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Comparing thermal stimulated current (TSC) with other thermal analytical methods to characterize the amorphous phase of polymers [α]

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Abstract

We compare thermal stimulated current (TSC) and relaxation map analysis (RMA) to the more traditional thermal analysis techniques DSC, DMA and DEA. It is suggested that TSC/RMA represents an important technological advance with regard to the study and characterization of the amorphous state of matter.

INTRODUCTION

This paper compares the most popular thermal analysis techniques to study relaxations and resonances in polymers. Relaxations in materials take place as the result of internal motions, which are induced by thermal, mechanical or electrical disturbances. Polymers that are processed by the usual molding methods have mechanical and electrical properties that depend on their internal structure, and it is therefore important to be able to characterize the local motions that define this internal structure, originating at the atomic (electronic), molecular, or even macro-molecular level.

Three types of experiments are commonly used to study relaxations in materials, (1) resonance methods, (2) damping methods, and (3) thermal activated methods.

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RESONANCE METHOD

The material is subjected to a periodic excitation, either mechanical or electrical in nature, applied at a determined temperature and pressure. The frequency of the excitation is swept, and the (mechanical or dielectric) storage and loss constants are determined at each frequency. Plots of the storage and loss functions versus (log) frequency display peaks which characterize the motions occurring in the structure, with the frequency at the maximum of loss corresponding to the resonance frequency for that particular internal motion. Working at different temperatures displaces the maximum, allowing one to determine the fundamental parameters of the rate-dependent process which gives rise to that internal motion.

A variation of this method subjects the polymer to an excitation at a fixed frequency while scanning the temperature. When the temperature reaches a level capable of thermally inducing the internal relaxation process, a resonance peak for the selected excitation frequency is observed.

It is possible to operate at various (fixed) frequencies and thus analyze the dependence between time and temperature (or frequency and temperature), providing information on the mechanism responsible for each internal motion. Note that resonance experiments apply the mechanical or electrical "deformation" as the measurement is made.

The field can be either an a.c. voltage polarization or a mechanical orientation within the sample, causing oscillation in the polymer which is at the same frequency as the field, but with a phase angle shift (δ). For dielectric analysis (DEA) the phase angle shift is measured by comparing the applied voltage to the measured current (which is separated into capacitance and conductance components), while for dynamic mechanical analysis (DMA) the stress and strain are compared to provide the elastic and loss moduli. The experimental resolution depends on the ability to measure changes in these variables, in particular the tan δ versus temperature (or frequency) loss peak.

DAMPING METHODS

Damping experiments consist of an excitation stage, e.g. submitting the specimen to a sudden torsion at a given temperature, followed by the interruption of the excitation and subsequent recording of the recovery curve as the polymer returns to equilibrium. The damping characteristics are direct functions of the polymer's internal state at this temperature; thus the molecular relaxations which govern the kinetics can be determined.

The classical torsional pendulum was popular in the 1950s to study "internal friction", while recent experiments have used sinusoidal pulses generated at ultrasonic frequencies to excite the polymer, analyzing the damping of the wave as it propagates through the sample to determine the complex modulus and complex viscosity at that frequency.

THERMAL ACTIVATED METHODS

These include both simple calorimetric measurements (DSC and DTA), and thermal stimulated methods: thermal stimulated current (TSC); thermal stimulated creep recovery (TSR) and thermal stimulated luminescence (TSL) which combine the influence of temperature and one other variable, which may be a mechanical or an electromagnetic (light) variable. In this paper we shall compare TSC with DSC, DMA and DEA.

RESULTS AND DISCUSSION

DSC

The classical output from a differential scanning calorimeter plots heat capacity versus temperature. The heat capacity increases as polymers cross the glass transition temperature, showing kinetic features which can be analyzed by the rate of change of the heat capacity or by the area of the endothermic peak. Melting and crystallization phenomena are characterized by endothermic and exothermic peaks, respectively.

There are several disadvantages to differential scanning calorimetry (DSC): (1) the technique cannot separate individual relaxation modes in the material; (2) DSC is insensitive to "secondary" internal movements for which the activation enthalpy is low; (3) for blends or block copolymers, the melting of one of the phases often obstructs the glass transition of the higher T_g component, so if one of the phases in a blend does not crystallize it may be impossible to determine whether the two phases actually mix or segregate since only one melting peak is visible; (4) due to shifted baselines on either side of a transition, the onset temperature and peak area are difficult to calculate (Fig. 1 shows incorrect calculation of an onset temperature by extrapolating the baseline from the high temperature side of the peak, rather than the low temperature side); (5) resolution can be poor for polymers which have been rapidly quenched (as normally seen in industrial polymer processing): compare the information in Fig. 1 for Vectra 900 (a liquid crystal) before and after annealing.

DSC is best suited for studying semi-crystalline materials, in particular melting and crystallization, and is an ideal tool to detect the presence of thermally active impurities, when these are present in sufficient concentration.

DMA and DEA

The outputs from a dynamic mechanical (or dielectric) analyzer are normally three types of curves: G′ (or ε′). G″ (or ε″) and tan δ, where tan

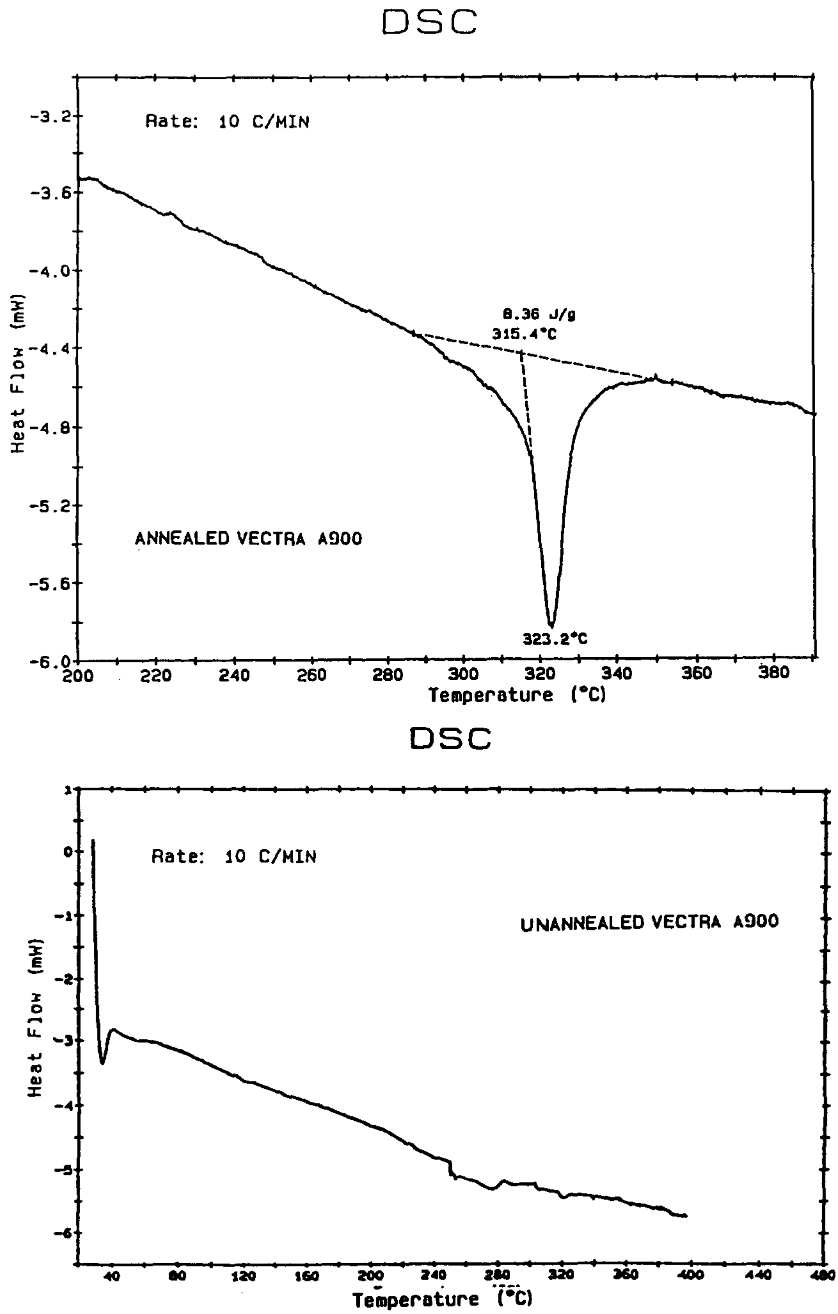


Fig. 1. DSC traces of annealed and unannealed Vectra A900 liquid crystal.

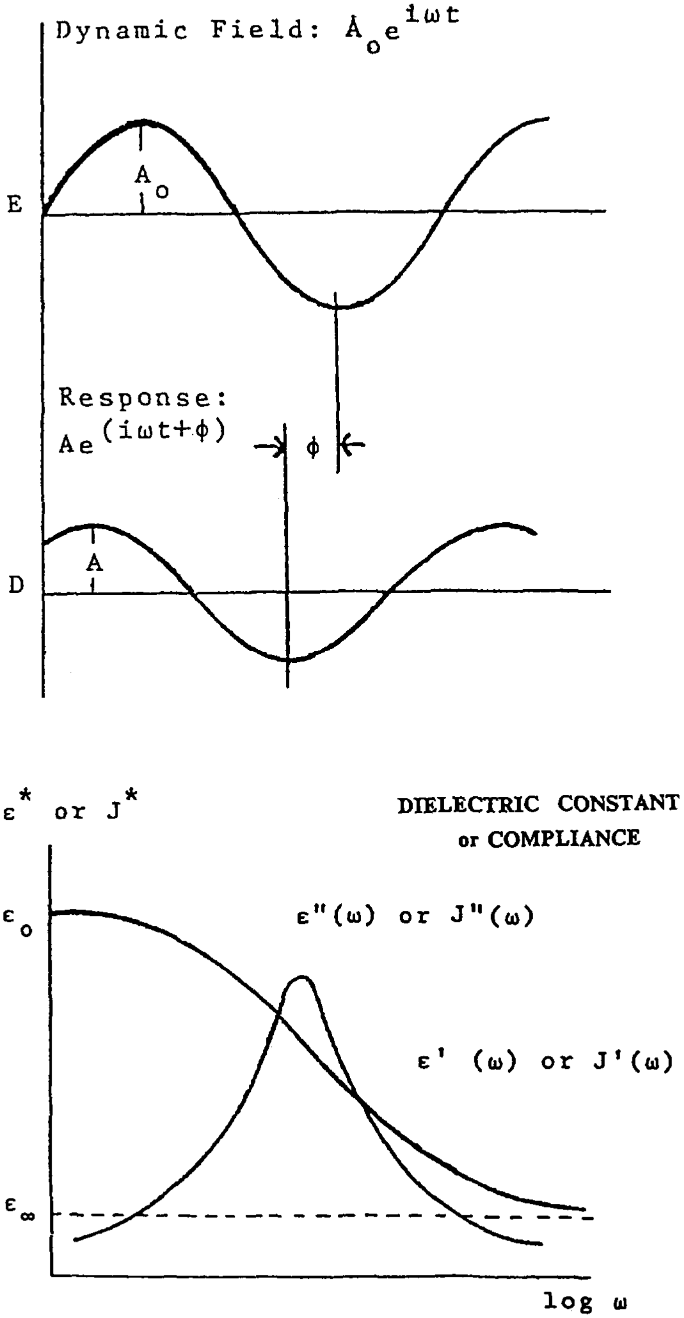


Fig. 2. Analysis of phase shifted information from DMA and DEA experiments.

δ is the ratio of the loss component (G'', ε'') to the elastic or in-phase component (G', ε') (see Fig. 2). The three curves are usually plotted together, with G'' and tan δ considered to be global peaks. Varying the

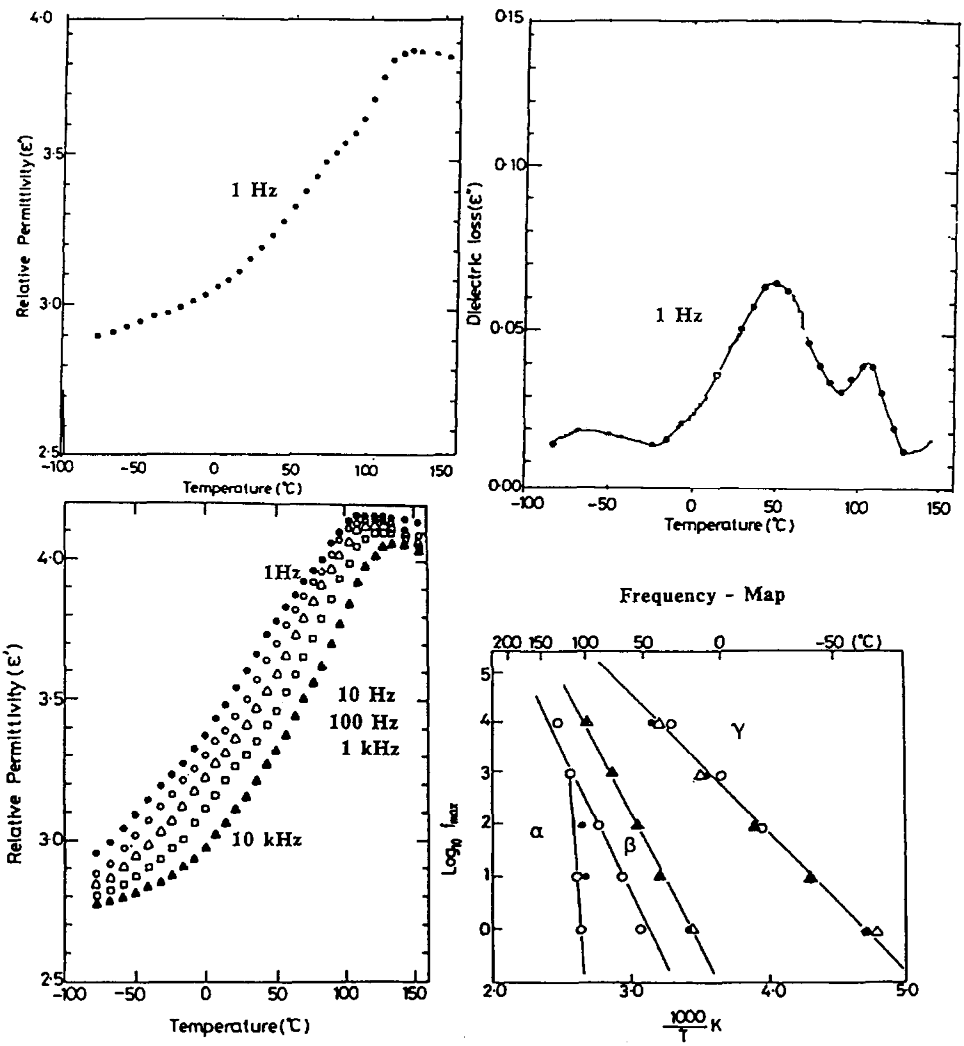


Fig. 3. Typical ε' and ε'' data for DEA experiments. The frequency map shows a typical analysis of the frequency/temperature data [11].

frequency shifts the maximum of the peaks, allowing calculation of a pseudo "activation energy" as shown in Fig. 3.

An alternative method is to work at constant temperature and to scan the frequency across the relaxation time spectrum.

The peaks observed in both DMA and DEA are more sensitive to the influence of internal structure than the peaks observed by DSC. These two techniques have been used to determine the properties of the amorphous phase from cryogenic temperatures up through the glass transition, including secondary transitions. However, there are limitations.

According to Hedvig [5], the low frequency range is best for studying polymer transitions by dynamic spectroscopy because of the increased

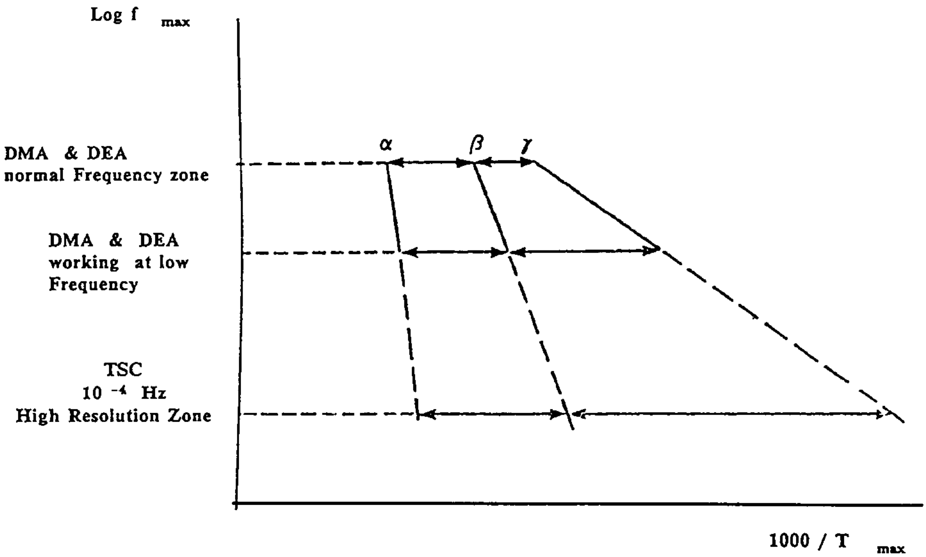


Fig. 4. Low frequency measurements provide better resolution than the frequencies used in DMA and DEA experiments. The effective frequency for TSC is calculated from the Debye equation.

information ("fine structure") at low frequencies: this is schematized in Fig. 4. At high frequencies the loss peaks can be shifted to high temperatures where chemical decomposition processes, depolymerization, crystallization or aging may occur. However, cryogenic transitions and problems connected with lattice vibrations are best studied using very high frequency methods. Hedvig [5] concludes that the very low frequency and the very high frequency ranges are best for monitoring polymer internal structures.

DMA

DMA has become very popular because the technique is simple to realize, to analyze, and the physical meaning of the input and output (stress and strain) are straightforward. Furthermore, it yields fundamental elastic constants of the materials since the deformation is chosen in the linear viscoelastic region. However, the frequency range is limited to the medium range (0.01–110 Hz) and time-temperature is often applied in order to extrapolate to a reasonable frequency range, which frequently leads to gross extrapolation errors [6].

Figure 5a and 5b shows a well-defined mastercurve for poly(*n*-octyl methacrylate), while Fig. 6 highlights the danger of superposition for a polystyrene mastercurve.

The dynamic mechanical behavior of most polymers can be measured with DMA provided the modulus exceeds 10^6 dynes cm^{-2} and tan δ is in the range 0.0001–1.7. The upper temperature limit is just above T_g for amorphous polymers (semi-crystalline polymers can be taken to T_m), explaining why DMA cannot be used to study uncrosslinked polymers in the rubbery and liquid flow regions without a substrate.

DEA

DEA is applicable to all polymers, provided that their conductivity is low, that their dissipation factor falls in the range of the instrument, and that the sample can be prepared with a thickness giving a capacitance within the range of the instrument. In a DEA experiment, ε' and ε'' are calculated

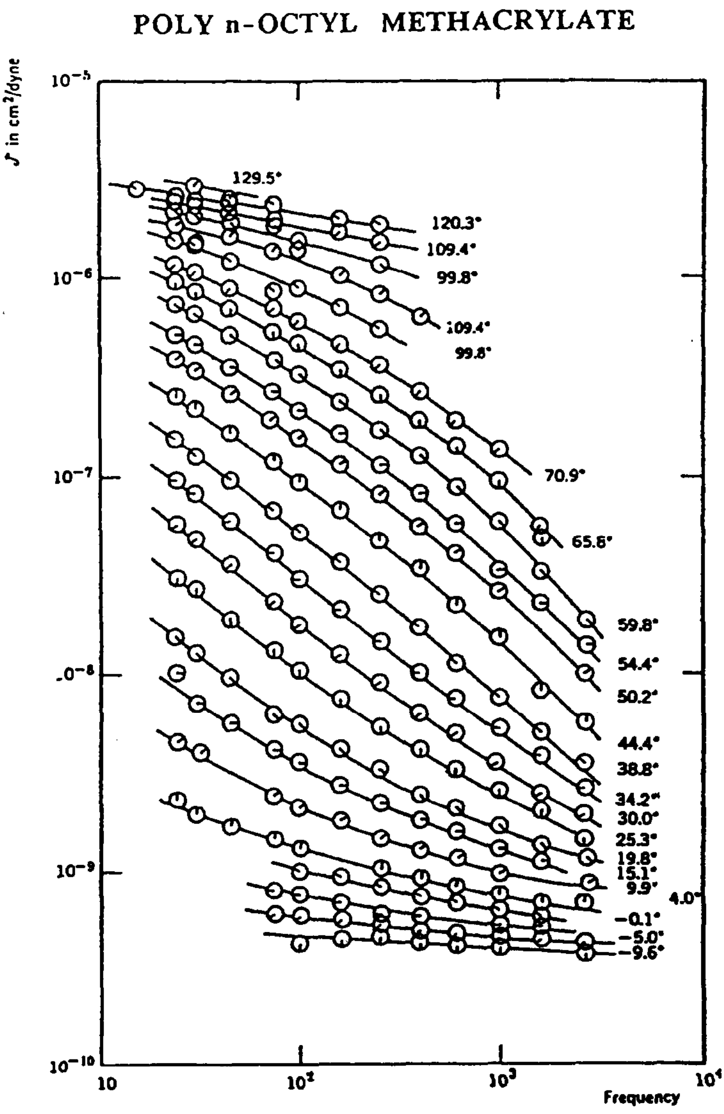


Fig. 5a. Compliance data to create a mastercurve for poly(*n*-octyl methacrylate).

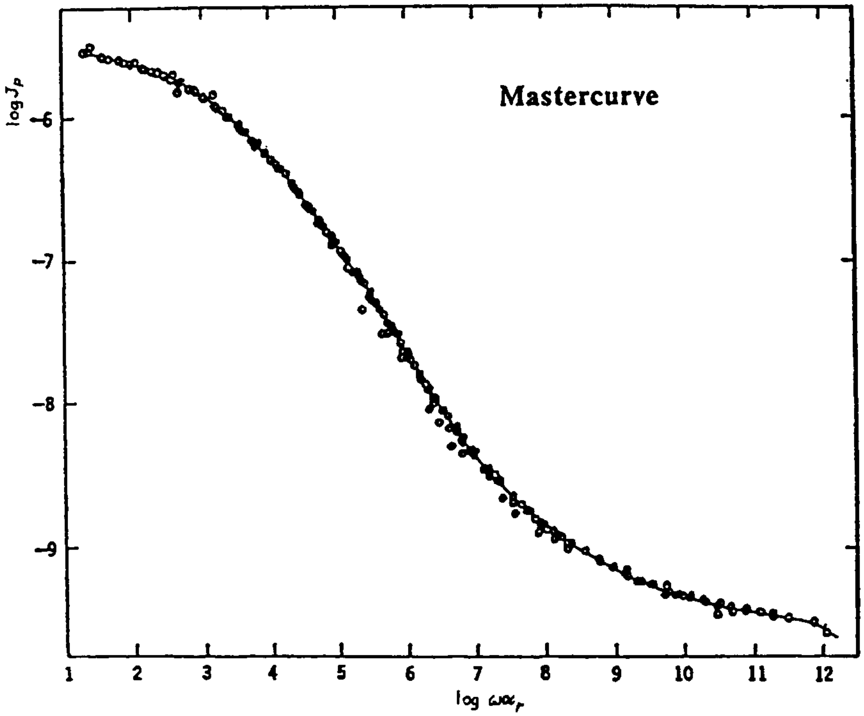


Fig. 5b. Result of the superposition of the curves in Fig. 5a.

from the capacitance and dissipation factor of a condenser with the polymer acting as the dielectric. The temperature of the experiment is selected so that the relaxation times of the motion are comparable to the frequencies used in the experiment.

The great advantage of the dielectric method is the possibility of exploring an extended frequency range, and therefore avoid reliance on the time-temperature superposition principle.

Small voltages (typically 1 V) are applied to the dielectric samples. These voltages are small enough to stay in the linear region, but are insufficient to dielectrically modify non-polar materials such as polyethylene, polypropylene and their derivatives.

A fundamental question for both DMA and DEA concerns the true physical meaning of the entropy and enthalpy of activation as determined from the frequency dependence of the loss peak. If the peak observed is "elementary", i.e. it describes a pure and unique relaxation process, then the value obtained by DMA and DEA is founded, but when a non-negligible degree of cooperation is responsible for the global peak, it is difficult to use any classical model to fit the data; both thermally activated and free volume analyses are unfounded.

An important limitation of a.c. dielectric devices at high frequencies is the inability to separate different transitions with close activation energies,

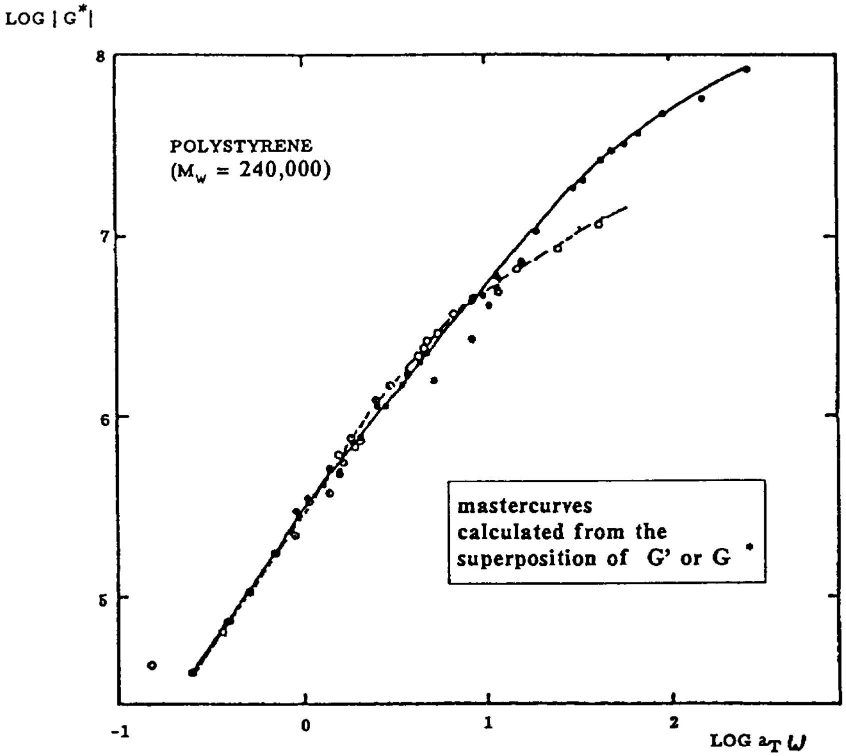


Fig. 6. Superposition onto a master curve of polystyrene, showing that mastercurve extrapolation needs the correct definition of the superposing variable.

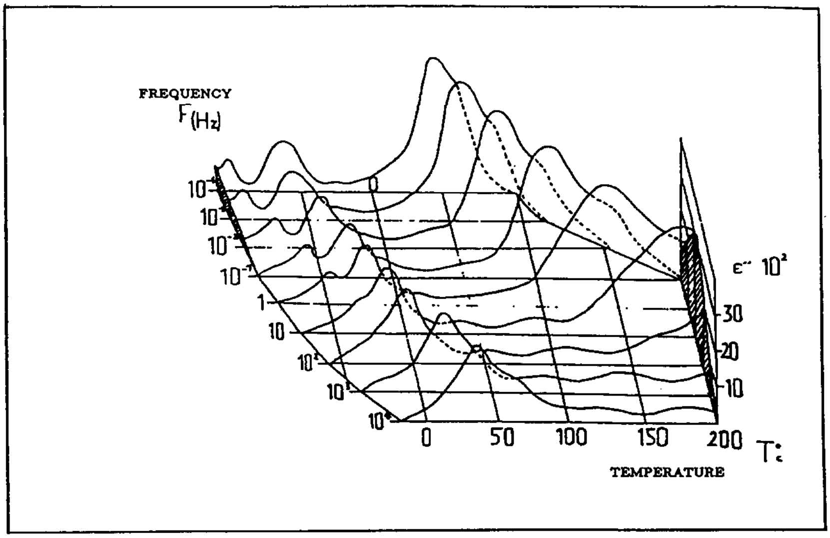


Fig. 7. Frequency versus temperature with the dielectric loss plotted on the *Z* axis. Results are calculated from TSC/RMA data. Note the improved peak resolution at low frequencies. From Goyaud [10].

because the effect of the high frequency is to merge neighboring peaks instead of resolving their fine differences. DMA and DEA cannot separate cooperative relaxation processes to isolate the coupling between elementary relaxation modes. Figure 7 shows how lower frequencies permit resolution of complex peaks.

TSC

Thermal stimulated current (TSC) is a technique of applying a d.c. voltage to a material in order to orient dipoles sensitive to the electric field [1–4]. The temperature is then lowered (with the field maintained) in order to reduce internal motions, "trapping" the polarized dipoles within the material. The sample is then reheated, allowing thermal energy to release the "trapped" molecular motions. As this occurs, a small current is observed, corresponding to one or more types of relaxations. This technique is used to characterize molecular motions in a variety of polymer types including films, coatings, fibres, powders and bulk specimens. TSC is used to study the

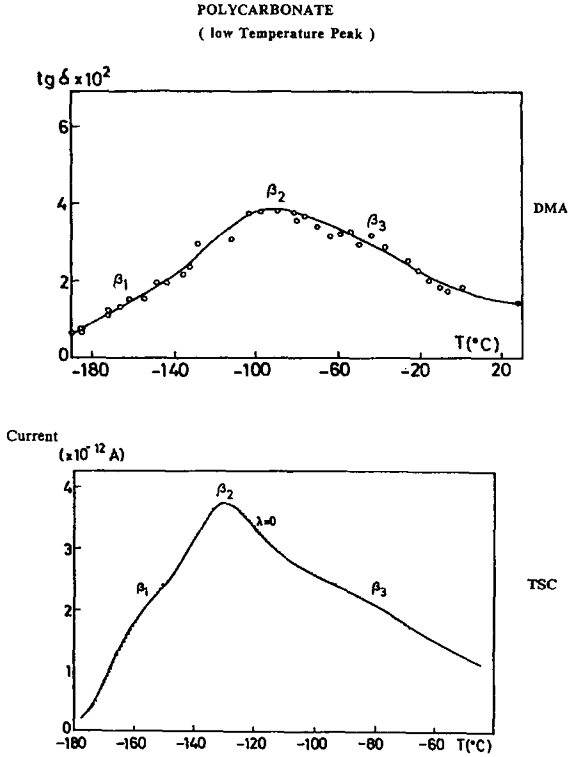


Fig. 8. A comparison of the resolution of DMA and TSC for the beta peak from polycarbonate. DSC data is from LeGrand as quoted by Vanderschueren [2] who also produced the TSC data.

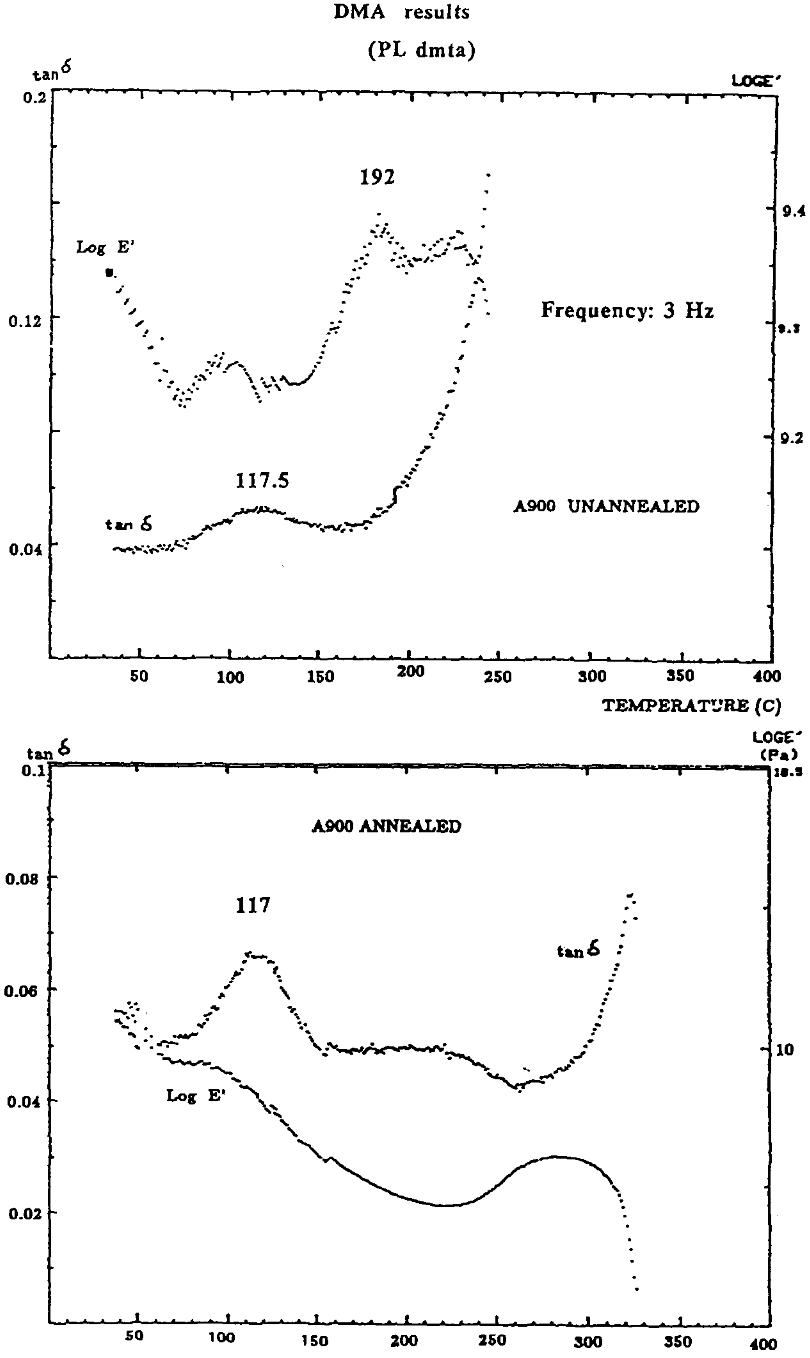


Fig. 9. DMA results for Vectra A900 liquid crystal, both annealed and unannealed. The unannealed results show jumps typical of sample motion during the experiment.

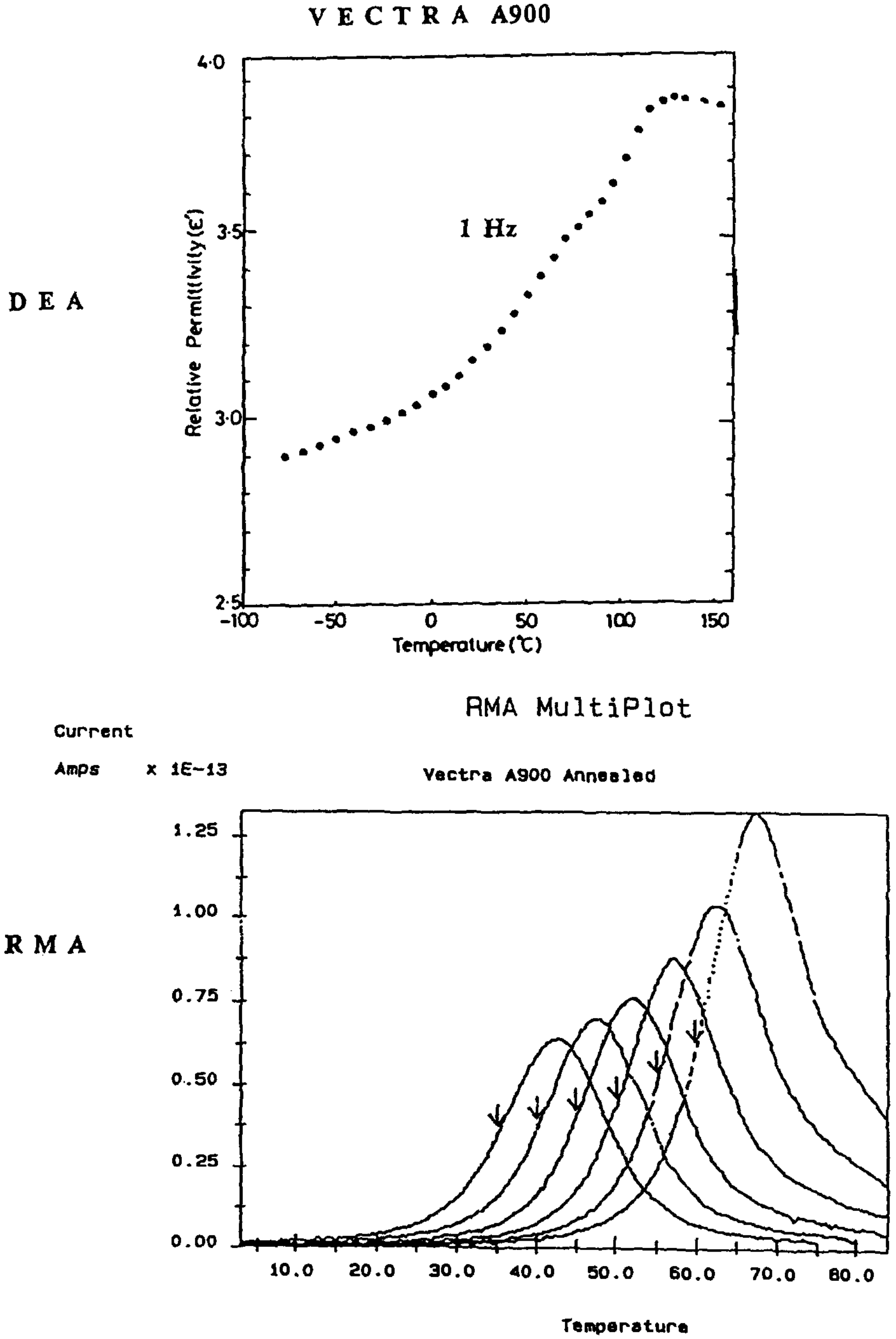


Fig. 10. Comparison of DEA and RMA results for Vectra A900. The "thermally windowed" TSC/RMA data is the analysis of the "bump" shown in the DEA graph at approximately 70 °C.

degree of curing, orientation, internal stress, aging, segregation of phases in copolymers and adhesion.

TSC provides advantages in both sensitivity and sample preparation. The output is a plot of depolarization current versus temperature, showing global peaks for each motion taking place during the recovery process. Temperature can be scanned from −150 °C to 400 °C, exploring the rubber and rubbery flow regions as easily as the solid state. The output is very similar to a plot of tan δ versus T obtained with DMA at very low frequencies, but with higher sensitivity. Figure 8 shows the polycarbonate β peak as measured by DMA and by TSC [2]. Sample preparation is simpler than for a normal DEA experiment and does not have the geometrical and temperature restrictions imposed by DMA. Paints, glues and other coatings can be studied directly on their normal substrates, which is a definite advantage for quality control applications, with the security that the coating is being studied in the same environment as it will be used in real life.

Figure 9 shows the results from a DMA for a liquid crystal material, Vectra A900. The annealed and unannealed graphs show differences, but it is hard to quantify them into kinetic parameters. Likewise, Fig. 10 shows a DEA graph for Vectra A900; note that there is a small "bump" at approximately 80 °C, but again it is difficult to quantify or even specify a peak temperature for this peak. In contrast, the bottom of Fig. 10 shows a TSC/RMA analysis (see discussion below) for the "bump". Peaks are well resolved and can be quantitatively defined. Figure 11 shows how these separated peaks together create the global peak. It is interesting to note that the maximum temperature in the global peak is not the same as the maximum temperature for the isolated local motion with the greatest peak height, bringing into question the attitude that the shift of a peak temperature with frequency as done by DMA or DEA without isolating cooperative motion reveals information that is quantitatively useful.

The TSC method also has disadvantages: it cannot be applied to conductive or semiconductor materials with resistances less than 10–9 $\Omega\ m^{-1}$ thickness, and the presence of space charges in the structures must also be handled with care to avoid pitfalls and artifacts.

The upper temperature limit of analysis is the onset of flow of the sample, which appears as a current discharge (the sample behaves as a battery which drains the charges accumulated at the surfaces). In that respect, a DSC and a TSC are complementary since DSC characterizes well semi-crystalline materials while TSC excels with amorphous materials.

Relaxation map analysis (RMA)

The polarization/depolarization parameters used for TSC analysis can be modified to separate the individual modes of relaxations from the global peaks. This is a very important advantage since the relaxation process during

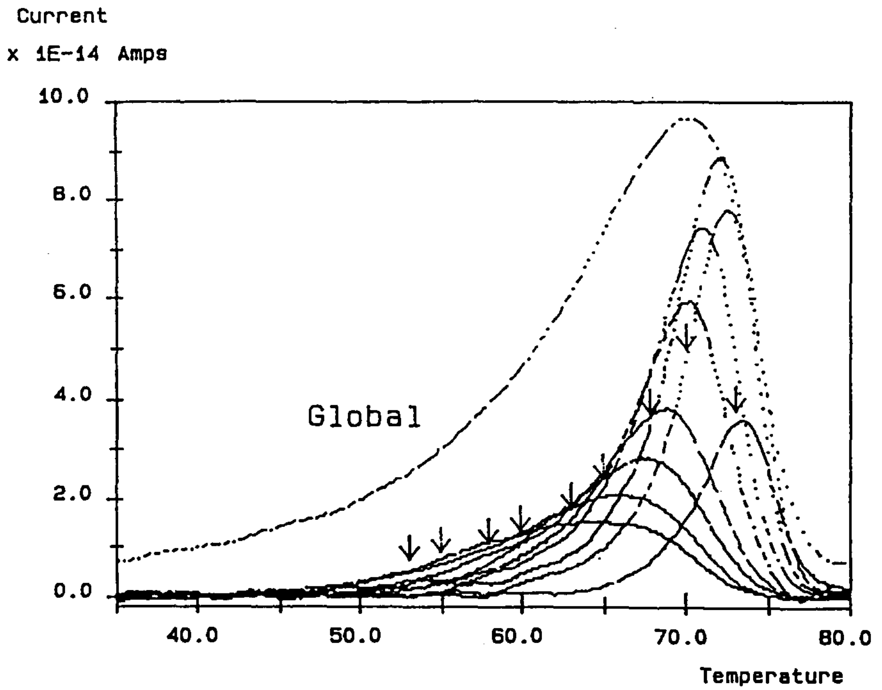


Fig. 11. Comparison of "thermally windowed" TSC/RMA peaks and the global TSC trace for Vectra A900.

the glass transition is due to a number of different relaxation modes, and by isolating each relaxation mode, a true understanding of the macroscopic properties of the material can be obtained.

"Thermal windowing", the process of isolating individual modes of relaxation, has been applied extensively for the last 15 years at the Laboratoire Physique des Solides in Toulouse, France [1–4]. Thermal windowing consists of first polarizing (orienting) only a fragment of the full spectrum of relaxations, then partially depolarizing (disorienting) to isolate or "window" a single relaxation process.

Thermal windowing is experimentally simple: (1) A voltage is applied to the sample for a short time, (2) Then cool slightly (typically 5 ° C) to trap the polarized segments. (3) Remove the polarizing voltage to allow some of the relaxation modes to return to equilibrium. (4) Then cool the sample further. (5) Finally, measure the depolarization current while reheating at a constant rate. These steps are repeated using different polarization and depolarization temperatures to separate the global peak into individual relaxation modes as shown in Figs. 10 and 11.

Each of these elementary relaxation curves can be mathematically transformed into its Arrhenius representation and plotted as log τ versus $1/T$,

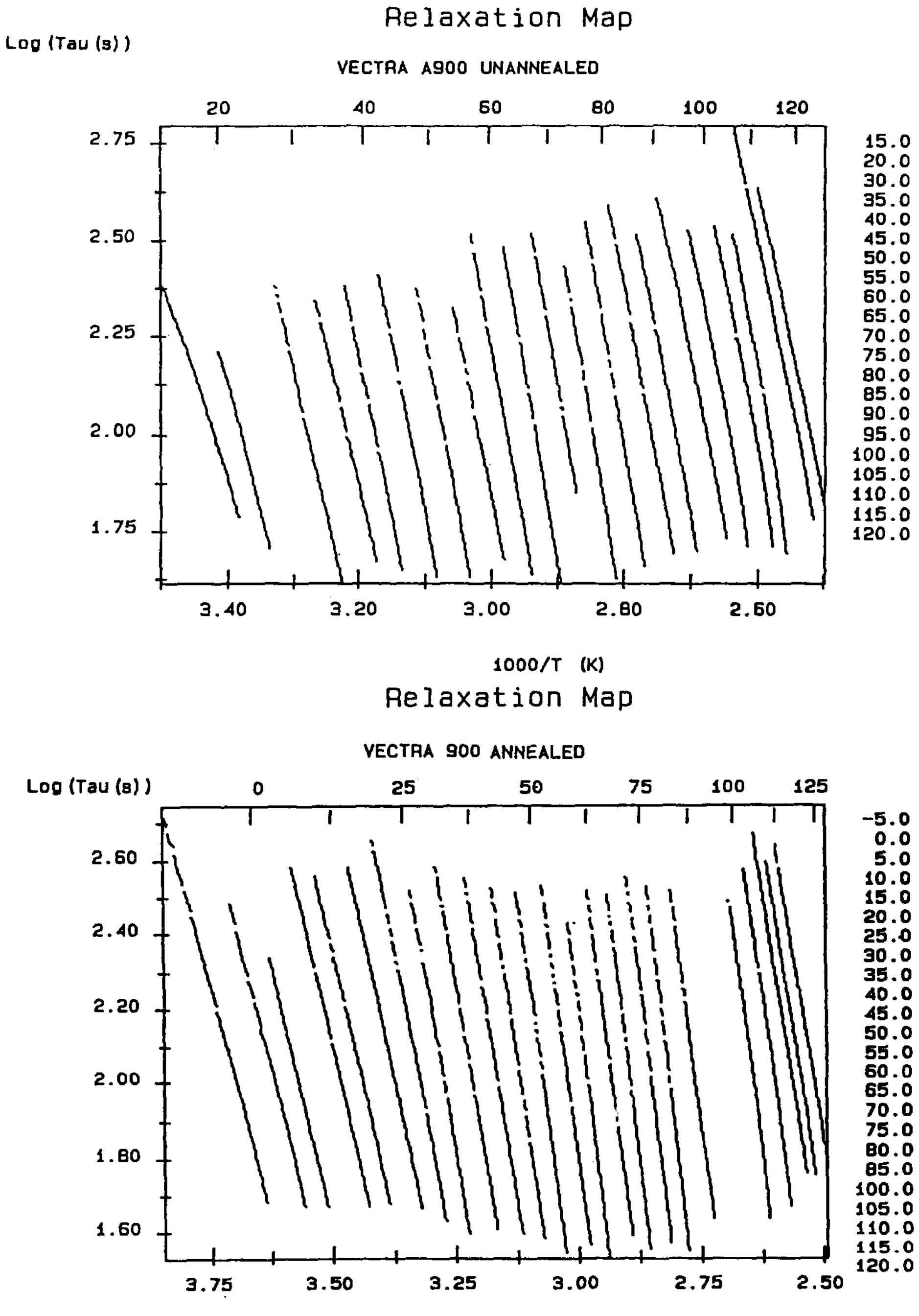


Fig. 12. Relaxation maps for unannealed and annealed Vectra A900. The right hand numbers are the polarization temperature (T_p). Each line corresponds to a certain T_p.

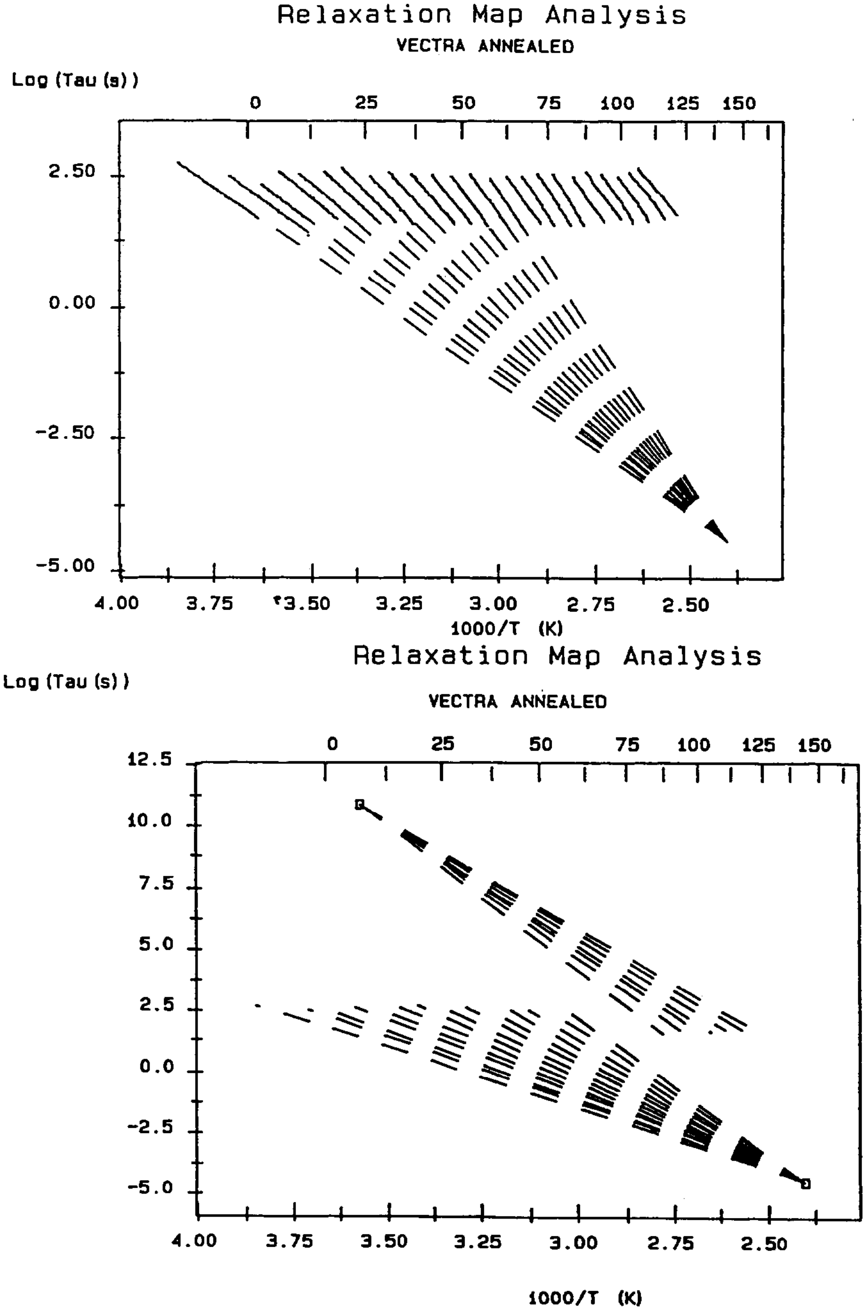


Fig. 13. Computer analysis to determine the T_g compensation point for annealed Vectra A900. The top graph shows a positive compensation, and the bottom graph displays both a positive and a negative compensation.

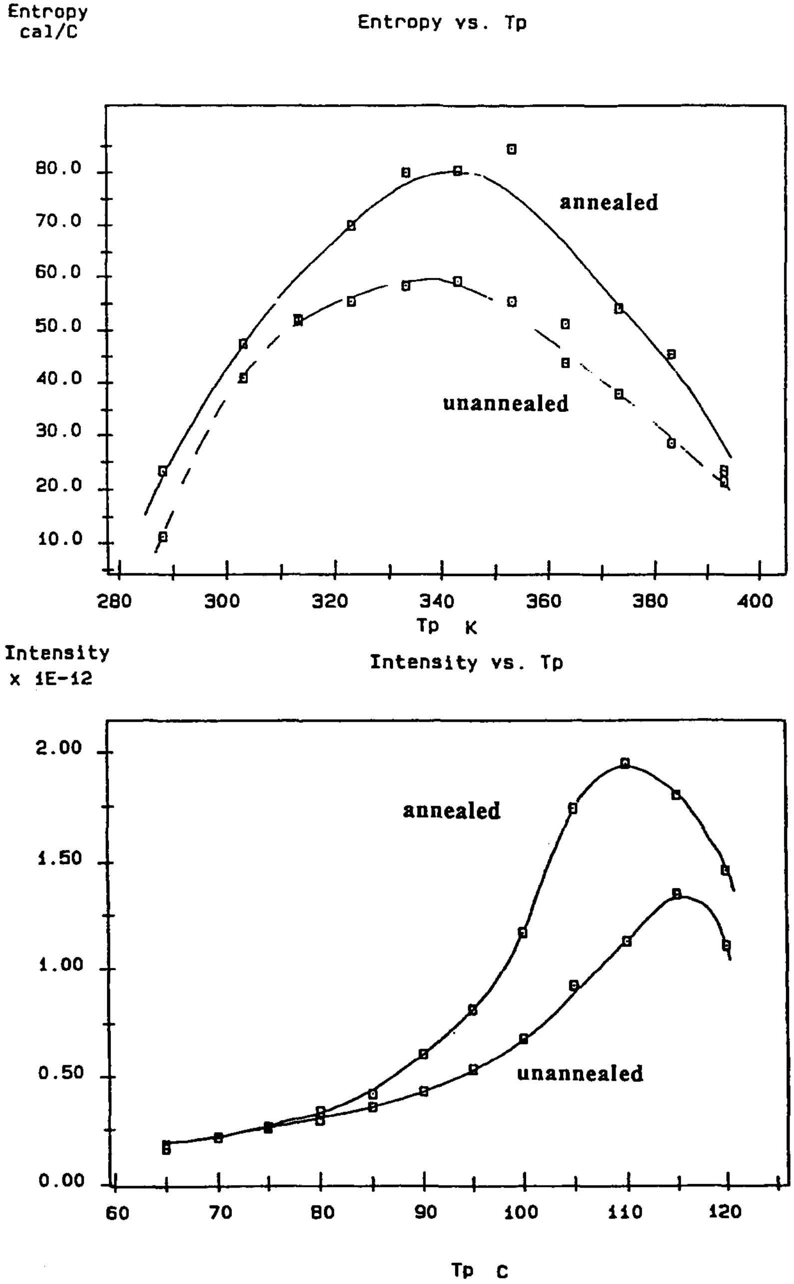
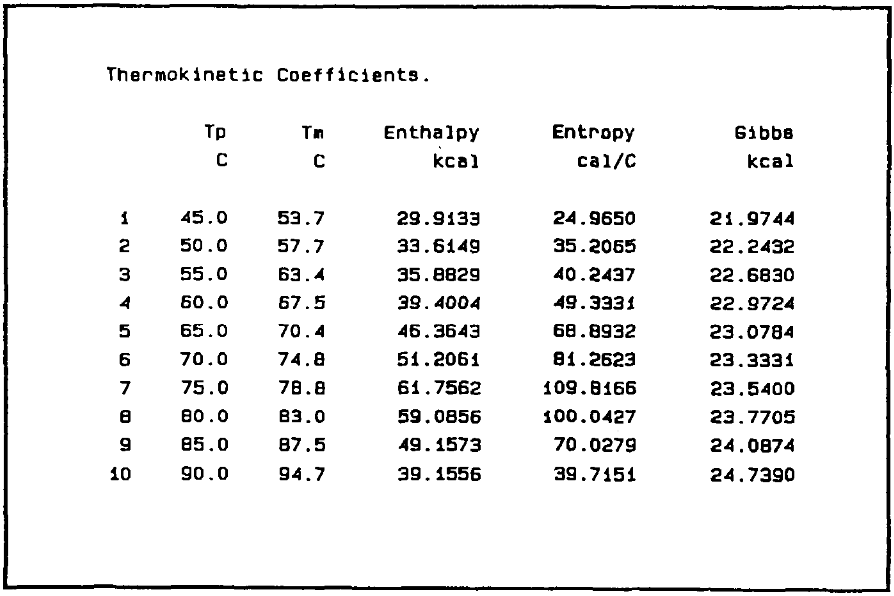


Fig. 14. The fitting of the individual Arrhenius lines (Fig. 12) results in calculation of the entropy, enthalpy and Gibbs free energy of the system. The plot of entropy versus polarization temperature (T_p) illustrates the entropic definition of T_g as a maximum. The intensity of the peaks (Fig. 10) at their maximum does not yield the same temperature for the transition.

which expresses the variation of relaxation time versus temperature as shown as the individual lines in Fig. 12.

A relaxation map (Fig. 12) is the result of transforming all of the



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Thermokinetic Coefficients.

          Tp       Tm      Enthalpy        Entropy         Gibbs
           C        C          kcal          cal/C          kcal

 1      45.0     53.7       29.9133        24.9650       21.9744
 2      50.0     57.7       33.6149        35.2065       22.2432
 3      55.0     63.4       35.8829        40.2437       22.6830
 4      60.0     67.5       39.4004        49.3331       22.9724
 5      65.0     70.4       46.3643        68.8932       23.0784
 6      70.0     74.8       51.2061        81.2623       23.3331
 7      75.0     78.8       61.7562       109.8166       23.5400
 8      80.0     83.0       59.0856       100.0427       23.7705
 9      85.0     87.5       49.1573        70.0279       24.0874
10      90.0     94.7       39.1556        39.7151       24.7390
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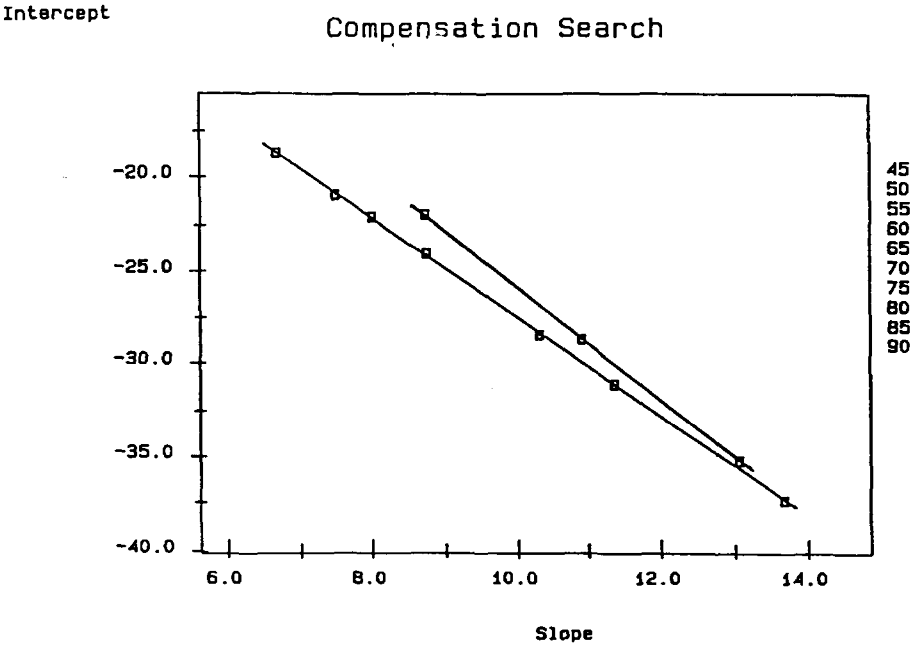

Fig. 15. Using a compensation search to calculate the compensation point characteristics for PMMA. Each point on the compensation search represents the intercept and slope for a single Arrhenius line of the relaxation map. The enthalpy and entropy can also be calculated from the Arrhenius lines (top).

elementary peaks obtained at various T_p into their Arrhenius representation. RMA (Relaxation Map Analysis) correlates the single relaxation modes to the thermokinetic (free energy, entropy and enthalpy) and/or other physical variables [6–8].

The data can also be represented as the free energy, entropy and enthalpy of activation versus temperature, and T_g is defined as the temperature at the

Dielectric constants
PPO

Frequency Hz.	-60°C		-55°C		-50°C	
	ε'	ε"	ε'	ε"	ε'	ε"
10^2	4.340	0.545	5.612	0.586	5.927	0.183
$3x10^2$	3.815	0.312	4.975	0.700	5.724	0.400
10^3	3.657	0.230	4.430	0.595	5.374	0.615
$3x10^3$	3.533	0.170	3.975	0.433	4.760	0.700
10^4	3.430	0.122	3.725	0.272	4.204	0.445
$3x10^4$	3.295	0.100	3.510	0.189	3.882	0.400
10^5	3.165	0.064	3.340	0.133	3.645	0.256
$6.3x10^5$	3.113	---	3.215	0.086	3.329	0.150
$3.3x10^6$	3.045	---	3.113	0.072	3.181	0.111

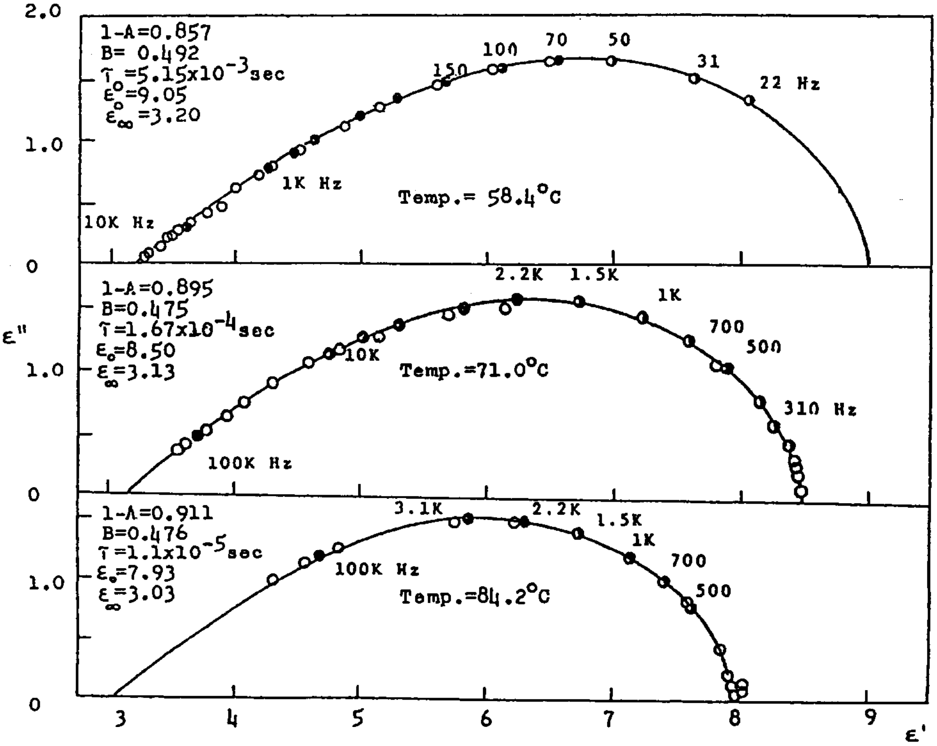

Fig. 16. Cole/Davidson plots for polyvinylacetate. These plots can be determined either from DEA or TSC/RMA experiments [9].

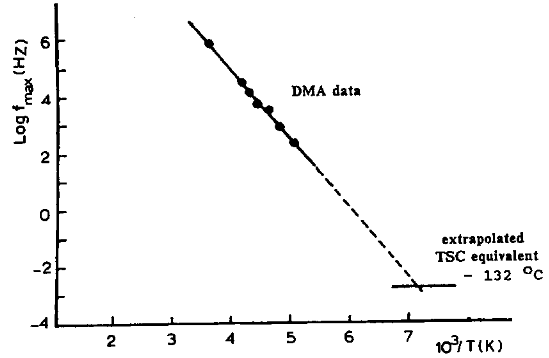

Fig. 17. Extrapolation on a frequency map from DMA information to the TSC equivalent temperature. From Vanderscheuren [2].

maximum of entropy (or enthalpy) (Fig. 14). Compensation phenomena (as shown by intercept versus slope plots in Fig. 15) determine the degree of coupling between the coupled relaxation modes which describe the thermo-kinetic state of the amorphous phase.

Thermal windowing data can also be converted into ε' and ε'' values, thus allowing an easy comparison with ordinary dielectric data. The great advantage of separating the individual relaxation times from global peaks using thermal windowing is not only being able to study their cooperation using a compensation search, but also to be able to calculate the response of the material at other frequencies and temperatures without resorting to time–temperature superposition. Comparison with a.c. data is remarkably good [9] as shown in Fig. 8 provided the a.c. data are extrapolated to the corresponding TSC equivalent frequency (Fig. 17). Cole/Davidson plots can be obtained from RMA and compare well with similar plots obtained by dielectric measurements (Fig. 16 shows such a plot).

RMA provides a unique opportunity to quantify the bonding strength, to both plastic and metallic supports of paints, coating and adhesives.

CONCLUSION

We have briefly compared the merits and limitations of the most popular thermal analysis techniques with a less known TSC technique recently introduced in a commercial instrument. The TSC technique's superior sensitivity allows detection of transitions that other techniques cannot see or separate.

Research scientists who have used other techniques will recognize the benefits of a new instrument and technique which combines the output from the traditional apparatus with a new understanding of the structure and behavior of polymers. In particular, it becomes rapidly clear to the users that the description of the elementary relaxation modes, their thermo-kinetic characteristics (activation energy and entropy), and quantification of the cooperative coupling is essential for a complete understanding of the macroscopic properties of materials.

ACKNOWLEDGMENT

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