Acetylacetonates of Nickel(II) and Copper(II) as Accelerators for the Epoxy Resin System

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SYNOPSIS

The acetylacetonates of nickel(II) and copper(II) serve as accelerators for the anhydride–curable epoxy resin system. An appreciable lowering in the cure gel time and a substantial increase in the rate of curing is observed with enhanced concentrations of the metal chelates. Cure kinetic studies and cure schedules have been followed using a differential scanning calorimeter. The thermal and electrical insulation characteristics of the cured epoxy system are little affected by the variation of temperature, voltage, and aging under UV radiation. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Epoxy resins are extensively used in electrical industries as insulating materials in equipment like motors, generators, transformers, and circuit breakers. There have been unstinted attempts by a number of workers to develop suitable latent accelerators for curing epoxy resins.[1,2] For the sake of convenience, the catalyzed resins are generally stored as one package system in large storage tanks in close proximity to the processing area. An adequate storage stability together with efficient reactivity at ambient conditions and cure at elevated temperatures are the necessary prerequisites for such resin systems. An ideal latent accelerator is expected to

(a) Unalter the storage life of the catalyzed resin system.
(b) Induce a rapid cure of epoxy resins at moderately elevated temperatures (370–460 K).
(c) Grossly maintain the properties of the cured resin system.

Although various compounds[3,4] have been used as latent accelerators for anhydride–epoxy resin systems, the most promising one is boron trifluoride monoethylamine.[5] Nevertheless, the compound has a setback in maintaining electrical properties at elevated temperatures. There are numerous patents[6–8] citing the use of organometallic compounds including acetylacetonates of transition metals as latent accelerators for the anhydride cure of bisphenol-A-based systems.[9–12] It is in this perspective that an attempt has been made to study the feasibility of using nickel(II) acetylacetonate [Ni(acac)$_2$] and copper(II) acetylacetonate [Cu(acac)$_2$] as accelerators for the bisphenol-A-based epoxy system, the results of which are described in this article.

EXPERIMENTAL

Raw Materials

Diglycidyl ether of bisphenol-A (DGEBA, CY 205) and anhydride hardener (HY 905) were procured from Ciba-Geigy India Ltd. and used as such. The characteristics of the resin and hardener are described in Table I. W$_{12}$-grade silica flour of 300 mesh used as the filler was also from Ciba-Geigy and was dried at 383 K for 3 h prior to its use. Ni(acac)$_2$ purchased from Fluka was used without further purification. Cu(acac)$_2$ was prepared and characterized as described elsewhere.[13]

Table I Characteristics of the Resin and Hardener

	Resin (CY 205)	Hardener (HY 905)
Density (g/cm³) at 298 K	1.15–1.20	1.15–1.25
Viscosity (mPas) at 298 K	9000–13000	150–230
Flash point (K) DIN 51758	> 473	423
Storage life	1 year	1 year
Epoxy content	5.0–5.4	—
Anhydride content	—	> 94%

Equipments and Tests

The gel-time characteristics of the resin system were determined according to the test tube gel time method described earlier.[14] Viscosity measurements were made using Brookfield viscometer. A differential scanning calorimeter DSC-2C with a data station (Perkin-Elmer) was employed for kinetic and specific heat measurements under a nitrogen atmosphere with a flow rate of 20 mL/min. The thermal stability studies were made using a thermal analyzer TA HE-20 (Mettler) maintained under an oxygen atmosphere with a flow rate of 20 mL/min and at a heating rate of 6°/min. Heat-distortion temperature (HDT) measurements were made using a Marten's HDT apparatus as per DIN 53458 specifications.

The volume-resistivity measurements were made using a megohm meter (Electronic Instruments) as per ASTM D 257. The dielectric constant and the loss factor (at 50 Hz) values were determined as per ASTM D 150 specifications using an Olman instrument.

Weathering studies were carried out as per ASTM D 2565 using the Xeno test 250 T (W. C. Heraeus) with a xenon lamp intensity of 2.7 kW at 180 kLX, 333 ± 1 K, and 55–95% RH with rain cycle of 18 min rain and 102 min dry.

Preparation of Specimens

Metal(II) acetylacetonates of varying proportions were individually blended with the filler using a mixer. Known quantities of the resin and hardener (1 : 1) were heated independently to 360–365 K (to reduce their viscosities) and mixed thoroughly. The hot resin hardener mixture was poured into the metal chelate–filler blend and stirred vigorously. The homogeneous mixture was then poured into different silicone grease (as the releasing agent) smeared dishes and dies (as per the dimensions of the specifications) and these were kept in an oven maintained at 400–410 K until gelation. The gelated samples were made grease-free using acetone and postcured at 423 ± 2 K for 10 h. During the course of cooling, the bending of the test specimens was avoided by placing them in between stainless-steel plates. The latter were loaded with heavy blocks whose weights were in the range of 2–5 kg. After cooling, the circular disks, each of about 3 mm thickness, were used for determining the electrical properties.

RESULTS AND DISCUSSION

Resin–Hardener Stoichiometry

The resin–hardener stoichiometry was determined using dynamic DSC runs by plotting enthalpy
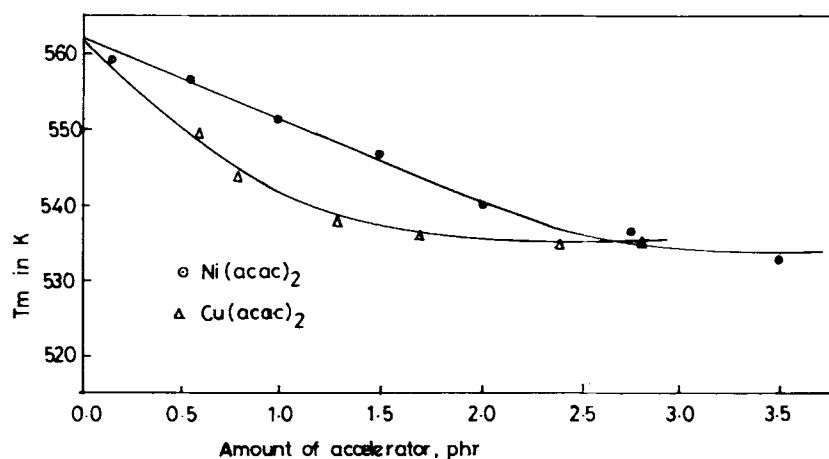
Figure 1 Effect of metal(II) acetylacetonates on T_m of the DSC cure exotherm.

Table II Gel Time and Storage Data for Epoxy System with Metal(II) Acetylacetonates

Accelerator (phr)	Gel Time Data (Min)[a] at Temperature (K)				Catalyzed Storage Lifetime (Days)[b]
	393	408	428	448	
Control system	625	305	155	75	80
Ni(acac)₂					
0.5	410	240	110	40	60
1.0	290	155	55	25	48
1.5	240	122	48	20	38
Cu(acac)₂					
0.5	520	290	145	69	90
1.0	480	250	115	48	85
1.5	450	225	112	40	83

[a] On 10 g impregnant sample in a test tube with a movable spiral wire.

[b] Time required for an increase of 10 times in viscosity at 298 K.

change ΔH against the amounts of hardener used and the stoichiometry was found to be 1 : 1.[14] For commercial applications, the epoxy systems will be generally associated with a suitable filler. In the present study, silica flour was used as the filler in such a way that the control system had the formulation of resin, hardener, and filler in the ratio 1 : 1 : 3.

Effect of $M(\text{acac})_2$, M = Ni or Cu

The curing rate of the resin system increased in the presence of the metal chelates as evidenced by the shift in the DSC cure exotherm (T_m) toward a lower temperature. Further, the rate also increased with increase in parts by weight of the metal chelate per one hundred parts by weight of the resin (phr). The T_m values decrease significantly with increase in the quantity of the metal acetylacetonates up to 1.5–2.5 phr and, thereafter, remain almost constant (Fig. 1). Hence, in the present study, the quantities of the metal chelates was limited to 2.0 phr.

The effect of the metal chelates on the gel time at various temperatures and the storage stability are given in Table II. The data indicate that the gel-time values for a given stoichiometry of the system are lower in the presence of Ni(acac)₂ than those with Cu(acac)₂. Further, the values are considerably lower than those of the control system. It is also evident that as the concentration of the given metal chelate increases the gel-time and storage-stability values of the resin system decrease.

Kinetic Studies

The dynamic DSC scans of the epoxy systems were carried out in the temperature range 315–650 K at
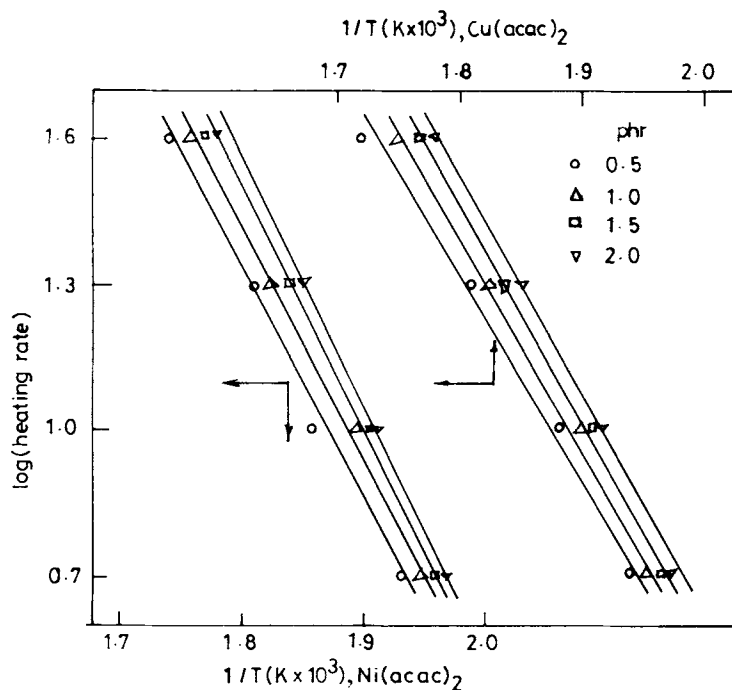
Figure 2 Arrhenius plots for the epoxy system with metal(II) acetylacetonates.

Table III Kinetic Parameters for Epoxy System in the Presence of Metal(II) Acetylacetonates

Accelerator (phr)	Activation Energy (E) (kJ/g)	Preexponential Factor (Z) 10^6 min^{-1}	Rate Constant (k) 10^{-3} min^{-1}
Control system	79.70	23.0–25.6	3.1
Ni(acac)$_2$			
0.5	79.32	16.4–21.2	3.0
1.0	78.48	17.5–21.9	4.1
1.5	77.86	17.2–18.1	4.3
2.0	75.89	12.1–14.2	5.6
Cu(acac)$_2$			
0.5	80.37	19.1–31.4	3.4
1.0	78.82	18.5–22.3	4.1
1.5	80.95	36.1–40.3	4.2
2.0	80.83	37.1–47.8	4.5

Table IV Cure Schedules $(t_f,$ h) for Epoxy System in the Presence of Metal(II) Acetylacetonates

Temperature (K)	Control System 0.0	Ni(acac)$_2$ (phr)			
		0.5	1.0	1.5	2.0
473	0.8–1.2	0.8–1.0	0.7–0.9	0.6–0.8	0.6–0.7
453	2.0–3.0	2.0–2.5	1.7–2.2	1.6–2.0	1.5–1.6
443	3.3–4.9	3.2–3.9	2.7–3.5	2.6–3.3	2.3–2.6
433	5.5–8.2	5.3–6.5	4.4–5.7	4.2–5.3	3.8–4.1
423	9.4–13.9	8.9–11.0	7.4–9.6	7.0–8.8	6.3–6.8
413	16.5–24.3	15.3–18.9	12.8–16.4	12.0–15.2	10.6–11.5
403	29.7–33.7	27.3–33.7	22.5–28.9	21.2–26.6	18.3–19.8
393	54.9–81.6	49.9–61.5	40.9–52.5	38.2–48.0	32.6–35.3

		Cu(acac)$_2$ (phr)			
		0.5	1.0	1.5	2.0
473		1.2–1.6	0.9–1.2	0.8–0.9	0.6–0.8
453		2.9–3.9	2.2–2.8	1.9–2.1	1.5–1.6
443		4.6–6.3	3.6–4.5	3.0–3.5	2.5–2.7
433		7.8–10.6	5.9–7.4	5.1–5.8	4.2–4.5
423		13.2–17.7	9.9–12.4	8.7–9.9	7.2–7.6
413		23.1–30.7	17.1–21.3	15.2–17.3	12.6–13.2
403		41.3–54.9	30.2–37.7	27.3–31.0	22.6–23.7
393		76.0–99.8	55.0–68.6	50.5–57.4	41.9–43.8

Table V Electrical[a] and Thermal Properties for the Epoxy System at 1.0 phr of Metal(II) Acetylacetonates

Accelerator	Loss Factor	Dielectric Constant	Volume Resistivity (ohm-cm) ($\times 10^{14}$)	Specific Heat (J/g deg)	Heat Distortion Temp (K)	Decomposition[b] Temp (K)
Control system	0.026	4.6–5.4	4.3	1.290	360–375	575
Ni(acac)$_2$	0.014	4.5–5.2	8.8	1.237	364–408	573
Cu(acac)$_2$	0.021	3.2–3.8	3.5	1.244	360–375	563

[a] At room temperature measured at 0.5 kV.
[b] At 10% weight loss.
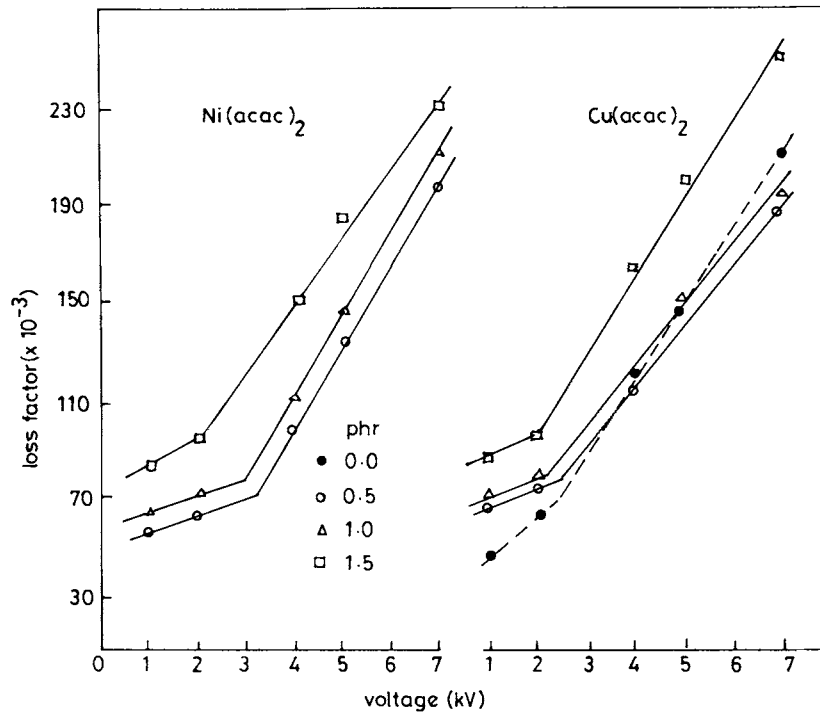
Figure 3 Variation of loss factor vs. voltage for the epoxy system with different phr of metal(II) acetylacetonates.

varying heating rates from 5 to 40 K/min. The temperatures corresponding to the peak minimum (T_m) and the peak final (T_f) of the curing exotherm were determined at various phr of the metal chelates.

The order of the curing reaction "n" was calculated using a single DSC profile at a constant heating rate[15] by plotting log k against $1/T_m$ and the best linear regression fit was observed when $n = 1$ at varied heating rates. The activation energy (E) for the curing reaction was calculated by plotting log (heating rate) vs. $(1/T_m)$ (Fig. 2). Using these values, the preexponential factor (Z) and also the rate
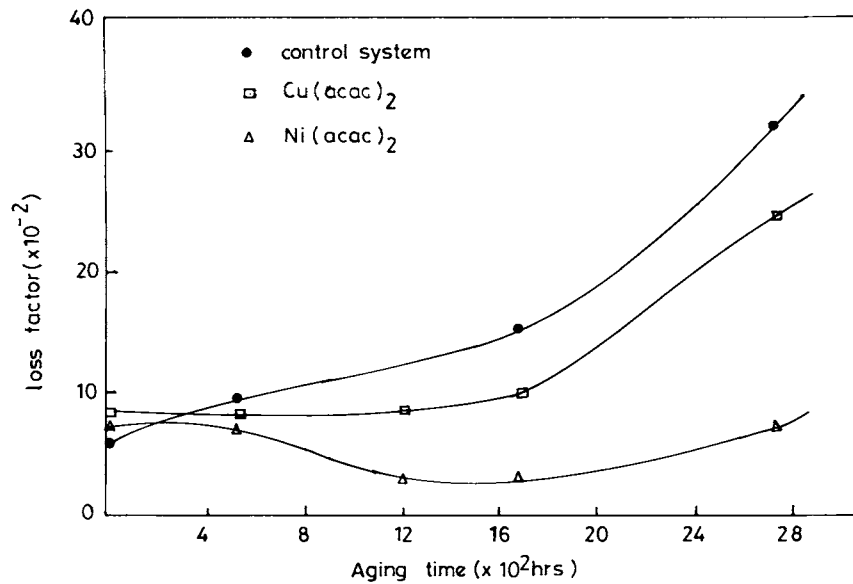
Figure 4 Variation of loss factor at 7 kV voltage stress.

constants (k) were evaluated[16,17] at 423 K. E for the curing epoxy system in presence of various phr of metal chelates has been found to be in the range 75–81 kJ/g (Table III). The rate constant increases with enhanced phr of the metal chelates. The values of n for the epoxy–anhydride system were determined in the presence of the accelerators from the slopes of the plot of log(rate constant) against log(phr) of the metal chelate and are 0.45 and 0.20 for Ni(II) and Cu(II) acetylacetonates, respectively.

Evaluation of Cure Schedules

According to Toop,[18] the degradation process can be considered as a single chemical reaction and, hence,

$$\log t_f = [E/2.303R\theta] + \log[EP(x_f)/BR]$$

where $\log P(x_f) = -2.315 - 0.547 (E/RT_f)$, E = energy of activation, R = gas constant, T_f = temperature at which specific change is observed, B = heating rate, θ = thermal condition, and t_f = time to condition at temperature θ.

For various insulating materials, the thermal ratings were evaluated from TGA thermograms run at varied heating rates.[18–21] The curing of the epoxy system is a process wherein one or more kinds of reactants are transferred from a low molecular weight material to a cross-linked network. The curing process is considered to follow the same mechanism throughout, and, hence, Toop's equation is extended to find the time-to-cure of epoxies.[21] The values of E and T_f determined from the dynamic DSC cure exotherm at different heating rates were substituted in the above equation and the range of cure schedules were calculated (Table IV). The results for the control system were found to be in accordance with the values reported elsewhere.[22] It is noticed that at a given temperature as the phr of the metal chelate increases the cure schedule order decreases. The cure activity of Ni(acac)$_2$ appears to be greater than that of Cu(acac)$_2$, which, in turn, has a higher activity than that of the control system.

## Thermal and Electrical Properties

Addition of a metallic impurity to an insulating material normally affects the thermal stability and other properties of the latter. The data of the thermal properties such as specific heat, heat distortion temperature, and decomposition temperature for the cured epoxy system at 1.0 phr of the metal chelates

are given in Table V. No appreciable change in these properties was noticed excepting a slight decrease in the decomposition temperature of the cured system in the presence of Cu(acac)$_2$ on subjecting it to dynamic TGA runs.

The electrical properties of the cured epoxy system with 1.0 phr of metal(II) acetylacetonates measured at room temperature (Table V) indicate not much variation. For high-voltage insulation applications involving generators, transformers, and ac motors, the limitations of electrical properties are usually dictated by the highest voltages used. Hence, the cured epoxy samples were subjected to variations of voltage. The loss factor data (Fig. 3) reveal that
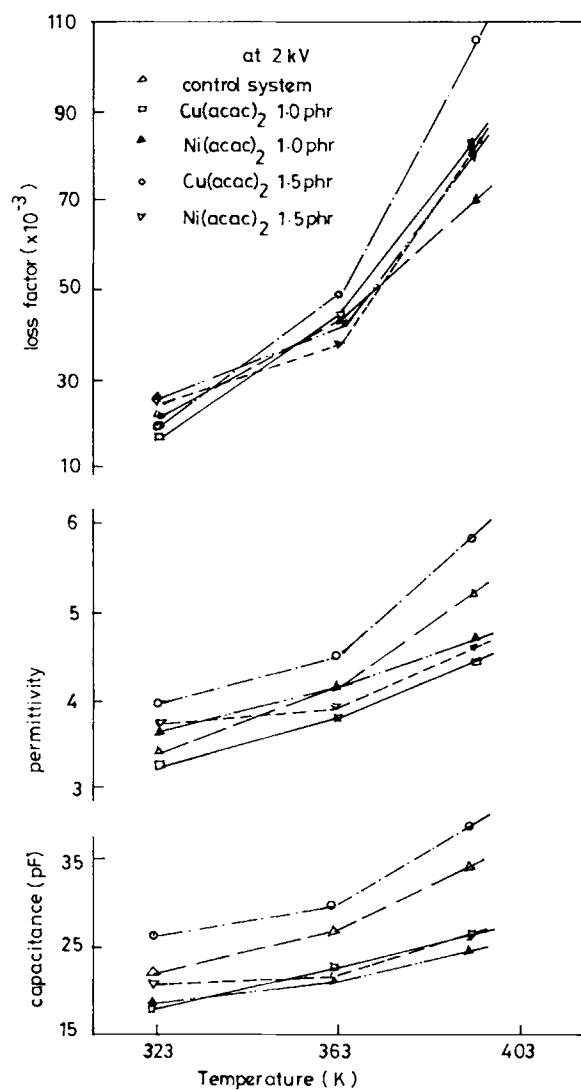
Figure 5 Variation of electrical properties with temperature for the epoxy system in the presence of metal(II) acetylacetonates.
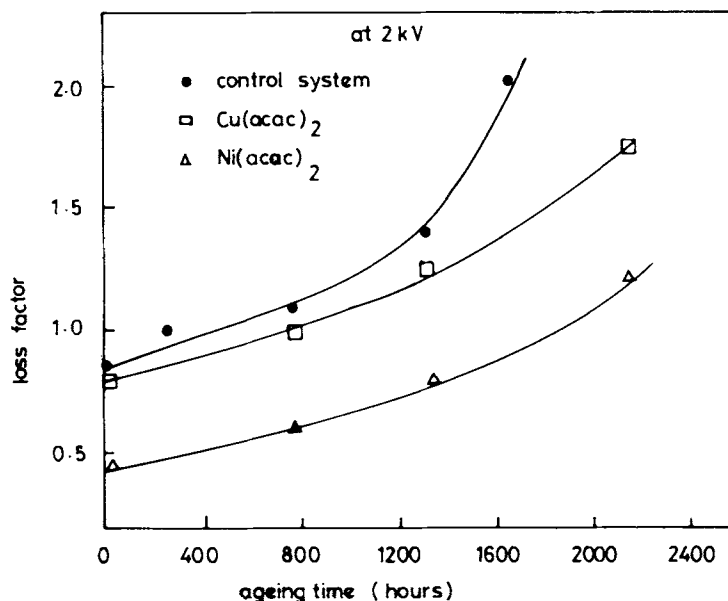
Figure 6 Variation of loss factor for the epoxy system with metal(II) acetylacetonates
(1 phr) at 90 kLx/50% RH/323 K.

for the epoxy system up to 1.0 phr of Ni(acac)$_2$ the values were comparable to those of the control system. A steep rise in the loss factor value was observed at 3 kV and higher. In the case of Cu(acac)$_2$ at 1.0 phr, the epoxy system exhibits higher loss factor values than those of the control system. Further, the values increase at 2.0 kV and higher. It is likely that at elevated temperature the degradation products formed from the copper(II) chelate while curing the epoxy system are more sensitive to voltage.

The voltage-withstanding capability of the resin material is important as many of the epoxy insulating systems will be under continuous voltage gradients. Therefore, the cured epoxy specimens in the presence of metal chelates (1.0 phr) were stressed at a 7 kV voltage gradient (determined on the basis of breakdown strength of the cured epoxy systems that are normally found to be greater than 15 kV/mm) for about 2800 h. The variation of loss factor values were comparable to those of the control system, and no deterioration of the resin material was noticed (Fig. 4).

The thermal endurance studies were carried out for the metal chelate-treated epoxy system, and the variation of capacitance, permittivity, and the loss factor values were plotted against temperature (Fig. 5). The results are almost equivalent to those of the control system for all the phr's (used here) of Ni(acac)$_2$ and up to 1.0 phr of Cu(acac)$_2$. Beyond 1.0 phr of Cu(acac)$_2$, the loss factor value was found to increase. In this case, copper oxide might be

formed and might behave as an oxidation catalyst so as to increase the loss factor.

Radiation and humidity are generally detrimental to the epoxy resin system. To determine the effect of these factors on the properties of the cured epoxy system in the presence of the metal chelates, the samples were aged in a xenon-arc weatherometer. The loss factor, volume resistivity, and change in weight of these aged samples were periodically measured. It was noticed that even after 2000 h of aging the above properties of the epoxy material in the presence of these metal chelates were comparable to those of the control system. A comparison of loss factor values is made in Figure 6.

CONCLUSIONS

The addition of Ni(acac)$_2$ and Cu(acac)$_2$ to the epoxy system decreases the cure time. The overall cure process follows first-order kinetics, the order with respect to Ni(acac)$_2$ and Cu(acac)$_2$ being 0.45 and 0.20, respectively. At the concentration levels studied, Ni(acac)$_2$ does not affect the thermal and electrical properties. However, in the case of Cu(acac)$_2$, a slight impairment of the insulation characteristics was noticed at 1.5 phr or higher.

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