

## MATERIALS TESTING BY DYNAMIC MECHANICAL ANALYSIS

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Applications of the new 980 Dynamic mechanical analyser (DMA) to the study of thermoplastic polymers, thermosetting polymers and metal glasses have been discussed in this paper. This instrument has also been used to study impact modified thermoplastics [2] elastomers [3] and metals. DMA is one of the thermo-analytical techniques available to the research or quality control chemist for evaluating the mechanical properties of materials. With the introduction of the 980 it is anticipated that the disadvantages due to long operation time and complexity inherent in older instrumentation will no longer hold back progress towards the full realisation of the technique.

Mechanical spectroscopy is the measurement of the ability of materials to store and dissipate energy imparted on deformation. If a material is deformed and then released, a portion of the stored deformation energy will be returned at a rate which is a fundamental property of the material. That is, the sample goes into damped oscillation. For an ideal elastic material with high  $Q$  (quality factor), the energy incorporated into oscillation will be equal to that introduced by deformation, with the frequency of the resultant oscillation being a function of the modulus (stiffness) of the material. Most real materials, however, do not exhibit ideal elastic properties, but rather show viscoelastic behavior in which a portion of the deformation energy is dissipated in other forms such as heat. The greater this tendency for energy dissipation, the larger the damping of the induced oscillation. On the other hand, if this dissipated energy is continually made up (by an in-phase drive signal applied to the system), the sample will stay in continuous natural frequency (compound resonance) oscillation.

The two properties of interest in mechanical spectroscopy, then, are resonant frequency and energy dissipation. Dynamic Mechanical Analysis (DMA) is a technique which measures these properties. This paper describes some applications of the new Du Pont 980 Dynamic Mechanical Analyser.

Central to this instrument is a pair of parallel stainless steel arms. (See Figure 1.) These arms are attached individually to the instrument's baseplate via a "flexure pivot" located near the centre of each arm, such that the arm-pivot combination is free to rotate in the horizontal plane. The "flexure pivots" are highly accurate torsional springs which possess essentially zero mechanical loss on rotation. In addition, the springs are very rigid in directions other than their torsional axis. The re-

sultant arm-pivot system, therefore, has a very low natural free oscillation frequency of approximately 2 Hertz. In fact, the resonant  $Q$  (quality factor) for the arm-pivot system, as determined by free decay, is in excess of 300, with the principal source of energy dissipation being air friction losses. The upper useful frequency limit of this system is about 100 Hertz due to the pivot rigidity along other axes.

The sample, in the form of a rectangle, is clamped between the arms as shown in Fig. 1 to form a compound resonance system, the resonant frequency of which is dependent almost entirely on the configuration and modulus of the sample. In os-

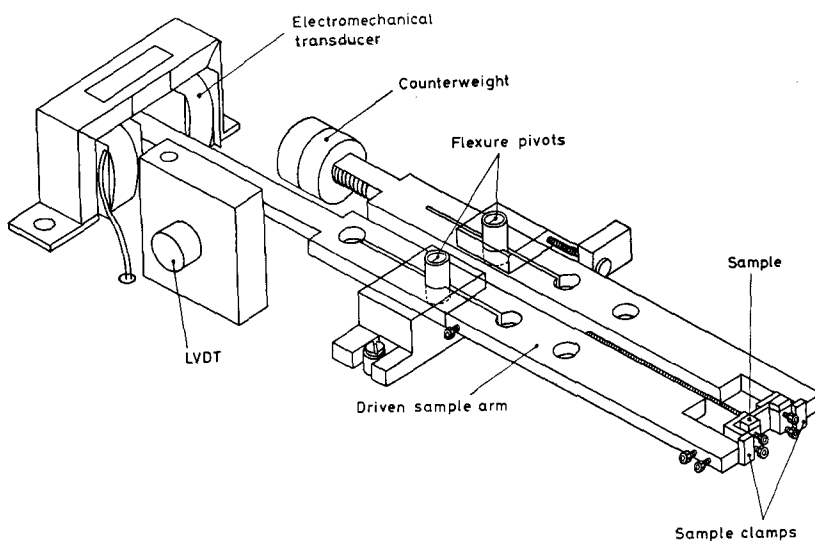


Fig. 1. DMA geometry

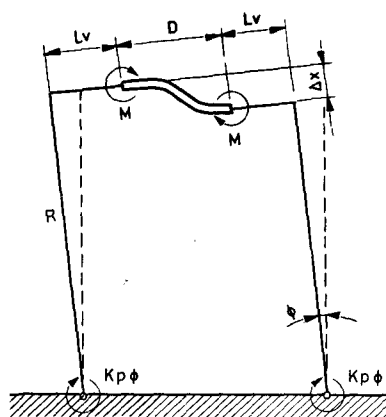


Fig. 2. Sample deformation by DMA

cillation, the sample deforms as shown in Fig. 2 in which the equilibrium position of the two arms is given by the broken lines.

The geometry of this system is similar to that treated by Timoshenko [1] except that the openings of the clamps do not start at the centerlines of each arm but extend a distance  $L_v$  (clamping distance) toward the opposite arm. If the compound resonance system is deflected away from the equilibrium position to a new position (represented by the solid lines in Fig. 2), the two ends of the sample remain parallel to each other and perpendicular to the arms. The centre of gravity of the sample and of the arms, however, translates to new positions.

This overall behavior is in direct contrast to the tuning fork where the centre of gravity remains fixed in space and only out-of-phase motion is possible.

It has been shown [2] that the resonant frequency of the system is related to the Young's modulus of the sample as follows:

$$E = \frac{(4\pi^2 f_0^2 J_0 - K)}{2H \left( \frac{D}{2} + L_v \right)^2} \left( \frac{D}{B} \right)^3.$$

Where:

- $E$  = Young's modulus in dynes  $\text{cm}^{-2}$
- $f_0$  = DMA frequency in Hz
- $J_0$  = Moment of inertia of arm in  $\text{g cm}^2$
- $K$  = Spring constant of pivot in dyne  $\text{cm rad}^{-1}$
- $L_v$  = Clamping distance in cm
- $H$  = Sample width in cm
- $B$  = Sample thickness in cm
- $D$  = Sample length in cm

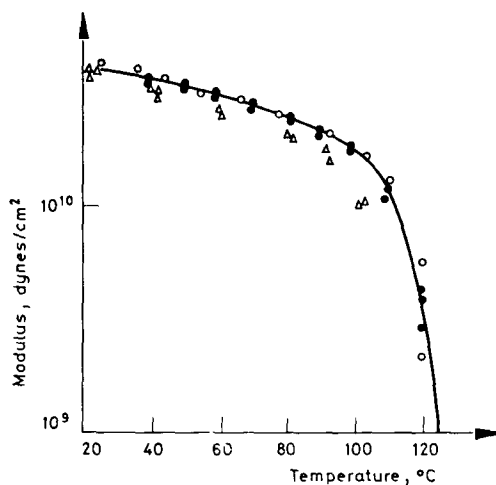


Fig. 3. Comparative modulus data. Polymethylmethacrylate. ● DMA ▲ torsion pend ( $\sim 1$  Hz) ○ driver (10 Hz).

The equation was derived from first principles and requires no empirical calibration with a sample of known modulus. Its validity has been tested by comparing the 980 DMA modulus data for polymethylmethacrylate with data from a torsion pendulum working at 1 Hz and from a driven mechanical testing system working at 10 Hz. The results are presented in graphical form in Fig. 3.

Energy dissipation is related to such properties as impact resistance, brittleness, and noise abatement. It is measured as a power input ratio on a logarithmic scale in units of decibels, and can be related directly to the more familiar  $\tan \delta$  values when certain instrumental voltages are measured that enable the actual power input to be calculated at different frequencies.  $\tan \delta$  is defined as (Loss Modulus) / (Elastic Modulus).

The 980 has been designed to measure very small changes in damping and is particularly sensitive at low temperatures where the frequencies of oscillation are often high. This is because the power required to keep a sample in oscillation increases as the frequency of the oscillation increases. A preliminary comparison of quantitative data from the 980 DMA with results from other types of instrumentation has been carried out successfully and will be the subject of a future publication.

To demonstrate the application of this instrument the following sections will give examples of its use with thermoplastic and thermosetting polymers, and amorphous metals (metal glasses).

### *Thermoplastic polymers*

The meaning of term "molecular spectroscopy" is illustrated by the results shown in Figs 4 and 5, which are the DMA scans of linear polyethylene and branched polyethylene respectively. The scans start at  $-150^\circ$  and are temperature programmed at a rate of  $5^\circ$  per minute. Both polyethylene samples exhibit damping peaks at around  $-100^\circ$  and  $50^\circ$ , which are due to long chain  $(-\text{CH}_2)_n$  crankshaft relaxations in the amorphous phase and motion in the  $(-\text{CH}_2-)$  crystalline phases of the polymer respectively. Both the temperature, position, and size of this latter damping peak are related to the crystallinity of the polyethylene [3]. In the second sample, there is a third damping peak at  $-9^\circ$ . This peak, which has been attributed to  $(-\text{CH}_3)$  relaxations in the amorphous phase, indicates that this latter sample is branched (low density) polyethylene. This conclusion is supported by the rapid decrease in frequency (modulus) of that sample as a function of temperature. In fact, the sample becomes so flexible (low in modulus) at  $90^\circ$  that it no longer contributes any restoring force to the compound resonance system; that is, it is pliant enough to be moulded.

Inert fillers and reinforcing agents are commonly added to thermoplastics and thermosets used in moulding processes to enhance the properties of the final product. Although thermoplastic moulding materials have inherent properties which permit their formulation and use without fillers, they can suffer from creep and dimensional stability problems especially at heavier loads and higher temperatures. Reinforced thermoplastics overcome many of these problems. Reinforce-

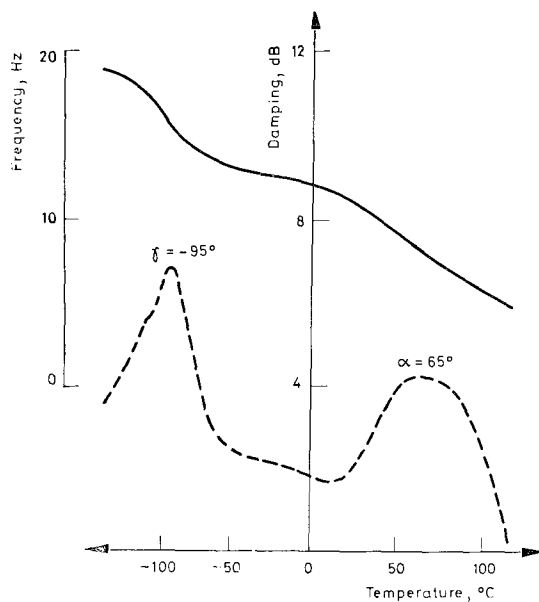


Fig. 4. DMA curve of linear polyethylene  
size:  $44 \times 395 \times 250$  mils, amp: 15 mils (p-p), prog:  $5^\circ/\text{min}$ , atm: N

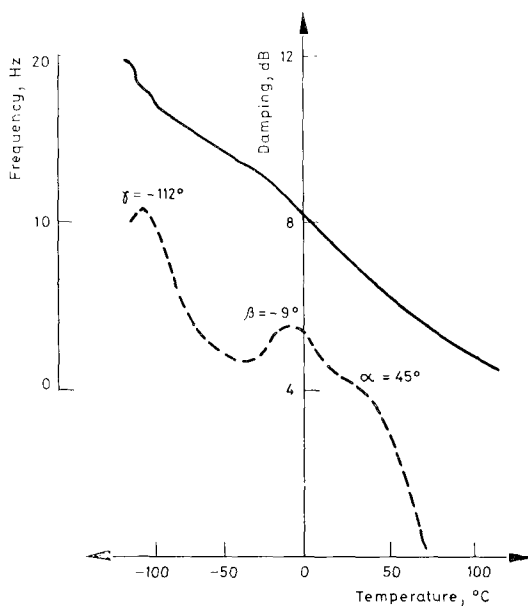


Fig. 5. DMA curve of branched polyethylene  
size:  $44 \times 385 \times 250$  mils, amp: 15 mils (p-p), prog:  $5^\circ/\text{min}$ , atm:  $\text{N}_2$

ments for plastics include a variety of fibrous and nonfibrous materials such as glass fibres, asbestos fibres, and glass spheres.

Fillers and reinforcing agents are often classified by the degree of their interaction with the polymer matrix. In the case of a glass fibre reinforced polymer the glass must normally be treated with some type of coupling agent which serves as a "binding interface" between the glass and the polymer [4]. This coupling agent will vary depending on the polymer being reinforced, and manufacturers of the glasses

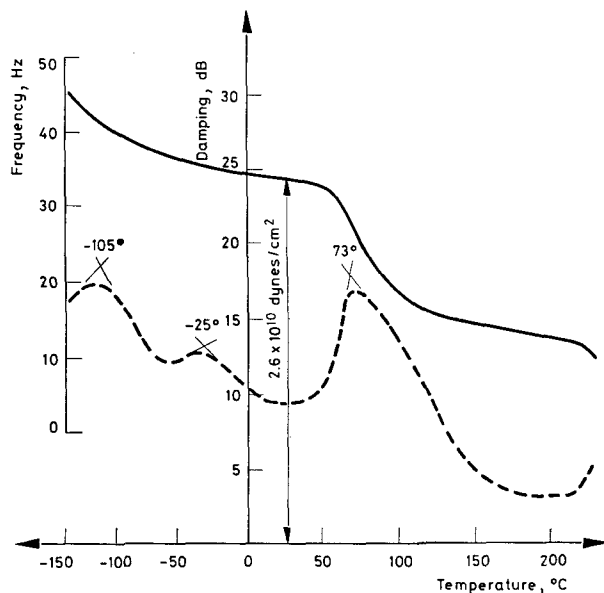


Fig. 6. DMA curve of unreinforced nylon 66  
size:  $0.13 \times 1.55 \times 0.663$  cm, amp: 0.10 mm, prog:  $5^\circ/\text{min}$

used for polymer reinforcement are continually evaluating new formulations. Both the quantitative modulus and the relative damping are used in evaluating the relative reinforcement merits of a given glass-polymer system. Fig. 6 is the DMA scan of unreinforced Nylon 66 and Fig. 7 is that of Nylon 66 reinforced with 33% by weight of glass fibre that has been coated with an experimental coupling agent. Numerous studies of the dynamic properties of polyamides have been made. In all cases where measurements on nylon have been made over a wide temperature range ( $-150$  to  $250^\circ$ ), three mechanical loss peaks are observed. These have been designated as  $\alpha$ ,  $\beta$ , and  $\gamma$  transitions and occur at approximately  $50^\circ$  to  $100^\circ$ ,  $-50^\circ$ , and  $-120^\circ$  respectively. The  $\alpha$  damping peak, corresponding to the glass transition, is of greater magnitude than the damping peaks at lower temperatures and is accompanied by the greater decrease in elastic modulus. The damping peak magnitude and temperature position have been shown to be sensitive to both the chemical

composition of the nylon and the effect of moisture. The  $\beta$  damping is attributed to the carbonyl group of the polyamide forming hydrogen bonds with the moisture present and its temperature will vary depending on the nylon moisture content. [5] Since all nylons adsorb water from the environment, moisture absorption characteristics must be considered in prospective uses of these materials [6]. Generally, moisture absorption by reinforced plastics is less than for the raw polymer. The low temperature  $\gamma$  transition is attributed to the "crankshaft" rotation of three or more methylene carbon atom chains between the amide groups.

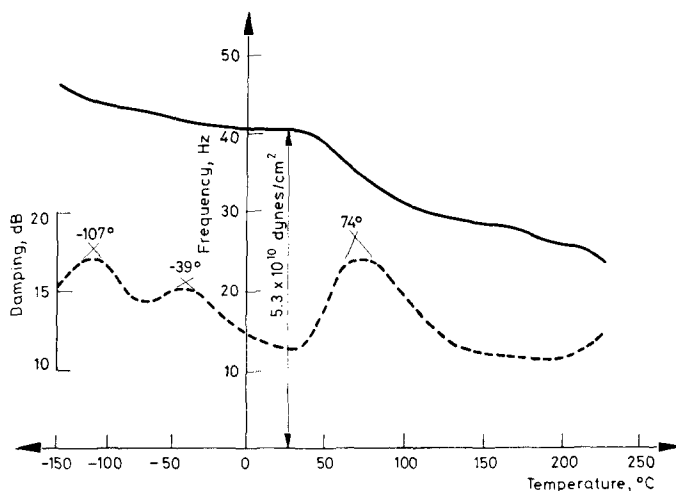


Fig. 7. DMA curve of 33% fiberglass reinforced nylon 66  
size:  $0.13 \times 1.55 \times 0.635$  cm, amp: 0.10 mm, prog:  $5^\circ/\text{min}$

These three major damping peaks are present in both the unreinforced and 33% glass reinforced nylon samples shown in Figs 6 and 7. Since any damping present is the result of energy dissipation by sample motion at that temperature, the damping display in the reinforced nylon sample should be entirely a function of the nylon present and not the glass reinforcing material which is transitionless (inert) at these temperatures. This is an important point, since samples of insufficient strength of their own, such as polymer films, can be evaluated by casting on a thin metal foil or other inert support. (This process is closely comparable to torsional braid analysis.)

Calculation of the modulus of the samples before and after the glass transition shows that the glass-reinforced nylon has twice the modulus before the glass transition, and five times the modulus after the glass transition, of the unreinforced nylon. The glass reinforcement of the nylon is therefore found to be effective in increasing the structural strength of the nylon, and the coupling agent being evaluated is satisfactory. A better indication of its commercial value can be obtained by comparison with other nylon-glass coupling agents.

### Thermosetting polymers

Thermosetting resins are a series of low molecular weight polymeric materials which can be cured, or hardened into a permanent shape. This curing is an irreversible chemical reaction involving crosslinking, and usually occurs on heating. For some thermosetting materials, however, curing is apparently initiated and completed at room temperature, but it is often the heat of reaction which actually cures the material. Commonly used thermosetting resins include alkyds, diallyl phthalates, polyesters and ureas. The following results relate to epoxy thermosetting resins which are characterized by the epoxide group. These are synthesized by reacting

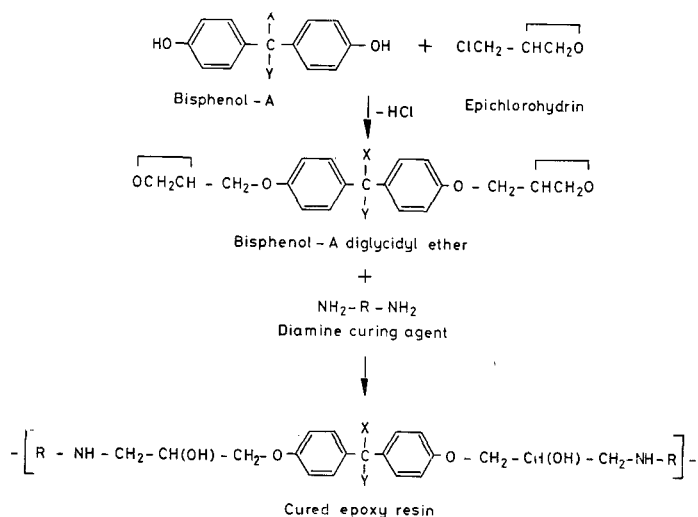


Fig. 8. Epoxy resin formation

epichlorohydrin with bisphenol *A* in the presence of an alkaline catalyst. By controlling the reaction conditions and varying the ratio of epichlorohydrin to bisphenol *A*, products of different molecular weight can be obtained (see Fig. 8). Epoxy resins are crosslinked using "active" or "passive" crosslinking agents during curing to yield their final desired rigid form. "Active" crosslinking agents serve as the actual crosslinks between chains in the final product, while "passive" agents serve only as catalysts for the crosslinking process. Useful epoxy crosslinking agents include amines, anhydrides, aldehyde condensation products, and Lewis acid catalysts. Careful selection of the proper curing agent is required to achieve a balance of the desired properties and initial handling characteristics. Epoxies cured with aromatic amines, for example, usually have a longer working life than do epoxies cured with aliphatic amines. On the other hand, aromatic amines usually



require an elevated temperature cure, and many of the aromatic amine curing agents are solids and must be melted into the epoxy, making them relatively difficult to use [7].

Dynamic mechanical analysis is a useful method for evaluating the mechanical properties of thermosets throughout the curing process. [14]. Figures 9 and 10 are DMA scans of an epichlorohydrin-bisphenol *A* epoxy resin cured using  $\text{BF}_3$ -

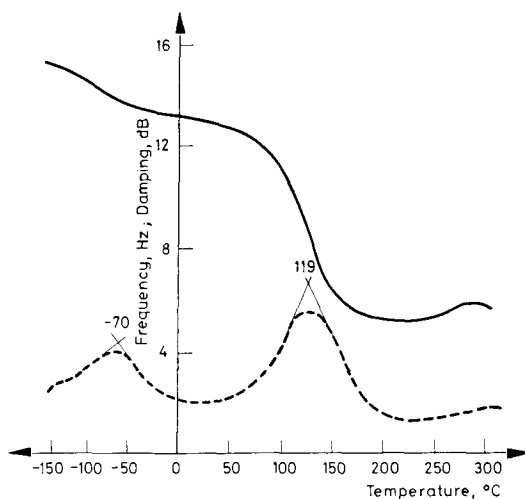


Fig. 9. DMA curve epoxy laminate  
size:  $45 \times 25 \text{ w} \times 720 \text{ mils}$ , prog:  $5^\circ/\text{min}$ , amp: 0.20 mm, mount: vertical, atm:  $\text{N}_2$

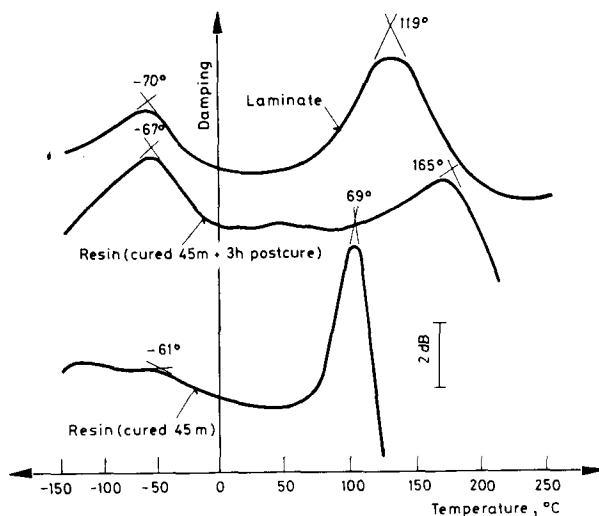


Fig. 10. Epoxy laminate cure. Comparative damping

ethylamine. This epoxy system has a high heat distortion temperature in the range 210–230°. This property, along with others such as excellent adhesion to both metallic and non-metallic surfaces, good electrical properties, dimensional stability, and good resistance to heat and chemical attack, makes it ideally suited for use in laminated printed circuit boards.

There are three basic regions of interest in the damping curve of the epoxy laminate shown in Fig. 9:  $-150^{\circ}$  to  $+20^{\circ}\text{C}$  where the modulus of the sample is slowly decreasing,  $20^{\circ}$  to  $210^{\circ}$  where the modulus undergoes a precipitous drop and then levels off, and  $210^{\circ}$  to  $330^{\circ}$  where the majority of glass-like structure is gone and the sample exhibits rubber-like properties. In the low temperature region, there is a single broad damping peak with a maximum at  $-70^{\circ}$ , which is the transition of the epoxy. It is thought that this peak is related to motion of the diglycidyl ether portion of the epoxy. Furthermore, it has been shown [8] that the area under the peak is proportional to the degree of cure. Hence, the relative size of this peak and its temperature maximum can be used to evaluate the degree of cure of the epoxy. Important to the eventual application of the final product is the fact that the presence and size of the peak appears to be related to the toughness of the epoxy, being present in the tougher diamine cured epoxies but absent in the more brittle anhydride cured epoxies [9]. The absence of an appreciable damping peak in the region  $-120^{\circ}$  to  $100^{\circ}$  indicates that this epoxy does not contain an aliphatic amine as its curing agent.

The other major damping peak (and associated large modulus change) at  $119^{\circ}$  represents the glass transition of the epoxy. This  $\alpha$  ( $T_g$ ) temperature is closely associated with the resin softening temperature of the epoxy. Not only is this  $T_g$  affected by the epoxy's degree of cure, but is also affected by substitution on the centre bridge methylene atoms of the bisphenol A [10]. The more steric hindrance exerted by the substituent groups, the higher is the  $T_g$ . This is obviously of interest in high temperature applications. The modulus of this laminate sample at room temperature is  $1.7 \times 10^{10}$  dynes  $\text{cm}^{-2}$ , which agrees well with literature values for similar systems [8, 10]. In laminates, the curing process has several stages. The first of these leads to a " $\beta$  stage" material which is flexible but still sufficiently hard to permit cutting, drilling, and similar processes, and it can be stored up to a year before further processing. In final preparation, several layers of these " $\beta$  stage" materials may be laminated together, sometimes with interspersed reinforcing fabric, and the cure completed to form the hard, durable final product. Therefore the ability to determine the degree of cure at these various stages of production is an important process control parameter. Thermal analysis techniques, such as differential scanning calorimetry (DSC) and thermomechanical analysis (TMA), have been widely used in this area. However, there are cases, particularly in laminates, where DMA because of its high sensitivity to minor transitions is more effective than DSC or TMA in evaluating degree of cure.

Figure 10 shows the comparative damping for the epoxy resin at various stages of cure, as well as that for the epoxy in its laminate end use. Both the glass transition ( $\alpha$  peak) maxima and the relative magnitude of the  $\beta$  damping peak indicate

that the postcure has a pronounced effect on the epoxy's properties, and that the laminate sample is intermediate in cure between the other two samples. With this laminate system neither DSC nor TMA were able to see the glass transition, and hence could not evaluate the degree of cure.

### *Amorphous metals*

In the last few years there have been rapid developments in the science of amorphous metals [11] (or metal glasses) and it now seems that there may be extensive commercial applications related to their unique mechanical, electrical and magnetic properties. Perhaps the most far-reaching application currently under investigation is their ability to provide an economic method for converting sunlight or waste heat into electrical energy [12].

Metal glasses have a random or non-crystalline structure in the solid phase, similar to that of a glass and unlike that of a conventional metal. They are currently produced by spraying a molten alloy onto a cooled, rapidly rotating copper drum so that the metal is quenched extremely rapidly, (at about one million degrees per second) and the random atomic structure of the liquid state is retained in the solid at ordinary temperatures. The grain boundaries found in normal crystalline metals are absent in metal glasses which means that the amorphous materials are frequently less subject to chemical attack or corrosion than the crystalline materials. Furthermore, unlike conventional glasses, metal glasses are not brittle and may be used in applications where impact resistance and mechanical strength are important.

It has been found that many metal glasses have a general chemical formula approximating to  $M_{80}X_{20}$  where  $M$  may be any one or more of the elements from

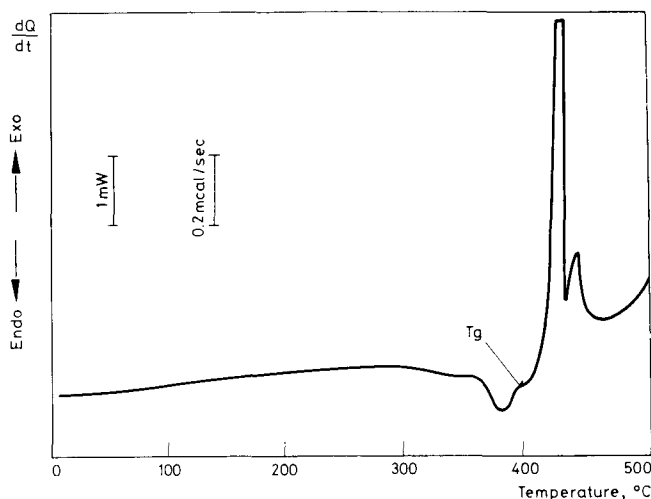


Fig. 11. DSC curve of Pb-Cu-Si metal glass  
size: 20 mg, prog: 20°/min, atm: N<sub>2</sub>

the group Fe, Ni, Cr, Co, Pd, and Cu, and  $X$  may be one or more from the group P, B, C, Al, and Si. Common formulations combine Fe Ni Co B and also Pd Cu Si, but many other elements may also be included in the alloy composition, such as Ti, Zr and Mo. It is the ability to "chemically modify" the composition of the metal glasses to optimise specific properties that make this class of material subject to so much research work. The amorphous materials currently being considered for

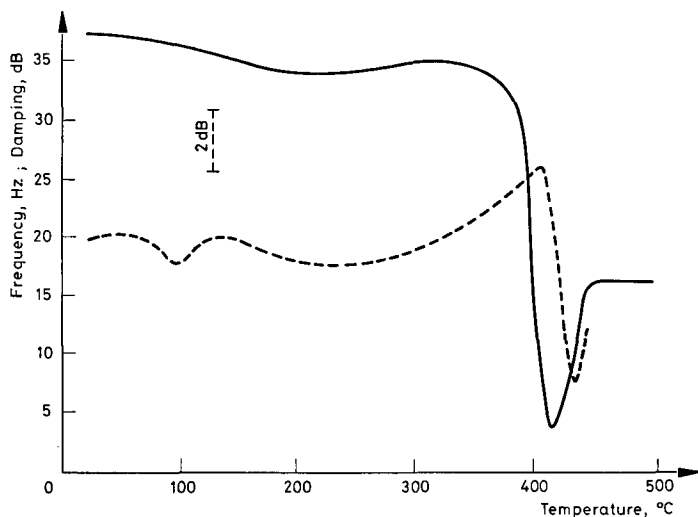


Fig. 12. DMA curves of Pb-Cu-Si metal glass  
size:  $0.06 \times 3 \times 7$  mm, prog:  $20^\circ/\text{min}$ , amp: 0.2 mm

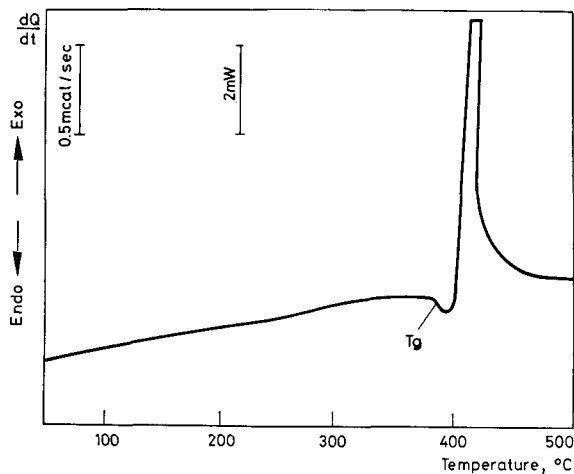


Fig. 13. DSC curve of Ni based metal glass  
size: 20 mg, prog:  $20^\circ/\text{min}$ , atm:  $N_2$

solar energy applications are based largely on silicon, but potential applications for other metal glasses include use as reinforcement elements in polymers and elastomers, corrosion resistant cables, magnetic shields and transformer cores.

Like common glasses, metal glasses show glass transitions at elevated temperatures. However, devitrification (crystallization) occurs very quickly after the  $T_g$  is passed. A DSC run on a fairly typical Pd-Cu-Si metal glass is shown in Fig. 11. The devitrification exotherm at about  $450^\circ$  is characteristically sharp. (The two peaks are thought to be due to two phases devitrifying separately – for a single

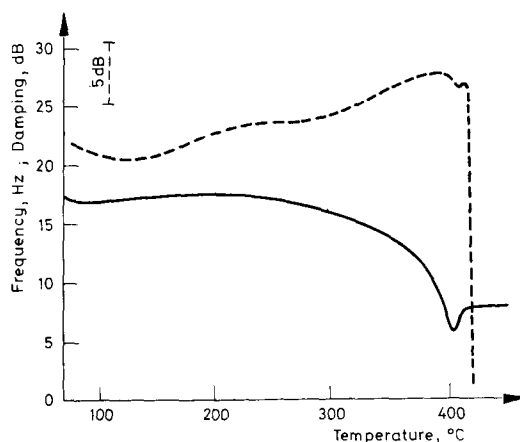


Fig. 14. DMA curve of Ni based metal glass  
size:  $0.06 \times 3 \times 7$  mm, prog:  $20^\circ/\text{min}$ , amp: 0.2 mm

phase metal glass the devitrification exotherm is usually a single sharp peak.) The DSC run shows a step in the baseline at  $370^\circ$  which in normal glasses would correspond to the glass transition. However, the result of the analysis of the same metal glass using the 980 Dynamic Mechanical Analyser (Fig. 12) shows quite clearly the true temperature of the glass transition. The centre of the damping peak occurs just below  $400^\circ$  and corresponds to the small deflection in the baseline in the DSC run at the same temperature. The DMA results also show that this particular metal glass has no marked deterioration in its mechanical strength up to a temperature of around  $350^\circ$ . The rise in frequency between  $420^\circ$  and  $440^\circ$  corresponds to the process of devitrification and consequent strengthening of the material as the structure becomes more crystalline. Above  $440^\circ$  the modulus is invariant with temperature.

Figures 13 and 14 are the DSC and DMA results for a metal glass with the approximate formula  $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ . Here, the DMA results show that the actual glass transition does correspond to the baseline step on the DSC run, but in this case the process occurs slowly and the metal glass steadily loses its mechanical strength as the temperature rises above  $250^\circ$ . These results show that a DMA run

on metal glass can give the glass transition temperature, the devitrification temperature and the useful mechanical working range of the material. DSC can give the heat and temperature of devitrification but is sometimes unable to give a definite glass transition temperature. It may be anticipated that dynamic mechanical analysis will be used increasingly to study amorphous inorganic materials as their application becomes more widespread.

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RÉSUMÉ — L'application du nouvel analyseur mécanique 980 à l'étude des polymères thermoplastiques, des polymères thermodurcissables et des verres métalliques est discutée. L'instrument a également été utilisé pour l'étude des thermoplastiques traités par percussion [2], des élastomères [3] et des métaux. L'analyse mécanique dynamique est l'une des techniques d'analyse thermique les plus utiles pour évaluer les propriétés mécaniques des matériaux, aussi bien en recherche que pour les opérations de contrôle de qualité. Avec l'introduction du modèle 980, il est prévisible que les inconvénients des instruments précédents, dus à la durée et à la complexité des opérations, n'entraveront pas le développement de cette technique.

ZUSAMMENFASSUNG — Der Einsatz des neuen 980 Dynamic Mechanical Analysers zur Untersuchung thermoplastischer und auf Hitzeinwirkung fest werdender Polymere, sowie Metallgläser, wird in dieser Veröffentlichung beschrieben. Dieses Instrument wurde auch zur Untersuchung von durch Stoss modifizierten thermoplastischen Stoffen [2], Elastomeren [3] und Metallen verwendet. Die dynamische mechanische Analyse ist eine der für den Forschungs- oder Kontrollchemiker bei der Bewertung der mechanischen Eigenschaften der Stoffe nützlichsten zur Verfügung stehenden thermoanalytischen Techniken. Die Einführung des Modells 980 gestattet die Folgerung, daß die bei den früheren Instrumenten als Nachteil verzeichnete lange Arbeitsdauer und Komplexität nunmehr dem Fortschritt in Richtung vollständiger Realisierung dieser Technik nicht mehr im Wege stehen werden.

Резюме — В статье обсуждено применение нового 980 динамического механического анализатора для изучения термопластичных полимеров, термореактивных полимеров и металлических стекол. Этот прибор был также использован для изучения термопластиков, эластомеров и металлов, модифицированных посредством ударного воздействия. Динамический механический анализатор является одним из самых широко используемых химиком термоаналитических методов, доступных для исследования количественного контроля при оценке механических свойств материалов. С введением 980 ожидается, что недостатки, обусловленные длительностью временем эксперимента и сложностью, присущие более старым инструментам, не будут больше сдерживать прогресс полного внедрения этой техники.