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COMPARISON OF DYNAMIC MECHANICAL AND DIELECTRIC THERMAL ANALYSIS ON CURE STUDIES FOR COMPOSITES

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Dielectric measurements covering a wide frequency range provide one of the few practical methods for monitoring the cure of thermosets (epoxy, etc.) using relatively non-intrusive sensors. The measurements form the basis of a manufacturing control cycle, in the autoclave, provided the rheological state of the thermoset can be related to the dielectric constant (ε') and loss factor (tan δ). The present paper concerns further investigations in our laboratory of the correlation between mechanical and dielectric behaviour during cure (1).

Theory

A. Dielectric

When a voltage is applied across an insulating material, such as a polymer or organic liquid, polarization occurs in three ways of importance in the present work. The polarization produces a nearly proportional dielectric constant described approximately by the Clausius-Mosotti equation (2).

$$\varepsilon'(\text{Total}) = \varepsilon'(\text{atomic}) + \varepsilon'(\text{dipolar}) + \varepsilon'(\text{space charge})$$

The term ε' (atomic) has a value always around 2 and is due to charge perturbation within atoms and bonds. The dipolar part of ε' gives rise to the "relaxation" behaviour of polar molecules when the frequency of applied field matches the molecular dipole re-orientation frequency. It is this dipole orientation term that is absent below a polymer's Tg and present well above Tg. It adds up to 3 to the dielectric constant total. The space charge term is absent in pure single phase organic systems. However, thermosets are far from pure and indeed usually have catalyst, cure promoters, added.

Ionic charges are thus pulled through a material in the fluid state, but are immobilised in the glassy state. The pseudo dielectric constant resulting from separation of these charges can be vast, in the order of 100's.

From the above brief resumê, it is apparant that when space charge polarization is present, it overwhelms the dipole term, which is the best molecular probe. By the very diffusional nature of the space charge polarization, its magnitude is reduced by measuring at higher frequencies. Dipolar effects on the other hand shift location with frequency, but do not drop in magnitude.

The schematic change in ε' and tanδ expected during an isothermal polymerization of a thermoset is shown in the lower part of Figure 1. The frequency of measurement is assumed to be high enough that the dipolar process (tan δ loss peak) is observed as the material is transformed from a fluid into an immobile glass. This can be regarded as equivalent to a Tg change produced by chemical change with time. When Tg passes the isothermal reaction temperature, the system becomes glassy and further cure at this temperature is minimal.

B. Mechanical

Also shown in Figure 1 are the schematic dynamic mechanical property changes expected during the same isothermal cure. These are more straight forward to interpret. The material is initially a fluid in a mildly viscoelastic state, with very low modulus (ε'). As the cross-linking reaction progresses a gel is first formed and under ideal conditions (3) a tan δ peak is observed as the polymer molecules are reduced in mobility by the gelling process. The main event in mechanical property change is the large (factor of 1,000) modulus change as Tg is driven up through the reaction temperature by the cross-linking process. The mechanical measurements do not sense the ionic migration which gives rise to space charge effects in the dielectric case.

Mechanical changes are relatively easy to study in the laboratory, but as yet a satisfactory remote sensor has not been devised for mechanical measurements.

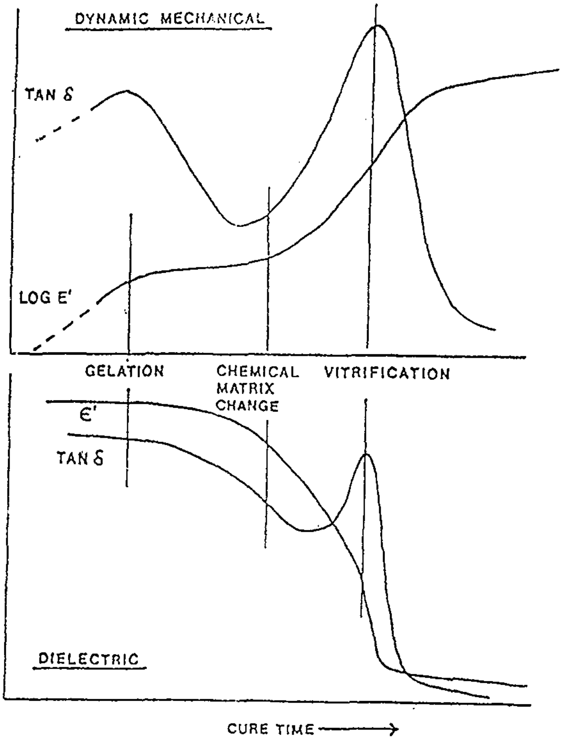
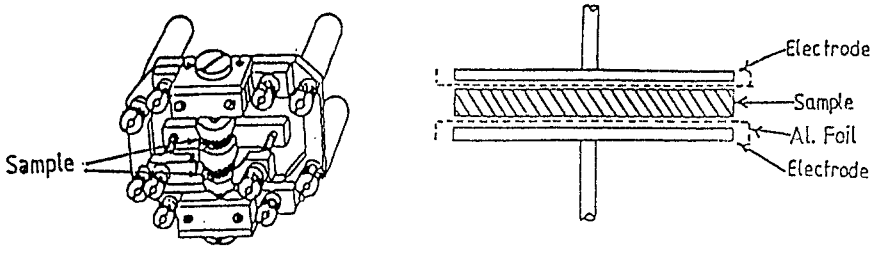


Fig. 1 Schematic changes in Dynamic Mecanical and Dielectric data during isothermal epoxy cure.

Experimental

Laboratory comparisons were made of dynamic mechanical and dielectric data during cure. For the mechanical case, the Polymer Laboratories Dynamic Mechanical Thermal Analyser(DMTA) was utilised in the shear mode. Rapid isothermal temperature rise was selected on software, so that the isothermal operating temperature was always achieved within 3 minutes. Cure time was recorded from the point of aquisition of the isothermal temperature.

The shear mode of clamping with the DMTA measured the epoxy directly with no added support. This required the use of the DMTA power head providing 14N maximum force. A shear plate was clamped in the DMTA drive and liquid epoxy placed above and below this, between clamping studs, to give the shear sandwich geometry, as shown in figure 2.



(a) (b)

Fig. 2 Clamping arrangements for cure studies.
(a) Shear head arrangement for the DMTA
(b) Parallel plate electrode arrangement for the DETA

Dielectric measurements were performed on a fully automatic system, the PL-Dielectric Thermal Analyser(DETA). The same epoxy resin systems which were employed in the DMTA measurements were measured as disc samples, approximately 1mm in thickness between parallel plate electrodes of the DETA. In order to allow removal of the sample after cure,the electrodes were completely covered in thin aluminium foil prior to insertion of the sample (Figure 2). The electrodes were locked at the required sample gap and any contraction of the epoxy was taken up by movement of the aluminium foil. The same isothermal temperature control conditions were employed as in the DMTA, with temperature rise again being achieved in 3 minutes or less.

Results and Discussion

The cross-linking with time in epoxy systems is usually via diamine reaction with terminal epoxide groups on the prepolymer. The effect of this is to progressively reduce molecular motion until the system becomes 'glassy' at the reaction temperature.

The behaviour is clearly illustrated in Figure 3, showing DMTA measurements in the shear mode on Araldite 'Rapid' at 40°C. The modulus (G') increases with time to glassy levels and during this chemically driven vitrification tan and

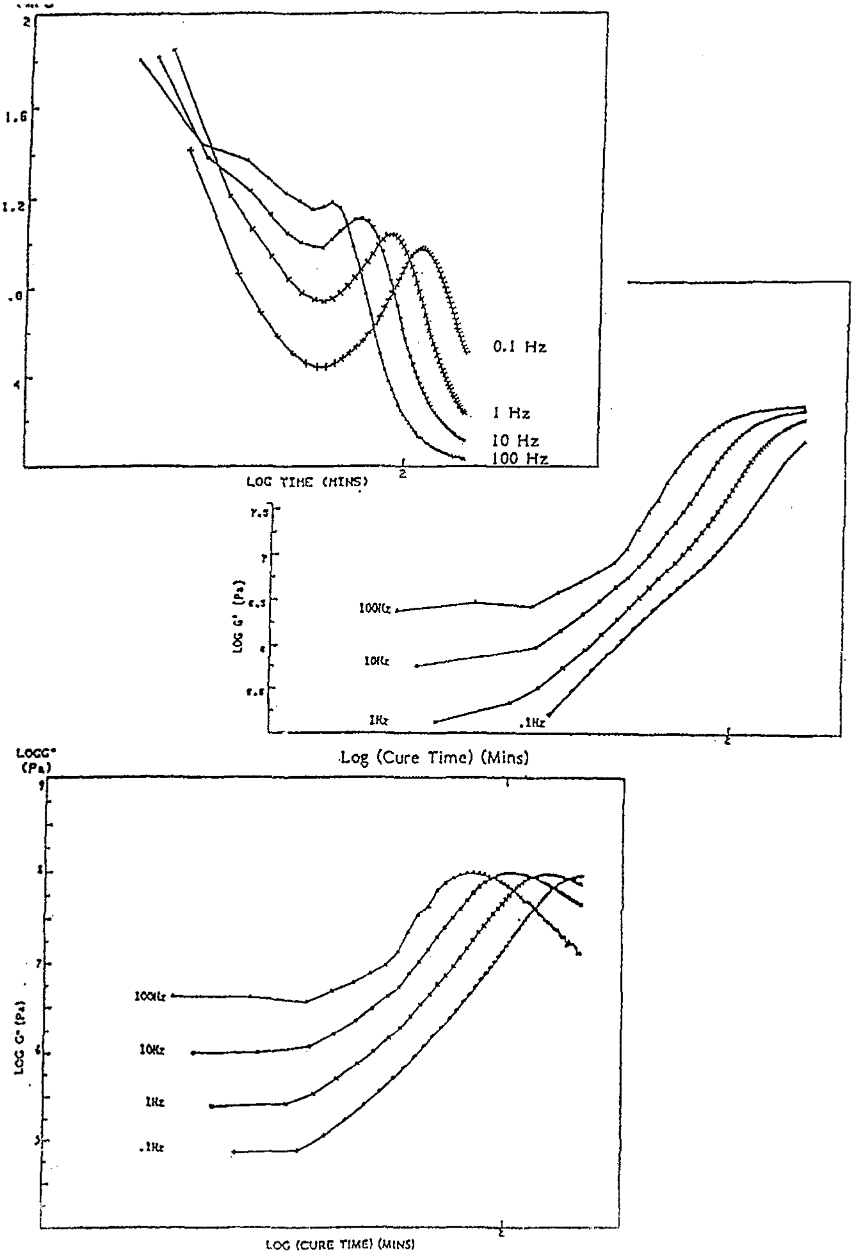


Fig 3

Dynamic Mechanical data for Araldite Rapid during cure at 40°C.

the loss modulus (G") exhibit maxima as expected. The loss peak positions as a function of measuring frequency are shown in Table 1.

TABLE 1

Frequency	Tan δ peak time (mechanical)	G" peak time
100Hz	40 mins.	72 mins.
10	57	108
1	82	159
0.1	120	210

A feature of any relaxation measurement of Tg phenomena, is its frequency dependence. The highest frequencies sense a vitrification process at shorter cure times because the rate of molecular motion is gradually being reduced by the cross-linking process. The difference in loss peak location between tan δ and loss modulus is seen in all relaxation measurements. The difference is greater, the broader the relaxation time spectrum for molecular motion. The times for maxima in G" compared to maxima in tan δ bear a constant ratio (1.8) in these results so any relationship between molecular motion and cure time will be the same whichever parameter is chosen.

Figure 4 shows plots of ln f versus ln t for the data in Figure 3. Both G" and tan δ loss peaks give the same dependence. On the same graph we have plotted dielectric results which will be referred to in detail later, but these are at a lower temperature.

Turning attention now to the dielectric thermal analysis results (DETA), it must be remembered that these measurements operate in a higher frequency range than the DMTA. From what we have seen in the mechanical data, higher frequencies detect shorter times to vitrification (tan δ peak position) during cure. This trend is continued for the DETA measurements. Figure 5 gives the dielectric tan δ at frequencies from 500 Hz to 10kHz for the same Araldite Rapid epoxy as

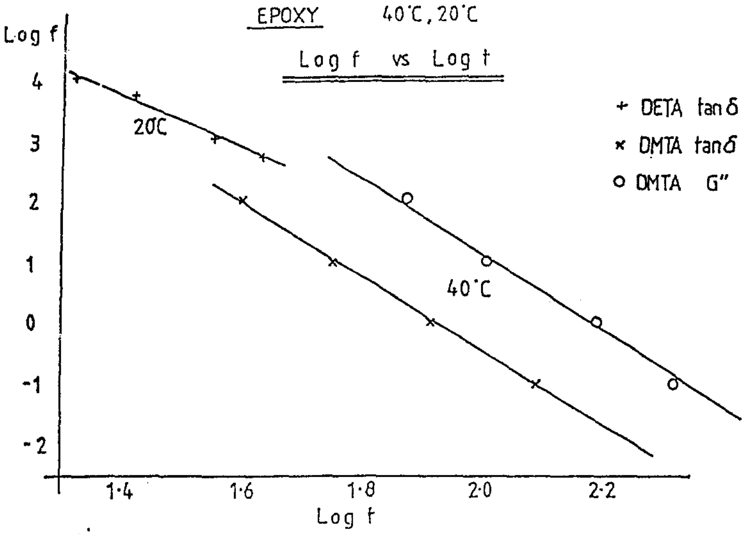


Fig. 4 . Loci of dynamic mechanical and dielectric loss peaks as a function of log (cure time) during isothermal cure of Araldite 'Rapid' under conditions shown.

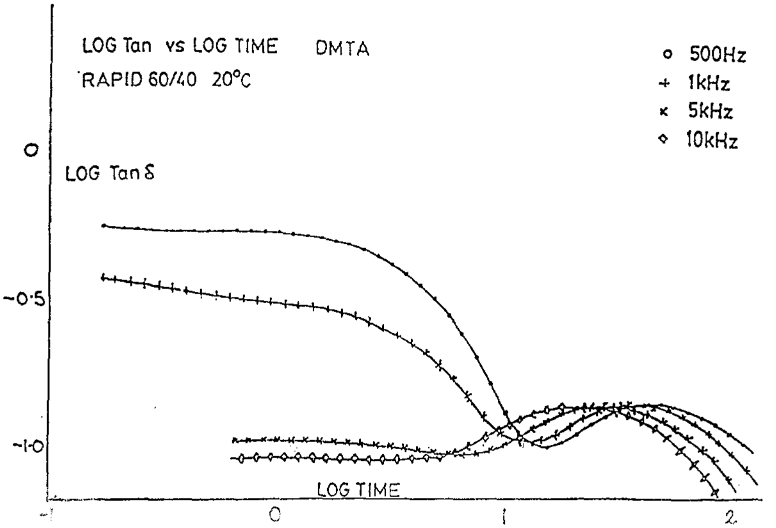


Fig. 5 Dielectric tan δ during cure of Araldite 'Rapid' at 20°C. Dipolar relaxation is shown to the right.

used in the DMTA work. The measurement temperature of 20°C was chosen because good separation of the ionic conductivity and polymer chain relaxation effects are achieved. The loss peaks occuring at log t values between 1 and 2 are due to polymer chain vitrification and it is this region which is directly analogous to the DMTA data. Thus in Figure 4 the dielectric peak positions at 20°C are also shown. When allowance is made for the lower temperature the DETA peaks occur at somewhat shorter cure times than predicted from the DMTA data. At higher temperatures, the low frequency ionic effects progressively swamp the molecular relaxation peaks. Figures 6 & 7 shows data for the same Araldite Rapid at 40°C. The background conductivity loss in the low cure region (short times) has skewed the loss peak locations for this system. The dashed line gives the predicted position of the dielectric loss positions. In fact the slope of the line is reversed, which makes detailed correlation by these plots difficult. Detailed comparisons of mechanical and dielectric loss locations needs analysis of the dielectric data in the frequency plane to allow subtraction of the conductivity losses. This analysis has been performed by Kranbuehl et al (4).

A problem of more general significance is that of selection of the most appropriate measuring frequency to access cure. It is clear from all the data presented that lowering the measurement frequency detects a longer time for vitrification at the cure temperature. It must be remembered that when an epoxy material is cooled from any reasonable cure state it will be glassy at room temperature, but that its modulus and Tg location will increase with cure time. Therefore it is a matter for the measurement frequency during cure to be chosen so that the cure time detected gives a suitable final product. It seems fairly clear that high frequencies >100Hz will be assessing cure at too early a time. It seems likely that frequencies of 1Hz or below will be needed to give sensible correlation with good performance. Dielectric loss measurements, however, will need extrapollating to these lower frequencies, from measurements at higher frequencies. Dielectric data below 10Hz in these systems becomes grossly distorted not only by the space charge effects, but also by actual build-up of charge at the electrodes.

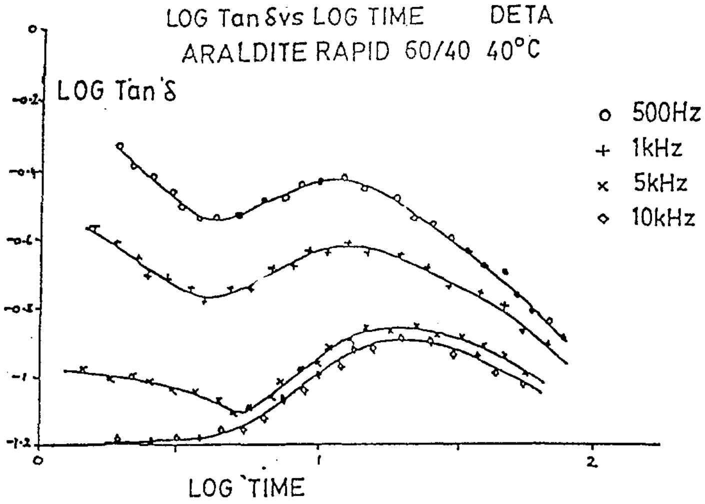


Figure 6

Dielectric data varies along cure time for Araldite Rapid at 40°C at frequencies shown.

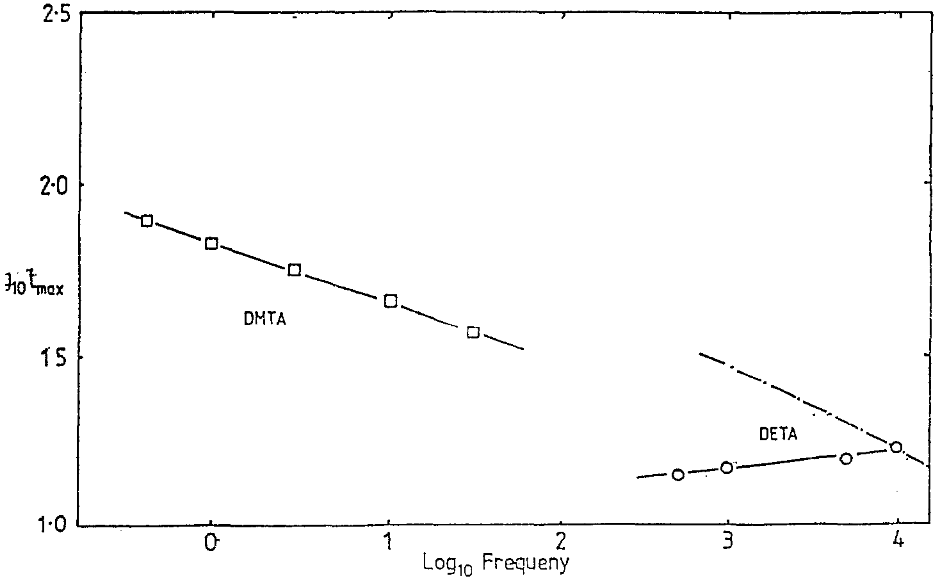
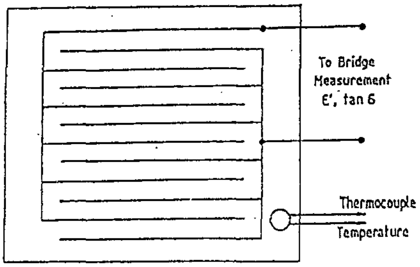


Figure 7

Dielectric and DMTA LOCI during curing of Araldite Rapid at 40°C. Note DETA results are skewed away from expected line by IONIC terms.

Remote Sensors

Fringe field dielectric measurements are quantitatively practicable with interdititating electrodes etched onto an inert material such as "Kapton" (DuPont Co.) or a ceramic. A typical construction is shown in Figure 8. The whole device measures 10mm x 12mm and has fine leads leading from it. The air capacitance of this device is 100pF which gives very good accuracy when this is buried in the curing epoxy. At the end of cure the leads are cut and the device is left in the cured system. There is also the potential for leaving the leads accessible to measure the material's ageing characteristics over prolonged times.



INTERDIGITATING ELECTRODE REMOTE SENSORS

Fig. 8 Remote sensor for in situ dielectric cure monitoring. Sensor - area approximately 1sq.cm., thickness .05cm.

Conclusions

The detection of cure time via the vitrification loss peak position in dynamic mechanical measurement depends on the measurement frequency via a linear relationship between ln f and ln t. High frequencies detect shorter cure times. Dielectric results correlate quite well with mechanical data at low temperatures, but at higher, more realistic cure temperatures, the molecular relaxation is swamped by conductivity losses. Remote sensors, coupled with good frequency plane data analysis, should yield the characterization required for proper cure process control.

References

1. Wetton R.E., Morton M.R., Rowe A.M. and Foster G.M. Proceedings of 6th International Conference on Composite Materials, London, July '87.
2. Glasstone S., Textbook of Physical Chemistry, p.535 MacMillan (1955)
3. Gillham J.K. in: Developments in Polymer Characterision-3 J.V. Dawkins, Ed., 1982, Applied Science Publishers, London, Chapter 5.
4. Kranbuehl D., Hoff M., Haverty P., Hamilton T., Haley W. and Clark R., Proceedings of 16th NATAS Conference, Washington 1987, p.70.

Zusammenfassung - Dielektrische Messungen über einem weiten Frequenzbereich stellen die eine Methode dar, um unter Anwendung verhältnismässig nicht-intrusiver Fühler die Aushärtung von Duroplasten /Epoxid usw./ verfolgen zu können. Die Messungen bilden die Grundlage für einen Fertigungsüberwachungskreis des Autoklaven, da der rheologische Zustand des Duroplast mit der Dielektrizitätskonstanten /ε'/ und dem dielektrischen Verlustfaktor /tan δ/ in Verbindung gebracht werden kann. Vorliegende Arbeit berichtet über weitere Untersuchungen unseres Laboratoriums über den Zusammenhang zwischen mechanischem und dielektrischen Verhaltens während der Aushärtung.

Резюме - Диэлектрические измерения, проводимые в широкой области частот, представляют один из практических методов контроля процесса отверждения термореактивных смол / напр. эпоксидной смолы и др. /. Такие измерения создают основу производственного контрольного цикла в автоклаве при условии, если реологическое состояние может определяться соотношением между диэлектрической константой /ε'/ и коэффициентом потерь /tanδ/ Представленная статья касается дальнейших исследований корреляций между механическим и диэлектрическим поведением в процессе отверждения.