The Effect of Cobalt Complex Addition on the Cure and Properties of an Epoxy Matrix Resin

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Synopsis

The effects of adding various cobalt complexes to a tetraglycidyl methylene dianiline-based epoxy resin were determined. The addition of cobalt(III) acetylacetonate was found to alter the epoxy cure and improve the flexural strength and fracture toughness of the cured resin. These effects were not duplicated by the addition of various other cobalt complexes.

INTRODUCTION

Previous studies at NASA Langley and Virginia Polytechnic Institute and State University have shown that the addition of metal salts and organometallic complexes to polyimides resulted in numerous desirable properties, including increased glass transition temperatures, improved adhesive strengths, and increased electrical conductivity.[1,2] Such properties made these polymers very attractive for aerospace applications where high temperature stability and the ability to dissipate space charging effects are important. Epoxies, however, are still among the most widely used aerospace resins because of their excellent processability, chemical resistance, and low cost. Some work has been performed on the addition of metal ions to epoxies.[3-8] This research has primarily focused on their use as catalytic hardeners for curing epoxies. A preliminary study was conducted at NASA-Langley, however, that evaluated the use of nine different metal ions in epoxies to improve their applicability as composite matrix resins for aerospace applications.[9] The metal salts and organometallic complexes were screened for resin compatability, reactivity, and their effect on the thermal stability and mechanical properties of an epoxy matrix resin. One of the results of that study was that the incorporation of approximately 5% by weight of cobalt(III) acetylacetonate ($Co(acac)_3$) into an epoxy system based on tetraglycidyl methylene dianiline (MY-720) substantially increased the mechanical strength of that highly crosslinked resin. Because the initial evaluation had included only one cobalt complex at one concentration, the current study was performed to more fully determine the effect of incorporating cobalt complexes into an aerospace epoxy resin. MY-720-based epoxies containing four different concentrations of $Co(acac)_3$ were prepared and characterized. Five other cobalt(II) or cobalt(III) complexes were also screened for comparison with the $Co(acac)_3$ epoxy system.

EXPERIMENTAL

Materials

The epoxy control in this study contained MY-720 as the major epoxy component, 4,4'-diaminodiphenylsulfone (DDS) curing agent, and an epoxidized phenolic novolac (SU-8). The MY-720 was obtained from Ciba-Geigy as Araldite MY 9512. The DDS was obtained from Fluka Chemical Co., and the Epi-Rez SU-8 from Celanese Polymer Specialties Co. The epoxy was formulated by dissolving the MY-720/DDS/SU-8 in Fisher Certified methyl ethyl ketone. The cobalt complexes evaluated included cobalt(III) acetylacetonate from Fluka, cobalt(II) acetylacetonate from Aldrich Chemical Co., and the following four complexes obtained from Dr. Larry T. Taylor at Virginia Polytechnic Institute and State University: trans-dichloro-bis-ethylenediamine cobalt(III) chloride([Co(en)$_2$Cl$_2$]Cl), trans-chlorothiocyanato-bis-ethylenediamine cobalt(III) thiocyanate ([Co(en)$_2$Cl(SCN)]SCN), chloropentaamine cobalt(III) chloride ([Co(NH$_3$)$_5$Cl]Cl$_2$), and potassium ethylenediamine tetraacetato cobaltate(III) (K[Co(EDTA)]).

Preparation of Epoxy Control

The MY-720/DDS/SU-8 epoxy control was formulated to simulate aerospace epoxies such as Narmco 5208[10] and contained 73.4% by weight MY-720 with 20.6% DDS and 6.0% SU-8. This resin was prepared in solution by first dissolving MY-720 and SU-8 in MEK and subsequently adding the DDS so that the resulting solution contained 62.5% by weight solids. To prepare neat resin specimens, the epoxy solution was poured into 2.25-in. diameter aluminum pans and degassed at 120°C under vacuum for 45–50 min to remove MEK. The vacuum was released, and the resin was then cured by gradually increasing the oven temperature to 150°C over a 3-h period, with a 1-h hold at 150°C and 2-h final cure at 177°C.

Preparation of Co(acac)$_3$/Epoxies

Two methods were used for the preparation of the Co(acac)$_3$/epoxies. In the first, or standard method of preparation (Fig. 1), Co(acac)$_3$ was added to the MY-720/DDS/SU-8 control solution and stirred for several hours at room temperature until the mixture changed from a grainy, dark green to an opalescent green. Shifts in the N—H stretch region of Fourier transform infrared (FTIR) spectra of the opalescent Co(acac)$_3$/epoxy solution after several hours of room temperature stirring indicated that this change in solution appearance was the result of an interaction between cobalt and the diamine curing agent (Fig. 2). In an effort to maximize the interaction of these two components, a second method of preparing the Co(acac)$_3$/epoxies was also used. In this premix method Co(acac)$_3$ was added to the DDS dissolved in MEK and stirred for several hours at room temperature before adding to an epoxy solution containing the MY-720 and SU-8 dissolved in MEK (Fig. 3). The procedures that were used for degassing and curing the epoxy control were also followed for the Co(acac)$_3$/epoxies. Four concentrations of Co(acac)$_3$ were used, based on molar ratios of cobalt ions to MY-720 polymer repeat units and varying from 1/50 to 1/5.
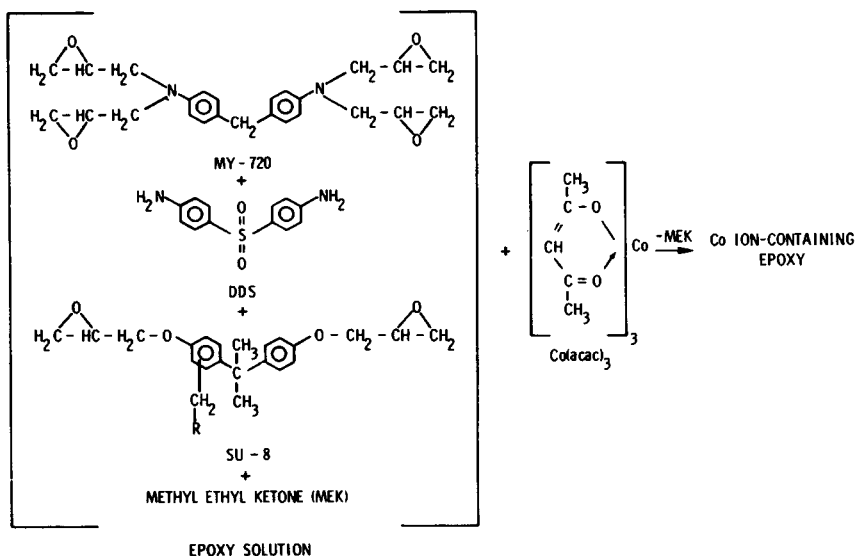
Fig. 1. Standard method of preparing Co(acac)₃/epoxies.

Preparation of Other Cobalt Ion-Containing Epoxies

The premix method was used to prepare epoxies containing Co(acac)$_2$, [Co(en)$_2$Cl$_2$]Cl, [Co(en)$_2$Cl(SCN)]SCN, [Co(NH$_3$)$_5$Cl]Cl$_2$, and K[Co(EDTA)]. These complexes were evaluated at the 1/10 concentration level only. The degassing and cure of these systems were the same as for the MY-720/ DDS/SU-8 control.
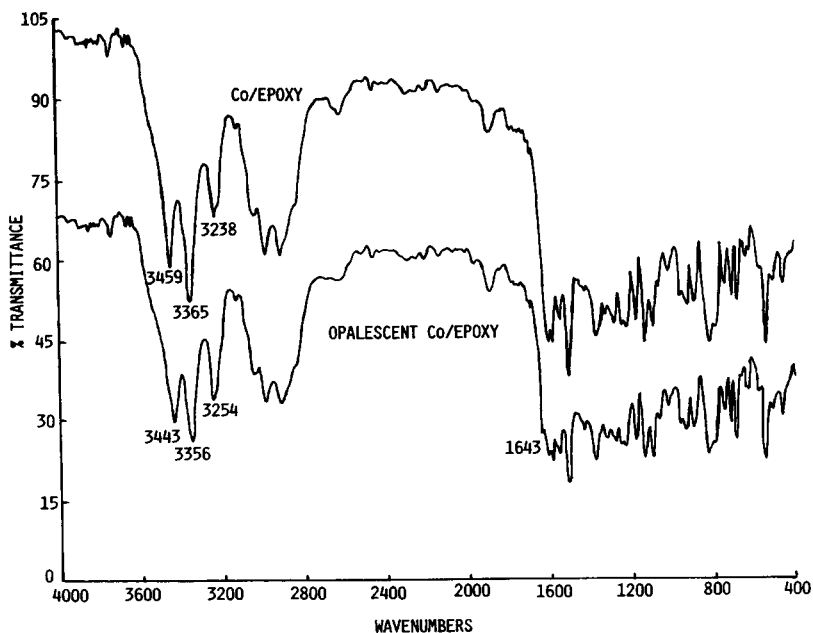

Fig. 2. FTIR spectra of Co(acac)₃/epoxies, initially and after room temperature stirring to achieve opalescence.

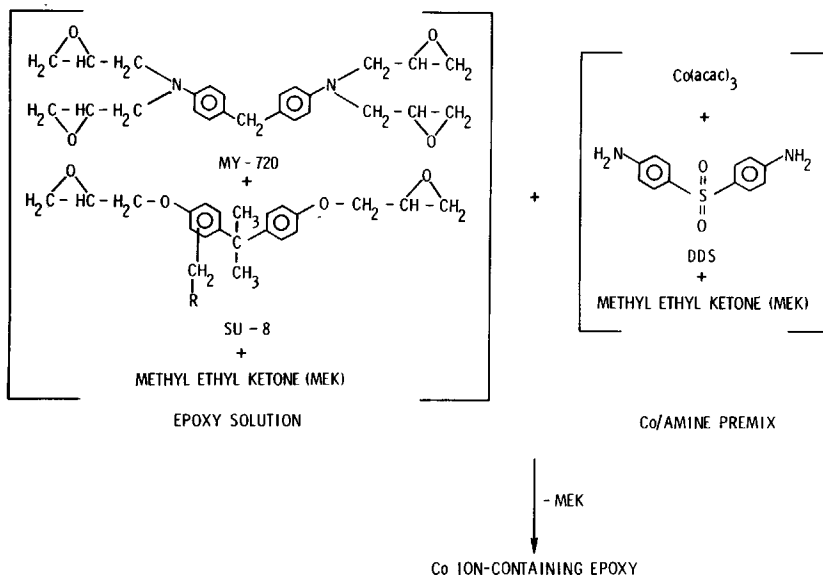Fig. 3. Premix method of preparing Co(acac)₃/epoxies.

Characterization

FTIR spectra were obtained on a Nicolet 60SX FTIR. Gel times were determined at 135°C on a Gel Timer Hot Pot manufactured by Shyodu Precision Instrument Co. using 35 g of degassed epoxy resin. Cure exotherms and heats of reaction were determined on a DuPont Series 990 Thermal Analyzer/Differential Scanning Calorimeter (DSC) at a programmed heating rate of 10°C/min. Glass transition temperatures (T_g's) of the cured epoxies were determined on a DuPont Model 943 Thermomechanical Analyzer (TMA) at a heating rate of 5°C/min using a penetration probe. Densities were obtained in a density gradient tube according to ASTM-D1505-60T. Elemental analyses were performed at Galbraith Laboratories, Knoxville, TN. The thermooxidative stability of powdered epoxy samples was measured in flowing air (15 cc/min) on a Perkin-Elmer Model TGS-2 Thermogravimetric System using an AR-2 Autobalance and a UU-1 Temperature Program Control at a heating rate of 2.5°C/min after an initial 30 min hold at 100°C. Flexural properties were determined at room temperature on neat resin castings of the epoxies using an Instron Testing Machine Model TT-C in a three-point bending mode. Five or six specimens, whose dimensions averaged 6.3 × 1.2 × 45.8 mm, were tested for each concentration. An average span to thickness of 16/1 was used, as specified by ASTM Standard D790-71. Compact tension testing was conducted at the Naval Research Laboratory (NRL), Orlando, FL and at United Technologies Research Center (UTRC), East Hartford, CT. Scanning electron microscopy (SEM) studies were conducted at the Virginia Institute of Marine Sciences (VIMS), Gloucester, VA, using an AMR 1000 Scanning Electron Microscope. Neat resin specimens of the control and of the 1/50 and 1/10 Co(acac)₃/ epoxies were etched in 98% formic acid for 1.5 h. Both etched and unetched specimens were coated on a Denton vacuum evaporator with an approximately 200 Å thick layer of 60:40 gold:palladium.

RESULTS AND DISCUSSION

Co(acac)$_3$/Epoxies

The addition of Co(acac)$_3$ to MY-720/DDS/SU-8 by the premix method was found to accelerate the epoxy cure, an acceleration that increased with increasing cobalt concentration as indicated by gel time measurements (Table I). Co(acac)$_3$/epoxies prepared by the standard method showed this accelerated cure, but to a lesser extent than for the premix systems at a given concentration. For example, the 1/10 Co(acac)$_3$/epoxy gelled in 26 min when prepared by the premix method, but took 45 min to gel when the standard method of preparation was used. This indicated that premixing the cobalt(III) acetylacetonate and the diamine curing agent did enhance the interaction between these two components.

As shown in the DSC curves in Figure 4, the MY-720/DDS/SU-8 control exhibited a single cure exotherm at 273°C. It is generally acknowledged that this cure exotherm may be attributed primarily to epoxy–primary amine reaction. A second and lower temperature exotherm was observed for the Co(acac)$_3$/epoxies. This additional exotherm peaked in a temperature range which is below the final cure temperature of this epoxy resin. As is evident from the scans, the intensity of this early exotherm increased dramatically with increasing Co(acac)$_3$ concentration. Although the exact nature of this cobalt-catalyzed portion of the epoxy cure has not been established, there is some evidence to suggest that it may be largely attributed to homopolymerization. In another study, MY-720/DDS/SU-8 epoxies containing the Lewis acid catalyst, boron trifluoride monoethylamine (BF$_3$:EtNH$_2$), were shown to have network structures that were significantly altered from the uncatalyzed system.[11] It has been suggested that the changes in this BF$_3$-catalyzed system were at least partially attributable to increased homopolymerization.

The heats of reaction (ΔH's) of the Co(acac)$_3$/epoxies listed in Table I were found to decrease with increasing cobalt concentration. These results are believed to be due to the accelerated epoxy cure caused by the presence of the metal. Prior to the DSC runs, the epoxy solutions were degassed under vacuum for 30 min at 100°C to remove the MEK. This degassing was conducted at a lower temperature and for a shorter period of time than during a normal epoxy cure, in an attempt to prevent or minimize any epoxy cure from occurring. Some reaction could not be avoided, however, particularly as the cobalt concentration was increased. As a result, the total heats of

TABLE I
Cure Characteristics of Co(acac)$_3$/Epoxies

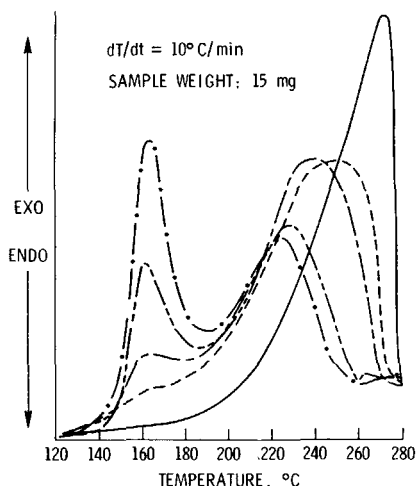| Mole ratio, Co/epoxy	Gel time at 135°C (min)	Heats of reaction (J/g)
0	190	496
1/50	127	483
1/25	102	471
1/10	26	440
1/5	8	395

Fig. 4. DSC curves of Co(acac)$_3$/epoxies: (—) MY-720/DDS/SU-8 control; (– – –) 1/50 Co/epoxy; (— — —) 1/25 Co/epoxy; (– – – –) 1/10 Co/epoxy; (—·—) 1/5 Co/epoxy.

reaction detected by DSC gradually decreased with increasing cobalt concentration due to this premature cure.

Densities of the cured Co(acac)$_3$/epoxies are listed in Table II. The densities were essentially unchanged by the addition of the cobalt complex. No differences in density were noted between samples prepared by the premix method and those prepared by the standard method. Elemental analysis indicated that the percent cobalt in the epoxies ranged from 0.18 to 1.69 as the Co(acac)$_3$/MY-720 mole ratio was increased from 1/50 to 1/5. These values were independent of the method of sample preparation. The appearance of the cured epoxy specimens changed from a transparent amber control to increasingly darker and less transparent discs with increasing Co(acac)$_3$ concentration.

Thermogravimetric analysis (TGA) data obtained on the Co(acac)$_3$/epoxies and epoxy control are compared in Figure 5. The presence of Co(acac)$_3$ caused a slight loss in epoxy thermal stability. Increasing cobalt concentration resulted in a difference of approximately 50°C between the temperature at 50% weight loss for the control and the 1/5 Co(acac)$_3$/epoxy. Curves for epoxies prepared by the premix and the standard methods were essentially identical.

Regardless of the method used for preparing these epoxies, the addition of Co(acac)$_3$ to the MY-720-based epoxy consistently lowered the apparent

TABLE II
Properties of Co(acac)$_3$/Epoxies

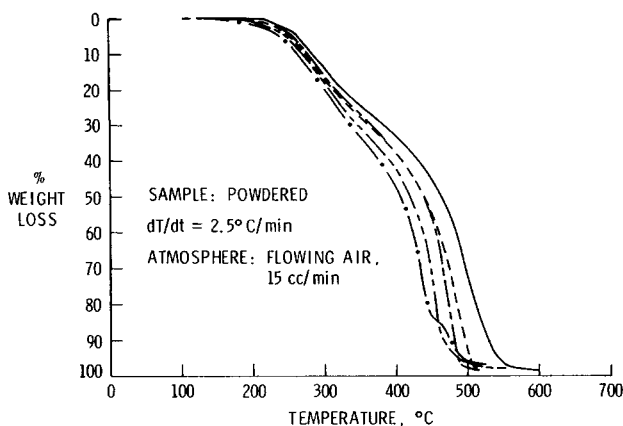| Mole ratio Co/epoxy	Density (g/cc)	Percent cobalt	Appearance of cured discs
0	1.271	0	Transparent amber
1/50	1.271	0.183	Transparent topaz
1/25	1.266	0.378	Transparent topaz
1/10	1.266	0.912	Transparent brown
1/5	1.266	1.690	Opaque dark brown

Fig. 5. TGA thermograms of Co(acac)$_3$/epoxes: (—) MY-720/DDS/SU-8 control; (---) 1/50 Co/epoxy; (————) 1/25 Co/epoxy; (— — —) 1/10 Co/epoxy; (—·—) 1/5 Co/epoxy.

T_g (Table III). This decrease in glass transition temperature became increasingly pronounced as the cobalt complex concentration increased. Differences between the methods of sample preparation also were apparent in these T_g measurements. At any given concentration of Co(acac)$_3$, the T_g was lower for the samples prepared using the more highly accelerated premix method.

Mechanical properties for the Co(acac)$_3$/epoxies prepared by the premix method are shown in Table IV. The flexural property data had an average deviation from the mean of ±7% for the flexural strength and ±5% for the flexural modulus. The addition of Co(acac)$_3$ resulted in a 33% increase in the epoxy flexural strength compared to the control. Stiffness of the epoxies as indicated by the flexural modulus data decreased with increasing Co(acac)$_3$ concentration. Although the 1/10 Co(acac)$_3$/epoxy in this particular series did not show improved flexural strength, previous preparations at this concentration did show an enhancement in the flexural strength.[9,12] Because of the brittle nature of these highly crosslinked polymers and the difficulty in precracking such systems, the compact tension testing at NRL was conducted without precracking the test specimens. The 1/50 concentration showed a substantial increase in the fracture toughness over that of the control. This effect was even more evident at the 1/10 concentration with a G_{I_c} value 3.6 times that of the MY-720/DDS/SU-8 control. Additional evaluation of compact tension specimens was conducted under a task agree-

TABLE III
Glass Transition Temperatures of Co(acac)$_3$/Epoxies

Mole ratio Co/epoxy	T_g by TMA (°C)	
	Standard prep	Premix method
0	206	—
1/50	198	193
1/25	185	180
1/10	186	167
1/5	158	131

TABLE IV
Mechanical Properties of Co(acac)$_3$/Epoxies

Mole ratio Co(acac)$_3$/ epoxy	Flexural strength (ksi)	Flexural modulus (ksi)	G_{Ic}[a] (J/m^2)	G_{Ic}[b] (J/m^2)
0	18.9	692	389	39
1/50	25.1	679	688	—
1/25	21.9	613	—	—
1/10	19.2	593	1398	165
1/5	24.3	539	—	—

[a]Tests conducted at NRL with a crosshead speed of 0.5 mm/min without precracking the specimens.

[b]Tests conducted at UTRC on precracked specimens with a crosshead speed of 0.25 mm/min.

ment with UTRC[13]. The control and the 1/10 Co(acac)$_3$/epoxy were evaluated, and, in this case, the specimens were precracked, accounting for the lower G_{Ic} values. The trend is the same, however. The 1/10 Co(acac)$_3$/epoxy had G_{Ic} values 4.2 times that of the control. The fracture surfaces of the precracked control specimens were shiny and smooth, indicating a characteristically brittle fracture. The Co(acac)$_3$/epoxies had a ridged fracture surface indicative of crack propagation and arrest (Fig. 6).

SEM's of acid-etched and unetched specimens revealed no significant structural differences between the control and the Co(acac)$_3$/epoxies at high magnification (10,000 ×). At low magnification (210 ×) the control and the 1/50 Co(acac)$_3$/epoxy appeared very similar to the unetched specimens except for occasional holes where polymer had been etched away. The 1/10 Co(acac)$_3$/epoxy, however, was pitted with larger and more numerous holes (Fig. 7). These results are perhaps consistent with an increase in the for-
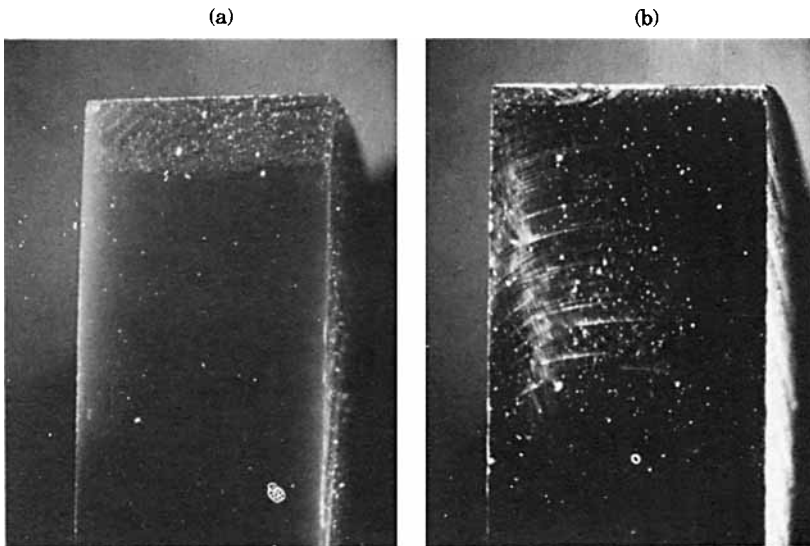

(a)   (b)

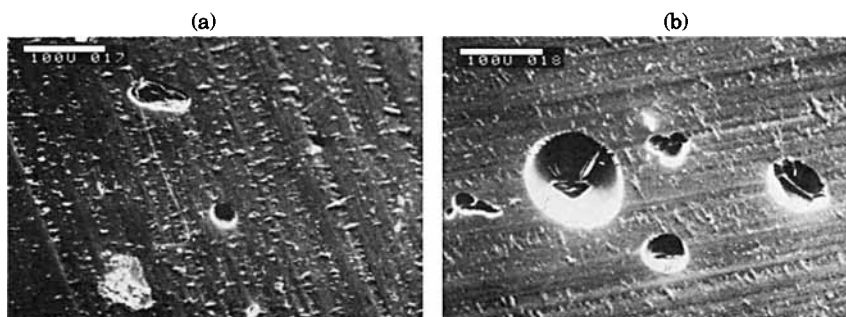Fig. 6.   Fracture surfaces of compact tension specimens: (a) MY-720/DDS/SU-8 control; (b) 1/10 Co(acac)$_3$/epoxy.

Fig. 7.   SEM photomicrographs of acid etched epoxies: (a) MY-720/DDS/SU-8 control; (b) 1/10 Co(acac)₃/epoxy.

mation of a more soluble homopolymer resulting from the cobalt-catalyzed cure.

Additional Cobalt/Epoxies

Cobalt(II) acetylacetonate and four cobalt(III) complexes were also added to the MY-720/DDS/SU epoxy at a concentration of 1/10 cobalt/epoxy. The complexes are listed in Table V along with the densities and appearances of the cured discs. The disc appearances gave some indication of the solubility problems encountered with these systems. None of the complexes were completely soluble at room temperature, and none of the solutions in MEK developed the opalescent appearance of the $Co(acac)_3$/epoxy system.

TGA's of all of these Co/epoxies showed a slight sacrifice in thermal stability due to the presence of the metal additive. Representative curves are shown in Figure 8. The least stable of the polymers prepared contained the $Co(acac)_2$ additive.

Some representative DSC scans of the epoxies containing various cobalt complex additives are shown in Figure 9. DSC scans of the 1/10 $Co(acac)_2$/epoxy (Fig. 9) and the 1/10 $[Co(en)_2Cl(SCN)]SCN$/epoxy showed the ap-
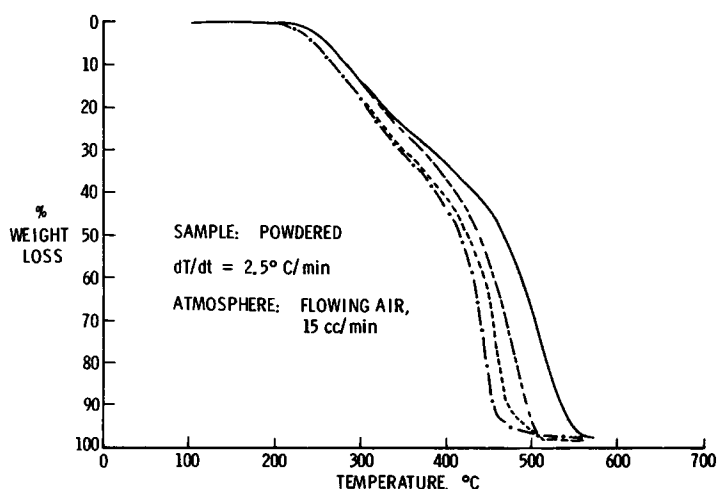

Fig. 8.   TGA thermograms of various Co/epoxies: (—) control; (- - - -) 1/10 $Co(acac)_3$; (- · · -) 1/10 $Co(acac)_2$; (— — —) 1/10 $[Co(en)_2Cl_2]Cl$.

TABLE V
Properties of Other Co/Epoxies

Cobalt complex	Density (g/cc)	Appearance of cured discs
Control	1.266	Transparent amber
Co(acac)$_3$	1.264	Transparent brown
Co(acac)$_2$	1.265	Transparent olive green
[Co(NH$_3$)$_5$Cl]Cl$_2$	1.271	Transparent amber with insoluble flecks of complex
[Co(en)$_2$Cl(SCN)]SCN	1.274	Opaque dark brown
[Co(en)$_2$Cl$_2$]Cl$_2$	1.280	Transparent green
K[Co(EDTA)]	1.288	Transparent amber with layer of undissolved complex on bottom

pearance of the additional cure exotherm that had been noted earlier for the Co(acac)$_3$ system. In these two systems, however, the exotherm occurred at a slightly higher temperature and was substantially lower in magnitude than for the Co(acac)$_3$/epoxy. As represented by the [Co(en)$_2$Cl$_2$]Cl/epoxy curve in Figure 9, epoxies containing the remaining three cobalt(III) complexes produced a single cure exotherm similar to the MY-720/DDS/SU-8 control, but occurring at a lower temperature.

Glass transition temperatures and flexural properties of the cobalt/epoxies are listed in Table VI. Unlike the 1/10 Co(acac)$_3$/epoxy which depressed the T_g from 206°C for the control to 167°C (Table III), these cobalt/epoxies showed no significant reduction in T_g. This was true even for the two systems that exhibited the additional DSC cure exotherm. These cobalt/epoxies did not show any increase in flexural strength. The Co(acac)$_2$/epoxy and the [Co(en)$_2$Cl(SCN)]SCN/epoxy did show a 9% reduction in flexural modulus compared to 14% for the 1/10 Co(acac)$_3$/epoxy previously shown in Table IV.

Gel time determinations on the Co(acac)$_2$ and thiocyante systems may explain why these two cobalt/epoxies did not more closely duplicate the cure and properties of the Co(acac)$_3$/epoxy. As was shown in Table I, the control gelled in 190 min at 135°C, while the 1/10 Co(acac)$_3$/epoxy gelled
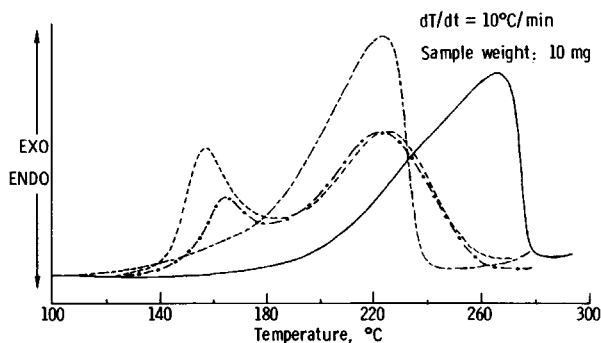

Fig. 9. DSC curves of various Co/epoxies: (——) control; (— — — —) 1/10 Co(acac)$_3$; (—·—) 1/10 Co(acac)$_2$; (— — —) 1/10 [Co(en)$_2$Cl$_2$]Cl.

Cobalt complex	T_g by TMA (°C)	Flexural strength (ksi)	Flexural modulus (ksi)
Control	206	18.9	692
Co(acac)₂	195	17.4	631
[Co(en)₂Cl₂]Cl	210	15.0	670
[Co(en)₂Cl(SCN)]SCN	214	16.0	628
[Co(NH₃)₅Cl]Cl₂	208	14.2	681
K[Co(EDTA)]	200	16.0	705

in only 26 min. The Co(acac)₂/epoxy took 190 min to gel, showing no acceleration at all. The [Co(en)₂Cl(SCN)]SCN gelled in 170 min, showing only minimal acceleration. The acceleration in cure above 160°C implied by the DSC scans of these two polymers was not demonstrated by the gel time determinations at 135°C. At this lower temperature the solubility of these two complexes was so limited that no acceleration occurred. For approximately the first 2 h of the cobalt/epoxy cure cycle, the temperatures are below 135°C. The solubility of the Co(acac)₂ or the [Co(en)₂(SCN)]SCN is limited at these lower temperatures compared to that of the Co(acac)₃, preventing cure acceleration or the altered mechanical properties that were seen in Co(acac)₃/epoxy system.

CONCLUSIONS

A Co(acac)₃/epoxy resin system has been prepared and characterized. The addition of Co(acac)₃ to an MY-720/DDS/SU-8 epoxy was found to accelerate the cure and produce an additional cure exotherm in the DSC scan of this polymer compared to a similar epoxy control containing no additive. FTIR spectra indicate that the catalytic species results from an interaction of Co(acac)₃ with the diamine curing agent. The concentration of the Co(acac)₃ and the extent of its interaction with the diamine determine the degree of this acceleration. The addition of this cobalt complex to the MY-720/DDS/SU-8 control lowered the T_g of the polymer, but did not effect the density and resulted in only a slight sacrifice in thermal stability. The Co(acac)₃/epoxy possesses improved flexural strength and increased fracture toughness, possibly the result of homopolymerization occurring early due to the cobalt-catalyzed cure. The evaluation of five additional cobalt ion-containing epoxy systems demonstrated the uniqueness of the Co(acac)₃/epoxy. Solubility of these complexes was limited and the resulting cobalt/epoxies did not show the acceleration of cure, reduction in T_g, or the improvement in flexural strength that was observed with the Co(acac)₃/epoxy.

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