The Development of Controllable Complex Curing Agents for Epoxy Resins. I. Preparation, Characterization, and Storage Behavior of Transition Metal–Diamine Complexes

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ABSTRACT: A series of complexes incorporating diamine (*o*-phenylene diamine and 2-aminobenzylamine—OPD and 2-ABA respectively) ligands and containing the acetato and chloro transition metal salts of Ni and Cu has been prepared and characterized using elemental analysis and spectroscopic methods. Infrared data show that complexation of the amino nitrogen atoms occurs to a high degree. The same curing agents have been incorporated into two commercial epoxy resins recognized as "industry standards" (MY721 and MY750), and their cure properties and shelf life assessed alongside commercial curative systems. The current work demonstrates that while complexes based on copper(II) and nickel(II) and containing OPD ligands may be prepared and incorporated into commercial epoxy resins, there are some advantages associated with using 2-ABA (as the diamine ligand) due to the higher complex solubility and better processing characteristics that it imparts to the formulated system. In general, the 2-ABA based complexes disperse well within commercial epoxy systems and display good storage stability over prolonged periods of time (up to 67 days at ambient temperature). Work continues to examine the thermal and mechanical characteristics of commercial epoxy resins cured using these complexes. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1489–1503, 2001

Key words: epoxy; curing agents; complexes; storage stability; controllable; preparation

INTRODUCTION

Epoxy resins are of considerable technological importance, and as we enter the 21st century they look set to continue to form the matrix resin for the majority of aerospace composites in use.[1,2] The highly strained epoxy group (comprising an oxirane ring) conveys a high degree of versatility to this family of materials and allows a surprisingly wide variety of chemicals to be employed as curing agents (acting as both nucleophiles or electrophiles).[3] It is our ultimate aim to develop novel curing agents with controllable, predictable cure characteristics. This must be accompanied by the ability to be formulated together with an epoxy resin and to possess a long shelf life (out life) of the order of 3 months at temperatures up to 40°C with minimal increases in resin viscosity.

The incorporation of transition metals in epoxy resins is not new and a number of groups have been working to this end. For example, the incor-

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poration of acetylacetonates of chromium and cobalt at low levels (1 mol %) in the commercial epoxy Epon 826 (based on bisphenol A diglycidylether, eew = 175 g mol^{-1}) has been reported to improve fracture toughness[4] compared to unmodified resin. Similarly, acrylates of zinc, chromium, and copper have been shown to improve electrical properties and thermal/chemical resistance[5–7] as have metal complexes containing aliphatic and aromatic diamines, organic acids, and N,N'-dimethylformamide.[8–10] However, all of the aforementioned studies have concentrated on the cure characteristics or final properties imparted to the polymer by the complexes with little or no discussion offered about the effect on storage properties.

The use of transition metals has also been explored as a means of imparting latent cure properties in, e.g., imidazole initiators, by means of forming dative covalent bonds between the ligand nitrogen atoms and the transition metal ions, and hence preventing the cure reaction to allow storage.[11] During cure, the ligands disscociate when a particular 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 polymerization.

Previous work at the University of Surrey has focused on the chemistry and properties of commercial epoxy resins after cure using imidazole-based initiators.[12–18] Various imidazoles (but principally 2-ethyl-4-methylimidazole) have been prereacted with phenylglycidylether to form organic ligands with structures resembling the backbone of epoxy oligomers. The ligands have then been complexed with a series of d-block transition metal salts (e.g. based on cobalt, copper, nickel, copper, zinc, and silver, etc.) to form a series of novel complexes.[18] The ultimate aim is to produce materials with the aforementioned latent cure properties and improved solubility in the epoxy (arising from the similarity in the backbone structure).

In the aerospace industry it is more common to use aromatic diamines (e.g., diaminodiphenylsulphone, DDS) or dicyandiamide (DiCy) to cure epoxy resins in order to achieve higher glass transition temperature (T_gs) than are possible using imidazoles (which essentially initiate a polyetherification reaction). Previously, we reported the results of a preliminary study[19] suggesting that aromatic diamines (in that case o-phenylene diamine and p-phenylene diamine) displayed interesting latent cure characteristics when com-

plexed with copper(II) and incorporated into MY750. In this latest study we have pursued this question in greater depth and have examined the effect of complex incorporation on a number of physical properties (principally shelf life and cure characteristics) of two common commercial epoxy resins.

MATERIALS

o-Phenylene diamine (OPD) and 2-aminobenzylamine (2-ABA) were obtained from the Aldrich Chemical Company. 2-ABA was used as received, while OPD was purified using a literature method[20] prior to use. Metal(II) acetates and chlorides were obtained from BDH and Aldrich in their hydrated forms and used as received. All solvents used (96% ethanol, acetone, and distilled water) were always degassed with nitrogen prior to use to remove carbon dioxide. The commercial epoxies used (both Ciba-Geigy products) were based on tetraglycidyldiaminodiphenylmethane (MY721), of epoxy equivalent weight 195.25, and the diglycidylether of bisphenol A (MY750) of epoxy equivalent weight 119.7. Epoxy equivalent weights were determined by a titrimetric method. The commercial curing agents were obtained from the following suppliers: CA-150 (*ex* Cytec), Curimid CN (*ex* Polyorganics), 4,4'-diaminodiphenylsulphone, DDS, (*ex* Ciba Speciality Chemicals as HT9664), and Diuron (*ex* SKW as Dyhard UR 200).

APPARATUS

The pH measurements were made on a Jenway 4330 Conductivity and pH meter (accuracy: ±0.003 pH units). Infrared absorption spectra were collected over the range 4000–400 cm^{-1} using a Perkin-Elmer model 841 spectrometer; the samples were analyzed as KBr disks. Visible spectra (over the range 400–800 nm) were obtained in ethanol solutions (at a resolution of 1 nm) on a Unicam UV-1 UV-visible spectrometer v 1.14 with a bandwidth of 2 nm. Differential scanning calorimetry (DSC) was carried out using a Perkin-Elmer DSC7. Analyses were carried out on samples (ca. 6 ± 1 mg) with a heating rate of 10 K min^{-1} between 50 and 300°C. Measurements were made under N$_2$ (40 cm^3 min^{-1}) using open 50 μL aluminum pans or sealed 30 μL aluminum pans (with a pierced lid) for volatile samples.

Table I   Selected Elemental Analyses for Transition Metal–Diamine Complexes[a]

Complex	% C	% H	% N
Ni(OPD)$_3$Cl$_2$			
Calculated for C$_{18}$H$_{24}$N$_6$Cl$_2$Ni	47.62	5.33	18.51
Found	47.82	5.41	18.52
[Ni(OPD)$_3$Cl$_2$]$_4$OPD			
Calculated for C$_{39}$H$_{52}$N$_{13}$Cl$_4$Ni$_2$	48.69	5.45	18.93
Found	48.60	5.46	18.96
Ni(OPD)$_3$Br$_2$			
Calculated for C$_{18}$H$_{24}$N$_6$Br$_2$Ni	39.82	4.46	15.48
Found	39.88	4.54	15.18
Cu(2-ABA)$_2$Cl$_2$			
Calculated for C$_{14}$H$_{20}$N$_4$Cl$_2$Cu	44.39	5.32	14.79
Found	43.89	5.35	14.54
(Literature value)[24]	(44.0)	(4.85)	(14.60)
Cu(2-ABA)$_2$(ac)$_2$			
Calculated for C$_{18}$H$_{26}$N$_4$O$_2$Cu	50.75	6.15	13.15
Found	50.78	6.35	13.11
Ni(2-ABA)$_3$Cl$_2$			
Calculated for C$_{21}$H$_{30}$N$_6$Cl$_2$Ni	50.84	6.10	16.94
Found	50.08	6.71	15.44
(Literature value)[24]	(50.00)	(5.70)	(16.10)
With 1 molecule of water added	49.06	6.27	16.35
Ni(2-ABA)$_3$(ac)$_2$			
Calculated for C$_{27}$H$_{36}$N$_6$O$_2$Ni	55.27	6.68	15.47
Found	52.15	7.13	14.27
With 1 molecule of water added	53.50	6.82	14.97
With 2 molecules of water added	51.83	6.96	14.51

[a] OPD: *o*-phenylenediamine; 2-ABA: 2-aminobenzylamine; ac: acetate ligand.

Storage life analyses were carried out by first heating the samples from −50 to 300°C at 10 K min^{-1}, then cooling them and rescanning the samples to 300°C at 10 K min^{-1}. Shelf life tests were carried out on OPD-containing blends using a Brookfield cone and plate CAP2000H viscometer. Analyses were carried out at 50°C with a spin rate of 350 rpm for a period of 15 s (although the spin rate was reduced as the viscosity increased). Elemental (C, H, and N) analysis was performed using an Exeter Analytical EA440 elemental analyzer using samples of 1–2 mg.

EXPERIMENTAL

General Preparative Methods for the Metal–OPD Chloro Complexes

The general method adopted for all of the metal(II) chloride–OPD complexes was based on a reaction procedure reported[21] for the analogous chromium–OPD complexes from CrCl$_2$ · 4H$_2$O. The full procedure is given for Cu(OPD)$_2$Cl$_2$, and modifications to the procedure are indicated in the following sections. Table I shows the analytical data for the complexes prepared during the course of this work and also gives the designations for each complex (which are used throughout this paper and also in Part II of this series[22]). The proposed structures for the complexes, based largely on the measurements of magnetic susceptibility reported herein, are given in Figure 1.

Cu(OPD)$_2$Cl$_2$

To a 250 cm^3 conical flask containing OPD (2.16 g, 0.02 mol) in ethanol (100 cm^3), was added CuCl$_2$ · 2H$_2$O (1.7g, 0.01 mol). Upon addition of the Cu(II) solution a blue/green precipitate was formed immediately and this became a khaki green over time. The contents of the flask were periodically shaken vigorously over the period of 1 h. After

Ni(2-ABA)₃.Cl₂

Ni(2-ABA)₃.(ac)₂

Cu(2-ABA)₂.Cl₂

Cu(2-ABA)₂.(ac)₂
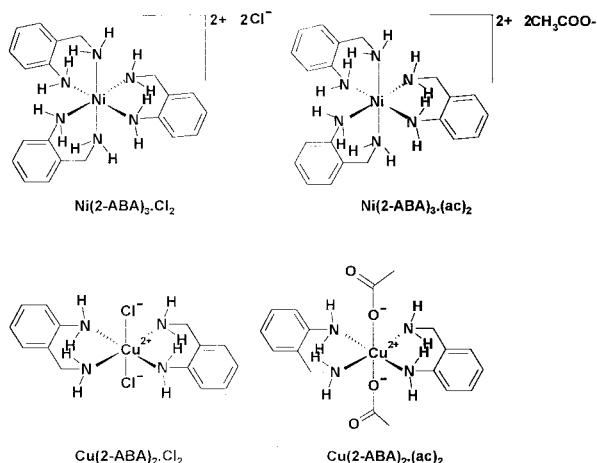
Figure 1 Proposed structures of the complexes studied in this work.

this time, the complex was filtered on a Büchner funnel and washed with cold ethanol to remove any uncomplexed OPD.

Cu(OPD)₃Cl₂

The general procedure was repeated using OPD (3.24 g, 0.03 mol), 96% ethanol (140 cm³), and $CuCl_2 \cdot 2H_2O$ (1.7g, 0.01 mol). Similar experimental observations were made and a khaki green solid was isolated.

Ni(OPD)₃Cl₂

A preliminary experiment was performed to determine the pH at which full complexation of the OPD to the Ni ion had been achieved. A 250 cm³ conical flask containing OPD (3.24 g, 0.03 mol) in ethanol (100 cm³) was heated to 40°C. To this mixture was added, via a burette in small portions, $NiCl_2 \cdot 6H_2O$ (2.38 g, 0.01 mol) in ethanol (40 cm³) while the pH was carefully monitored. Upon addition of the Ni(II) solution a light blue precipitate formed immediately. The graph (Fig. 2) demonstrates that at ca. 5.3 the apparent pH of the solution starts to rise significantly on further addition of OPD, indicating that these ligands are not undergoing complexation.

Having determined the apparent pH at which full complexation occurs, a 250 cm³ round-bottom flask containing ethanol (100 cm³) was heated to 40°C and maintained at this temperature. In two separate 50 cm³ dropping funnels were placed OPD (3.24 g, 0.03 mol) in ethanol (40 cm³) and $NiCl_2 \cdot 6H_2O$ (2.38 g, 0.01 mol) in ethanol (40 cm³). Each of the solutions was added in 10 cm³ portions to the round bottom flask in the following manner: (1) addition of the nickel solution with stirring, (2) initial apparent pH measurement, (3) addition of the OPD with stirring to allow complexation to occur, and (4) further pH measurement. The apparent pH was allowed to reduce by

pH Trend of Ni (II) Chloride addition to OPD (1:3)
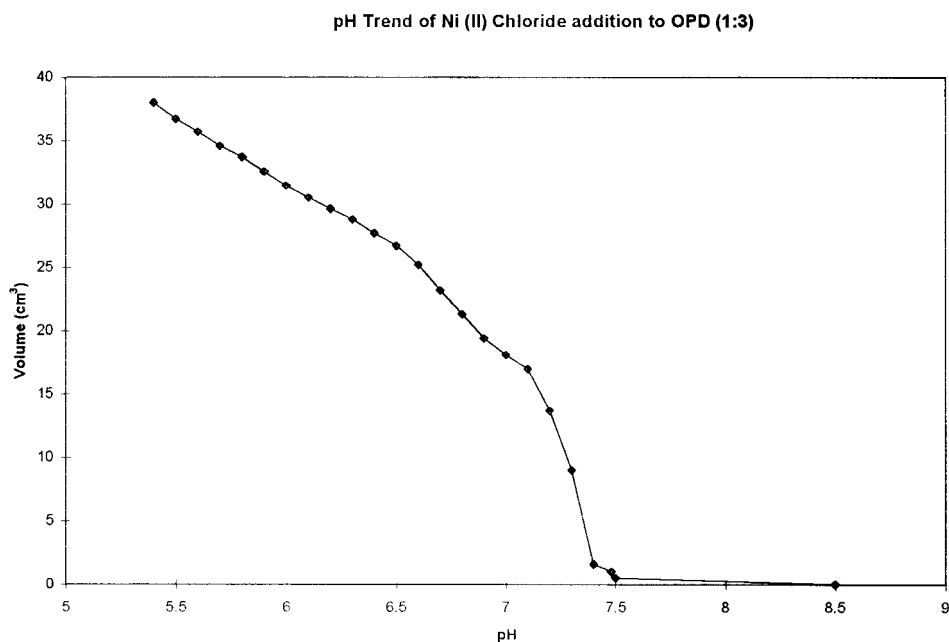
Figure 2 Plot of apparent pH as a function of nickel(II) chloride volume added to OPD solution.

one pH unit (initially to around pH 5) when the next portion of nickel was added and so on.

Upon addition of the Ni(II) solution a lilac precipitate was obtained. This solid was isolated by vacuum filtration, washed with hot ethanol to remove any uncomplexed OPD and dried overnight in a vacuum oven at 50°C (1 bar) to yield a lilac powder with elemental analysis consistent with literature reports.[23]

Ni(OPD)$_3$Br$_2$

The procedure outlined for Ni(OPD)$_3$Cl$_2$ was repeated using OPD (3.24 g, 0.03 mol) and NiBr$_2$ · 6H$_2$O (2.73 g, 0.01 mol). A blue solid was isolated with elemental analysis consistent with literature reports.[23]

General Preparative Methods for the Metal–2-ABA Chloro Complexes

The general method adopted for all of the metal(II) chloride–2-ABA complexes was used with minor modifications. The full procedure is given for Ni(2-ABA)$_3$Cl$_2$ and modifications to the procedure are indicated in the following sections.

Ni(2-ABA)$_3$Cl$_2$

A 1000 cm^3 round bottom flask containing ethanol (150 cm^3) was heated to 40°C and maintained at this temperature by constant stirring. In two separate 250 cm^3 dropping funnels were placed 2-ABA (3.74 g, 0.03 mol) in ethanol (75 cm^3) and NiCl$_2$ · 6H$_2$O (2.43 g, 0.01 mol) in ethanol (75 cm^3). Each of the solutions was added simultaneously to the round bottom flask. Upon addition of the Ni(II) solution, a light purple precipitate was obtained. This solid was isolated by vacuum filtration and dried overnight in a vacuum oven at 50°C (1 bar) to yield a solid with elemental analysis consistent with literature reports.[24]

Cu(2-ABA)$_2$Cl$_2$

The procedure outlined for Ni(2-ABA)$_3$Cl$_2$ was repeated using 2-ABA (3.74 g, 0.03 mol) and CuCl$_2$ · 2H$_2$O (1.74 g, 0.01 mol). A dark green solid was isolated by vacuum filtration and dried overnight in a vacuum oven at 50°C (1 bar) to yield a solid with elemental analysis consistent with literature reports.[24]

General Preparative Methods for the Metal–2-ABA acetato (ac) Complexes

Two general methods were adopted for the metal(II) acetato–2-ABA complexes, the first involving a solvent complexation, the second involving the use of a greatly reduced volume (virtually a solid blend method).

Ni(2-ABA)$_3$(ac)$_2$

A 1000 cm^3 round-bottom flask containing ethanol (150 cm^3) was heated to 40°C and maintained at this temperature by constant stirring. In two separate 250 cm^3 dropping funnels were placed 2-ABA (3.74 g, 0.03 mol) in ethanol (75 cm^3) and Ni(CH$_3$COO)$_2$°4H$_2$O (2.49 g, 0.01 mol) in ethanol (75 cm^3). Each of the solutions was added simultaneously to the round-bottom flask. Upon addition of the Ni(II) solution, a light purple precipitate was obtained. This solid was isolated by vacuum filtration and dried overnight in a vacuum oven at 50°C (1 bar) to yield a solid with elemental analysis consistent with literature reports.[24]

Cu(2-ABA)$_2$(ac)$_2$

The procedure outlined for Ni(2-ABA)$_3$Cl$_2$ was repeated with a slight modification. A 1000 cm^3 round-bottom flask containing ethanol (150 cm^3) was heated to 40°C and maintained at this temperature by constant stirring. In two separate 250 cm^3 dropping funnels were placed 2-ABA (3.74 g, 0.03 mol) in ethanol (100 cm^3) and Cu(CH$_3$COO)$_2$·H$_2$O (2.00 g, 0.02 mol) in degassed distilled water (100 cm^3). Each of the solutions was added simultaneously to the round-bottom flask. A blue solid was isolated by vacuum filtration and dried overnight in a vacuum oven at 50°C (1 bar) to yield a solid with elemental analysis consistent with literature reports.[24]

Ni(2-ABA)$_2$(ac)$_2$

A second preparation was attempted using a reduced volume of solvent. To 2-ABA (0.374 g, 0.003 mol) and Ni(CH$_3$COO)$_2$·4H$_2$O (0.249 g, 0.01 mol) in a mortar was added acetone (to a total of 10 cm^3) and the mixture heated gently with an air gun. The solution began to turn cloudy until a light green precipitate formed and fell out of solution. The solid had an elemental analysis consistent with literature reports.[24]

Formulation of Epoxy-Curing Agent Samples

The levels of curing agent incorporation were based on the relevant epoxy equivalent weights

Table II Mixing Ratios for OPD-Based Curing Agents (Based on 1 g of Epoxy)[a]

Epoxy	Curing Agent				
	DDS	OPD	$Ni(OPD)_3Br_2$	$Ni(OPD)_3Cl_2$	$Cu(OPD)_2Cl_2$
MY721 (eew 119.7)	0.5185	0.2259	0.3779	0.3162	0.3195
MY750 (eew 195.25)	0.3179	0.1385	0.2317	0.1938	0.1959

[a] eew: epoxy equivalent weight; DDS: 4,4′-diaminodiphenylsulphone; OPD: *ortho*-phenylene diamine.

(eew) of the epoxies and the number of active amino hydrogen atoms in each complex. For example, $Ni(OPD)_3Br_2$ has a relative molar mass (RMM) of 542.93 and contains 12 active hydrogen atoms. Therefore, one 1 mole of active hydrogen atoms represents 45.24 g (542.93 ÷ 12). This figure is the stoichiometric equivalent of the eew and, hence, for every 195.25 g of MY750, 45.24 g of $Ni(OPD)_3Br_2$ are required. These calculations led to the following levels of incorporation for both the OPD and 2-ABA complexes (Tables II and III). After drying, each complex was ground to a powder using a pestle and mortar to remove the larger particles. To each commercial epoxy was added the calculated quantity of the solid complex and the mixture was stirred manually until the curing agent was well dissolved in the epoxy.

Storage Stability Testing ("Shelf Life")

Shelf life tests were carried out on samples of MY721 and MY750 containing selected examples of OPD- and 2-ABA-based curing agents (see Tables II and III for incorporation levels). After formulation was complete, the mixtures were stored at "room" temperature (thermostated at 19°C). Then the viscosities of mixtures were periodically

measured using a cone and plate viscometer at 50°C at an initial spin rate of 350 rpm for a period of 15 s.

RESULTS AND DISCUSSION

Preparation of Transition Metal Complexes Containing OPD

Complexes containing OPD ligands based on the corresponding chloro and acetato salts of nickel and copper were prepared using a literature method in quantitative yields. The analytical data for $Ni(OPD)_3Cl_2$ (see Table I) suggest that a single OPD molecule may be trapped in the lattice as $[Ni(OPD)_3Cl_2]_4OPD$, for which the calculated figures are in close agreement (and the IR spectral data do support this, showing the presence of "free" N—H stretches due to the partially complexed diamine). The preference for the formation of the *bis*-(bidendate) and *bis*-(monodentate) complexes in the nickel(II) chloride case could be due to the chloride counterion being tightly bound to the nickel ion. This would, in turn, lead to the bidentate ligands being located at the equatorial positions of the Ni(II) in preference to the axial-

Table III Mixing Ratios for 2-ABA Based Curing Agents (Based on 1 g of Epoxy)[a]

Epoxy	Curing Agent				
	DDS	2-ABA	$Cu(2\text{-}ABA)_2 \cdot Cl_2$	$Cu(2\text{-}ABA)_2 \cdot ac_2$	$Ni(2\text{-}ABA)_3 \cdot Cl_2$	$Ni(2\text{-}ABA)_3 \cdot ac_2$
MY721 (eew 119.7)	0.5185	0.2551	0.3956	0.4449	0.3454	0.3782
MY750 (eew 195.25)	0.3179	0.1564	0.2425	0.2727	0.2117	0.2319

[a] eew: epoxy equivalent weight; DDS: 4,4′-diaminodiphenylsulphone; 2-ABA: 2-aminobenzylamine.

equatorial positions. It has been shown[23] that it is possible to promote the formation of the *tris*-(bidentate) ligands (which would be preferable in this application) to the Ni(II) ion by reacting the complex with bromine gas to form the less tightly bound bromide counter-ion. In this study, the di-equatorial bidentate OPD was successfully prepared with $NiBr_2$. The reaction conditions were designed to promote the production of *tris*-(bidentate) ligands, but owing to the insolubility of the *bis*-(bidentate) OPD in the reaction solution, only the *bis*-(bidentate) complex was obtained—precipitating on formation.

Eventually, the study of the formulation of OPD complexes in the commercial epoxy systems (see below) demonstrated some shortcomings in their solubility. This was thought to be due to the stability of the complex preventing solvation in nonpolar solvents, coupled with the ligands forming a hydrophobic casing around the transition metal further preventing solvation in polar solvents—although when exposed to strong solvating agents (e.g., DMSO and dimethyl formamide) the ligands did dissociate.

2-Aminobenzylamine was chosen as an alternative ligand for two principal reasons: the incorporation of a short aliphatic chain in the molecule was hoped to aid the solubility in epoxy and the incorporation of both an aliphatic and aromatic amino group would offer greater processing versatility. It is well known that aliphatic and aryl primary amines display differing reactivity towards epoxy resins.[2] The former react very readily at low (even room) temperatures, whereas in aryl amines, the delocalization of the nitrogen lone pair in the *p*-orbital into sp^2 orbitals of the phenyl ring lowers their reactivity. In this way it is hoped that two different types of amino groups will offer greater versatility in subsequent resin processing operations.

## Preparation of Transition Metal Complexes Containing 2-ABA

Complexes containing 2-ABA ligands based on the corresponding chloro and acetato salts of nickel, copper, and cobalt were prepared by several preparative methods in a variety of yields (of between 80 and 100%). Like OPD, 2-ABA is air and light sensitive, discolors readily, and reacts slowly with atmospheric (or solvent-borne) carbon dioxide. Kovala-Demertzi et al.[24] reported the preparation of 2-ABA complexes of chloro and bromo salts of nickel, copper, and cobalt. Their

results suggested that only mono- and *bis*-(bidentate) copper complexes, Cu(2-ABA)Cl_2, Cu(2-ABA)$_2Cl_2$, and Cu(2-ABA)$_2Br_2$ appeared to form, with the mono-(bidentate) structure having a polymeric form. This latter structure would be of limited use in our study given the need for high solubility of the complexes within the epoxy resin. Furthermore, they found that it was only possible to obtain the *tris*-(bidentate) complex with nickel and cobalt salts.

In our work, initially, solution methods (similar to those employed earlier for OPD) were examined with some success but the procedures had to be carried out under nitrogen. Elemental analysis of the complexes showed only reasonable agreement with calculated values, although the data were similar to those previously reported.[24] For example, Table I shows selected elemental data for 2-ABA complexes prepared in this work, along with those reported in the literature. Generally, the nickel complexes displayed a poorer correlation (than the corresponding copper complexes) between the analytical figures and those calculated for the desired structures. The complexes did appear slightly susceptible to moisture absorption on standing. In these cases, either one or two molecules of water of crystallization have been "added" to the analyses and this appears to bring the values much closer to the accepted value. This might present potential problems in later use with this complex in an epoxy formulation as the presence of water may have deleterious effects on the storage (and final) properties of the epoxy resin and work is underway to assess its impact.

One drawback that had been experienced with the OPD preparations was the occlusion of free (uncomplexed) diamine present in the isolated complex. Clearly, this would be of little use in an application requiring an "inert" curing agent with no amino groups free to react with epoxy groups. Consequently, during the course of the study, the volume of solvent was progressively reduced in the mixture until a virtually solvent-free method was developed that ensured high yielding preparations.

In order to obtain the Ni(2-ABA)$_3 \cdot Cl_2$ complex it was necessary to use a minimum level of solvent as the complex precipitated more readily upon standing. The elemental analysis and Fourier transform infrared data obtained for this complex suggest a structure in which the bidentate ligands are octahedrally bound to the nickel with the counterions balancing out the charge on

(a)

(b)
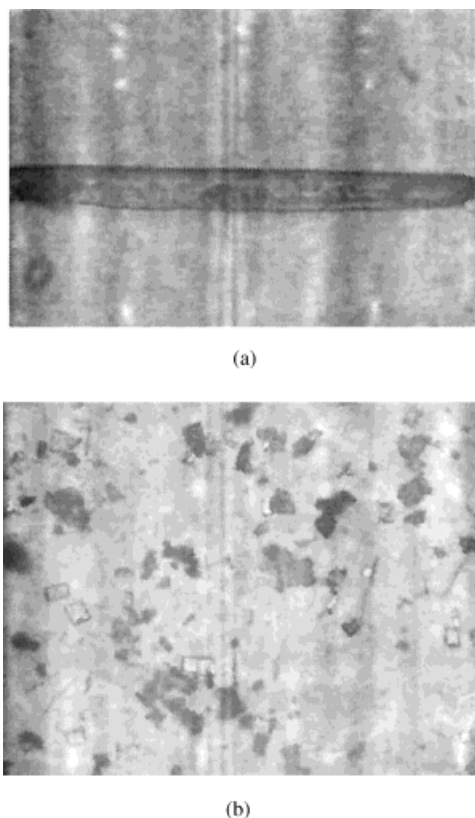
Figure 3 Photographs of (a) needle shaped crystals of $Cu(2\text{-}ABA)_2 \cdot (ac)_2$ and (b) rhomboid shaped crystals of $Cu(2\text{-}ABA)_2 \cdot Cl_2$.

the outer sphere. Similarly, $Ni(2\text{-}ABA)_3 \cdot (ac)_2$ was obtained using a minimum of solvent to dissolve the complex and then precipitating the complex with an excess of diethyl ether. Like its chloro analogue, $Ni(2\text{-}ABA)_3 \cdot (ac)_2$ has three bidentate ligands octahedrally bound to the nickel center, with the acetato counterions not directly bound to the metal. Unlike the nickel complexes, the copper complexes are *bis*-bidentate with the counterions attached to the central transition metal ion. $Cu(2\text{-}ABA)_2 \cdot (ac)_2$ forms deep blue crystalline needles [Fig. 3(a)] that are soluble in ethanol. In order to obtain the final complex it was necessary to use a minimum level of solvent to dissolve the complex and then reprecipitate it with an excess of diethyl ether. $Cu(2\text{-}ABA)_2 \cdot (ac)_2$ appears to have a structure in which the acetato counterions are placed in an axial position. $Cu(2\text{-}ABA)_2 \cdot Cl_2$ is a dark green crystalline solid [rhomboid in shape, Fig. 3(b)] with a small particle size (a somewhat crude estimation of size may be gained using an optical microscope with a graduated scale that gives a size of ca. < 0.1 μm

for the needles of $Cu(2\text{-}ABA)_2 \cdot (ac)_2$ and 0.05–0.1 μm for the rhomboids of $Cu(2\text{-}ABA)_2 \cdot Cl_2$). Both the nickel complexes were estimated to be less than 0.1 μm in diameter. While this only a crude estimate, it is clear that the choice of acetato or chloro counterion has a significant effect on both the particle size (due to precipitation during crystal growth) and solubility properties. The $Cu(2\text{-}ABA)_2 \cdot Cl_2$ complex precipitated readily on formation in ethanol and is water soluble. Like the chloro analogue, the complex appears to be *bis*-bidentate with the counterions attached to the central copper(II).

IR Characterization of Transition Metal–Diamine Complexes

Infrared (IR) spectroscopy was used extensively in this work to determine whether complexation had been achieved. Barvinok et al.[25–28] and Marks et al.[23] have reported the influence of coordination of a number of transition metals to the IR spectrum of, e.g., aniline and OPD (the latter is of particular interest in this work). They observed not only the expected shift in the NH_2 asymmetric and symmetric stretches to lower wavenumbers on complexation (from 3472 to below 3320 cm^{-1} for the symmetric stretch and from 3390 to 3260 cm^{-1} for the asymmetric stretch in aniline), but that a shift in the frequency of the band could also be effected by changing the nature of the (halide) counterion.

In the current work, two principal areas within the spectra were monitored: 3500–3000 cm^{-1} (NH_2 asymmetric and symmetric stretch) and 1650–1590 cm^{-1} (NH_2 deformation, $\delta(NH_2)$). Owing to the complexity of the spectra, it was difficult to determine the 1290–1220 cm^{-1} region (C—N stretch) with certainty, although it is included in Table IV for completeness. However, the remaining two vibrational frequencies yield information about the bonding (and more particularly the degree of association) within the complex. The stronger the nitrogen–metal (N—M) bond within the complex, the greater is the observed shift of the vibration to lower wavenumber from that observed for the free ligand (OPD or 2-ABA respectively). Kovala-Demertzi et al.[24] extensively examined the complexation chemistry of 2-ABA to first row transition elements and, in doing so, reported changes in both physical (e.g. magnetic moment and molar conductance) and spectroscopic (e.g., IR and UV-visible) characteristics of the free and complexed ligand.

Table IV   Selected IR Data for Complexes

Complex	Characteristic Bands in Mid-IR Indicative of Complexation		
	3500–3000 cm^{-1}	1700–1400 cm^{-1}	1290–1220 cm^{-1}
OPD	3384, 3361, 3279 (mb), 3175 (mb)	—	1274
Cu(OPD)$_2$Cl$_2$	3380, 3152	—	1240
Cu(OPD)$_3$Cl$_2$	3400, 3190	—	1280, 1240
Ni(OPD)$_3$Cl$_2$	3395, 3287, 3221, 3142	—	1282, 1241
Ni(OPD)$_3$Br$_2$	3348, 3259, 3139, 3083	—	1257
2-ABA	3399, 3282	1652	—
Cu(2-ABA)$_2$Cl$_2$	3288, 3216, 3112, 2999	1622	—
Cu(2-ABA)$_2$(ac)$_2$	3342, 3230, 3189, 3113, 3068	1627 (sh), 1611 (sh)	—
Ni(2-ABA)$_3$Cl$_2$	3413,^{a} 3308, 3224, 3127	1617	—
Ni(2-ABA)$_3$(ac)$_2$	3318, 3234, 3193	1626	—

^{a} O—H stretch (associated with water in sample); sh: shoulder on main acetato peak.

A close inspection of the IR spectra (Fig. 4) of the 2-ABA based complexes prepared in our study shows several points of note (the principal bands of interest included in Table IV are those used to demonstrate that complexation has occurred). Of particular interest to us, considering the proposed application of the complexes, is the finding that there is no evidence of a free N—H stretch in any of the complex spectra—indicating that complexation is apparently complete (unlike the data obtained for the corresponding OPD complexes). The $\delta(NH_2)$ (scissoring) band is generally located at around 1652 cm^{-1} for 2-ABA. In all cases there is a significant shift in this band on complexation. The IR spectra of the nickel complexes displayed a marked shift from 1652 in the 2-ABA ligand to 1617 cm^{-1} for the chloro complex and to 1626 cm^{-1} for the acetato complex. Similarly, the copper complexes display a smaller but significant shift in the $\delta(NH_2)$ band from 1652 to 1622 cm^{-1} for the chloro complex and to 1627 cm^{-1} for the acetato complex.

A further complication arises through the use of the acetate anion with its two prominent vibrations that can mask some vibrations associated with the diamines. Nakamoto[29] discusses the different ways in which this anion may complex with transition metals, although in the current work, only two forms are observed (i.e., as a monodentate ligand or an associated counterion). Literature studies have shown[29] that although there is no marked effect on the band shifts of the acetate, due to the symmetry of the free ion being low, variations in frequency are observed when changing the nature of the metal.

In general, in nickel (and cobalt and silver) complexes the absorption for the COO vibrations occur below the bands associated with the NH$_2$ deformations, although this is not the case for copper (and manganese). In addition, the acetate bands in the 1700–1300 cm^{-1} region are very distinctive for acetates of copper and nickel (and cobalt), which display two strong bands at around 1550 and 1420 cm^{-1} (Fig. 4).

Magnetic Susceptibility Measurements of Complexes Containing 2-ABA

Magnetic susceptibility measurements were undertaken for four of the complexes prepared in this study. Both chloro complexes display values very close to those reported by Kovala-Demertzi et al.[24] Cu(2-ABA)$_3$Cl$_2$ yields a μ_{eff} value of 2.90 B.M. *cf* 2.91 B.M.,[24] whereas Cu(2-ABA)$_2$Cl$_2$ yields a μ_{eff} value of 1.82 B.M. *cf* 1.84 B.M.[24] Simple Cu(II) complexes, i.e., those that do not have Cu–Cu interactions, generally fall in the region 1.75–2.20 B.M., regardless of symmetry and at normal temperatures.[30] Measurements of Ni(2-ABA)$_3$Cl$_2$ also showed a value in close agreement with the literature value.[24] These data tend to support the formation of discrete complexes rather than associated "polymeric" forms.

Shelf Life Studies of Epoxy-Curing Agent Samples

One of the main drawbacks associated with the use of conventional high melting curing agents
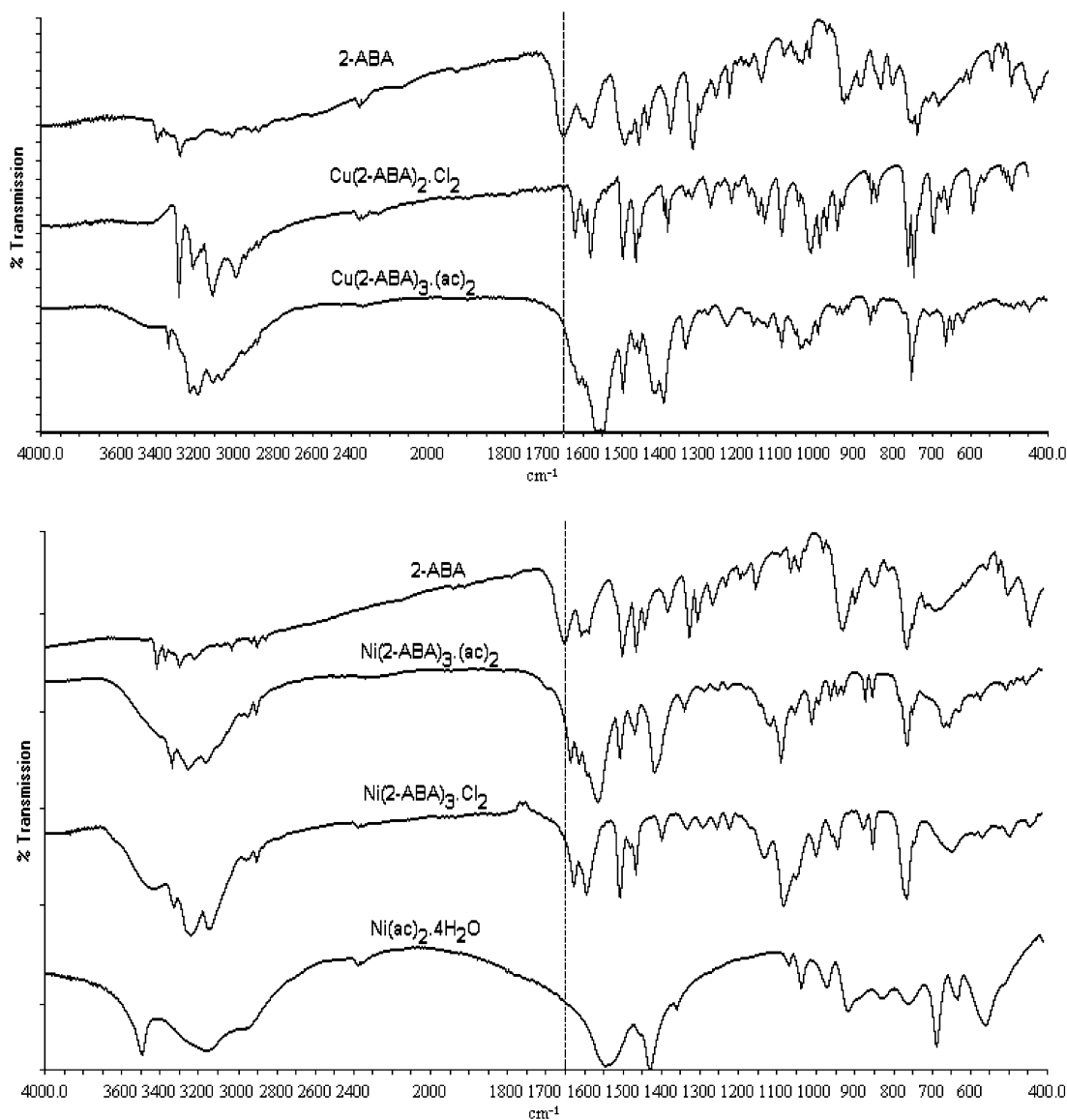
Figure 4 IR transmission spectra of selected complexes and ligands. The $((NH_2)$ (scissoring) band is indicated with a solid line at 1652 cm^{-1}.

[e.g., DiCy or aryldimethylureas such as CA-150 and Diuron] is their low solubility in common commercial epoxies such as MY721 or MY750. In order to produce a homogeneous formulation it is necessary to reduce the compounds to a fine powder (i.e., micronize) prior to mixing to allow a more even dispersion and thus prevent "hot spots" of concentrated curing agent.

Epoxy–OPD Complexes

Only three of the OPD complexes were chosen for incorporation into the epoxy resins (MY721 and

MY750) for shelf life tests. The initial screening step was based on the absence of free N—H stretches in their IR spectra and this eliminated $Ni(OPD)_3Cl_2$ as having poor potential as a latent curing agent. The levels of incorporation for the OPD-based curing agents are shown in Table II (note that OPD and DDS were included as baseline measures in later tests). In practice, for comparison DiCy (with 3–7 active hydrogen atoms *per* molecule)[31] would be added at a level of 0.077g to 1 g of MY721 of eew 119.7.

After drying, $Ni(OPD)_3Br_2$ had a chalky appearance and retained some lumps after grinding. Furthermore, the powder appeared to form ag-

glomerates, further hampering addition to the epoxy. On standing, the finer particles remained suspended in the epoxy, but the larger agglomerates settled to the bottom of the vessel. $Cu(OPD)_3Cl_2$ initially suffered from similar problems, but the size of the agglomerates decreased with time and after a period of seven days had elapsed the epoxy/complex mixture appeared homogeneous. After drying, $Ni(OPD)_3Cl_2$ formed smaller, more uniform particles making mixing somewhat easier to achieve. However, in the lower viscosity MY750 some settling out did occur on storage. It should be borne in mind that these simple formulations did not incorporate fillers to modify the viscosity of the mixture.

In order to determine the utility of these curing agents in one-pot formulations, shelf life tests were carried out on mixtures containing one of each of the OPD-based curing agents in both MY721 and MY750 (see Table III). A Brookfield viscometer was used to determine the gel times for each of the commercial epoxy resins containing a series of curing agents. A commercial curing agent (DDS) was also analyzed to yield baselines for the unmodified (uncomplexed) curing agents for comparative purposes. While the method is not ideal (it is a dynamic measurement that encourages mixing of the blend components or thinning), it does provide a comparative measure of the curative systems analyzed under identical conditions.

The results are presented as plots of viscosity (in centipoise, cP) against storage time (in days) and a number of observations can be made. The dynamic viscometric data for formulations containing MY721 are shown in Figure 5(a). The presence of OPD caused the viscosity to rise markedly after a period of only three days, with the formulation having achieved a viscosity of 2 cP after only a week. For comparison, the MY721 formulation containing $Cu(OPD)_3Cl_2$ had reached this same viscosity after a period of 22 days.

The formulations containing MY750 are shown in Figure 5(b). In comparison with MY721, the presence of OPD caused the viscosity to rise still more markedly after a period of only two days, with the formulation having achieved a viscosity of 2 cP after only three days. The MY750 formulation containing $Cu(OPD)_3Cl_2$ had reached this same viscosity after a period of 30 days.

Both of the epoxies containing the $Ni(OPD)_3Cl_2$ complex had shown no significant increases in viscosity during the test period, while those containing the $Ni(OPD)_3Br_2$ complex 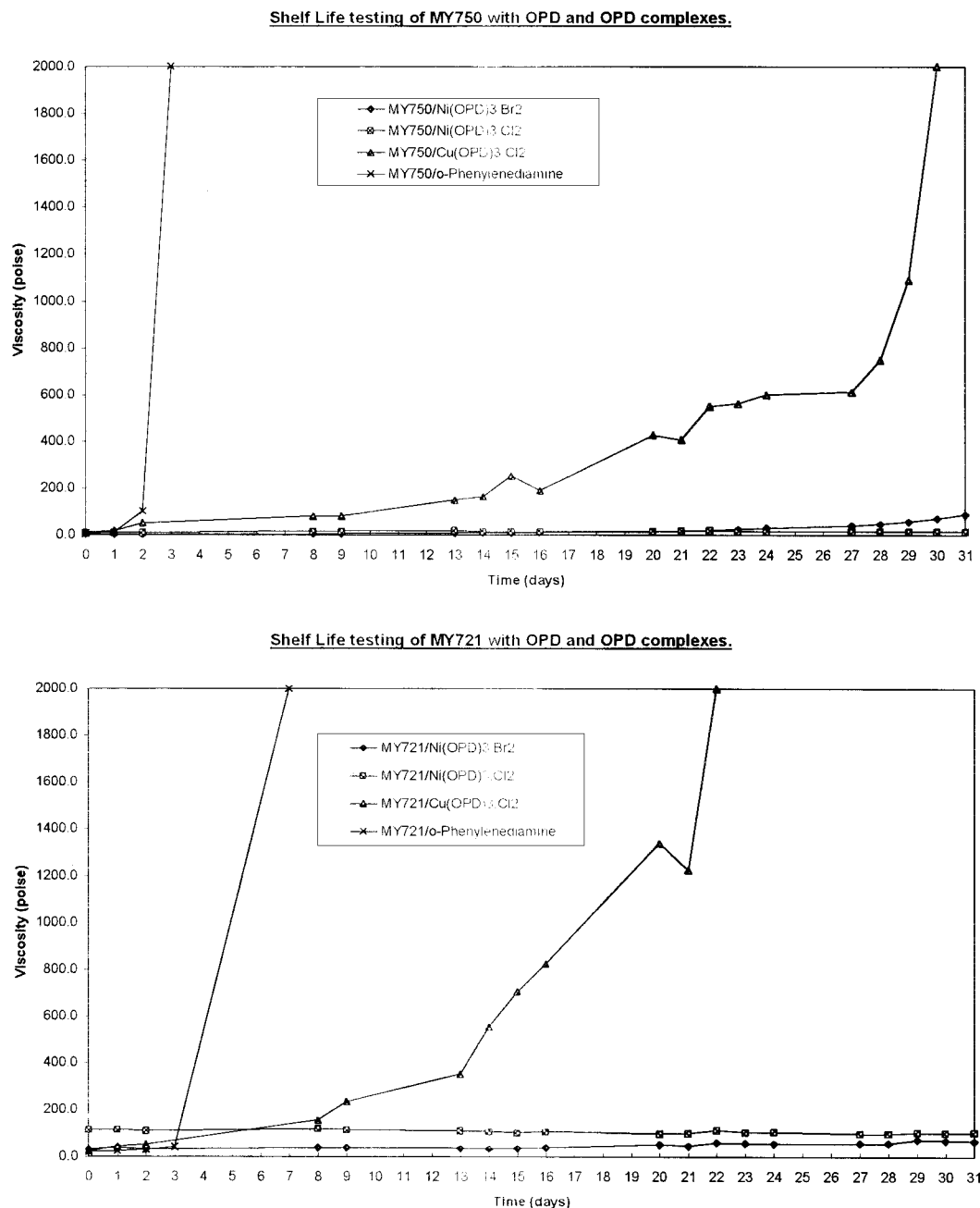had started to undergo cure after ca. 31 days. These observations suggest that complexation of the amino groups has significantly slowed the initiation of the cure reaction. Furthermore, the complexes may well be functioning in a similar fashion to DiCy, in that their relatively poor solubility in epoxy (and relatively high melting points) hinders the reaction.

Epoxy–2-ABA Complexes

Four of the 2-ABA complexes were chosen for incorporation into the epoxy resins (MY721 and MY750) for shelf life tests. The levels of incorporation for the 2-ABA-based curing agents are shown in Table III (note that 2-ABA and DDS were included as baseline measures in later tests). The $Ni(2\text{-}ABA)_3 \cdot Cl_2$ complex has a powdery texture and did not dissolve directly in MY721; however, it did display a higher degree of solubility in organic solvents than $Ni(2\text{-}OPD)_3 \cdot Cl_2$ as it was soluble in ethanol. $Ni(2\text{-}ABA)_3 \cdot (ac)_2$ also has a powdery texture and did not dissolve in MY721 although it is also soluble in ethanol. $Cu(2\text{-}ABA)_2 \cdot (ac)_2$ is a dark green crystalline [rhomboid in shape Fig. 3(b)] water-soluble solid with a small particle size. It is partially soluble in MY721. $Cu(2\text{-}ABA)_2 \cdot Cl_2$ also partially dissolves in MY721 and is soluble in ethanol.

A series of storage stability tests was carried on samples of MY721, containing the 2-ABA based complexes, over a period of 67 days in order to examine changes in the thermal characteristics during the storage period. All complexes were incorporated in a stoichiometric blend with MY721 and stored under identical conditions (in a room thermostated at 19°C).

In order to examine the effect of storage on the thermal characteristics of the formulations, DSC analysis was performed on blends containing MY721 and each 2-ABA based curing agent over the storage period of 67 days. There is little apparent change in the position of the peak maximum over the period (dropping from ca. 141 to 137°C), but the cure onset drops from ca. 119 109°C during the same time. The exothermic peak undergoes very subtle changes in shape and magnitude [Fig. 6(a)] with the peak being reduced from 498 to 472 J g^{-1} after 63 days. The formulation containing the copper analogue, $Cu(2\text{-}ABA)_3 \cdot (ac)_2$ behaves in a similar fashion: the exothermic peak maximum (140°C) remains unchanged on storage, while the peak onset falls from 127 to 118°C. The changes in the exothermic peak are more marked in this case [Fig. 6(b)]. The peak becomes significantly broadened, the shoul-

Shelf Life testing of MY750 with OPD and OPD complexes.

Shelf Life testing of MY721 with OPD and OPD complexes.

**Figure 5**   Dynamic viscometry data for OPD-based curing agents when blended with (a) MY721 and (b) MY750.

der following the main exothermic peak becomes smaller and the value of ΔH falls from 384 to 241 J g^{-1} after 67 days. Incidentally, both formulations showed practically no change over the first 14 days of storage (a realistic period during which processing might take place).

DSC Measurements of Commercial Epoxy/OPD-Based Curing Agents

A thorough study of the thermal characteristics of the formulations is outside the scope of this paper

and forms the basis of a second, related paper.[22] However, a brief DSC characterization was carried out on each of the MY750 and MY721 formulations to determine simple parameters (e.g., cure onsets and heats of reaction).

Both MY750 and MY721 formulations (Table V) displayed similar cure characteristics in that all but one of the novel curing agents have a higher cure onset than the commercial curing agents. The thermal data demonstrate that OPD (in the uncomplexed form) displays a similar cure
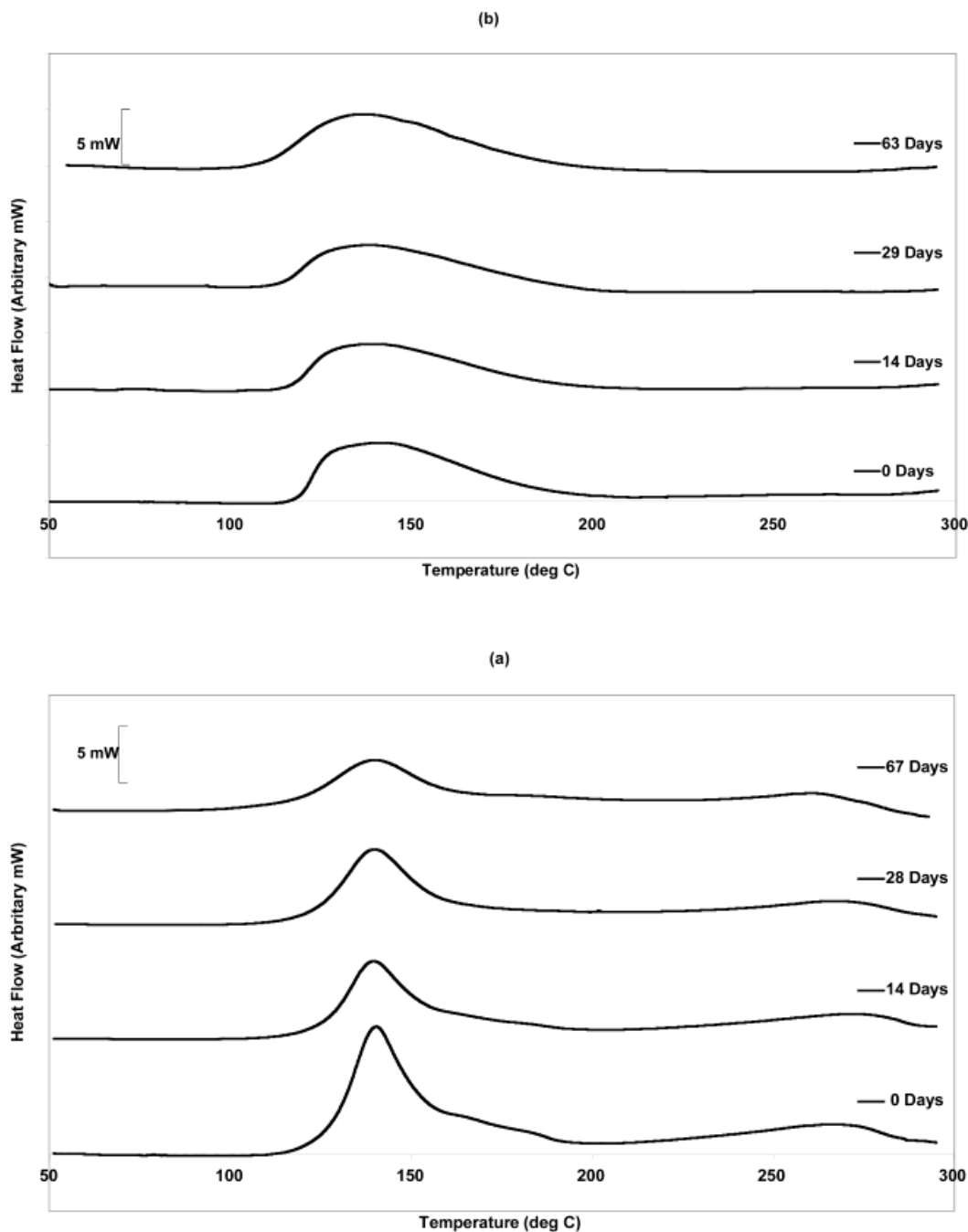
Figure 6 Selected DSC data for (a) Ni(2-ABA)$_3$ · (ac)$_2$ in MY721 and (b) Cu(2-ABA)$_2$ · (ac)$_2$ in MY721 during the storage period.

onset to the commercial curative systems. This is related to the melting points of the complexes and to the dissociation temperatures of the M—N bonds and will be discussed in more detail in the relevant paper.[22]

It is noteworthy that there is a marked difference in the thermal behavior of the novel curing agents when produced via different methods (i.e., those denoted with superscripts in Table V). Ini-

tially, the two reagents were simply mixed together and shaken vigorously, whereas the later materials (denoted with a superscript "c") were mixed in the same fashion as the production of the nickel OPD complexes. The latter method employs stoichiometric addition to the reaction vessel, thus ensuring a constant 3:1 ratio of OPD to Cu(II). We believe that the second method is more effective in yielding products of higher purity (viz.

Table V Thermal Characteristics of Epoxy Blends with Different Curing Agents

Epoxy	Curing Agent	$T_o{}^a$ (°C)	$T_{max}{}^a$ (°C)	ΔH^a (J/g)
MY750	Curimid CN	135	146	124
	DiCy/CA150	142	147	282
	Diuron/DiCy	144	150	612
	$Cu(OPD)_3Cl_2$	151	160	84
	$Ni(OPD)_3Cl_2{}^b$	156	168	191
	$Ni(OPD)_3Cl_2{}^c$	163	172	207
	$Ni(OPD)_3Br_2{}^b$	164	174	146
	$Ni(OPD)_3Br_2{}^c$	164	175	193
	OPD	139	167	290
MY721	Curimid CN	142	176	704
	DiCy/CA150	136	143	361
	Diuron/DiCy	141	147	567
	$Cu(OPD)_3Cl_2{}^b$	176	206	698
	$Cu(OPD)_3Cl_2{}^c$	136	153	519
	$Cu(OPD)_2Cl_2{}^b$	228	286	709
	$Ni(OPD)_3Cl_2{}^b$	158	169	643
	$Ni(OPD)_3Cl_2{}^c$	161	172	233
	$Ni(OPD)_3Br_2{}^b$	163	174	739
	$Ni(OPD)_3Br_2{}^c$	164	173	791
	OPD	158	182	487

[a] T_o: onset of polymerisation exotherm; T_{max}: peak maximum of polymerization exotherm; ΔH: magnitude of polymerisation exotherm.
[b] Complex prepared by simple mixing and vigorous shaking.
[c] Complex prepared by stoichiometric addition.

the elemental analyses in Table I) and the possible presence of an uncomplexed OPD molecule within the crystal lattice could lead to the observed reduction in the cure onset temperature (and peak maximum) which approaches the value observed for OPD.

CONCLUSIONS

The current work has demonstrated that while complexes based on copper(II) and nickel(II) and containing OPD ligands may be prepared and incorporated into commercial epoxy resins, there are some advantages associated with using 2-ABA (as the diamine ligand) due to the higher complex solubility and better processing characteristics that it imparts to the formulated system. In general, the 2-ABA based complexes disperse well within commercial epoxy systems and display good storage stability over prolonged periods of time. Work continues to examine the thermal and mechanical characteristics of commercial epoxy resins cured using these complexes.

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