Study on the Catalytic Behavior of Metal Acetylacetonates for Epoxy Curing Reactions

Zhuqing Zhang, C. P. Wong

School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

ABSTRACT: Metal acetylacetonates are effective latent catalysts for epoxy/anhydride systems. A screen test on the catalytic behavior of metal acetylacetonate shows that this system offers a wide range of curing latency and material properties. It can be inferred that the curing behavior is closely related to the bonding strength of the metal ion to the ligand. Isothermal kinetic study on the catalytic behavior of metal chelates with first-row transition metal ions is conducted and analyzed by using an autocatalytic model. It is found that the activation energy of the system containing the divalent metal chelates follows the Irving and Williams rule. The activation energies of the reaction obtained in the kinetic study are compared with the dissociation energies of the metal/ligand bond and the results are discussed. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1572–1579, 2002

Key words: metal acetylacetonates; epoxy/anhydride system; catalytic behavior; kinetics; activation energy

INTRODUCTION

The development of latent catalysts for epoxy resins has achieved much attention in recent years. Organometallic compounds have been explored as the latent catalysts for various epoxy resin systems.[1,2,3] Metal acetylacetonates (AcAcs), in particular, are found to be effective latent accelerators for anhydride-cured epoxy resins.[4,5,6] Successful encapsulant materials have been developed on the basis of this system for flip-chip underfill applications in electronic packaging.[7,8] The usefulness of metal AcAcs as catalysts for epoxy-curing reaction lies not only in their high catalytic latency, but also in the wide range of curing temperature they can offer.

Despite the fact that metal AcAcs have been used extensively as catalysts for epoxy resins, there has been a lack of systematic study on their catalytic behaviors. Reddy's work was focused on the curing kinetics of epoxy/anhydride/Co (III) AcAc system.[5] Their results showed that it followed first-order kinetics. Smith studied the curing behavior of the epoxy/anhydride/metal AcAcs system for a number of different metal AcAcs.[4] He suggested that the decomposition products of the metal AcAcs might be the active species responsible for initiating polymerization in epoxy/anhydride resin systems. A systematic study on metal chelate cured epoxy resins was conducted by Kurnoskin.[9–13] The study included the reaction mechanisms, structures, and various properties of epoxy/

metal chelate matrices. Although the work was mainly for epoxy resins cured by metal chelate, there were some revealing points that can be applied to the epoxy/anhydride/metal chelate system as well. In this work, a variety of metal AcAcs are investigated as the catalysts of epoxy/anhydride system. The curing kinetics study on this system can provide us with more insight into the nature of the reactions.

EXPERIMENTAL

Materials

Two types of epoxy resins were used in this study. They were bisphenol-A-type epoxy resins (EPON 828 from Shell Chemical Company, Houston, TX) and cycloaliphatic epoxy resins (ERL 4221 from Union Carbide Corporation, Danbury, CT). The epoxy equivalent weight (EEW) of ERL 4221 was 134 g/mol, and the EEW of EPON 828 was 188 g/mol. The curing agent used in this study was hexahydro-4-methylphthalic anhydride (HMPA), purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI). The molecular weight of HMPA was 168.2 g/mol and its purity was >97%. The chemical structures of the epoxy resins in this study and HMPA are shown in Figure 1.

The metal AcAcs studied are included in Table I. Most of the metal AcAcs were purchased from Research Organic/Inorganic Chemical Corp. (Bellville, NJ) and stored in the lab for more than 10 years. However, Co (II) AcAc, Co (III) AcAc, Fe (II) AcAc, Fe (III) AcAc, and Ni (II) AcAc were newly purchased from Aldrich Chemicals, Inc. For study on the curing kinetics, Cu (II) AcAc and Cr (III) AcAc were purchased from Avocado Research Chemicals Ltd. (Ward
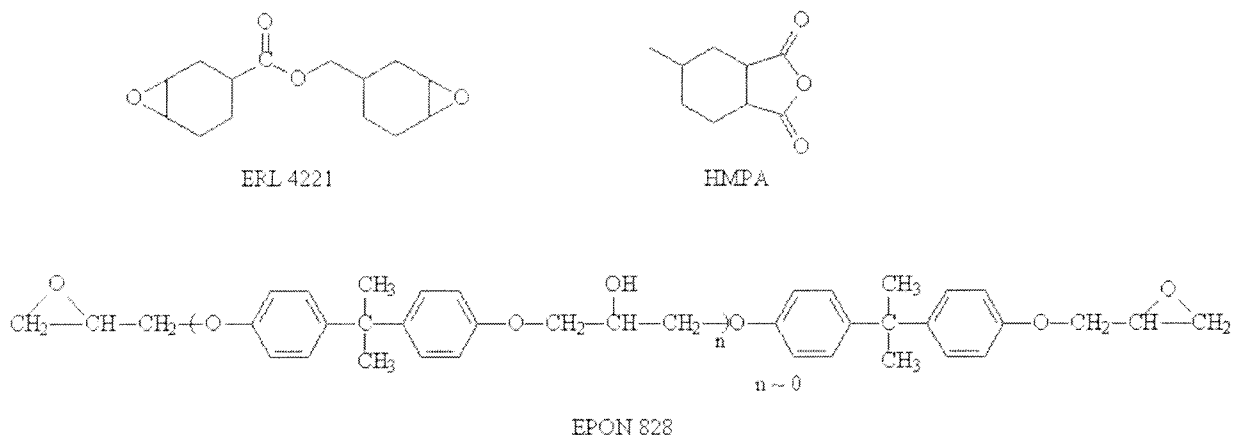
Figure 1 Chemical structures of epoxy resins and hardener in study.

Hill, MA). Mn (II) AcAc and Mn (III) AcAc were purchased from TCI America (Portland, OR). The melting points of the metal AcAcs were obtained either from the literature or from DSC experiments and are listed in Table I.

For formulations based on cycloaliphatic epoxy resin, the mixing weight ratio of ERL 4221 : HMPA : metal AcAc was 100 : 100 : 0.80. The metal AcAcs were dissolved in the epoxy resins at high temperature before the addition of HMPA. The dissolving temperature depended on the solubility of the metal AcAcs in ERL 4221. The dissolving behavior of the metal AcAcs was recorded and included in Table I. In the case of formulations based on bisphenol-A resin, the weight ratio of EPON 828 : HMPA was 100 : 71.2. A molar concentration of 0.005 mol metal ion per mole epoxide was used in this case.

Instruments

The thermal stability of a metal AcAc was investigated by using a thermal gravimetric analyzer (TGA), model 2050 by TA Instruments. A sample of $\sim$ 20 mg was placed in a platinum pan and heated to 400°C at a heating rate of 5°C/min under N_2 purge (77 mL/min in the vertical direction and 12 mL/min in horizontal direction). A curve of weight loss versus temperature can be obtained.

The dynamic curing profile of a formulation was obtained using a modulated differential scanning calorimeter (DSC), model 2920 by TA Instruments. A sample of $\sim$ 10 mg was placed into a hermetic DSC sample pan and heated in the DSC cell from room temperature to 350°C at a heating rate of 5°C/min under N_2 purge (40 mL/min). The reaction heat was recorded as a function of temperature. The onset temperature and the peak temperature of the curing reaction were recorded. For the kinetics study, isothermal DSC experiments were conducted. The sample was placed into a hermetic DSC sample pan and kept at a certain temperature for a sufficient amount of time. For each formulation, four isothermal temperatures were chosen within ±20°C of the onset curing temperature in a dynamic DSC curing profile at a heating rate of 5°C/min. The reaction heat was recorded as a function of time.

RESULTS AND DISCUSSION

Screen test

The screen test of the catalytic behavior of metal AcAcs was performed on an ERL 4221/HMPA/metal AcAc system. Altogether, 43 formulations were investigated in terms of the solubility of metal AcAc in the epoxy resin, the DSC curing profile at a heating rate of 5°C/min, and the qualitative properties of cured resins after curing at 170°C for 30 min and then at 230°C for another 30 min. These results are included in Table I. As can be observed in the table, metal AcAcs offer a wide range of curing temperatures and curing properties for the ERL 4221/HMPA system. We are interested in understanding what causes the difference in the catalytic behavior among these metal AcAcs.

As mentioned in Smith's work,[4] insolubility of some metal AcAcs may have been a contributing factor in determining the catalytic behavior. However, some lanthanide ions (e.g., Nd, Sm, Gd, etc.) did not dissolve into the epoxy resins but showed a catalytic effect at a low-onset curing temperature. Also, according to Smith, the mechanism of reaction may be related to the tendency of some metal AcAcs to decompose or dissociate at an elevated temperature. Hence, TGA studies on the decomposition of some metal AcAcs were conducted. TGA results on these metal AcAcs did not show a strong correlation between the decomposition temperature of the metal AcAcs and the curing temperature of epoxy/anhydride/metal AcAc system, as shown in Table II. For instance, Co (II) AcAc and Fe (II) AcAc displayed similar weight

TABLE I
Basic Curing Properties of ERL 4221/HMPA/Metal AcAc System

Metal Chelate	Melting point (°C)	Solubility in ERL 4221	Onset temperature (°C)	Peak temperature (°C)	Curing property	
					30 min @ 170°C	30 min @ 170°C + 30 min @ 230°C
Li(I) AcAc	250	150°C	168	219, 322	Cured	—
Na(I) AcAc	210	150°C	152	176	Air bubble, brittle	Cured
Be(II) AcAc	108	60–70°C	162	198, 259	Not cured	Cured
Mg(II) AcAc	259	Not dissolved	—	315	Not cured	Brittle, crack
Ca(II) AcAc	175	150°C	112	257	Not cured	Brittle, crack
Sr(II) AcAc	220	150°C	101	227	Not cured	Brittle, crack
Ba(II) AcAc	320	150°C	165	282	Not cured	Cured
Ga(III) AcAc	194	150°C	100	181	Cured	Cured
In(III) AcAc	186	Not dissolved	76	132	Soft material	Brittle, crack
TI(III) AcAc	160–165	Not dissolved	75	135	Cured	Cured
Pb(II) AcAc	141–144	Not dissolved	83	179	Cured	Cured
La(III) AcAc	150	110°C	168	209	Cured	Cured
Pr(III) AcAc	139	Not dissolved	98	209	Cured, brittle	Cured, brittle
Nd(III) AcAc	140	Not dissolved	88	204	Cured, brittle	Cured, brittle
Sm(III) AcAc	138	Not dissolved	94	203	Cured, brittle	Cured, brittle
Gd(III) AcAc	100	Not dissolved	88	195	Cured, brittle	Cured, brittle
Tb(III) AcAc	101	Not dissolved	92	206	Cured, brittle	Cured, brittle
Dy(III) AcAc	103	Not dissolved	152	199	Cured	Cured
Ho(III) AcAc	104	110°C	148	189	Cured	Cured
Er(III) AcAc	103	Not dissolved	97	187	Cured, brittle	Cured, brittle
U(II) AcAc	225	Cured	—	—	—	—
Tm(III) AcAc	97	Not dissolved	165	202	Not cured	Cured
Th(II) AcAc	171	130°C	120	169	Not cured	Cured
Cd(II) AcAc	235	Not dissolved	95	200	Cured, brittle	Cured
Sc(III) AcAc	187–190	90°C	121	160	Cured, brittle	Cured
Y(III) AcAc	102	90°C	97	158	Cured, brittle	Cured
Cu(II) AcAc	284	90°C	199	232	Cured	Cured
Ti(IV) AcAc	subl. 200	Not dissolved	140	266	Not cured	Cured
Zr(IV) AcAc	—	Cured	—	—	—	—
Hf(IV) AcAc	193	150°C	200	288	Not cured	Cured
Co (II) AcAc	166	60°C	156	207	Not cured	Cured
Co (III) AcAc	210–213	60°C	180	217	Not cured	Cured
Fe (II) AcAc	175	60°C	124	176	Cured	Cured
Fe (III) AcAc	182–185	60°C	50	149	Cured	Cured
V(III) AcAc	184	90°C	148	193	Cured	Cured
Mo(III) AcAc	179	Not dissolved	167	212	Cured	Cured
Mn(II) AcAc	261	150°C	166	205	Cured	Cured
Ru(III) AcAc	260	90°C	199	263	Not cured	Crack
Rh(III) AcAc	263	90°C	174	235	Cured	Cured
Pd(II) AcAc	132–205	Not dissolved	94	205	Cured, brittle	Cured, brittle
Pt(II) AcAc	250	130°C	220	248	Not cured	Crack
Ni(II) AcAc	240	90°C	185	249	Not cured	Cured
Lu(III) AcAc	—	Not dissolved	169	193	Cured, brittle	Cured

loss over heating, as shown in Table II. However, their catalytic reactivities were quite different. However, considering the behavior of metal AcAcs as solids in the nitrogen atmosphere might differ from that in a solution of epoxy resins, it is possible that the metal–ligand bonding strength or energy is responsible for their reactivity in catalyzing the curing reaction.

According to the crystal field theory (CFT), the metal complexes are stabilized through the crystal field stabilization energy (CFSE) generated by the deformation of the *d* electron cloud when the metal ion is surrounded by the ligands.[14] If the catalytic behavior of metal AcAcs is related to the dissociation of the bond between the metal ion and the ligand, the curing reactivity of these formulations should be able to correlate to the CFSE of the metal complexes. Most of the metal AcAcs investigated here can be classified into three categories in terms of their catalytic behavior.

The first group consists of chelates with alkali and alkaline earth metal ions. They typically give a low-onset curing temperature and a high curing peak temperature with relatively poor properties of cured resins. As these ions do not have *d*-orbitals or only filled *d*-orbitals, crystal field stabilization cannot occur.

TABLE II
Onset Temperatures of Decomposition of Some Metal AcAc's Compared with Their Catalytic Behavior in ERL 4221/HMPA System

Metal ion	Onset decomp. temp.	Onset curing temp.	Peak curing temp.
Co (II)	170°C	156°C	207°C
Fe (II)	172°C	124°C	176°C
Mn (II)	215°C	166°C	205°C
Ni (II)	212°C	185°C	249°C
Cu (II)	200°C	199°C	232°C

There is only electrostatic bonding between the ion and the ligand and the bonding strength is poor. Therefore, the metal chelates easily dissociate in the epoxy resins and start the reaction at low temperature. However, because the metal ions cannot form strong bonds with epoxy or HMPA because of the nature of their electron configuration, they do not show an effective catalytic behavior, resulting in high curing peak temperature and poor material properties. Exceptions in this group include Li (I) AcAc and Be (II) AcAc, which showed sufficient catalytic effects for ERL 4221/HMPA system. These two ions have low atomic number and small radius. Hence, the bonding of the ions to the ligand possesses a high portion of covalent bonding rather than pure electrostatic bonding. Therefore, the bonding strength of Li (I) and Be (II) to the ligand is substantially higher than that of the other ions in this group, which makes their catalytic behavior different from other alkali and alkaline earth metal ions.

The second group consisted of chelates with lanthanide and actinide ions. Although these ions possess partially filled *f*-orbitals, the *f*-electrons are not effective in forming coordination bond. Therefore, they showed similar behavior to the first group, namely, low curing onset temperature, high curing peak temperature, and poor material properties of cured resins.

The third group contained chelates with transition metal ions with partially filled *d*-orbitals. They displayed a variety of curing reactivities and usually better material properties after curing, as indicated in Table I. To take a close look at these metal AcAcs, studies were conducted on EPON 828/HMPA/metal AcAc system. BisA-type epoxy was chosen in the kinetic study because it possesses a symmetric structure, unlike ERL 4221, whose two epoxide groups might have different reactivity, which introduced complexity in curing kinetics. The metal chelates containing the first row of transition metal ions were investigated, including Cr, Mn, Fe, Co, Ni, Cu, and Zn. To keep a consistent ratio of metal ion to epoxide group, a molar concentration of 0.005 mol/1 mol epoxide was adopted for all formulations.

Curing kinetics study

To further investigate the catalytic behavior of some transition metal AcAcs, kinetics studies were conducted on EPON 828/HMPA/metal AcAc system. The metal chelates containing the first row of transition metal ions were investigated, including Cr, Mn, Fe, Co, Ni, Cu, and Zn. First, a DSC dynamic curing profile at a heating rate of 5°C/min was obtained for each EPON 828/metal AcAc formulation and EPON 828/HMPA/metal AcAc formulation. Results showed that even without anhydride, metal AcAc had the ability to cure epoxy resins. However, the reaction occurred at a much higher temperature. Figure 2 shows the curing diagram of the two systems when Co (II) AcAc was used. This indicates that the metal
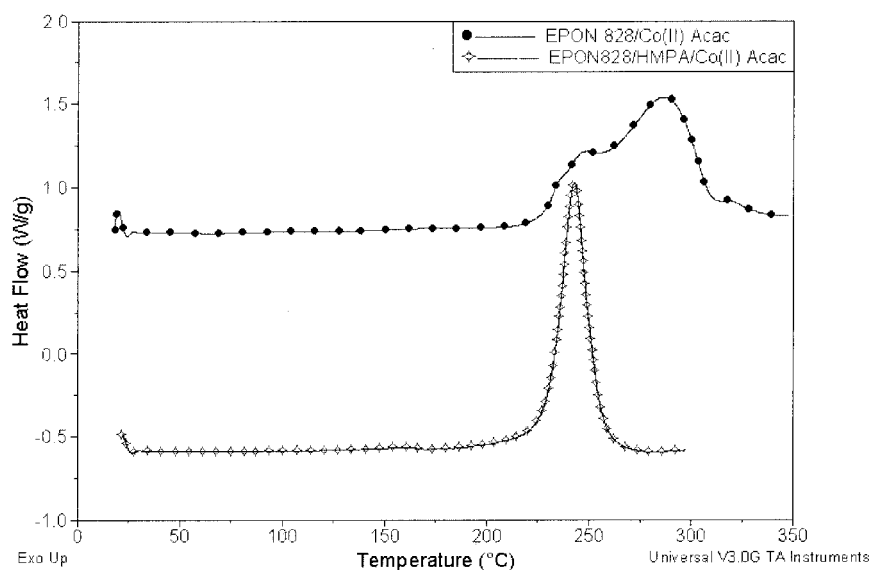
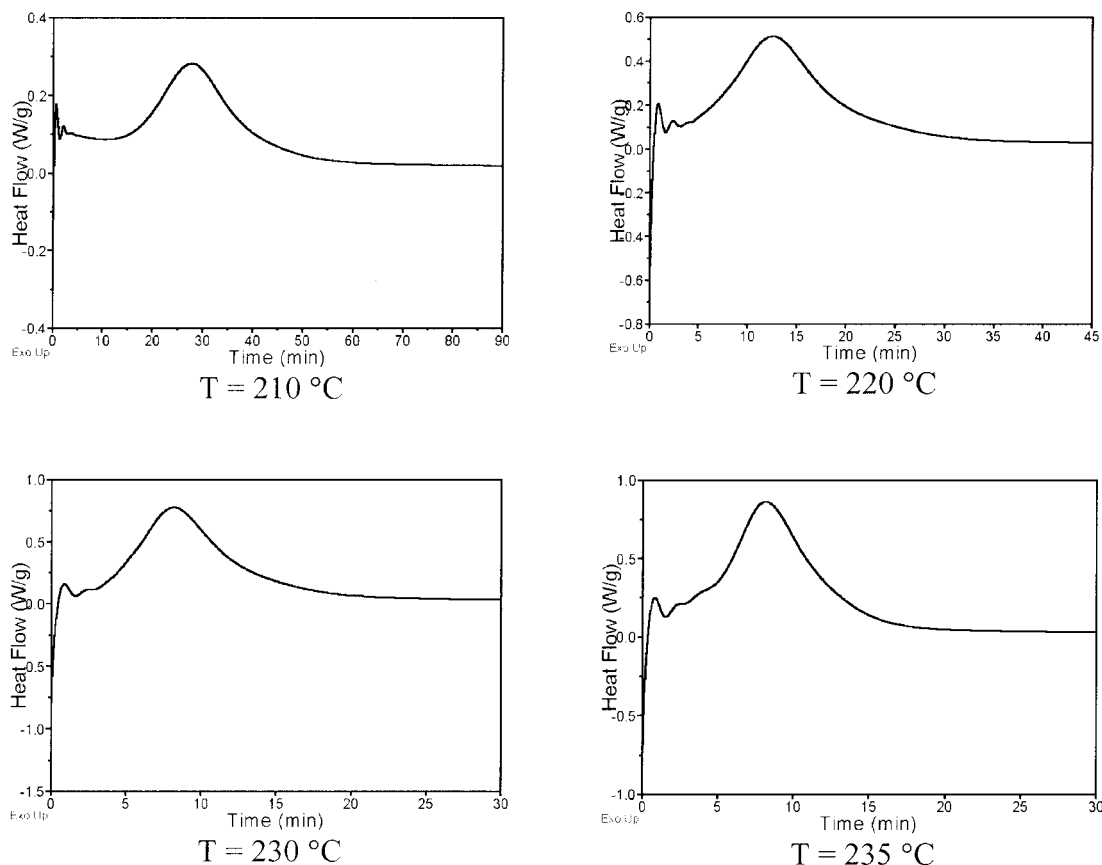**Figure 2** DSC curing profile of EPON 828/Co (II) AcAc and EPON 828/HMPA/Co (II) AcAc.

Figure 3 Isothermal curing profiles for Co(II) AcAc catalyzed epoxy reaction at different temperatures.

AcAcs probably reacted with HMPA first to form a transition state that proceeded to cure the epoxy resins.

Following the dynamic curing studies, isothermal curing behavior of EPON 828/HMPA/metal AcAc system was investigated. Figure 3 shows the isothermal curing profiles of EPON 828/HMPA/Co (II) AcAc at four different temperatures. The choice of the isothermal temperature is very important. At high temperatures, reaction takes place so quickly that the initial instability in heat flow created great inaccuracy. On the other hand, if the isothermal temperature is too low, the reaction takes a long time to finish and the heat flow is so low that the DSC is not sensitive enough to recognize the signal.

At each temperature, an autocatalytic kinetic model is utilized to obtain the reaction order and the rate constant. The model can be expressed as

$$\frac{dC}{dt} = kC^m (1 - C)^n$$

where C is the fractional conversion, n is the reaction order, m is the independent order, and k is the rate constant. Figure 4 shows the kinetic analysis for the reaction of ERL 4221/HMPA/Co (II) AcAc at 220°C.

Results indicate that the reaction follows the autocatalytic model well.

According to the kinetic theory, reaction constant k is related to temperature and activation energy of the reaction by Arrhenius equation:

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right)$$

where E_a is the activation energy and k_0 is the frequency factor. Figure 5 shows the plot of ln k versus $-1/T$. From the slope of the plot, E_a is calculated to be 98 KJ/mol.

Isothermal kinetic parameters of other formulations were obtained in the same way and listed in Table III. The onset and peak temperatures of the dynamic curing profiles of the EPON 828/HMPA/metal AcAc system, together with the activation energy obtained from the isothermal studies, are illustrated in Figure 6.

From the onset and peak curing temperatures of EPON 828/HMPA/Metal AcAc system, the trend cannot be easily interpreted because these systems possess different reaction orders. However, the activation energy of these reactions can provide better understanding on the catalytic behavior of metal AcAcs. Theoretical studies have shown that the charge and
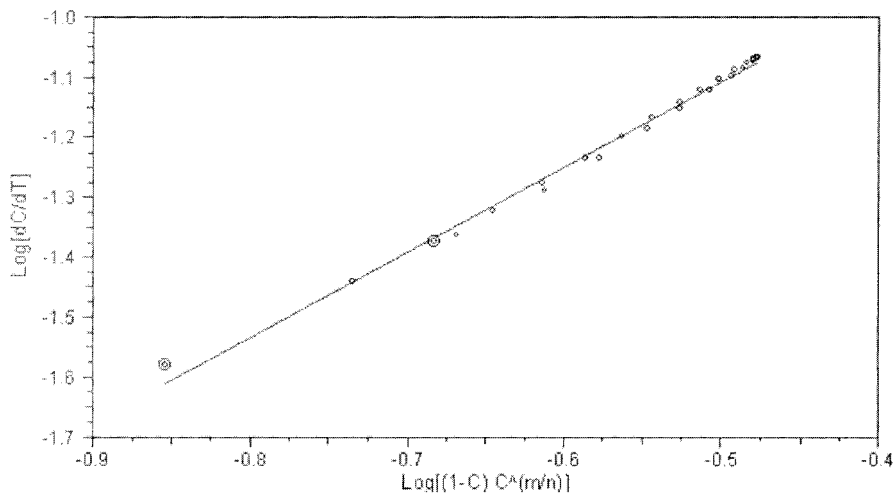
Figure 4 Kinetic analysis for ERL 4221/HMPA/Co (II) AcAc at 220°C.

radius of the ion, and the stability due to orbital splitting, are the important factors determining the stability of the metal complexes.[15] The covalency of the bond and the stability of the metal complexes formed with the same ligand generally increase with increasing oxidation number of the metal ion. As can be observed in Figure 6, trivalent metal AcAcs have higher activation energy in catalyzing the epoxy curing reaction than the divalent metal AcAcs. For divalent metal AcAcs, the activation energy follows the rule discovered by Irving and Williams[16] that the order of complex-forming ability in the series of similar, divalent metal ions is as follows:

$$Mn < Fe < Co < Ni < Cu > Zn$$

The order can be explained by the decrease in metal-ion radius from Mn to Zn, and by the increase of crystal-field stabilization energy from Fe to Cu. The d-orbitals of Zn (II) are full, so no stabilization energy is gained through the complex, which is the main reason that Zn (II) AcAc behaved similarly to that of the alkaline earth metal ions and the lanthanide and actinide ions, initiating curing at low temperature but giving poor curing properties. Figure 7 shows the DSC dynamic curing heat flow of EPON 828/HMPA/Zn (II) AcAc system. The isothermal diagram cannot be obtained because of the fact that the heat flow was too low to be captured.

The activation energy reflects the energy barrier the reactants need to overcome to start the reaction. It is
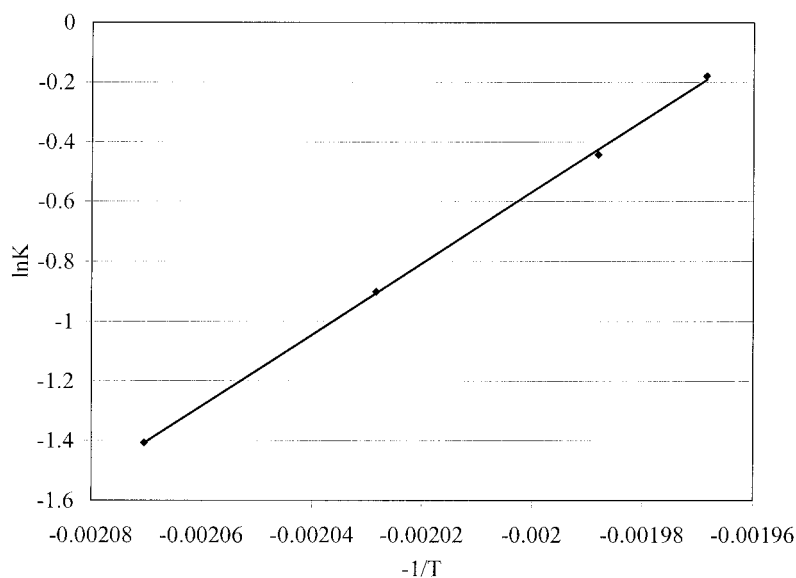

Figure 5 Arrhenius plot for the reaction of ERL 4221/HMPA/Co(II) AcAc.

TABLE III
Isothermal Kinetic Parameters of EPON
828/HMPA/Metal AcAc System

Catalyst	E_a (kJ/mol)	log K	n	m
Mn (II) AcAc	73.2	6.59	0.339	0.230
Fe (II) AcAc	74.8	7.95	0.821	0.260
Fe (III) AcAc	103	11.0	0.823	0.195
Co (II) AcAc	98	10.0	1.42	0.925
Co (III) AcAc	122	12.7	1.46	0.913
Ni (II) AcAc	101	8.88	0.657	0.045
Cu (II) AcAc	133	12.8	0.89	0.47

closely related to the dissociation energy of metal AcAc in a solution of epoxy resin and HMPA. The metal–ligand bond energies have been studied by using a number of methods,[17] including theoretical calculation,[18] ion-molecule reactions, ion beam, photodissociation, mass spectrum,[19] and collision-induced dissociation (CID),[20] etc. Rodhers and Armentrout did a systematic study on the metal–ligand bond energies for a wide variety of metal ions and ligands using the CID technique.[20] Although metal AcAcs were not included in their study, the general trend for the first row transition metal ions was proved to be a decrease from Ti to Mn and an increase from Mn to Cu. However, in each particular case, the change in the bond energies depended largely on the ligands. The bond energies in their study varied from 50 to 250 kJ/mol, which is of the same order of magnitude as those from the current isothermal curing study. The study by Reichert and Westmore was performed on metal (II) AcAcs by using the mass spectrum.[19] The dissociation energies from their study were 9, 30, and 51 kcal/mol for Mn (II) AcAc, Fe (II) AcAc, and Co (II) AcAc, respectively. Although they followed the same general trend, the differences between these metal AcAcs were

greater than what was obtained from the current study. However, noticing that in the current study, the metal AcAcs were in a solution of epoxy resin and HMPA, the energy states of the metal ions were more complicated, as compared to those in the literature where only pure metal complexes were investigated. The transition state of the reaction was considered to be
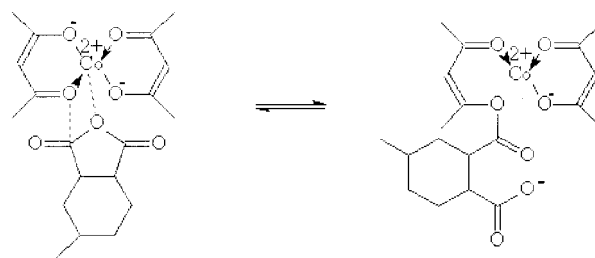
where both the breakage of the coordinate bond between the metal ion and AcAc and the establishment of the bond between AcAc and HMPA should be taken into account in addition to the solvation effect from epoxy resins. Despite all these complications, the activation energies obtained from isothermal curing study of epoxy/HMPA/metal AcAc can provide us with an insight into the coordinate bond energy of metal AcAcs and curing reaction mechanism of this system. This understanding can be used as a guideline for designing epoxy curing systems in a wide variety of applications.

CONCLUSION

Metal acetylacetonates offer a wide range of catalytic latency and curing behavior for epoxy/anhydride system. The DSC dynamic curing profiles at a heating
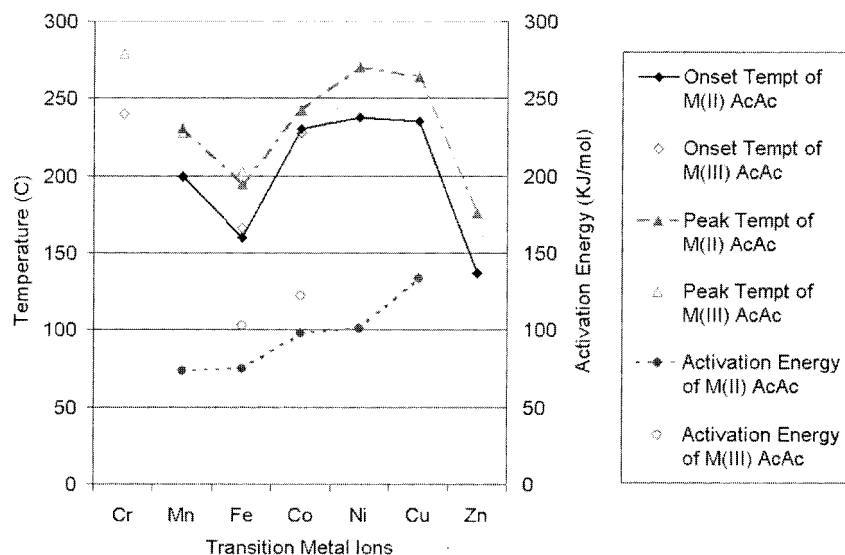
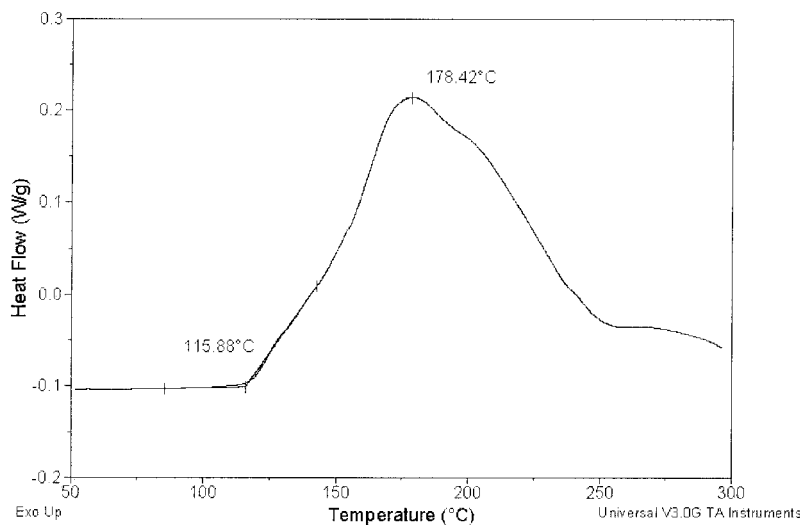**Figure 6** Kinetic parameters of curing reactions of EPON 828/HMPA/metal AcAc system.

Figure 7 DSC curing profile of EPON 828/HMPA/Zn (II) AcAc.

rate of 5°C/min were obtained for 43 formulations of ERL 4221/HMPA/metal AcAc system. The results showed that the curing latency was closely related to the bonding strength of the metal ion to the ligand. The DSC isothermal curing study at different temperatures was performed on EPON 828/HMPA/metal AcAc containing the first row transition metal ions. Most curing reactions can be analyzed by using the autocatalytic kinetic model. The activation energy of the system containing the divalent metal AcAcs followed the Irving and Williams rule, which was determined by the decrease in metal–ion radius from Mn to Zn, and by the increase of crystal field stabilization energy from Fe to Cu. The activation energies of the reaction obtained in the kinetic study were comparable with the dissociation energies of the metal/ligand bond from the literature. Because the metal AcAcs were in a solution of epoxy resin and HMPA, the energy states of the metal ions were more complicated. The isothermal curing kinetic study provided us with an insight into the coordinate bond energy of metal AcAcs and curing reaction mechanism of this system.

References

1. Starck, H.; Schlenker, F. U.S. Pat. 2,801,228, 1957.
2. Naps, M. U.S. Pat. 2,876,208, 1959.
3. Markovitz, M. U.S. Pat. 3,812,214, 1974.
4. Smith, J. D. B. J Appl Polym Sci 1981, 26, 979.
5. Reddy, P. V.; Thiagarajan, R.; Ratra, M. C. J Appl Polym Sci 1990, 41, 39.
6. Stoakley, D. M.; St. Clair, A. K. J Appl Polym Sci 1986, 31, 225.
7. Wong, C. P.; Shi, S. H.; Jefferson, G. IEEE Trans Components, Packag, Manufac Technol—Part A 1998, 21 (3), 450.
8. Wong, C. P.; Shi, S. H. U.S. Pat. 6,180,696, 2001.
9. Kurnoskin, A. V. J Appl Polym Sci 1992, 46, 1509.
10. Kurnoskin, A. V. J Appl Polym Sci 1993, 48, 639.
11. Kurnoskin, A. V. Polymer 1993, 34 (5), 1060.
12. Kurnoskin, A. V. Polymer 1993, 34 (5), 1068.
13. Kurnoskin, A. V. Polymer 1993, 34 (5), 1077.
14. Basolo, F.; Johnson, R. Coordination Chemistry; W. A. Benjamin, Inc.: New York, 1964.
15. Inczedy, J.; Tyson, J. in Chapter 1: Complexes and Their Properties; Analytical Applications of Complex Equilibria; Wiley: New York, 1976.
16. Irving, H.; Williams, R. J. P. J Chem Soc 1953, 3192.
17. Freiser, B. S. (Ed.). Organometallic Ion Chemistry; Kluwer Academic: The Netherlands, 1996.
18. Rosi, M.; Bauschicher, Jr., C. W. J Chem Phys 1990, 92 (3), 1876.
19. Reichert, C.; Westmore, J. B. Inorg Chem 1969, 8 (4), 1012.
20. Rodhers, M. T.; Armentrout, P. B. Mass Spectrom Rev 2000, 19, 215.