

**COMPLEX MODULUS MEASUREMENTS OVER  
A WIDE RANGE OF FREQUENCIES AND  
MATERIAL CHARACTERISTICS THROUGH  
THE CONFRONTATION OF TWO INSTRUMENTS**

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**ABSTRACT**

Two instruments are used to measure the viscoelastic properties of polymers. The instruments are presented and three different applications are shown. The measurement of the magnitude modulus and damping characteristics of a damping material is used to illustrate the compatibility of both instruments. The curing of two different materials is shown. In particular, the information contained in viscoelastic measurements proves to be quite helpful in following the evolution of the polymer structure throughout the process. Mechanical spectrometry of two homopolymers and a blend further exemplifies this concept.

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**INTRODUCTION**

A number of techniques are commonly used to obtain viscoelastic material data. Methods such as the vibrating beam where material characteristics are deduced from the dynamics of simple systems can be referred to as indirect while methods where a force is directly applied to a material sample and the resulting displacement measured fall under the direct category. This paper will concentrate on two direct measurement instruments : the VISCOANALYSER and the MICROMECHANALYSER from METRAVIB INSTRUMENTS.

Modern design techniques for sophisticated technical products require accurate, consistent data for a variety of materials and configurations. It is also very important to manufacturers of finished products to have a data base over a given temperature and frequency range for many materials in order to compare them from one supplier to the next. In many instances, material makers themselves need good data as they have a difficult time reproducing mechanical and damping characteristics with sufficient precision from batch to batch. Variations of to 25 % are not uncommon in natural and synthetic rubbers. Furthermore, scientific research calls for precise phase angle data since it is becoming a popular tool to understand the physics and micromechanics of molecular structure.

A problem is indeed that various instruments using different operating principles usually yield slight discrepancies in measured data. This can be for several reasons.

- i) The mode of strain can differ. For example, the use of 3 point bending to measure Young's modulus can induce errors due to the variable shear component of strain which appears in such a configuration.
- ii) Different techniques for holding the sample. Various mechanical stresses due to sample holding (clamped, simply supported ...) can perturb measurements. Adhesive bonding is mechanically clean but is problematic with porous materials, extreme temperatures and certain polymers for which glueing is excessively difficult.

- iii) Inertial effects can, for certain high frequency measurements, yield polluted data (for instance 3-point bending in the case of solids and annular pumping in the case of liquids). The importance of the inertial term can easily be evaluated but it is nonetheless a limitation to be reckoned with.
- iv) Another reason comes the design of any instrument. They are almost all designed with a specific application in mind. This gives the instrument a design philosophy making it more suited to particular materials or stiffness and temperature ranges. Of course, the quality of data usually increases as the instrument's optimal domain is reached. For example, the Viscoanalyser was designed to measure the glass transition of most solid polymers while the Micromecanalyser was conceived with mechanical spectrometry in mind.

Ideally, all techniques should yield the same result, and when they do the benefit is great due to the number of applications. Damping predictions, design of load bearing structures and scientific research have been mentioned. Process control, the study of curing and data bases for computer F.E.M. codes can be added to this non exhaustive list.

The purpose of this paper is to show how, when two instruments are compatible and complementary, the domain of validity of measurements and the confidence level in the results are increased. The two instruments must show consistant data when measuring the same material under similar conditions while having distinct preferred applications.

### THE VISCOANALYSER

This instrument measures the force and the displacement acting on a sample submitted to an oscillatory regime. The schematic diagram of figure 1 illustrates the basic mechanics of the instrument. From the sample outward this diagram runs as follows. The sample is placed on a rigid column, incorporating a force transducer, which links it to a fixed, solid, metallic base. The sample is surrounded by a furnace, capable of temperatures of up to 350°C using electric heating elements, and of temperatures as low as -100°C obtained by liquid nitrogen cooling. The upper part of the sample is attached to an electrodynamic shaker via a rigid column similar to the lower one. The shaker is fastened to an upper chassis. The displacement and acceleration of the upper column are recorded by two transducers.

The height of the upper chassis can be adjusted, as well as the pre-strain on the specimen.

Many sample holders exist : tension compression, shear, 3 point bending, annular shear and annular pumping. These allow the measurement of characteristics of materials ranging from oils to rigid reinforced polymers.

The general characteristic of the instrument are the following :

- Frequency : 5 Hz - 1000 Hz
- Displacement : 0.1  $\mu\text{m}$  - 500  $\mu\text{m}$  (option 3000  $\mu\text{m}$ )
- Strain :  $10^{-4}$  -  $10^{-1}$
- Force : 0.1 N to 100 N (option 150 N)
- Temperature : 200 K - 600 K
- Loss angle :  $0.5^\circ$  -  $90^\circ$

### THE MICROMECHANALYSER

This inverted torsion pendulum operates under forced oscillations. The oscillations are created by a sinusoidal electromagnetic force obtained by running an A.C. current through Helmholtz coils (figure 2). The angular displacement is measured using an optical sensor to detect a light beam reflected off a mirror placed on the sample holder connection rod. The sample can be placed in a sealed compartment filled with air or an inert gas.

This instrument allows creep with D.C. current through the coils. Its extreme sensitivity in phase angle makes it ideal for mechanical spectrometry. Indeed, the apparatus can measure phase angles as small as  $0.03^\circ$  and theoretically as large as  $90^\circ$ , though no solid is entirely viscous. More generally, the characteristics are :

- Frequency :  $10^{-5}$  Hz - 5 Hz
- Angular displacement :  $0^\circ$  -  $0.5^\circ$  (option  $10^\circ$  in creep)
- Strain :  $10^{-6}$  -  $10^{-3}$
- Torque :  $2 \cdot 10^{-7}$  Nm -  $1.5 \cdot 10^{-2}$  Nm
- Temperature : 100 K - 670 K
- Loss angle :  $0.03^\circ$  -  $90^\circ$

In practice, the  $10^{-5}$  Hz range is seldom used. The principal advantage of this feature is to aid in the separation of relaxation peaks in very temperature-sensitive materials. An application of this is with polymer alloys.

### DYNAMIC STIFFNESS, MODULUS AND VISCOSITY

It is common when dealing with harmonic systems to represent physical concepts such as stiffness, modulus or viscosity in the complex plane.

A viscoelastic sample has a dynamic stiffness  $K^*$  defined by its response to sinusoidal sollicitation :

$$K^* = \frac{F^*}{U^*} \quad (1)$$

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where  $F^*$  is the forcing function :

$$F^* = F_0 \exp i(\omega t + \delta) \quad (2)$$

and  $U^*$  the harmonic displacement :

$$U^* = U_0 \exp i\omega t \quad (3)$$

The phase shift,  $\delta$ , is linked to the vibration damping characteristics of the material and its tangent,  $\tan \delta$ , is often called the loss factor.

From equations (1) to (3), the stiffness  $K^*$  becomes :

$$K^* = (F_0 / U_0) \exp i\delta$$

The real and imaginary parts of  $K^*$ ,  $K'$  and  $K''$  respectively, are thus given by :

$$\begin{aligned} K' &= F_0 / U_0 \cos \delta \\ K'' &= F_0 / U_0 \sin \delta \end{aligned}$$

The Viscoanalyser yields directly  $F_0 / U_0$  and  $\delta$ .

The same equations can be written in torsion where force is replaced by torque and displacement by angular displacement.

The instrument's software then proceeds to calculate the modulus of the material, which is an intrinsic value, and ideally should not depend on the type of apparatus employed. In this respect, the general equation (4) is used :

$$M^* = K^* \frac{e}{S_e} F_s \quad (4)$$

where  $M^*$  is the complex modulus, for example  $M^* = E^*$  (Young's modulus) in tension and  $M^* = G^*$  (shear modulus) in shear,  $S_e$  is the excited surface,  $e$  is the distance between sollicitation surfaces and  $F_s$  is the shape factor.

The shape factor is the biggest source of incertainly when trying to determine the modulus of a material, especially in the case of fibrous or anisotropic materials. It is also a problem in the case of shear-rate dependent viscosity liquids. In general, however the shape factor can be chosen close to unity (tall and slender in tension-compression, short and fat in shear) to minimize error.

In the complex plane, harmonic displacement ( $U^*$ ) is proportional to harmonic velocity ( $V^*$ ) :

$$V^* = i\omega U^*$$

The complex shear modulus is therefore related to complex viscosity ( $\eta^*$ ) by:

$$G^* = i\omega \eta^* \quad (5)$$

They represent the same intrinsic quantity in the overall description of a material.

There is a difference however, in the sense that the usual terminology differs according to whether the material flows under constant stress or not.

Viscoelastic materials can of course be either clearly solid or clearly liquid, but they can also be somewhere in between. The shear modulus applies to mostly solid-like materials while the viscosity applies to mostly liquid-like materials. Materials can change in a continuous fashion from liquid to solid. This is typically a curing process.

### MECHANICAL PROPERTIES OF USUAL MATERIALS

Figure 3 shows usual materials in relation to each other with respect to their mechanical characteristics. The vertical direction reflects intrinsic dynamic stiffness while the horizontal axis represents damping.

The numbers shown on the modulus, viscosity and loss factor scales are indicative "ball-park" figures and should not be considered otherwise.

On the figure, the domain of validity of both the Micromecanalyser and Viscoanalyser appears.

One notices that the Viscoanalyser is more suited to the softer, higher loss materials while the Micromecanalyser is best for high modulus materials.

For example :

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Metals and composites are typically materials which can be measured most accurately with the Micromecanalyser while oil, tar, pastes and gels are reserved for the Viscoanalyser.

Both instruments have a wide overlapping range in which most polymers including vibration damping materials can be found.

Curing which can be studied using both instruments is, mechanically, the evolution from a viscous liquid-like substance to a complete solid.

The specific qualities required of the instrumentation here is the capacity to measure properties over a wide range without changing sample holders.

It can be noted that most materials are covered by the measurement ranges of these instruments. In fact, one is hard put to think of a material of very low modulus and very low loss factor ! As it is seen from the graph, the materials are all along a diagonal going from high loss or viscous liquids to elastic solids.

#### DAMPING MATERIAL CHARACTERIZATION

Two master curves are shown.

The material is GE. SMRD. The measurements were made at METRAVIB but the data were compiled and exploited by Dr. Lynn ROGERS.

Figure 4 was obtained with Viscoanalyser while figure 5 was derived from Micromecanalyser data.

The Viscoanalyser's measurement parameters were :

Frequency : 5 Hz → 500 Hz  
Temperature : -10°C → + 60°C

In the case of the Micromecanalyser, these were :

Frequency : 0.0078 Hz → 1 Hz  
Temperature : 0°C → + 50°C

The two graphs have different scaling factors, but overall, if one looks at the actual numbers, the two curves are consistant.

For example :

Consider the values of the real modulus and loss factor at the glass transition peaks in table 1.

	Elastic shear Modulus G' (MPa)	Loss factor
Micromecanalyser	28.80	1.01
Viscoanalyser	31.20	.866
Δ %	+ 8.3%	- 14.2%

In view of the fact these measurements were obtained using two instruments with different techniques (plane shear versus torsion), these are quite acceptable. In fact this is confirmed by the loss factor versus magnitude modulus plots of figures 6 and 7 for the Viscoanalyser and Micromecanalyser respectively. The two plots superpose quite neatly.

### POLYMER CURING

Figures 8 and 9 show the curing kinetics of two polymers.

Figure 8 shows the constant temperature (160°C) cure of a two component adhesive. The test was performed with a Viscoanalyser using an annular pumping sample holder.

The various stages are as follows :

- 1) In the first few minutes of cure, the resin - a polymeric liquid at first - fluidifies under the effect of temperature and the stiffness decreases.
- 2) As the chemical reaction progresses the molecular chains grow to form ramifications and finally a complete network. During this time, the stiffness increases while the loss factor at first decreases then increases to a maximum. This maximum defines the gelation time (here 16 mins). This peak is accompanied by a change in slope in the stiffness ( $\log(K)$ ) curve and is a result of the competition between the rates of increase of viscosity  $K''$  and elasticity  $K'$ . Indeed, a various times during the gelation process, the increase in total stiffness ( $K$ ) is at times mostly due to an increase in elasticity, and at other times mostly due to an increase in viscosity.
- 3) After about 40 minutes, the material is fully cured. The curing temperature here was above the glass transition temperature of the finished product; the chemical structure is therefore stable.

In figure 9 the curing spectrum is that of a braid impregnated with resin. The study was done with the Micromecanalyser. Here, the material was slowly heated from 100 K to 500 K.

From 100 K to 250 K, the material is literally frozen. The loss factor spectrum shows two minor relaxations associated with the uncured epoxy components.

Above 250 K thaw takes place. The resin fluidifies, the loss factor tends to infinity (loss angle = 90°) and the stiffness decreases to reveal the stiffness of the glass fiber braid. Around 400 K, gelation starts to take place followed by vitrification (around 420 K). The glassy polymer then reaches its glass transition temperature (460 K) and the classical glass transition peak and drop in modulus is observed.



**MECHANICAL SPECTROMETRY**

Figures 10 and 11 show the micromechanical property-temperature spectra of BuA (Butyl Acrylate) and VAc (Vinyl Acetate) homopolymers.

Three frequencies (0.01, 0.1 and 1 Hz) are represented. Four sets of curves labeled a, b, c and d are shown.

Set a :  $\log (G'/G_0)$  (with  $G_0 = 1.5 \cdot 10^9 \text{ N/m}^2$ ) as a function of temperature for pure poly (BuA)

Set b :  $\log (\tan \delta)$  (loss factor) for pure poly (BuA) as a function of temperature

Set c :  $\log (G'/g_0)$  (with  $G_0 = 1.5 \cdot 10^9 \text{ N/m}^2$ ) as a function of temperature for pure poly (VAc)

Set d :  $\log (\tan \delta)$  (loss factor) for pure poly (VAc) as a function of temperature

What is clear here is that the two polymers have radically different spectra. The loss factor curves reveal not only that the two have different transition temperatures but that the BuA peak is much smaller than the VAc. The drop in modulus is 3.5 decades in both cases.

The micromechanical spectrum of the blend of the previous homopolymers is shown figure 12. The blend was obtained using equal masses of both BuA and VAc coalesced at room temperature.

The graph indicates that the loss factor peak of ABu (first transition) is much smaller than appeared before (10 time smaller) while the VAc peak suffers only a slight drop (25 %). The same is true of the drop in modulus. The first drop is much smaller than the second drop (VAc).

However both peaks are very clearly apparent which shows that micromechanical spectrometry holds a trace of the structure of the material, and the various polymers in the blend can be readily identified.

**CONCLUSION**

Two principal uses of dynamic mechanical measurement are illustrated through two different instruments.

- 1 - Obtention of viscoelastic data
- 2 - Determination of structural properties

When used in a complementary fashion, each instrument allows the extension of the other's measurement capacity.

For example :

- 1) They combine to cover 8 decades in frequency ( $10^{-5}$  Hz to  $10^3$  Hz)
- 2) They can measure practically all materials known.

The instruments are consistent and both can be used for scientific research, quality control and design.

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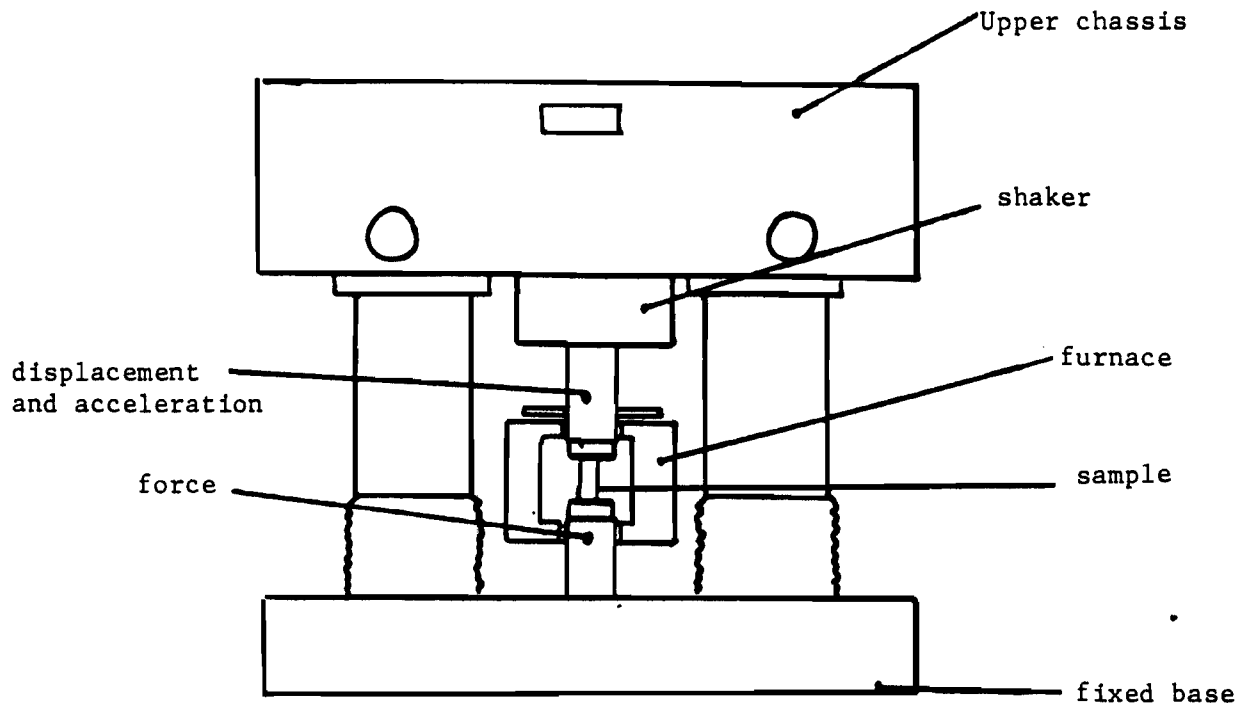


Figure 1 : VISCOANALYSER

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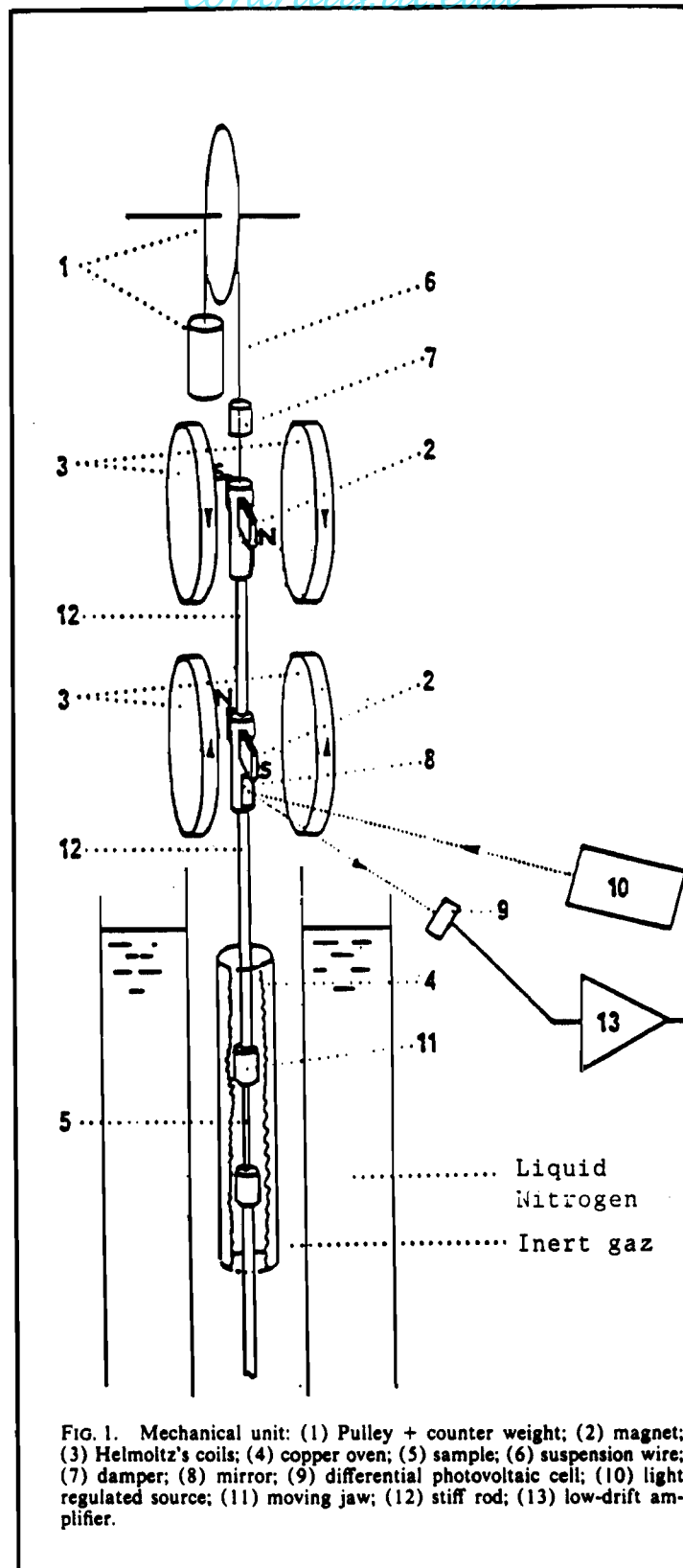
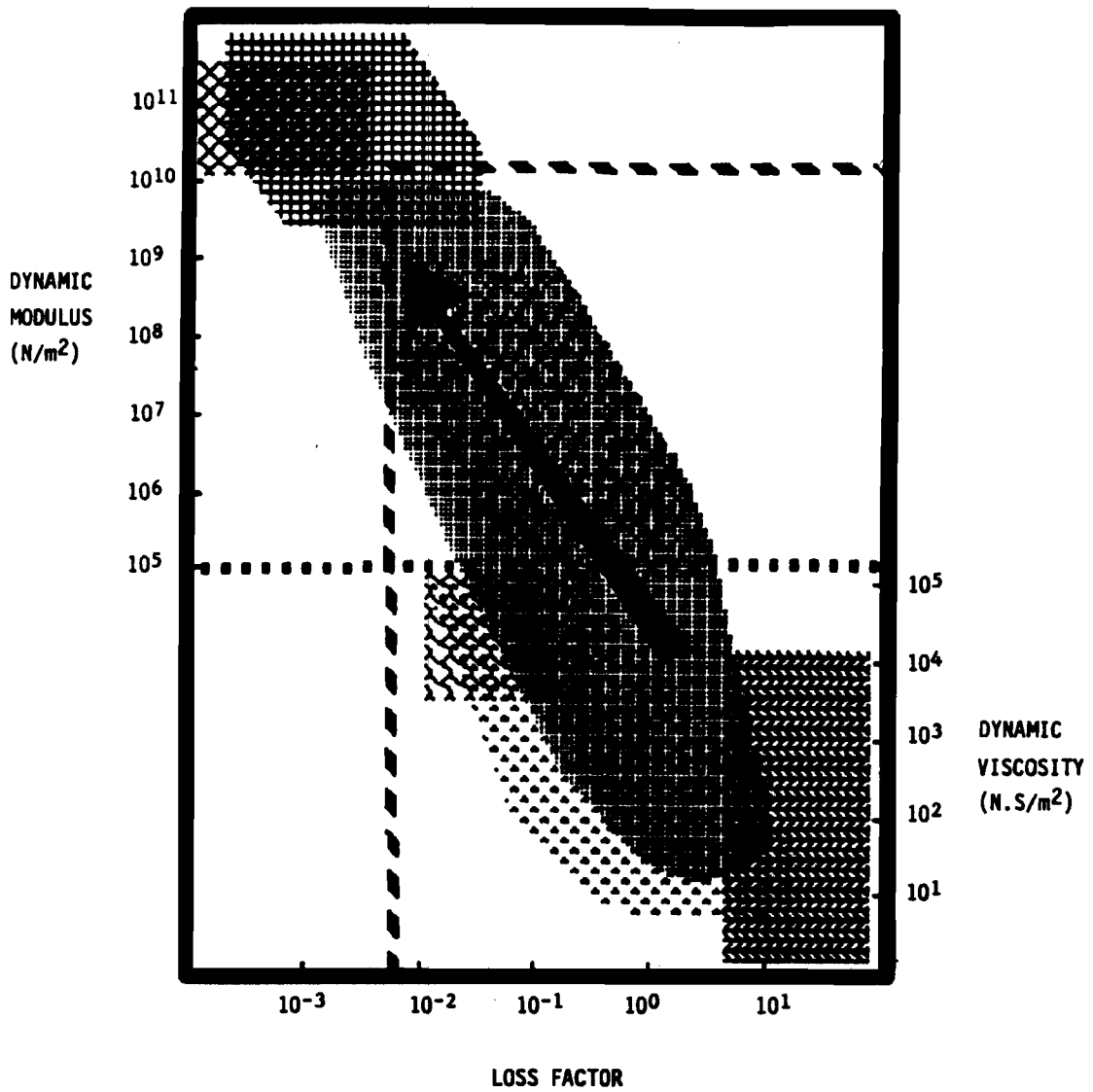


Figure 2 : MICROMECHANALYSER

### MECHANICAL PROPERTIES OF USUAL MATERIALS













-  METALS
-  OILS
-  GELS (FOOD INDUSTRY)
-  POLYMERS
-  COMPOSITES
-  TARS & BITUMINOUS MATERIALS
-  RUBBERS AND USUAL DAMPING MATERIALS
-  POLYMER CURING
-  VISCOANALYSER MEASUREMENT LIMIT
-  MICROMECHANALYSER MEASUREMENT LIMIT

Figure 3

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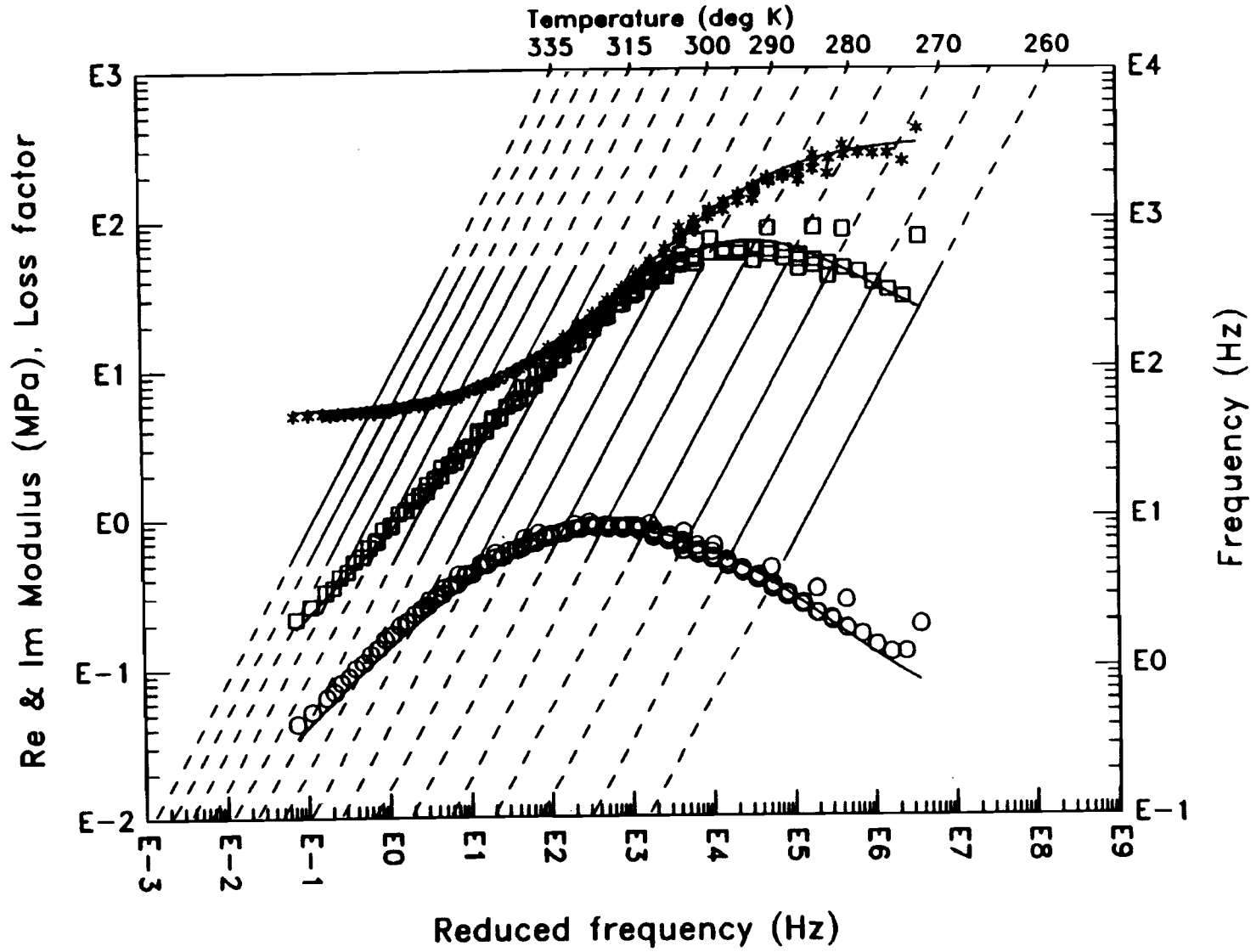


Figure 4 : GE SMRD Master curve  
obtained using the VISCOANALYSER

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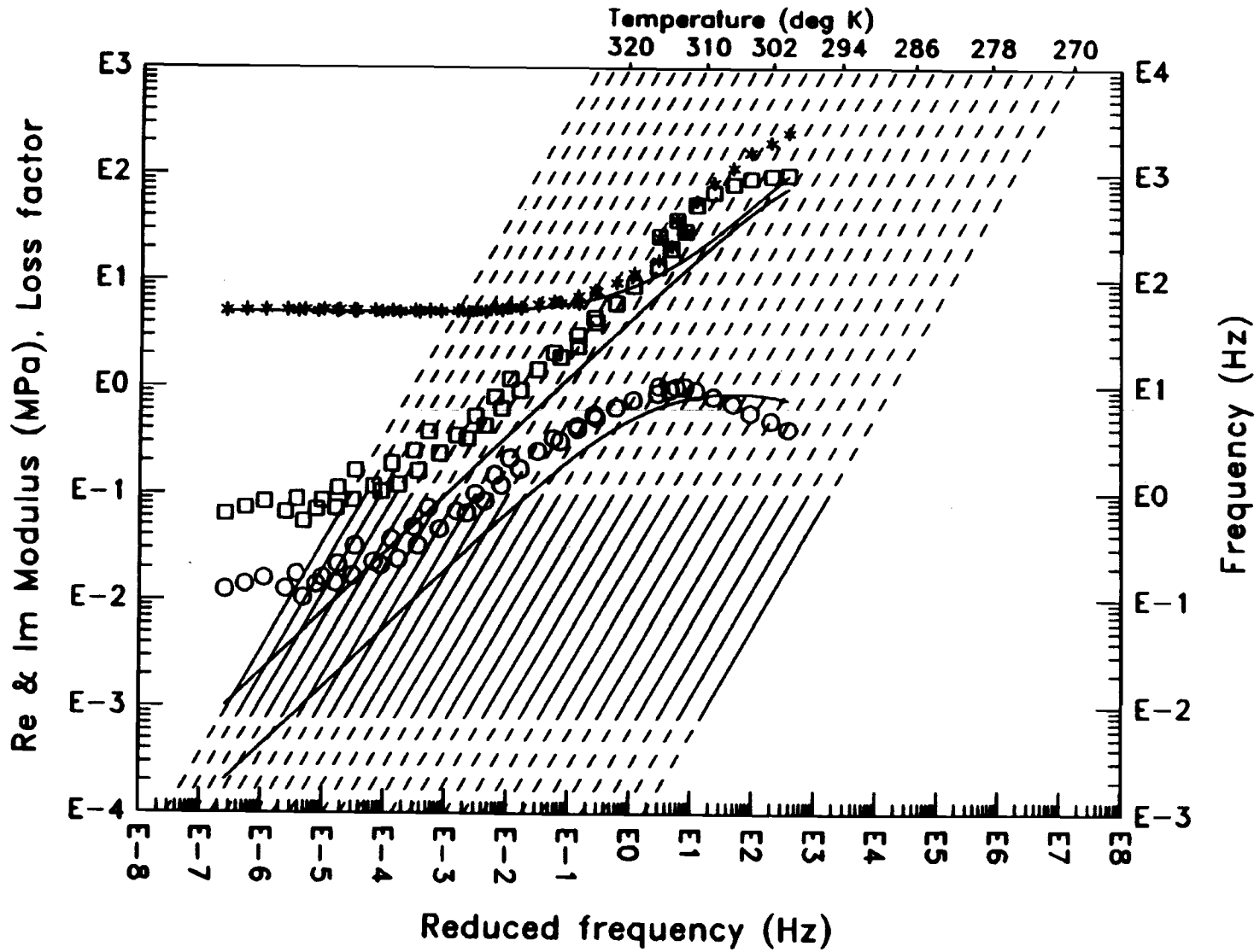


Figure 5 : GE SMRD - Master curve obtained using the MICROMECHANALYSER

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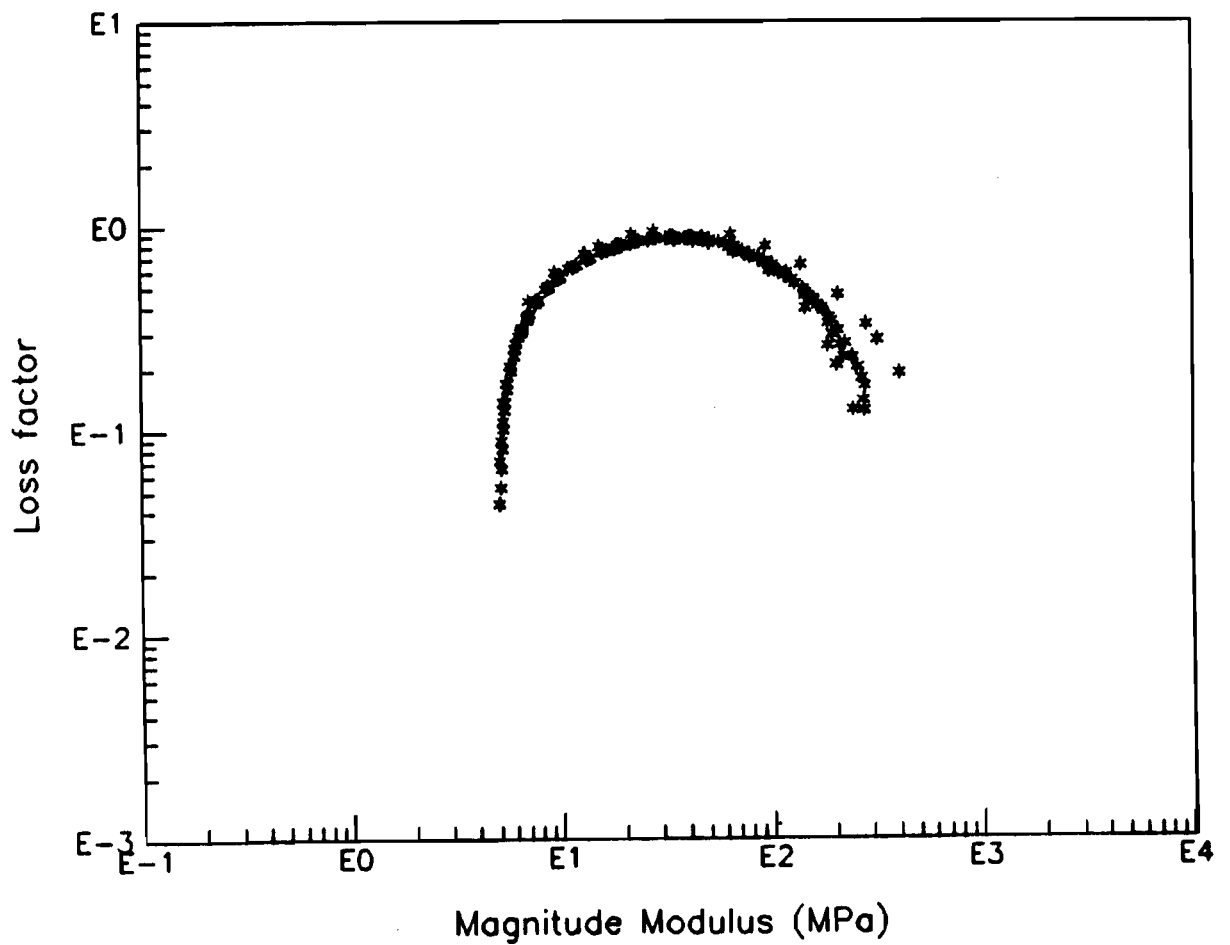


Figure 6 : Loss factor v/s modulus for GE SMRD  
obtained using the VISCOANALYSER

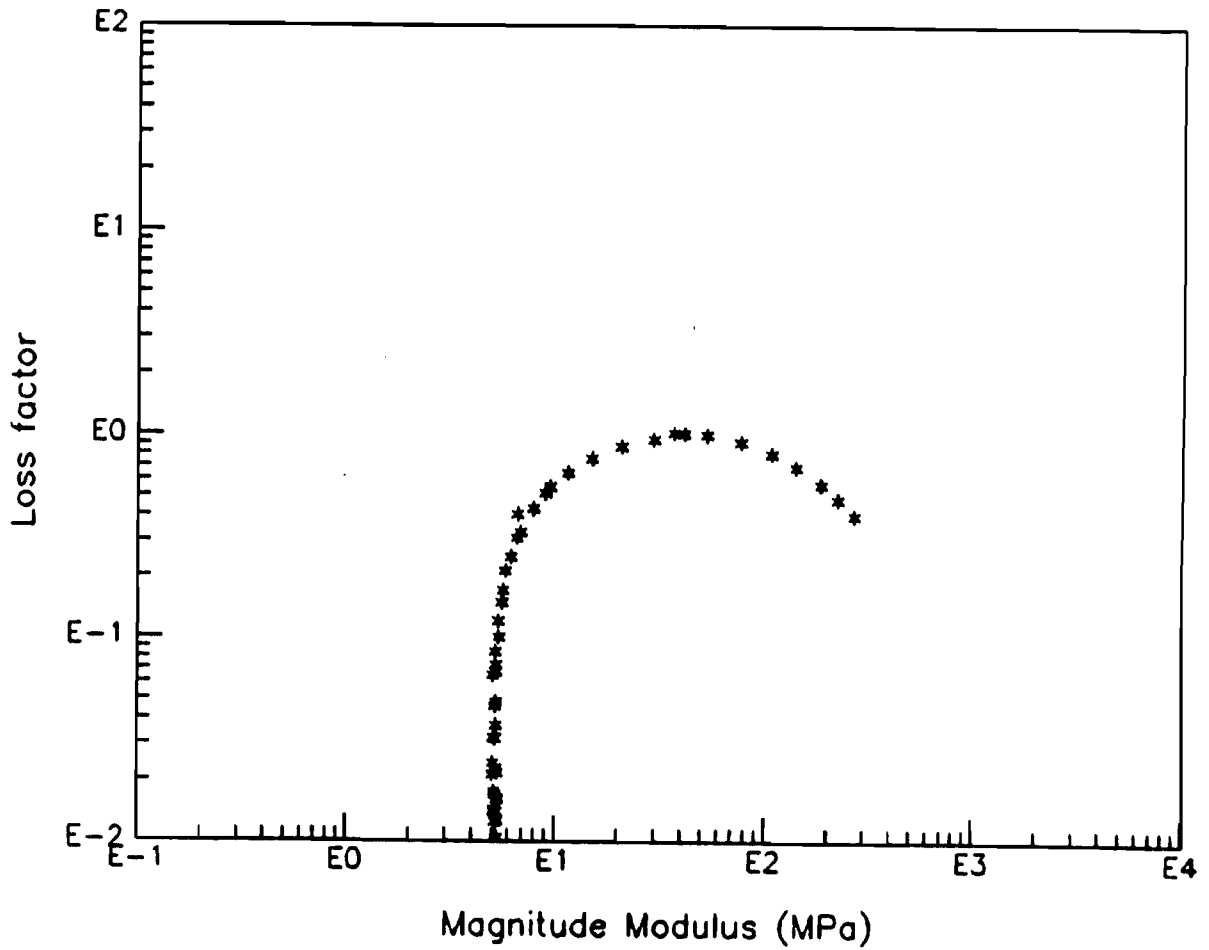


Figure 7 : Loss factor v/s modulus for GE SMRD  
 obtained using the MICROMECHANALYSER

### CURING OF AN ADHESIVE

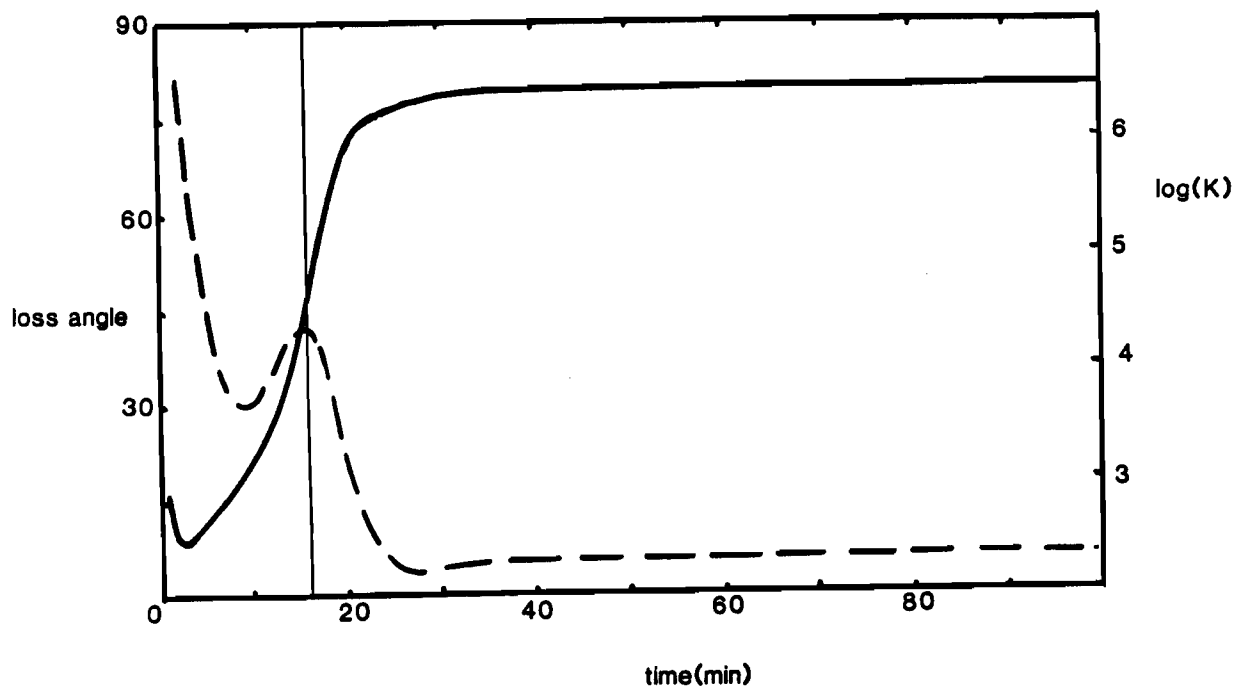


Figure 8

**TORSION HEATING SPECTRUM**

**GLASS FIBER IMPREGNATED WITH EPOXY RESIN**

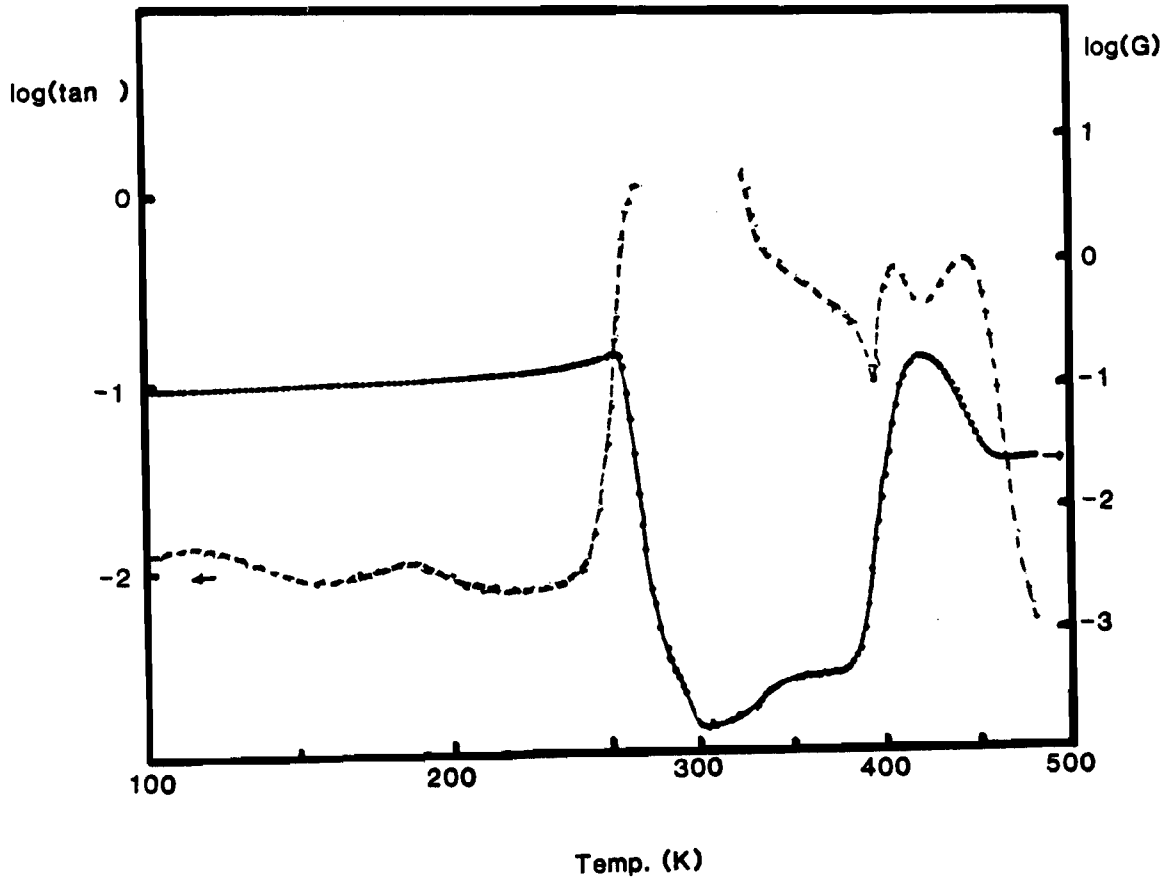


Figure 9

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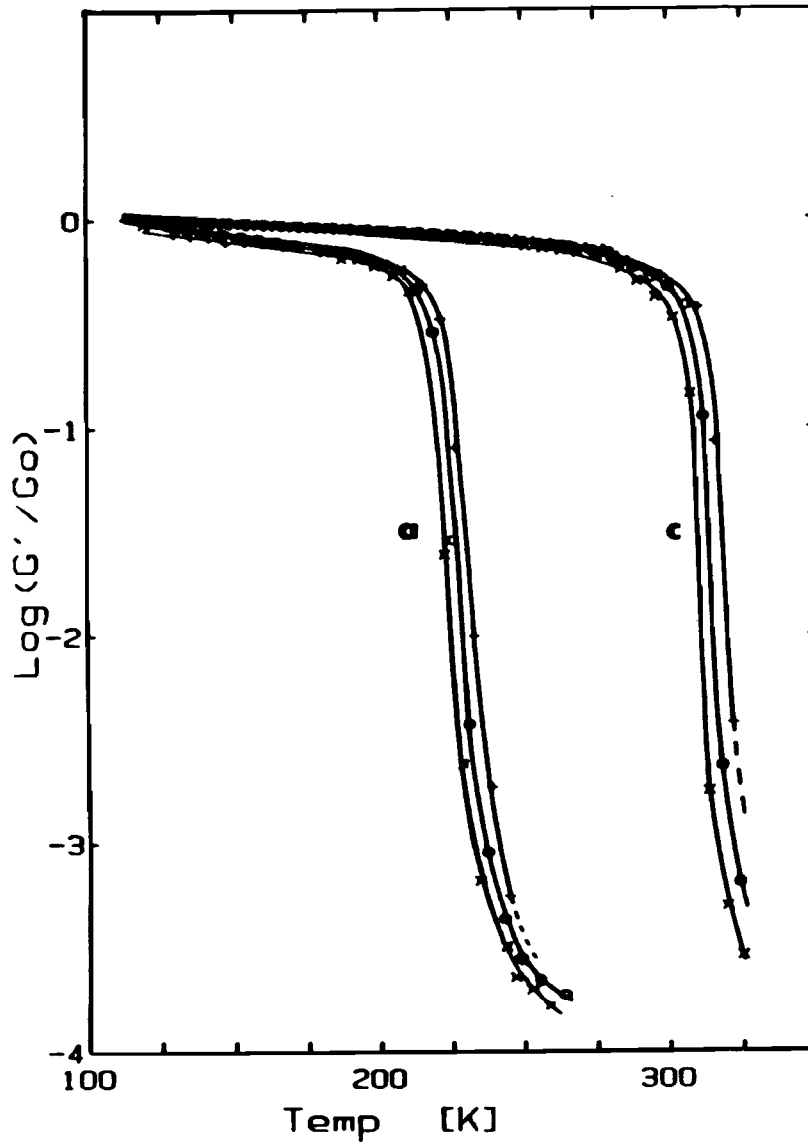


Figure 10 : Micromechanical  $G'$  - temperature spectra ( $G_0 = 1.5 \cdot 10^9$  Pa)  
 a) poly (BuA)      c) poly (VAc)

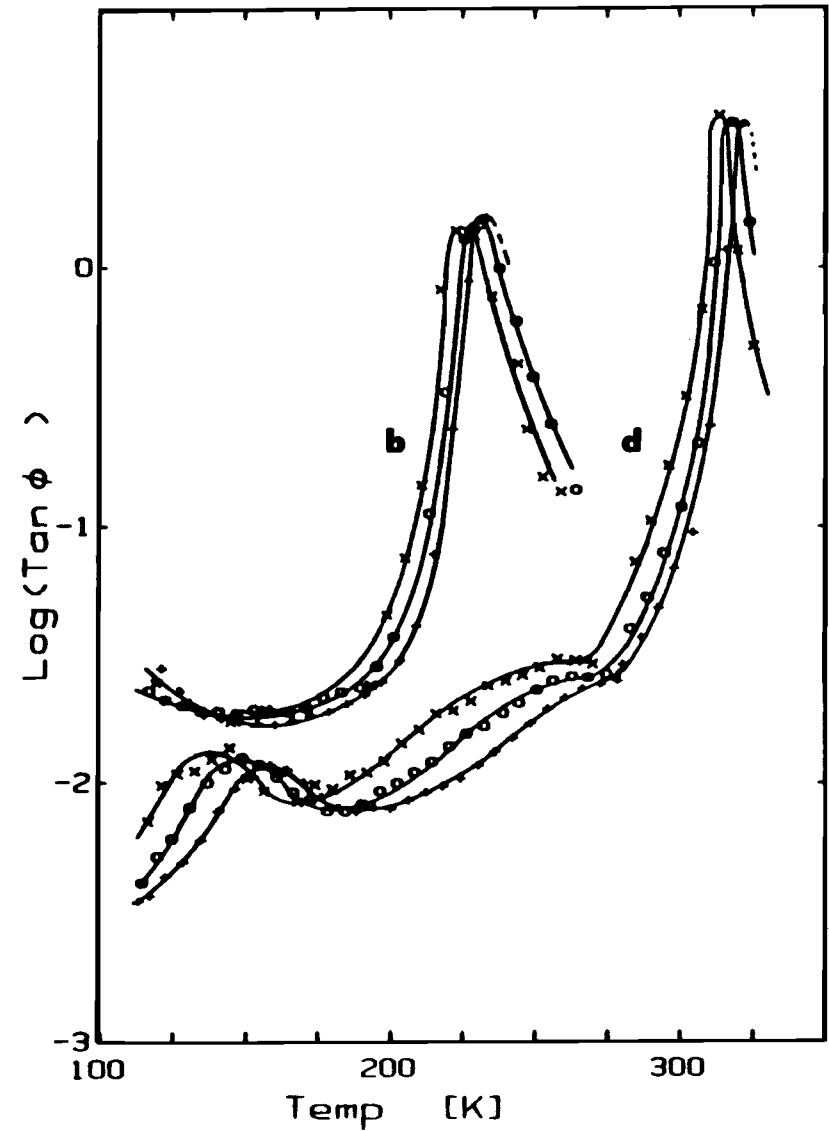


Figure 11 : Micromechanical  $\tan \delta$  - temperature spectra  
 b) poly (BuA)      d) poly (VAc)

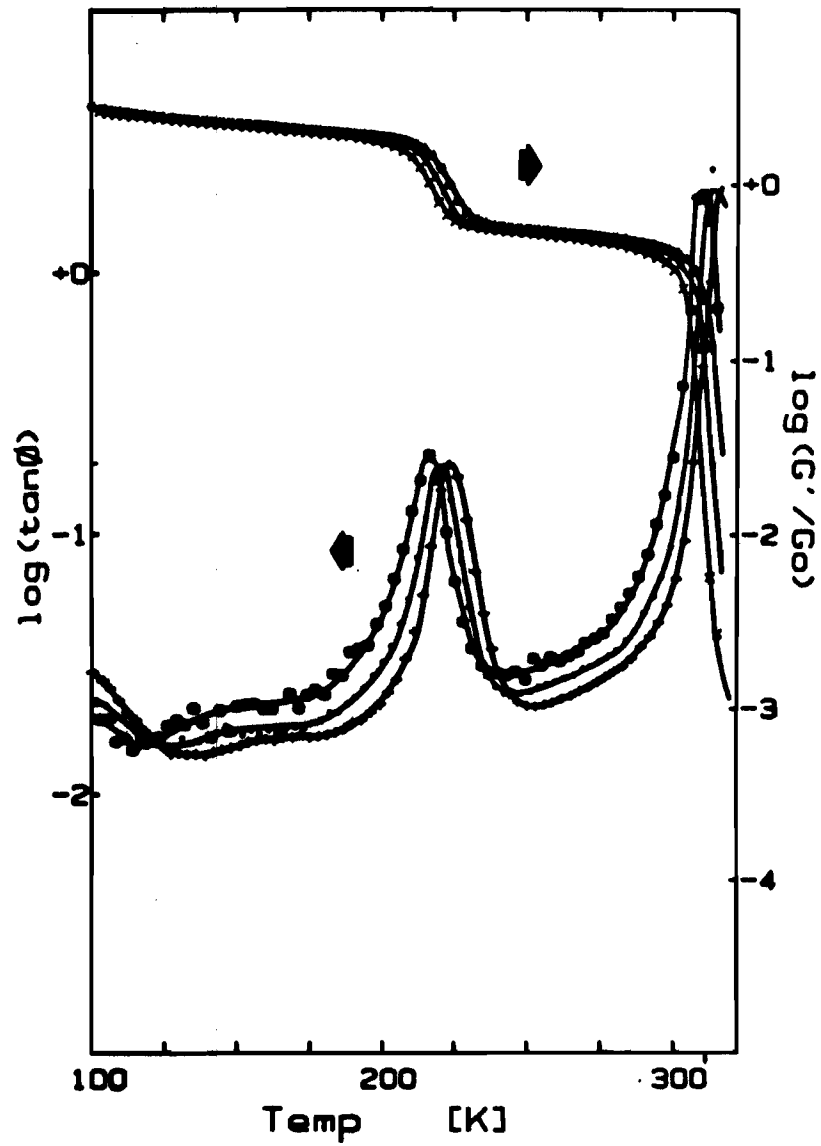


Figure 12 : Micromechanical property-temperature spectra for BuA - VAc copolymer