal strain which lags behind the stress by a phase angle δ. From the recorded data modulus and damping values can be calculated. Creep, stress relaxation and DMA are all dependent on the rate of frequency of testing as well as the temperature. When DMA is conducted over a range of temperatures, the technique is more correctly referred to as dynamic thermomechanical analysis or dynamic thermomechanometry [1]. A number of DMA techniques are available, using different vibrational principles at various frequencies. These can be divided into four basic categories: free oscillation, resonance forced oscillation, non-resonance forced oscillation and wave or pulse propagation.

An inherent feature of dynamic mechanical tests is that they are prone to appreciable errors, arising partly from limitations in the theoretical methods of data analysis and partly from spurious external influences on the measured stiffness and damping [2]. Thus data obtained by different techniques as well as by the same technique at various laboratories, often shows large discrepencies. Read et al. [2] have prepared a monograph wherein they review the underlying theory of a number of techniques thereby elucidating the limitations in the basic model and in addition they discuss external sources of error. Wedgewood [3] similarly investigates the Rheovibron viscoelastometer.

One of the newest commercial instruments is the du Pont 981 DMA and to date there has been no extensive work published on its reproducibility. This paper

highlights the critical parameters, control of which enables much greater accuracy and reproducibility to be obtained with the du Pont instrument.

Experimental

Material

PMMA sheet, supplied by AECI, was used to evaluate the response of the instrument to a number of variables.

Sample preparation

Samples were cut from sheets of PMMA and milled to the correct length and width. The sheet thickness varied slightly but areas of constant thickness were chosen. For experiments requiring varying thicknesses, thicker or thinner areas on the sheet were selected or alternatively specimens were pressed on a Buehler mounting press at 130° and 30 MPa for 10 minutes.

There was no significant difference between samples of the same thickness which were pressed or not pressed, provided there were no residual stresses.

Instrumentation

The du Pont 981 Dynamic Mechanical Analyser (DMA) with the 990 console.

The du Pont 981 DMA has been described in detail elsewhere [4–7]. Essentially it is a driven oscillation resonant technique which measures the natural sample resonance frequency as well as the energy dissipation over a wide temperature range at constant amplitude.

The resonance frequency is related to the Young's modulus of the sample via the equation.

$$E = \left[\frac{4\pi^2 f^2 J - K}{2W\left(\frac{L}{2} + D^2\right)}\right]\left(\frac{L}{T}\right)^3\left[1 + 0.71\left(\frac{2T}{L}\right)^2 - 0.1\left(\frac{2T}{L}\right)^3\right] \quad (1)$$

where:

E = Young's modulus
f = Resonance frequency
J = Moment of intertia of arm
K = Spring constant of pivot
D = Sample clamping distance (see Fig. 1)
L = Sample length
W = Sample width
T = Sample thickness

The dissipated energy or damping can be directly converted to tan δ values:

$$\tan \delta = \frac{Vc}{f^2} \tag{2}$$

where:

V = damping signal
c = system constant
f = resonance frequency

or loss modulus $E'' = E \tan \delta$.

Both E'' and tan δ curves show maxima when the test frequency equals some reciprocal average relaxation time.

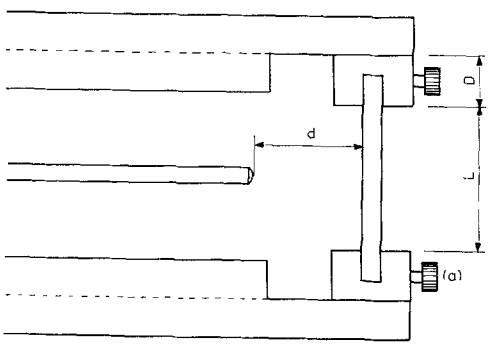

Fig. 1. Schematic diagram showing clamping length (D), sample working length (L), sample-thermocouple distance (d) and cap screws (a)

The tan δ maxima occurs at a higher temperature since it is governed by a larger but related relaxation time (τ_1) [8]

$$\tau_1 = \tau\sqrt{E_u/E_R} \tag{3}$$

where:

τ = relaxation time governing the loss modulus
E_u = unrelaxed modulus
E_R = relaxed modulus

In these experiments the peak in the damping signal was used as a measure of Tg since we were only interested in shifts in Tg. From equation (2) we see that the damping signal is proportional to tan δ provided the frequency remains constant, i.e. provided the sample dimensions remain constant.

Results and discussion

Isothermal studies (room temperature)

a) *Sample mounting:*

The effect of varying the torque on the cap screws (Fig. 1) when mounting the sample in the sample clamp, is clearly indicated in Fig. 2. Obviously if the sample is simply clamped according to the operator's whim, then the modulus can vary by a factor of 2, i.e. a 100% variance in results. The curve indicates that a torque of at least 7 N. cm. should be used. In all other experiments discussed, a torque meter was used to tighten the cap screws to 15 N. cm.

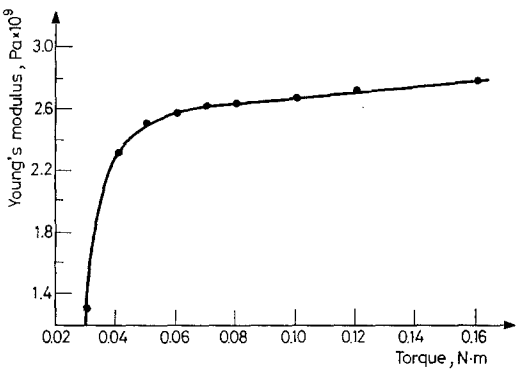

Fig. 2. Relationship between Young's modulus and the torque with which the cap screws are tightened

If the sample is made to fit exactly between the passive and driving arm, then alignment of the sample is not a problem. However, in practice the sample length is invariably slightly shorter and variances in Young's modulus may arise if the clamped length varies, as in Fig. 3. It is clear that centering the sample in the clamp goes a long way towards reducing the variance, i.e. the same length of sample must be placed in each arm clamp.

The non-parallel alignment (skewing) of a sample however had only a negligible effect on the sample modulus.

b) *Sample dimensions:*

DuPont recommend the use of samples 19, 25 or 31 mm long, 0.1–13 mm wide and 0.1–1.6 mm thick with an aspect (length: thickness) ratio of greater than 10. However, consistent sample dimensions appear to be essential for reproducable modulus values as can be seen from Figs 3, 4 and 5. Fig. 4 shows that Young's modulus will vary with changing aspect ratio. The curve indicates that the most reproducible results can be obtained if one works within a ratio region of 14–20.

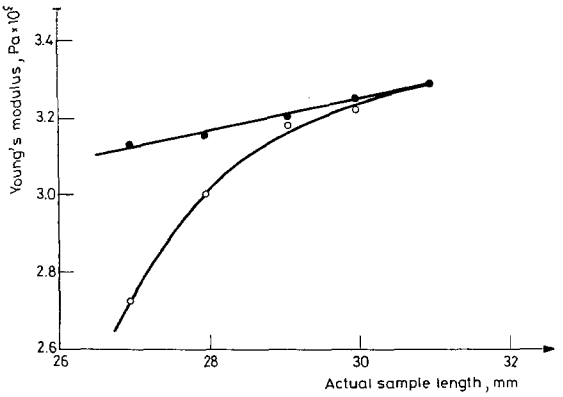

Fig. 3. Dependence of Young's modulus on the actual sample length: • sample centered in clamps; ○ sample offset to one side

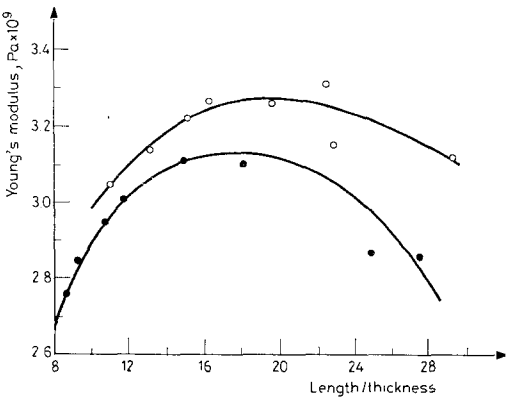

Fig. 4. Variation of Young's modulus with aspect (length/thickness) ratio for two different sample lengths; • $L = 12.23$ mm; ○ $L = 18.60$ mm

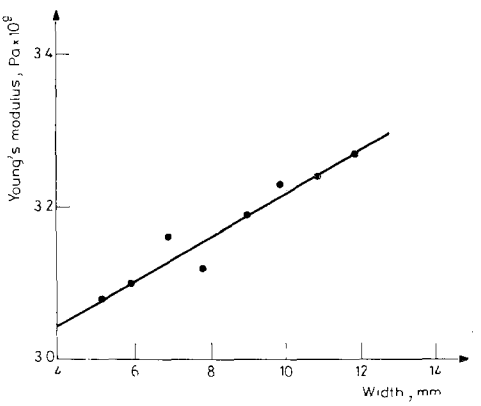

Fig. 5. Variation of Young's modulus with the width of sample

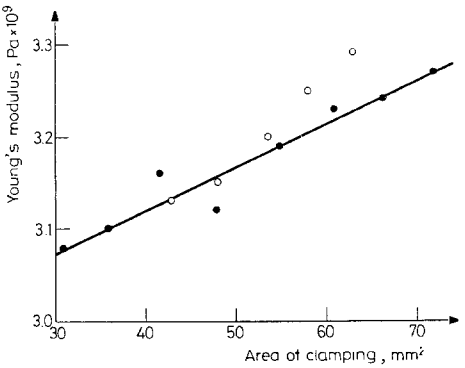

Fig. 6. Relationship between Young's modulus and area of sample which is clamped: • data from Fig. 5; ○ data from Fig. 3 (centered sample)

In addition it is seen that varying the length whilst keeping the aspect ratio constant, will also affect the modulus. Fig. 5 shows a small but steady increase in modulus with an increase in the width of the sample. It is interesting to note that if one plots the area of contact between the sample and the clamp versus the Young's modulus for the data in Figs 3 and 5, then there is a reasonable correlation between the two sets of data (Fig. 6). This seems to indicate that the variations may be due to slippage at the clamps since the greater the clamping pressure and the greater the contact area, the greater is the recorded modulus.

Thermal studies

The modulus and damping curves were monitored from 30° to 150°. The major variables affecting the recorded position of the glass transition temperature were the flow rate of the N_2 gas (Fig. 7) and the positioning of the sample thermocouple

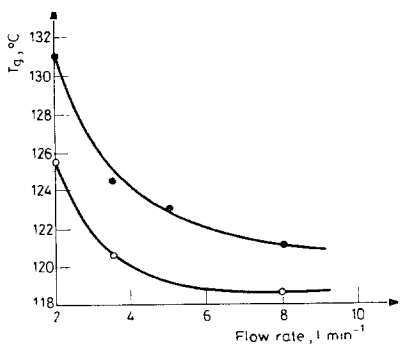

Fig. 7. Dependence of the glass transition temperature (Tg) on the flow rate of N_2 gas for various sample to thermocouple distances (d): • d = 4.45 mm; ○ d = 0.5 mm

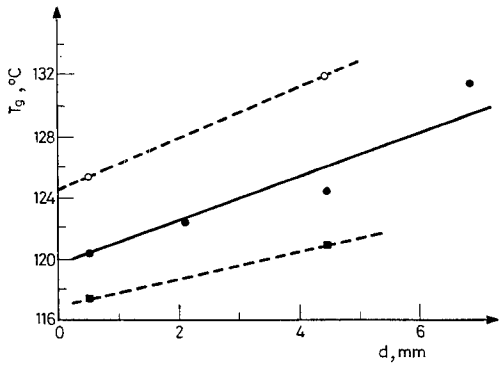

Fig. 8. Dependence of the glass transition temperature (Tg) on the sample to thermocouple distance (d) for various flow rates: • flow rate = 2 l min^{-1}; ○ flow rate = 3.5 l min^{-1}; ■ flow rate = 8 l min^{-1}

(Figs 1 and 8). Figure 9 is a schematic diagram of the heating arrangement. Heating occurs via the hot N_2 which flow from the end of the heating block and by direct radiation from the heating block. Since polymers are poor thermal conductors, it becomes difficult to record the exact sample temperature. In the instrument the sample thermocouple is insulated to retard its response and in so doing the actual sample temperature is more closely matched. However, how well the matching occurs will depend on a number of variables.

From Fig. 9 it is evident that increasing the flow rate of hot N_2 should have a greater effect on heating the sample than on heating the sample thermocouple which is shielded to some extent by the sample. Thus the sample would reach its glass transition temperature at a lower recorded value. This behaviour is shown in Fig. 7. Similarly by moving the sample thermocouple away from the sample (increasing *d* [Fig. 1]) it becomes less shielded and hence will be heated more rapidly by the hot N_2 gas flow, thus causing the recorded *Tg* to increase (Fig. 8).

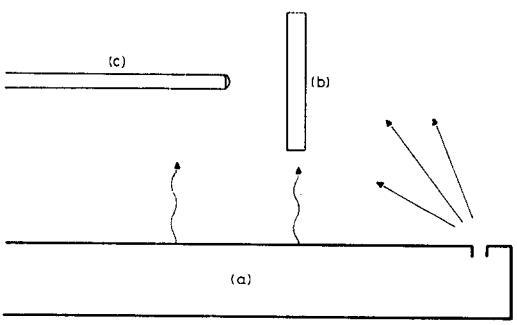

Fig. 9. Schematic diagram of the heating arrangement showing heating of sample and thermocouple by radiation and by gas flow: (a) heating block; (b) sample; (c) thermocouple

In an attempt to determine the actual glass transition temperature, we inserted a thermocouple in a sample and compared the actual sample temperature to the sample thermocouple temperature at a variety of flow rates. The results are shown in Fig. 10 where the temperature difference plotted represents the actual temperature minus the sample thermocouple temperature. It is seen that at low temperatures the sample temperature lead is greater for low flow rates, since heat loss to the sample from the decreased volume of gas is greater and less hot air reaches the thermocouple. At higher temperatures radiation from the heating block plays a greater role and since it heats the thermocouple more readily than the sample, the sample temperature lead decreases and ultimately becomes negative, i.e. the

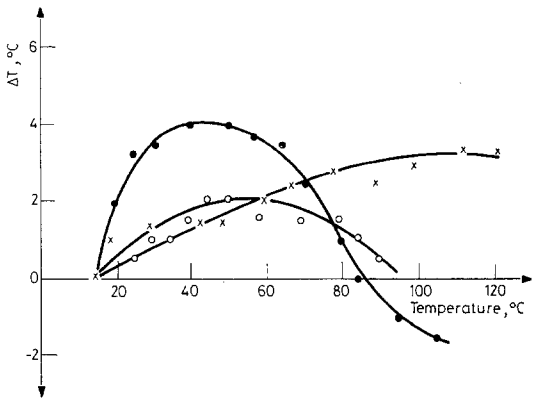

Fig. 10. Variation of the sample temperature lead (ΔT) versus temperature for various flow rates: • flow rate = 2 l min^{-1}; ○ flow rate = 5 l min^{-1}; × flow rate = 8 l min^{-1}

sample temperature lags behind the recorded temperature. At higher flow rates more heat is conveyed to the system by the N_2 gas and as a result radiation effects from the heating block contribute less to the heating process. Thus the initial sample temperature lead is diminished and the point at which it becomes negative is delayed.

In theory then it is possible to use Fig. 10 to correct the *Tg* values by adding the temperature difference to the observed temperature. In this manner we could obtain a *Tg* which is independent of flow rate and thermocouple-sample distance. Fig. 10 represents a particular thermocouple-sample distance but similar curves can be obtained at different values of *d*. If *d* is increased, then the *Tg* versus flow rate curve will move upwards (Fig. 7) but the sample temperatures lead will decrease, resulting in the same value for *Tg*. Establishing a correction curve of this nature, is very tedious, and when simply comparing *Tg* values, possibly pointless. It does, however, emphasize the need to control the operating variables. Thus Fig. 10 shows that discrepancies of the order of 4° could exist between the sample and the recorded temperature as in our case.

Furthermore it shows that the temperature difference varies with temperature and flow rate and can be both positive and negative. Finally it predicts that a transition in the region of 50° would shift to higher values as the flow rate increases, since the sample temperature lead decreases with an increase in flow rate. This is the opposite of the behaviour shown in Fig. 7 where *Tg* is in the region of 120°. *Tg* is also seen to vary with a change in width of sample (Fig. 11). This cannot be ascribed to an increase in shielding of the thermocouple as such shielding should increase the sample temperature lead and therefore decrease the recorded *Tg*. Furthermore, differences in frequency as a result of different dimensions are small and give rise to negligible changes in *Tg*. The increase in T*g* is probably associated with the increase in Young's modulus with width noted at room tem-

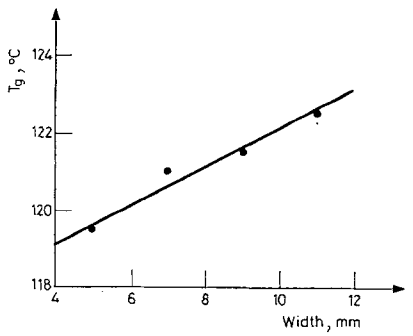

Fig. 11. Variation of the glass transition temperature (*Tg*) with the width of the sample

perature (Fig. 5) and which, in fact, holds at all temperatures. Thus the inflection point and hence damping maximum or *Tg* will occur at higher temperatures.

Changing the rate of heating from $0.5-10\,^{\circ}\,\mathrm{min}^{-1}$ caused a negligible shift in the curves as did varying the proportional band. Scratches introduced onto the sample surface did not alter the modulus, highlighting the use of a non-destructive test rather than a destructive tensile test in which sample preparation is only critical in as far as the sample dimensions must be accurately reproduced.

Quantitative tan δ values will also vary with changes in clamping and sample dimensions (similar manner to that depicted for Young's modulus in Figs 2–5) and are being investigated more fully.

In a preprint just to hand Lear and Gill [9] point to the need to give careful consideration to clamp end effects in all mechanical methods involving visco-elastic materials. They suggest a 1.5% compression to compensate for slippage inducing tensile stress at the sample-clamp boundary surface. New data analysis equations are presented, incorporating sample and correction factors which are shown to lead to improved dimensional independence of E values for samples of aspect ratios in the region of 2 to 6.

Conclusion

Since a number of variables affect both the Young's modulus and the glass transition temperature, extreme care must be exercised in comparing data with that obtained in separate experiments or in other laboratories. If trends or shifts in peaks are to be noted, then the accuracy can be greatly enhanced by:

(i) keeping all sample dimensions constant with an aspect ratio of between 14 and 20;
(ii) mounting the sample consistently, i.e. centering the sample carefully and tightening the cap screws to a constant torque of 10 – 15 N.cm;
(iii) maintaining a constant gas flow rate;
(iv) maintaining a constant sample thermocouple position.

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We wish to thank the South African C. S. I. R. for financial assistance.

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ZUSAMMENFASSUNG — Es wurden die den Young Modulus und die Glasübergangstemperatur beeinflussenden Parameter untersucht. Die Probengröße und die Packungsdichte der Probe erwiesen sich als kritisch. Für Analysen oberhalb der Raumtemperatur sind die Geschwindigkeit der Gasströmung und die Lage des Thermoelements in der Probe besonders wichtig.

Резюме — Исследованы параметры, затрагивающие модуль Юнга и температуру стеклообразования. Пиказано, что решающими факторами являются размеры образца и держател образцов. Скорость потока газа и положение термопары являются также вамными для анализа при необычных температурах.