Dielectric Relaxation and Crosslinking in Unsaturated Polyester Resins

GEORGE S. LEARMONTH, *Reader in Polymer Technology at the University of Aston in Birmingham, England,* and GEOFFREY PRITCHARD, *Lecturer in Polymer Science at the Kingston College of Technology, Kingston on Thames, England*

Summary

The properties of crosslinked thermosetting resins depend markedly on the completeness of the crosslinking process. Determination of the degree of cure of an unsaturated polyester resin has been studied previously by mechanical, spectroscopic and volume resistivity methods. In this respect the effect of cure time and temperature on the ac dielectric constant and dissipation factor at 1 kc/s and 10 kc/s is considered. The dissipation factor appears to be a most useful parameter for detecting changes in the degree of cure in the later stages of reaction.

The electrical properties of the cured resin are discussed, and values for the energy of activation for electrical conduction are compared with literature reports on similar materials.

INTRODUCTION

Thermosetting polymers possess properties which depend greatly on the completeness of the crosslinking reaction. Undercure results in poor mechanical properties, weathering, water resistance and heat resistance. Undercured samples are sometimes found to continue to crosslink at an almost imperceptible rate for long periods, resulting in shrinkage and departure from intended dimensions. Determination of the completeness of crosslinking by following the reaction chemically is usually difficult and uncertain, and consequently many instrumental techniques have been utilized.

Phenol-formaldehyde resin cure has been monitored by ultrasonic pulse propagation,[1] and by differential thermal analysis.[2] Epoxide polymerization has been followed by dynamic mechanical measurements with a vibrating reed specimen.[3] Attenuated total reflectance spectroscopy has been suggested for use with coatings.[4] Unfortunately, some methods are insensitive in the later stages of cure. Wohnsiedler et al. found no change in Young's modulus for melamine-formaldehyde resins while several other properties were undergoing sigmoidal changes.[5] Turanov and Sokolov found that the calorimetric determination of degree of cure of unsaturated polyester resins indicated complete reaction when the use of a plastimeter

and a dilatometer still showed some changes occurring.[6] Second moments of NMR lines from spectra of polyester resins were found by Grad and Al'shits to be unchanged after ten days,[7] but usually cure is believed to continue for very much longer than this unless the cure temperature is very high.

The present authors crosslinked an unsaturated polyester resin, Beetle 4116 (obtained from B.I.P. Chemicals Ltd., Oldbury, Birmingham, England) with styrene using a benzoyl peroxide-tertiary amine initiating system. Several properties were measured during isothermal crosslinking. One property could then be correlated with another. The dynamic shear modulus and logarithmic decrement were measured with a torsional pendulum,[8,9] and Young's modulus was determined from the velocity of sound as measured by a resonant rod technique.[9] Chemical changes were observed[10] spectroscopically using the 1737 cm^{-1} carbonyl peak as an internal reference standard, and measuring the decreases in the intensity of the absorption at 915 cm^{-1} and 985 cm^{-1}. Refractive index[10] and volume resistivity[11] were also measured as a function of cure time.

It was found that the mechanical logarithmic decrement as determined by the torsional pendulum was the most sensitive to changes in cure in the later stages of reaction. Therefore it seemed important to measure the electrical analogue, the dielectric dissipation factor or loss tangent (tan δ). This was measured at two frequencies, 1 kc/s and 10 kc/s, together with the dielectric constant.

Dielectric Constant and Loss as Cure Parameters

Tan δ is usually high in the early stages of cure because of ionic conductance arising from impurities and from catalyst or accelerator. The dielectric loss then falls and later exhibits a peak. Dielectric constant falls during cure because of gradual immobilization of the polar groups. Ehrlich and de Lollis observed these changes during the copolymerization reaction between styrene and acrylonitrile;[12] van Beek measured the changes in dielectric properties of a resin made from a novolak and 1,3 dioxolane over a period of 25 days.[13] In this reaction, water is produced which interferes with the electrical measurements by increasing the electrical losses. Some of the loss was attributed to the acid catalyst used. As a result, not much change was observed in dielectric constant, ϵ', or loss in the latter stages, but a considerable change was found in the frequency of maximum loss, which is raised by the water produced.

Delmonte[14] observed the changes in ϵ' and tan δ during the cure of epoxide polymers. He found these properties more informative than resistivity. The peak values of tan δ which appeared in the region of gelation or just after (depending on the frequency) were the same for all resins. These peaks coincided with the midpoint of the maximum slope of ($d\epsilon'/dt$), i.e. the greatest change in dielectric constant. The levelling off value for the dielectric constant ϵ' was the same for all resins.

Delmonte's work aroused the interest of Haran, Gringras and Katz, who attempted[15] to devise a method for detecting the onset of gelation in epoxy resins, to enable metal inserts to be extracted at the appropriate time. They examined the factors affecting the time elapsing before a peak in the dielectric loss tangent was found.

Recently Holdsworth patented a device[16] for determining simultaneously the thickness and degree of cure of coatings using dipole orientation.

In view of these and other promising investigations of the cure of resins using dielectric tests, it seemed important to measure the dielectric constant and loss of the unsaturated polyester resin mentioned previously, whose mechanical and spectroscopic absorption properties had already been studied. The same catalyst system (1% by weight of benzoyl peroxide and 0.007% N,N' p-dimethyl toluidine) was used as in previous studies.[8-11]

Experimental

A polymerization cell was made from two parallel glass plates, 5 in. square and $3/16$ in. thick. These were separated by nitrile rubber gaskets (0.1 in. thick) to which both plates were cemented by a suitable epoxide-based adhesive. Circular aluminium foil electrodes were adhered to the inside face of each plate and rolled until quite flat. Nonoverlapping, projecting tabs were provided to connect the electrodes to the measuring instrument. This was a Marconi Ltd. (England) TF 1313A 0.1% Universal bridge. Corrections for edge capacitances were made according to ASTM-D-150-65 T.

The mixed (catalyzed) resin was poured into the preheated cell and cured in an accurately thermostatted air oven. Readings were taken almost immediately although it was recognized that isothermal conditions were not attained for some time because of the low thermal conductivity of the resin. Cure was then continued for up to 120 hr at 45°C (rather less at higher temperatures). Post-curing was carried out at 80°C for 20 hr, 100°C for 24 hr, 130°C for three hours and finally at 165°C until no further change occurred in volume resistivity. An increase in the latter quantity, ρ, measured simultaneously with dielectric constant and loss, was observed for up to four days. The cell was so designed that air was almost entirely excluded from the resin during cure and postcure.

Additional runs were carried out using a cobalt-naphthenate (0.17%) and cyclohexanone peroxide (0.75%) initiating system.

DISCUSSION

Dielectric Constant

The dielectric constant, measured at 10 kc/s, changed during cure at 45°C from about 6.0 to about 3.7. This was a much smaller change than had been found in volume resistivity (about five decades) and also less striking than the change in the dissipation factor. Moreover, the changes which did occur were largely confined to the second stage of the crosslinking
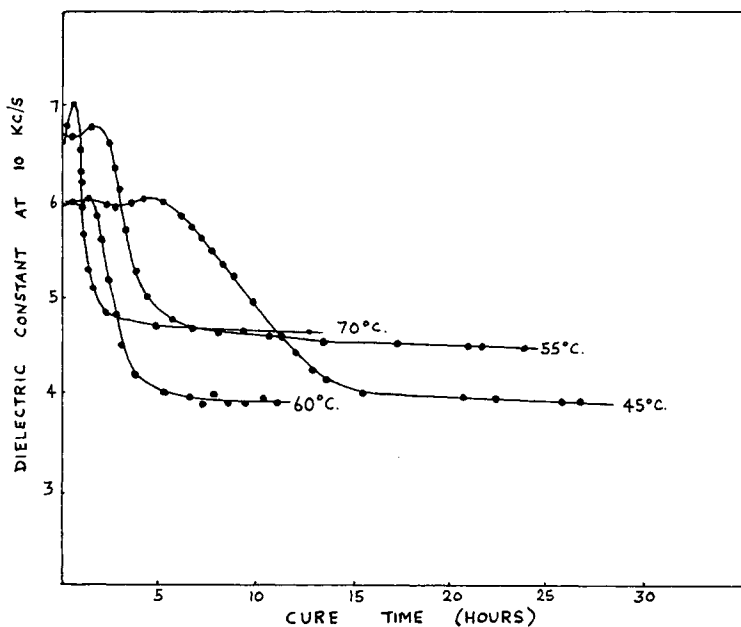
Fig. 1. The effect of curing time on dielectric constant at various temperatures.

process, i.e., after gelation, but before immobilization of the network caused propagation reactions to decline sharply in rate.   This is in accordance with the theory that the third stage of crosslinking is primarily the incorporation of styrene into the existing network by diffusion of monomer through the structure.

Figure 1 shows the changes in dielectric constant, measured at 10 kc/s. (Changes at 1 kc/s were similar, and are not shown.)   The terminal values of ϵ' are not in the same order as the cure temperatures.   This is probably because the terminal values of the dielectric constant depend on two competing effects.   The higher the degree of crosslinking (higher crosslinking is found at higher cure temperatures), the lower the expected dielectric constant.   On the other hand, the higher the cure temperature, the higher the dielectric constant would be expected to be since the value rises with measurement temperature over most of the temperature range of interest. Cure at 60° or 70°C would give much higher crosslinking than at 45° or 55°C, because the threshold temperature for spontaneous thermal decomposition of benzoyl peroxide is about 60°C.   (The tertiary amine accelerator concentration was too low for the benzoyl peroxide to be very readily decomposed at lower temperatures, though some activation did occur.)

Dissipation Factor

Figure 2 shows the changes in dielectric dissipation factor, tan δ, during cure.   The frequency of measurement is more important here than for di-
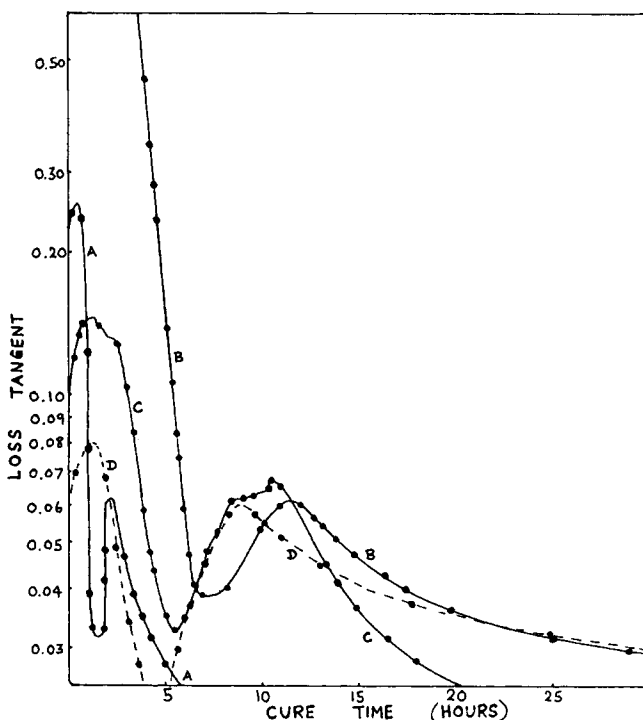
Fig. 2. The effect of curing time on electrical dissipation factor at various cure temperatures.

A: 60°C; 10 kc/s: benzoyl peroxide/amine system.
B: 45°C; 1 kc/s: benzoyl peroxide/amine system.
C: 45°C; 10 kc/s: benzoyl peroxide/amine system.
D: 45°C; 1 kc/s: cyclohexanone peroxide/cobalt naphthenate system.

electric constant.   At low frequencies the loss angle of the uncured resin is much greater than at about 10 kc/s.   Because of the overlapping effects of temperature and polymerization in the early, pregelation region, it is not possible to distinguish with certainty what changes the loss tangent undergoes.   After gelation, it decreases very steeply to a minimum and then rises to a peak, the position of which is frequency-dependent.   This peak occurs because the initially short relaxation times have lengthened until the polar groups can only partly follow the applied field, and lag behind it. The result is that energy is dissipated by frictional forces.   It is analogous to the peak found in the loss tangent of the cured resin (measured as a function of temperature) and was found here to be of a similar magnitude (about 0.063).   The higher the frequency, the sooner this peak appears.[17]

At the beginning of cure, the loss tangents at one and ten kilocycles per second differed by a factor of ten.   Thereafter, the two values began to converge and towards the completion of cure the two values were quite similar.

The changes in loss tangent at an advanced stage in the crosslinking reaction were still quite appreciable, suggesting that this property may be a useful parameter for determining the degree of cure of casting resins.

Comparison with Other Properties

The peaks in the dissipation factor (Fig. 2) may be regarded as locating a frequency-dependent transition from a rubbery to a glassy material. It is significant that the peaks at 1 kc/s and 10 kc/s roughly coincide with a rather sudden fall-off in the rate of change of volume resistivity.[11] This is indicated in Figure 3. At this point diffusion control, which impedes termination reactions quite early, affects propagation as well. Thereafter, the crosslinking process is dependent on the diffusion of small monomer or microradicals to frozen macroradical sites.

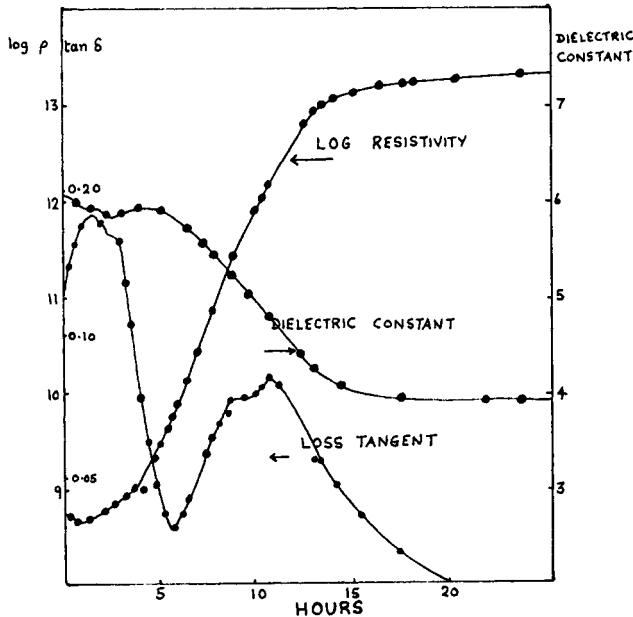Table I shows some of the changes in properties of Beetle 4116 during cure at 45°C.

Fig. 3. D.c. volume resistivity, dielectric constant and loss during cure at 45°C.

Electrical Properties of the Cured Resin

Warfield and Petree have studied the temperature dependence of the volume resistivity of epoxide polymers and, in some cases, polyesters. They concluded that when the plot of log resistivity against temperature has become a reproducible straight line then the resin is fully cured. Further, more drastic heating was found to cause a decrease in the slope of this line and in the corresponding energy of activation for electrical conduc-

TABLE I
Changes in the Properties of Beetle 4116 during Isothermal Cure at 45°C

Time (hr)	ϵ^a	tan^a δ	log ρ	Shear^b modulus (1 c/s)	log dec (1 c/s)	Tensile strength (psi)	Refr. index
1	5.98	0.145	8.63	—	—	—	1.53516
2	5.91	0.137	8.81	—	—	—	1.53534
3	5.91	0.107	8.84	—	—	—	—
4	5.98	0.055	9.06	—	—	—	—
5	5.93	0.035	9.53	—	—	60	1.53966
$7^1/_2$	5.62	0.050	10.72	0.69	0.40	120	1.55000
10	4.99	0.063	11.87	0.90	0.26	225	1.55568
15	4.04	0.037	13.08	1.05	0.19	3840	—
25	3.91	0.022	13.25	1.11	0.16	5800	1.56160
100	3.76	0.014	13.45	1.20	0.12	6600	1.56250

^{a} Measured at 10 kc/s.

^{b} Dynes per sq. cm, $\times$ 10^{-10}. All electrical properties were measured at the cure temperature. Refractive index was measured at the cure temperature. Mechanical properties were measured at 25°C.

tion, E_c. The values of E_c were used as a basis for classifying polymers according to their crosslink density.[18,19]

Postcuring of Beetle 4116 was carried out in this present work until a reproducible straight line plot was obtained. The expected kink at the glass transition temperature was not at all prominent. This postcuring was carried out in virtual absence of air; it has been shown that the absence
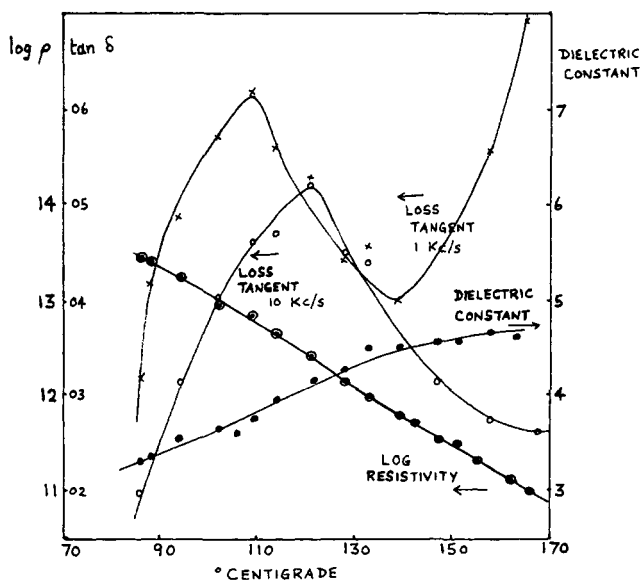

Fig. 4. Temperature dependence of volume resistivity, dielectric constant, and dielectric loss for the benzoyl peroxide/amine cured resin.

of air can in some cases preclude the possibility of degradation which would otherwise be rapid at the same temperature.[20]

Figure 4 shows the electrical properties of the cured resin as a function of temperature in the range 70° to 170°C. The dielectric constant rises gradually in the dispersion (transition) region, but does not show any fall at the high end of this range; thermal agitation is therefore insufficient at 170°C to prevent orientation. An upswing in the dielectric loss at this temperature indicates ionic conductance as more ions are formed by thermal dissociation. The transition temperature is not clear from the resistivity but appears to be in the region of 125°C.

E_c was found to be 27.5 kcal per mole, which appears to be low in view of Taylor's assertion that all dry amorphous substances should have values[21] greater than 25, and in the light of Warfield's value of 46 for the identical resin Laminac 4116. (The differences between Laminac and Beetle 4116 are probably limited to small discrepancies in manufacturing procedure between the American and British firms concerned, but it may be that such small differences do in fact affect the electrical properties.)

It was found that the constant ρ_0 in the compensation law expression for the temperature dependence of the resistivity, ρ,

$$\rho = \rho_0 e^{-E_c/RT}$$

was $10^{-2.8}$, which lies exactly on the straight line plotted by Warfield and Petree using data for polymers, monomers and inorganic liquids.[22]

CONCLUSIONS

Since the curing of unsaturated polyesters continues almost imperceptibly in the glassy state for long periods, those properties used to monitor the curing process should be able to reflect the gradual incorporation of styrene monomer into a largely immobilized three-dimensional network. Damping terms, whether electrical or mechanical, are indicative of the loose ends present and of network imperfections found in networks based on chains of low primary molecular weight. These terms are probably preferable to many others which have been suggested for determining the degree of cure of resins. Like all electrical property tests, the measurement of dissipation factor requires strict purity and reproducible conditions of temperature and humidity. It does however have the advantage that any departures from standardized conditions, such as improper mixing or the presence of impurities, or incorrect temperature, is quickly shown in dielectric properties.

References

1. G. A. Sofer, A. G. H. Dietz, and E. A. Hauser, *Ind. Eng. Chem.*, **45**, 2743 (1953).
2. R. H. White and T. F. Rust, *J. Appl. Polymer Sci.*, **9**, 777 (1965).
3. R. Jenkins and L. Karre, *J. Appl. Polymer Sci.*, **10**, 303 (1966).
4. H. Dannenberg, J. W. Forbes, and A. C. Jones, *Anal. Chem.*, **32**, 3, 365 (1960).
5. H. P. Wohnsiedler, I. H. Updegraff, and R. H. Hunt, *Ind. Eng. Chem.*, **48**, 1, 82 (1956).

6. A. Turanov and A. D. Sokolov, Plast. Massy, No. 7, 17 (July 1965).

7. N. M. Grad and I. M. Al'shits, *Vysokomol. Soed.*, **A9**, 4, 832 (1967).

8. G. S. Learmonth, G. Pritchard, and J. Reinhardt, *J. Appl. Polymer Sci.*, **12,** 4, 619 (1968).

9. G. S. Learmonth and G. Pritchard, *S. P.E. Journal*, **24,** 11, 47 (1968).

10. G. S. Learmonth and G. Pritchard, *S. P. E. Journal*, **23,** 12, 46 (1967).

11. G. S. Learmonth and G. Pritchard, I & E C. Prod. Res. Dev. Quart., **8,** 124 (1969).

12. P. Ehrlich and N. J. de Lollis, *J. Res. Nat. Bur. Stand.*, **51,** 3, 145 (Sept. 1953).

13. L. K. H. van Beek, *J. Appl. Polymer Sci.*, **8,** 2843 (1964).

14. J. Delmonte, *J. Appl. Polymer Sci.*, **2,** 4, 108 (1959).

15. E. N. Haran, H. Gringras, and D. Katz, *J. Appl. Polymer Sci.*, **9,** 3505 (1965).

16. D. W. Holdsworth, U.S.P. 3,234,462.

17. M. Olyphant, *Insulation*, **12,** 8, 37 (July 1966) and **12,** 9, 42 (August 1966).

18. R. W. Warfield and M. C. Petree, *S.P.E. Trans.*, 1, 80 (April 1961).

19. R. W. Warfield, *S.P.E. Journal*, **14,** 11, 39 (Nov. 1958).

20. E. S. Ebers, W. F. Brucksch, P. M. Elliott, R. S. Holdsworth, and H. W. Robinson, *Ind. Eng. Chem.*, **42,** 114 (1950).

21. C. P. S. Taylor, *Nature*, **189,** 388 (1961).

22. R. W. Warfield and M. C. Petree, U. S. Dept. Com., Office Tech. Serv., A. D. 276,575 (1962).