

The Development of Controllable Complex Curing Agents for Epoxy Resins. II. Examining the Dissociation and Thermal Behavior of Transition Metal-Diamine Complex-Epoxy Blends

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ABSTRACT: A series of complexes incorporating diamine (*o*-phenylene diamine and 2-aminobenzylamine) ligands and containing the acetato and chloro salts of Ni(II) and Cu(II) was incorporated into two commercial epoxy resins recognized as industry standards (MY721 and MY750). The cure properties of the complexes are assessed alongside commercial curative systems. Thermal analysis (principally differential scanning calorimetry) shows that the nature of the cure mechanism can be dramatically affected by the nature of the transition metal and counterion (and the level of curing agent incorporation). For example, by using a nickel(II) acetato complex rather than its chloro analog, the onset of the cure reaction of MY721 may be reduced by 40 K. Thermogravimetric analysis, and visible, infrared, and electron spin resonance spectroscopy are employed to determine the point at which the complexes undergo dissociation. The data show that $\text{Cu}(2\text{-ABA})_2(\text{ac})_2$ appear to dissociate at temperatures between 70 and 80°C in octan-1-ol. A multivariate approach is applied to the analysis of infrared data obtained for solvated complex samples subjected to a heating program and the results are consistent with the dissociation temperature obtained from the other spectral data. The data suggest that the aromatic amino function in the complex undergoes dissociation from the metal at a lower temperature than the aliphatic amine. The 2-ABA-based complexes containing chloride counterions undergo gelation at higher temperatures than their acetato analogs (for both commercial epoxy systems). The newly prepared complexes generally display η_{min} values comparable with the commercial curative systems [the exceptions being $\text{Cu}(2\text{-ABA})_2\text{Cl}_2$ and $\text{Ni}(\text{OPD})_3\text{Cl}_2$, which produce markedly higher values of 14 and 10 P, respectively], but it is believed that this is due to agglomeration and settling of the complex as the resin viscosity decreases during the heating cycle. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2411–2424, 2002

Key words: epoxy; curing agents; complexes; storage stability; thermal analysis; spectroscopy; multivariate analysis; viscometry

INTRODUCTION

Our work continues to develop novel curing agents with controllable, predictable cure charac-

teristics for epoxy resins. The latter are of considerable technological importance and continue to form the matrix resin for the majority of aerospace composites in current use.^{1,2} Furthermore, this appears set to continue in the 21st century. Our eventual aim is to produce versatile curing agents that have the ability to be formulated together with an epoxy resin in one pot and to possess a long shelf life on the order of > 3 months

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at temperatures up to 40°C with minimal increases in resin viscosity. In a previous article,³ we reported the preparation and full characterization of a series of transition metal complexes containing diamino-substituted ligands (*o*-phenylene diamine, OPD, and 2-aminobenzylamine, 2-ABA) and the storage stabilities of commercial resins formulated with these materials.

It is well known that the use of transition metals can impart latent cure properties in imidazole initiators when mixed with epoxy resins, for example.^{4–7} The formation of dative covalent bonds between the ligands' nitrogen atoms and the transition metal ion act to prevent the cure reaction (otherwise initiated by lone pairs of electrons undergoing a nucleophilic attack on the strained oxirane ring of the epoxy). Previous work has shown that during cure, the ligands dissociate when a critical temperature (dependent on the nature of the transition metal, ligand stereochemistry, and counterion) is reached, allowing the lone pairs of electrons on the nitrogen atoms of the free ligands to initiate the polymerization reaction.^{6,7}

In the aerospace industry, curing agents based on aromatic diamines (e.g., diaminodiphenylsulfone, DDS) are commonly used to cure epoxy resins to achieve optimal glass transition temperature (T_g 's) in the cured resins.⁸ The results of a previous⁹ study suggested that aromatic diamines (in that case OPD) and *p*-phenylene diamine displayed interesting latent cure characteristics when complexed with copper(II) species and incorporated into MY750. Our previous article³ extended this work to study OPD and 2-ABA and found that the latter was particularly interesting, as it displayed good latent cure properties. Furthermore, the physical and thermal properties of complexes containing 2-ABA were also amenable to tailoring by changing the nature of the transition metal and counterion. In this article, we now examine the thermal characteristics of these formulations in greater detail.

EXPERIMENTAL

Materials

OPD and 2-ABA were obtained from the Aldrich Chemical Co. 2-ABA was used as received, whereas OPD was purified by using a literature method¹⁰ prior to use. Metal(II) acetates and chlorides were obtained from BDH and Aldrich

Chemical Corp. in their hydrated forms and gave acceptable analytical results: these materials were used without further purification. Octan-1-ol (GPR) was obtained from BDH and used without further purification. The commercial epoxies [MY721, of epoxy equivalent weight 195.25, and MY750 of epoxy equivalent weight 119.7, as determined by an in-house (Cytec-Fiberite Ltd., Wrexham) titrimetric method] were obtained from Ciba-Geigy products. The complexes prepared in a previous publication³ are depicted in Figure 1.

In the same publication,³ the rationale for the selection of formulations was discussed. In short, the levels of curing agent incorporation were based on the relevant epoxy equivalent weights (eew) of the epoxies and the number of active amino hydrogen atoms in each complex. For instance, Ni(2-ABA)₃Cl₂ has a relative molar mass (RMM) of 496.16 and contains 12 active hydrogen atoms. Therefore, 1 mol of active hydrogen atoms represents 41.35 g (496.16 ÷ 12). This figure is the stoichiometric equivalent of the eew and, hence, for every 195.25 g of MY750, 41.35 g of Ni(2-ABA)₃Cl₂ is required. These calculations led to the quantities of the curing agents (based on 1 g of epoxy) in the formulations studied shown in Table I. These curing agent loadings were used for the subsequent spectral, thermal, and viscometric measurements (with the exception of the DSC study of thermal behavior as a function of curing agent concentration, in which the loading was of necessity changed incrementally). The commercial curing agents were obtained from the following suppliers: DiCy and CA-150 (Cytec) and Curimid CN (Polyorganics) and were incorporated in line with accepted in-house (Cytec-Fiberite, Ltd.) formulations.

Apparatus

Differential scanning calorimetry (DSC) was carried out by using a Perkin-Elmer DSC7 on samples (ca. 6 ± 1 mg) over the range 30–300°C at a variety of heating rates (5, 10, 15, and 20 K min⁻¹). Measurements were made under N₂ (40 cm³ min⁻¹) using open 50-μL aluminum pans or sealed 30-μL aluminum pans (with a pierced lid) for volatile samples. Thermogravimetric analyses (TGA) were performed by using a Pyris™-operated Perkin-Elmer TGA7 on samples (ca. 5 ± 1 mg) at a heating rate of 10 K min⁻¹ between 50 and 1000°C. Measurements were made under N₂ (40 cm³ min⁻¹) by using a platinum boat. Visible

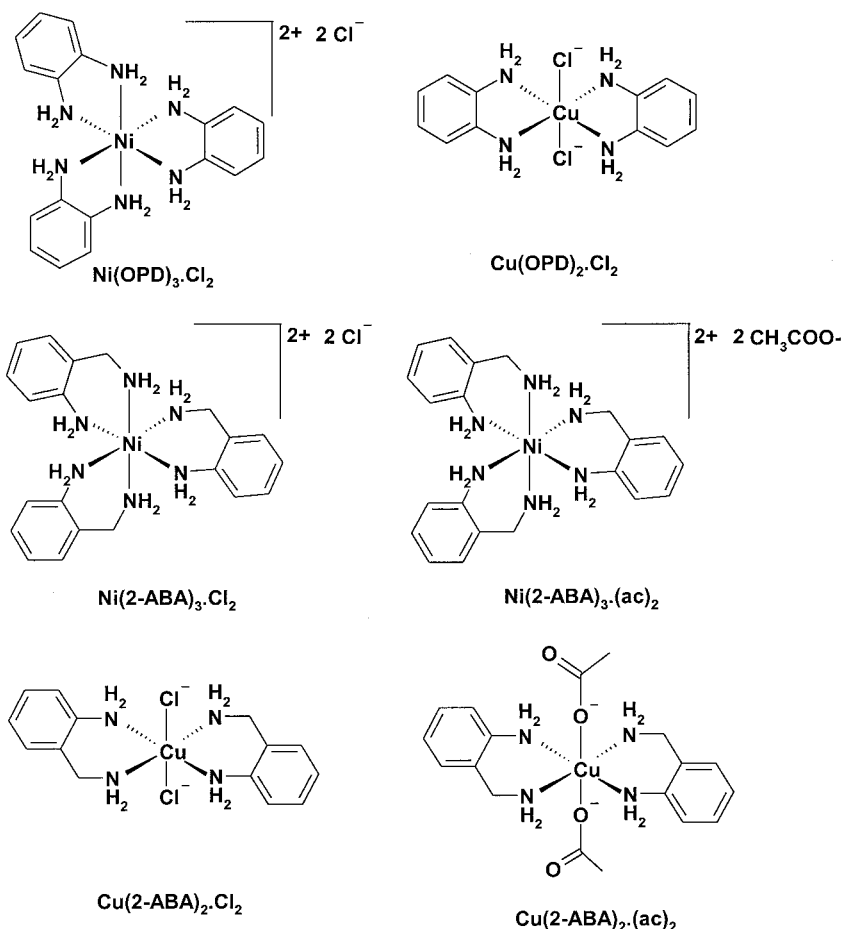


Figure 1 Proposed structures of the complexes studied in this work.

spectroscopy was performed by using a Hewlett-Packard 8452A diode array spectrometer and a Cecil CE7200 (7000 series) UV-visible spectrometer.

A sample of $\text{Cu(2-ABA)}_2(\text{ac})_2$ (6.4×10^{-3} g) was dissolved in octan-1-ol (50 cm^3 , 3×10^{-3} M) and the solution heated from 22 to 30°C (to provide an initial visible spectrum of the complex prior to thermal treatment). The solution was then heated further by means of a thermostated silicone oil bath and aliquots of the solution were withdrawn and placed into a standard cuvette (with a path length of 1 cm) and the visible spectrum (400–800 nm) was recorded. Measurements were then made at sampling intervals of 10 K between 30 and 140°C . For electron spin resonance (ESR) spectroscopy measurements, a similar methodology was adopted. In this case, a small sample of $\text{Cu(2-ABA)}_2(\text{ac})_2$ (the minimum observable, ca. 0.01 g) was dissolved in octan-1-ol (5 cm^3) and the solution heated from 25 to 30°C (when the first reading was taken) and on to 130°C with

further readings taken at intervals of 10 K after the sample was allowed to reach equilibration at each stage. Spectra were recorded by using a JEOL RE1X ESR spectrometer operating at X-band frequencies. Gelation measurements were determined by using a TA Instruments AR1000 rheometer using 4-cm-diameter (open) disposable plates (as these are thermosetting systems). A heating rate of 2 K min^{-1} was used between 50 and 250°C to simulate a conventional cure cycle. The gel point of each epoxy/curing agent formulation was determined by the intersection of the plots of storage (G') and loss (G'') moduli data.¹¹ Infrared data were acquired by grinding the sample and incorporating it in a KBr disk, which was placed in a temperature-controlled heating accessory. This was placed in the sample compartment of a Perkin-Elmer System 2000 FTIR spectrometer. Spectra were obtained with a resolution of 4 cm^{-1} under strong apodization, and 16 scans were co-added to improve the signal-to-noise ratio, at temperatures between 20 and 160°C .

Table I Amount of Curing Agent Added to Blend (Based on 1 g of Commercial Epoxy)

Epoxy	Curing Agent							
	Ni(2-ABA) ₃ Cl ₂	Ni(2-ABA) ₃ (ac) ₂	Cu(2-ABA) ₂ Cl ₂	Cu(2-ABA) ₂ (ac) ₂	Curimid CN	OPD	Ni(OPD) ₃ Cl ₂	DiCy/CA-150
MY721 (eew 119.7)	0.3454	0.3782	0.3956	0.4449	0.0273	0.2259	0.3162	—
MY750 (eew 195.25)	0.2117	0.2319	0.2425	0.2727	0.0267	0.1385	0.1938	0.0725

RESULTS AND DISCUSSION

Thermal Dissociation of Complexes

All of the complexes were analyzed in isolation by using TGA (see below) and most underwent dissociation on reaching their melting points (the latter were determined by using an electrothermal melting point apparatus); the exceptions are noted in the text. Both OPD-based complexes, Cu(OPD)₂Cl₂ and Ni(OPD)₃Cl₂, displayed melting points in excess of 250°C. During TGA measurements, Cu(OPD)₂Cl₂ appeared to undergo a series of dissociation steps between 135 and 585°C (Fig. 2). Two significant thermal events at ~ 162°C (4.6%/min) and 204°C (7%/min) preceded the main breakdown of the complex (204–580°C). Ni(OPD)₃Cl₂ displayed a similar plot, with a series of dissociation steps occurring in a slightly higher temperature regime between 170 and 600°C (Fig. 2), albeit with a lower rate of degradation. Two significant thermal events at ~ 210°C (9.2%/min) and 300°C (6.6%/min) preceded a final breakdown of the complex (360–600°C).

The 2-ABA analogs were also analyzed by using TGA. Ni(2-ABA)₃Cl₂ [melting point (mp) > 250°C, with evident discoloration at 190°C] appeared to undergo a series of dissociation steps between 60 and 960°C (Fig. 3). There was evidence of a small loss in mass at temperatures up to 100°C, probably due to the complex absorbing atmospheric moisture (a characteristic noted in a previous article³). The main breakdown of the complex occurred at 190°C and was accompanied by a markedly higher rate of weight loss of 5.2%/min.

Unlike its chloro analog, Ni(2-ABA)₃(ac)₂ displayed a rather less complex dissociation pattern when observed using TGA between 80 and 340°C (Fig. 3). The 10% loss in mass at temperatures up to 200°C (0.06%/min) is probably due to the complex having absorbed atmospheric moisture on standing.³ The main breakdown of the complex occurred between 200 and 350°C (rate of weight loss of 0.43%/min); this corresponds well with a loss in mass of 68% (which equates to the combined masses of the 2-ABA ligands—the acetato ligands are not bonded to the metal center). This observation appears to suggest that ligand dissociation occurred via a single (or two very closely linked) step(s). The mp of Ni(2-ABA)₃(ac)₂ was determined to be around 110°C (as evidenced by the presence of

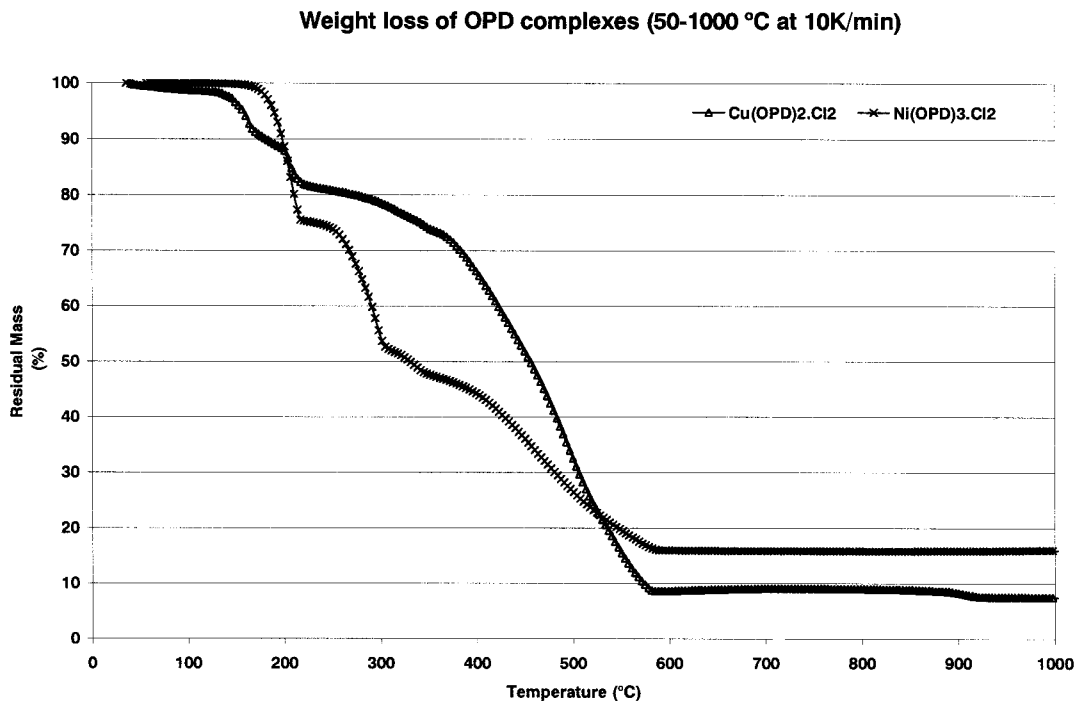


Figure 2 Dynamic TGA data (10 K min^{-1}) obtained under nitrogen for the OPD-based complexes studied in this work.

brown liquid condensing on the side of the capillary tube), although under the conditions of the TGA analysis of this complex, it is possible that the complex has already undergone some

dissociation before this temperature was reached.

$\text{Cu}(2\text{-ABA})_2\text{Cl}_2$ (mp $\sim 200^\circ\text{C}$, with darkening at 190°C) also displayed a complex dissociation

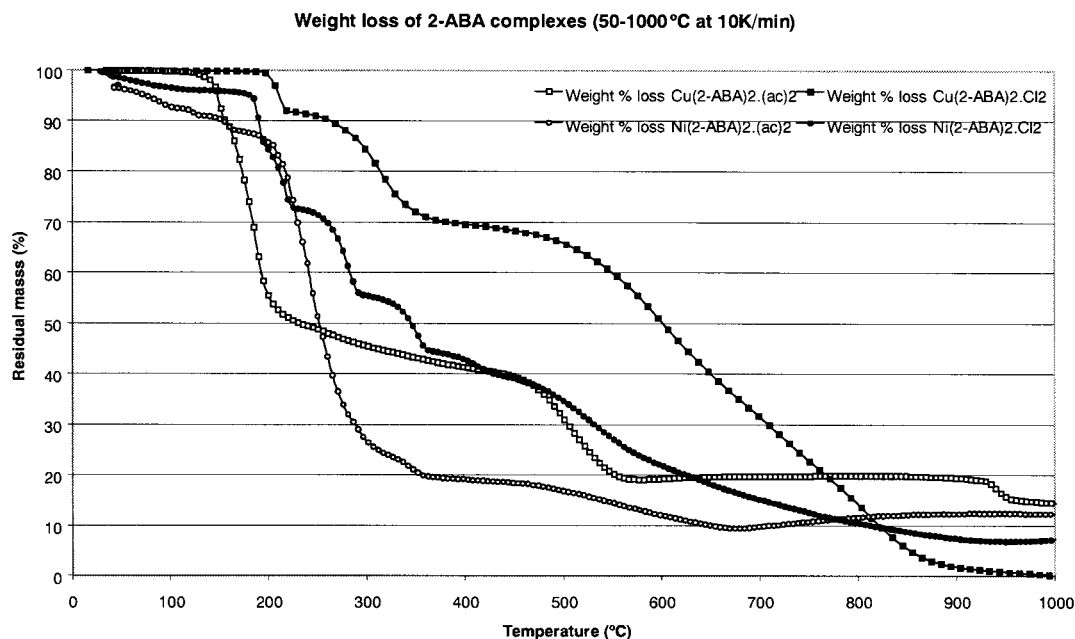


Figure 3 Dynamic TGA data (10 K min^{-1}) obtained under nitrogen for the 2-ABA-based complexes studied in this work.

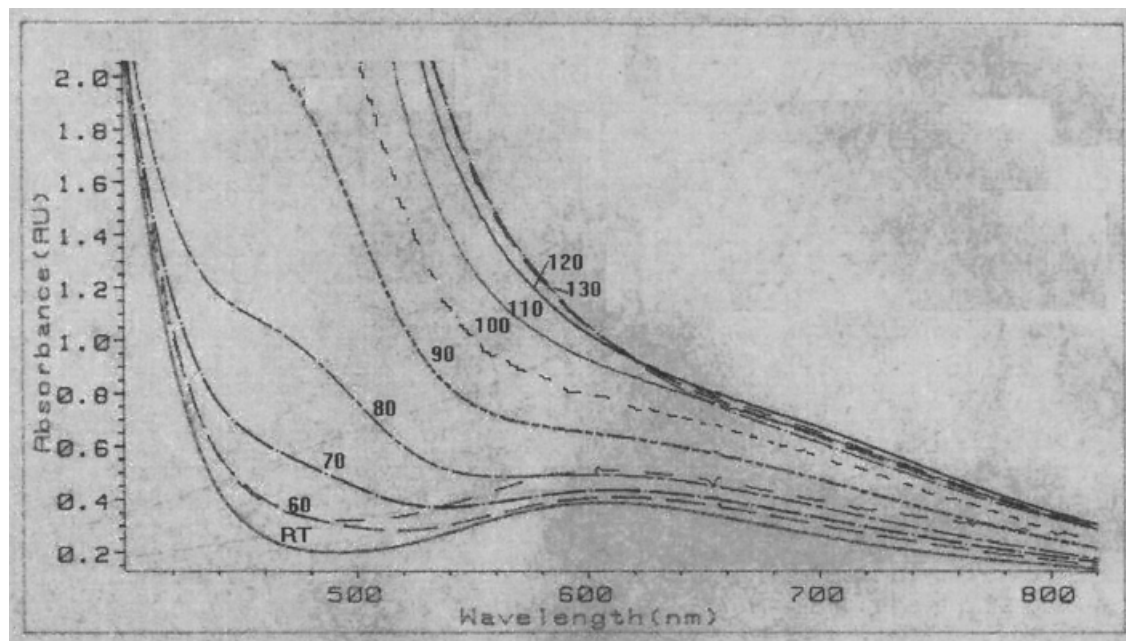


Figure 4 Visible spectra of $\text{Cu}(\text{2-ABA})_2(\text{ac})_2$ in octan-1-ol between 25 and 130°C.

pattern that extended over a wide temperature range (200–900°C, with a maximum rate of weight loss of 0.22%/min), before both 2-ABA ligands appeared to have undergone full dissociation. The high apparent stability of the complex is probably due to the presence of the chloride ions bonded to the copper center. These would, in turn, draw electrons away from the copper, making the 2-ABA ligands more tightly bound. $\text{Cu}(\text{2-ABA})_2(\text{ac})_2$ (mp 135–140°C) displayed an initial loss of mass at 185°C and had lost 55% of its mass by 200°C (there is a further 10% loss up to 400°C). This corresponds to the dissociation of the ligands in a multistep process over a relatively small range of temperature (145–200°C, with a maximum rate of weight loss of 9.5%/min).

Study of the Dissociation of Complexes in Solution by Using Spectroscopic Analysis

The TGA measurements gave an indication of the relative thermal stability of the complexes studied in this work. However, these studies were carried out on isolated complexes and it might be argued that these conditions bear little resemblance to the environment of the curing agent in an epoxy resin, undergoing cure. Consequently, a spectroscopic study was carried out on $\text{Cu}(\text{2-ABA})_2(\text{ac})_2$ in a solvated form to determine whether the thermal dissociation characteristics observed by using TGA were reproduced while

dispersed within an organic phase. Octan-1-ol was selected as a suitable solvent because it not only dissolved the complexes satisfactorily, but its boiling point of 190°C would allow a number of spectroscopic measurements to be made over a wide temperature range. The initial reading (taken at 30°C) showed a λ_{max} value of ~ 610 nm (the peak was quite broad and spanned ~ 300 nm), presumably because of a $d-d$ transition in the copper (2-ABA) complex. The intense purple color of the complex supports this conclusion, whereas the solvent cut-off (octan-1-ol) appeared at ~ 420 nm (Fig. 4). As the temperature is progressively raised, little change is seen in the spectrum obtained at 60°C. However, between 70 and 80°C, there is an incipient peak revealed at ~ 460 nm. The band is initially obscured by the solvent, but is clearly visible at 80°C and continues to grow in intensity quite markedly at higher temperatures. The band may be tentatively assigned to the dissociation of the complex, as evidenced by the corresponding color change, and is probably a copper-acetate-octan-1-ol complex.¹² There is evidence of a small degree of reassociation on cooling, to take the spectroscopic measurement, although subsequent association with the alcoholic solvents largely prevents this. A blank experiment containing octan-1-ol run under the same conditions, but lacking the complex, showed no apparent color change up to 140°C. Further-

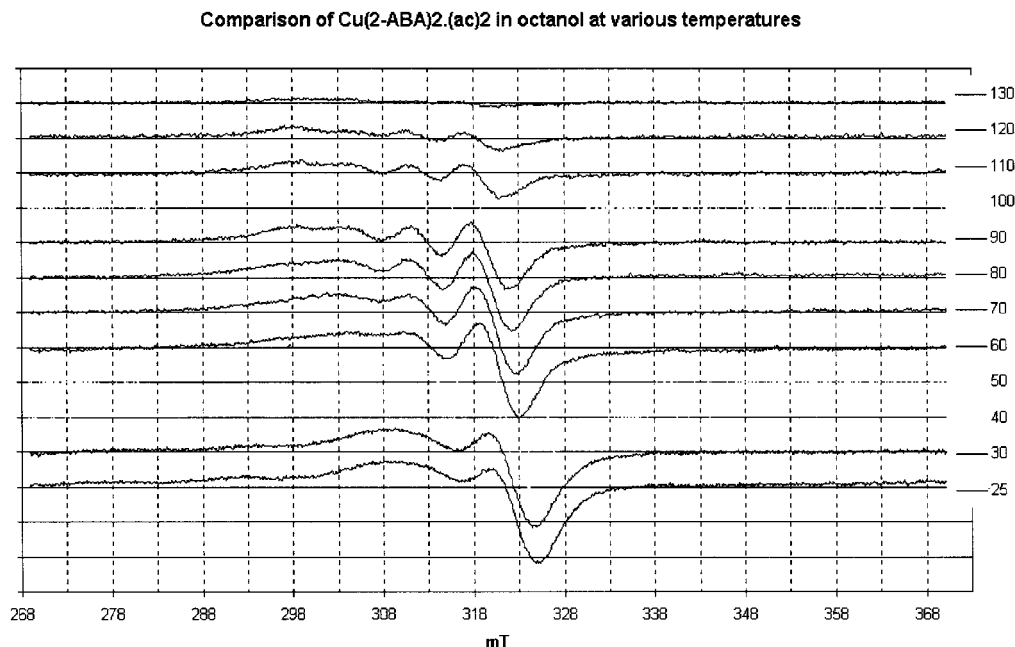


Figure 5 ESR spectra of Cu(2-ABA)₂(ac)₂ in octan-1-ol between 25 and 130°C.

more, during the experiment, the majority of the variations occurred between 190 and 230 nm (well below the λ_{\max} of octan-1-ol), although these changes were very small ($\sim \pm 0.03$ absorbance units).

The same experiment was effectively repeated by using the same complex/solvent combination to confirm the data with the use of a complementary technique. ESR spectroscopy was carried out on similar samples. The spectra (Fig. 5), with a g factor of approximately 2.1, indicate a hyperfine coupling to copper of approximately 6 mT, giving rise to four lines of equal intensity but progressively increasing line width from high field to low field. This is caused by molecular rotation and with increasing temperature there is evidence of the expected line narrowing. The spectra exhibit additional complexity consistent with the presence of dynamic exchange that is not susceptible to analysis. The data indicate that the initial dissociation commences at between 70 and 80°C.

The data were also treated by using principal components analysis (PCA), a multivariate analysis technique¹³ that utilizes all the ESR data and uses a holistic approach to determine similar and dissimilar spectra. This approach shows how extracting the principal components (PCs), which account for the variance in data, enables the analysis to be simplified. A plot of PC1, which accounts for 72% of the variance in the spectral data, against PC2, which accounts for 21%, is

shown in Figure 6 and displays a turnover point around 72°C.

Similar data were obtained by forming a dilute mixture of Cu(2-ABA)₂(ac)₂ in a KBr disk, fitting the pellet into a temperature controlled stage, and obtaining the transmission spectra at 10° intervals between 20 and 160°C. The active Cu(2-ABA)₂(ac)₂ migrates away from the measurement area, and so the acetate band around 1567 cm⁻¹ is used to normalize the data, as seen in Figure 7.

The infrared data are highly revealing of the changes that occur in the thermal treatment of Cu(2-ABA)₂(ac)₂. Although the separation between the two carboxyl acetate bands stays the same as in Cu(ac)₂, at 133 cm⁻¹, both bands are shifted some 50 cm⁻¹ in the complex. The intensity of these bands, together with the O—C=O in-plane deformation near 753 cm⁻¹, seem to stay reasonably constant over this temperature range. Similarly, the 2-ABA aromatic semicircle stretch bands at 1495 and 1458 cm⁻¹ change little in intensity. However, the asymmetric aromatic NH₂ stretch is not seen in the complex, whereas the symmetric component decreases by 50% above 130°C. Although there are small changes in the spectra, the biggest differences are seen above this temperature.

As with the ESR data, the infrared data were also subjected to PCA. The model requires just two PCs to describe 99% of the variance in both

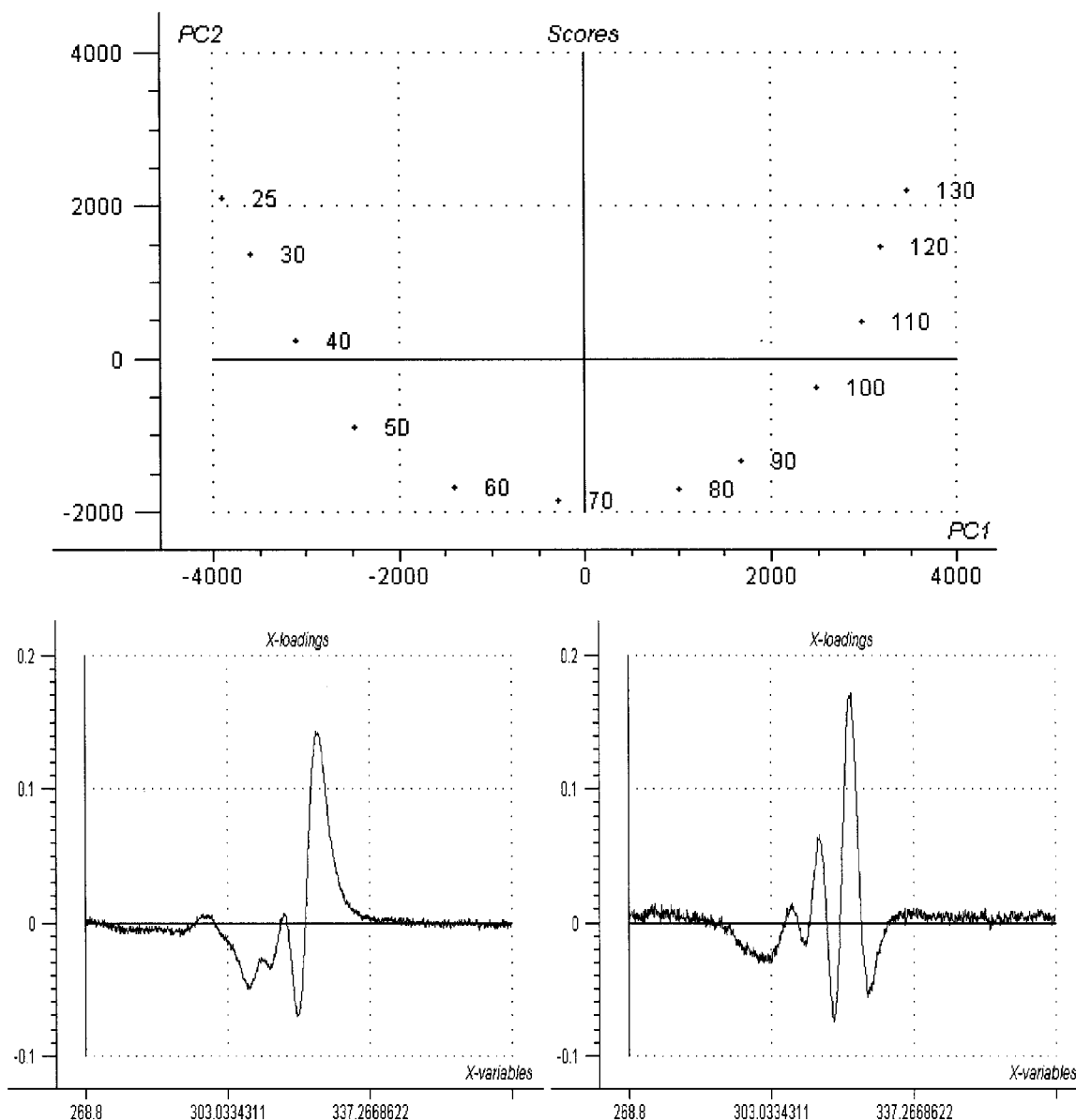


Figure 6 Principal component analysis applied to the ESR data (top), and plots of PC1 (below left) and PC2 (below right).

the spectral data and the temperature, and these are shown in Figure 8. This analysis reinforces the major change seen above 130°C, but also suggests smaller changes at lower temperatures. By removing the samples at 140°C and above, the smaller variations at lower temperatures are more easily visible [Fig. 8(a)]. The plot of PC2 against PC1 shows a similar shape to Figure 6 and suggests that both the ESR and the IR are monitoring the same molecular changes, which exhibit a change between 70 and 80°C. In Figure 8(b), PC1 describes 86% of the spectral variance in the 20–130°C data set

and corresponds closely to PC2 [Fig. 8(c)], which describes 15% of the spectral variance in the 20–160°C data set.

These PCs can be interpreted spectrally and show the most significant bands that contribute to the regression against temperature. In both cases, the 754 cm^{-1} band (aromatic ring bending) shows a shift to lower frequency as the temperature increases. In particular, the 20–130°C set shows a large decrease in the intensity of the 1547 cm^{-1} band (aliphatic amine) and an increase in the 1623 cm^{-1} band (aromatic amine), suggesting the freeing-up of the latter (presumably brought

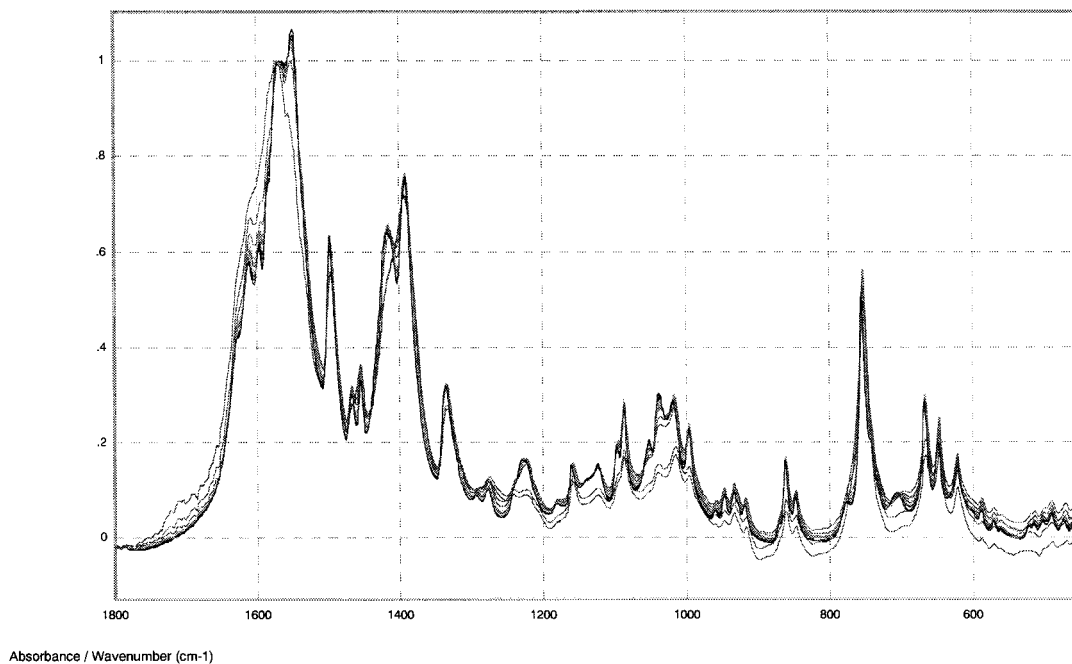
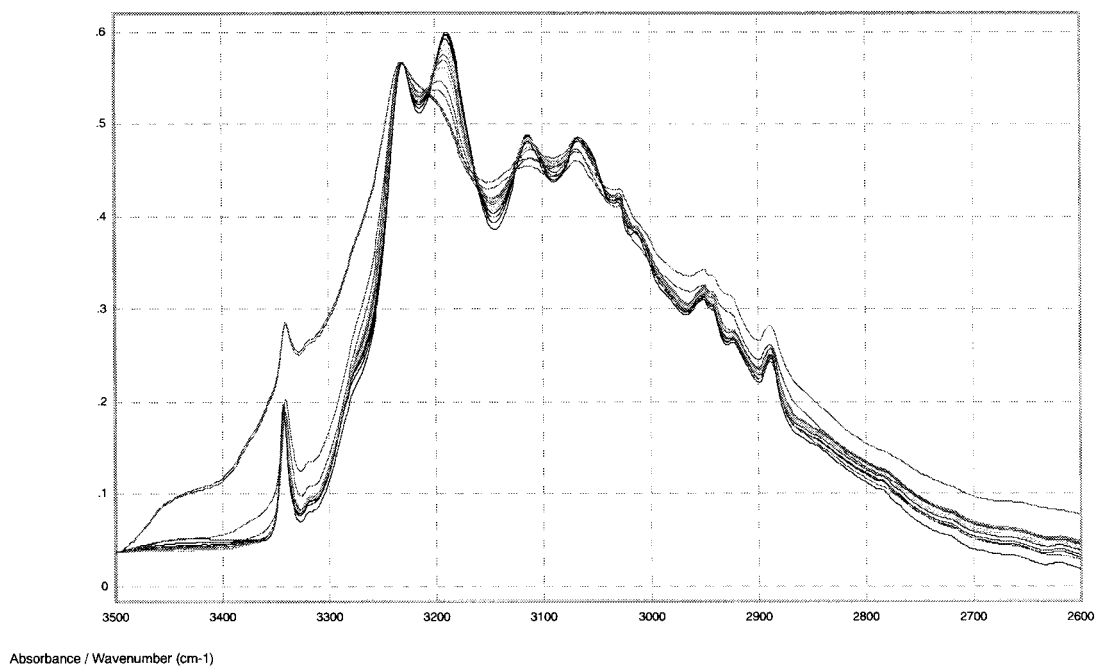


Figure 7 IR Spectra of $\text{Cu}(\text{2-ABA})_2(\text{ac})_2$, between 3500 and 2600 and 1800 and 450 cm^{-1} .

about by dissociation from the metal). A more complete interpretation is in progress.

Effect of Blend Composition on Polymerization Mechanism

Table II contains the DSC data obtained for MY721 when blended with selected commercial

curing agents or OPD-based systems. This allows the thermal behavior of the new blends to be compared with materials that are already in use in an industrial context. A cursory examination reveals that the introduction of OPD into MY721 leads to an onset temperature (and an exothermic peak maximum) that is comparable with the com-

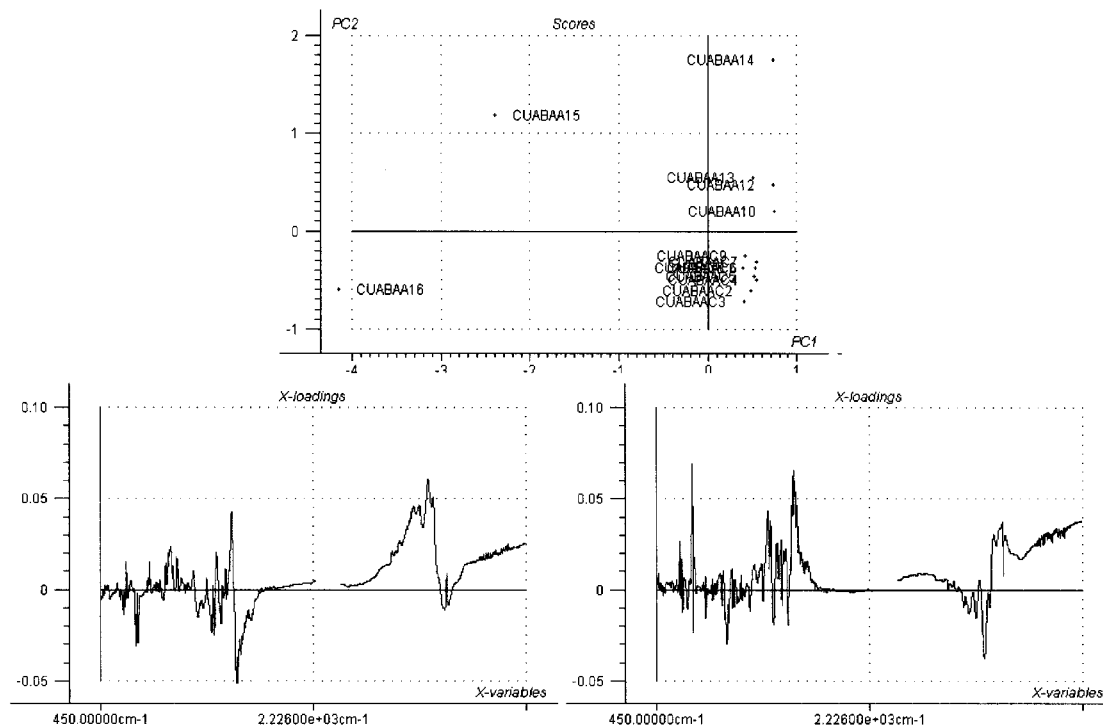


Figure 8 Principal component analysis applied to the IR data (top) and plots of PC1 (below left) and PC2 (below right).

mercial curing agents (and markedly lower than that recorded for DDS). Of the OPD complexes, $\text{Cu(OPD)}_2\text{Cl}_2$ is least impressive, because the onset temperature (228°C) is somewhat higher than DDS, although the nickel analog provides an onset temperature (162°C) that should facilitate a lower cure.

In Table III, DSC data are presented for MY721/2-ABA-based curing agent blends as a function of heating rate (2-ABA and DDS are also

Table II DSC Data (10 K min^{-1}) for MY721/Commercial Curing Agent Blends and OPD and Complexes

Curing Agent	Cure Onset ($^\circ\text{C}$)	Peak Max ($^\circ\text{C}$)	ΔH (J g^{-1})
DDS	202	236	590
Curimid CN	143	176	704
DiCy/CA150	136	143	361
Diuron/DiCy	140	147	567
OPD	158	182	487
$\text{Cu(OPD)}_2\text{Cl}_2$	228	286	709
$\text{Ni(OPD)}_3\text{Cl}_2$	162	172	233

included for comparison). As expected, increasing the heating rate leads to the cure onset and peak maximum being elevated to slightly higher temperatures. In general, the 2-ABA systems give rise to lower onset temperatures than the OPD analogs. Of the 2-ABA complexes tested, $\text{Ni(2-ABA)}_3(\text{ac})_2$ yielded the lowest onset (and exothermic peak) temperature.

Table IV depicts the effect of changing the concentration of the complex in the blend (while the MY721 content is held constant). A series of complex concentrations was chosen to represent a stoichiometric blend (denoted 1 : 1) through to a catalytic concentration (denoted 20 : 1). In general, as one might expect with an amine–epoxy reaction and polyetherification mechanism in direct competition, as the complex concentration is increased, the amine–epoxy reaction is favored.

This is shown graphically for the case of $\text{Ni(2-ABA)}_3\text{Cl}_2$ by means of a thermogram (Fig. 9) from which it is clear that the first exothermic peak (corresponding to the amine–epoxy reaction) is suppressed as the complex concentration decreases, whereas the homopolymerization peak becomes markedly more pronounced at around 230°C . In the case of $\text{Cu(2-ABA)}_2\text{Cl}_2$, a reduction

Table III DSC Data for MY721/Curing Agent Blends as a Function of Heating Rate

Curing Agent	Heating Rate (K min ⁻¹)	Cure Onset (°C)	Peak Max (°C)	ΔH (J g ⁻¹)
DDS	5	193	219	573
	10	202	236	590
	15	208	245	663
	20	220	257	572
2-ABA	5	103	119	341
	10	104	131	260
	15	106	138	337
	20	113	149	274
Ni(2-ABA) ₃ Cl ₂	5	149	152	340
	10	149	162	563
	15	152	166	580
	20	159	173	540
Ni(2-ABA) ₃ (ac) ₂	5	118	131	536
	10	109	129	554
	15	119	144	573
	20	124	157	578
Cu(2-ABA) ₂ Cl ₂	5	157	168	607
	10	165	176	610
	15	169	179	688
	20	180	188	548
Cu(2-ABA) ₂ (ac) ₂	5	128	137	450
	10	136	145	497
	15	133	144	462
	20	141	152	484

in the concentration of the curing agent again leads to a reduction in the exothermic peak associated with the amine–epoxy reaction ($\sim 180^\circ\text{C}$) and an increase in the peak associated with the homopolymerization. This feature is less marked in the case of the corresponding acetato complexes, Ni(2-ABA)₃(ac)₂ and Cu(2-ABA)₂(ac)₂, for although a decrease in the complex concentration is accompanied by a decrease in the amine–epoxy exothermic peak at 140°C , the homopolymerization peak appears little changed. What is clear, however, is that at the level of incorporation of 5%, neither acetato complex appears to be present in sufficient quantity to initiate significantly the epoxy–amine reaction.

Effect of Complex on Polymerization Mechanism

A cursory examination of the thermal data reveals two factors contributing to the nature of the polymerization mechanism: the nature of the transition metal and the nature of the counterion. Both features offer a means of tailoring the way in which the polymers might ultimately be pro-

cessed or altering the formation of the resulting network. The thermal data, collected in Table III, demonstrate that the incorporation of Ni(II) rather than Cu(II) results in the reduction of the onset of polymerization. For example, in the case of the complexes containing acetate, there is a reduction of ~ 30 K (and a broadening of the exotherm), while the corresponding chloro complexes experience a reduction of 20 K. Incidentally, the appearance of the thermograms appears less affected by the change of transition metal in this case.

The nature of the counterion appears to have a more significant effect on the thermal behavior of the epoxy formulation. The incorporation of acetato, rather than chloride, counterions not only reduces the onset of polymerization (by around 40 K in both cases), but it appears to alter the reaction pathway. The observations of the DSC thermograms are consistent with the TGA data reported here. For example, the epoxy formulation containing Cu(2-ABA)₂(ac)₂ exhibits the least complex thermogram with a regu-

Table IV Dynamic DSC Data (10 K min⁻¹) for MY721 as a Function of Curing Agent Composition

Complex	Molar Mixing Ratio (E : A) ^a	Mass of Complex (per 1 g epoxy)	Cure Onset (°C)	Peak Max (°C)	ΔH Total (J g ⁻¹ mixture) ^b
Ni(2-ABA) ₃ Cl ₂	20 : 1	0.02	139	159	733
	5 : 2	0.14	143	163	721
	5 : 3	0.21	146	162	587
	5 : 4	0.28	147	162	619
	1 : 1	0.34	149	162	563
Ni(2-ABA) ₃ (ac) ₂	5 : 2	0.22	118	145	752
	5 : 4	0.37	117	140	630
	1 : 1	0.38	109	129	554
Cu(2-ABA) ₂ Cl ₂	5 : 1	0.08	172	181	n/a
	5 : 2	0.16	170	181	877
	5 : 3	0.24	169	180	725
	5 : 4	0.32	165	177	756
	1 : 1	0.40	165	176	610
Cu(2-ABA) ₂ (ac) ₂	20 : 1	0.02	109	121	n/a
	5 : 1	0.09	117	130	103
	5 : 2	0.18	123	137	222
	5 : 3	0.27	127	138	323
	5 : 4	0.36	129	140	469
	1 : 1	0.44	135	145	497

^a A, amine; E, epoxy. MY721 is a tetrafunctional epoxy and each primary amine (on the 2-ABA ligand) may react with two epoxy groups.

^b Refers to total mass of formulation analyzed. n/a, at this level of catalysis, measurement of the polymerization enthalpy was difficult to achieve due to baseline drift.

lar, almost Gaussian, exothermic peak (and this may be due to the release of the ligands from the metal center in a single step as evidenced by

the TGA measurements). In contrast, the formulation containing the chloro analog, Cu(2-ABA)₂Cl₂, displays a more complex thermogram

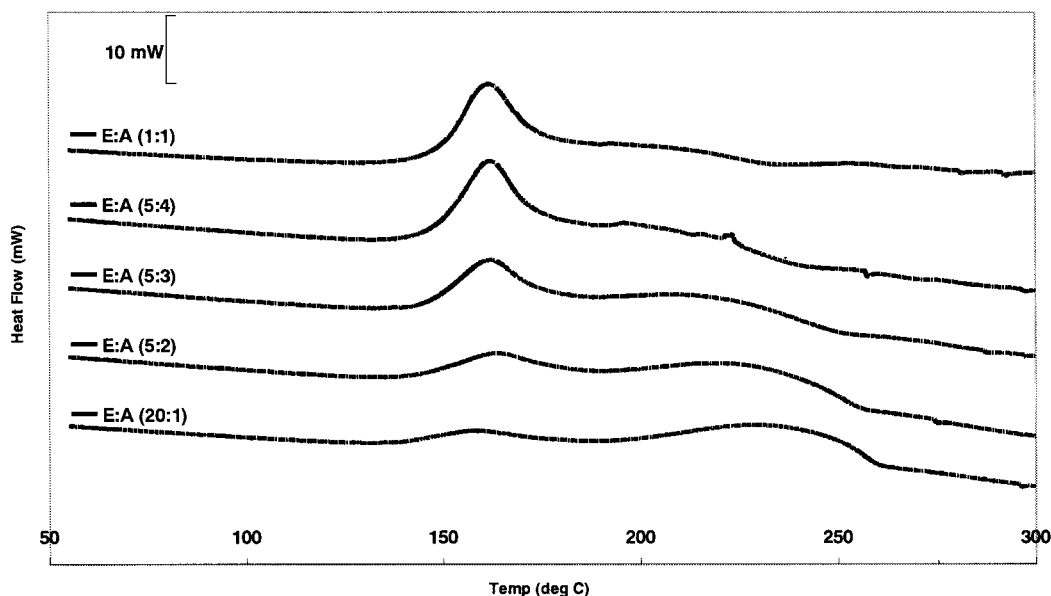


Figure 9 Dynamic DSC data (10 K min⁻¹) obtained under nitrogen for Ni(2-ABA)₃Cl₂ in MY721 shown as a function of complex concentration.

Table V Gelation Behavior of Epoxy Resins Containing Different Curing Agents

Epoxy	Curing Agent	η_{\min} (P)	Gel Point (°C)
MY721	Ni(2-ABA) ₃ Cl ₂	3	150
	Ni(2-ABA) ₃ (ac) ₂	5	136
	Cu(2-ABA) ₂ Cl ₂	14	160
	Cu(2-ABA) ₂ (ac) ₂	8	133
	Curimid CN	3	131
	OPD	3	136
	Ni(OPD) ₃ Cl ₂	2	192
MY750	Ni(2-ABA) ₃ Cl ₂	0.5	174
	Ni(2-ABA) ₃ (ac) ₂	0.8	161
	Cu(2-ABA) ₂ Cl ₂	0.3	174
	Cu(2-ABA) ₂ (ac) ₂	0.9	144
	DiCy/CA-150	4	132
	Curimid CN	7	131
	OPD	5	137
	Ni(OPD) ₃ Cl ₂	10	172

η_{\min} , Minimum viscosity recorded during experiment. See Table I for curing agent concentrations.

with several apparent exothermic transitions (one of which is seen as a shoulder on a larger peak). This is, in turn, consistent with the TGA findings that Cu(2-ABA)₂Cl₂ displayed a complex dissociation pattern, extending over a wide temperature range. Although these data strongly suggest that the polymerization mechanism changes with the nature of the complex, this hypothesis is not conclusive and work continues to clarify this aspect.

Viscometric Measurements of the Commercial Epoxy/Curing Agent Blends

Two commercial curing agent/accelerator systems (e.g., DiCy/CA-150 and Curimid CN) were selected for comparative purposes. Of the OPD-based curatives, both OPD and Ni(OPD)₃Cl₂ were tested in the commercial epoxy resins, as the Ni(OPD)₃Br₂ remained poorly dispersed in the resins. Winter¹¹ has described the detection of gel point in a network-forming polymer by using rheological measurements, in which storage modulus (G') and loss modulus (G'') are monitored as a function of reaction time during an analysis performed under conditions of fixed-frequency/small-amplitude oscillatory shear. Under these conditions, the point at which the G' and G'' data intersect is taken to indicate the vicinity of the gel point. The rheological data are shown in Table V and the following general observations can be made. For the

2-ABA-based complexes, those containing chloride counterions underwent gelation at higher temperatures than their acetato analogs (for both commercial epoxy systems). In general, the newly prepared complexes generally displayed minimum viscosity (η_{\min}) values comparable with the commercial curative systems [the exceptions being Cu(2-ABA)₂Cl₂ and Ni(OPD)₃Cl₂, which produced markedly higher values of 14 and 10 P, respectively]. However, it was noted that during the cure cycle, Ni(OPD)₃Cl₂ settled to the bottom of the sample as the viscosity of the resin decreased, leading to a heterogeneous reaction mixture (and possibly accounting for the unexpectedly high figure recorded).

CONCLUSION

The cure of commercial epoxy resins (MY721 and MY750) can be effected by using novel coordination compounds under a conventional cure cycle, and gelation occurs at temperatures between 131 and 192°C, depending on the complex/curative system employed. This approach demonstrates that by altering different aspects of the complex's composition (i.e., the nature of the transition metal, ligands, or counterions), it is possible to alter significantly the solubility of the complex in epoxy and the thermal behavior of the resulting formulation. The latter is of particular interest because it allows the selection of different cure schedules to facilitate the cure of epoxy resins of differing reactivities and the ability to affect the nature of the eventual network formed. Work continues to examine the thermal and mechanical properties of epoxy resins cured by using these new curative systems.

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