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The Use of AC Measurements to Determine Physical Processes Occurring in Thin Film Dielectrics

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One of the major problems encountered in quantitative investigations of thin films (thickness $<1\ \mu$m) is that of obtaining information on structure and composition. Basically this is due to the small amount of material available yielding results below the detection limit of the usual non-destructive analytical equipment.

This paper gives an analytical technique which is a modification of that used for bulk dielectrics, and describes its application to one type of ultra-violet radiation-formed thin film polymer. From the experimental results, conclusions are drawn relating to the "electrical" structure of the material, and suitable ways of extending the range of the technique are outlined.

1. Introduction

The greatest difficulty encountered in working with thin film dielectrics, especially polymer films, which can be as thin as 100 Å, is in determining either the composition or the structure of the material. This is primarily because of the small amount of material available. The method of attack used here yields some insight into the "dipole" properties of the thin film dielectric, provided that there is sufficient dipole interaction present to be detected. This last condition, unfortunately, is not always fulfilled with low loss thin film dielectrics.

2. Theory

The theory behind this method of investigation is outlined in references 1 and 2. The significant expression extracted from these articles is the equation linking f_m, the frequency of maximum absorption ("dissipation factor" or "power factor") with temperature

$$f_m = f_0/\pi \exp - (\Delta F/RT) \qquad (1)$$

Whence

$$f_m = \tfrac{1}{2}\pi\tau = f_0/\pi \exp(\Delta S/R) \exp(-\Delta E/RT) \qquad (2)$$

where: τ is the period of oscillation of the absorption "centres" at maximum absorption; ΔS is the entropy change on dipole rotation; ΔF is the free energy of activation; ΔE is the dipole rotation thermal activation energy; R is the gas constant; f_0 is the natural frequency of oscillation of a dipole in its potential well.

If the theory of absolute reaction rates is applied to the phenomenon of dielectric absorption, the term f_0/π in the above equation can be replaced by kT/h, where k is Boltzman's constant, T is the absolute temperature, and h is Planck's constant. Thus we have

$$f_m = kT/h \exp \Delta S/R \exp -\Delta E/RT \qquad (3)$$

Assuming a one dipole system therefore, we have a relationship of the form

$$f_m = A \exp -\Delta E/RT \qquad (4)$$

Thus $\log_e f_m$ should be a linear function of $1/T$.

Information concerning the nature of the rotation process may be obtained by dividing up the free energy of activation ΔF into thermal energy ΔE and an entropy term ΔS. ΔF is obtained from equation 1, ΔE from the slope of the plot of equation 4 and ΔS from the difference since

$$\Delta F = \Delta E - T\Delta S \qquad (5)$$

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The values of entropy of activation thus obtained give an indication of the magnitude of rearrangement occurring on dipole rotation. In the specific case of polymer dielectrics it can indicate whether the polymer chain as a whole or a side chain is contributing to the absorption process.

3. Experimental

The dielectrics used in this work were ultraviolet and glow discharge formed polymer films, which could be laid down at thicknesses between 100 Å and 3000 Å [3]. The electrode area of the samples was 0.3 cm^2, which for a 500 Å film of permittivity 2.65 gave a capacitance of 14000 $\mu\mu$F. The samples were measured in an evacuated copper cryostat which was immersed in liquid nitrogen, and were cooled to that temperature by admitting pure helium gas. The samples were heated using a DC heater clamped on the back of the substrate holder.

Consider the hypothetical series of loss peaks shown in fig. 1, for a material whose dielectric absorption obeys equation 4, the plot of which is fig. 2. The temperatures indicated in fig. 1 are taken from fig. 2 using an arbitrary activation

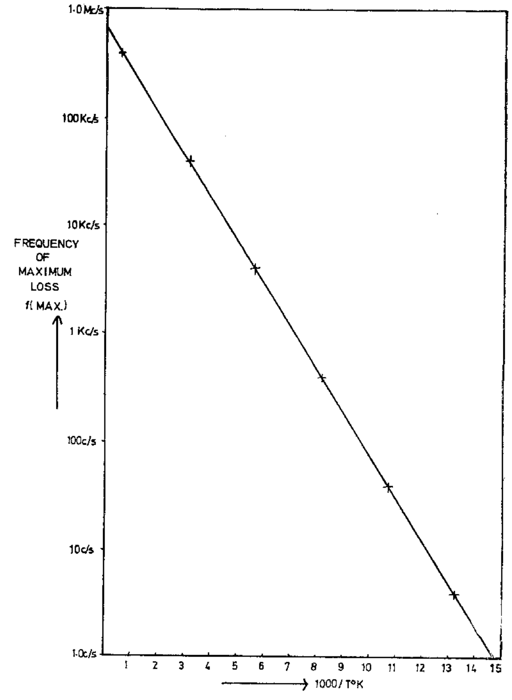

Figure 2 $f_{max}/[1/T(°\,K)]$ curve for theoretical case.

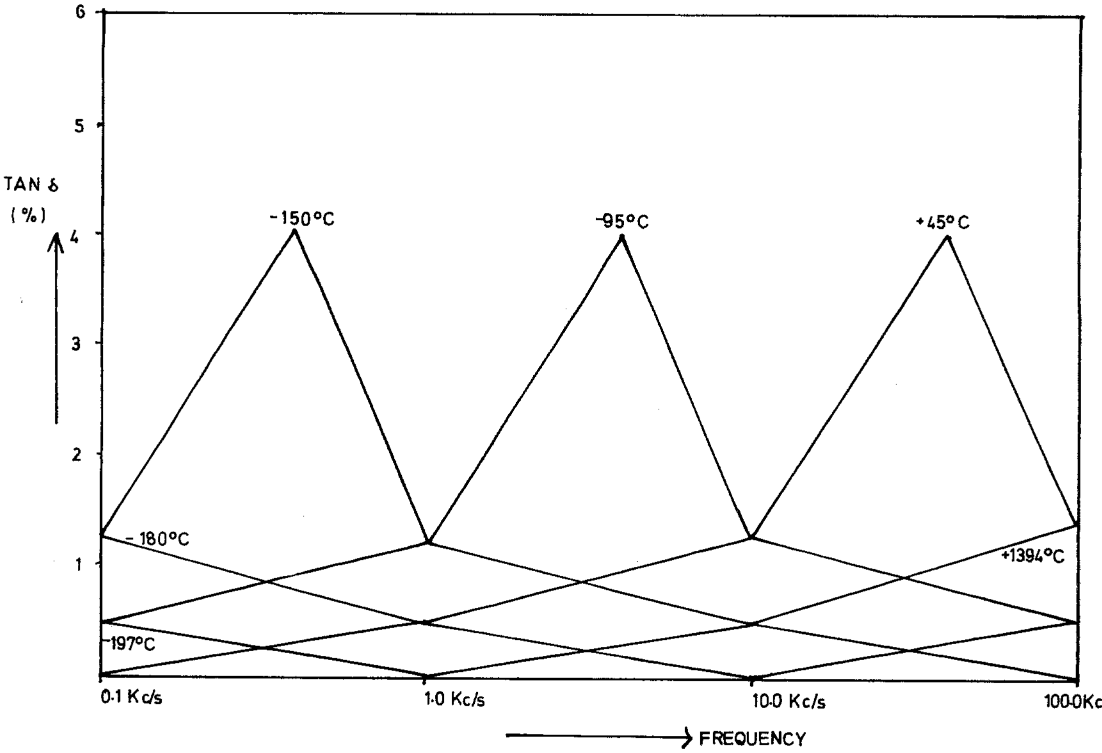

Figure 1 Loss factor/frequency/temperature curves for theoretical case.

energy of 0.08 eV. It can be seen that the greater the activation energy the more sensitive is the variation of the frequency of maximum absorption with temperature. Thus, in an experiment to measure the variation of dielectric loss with frequency at spot temperatures, the cryostat would have to be controlled to a very fine degree, or the curve would become "smeared out" and possibly the peak "lost". The alternative is to measure the variation of loss with temperature at spot frequencies. Frequency can of course be controlled to a much greater degree than temperature. The question then arises however, whether or not one can transpose curves thus obtained to give the correct activation energies. To test this the curves in fig. 3 were drawn from information in fig. 1. These, as it can be seen, have peaks occurring at different temperatures. The frequencies and temperatures of these peaks were plotted assuming a relationship of the form of equation 4, in fig. 4. The activation energy obtained from this graph, within the limits of drawing error, is the same as that originally used in plotting fig. 2. Thus it would seem that it is possible to carry out the work in this "transposed" way and obtain the same result.

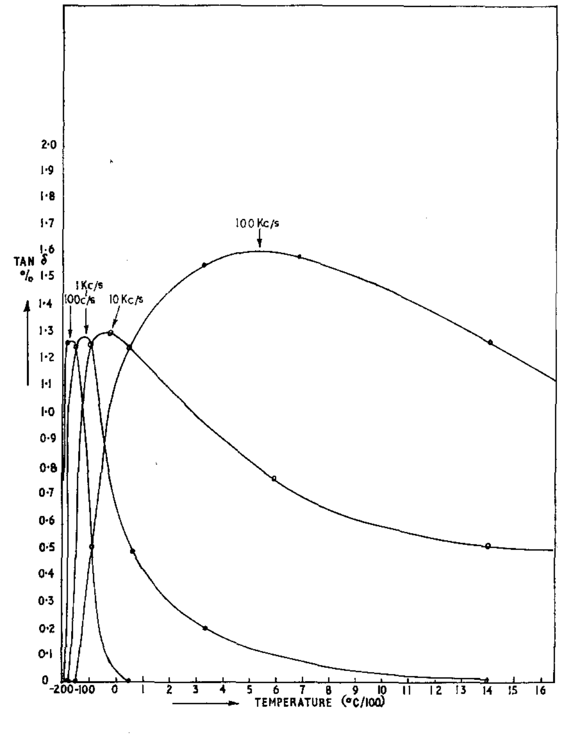

Figure 3 Loss factor/temperature/frequency curve for theoretical case.

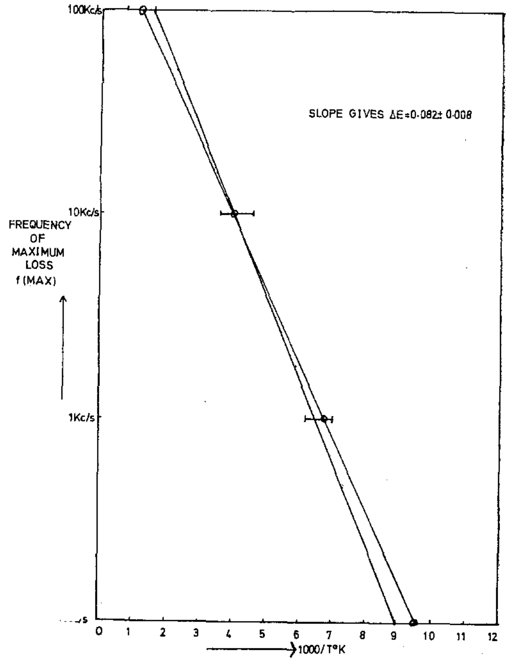

Figure 4 $f_{max}/[1/T(^{\circ}\,K)]$ curve taken from fig. 3.

4. Results

Fig. 5 is a set of experimental curves obtained for acetylene dicarboxylic acid dimethyl ester polymer. Of the polymer dielectrics used this was the only one which showed peaks in the loss/temperature curve. It was decided to try a possible large-side-chain polymer after failure to observe any such peaks using other polymers such as polystyrene, polyacetylene, or polycyanogen. Fig. 6 is a possible empirical structure for the polymer.

An activation energy for dipole rotation was obtained from fig. 5 by plotting fig. 7. This resulted in a straight line. The following table is a summary of the values of ΔF, ΔE and ΔS obtained for this polymer from fig. 6.

5. Conclusions

The value -0.0009 eV/° K, or expressed in normal entropy units, -9 eu, is extremely small and it indicates very little rearrangement occurring in the polymer during dielectric absorption. A close study of fig. 6 reveals the most likely seat of the absorption involving a small part of the polymer would be the C=O group, which is known to have a dipole moment. It seems

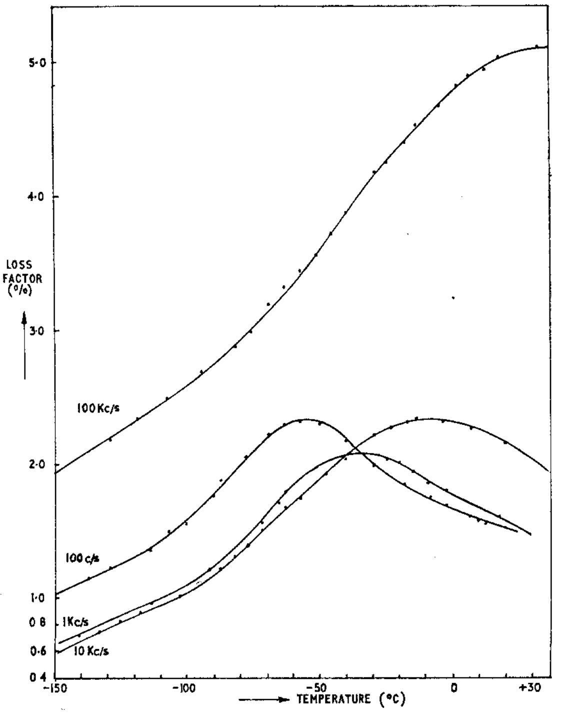

Figure 5 Loss factor/temperature/frequency curves for poly(ADADE).

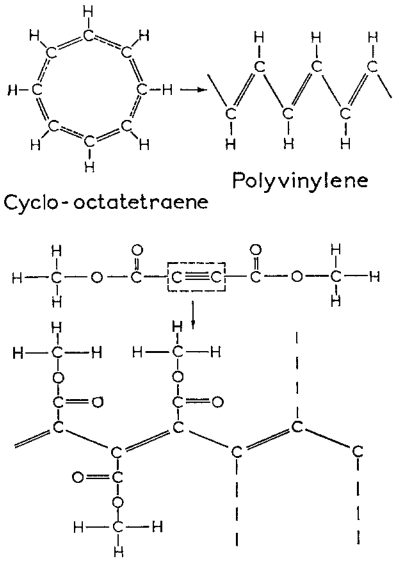

Figure 6 Possible polymerised products of ultra-violet irradiated monomers.

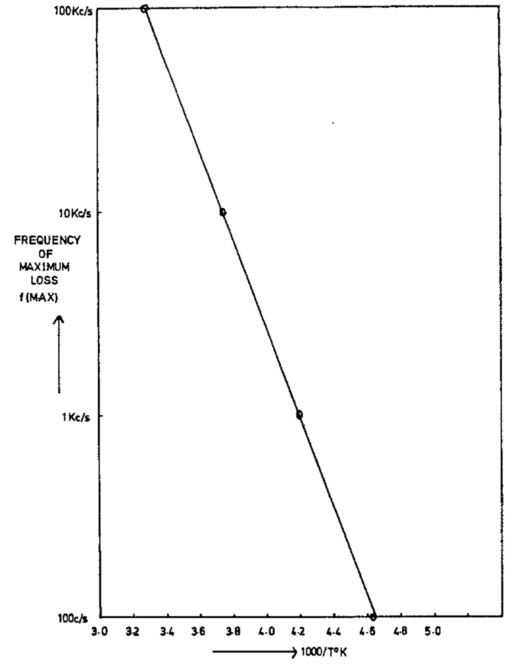

Figure 7 $f_{max}/[1/T(° K)]$ curve for poly(ADADE).

TABLE I

Temp (° K)	f_{max} (cycles/sec)	Constant A	ΔF(eV)	ΔE(eV)	ΔS(eV/T)
216	10^2	9×10^{11}	0.506	0.43	−0.0008
238	10^3	9×10^{11}	0.514	0.43	−0.0009
265	10^4	9×10^{11}	0.555	0.43	−0.0009
311	10^5	9×10^{11}	0.557	0.43	−0.0009

justified therefore to conclude that the whole structure of the polymer does not take part in the dielectric absorption process, only the carboxyl group, at frequencies above 100 c/sec at room temperature.

6. Discussion

The aim of this paper was to indicate the problems involved in the analysis of thin layers and a possible method of overcoming some of them. It has been shown that the method described can be used to find major "structural" units, although the basic difference between bulk materials and thin films is the main stumbling block. Compared with bulk materials thin films are strained, which effects a spread in relaxation times and "peak broadening". Thin films also contain more anisotropy than bulk materials because of their method of formation, expecially these polymerised films where the material is chemically formed on the substrate. The assumption made previous to equation 4 therefore needs modifying in some way to allow both for these deviations and for a range of relaxation times.

This approach could be extended to yield more information in two ways: the extension of the measurements to temperatures above ambient would raise the frequency of the sub-audio peaks into a more accessible region. Increasing the measurement frequency into the radio-frequency region would yield the loss peaks of those materials with smaller structural units, and so be useful with a much wider range of materials, particularly those used for low loss capacitor dielectrics.

References

1. "Progress in Dielectrics", Vol. 3 (Heywood, London) p. 153.
2. G. GLASSTONE *et al* in "Theory of Rate Processes", edited by L. P. Hammett (McGraw-Hill, New York, 1941) p. 544.
3. M. E. FABIAN, *J. Matls. Sci.* **2** (1967) 424.