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THEORY AND APPLICATION OF DYNAMIC MECHANICAL THERMAL ANALYSIS

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ABSTRACT

The dynamic mechanical technique of applying a sinusoidally oscillating stress to a material and the analysis of the resultant strain is now widely practised. The basic theory underlying this method is discussed and the application of dynamic mechanical analysis (DMTA) to a wide range of materials ranging from solid composites through to polymer melts is considered.

Data may be collected under computer control in the temperature plane; in the frequency plane at a set of pre-selected temperatures; or isothermally as a function of time. Thus, the dynamic mechanical technique has been applied to a wide variety of different systems.

Examples which are considered in this paper include; The study of polymer blends and phase morphology; The effect of orientation on the mechanical properties of solid polymers; The deviation of master curves using the time-temperature superposition principle; Investigation of the cure properties of thermosetting resins and fibre reinforced composites and finally, the study of melting semi-crystalline polymers.

This list of applications is by no means exhaustive but will serve to illustrate the flexibility of this method for materials characterisation.

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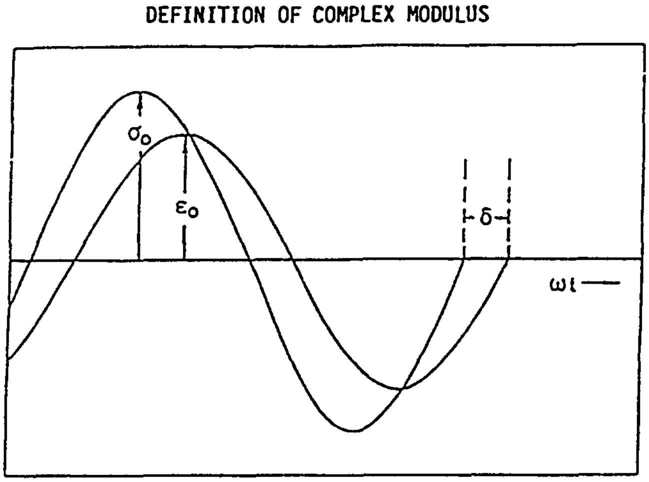
RESULTS AND DISCUSSION

Dynamic mechanical thermal analysis has become a widely practised polymer characterisation technique. It has far greater sensitivity to both macroscopic and molecular relaxation processes than thermal analysis techniques based upon a temperature probe alone.

It is the viscous or time-dependent behaviour of polymers that makes dynamic mechanical testing such a useful characterisation technique. There are many excellent references on the subject of dynamic mechanical testing (1-3) and only a brief summary shall be presented here. The technique usually applies a sinusoidal load to a sample (although other loading schedules could be used) and a real or inphase modulus (E') and an imaginary or out-of-phase modulus (E'') are obtained (see figs 1 & 2). The real and imaginary moduli represent the elastic and viscous behaviour of the sample respectively. Their ratio (E''/E') defines the loss tangent often referred to as tan δ. The ability to measure both of these moduli enables the full characterisation of a viscoelastic material. Increases in E'' or tan δ can be due to microscopic factors such as molecular relaxations or macroscopic factors such as phase boundary motion, interfacial failure.

Good dynamic mechanical test equipment should enable the testing of samples over a wide range of frequency and strain. For obtaining moduli within the linear viscoelastic range it is important that the applied strain level should be kept small, typically 10^{-3} . Large strain levels may lead to non-linear effects, particularly in semi-crystalline or filled systems (4).



Out-of-phase oscillatory stress (σ) and strain (ε) for a linear viscoelastic material

$$\sigma(t) = \sigma_0 \exp[i(wt + \delta)]$$

$$\varepsilon(t) = \varepsilon_0 \exp(iwt)$$

$$M^* = \frac{\sigma_0}{\varepsilon_0} \exp(i\delta)$$

FIG 1

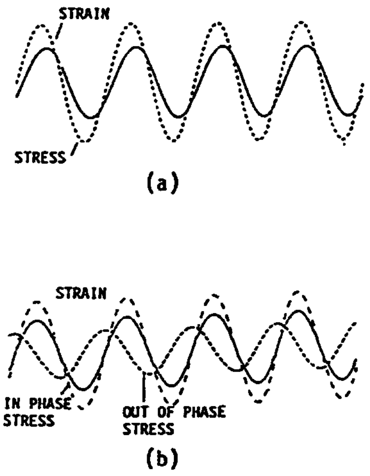


FIG 2. (a) Schematic representation of the response of a viscoelastic material to an applied sinusoidal stress.

(b) Schematic resolution of in phase and out of phase stress components with respect to strain.

One of the most common uses of dynamic mechanical testing is the determination of the glass transition temperature (Tg) of a sample. This is where the molecular chains of a polymer obtain sufficient energy (usually from thermal sources) to surmount the energy barriers for bond rotation.

Under these conditions, the material goes from a frozen glass-like condition with very limited mobility to a totally mobile system that achieves thermodynamic equilibrium instantaneously. The fall in modulus (E′) associated with this change is typically three orders of magnitude for an amorphous polymer. Large peaks occur in the values of E" and tan δ, corresponding to the onset of such motion. One of the advantages of this method of Tg determination is that it is a direct method. A material's mechanical properties are desired and it is a mechanical response which is being measured. Within experimentally achievable heating rates, Tg will be constant, but it will depend very strongly on the frequency of deformation. This means Tg can be measured under conditions that resemble the material application as closely as possible.

Polymer blends (polyblends) or polymer alloys are an important topic and of significant interest to polymer producers and processors. Figure 3 shows the dynamic mechanical relaxation spectrum for an incompatible blend.

The glass transitions of the pure components are clearly discernable, 112°C for styrene-acylonitrile and 150°C for polycarbonate. The β relaxation process can also be seen for polycarbonate. Such relaxations are indicative of energy absorption mechanisms which will relate to a material's toughness.

The glass transition is affected by molecular orientation. Figure 4 shows how increasing levels of orientation in natural rubber decrease the glass transition temperature by up to 150°C. Such experiments are readily performed in the DMTA tensile system. The magnitude of the orientational stress can be found in samples with unknown levels of orientation. One of the emerging application areas for DMTA is the generation of master curves. The William-Landel Ferry (WLF) equation usually forms the basis of the necessary shifts to produce a master curve. Measurements made over a narrow range of frequencies, but a wide range of temperatures are assumed to be equivalent to measurements made at one temperature over a wide range of frequencies, hence the name time-temperature superposition.

However, it should be noticed that this equivalence does not hold for many materials. The data presented in Figure 5 shows a set of isotherms for an acrylic resin. Figure 6 is the mastercurve for a reference temperature of 30°C. The quality of the curve is low, particularly with reference to the tan S curve. Figure 7 shows a 'wicket plot'. This is a plot of tan S vs modulus. The limiting values of modulus are E' glass and E' rubber. The fact that a smooth curve is not obtained between these limits shows that data from this material does not time-temperature superimpose very well. Conversely, Figures 8 & 9 show a good master curve and a smooth 'wicket plot'. This plot is a good measure of the quality of a time-temperature analysis and any predictions made by the master curve can be judged accordingly.

Another important application area for DMTA is the cure of resins. DMTA is very sensitive to the cure process and isothermal experiments enable the developments of an ideal curing schedule. Some results are shown in Figures 10 & 11. Figure 10 shows the increase in modulus with time as the cross-linking reaction progress. Figure 11 shows the tan S plot with time and exhibits a large initial peak (gelation) with a subsequent peak occurring as the material becomes a cross-linked glass. Note that its occurrence is frequency dependent, a result which is expected due to the viscoelastic nature of these materials.

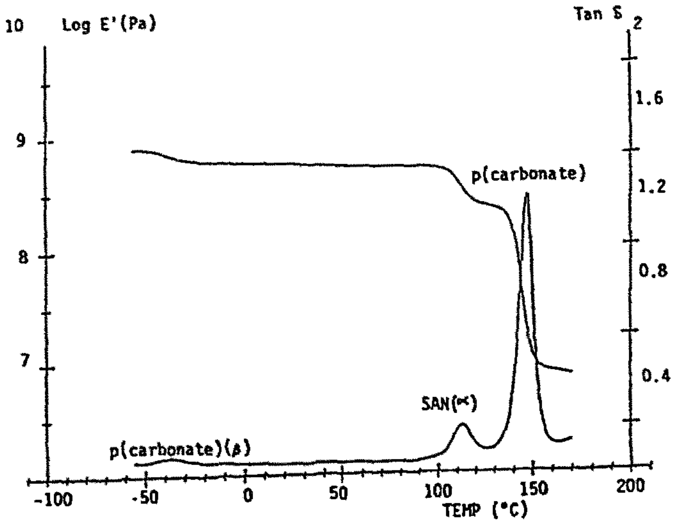


FIG. 3. Dynamic mechanical properties for SAN/PC incompatible blend

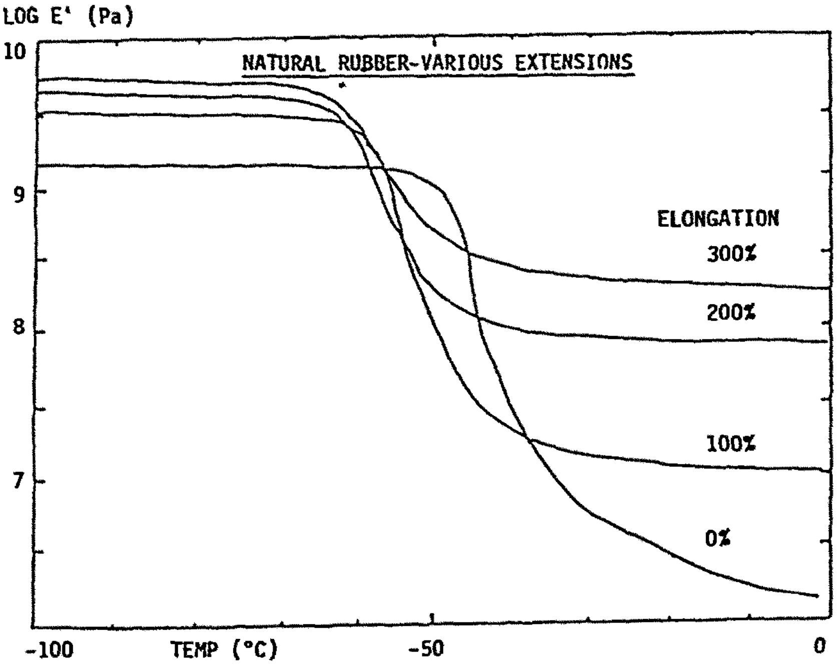


FIG 4a. Dynamic modulus of cross-linked natural rubber measured at various extension ratios. Frequency = 10Hz.

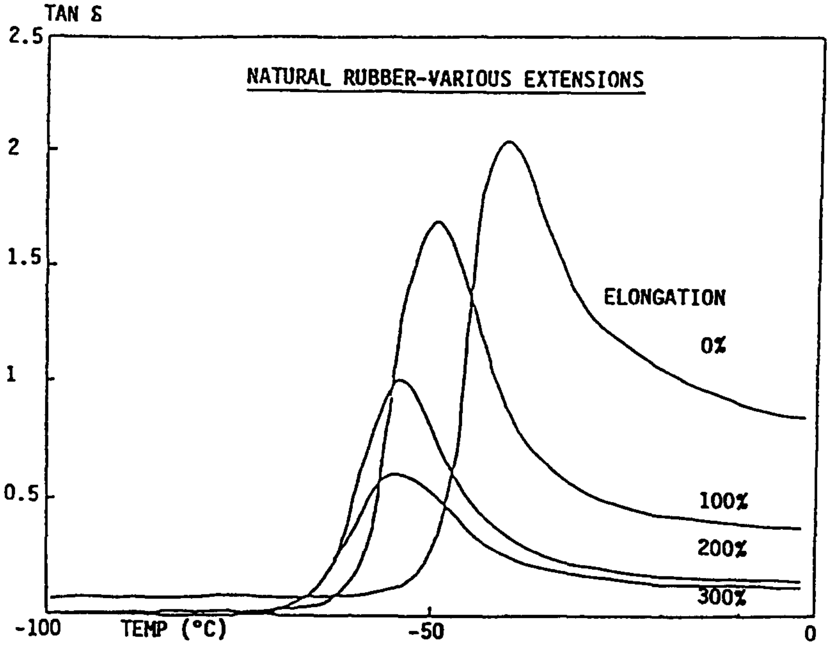


FIG 4b. As 4a, Tan δ values

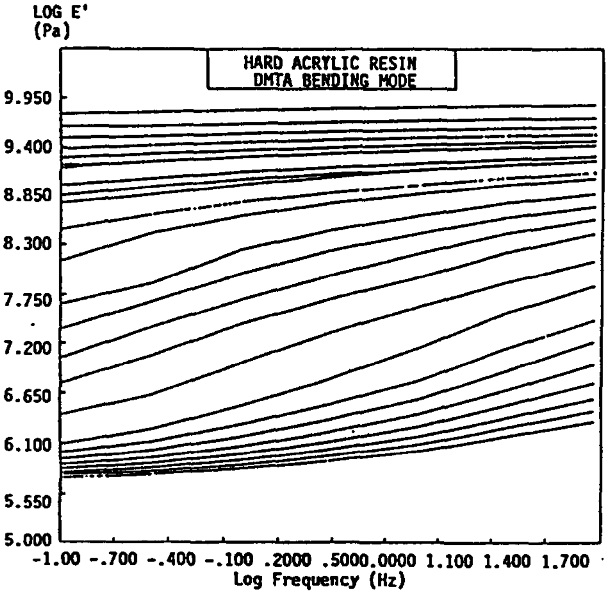


FIG 5. Storage modulus of a hard acrylic resin as a function of frequency at a series of measurement temperatures

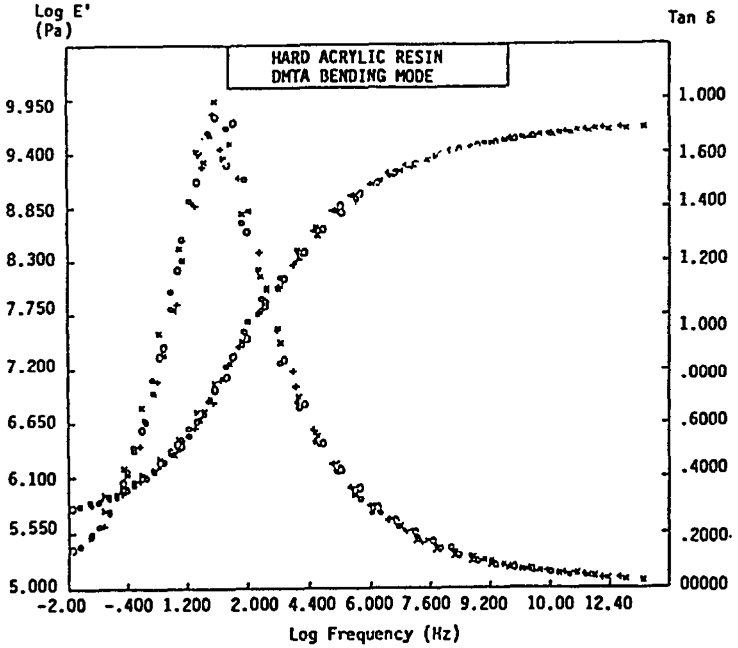


FIG 6. Master curve of a hard acrylic resin at 30°C, generated from the data in Figure 5

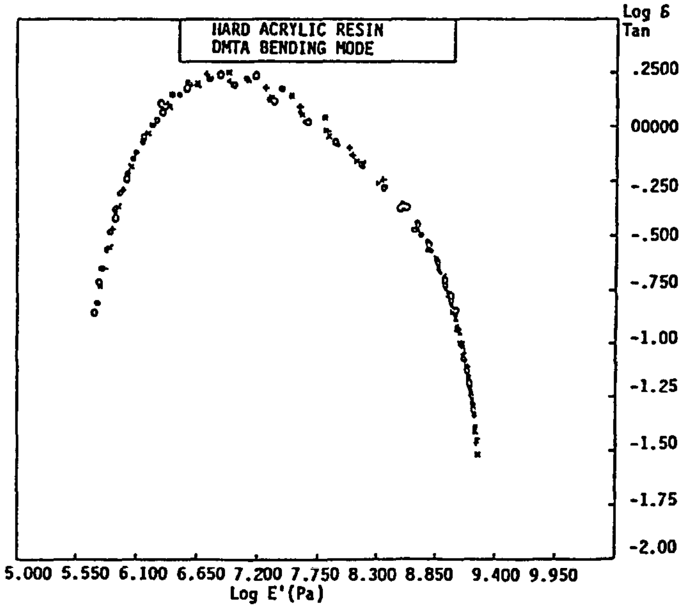


FIG 7. Wicket plot of a hard acrylic resin at 30°C, generated from the data in Figure 5

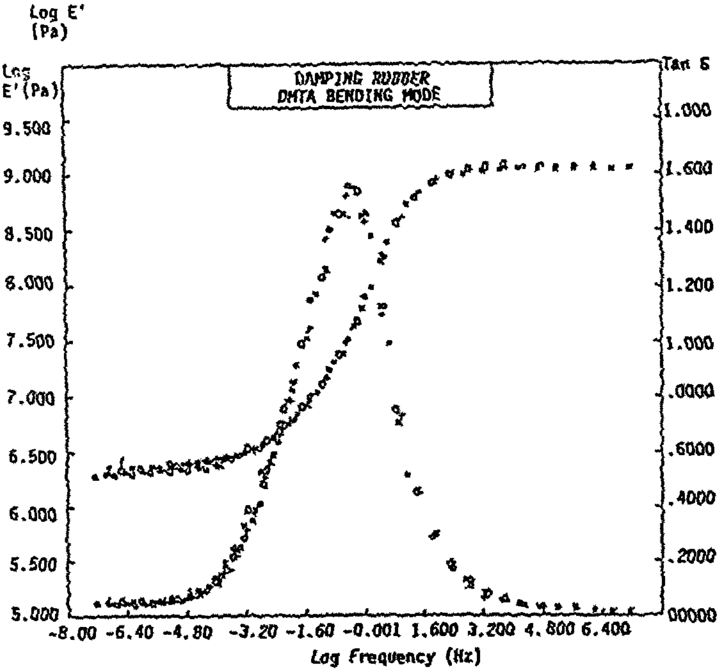


FIG 8. Master curve of damping rubber at -56°C

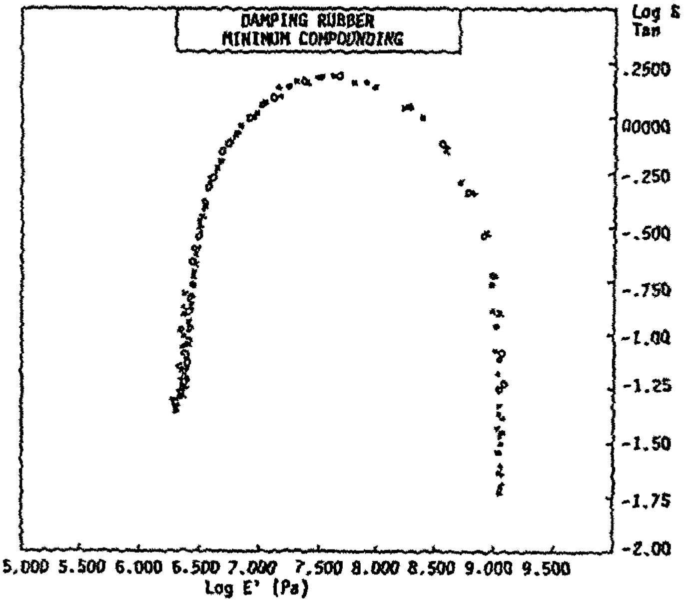


FIG 9. Wicket plot of damping rubber at -56°C

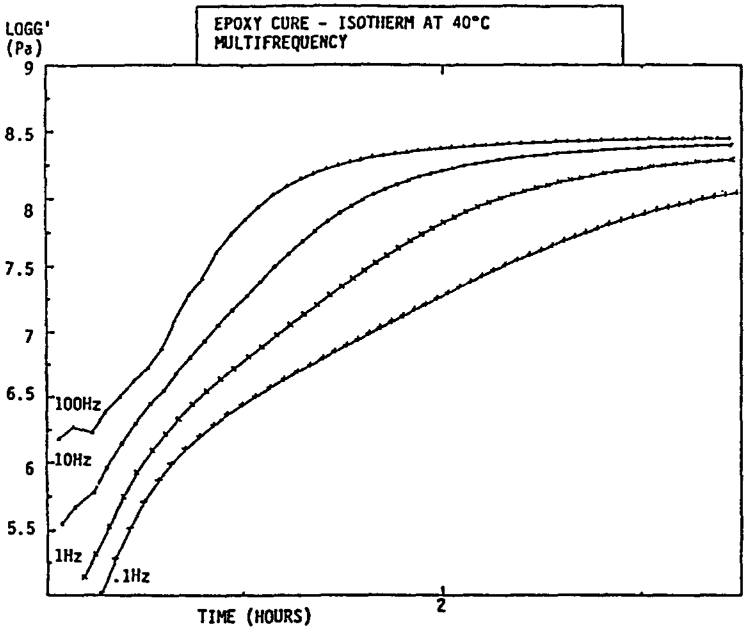


FIG 10. Shear modulus as a function of time for an epoxy resin cured at 40°C.

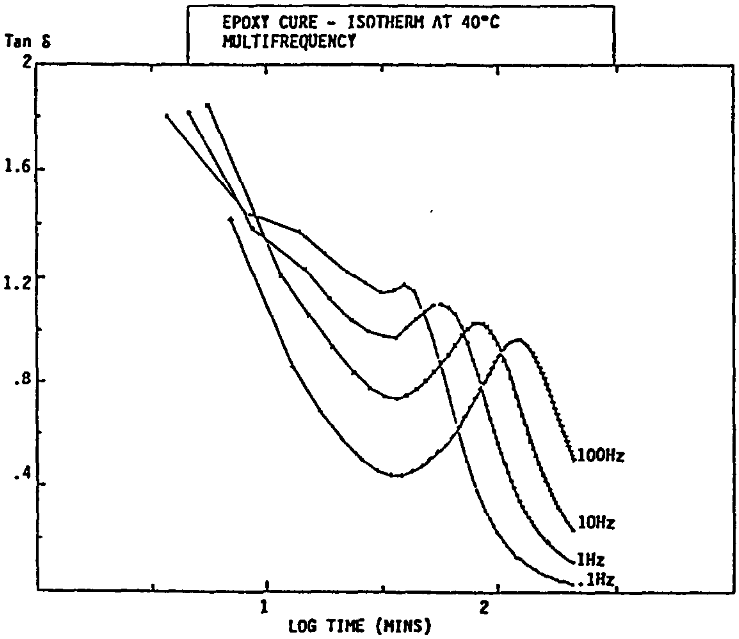


FIG 11. Tan δ as a function of time for an epoxy resin cured at 40°C

It is hoped that this brief presentation of results, whilst by no means exhaustive, clearly illustrates the wide applicability of dynamic mechanical thermal analysis for materials characterisation.

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