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ETMA: THE COMBINED ELECTRICAL, THERMAL, MECHANICAL ANALYSIS OF THE BEHAVIOR OF MATERIALS WITH UNIRELAX

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ABSTRACT

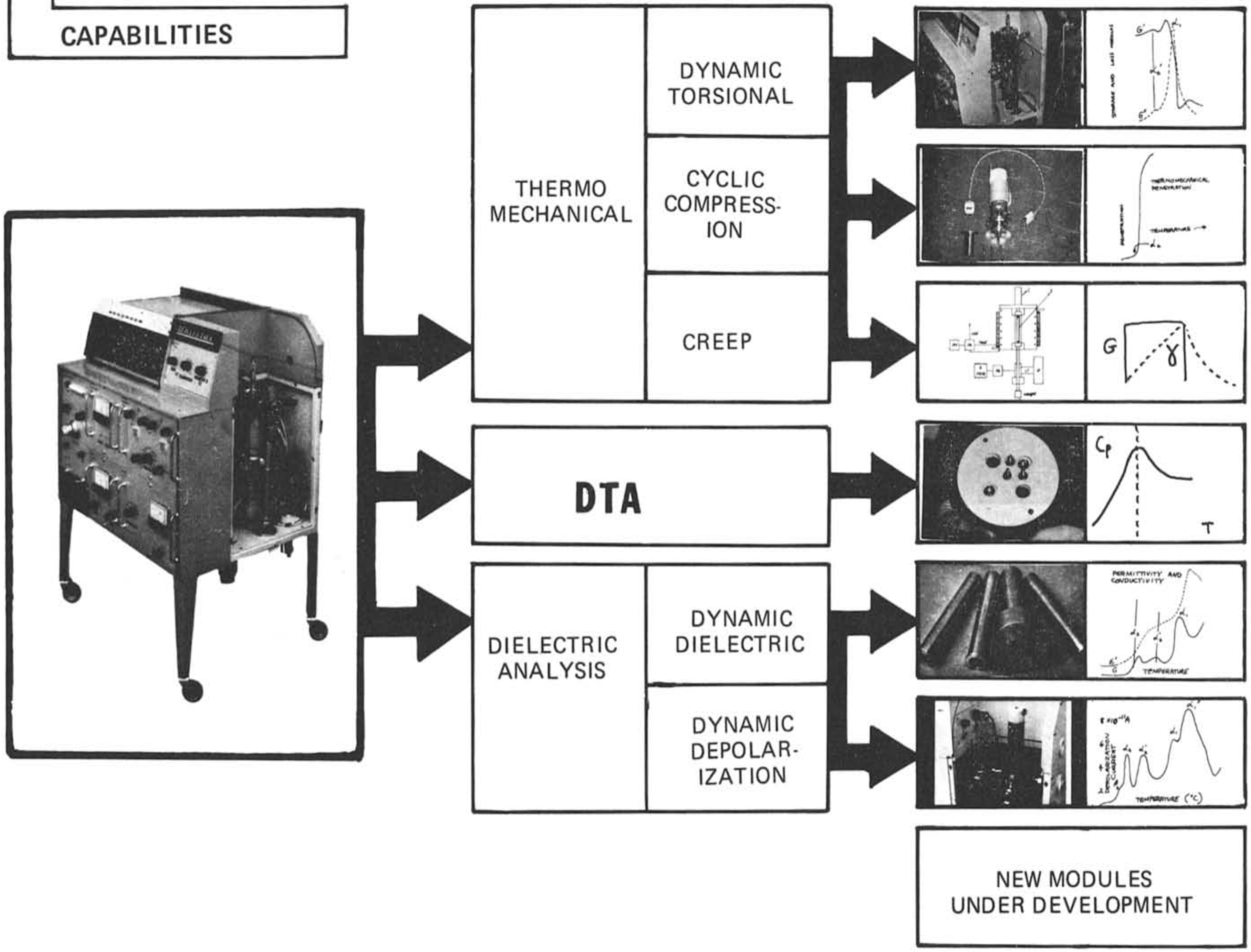
Relaxation behavior involves the strain of a volume element of a material due to an applied stress. Stresses may be either dynamic or static and may take many forms; electrical, as for a dielectric measurement; mechanical, as for dynamic mechanical and viscosity testing; thermomechanical, as in creep, torsion, compression, penetration and flow tests; thermal, as in DTA and DSC; polarization, such as in depolarization analysis (DPS); NMR effects; etc. All of the above relaxation effects are related together both in theory and in experimental findings. A Universal Relaxation Spectrometer (Unirelax) has been developed which has the capabilities of performing all of the preceding tests, excepting NMR. Not only can tests be cross-checked against each other, permitting unequivocal identification of responses, but various elusive quantities such as the defect structure of polymers, the ultra-low frequency dielectric response of polymers, etc. can be obtained through a combination of methods and mathematical techniques such as Fourier transforms. Work performed with this method is extremely varied, covering not only the ETMA responses of inorganic and organic materials during softening, curing and other transformations, but also allowing us to often trace these responses to their microscopic origins.

INTRODUCTION

Over the past decade or so, dielectric, mechanical and thermal measurement methods have evolved into analytical tools for analyzing material behavior and probing underlying structures.

These methods have been applied in fields so widely separated in objective and philosophy, from published research to proprietary process control, from quantum chemistry to asphalt manufacture, that it was unlikely that they would be drawn together into a common body of theory and data or appear in related publications. However, an evolution into a common body is now taking place in several planes: theory, development of new techniques, experimental laboratory findings, process control. All of these are forms of relaxation behavior, which serves as the basis for

CAPABILITIES



both their common understanding, and their measurement[1]. In this paper, the authors shall attempt to bring together these factors in an introductory fashion to show what can and has been done. A relaxation spectrometer, Unirelax™ (universal relaxation spectrometer) has been developed for this work and its performance is described.

INSTRUMENTATION/THEORY AND PRACTICE

Dielectric spectroscopy

Dielectric behavior involves dipoles and their interactions with electric fields. A dipole consists of positive and negative charges $\pm Q$, separated by a distance d. An electric field E applies a torque force T to these dipoles tending to align them in the field's direction, and this ability to align is affected by molecular hinderances such as polymer shape and degree of cross-linking. These microscopic factors could also affect the other ETMA techniques.

In dynamic dielectric measurements we measure the storage and dissipation of the alignment energy, which are termed capacity C and dissipation D, over a range of frequencies, up to 100 kHz for polymers. A block diagram of a combined dielectric spectrometer/DTA system is shown in Fig. 2. The block labeled Audrey 300U™ is a wide range dielectrometer system for driving both dielectric and mechanical test cells. Dielectric tests cells can be adapted to almost any material configuration: liquids, films, powders, cables, composites, etc.

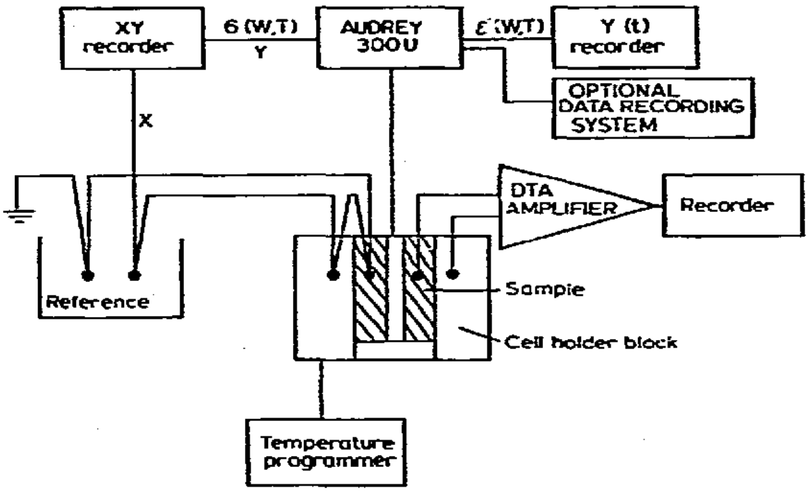


Fig. 2. Audrey/DTA system.

Mechanical spectrometry

Unirelax may be operated as a mechanical spectrometer and, quite interestingly, this function is electronically directed by the dielectric spectrometer, via an external control adaptation. But, this is what one might expect from the close theoretical analogy between mechanical and dielectric relaxation.

It is more difficult to monitor the mechanical than the dielectric behavior of materials. We are always operating through a test fixture such as a clamp which not only influences results, but can modify them to the opposite of expectations. For example, we would probably experience increasing losses with temperature due to molecular motion. Losses may seem to drop with softening or degradation, because of poor clamp coupling, but they would almost certainly still be climbing. In such an instance, the imposed electric field of a dielectric measurement would be more likely to bring out the correct picture[2].

It is also fortunate that available mechanical test frequencies are those which are important for structural and acoustic applications, i.e., frequencies below 10,000 Hz. However, responses to frequencies from as low as 0.001 Hz up through several MHz are often critically revealing, and only electronic and optical techniques can scan such a vast range—covering liquid to rubber to leather to glass transitions and the motions of the individual polymer segments—all of this over a broad temperature range.

The torsion or forced oscillation method, where the sample is forced to oscillate in compression, extension or torsion, is used in Unirelax because of its wider frequency range possibilities, from 1 to 30 Hz in Unirelax, and because it lends itself to automatic operation. The block diagram of the Unirelax forced oscillation mechanical spectrometer is shown in Fig. 3. It measures the storage torsional modulus G' and the loss modulus G'' over a wide temperature range.

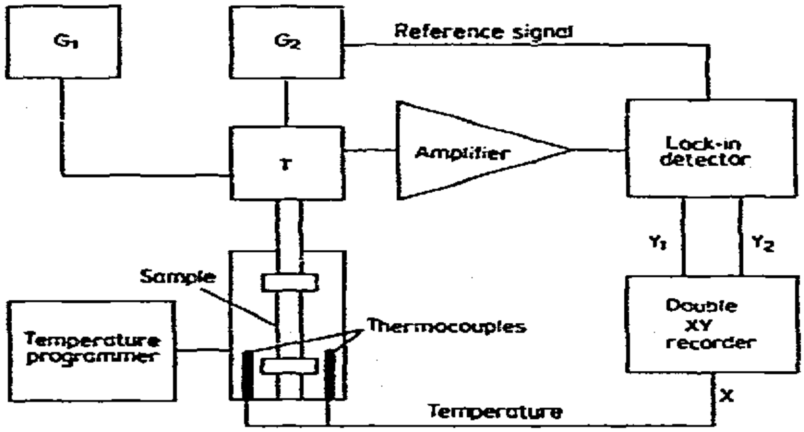


Fig. 3. Dynamic mechanical spectrometer. G1 and G2 are controlled by Module 41 through the dielectric spectrometer.

When the load is purely elastic, e.g., if a lossless spring is used, the in-phase component of current, representing energy storage, would be maximum and the 90° out-of-phase component, representing loss, would be minimum. On the other hand if a purely viscous load were to be inserted, e.g., a cylinder moving in a viscous fluid, the in-phase component would be minimum and the out-of-phase component maximum. We can thus measure the mechanical response of a sample to a periodic load, separating this response into its viscous and elastic components.

The mechanical spectrometer can also be operated in a differential manner by biasing one balance motor with a standard sample for enhanced resolution. Samples may be films, rods, fibers of approximately 50 × 8 mm.

Dynamic viscometry

In principle, this is similar to mechanical relaxation. The same measurement and control electronics are used, but we now operate on liquid rather than solid samples. The test module consists of a cylindrical or double-cone shaped rotor connected to the module's vibrating transducer and immersed within the fluid to be measured (Fig. 4). This device can also be operated in a differential manner by biasing against a reference solution. The viscosity of the reference solution can be controlled by varying its temperature. Dynamic viscometry simultaneously records both viscous loss and elastic components and is particularly useful for studying such viscoelastic liquids as polymer melts.

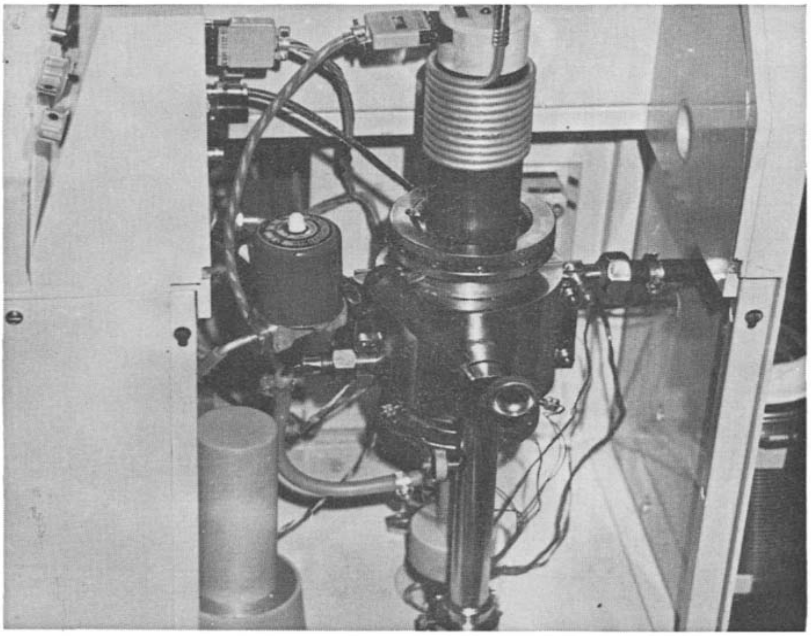


Fig. 4. Vibrating Viscometry in operation. The reference rotor is off to the right and not visible in this photo. The dynamic mechanical module set-up closely resembles this installation.

It can also be used in the rotating regime which is useful for measuring polymer melts of extremely high viscosities in the region of 50,000 to 100,000 poises, where the vibrating method becomes difficult to use.

Definition

Thermal analysis involves the measurement of heat absorbed, emitted and conducted through a material via such methods as DTA, DSC and calorimetry. Because the concept of free volume enters into both dynamic and quasi-static dielectric and mechanical behavior, all of these methods quite often agree, each in its own particular way, each with its own particular advantages and limitations. Thermal analyses are limited to test cells and special programming methods and are incapable of providing highly specific excitations for the fine probing of materials structures[3].

Measurement methods

With Unirelax, DTA, DSC and calorimetry tests may be run separately or simultaneously with dielectric tests. The time constant of the thermal cells is 2 min; their signal-to-noise ratio is 10:1 in the isothermal regime; with temperature scan, the sensitivity is about 10 times less due to baseline shift; typical cell sensitivity is $70\,\mu\text{V}\,\text{mcal}^{-1}\,\text{sec}^{-1}$. For measuring melting peaks of polymers, the full-scale reading should be about $10\,\text{mcal}\,\text{sec}^{-1}$ and for polymerization reactions we usually require about 1/100 of this sensitivity; for cross-linking reactions, even less sensitivity is needed. The calorimeter/DTA/DSC test cell consists of a battery of 120 copper–constantan thermocouples arranged symmetrically on the surface of the sampling area. Sample and reference materials can be placed within pyrex-glass holders into the calorimeter, where the sample can be evacuated or subjected to various atmospheres (Fig. 5). This calorimeter is a compromise between the Calvet-type, which was designed for the study of isothermal reactions, and the Perkin-Elmer type, which was designed for phase transitions. For practical work we have found that using sealed

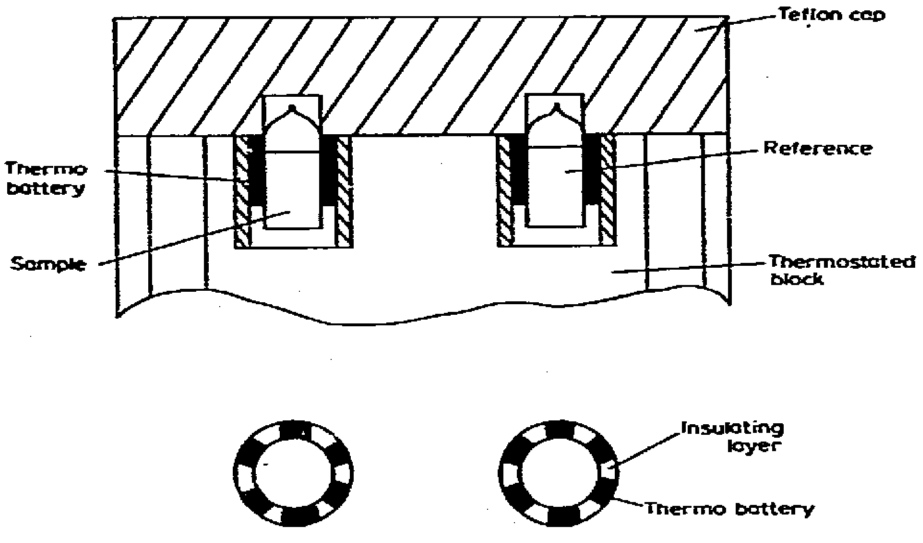


Fig. 5. DSC calorimeter.

glass sample holders is very comfortable, being adaptable to any atmosphere. Our temperature scan goes up to 9 °C min^{-1}, but we usually go no higher than 1 °C min^{-1}. The speed matches better with that of the thermomechanical and dielectric measurement than the high speeds used in the P–E type DSC systems. Although sensitivity increases at high speeds, we prefer lower speeds for making comparisons, even for studying phase transitions. Also, for chemical work it sure is nice occasionally to work with palpable quantities of materials in the order of 0.2 to 0.5 g. For chemical work, the Calvet calorimeter is more suitable than the P–E, but it can not be scanned.

QUASI-STATIC METHODS

Depolarization spectroscopy

In dielectric, mechanical and thermal testing we usually assume our samples to be uniform and homogeneous, and for mixtures also ideally dispersed. Unfortunately, this is not usually the case, and a spread of test data and a loss of correlation result from such deviations from ideality. These deviations we call "defects". Defects are discontinuities in the regular matrix structure of such diverse dielectric material as polymers, ceramics and glasses. They include amorphous regions, internal strains, electronic charge centers, variations in filler concentrations, voids, non-wetting of particles, etc. These defects, although irregularly dispersed and low in concentration, often strongly influence or control material behavior and reaction rates. It has been proposed that the basic electrical, mechanical and thermal properties of a polymer are mainly determined by the collective states of the defect phase and not by those of the matrix or background phase[4,5].

At the Institute for Plastics Research in Budapest, Hedvig's group has shown that if a very strong electric field is passed through a material, charges will pile up along fault lines (Fig. 6) revealing such variations in the background structure as internal strains, voids, free radical effects such as ageing and radiation induced changes, and particle variations. The technique involves depolarization currents and is known as DPS or depolarization spectroscopy[6].

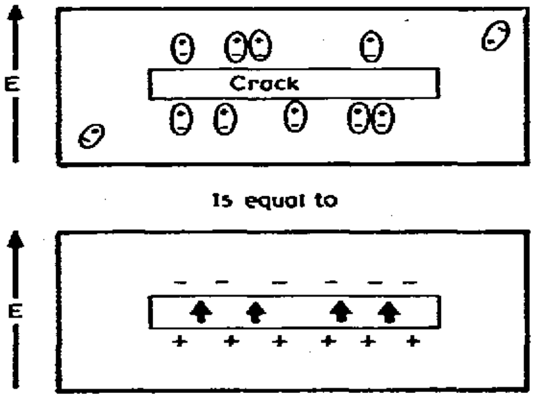


Fig. 6.

The measurement procedure involves placing the material between two flat electrodes; heating it to its melting point; allowing it to cool under a strong electrical field. On removing this field, the material will be found to be polarized, with the dipoles frozen into alignment. On programmed re-warming, the interfacial trapped charges are gradually released, often in a complex and revealing sequence corresponding to particle sizes, polymer chemistry and lattice defect types (strains, voids, impurity centers, etc.). Examples of results are given further on in this article.

Conductivity measurements

The experimental arrangement for measuring DC conductivity k_0 is similar to that used for DPS. By recording k_0 as a function of the temperature, we usually find that $k_0(T)=k_0^0 \exp(-E_0)/KT$ where E_0 is the activation energy of conduction, k is the Boltzmann constant and k_0^0 is a constant. By measuring at two temperatures, T_1 and T_2, we can calculate E_0 directly through relationships such as

$$E_0\,(\mathrm{kcal\ mol^{-1}})=\frac{20.0\ln(k_0^{(1)}/k_0^{(2)})}{1/T_2-1/T_1}\times 10^{-4}.$$

Examples of DC conductivity methods cross-checked against other Unirelax functions are depicted in the Applications section of this article.

Very low frequency measurements

DPS spectra can be Fourier transformed into dielectric spectra at the very low, difficult to monitor frequencies from 1 down to 1×10^{-4} Hz with computer assistance. Relaxation responses in this ultra low frequency range are quite interesting, particularly for cured systems and measurements at low temperatures.

Creep and stress relaxation

Creep and stress relaxation are time and temperature dependent processes. For creep measurements, we record sample deformation as a function of time at constant temperature (strain behavior with constant stress). Stress relaxation involves the measurement of stress deformation as a function of temperature at constant strain (Fig. 7).

By selecting the load, the temperature or the speed of temperature sweep, structural transitions will appear as breaks on the recorded curves. From these curves the rate constant of the process can be determined in the tensional regime [$k_c(\text{tension})=\mathrm{d}E_0/\mathrm{d}t$] and the torsional regime [$k_c(\text{torsion})=\mathrm{d}G_0/\mathrm{d}t$], where E_0 and G_0 are the tensional and torsional moduli, respectively. Activation energies can be obtained by measuring the rate constant at two different temperatures

$$E\,(\text{creep})=\frac{R\ln\dfrac{k_c(T_1)}{k_c(T_2)}}{1/T_2-1/T_1}$$

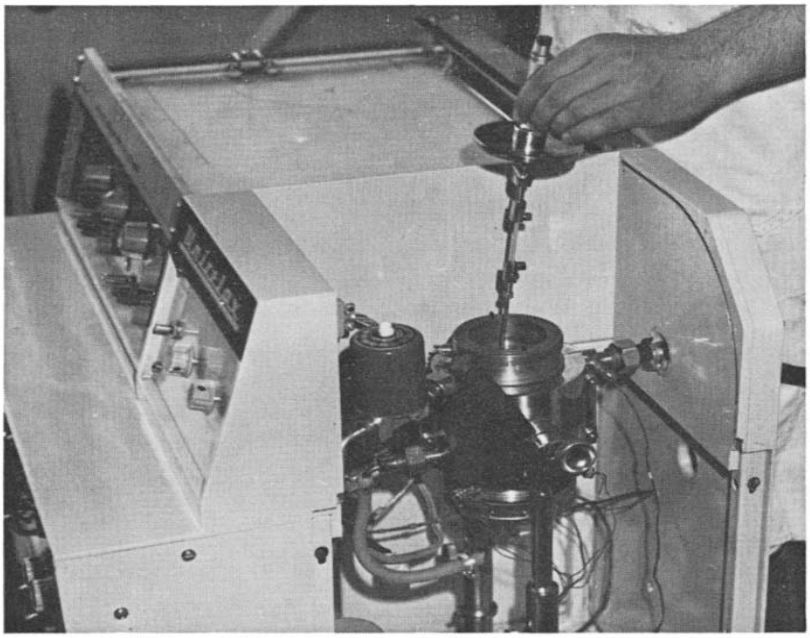


Fig. 7. Inserting a creep sample in Unirelax.

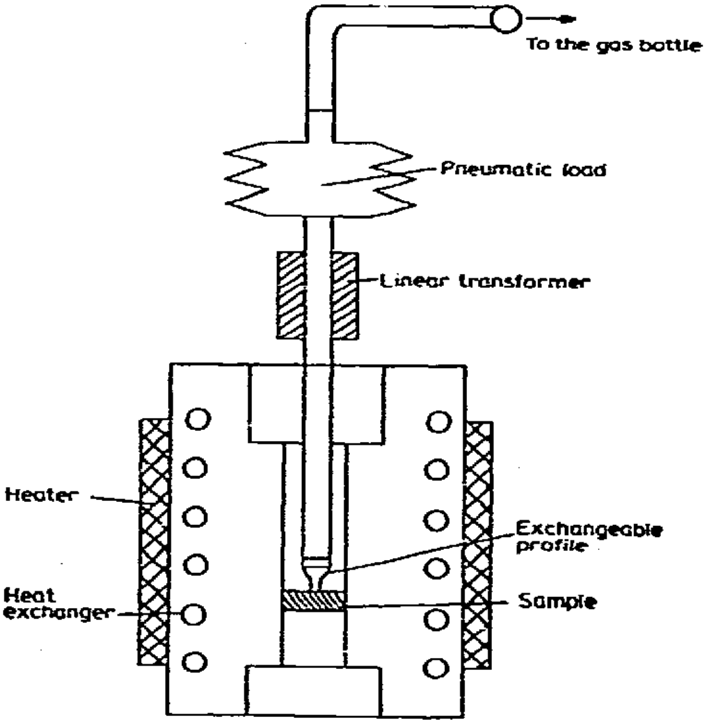


Fig. 8. Thermomechanical module where load is applied to the fixture via a pneumatic driver. A penetration profile fixture is in place.

which is the quasi-static mechanical analog to the activation energy calculated from quasi-static conductivity measurements. In oriented samples the relaxation of the internal stresses may result in contraction before creep sets in, which is useful in studying orientational effects.

The analysis of cyclic creep results can yield unexpected insights into material behavior through careful measurement and computer analysis of the static and transient changes between loaded and unloaded conditions, as shall be shortly reported upon by Forgacs and Hedvig, both of the Research Institute for Plastics, Budapest, Hungary. Although creep testing is commonplace, it is quite probable that through modification of test procedures and refined methods of data analysis, the use and importance of this method will grow. In the near future, Forgacs and Hedvig will be reporting upon the results. Loads can be compressional, extensional or torsional which are applied via a pneumatic load system.

Flow viscometry

The pneumatic system used for creep measurement can also be used as a simple, effective flow viscometer, as configured approximately as shown in Fig. 8. It is adaptable to capillary extrusion rheometry, where we measure the apparent melt viscosity of plastic materials at various temperatures and shear rates, permitting us to determine processing conditions and distinguish between good and bad batches. The material to be tested is melted within this cell, then cooled below its melting or glass temperature; then after a heat soak at test temperature, a load is applied and the movement of the plunger is recorded as a function of time while the sample extrudes through an orifice.

Thermal expansion measurements

The cell shown in Fig. 8 can also be used for measuring volume expansion coefficients by filling the sample area with a fluid or polymer melt. It would also be possible to record thermal dilation at different pressures by applying pressure during the temperature scan.

Penetration

This simple but revealing test is shown in Fig. 8 and involves the measurement of depth of penetration of various indentors into a material, vs. time and temperature.

APPLICATIONS

Extent of cure

Dielectric methods are particularly useful for following and extracting the optimum cure from polymeric material. We have found, for example, that cure at any particular temperature is quite self-limiting with a progressive inability to structurally expand. Improvements in the degree of cure and material performance can be obtained through the use of unorthodox processing cycles, such as is shown in Fig. 9[7,8].

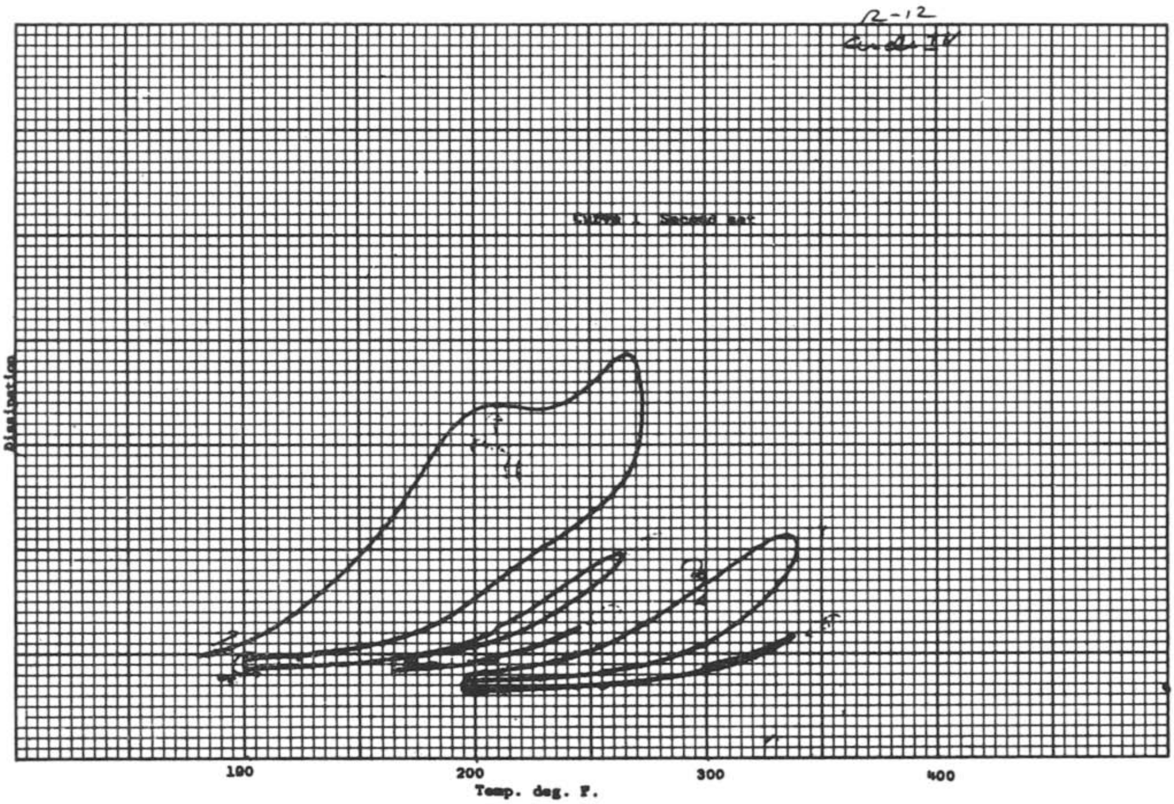


Fig. 9. Extent of cure curve. There is an equilibrium cure structure characteristic of particular temperatures which we can perceive as loops within dissipation vs. temperature curves, the area of the loop representing the concentration of conversion during a temperature cycle. In this example, a phenolic resin was cycled several times in temperature up to a particular temperature limit, successively reducing loop area to a single line curve, indicating that no further reaction was occurring. With an increase of temperature, some further reaction was generated, as indicated by the loops to the right.

In Fig. 10, the curing response of a polyester resin as determined with dielectric and DTA measurements is shown. Dielectric analysis reveals a first conductive peak (σ) at −50°C, occurring approximately at the center, or deflection point of a rise in E' which represents softening behavior for the resin. It is barely detected by DTA. The 70°C peak is due to polymer cure, and is picked up by both dielectric and DTA methods.

The effect of thermal history is just beginning to be appreciated in plastics production, process control and testing. Its great influence arises because polymers, by their viscoelastic nature, rarely reach thermodynamic equilibrium in the solid state because of the finite times required to achieve a free volume characteristic of any particular temperature. These holes may be considered to be defects in the polymer structure and under an electric field, local charge concentration will build up around them. A polarization of the field P is directly proportional to the defect concentration N_d, and when we pass through a structural transition, the defect concentration will

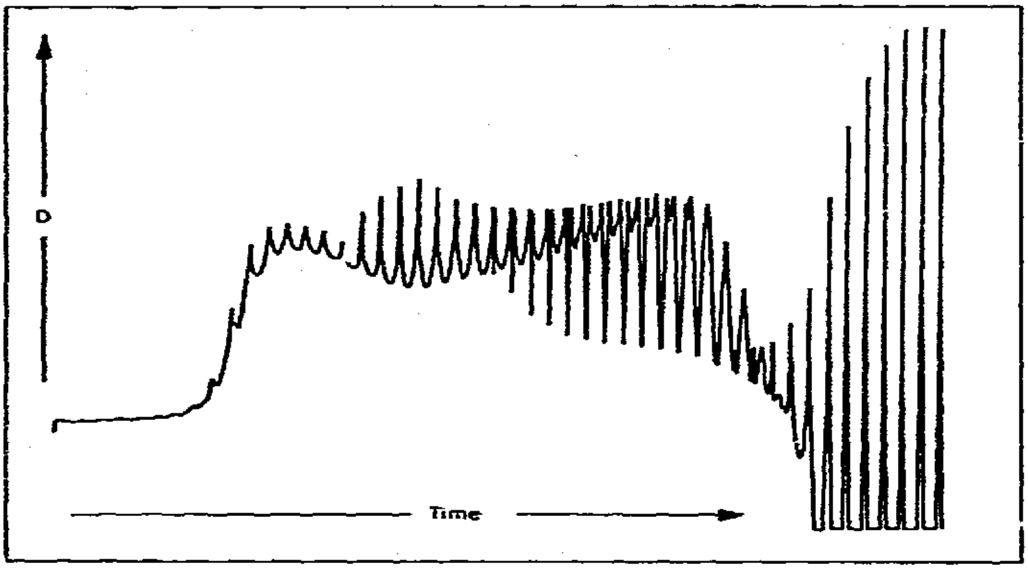


Fig. 10. Curing response of a polyester resin determined with dielectric and DTA measurements.

change abruptly, causing a change of polarization. This change causes a current peak I, where:

$$I \propto \left(\frac{dP}{dT}\right) T_0 \propto \left(\frac{dN}{dT}\right) T_0$$

After rapid cooling, a high concentration of defects would be frozen into a material and with subsequent reheating, the change in this concentration would be less than after slow cooling. This signifies that the depolarization peak is a measure of the texture and morphology of the polymer at that temperature where the heating-up had started.

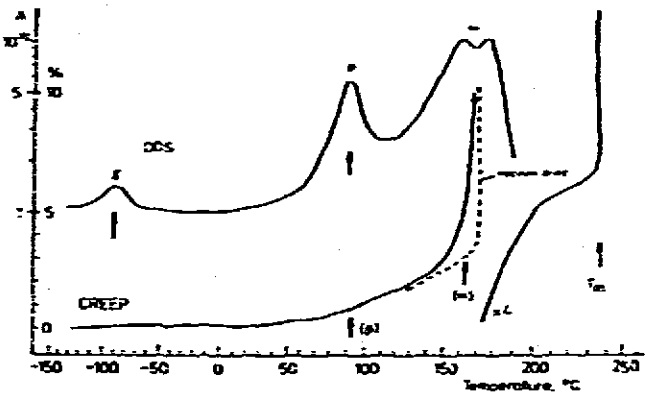


Fig. 11. Depolarization and creep curve for cellulose triacetate.

Figure 11 contains both a depolarization and a creep curve for cellulose triacetate where α is the T_g peak for CTA, T_m is the crystalline melting temperature and β and γ are T_{gg} transitions, which may also be readily measured by dielectric spectroscopy[9].

Thermoplastics

Both organics and inorganic thermoplastic materials such as polymers, biological materials, glasses and ceramics can be followed through their reversible and irreversible changes via dielectric analysis, as shown in Fig. 13b for an unsaturated cross-linked PVC[10].

Creep behavior of cellulose triacetate (CTA) combined with polyacrylamide (PAA)

This most interesting experiment had as its objective the determination of the effect of heterogeneous inclusions on mechanical properties and how well they might be detected by DPS. PAA was polymerized within a water solution by radiation into a colloid form and dispersed within the medium (HET). The HOM polymer was prepared by using a common solvent for CTA and PAA. It is evident in Fig. 12 that even though the heterogeneities were of low concentration, they had a dominant and overriding effect on overall creep performance.

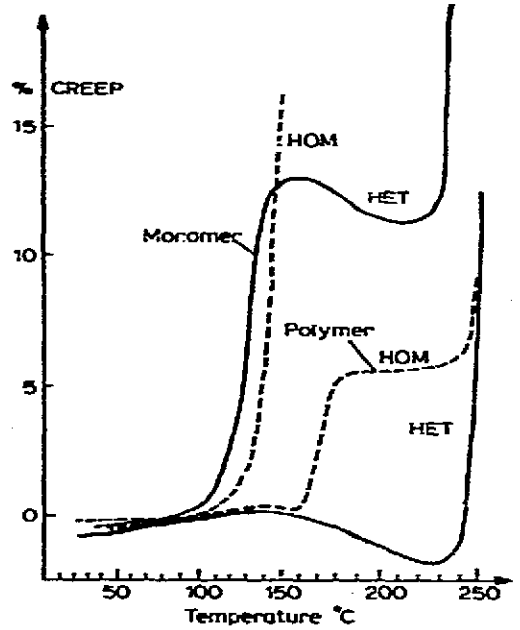


Fig. 12. Creep behaviour of cellulose triacetate combined with polyacrylamide.

PVC/rubber blends

Blends of this type are commonly used in industry, and a study was performed on the various ETMA responses of these materials, including the effects of particle size and particle dispersion (Fig. 13). Figure 13a compares the dielectric depolarization spectrum of the rubber phase with the corresponding dielectric analysis spectrum at 1 kHz, and in Fig. 13b the depolarization spectrum is compared with that for mechanical relaxation. It is seen that the α_1 transition, the T_g for PVC, is quite sharp but the α_2' transition, the glass–rubber transition of the elastomer phase, is quite well defined in the depolarization domain but is only slightly indicated in the

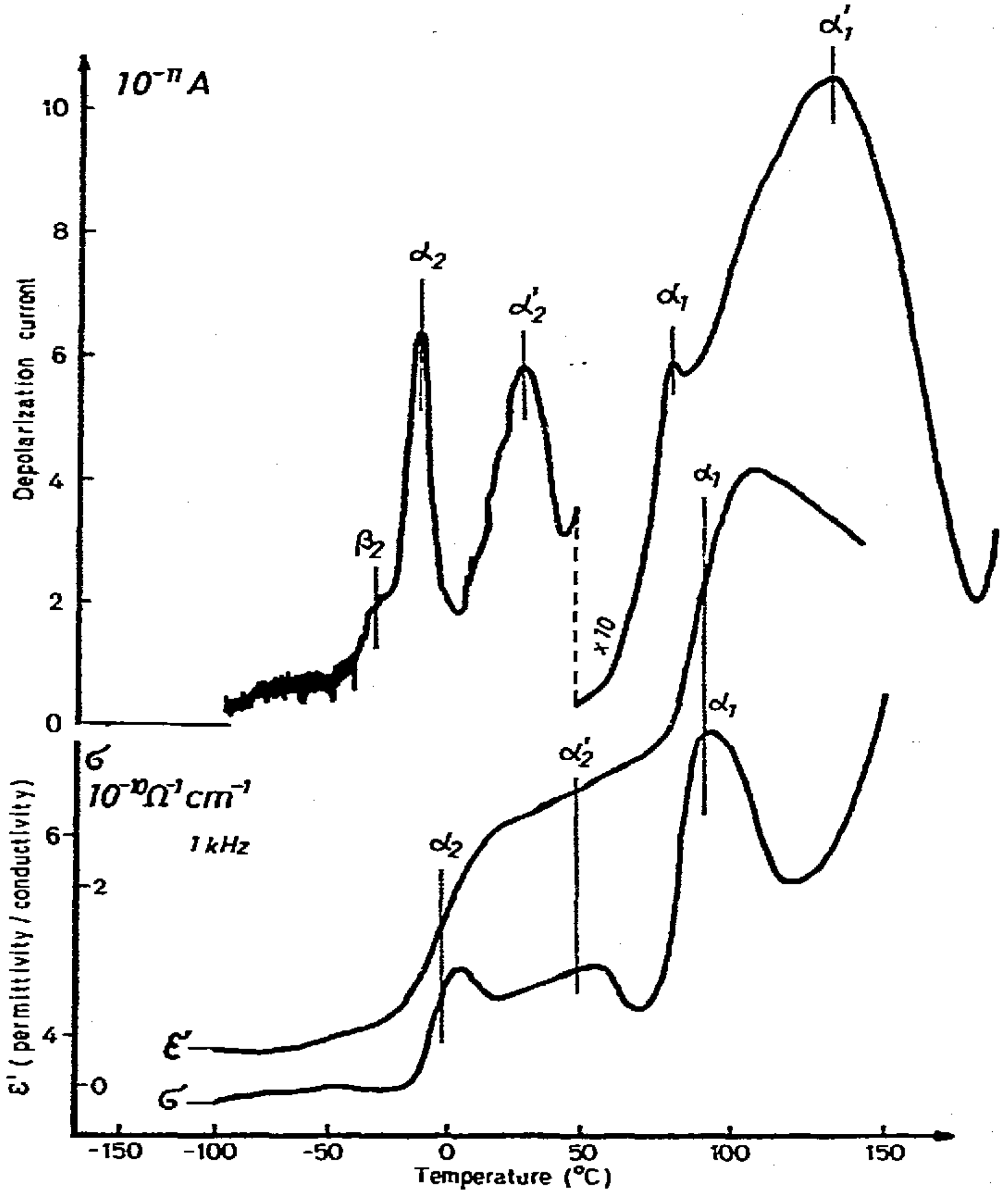


Fig. 13a. Dielectric depolarization and dielectric property response vs. temperature for a PVC/rubber blend.

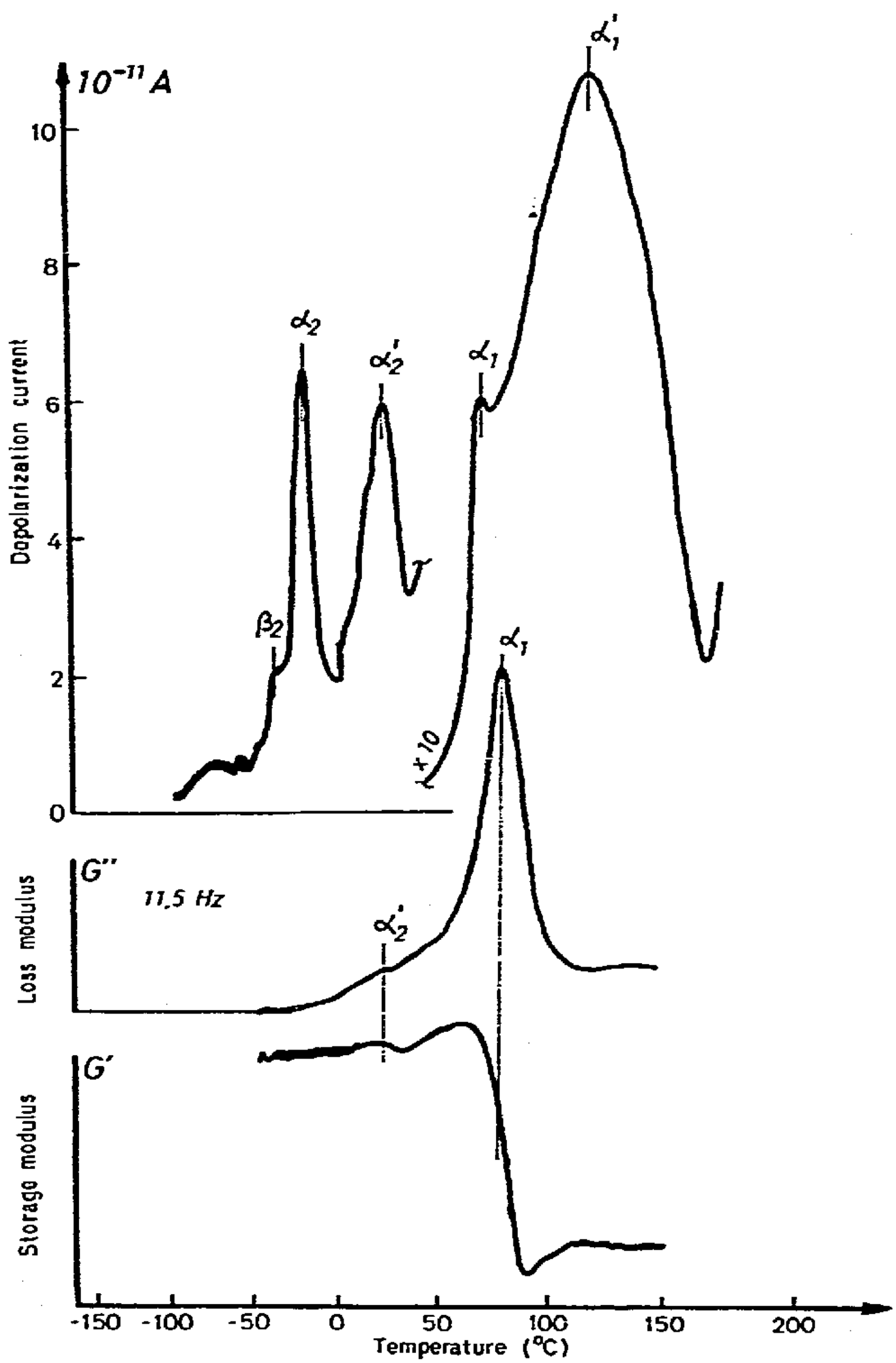


Fig. 13b. Comparison between depolarization, mechanical loss and storage modulus for a PVC/rubber blend.

mechanical modulus curves[11]. In Fig. 13c, dielectric depolarization of the rubber phase was compared with dynamic mechanical and thermal mechanical curves. The α_2' transition appears as a shoulder in the dynamic relaxation curve and as a very well-resolved peak in the depolarization spectrum.

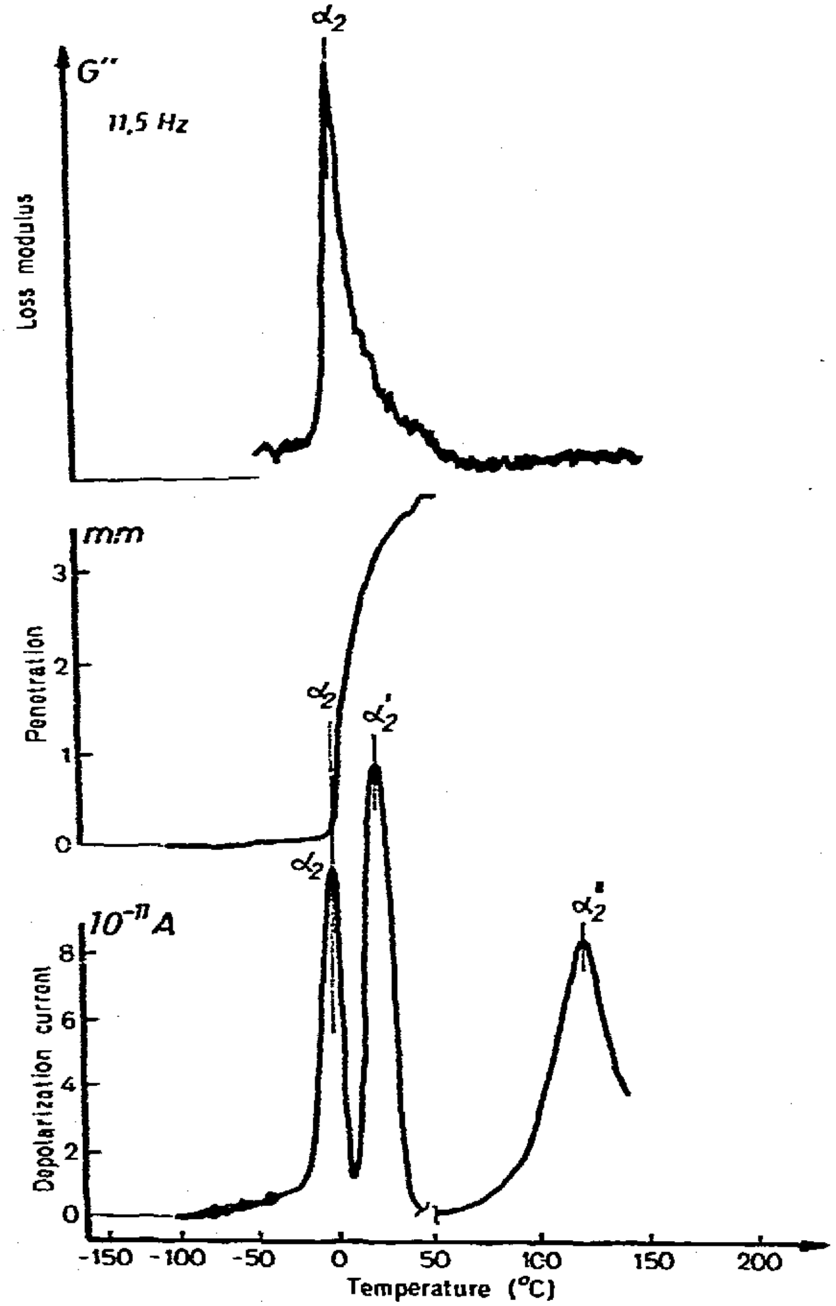


Fig. 13c. Comparison between depolarization and thermal mechanical properties for the rubber phase extracted from the PVC/rubber blend.

Radiation curing and degradation

DPS, supported by calorimetry and other ETMA methods, is particularly suited for studying free radical reactions involving the usual initiation, propagation and termination steps. Such reactions involve a defect mechanism, where changes although of low concentrations are capable of producing a large effect in properties[12].

Using a variety of sources including UV, Co^{60}, the electron beam and X-ray radiation, a variety of studies have been performed. These include: the effect of dose rate on curing; competition between addition and condensation polymerization; the effectiveness of inhibitors; degradation effects (particularly of elastomers and thermoplastics associated with radiation curing) have been studied. A typical study is shown in Fig. 14.

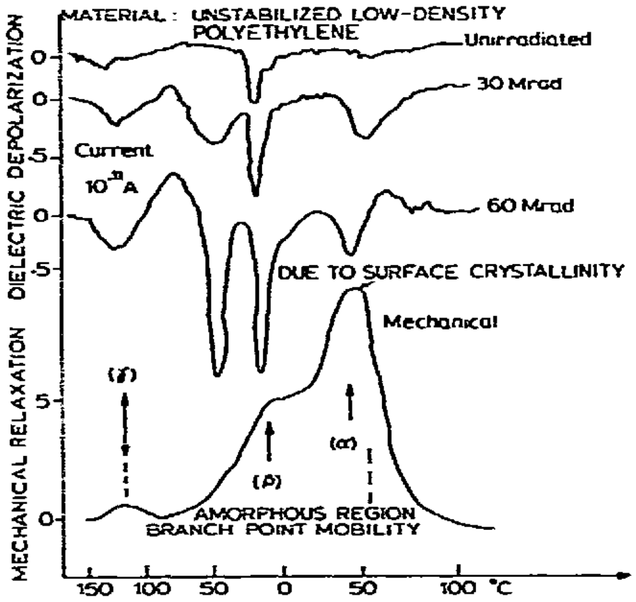


Fig. 14. Mechanical and dielectric depolarization property changes as a function of irradiation for a low density polyethylene.

CONCLUSIONS

Methods by themselves have limited applicability. When combined together, such as with ETMA, we often obtain insights which we would otherwise not gain. Additionally, with the reinforcement of our viewpoints through the obtaining of complementary data, we can often extend the method into new areas, such as the creep and depolarization transformations mentioned within this article. Dielectric analysis and ETMA are relatively recent and until the publication of this review article, information has been dispersed throughout the literature. Naturally a more detailed presentation cannot be made within the confines of *Thermochimica Acta*, but we would welcome any specific questions.

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