

Polymerization Behavior of Silver-Filled Epoxy Resins by Resistivity Measurements

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Synopsis

The cure of heavily silver-loaded epoxy resins with several amines has been investigated by resistivity-time measurements under isothermal conditions. For favorable cases activation energies in the range of 14-17 kcal./mole have been derived from slope analyses of the ρ - t plots. The relationship of the technique to similar measurements on unfilled or lightly loaded resins is discussed. Many aspects of the electrical behavior of silver-based conductive adhesive systems are clarified by the kinetic data.

INTRODUCTION

The behavior of metal dispersions in thermosetting resins at concentrations sufficient to develop high conductivity depends on the variation in electrical properties with polymerization of the continuous insulating phase. Recorded, four-point potentiometric measurements of resistivity on silver-loaded epoxy composites have been used here to follow the rate of cure as a function of temperature. The implications of such measurements as a method of observing resin cure parameters are discussed.

The rate of polymerization of thermosetting polymers has been studied through measurements of electrical resistivity by Warfield and Petree.^{1,2} In such cases the resistivity changes from the 10^6 ohm-cm. values of the fluid resin-hardener to the 10^{14} ohm-cm. region characteristic of cured epoxies. The maximum slope of the log resistance versus time plot, $(1/R)dR/dt$, is taken as a measure of rate and $\log \max [(1/R)dR/dt]$ versus $1/T$ used for activation energy estimation.

More recently Chadwick³ has reported a resistivity technique involving incorporation of approximately 1% of finely dispersed powdered graphite into the thermosetting resins. Indicated resistance changes are within an order of magnitude of initial values (about 10^5 ohms) and are used as qualitative measure of the progress of cure and degradation.

EXPERIMENTAL

In the present work samples are cast as bar shapes ($0.5 \times 0.5 \times 4$ cm.) in Silastic RTV 501 (Dow Corning Corp.) blocks containing copper wires inserted through the mold for current and voltage contacts. Resistivity-time plots are obtained by means of the apparatus diagrammed in Figure 1.

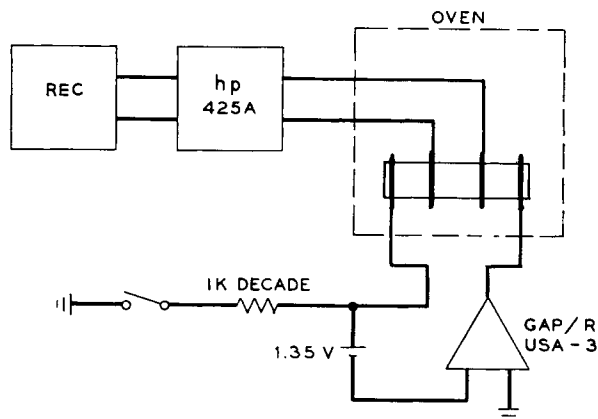


Fig. 1. Schematic of constant current-probe voltage, four-point technique for isothermal resistivity measurements.

The sample is weighed out, thoroughly mixed, transferred to the preheated mold, and inserted in the constant temperature ($\pm 1^\circ\text{C}.$) oven. The probe voltage at constant current is monitored on a strip chart recorder. The operational amplifier (Model USA-3, G. A. Philbrick Researches, Inc.) circuitry provides known currents from $1\text{ }\mu\text{a.}$ to 10 ma. For the lowest levels of resistivity a Harrison Laboratories Model 865B supply of 0.5 amp. capacity is switched in at the output of the USA-3. The Hewlett-Packard 425A microvoltmeter is useful over the required range of $100\text{ }\mu\text{v.}$ to 1 v. Resistance is converted to resistivity (ohm-cm.) by applying the cross-sectional area of the bar (normally 0.25 cm.^2) and the distance between voltage probes (about 1.5 cm.).

DER 332-LC (Dow Chemical Co.), high purity diglycidyl ether of bisphenol A, and phenyl glycidyl ether (Eastman White Label) in an 80/-20 w/w mixture were adopted as standard for a low viscosity medium capable of high filler loadings. For contrasting higher reactivity, ERL 3794 epoxy resin (Union Carbide Plastics) containing different phenolic functionality was substituted for DER 332-LC. The two systems are referred to as 80/20 332 and 80/20 3794. The following four amines were obtained from commercial sources and redistilled where required: diethylenetriamine (DETA), diethylaminopropylamine (DEAPA), menthane diamine (MDA), and triethanolamine (TEA).

The conductive filler was normally a silver flake, MD-755 (Metals Disintegrating Co.) containing 0.5% stearic acid but used as received since surface treatments degraded its dispersibility.

RESULTS

Diethylenetriamine (DETA)

The family of resistivity-time curves for 77% (wt.) silver flake (approximately $27\text{ vol.}\%$) in 10 phr DETA-80/20 332 resin at various tem-

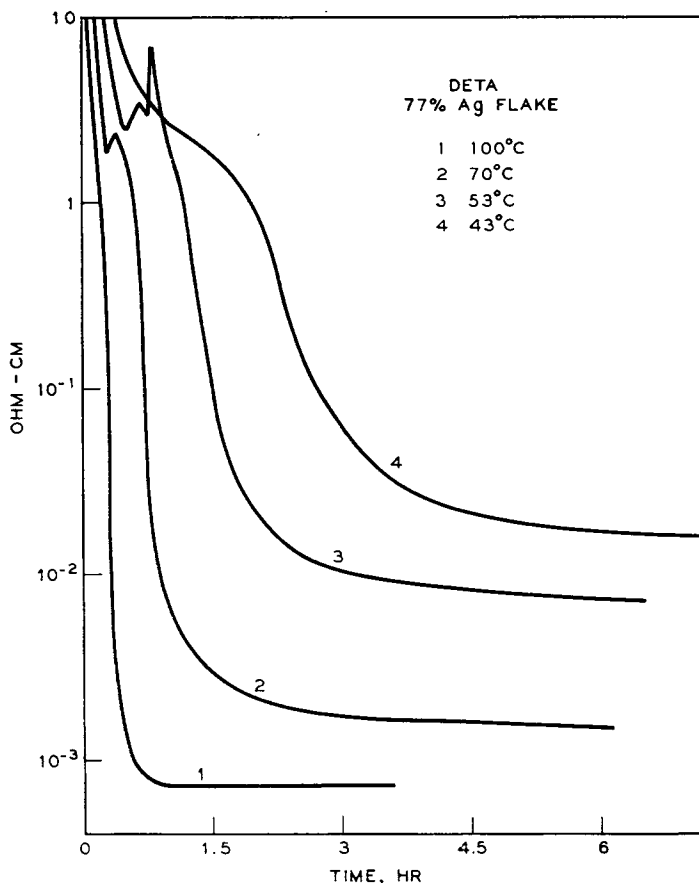


Fig. 2. Resistivity-time curves for 10 phr DETA in 80/20 332 resin at 77% silver flake.

peratures is given in Figure 2. The initial values of resistance are beyond the input impedance of the apparatus, but valid readings are obtained after a temperature-dependent period most probably corresponding to the onset of gelation. After the initial drop the resistance is characterized either by a plateau region or a peak, depending again on temperature, in which the signal is noisy. Immediately after this stage the resistance decreases steadily to a final level determined by the curing temperature as shown in Figure 3, curve 1.

Warfield and Petree¹ found the curves with DETA and Epon 828 resin (Shell Chemical Co.) to be smoothly sigmoidal in shape, showing no complications like those of Figure 2, with the maximum slope portions corresponding to crosslinking after gelation of the polymer. Activation energy derived from their Arrhenius plot was 14 kcal./mole, in reasonable agreement with other data.¹ The Arrhenius plot constructed from the maximum slopes of the regions beyond the initial peak or plateau in Figure 2 also yields 14 kcal./mole for the process (Fig. 4). The coincidence of

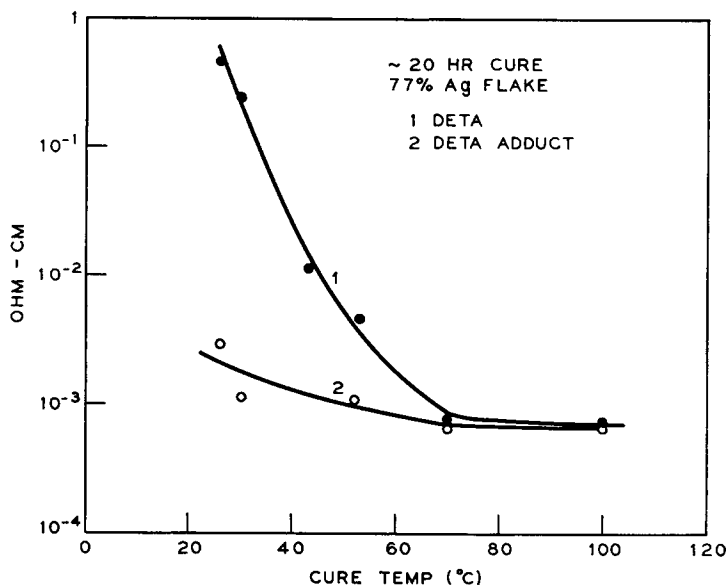


Fig. 3. Resistivity after cure for 10 phr DETA in 80/20 332 resin and for the same composition with DETA-phenyl glycidyl ether prereacted to form an adduct.

these two values, considering the different epoxy resin phases and the presence of a stearic acid-coated conductive particle is possibly fortuitous. However, basically similar values might be expected if the conductivity of silver-DETA-80/20 332 involves crosslink-dependent formation of a continuous network of silver flakes whose contact area is determined by the temperature-defined degree of resin contraction.

An explanation for the peak at intermediate temperatures (50–70°C.) and plateau slope for higher and lower ranges lies in the opposing effects of (a) thermal expansion and relaxation of the just gelled polymer decreasing contact area of particles and increasing resistance and (b) rate of cross-linking causing the decrease in resistance shortly to be dominant. At higher temperatures (b) overcomes (a) with only a slight plateau or lower slope through the gelation period. At lower temperatures the thermal pulse is sufficiently diminished to have only the lower slope region. The intermediate (50–70°C.) peak is then viewed as effect (a) momentarily dominating. Some support for this supposition comes from the resistance-time behavior shown by DETA composites when subjected to a temperature increase of about 1–2°C./min after stabilizing under normal cure. A sample cured 20 hr. at 26°C., then heated to 70°C. in about 25 min., showed a rise in resistivity of about three orders of magnitude. On maintenance of 70°C. the resistivity then decreases but, even after extended periods, does not drop very much below the original 26°C. level, in contrast to the value achieved if the cure had been carried out directly at the higher temperature. The loaded resin here resembles the gel stage in reaction to sudden heating, thus duplicating on a longer time scale the 70°C. cure

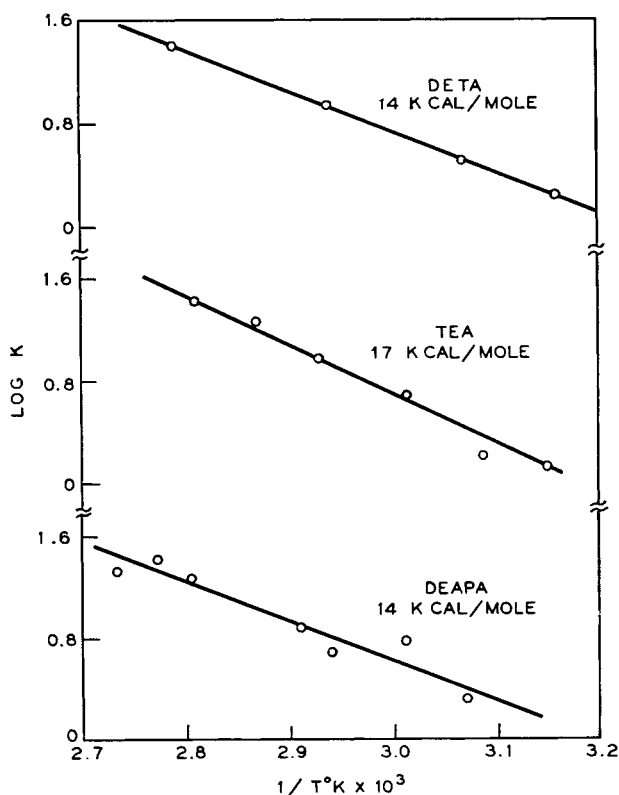


Fig. 4. Activation energy plots for 77% silver flake in 80/20 332 resin with the indicated curing agents.

type peak. Similar treatment of a 53°C. cure (heating to 100°C.) causes no resistivity pulse at these heating rates but brings the resistivity down to an order of magnitude higher value than direct 100°C. cures. With DETA the path to the final temperature determines the resistivity.

The geometry of particles has a strong effect on ultimate conductivity; a fine spherical silver powder does not yield conductive dispersions until nearly maximum (90%) loading. In this work a silver powder of irregular geometry (Silpowder 130, Handy and Harman, Inc.) was examined up to its maximum wettable loading in 80/20 332 where, with the higher temperature DETA cures (100°C.), the conductivity is as good as that achieved with the flake. Below this high loading range the powder composites fall off more sharply in conductivity, the more two-dimensional, albeit stearic acid-coated, flake being more suitable for practical use than the pure crystalline powder.

Kinetic runs with Silpowder 130 in the 10 phr DETA-80/20 332 matrix indicate similar strong dependency of final resistivity on cure temperature as for flake runs. However, the contact geometry appears sufficiently different at these loadings that the pronounced maxima effects seen with the

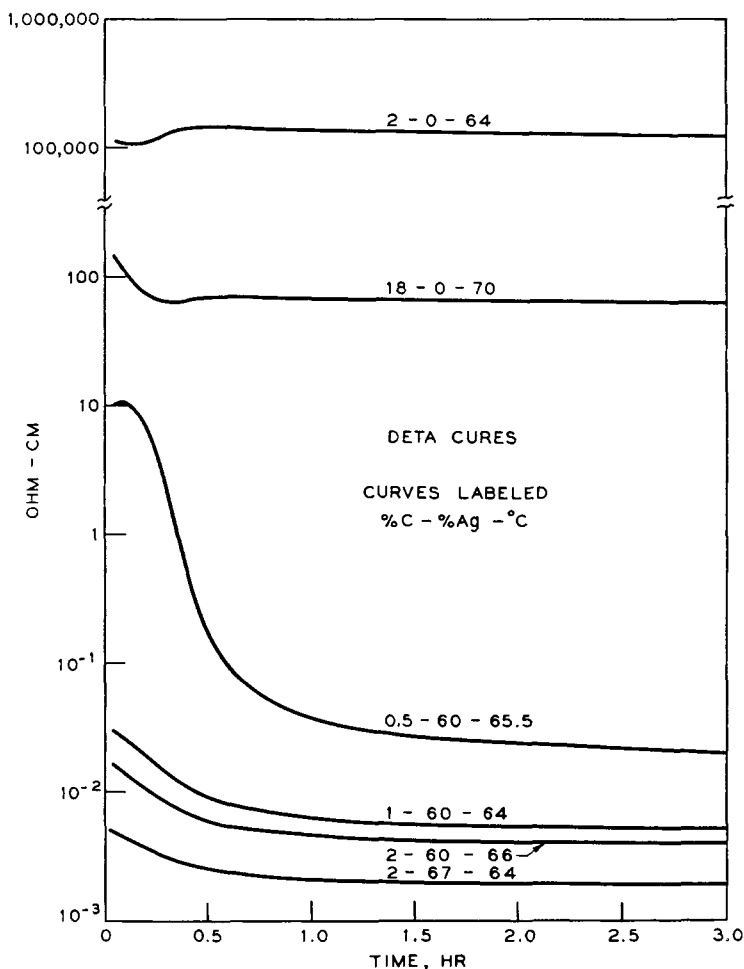


Fig. 5. DETA cures in 80/20 332 resin with the specified conditions of carbon and silver content and temperature.

flake are damped to less well-defined slope changes, not permitting rate calculations. Cure times to achievement of stable values are similar to those with the flake.

Examination of a number of carbon black-silver mixtures indicated qualitatively that, as an additive, carbon does not drastically affect the final level of resistance where the appropriate quantity of silver is present. Followed resistively, such systems illustrate the transition from all carbon, to mixed silver-carbon, to high silver paths as inferred from curve shapes and ultimate resistance value.

In Figure 5, the upper two curves representing 2% and 18% (maximum loading) of Vulcan XC 72 (Godfrey L. Cabot Co.) show relatively small changes with time and quite noise-free, readily measurable resistance in the original mix. Gelling and hardening produce changes only within a factor of two from the first resistance value measured after time zero (in-

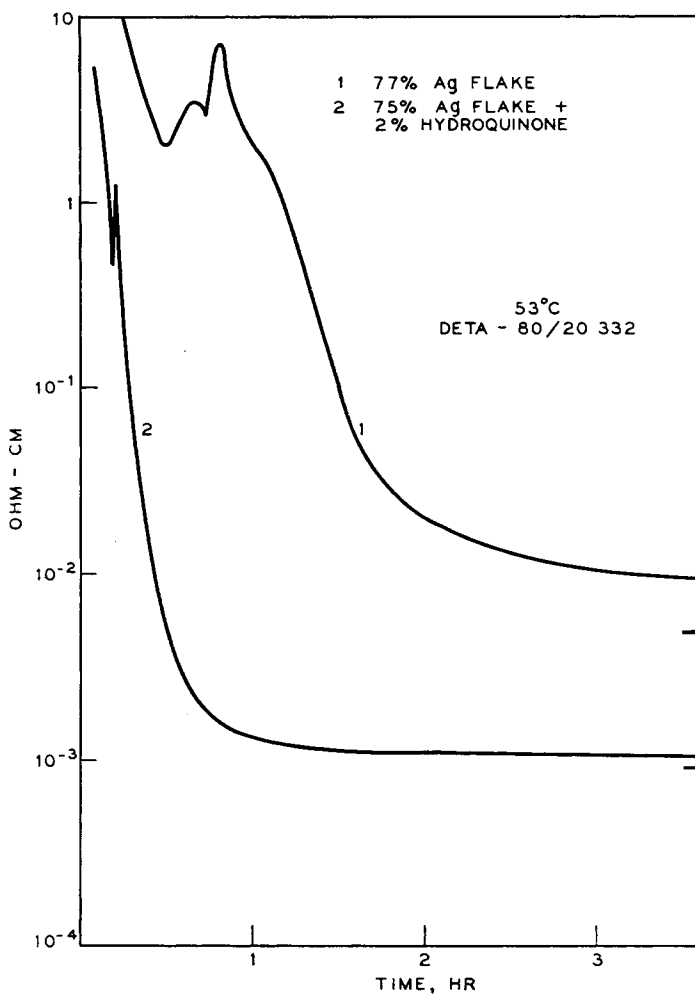


Fig. 6. Resistivity-time curves for hydroquinone-catalyzed and uncatalyzed composites.

section of sample into oven). This type of variation is of the order of that described by Chadwick.³ The carbon particles have continuity initially, and the direction of change is variable with resin cure. In the 2% and 18% C cases the resistance at first drops, increases to a broad maximum, and then tends to drop slightly over an extended interval.

The bottom two curves with 2% carbon and 60 and 67% silver flake vary less than a decade in resistivity with time and exhibit equilibrium values in keeping with their silver content. As the carbon concentration is lowered (1% and 0.5% mixtures) the curing curve takes on the cure shape for silver. In the 0.5% C system there is even a small peak and sharp drop as in the absence of carbon, presumably as essentially silver paths determine the resistance early in the cure.

Quite different kinetic behavior is exhibited by DETA cures when the ERL 3794 resin is substituted for DER 332-LC, other factors remaining

constant. The dispersions from the beginning of a run show considerable conductivity and, though final levels are expectedly concentration dependent, even down at 60% silver there is no marked variation with time on curing. Addition of DETA to 80/20 332-silver mixes causes no immediate physical effect, while with 80/20 3794 substituted, immediate increase in viscosity is observed on mixing in the DETA. Actual hardening of the resin is faster than for 80/20 332 but other factors dominate, and the electrical data are more significant for the practical problem of conductive plastics than they are for resin cure kinetic information. Two properties of the 3794 resin appear important: with amines present it is observed to be reductive to silver compounds, its polyhydroxy phenolic content accelerates the initial polymerization reactions.^{4,5}

These two effects can be partly duplicated in the purer resin by the addition of hydroquinone or DETA-adduct curing agent. The 53°C. runs with 77% Ag and 75% Ag-2% hydroquinone are contrasted in Figure 6. The marked catalysis and the improvement in conductivity attained are evident for the additive, starting in both cases from a high resistance mixture. Hydroquinone is only slightly soluble in the resin, and this probably controls its effect. Both phenolic acceleration of amine-epoxy reactions and surface compound reduction are operative.

DETA-adduct curing agents with DER 332-LC are similar to ERL 3794 with DETA alone. In these examples the phenyl glycidyl ether is reacted with DETA for time sufficient to form an adduct with excess amine function. Runs with the more active adduct curing agent show immediately measurable resistance values in which the network of silver conduction is established from point of mixing into the partially reacted matrix. As is found in 3794 resin, the curing temperature effect on equilibrium resistivity at constant per cent silver is greatly reduced (Fig. 3, curve 2).

Triethanolamine (TEA)

The family of curves (Fig. 7) for this tertiary epoxy-opening base at 12 phr in 80/20 332 at 44-83°C. omits an initial period of unstable signal but shows the subsequent apparent gelation effect. A DETA-like decrease in resistance then proceeds but with the final conductivity for all runs lying in the narrow range of the I-bar on the plot around 4×10^{-4} ohm-cm., a consistently excellent value for such a composite. With TEA the final state in electrical terms is essentially independent of cure temperature, though the rates to that state vary widely, as indicated by the 17 kcal./mole activation energy (Fig. 4).

The similarity of TEA and DETA with respect to 80/20 3794 cures is strong: even at reduced contents of silver flake, low resistance values are immediately reached. TEA cures, which evidently are not highly cross-linked as implied by low softening point and strength, still yield excellent conductors, indicating that surface effects on the metal contacts as well as (or more than) bulk structural shrinkage can determine this feature. Such reasoning must be involved for both TEA and DETA in the 3794 system and perhaps more strongly yet in the cases of very poor conductors formed

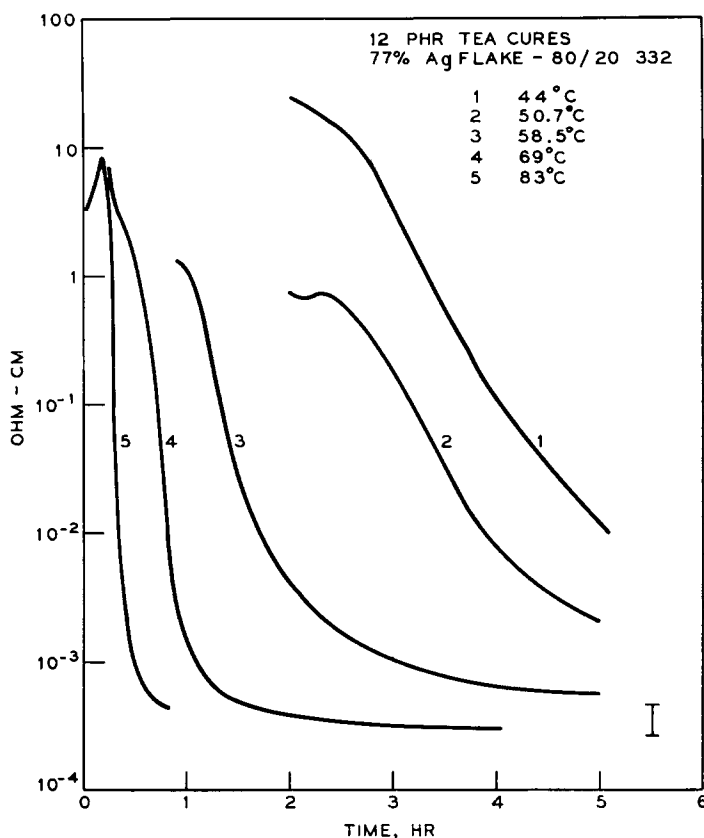


Fig. 7. Resistivity-time curves for TEA cures in the 80/20 332 resin.

with many other curing agents where resulting internal pressures are little different from those of suitable hardeners.

Diethylaminopropylamine (DEAPA)

The curves for DEAPA over a 34°C. range (Fig. 8) indicate a more complex course of reaction than the previous flake systems with a second step in the intermediate region of temperature. The activation plot (Fig. 4), yielding 14 kcal./mole, is taken from the slope of the first steep region after the initial pause, as with the previous amines. The scatter of the points is in keeping with the averaged complexities of the curing curve of the mixed crosslinking and tertiary amine functions. The final level of resistivity is intermediate in degree of temperature effect ($1-7 \times 10^{-3}$ ohm-cm., 93-59°C.) compared to DETA and TEA.

Menthane Diamine (MDA)

Polymerization of MDA-epoxy resins to a hard state requires higher temperatures for reasonable rates than those of the previous amines, as is expected from the sterically hindered *tert*-alkylamine structure. Runs at the

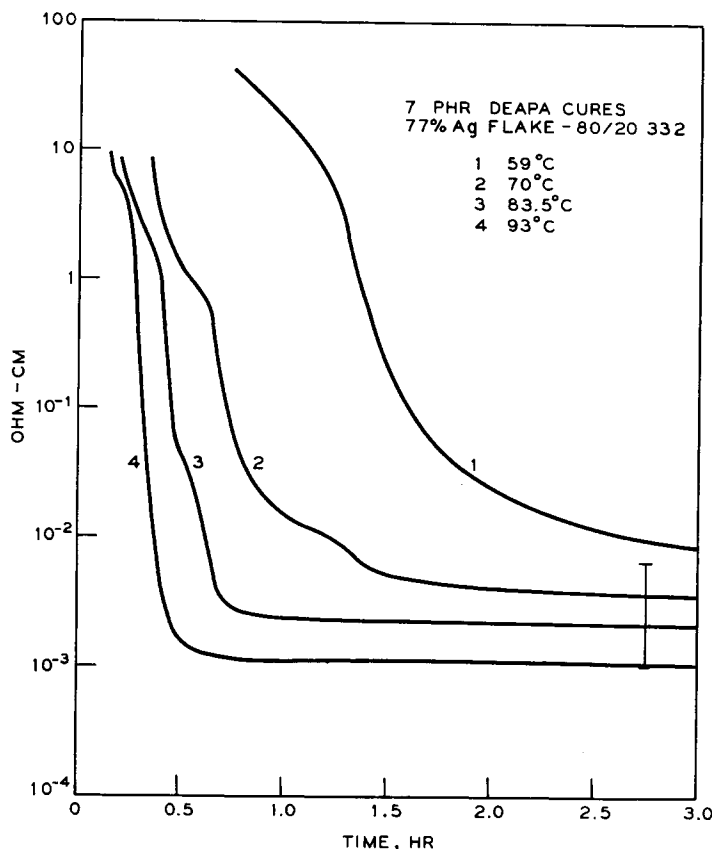


Fig. 8. Resistivity-time curves for DEAPA cures in the 80/20 332 resin.

stoichiometric quantity of 23 phr need appreciably more low viscosity curing agent than the other amines discussed (7–12 phr), and the elevated temperature cure and subsequent initial fluidity are detrimental to reproducibility at the slower rates of the lower range (70–80°C.). Figures 9 and 10 compare three temperature runs each for 77% silver and both resins, indicating a lack of a clear-cut rate difference for this curing agent vis à vis the two resins. Final resistance is strongly curing temperature-dependent. At higher temperatures (115–120°C.) than those feasible for fast cure thermostated runs by this method, the 80/20 resin at 77% silver flake cures to 5×10^{-4} ohm-cm. room temperature resistivity.

The absence of a resin effect (3794 versus 332-LC) possibly indicates an ineffective catalysis by hydroxyl on the sterically hindered amine-epoxy reaction. Furthermore the reducing aspects of the medium show basically no influence during cure, since the achievement of a gelled, then hardened, state is here more essential for particle continuity than any such surface differentiation as is probably operative for TEA. The higher temperatures may substantially moderate the latter effects. The MDA 80/20 332 matrix shows a second step at higher temperatures as it passes through the $5 \times$

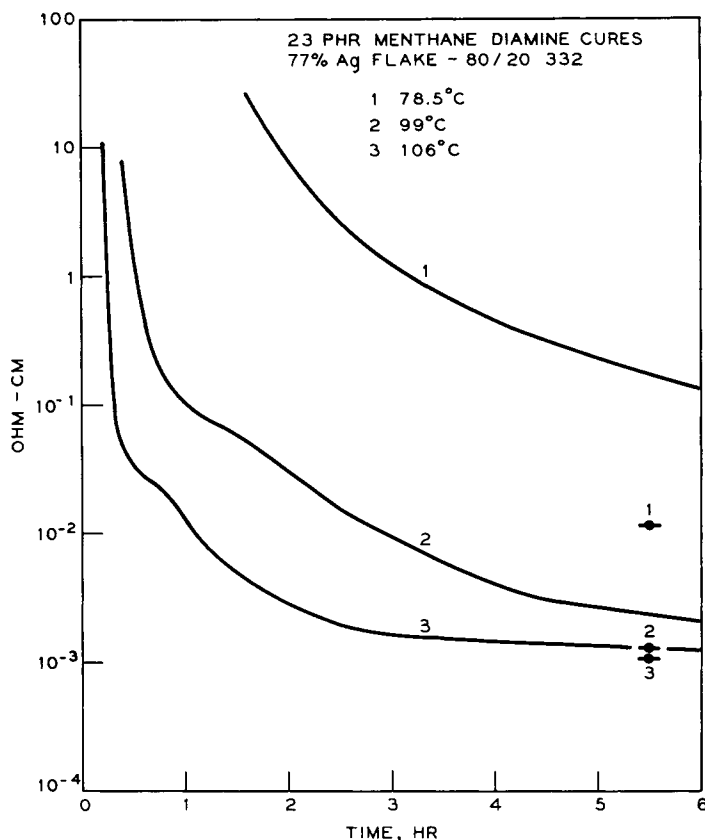


Fig. 9. Resistivity-time curves for MDA cures in the 80/20 332 resin.

10^{-2} ohm-cm. region. The 80/20 3794 plots do not show a clear stepwise sequence. The slope approach to rate data from these plots cannot be satisfactorily applied.

DISCUSSION

A conductive filler such as silver flake with its surface coating and necessarily high concentration may quite conceivably alter the course of the polymerization reactions as opposed to the minimal effect of low concentrations of heat-treated graphite claimed by Chadwick.³ Whatever the extent of this metal effect it is also true that such fillers are typically more sensitive probes of the progress of curing reactions than the low level carbon cases. The use of such techniques for rate information awaits more comparison than is available for the data of this work; it may, however, be stated that for the purposes of understanding the electrical life history of such conductive thermosetting composites, it is likely the most informative method of approach.

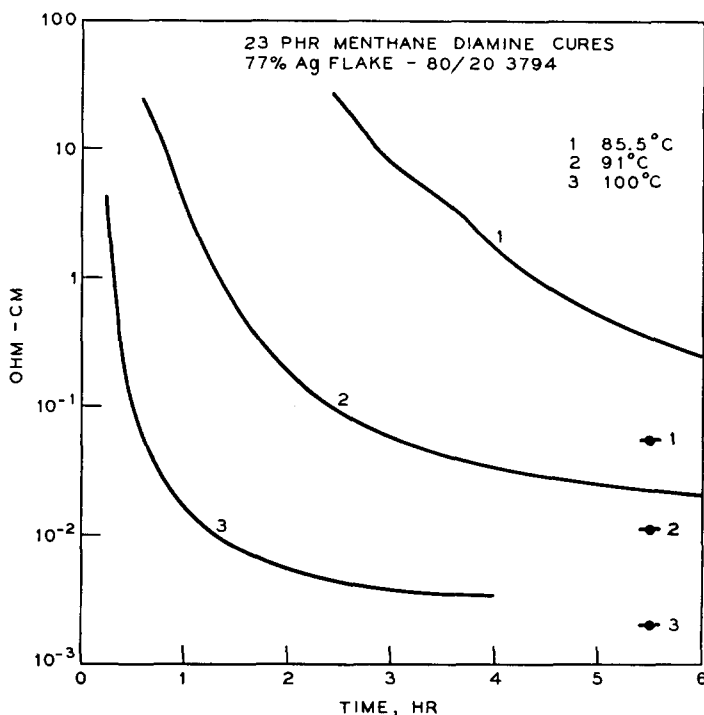


Fig. 10. Resistivity-time curves for MDA cures in the 80/20 3794 resin.

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Résumé

Le recuit des résines époxy chargées d'argent en présence de nombreuses amines a été étudié par des mesures de résistivité dans des conditions isothermes. Dans les cas favorables, des énergies d'activation à partir de 14-17 Kcal/mole ont été obtenues au départ de l'analyse de tangentes des diagrammes- ρ en fonction de t . L'application de la technique à des mesures semblables sur les résines non chargées et légèrement chargées est discutée. De nombreux aspects du comportement électrique de systèmes adhésifs conducteurs à base d'argent ont été classifiés au moyen de ces données cinétiques.

Zusammenfassung

Die Härtung stark silbergefüllter Epoxyharze mit einigen Aminen wurde durch Widerstandsmessung in Abhängigkeit von der Zeit unter isothermen Bedingungen untersucht. In günstigen Fällen wurden Aktivierungsenergien von 14-17 kcal/Mol aus der Neigung der ρ - t -Diagramme abgeleitet. Die Anwendbarkeit des Verfahrens auf ähnliche Messungen an ungefüllten oder schwach gefüllten Harzen wird diskutiert. Viele Aspekte des elektrischen Verhaltens von leitenden Adhäsionssystemen auf Silberbasis werden durch die kinetischen Daten geklärt.

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