The development of controllable complex curing agents for epoxy resins Part 3. An investigation of the shelf life and thermal dissociation behaviour of bis(acetanilido)-tris(acetato)dicuprate(II)

Ian Hamerton, Alan M. Emsley, John N. Hay, Henryk Herman, Brendan J. Howlin and Peter Jepson

A copper(II) complex, containing anthranilamide ligands, has been shown to display latent behaviour over a prolonged period of ambient temperature storage when formulated within MY721, a commercial epoxy resin recognised as an industry standard. The onset of cure occurs just above 100 °C to yield a polymer with a dry Tg of 128 °C.

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The development of controllable complex curing agents for epoxy resins

Part 3.† An investigation of the shelf life and thermal dissociation behaviour of bis(acetanilido)-tris(acetato)docuprate(II)

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Bis(acetanilido)-tris(acetato)docuprate(II), $[\text{Cu}_2(\text{C}_7\text{H}_8\text{N}_2\text{O})_2(\text{CH}_3\text{CO}_2^-)_3]$, is incorporated into MY721, a commercial epoxy resin recognised as an 'industry standard'. Infrared spectroscopy and thermogravimetry are employed to examine the structure and thermal dissociation behaviour of the newly prepared complex. Multivariate analysis techniques (*e.g.* principal components analysis) are used to examine the spectral data to corroborate the dissociation temperature. The shelf life and cure characteristics of the commercial epoxy/curing agent formulation are determined using differential scanning calorimetry and vibrational spectroscopy.

Introduction

The market for thermoset polymers is substantially smaller than the demand for thermoplastics, *e.g.* in 2003 the total consumption of thermoplastics in Western Europe was 38 148 000 tonnes, compared with 10 640 000 tonnes of thermosets.¹ Despite this, epoxy resins still form a substantial market and in their consumption totals around 900 000 tonnes in the USA, Western Europe and Asia/Pacific combined, with Asia taking a 35% share.² The principal uses for epoxy resins are (in approximate order of consumption) surface (protective) coatings, electrical/electronic components, composites (reinforced resins), bonding and adhesives, flooring (construction) and tooling and casting.

The conversion of epoxy resins from liquid or semi-solid monomers into hard, infusible thermoset networks occurs *via* the introduction of cross-linking agents and the initiation of polymerisation by thermal, ultraviolet or microwave radiation, *etc.* Polyamines are among the most commonly used curing agents for epoxy resins and make up around 22% of the commercial market;³ primary, secondary and tertiary amines may all be used to initiate cure in epoxy systems. Primary and secondary amines are generally employed in stoichiometric amounts (as the amine becomes incorporated within the epoxy polymer network), but tertiary amines are used in catalytic quantities. Where tertiary amines are used, ring-opening of the oxirane group occurs prior to polymerization taking place *via* a polyetherification mechanism. The choice of amine governs the formation of polymer networks that differ in terms of their cross-link density, and hence glass transition temperature

which, in turn, has serious implications for the resin performance and ultimate application.

Epoxy resins are often formulated as 'one-pot' systems, which contain the monomer or prepolymer, curing agent(s) and additives, for sale or shipment. However, in order to formulate a curative system with a long shelf life (to enable storage either prior to shipment or between periods of use) each reactive component has to remain inert in the presence of any other co-reactants at the storage temperature. The curing agent may be rendered temporarily unreactive towards the epoxy group by complexation, thus preventing the lone pairs of electrons on the amino nitrogen atoms from participating in a nucleophilic attack. The association should be sufficiently strong to prevent premature reaction, but sufficiently labile to allow the initiation and polymerisation reactions to proceed, once a pre-determined cure temperature has been achieved.

Since the 1970s, transition metal complexes have been added to catalyse the reaction between curing agents and epoxy resins⁴ and their use has recently been reviewed.⁵ Our previous work has examined the potential of a variety of nitrogenous ligands, including complexes based on parent imidazoles^{6,7} and aromatic amines such as *o*-phenylene diamine (OPD)⁸ and 2-aminobenzylamine (2-ABA)^{8,9} (containing aliphatic and aromatic amino functions). In these preceding papers we have outlined both the benefits and the potential drawbacks of the ligands employed and this paper details the latest work in this process, by seeking to exploit the beneficial properties of the anthranilamide ligand.

Apparatus

Differential scanning calorimetry (DSC) was carried out using a Perkin-Elmer DSC7 on samples (*ca.* 6 ± 1 mg) over the range 30–300 °C at a range of heating rates (5, 10, 15 and 20 K min⁻¹). Measurements were made under N₂ (40 cm³ min⁻¹) using sealed 30 µl aluminium pans with a pierced lid. Glass transition temperatures (T_g) were determined by performing a rescan experiment (10 K min⁻¹) directly after quenching and cooling the scanned sample. The apparent T_g is

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† For Parts 1 and 2, see refs. ? and ?.

quoted as the midpoint of the inflection in the baseline. The differential kinetic equations were solved by using a commercial software package (ModelMaker v3.0.4 from Cherwell Electronics). Thermogravimetry (TG) was performed using a Pyris[®] operated Perkin-Elmer TGA7 on samples (*ca.* 5 ± 1 mg) at a fixed heating rate of 10 K min⁻¹ between 50 and 1000 °C. Measurements were made under flowing N₂ (40 cm³ min⁻¹) using a platinum boat. Mid infrared data were acquired using a Perkin-Elmer System 2000 FT-IR spectrometer using KBr disks and also an ATR accessory, which was placed in conjunction with a temperature controlled heating accessory. Spectra were obtained with a resolution of 4 cm⁻¹ under strong apodisation, and 16 scans were co-added to improve the signal-to-noise ratio, at temperatures between 20 and 160 °C. Near infrared (NIR) spectra were acquired by placing a sample, comprising a blend of MY721 and the anthranilamide complex, between microscope cover slips in a temperature controlled heating accessory. This was placed in the sample compartment of a Perkin-Elmer System 2000 FT-NIR spectrometer. Spectra were acquired at 15 min intervals (corresponding to a heating rate of 0.1 K min⁻¹) with a resolution of 4 cm⁻¹ under strong apodisation, and 32 scans were co-added to improve the signal-to-noise ratio, at temperatures between 60 °C and 150 °C. Magnetic susceptibility data were acquired using a Stanton Instruments SM12 Gouy balance: samples were placed in a cylindrical glass vessel and suspended in a non-homogeneous magnetic field and the application of a current (1 A) induced an increase or decrease in the sample weight. Elemental analysis was performed on samples (1–2 mg) using an Exeter Analytical EA440 CHN/O/S elemental analyser by combusting the samples in oxygen in a high temperature furnace (1800 °C) using helium as the carrier gas.

Materials

Copper(II) acetate tetrahydrate and anthranilamide were obtained from Aldrich Chemical Corp. The commercial epoxy (MY721) was obtained from Ciba-Geigy products and its epoxy equivalent weight (EEW) was determined to be 119.70 g using an in-house (Cytec-Fiberite Ltd., Wrexham) titrimetric method (hydrochloric acid 0.44 N, bromophenol blue). All commercial materials gave acceptable analytical results and were consequently used without further purification unless otherwise stated in the text.

Preparation of bis(acetanilido)-tris(acetato)dicuprate(II)

Copper(II) acetate tetrahydrate (0.01 mol) was dissolved in ethanol (100 cm³) in a 500 cm³ three necked round bottomed flask and heated with constant stirring to 40 °C. Anthranilamide (0.02 mol) was dissolved in ethanol (50 cm³) and added dropwise to the solution with constant stirring over a period of 15 minutes. The resulting precipitate was filtered and washed three times with ethanol (3 × 50 cm³) to produce a light green solid (yield 92%) of melting point greater than 230 °C and μ_{eff} 1.29 B.M. Elemental analysis calculated for C₂₂H₃₃N₄O₁₀Cu₂ (*i.e.* a dimer, containing one molecule of water and one molecule of ethanol of crystallization) 40.93% C, 5.11% H, 8.68% N; found 41.35% C, 4.44% H, 8.57% N.

Procedure for the formulation of complex–epoxy resin mixture

The amount of curing agent incorporated in the epoxy formulations was based on the EEW of the commercial monomer and the number of active amino hydrogen atoms in the dimeric complex. [Cu₂(C₇H₈N₂O)₂(CH₃CO₂⁻)₃] has a relative molar mass of 576 g mol⁻¹ and contains 8 active hydrogen atoms and one mole of active hydrogen atoms represents 72 g (576 ÷ 8): the stoichiometric equivalent of the EEW. Hence, for every 119.70 g of MY721, 72 g of [Cu₂(C₇H₈N₂O)₂(CH₃CO₂⁻)₃] are required and this curing agent loading was used for the subsequent spectral and thermal measurements.

Results and discussion

Rationale behind the selection of the ligand

During previous work to examine potential curing agents containing OPD⁸ and 2-ABA ligands,^{8,9} it was observed that the formulated curing agents displayed excellent shelf lives (of the order of 67 days at room temperature when mixed in MY721) and were able to effect cure in commercial epoxy resins within reasonable timescales. However, the volatility of the curing agents during the cure process, observed during rheological measurements, caused voids in the curing resins, as the liberated ligands underwent volatilisation, but were entrapped in the gelling mixture. This phenomenon, if translated to cured composite specimens, would obviously compromise the mechanical properties of the polymer and rendered the curing agents of limited use.

Anthranilamide has similar binding characteristics to the previous ligands, but has a higher melting point (*ca.* 114 °C) than 2-ABA and OPD and should not volatilise when undergoing dissociation from the metal centre. To prolong the shelf life, the polydentate ligand should coordinate as completely as possible, in this case *via* the nitrogen of the amine and the oxygen and/or nitrogen of the amide group. The latter is electron withdrawing and should reduce the ability of the amido nitrogen to co-ordinate to the metal centre, consequently leading to a reduction in the temperature at which the amido–metal bond is broken. The selection of a commercial material is also important to keep costs down.

Evidence for the structure of the complex prepared during this study

Allan *et al.* carried out,^{10,11} thermal, structural and electrical studies on chloro complexes of Co(II), Ni(II) and Cu(II) containing anthranilamide ligands and their data suggested that the ligand complexed through the amino nitrogen and the amido oxygen when introduced to Ni(II) and Co(II), but only through the amino nitrogen when introduced to Cu(II). In the present study, model ligands anthranilamide and aniline were examined to determine whether complexation was occurring through the amino or amido groups (or both). The amine bending bands are in close proximity to those of the amide, although the $\delta_{\text{N-H}}$ bands of aniline are found at slightly lower wave numbers (1619 cm⁻¹ and 1601 cm⁻¹).

There is general consensus concerning the assignment of amido bands in the mid-infrared. Kemp¹² has studied the

Fig. 1 Infrared absorption spectrum of bis(acetanilido)-tris(acetato)dicuprate(II) in KBr (blue) and analysed using ATR (red).

bands in the spectrum of benzamide and stated that there are two sets of bands that are characteristic of primary amides, $\nu_{\text{N-H}}$ near 3400 cm^{-1} and 3200 cm^{-1} and $\nu_{\text{C=O}}$ (amide I) and $\delta_{\text{N-H}}$ (amide II) which occur at around 1650 cm^{-1} (and the data presented in Fig. 1 and Table 1 agree with these assignments). Weast and Grasselli¹³ also describe the $\nu_{\text{N-H}}$ for the amide to be at 3448 cm^{-1} and 3226 cm^{-1} and $\delta_{\text{N-H}}$ 1639 cm^{-1} for both the anthranilamide and the benzamide (with a shift to higher wave numbers for the $\nu_{\text{C=O}}$ in the anthranilamide). Lin-Vien *et al.*¹⁴ state that unsubstituted amides in the hydrogen bonded state have asymmetric NH_2 stretch bands near 3350 cm^{-1} and symmetric NH_2 stretch bands near 3180 cm^{-1} . The C=O stretch band ($1680\text{--}1640\text{ cm}^{-1}$) and the NH_2 scissors deformation band ($1640\text{--}1620\text{ cm}^{-1}$) overlap in the hydrogen bonded state, with the former being the more intense of the two bands in the IR.

Table 1 contains the assignments that Allan *et al.* reported for three complexes of anthranilamide and the data for the newly-prepared complex. These suggest that the $\nu_{\text{N-H}}(\text{NH}_2)$ band has some similarities to those bands reported for free anthranilamide, whilst those for $\nu_{\text{N-H}}(\text{CONH}_2)$ are somewhat higher than the values quoted for the copper, cobalt and nickel complexes reported by Allan *et al.* The $\nu_{\text{C=O}}$ band of the new complex is also closer to the value observed for those

complexes containing bidentate anthranilamide,¹⁰ suggesting that, in contrast with the findings of Allan *et al.*, our complex contains monodentate anthranilamide ligands bonded to the copper through the amido nitrogen, with the ligands bearing free primary aryl amines. Consequently, future studies might involve *e.g.* cobalt in order to increase the likelihood of achieving full complexation.

Having ascertained the denticity of the ligands, it was necessary to determine whether the complexes were polymeric. Magnetic susceptibility values for Cu(II) complexes in an octahedral environment tend to lie between 1.75 and 2.20 B.M. regardless of symmetry and at normal temperatures¹⁵ and $[\text{Cu}(\text{2-ABA})_3\text{Cl}_2]$ and $[\text{Cu}(\text{2-ABA})_3\text{Cl}_2]$ yield μ_{eff} values of 2.90–2.91 B.M. and 1.82–1.84 B.M. respectively.^{7,16} A μ_{eff} value of 1.29 B.M. was obtained for the newly-prepared complex, suggesting that the Cu(II) metal centre is in a polymeric or bi-nuclear environment with Cu–Cu interactions. These data lead to a possible structure for the complex in which the acetate ligands bridge the bi-nuclear centre and in which two anthranilamide ligands are coordinated *via* the amido nitrogen atoms, thus leaving a free amino group on each ligand. Similar structures are also possible in which the aromatic amine is coordinated to the metal centre (or a mixture of the two).

Table 1 Selected infrared spectral assignments of model compounds and selected complexes containing anthranilamide ($\text{C}_7\text{H}_8\text{N}_2\text{O}$)

Compound	$\nu_{\text{N-H}}(\text{NH}_2)$	$\nu_{\text{N-H}}(\text{CONH}_2)$	$\nu_{\text{C-O}}(\text{CH}_3\text{CO}_2^-)$	$\nu_{\text{C=O}}$
Anthranilamide*	3406 (s) 3316 (s)	3378 (s) 3192 (s)	—	1656 (s)
Benzamide	—	3368 (s), 3173 (s)	—	1658 (s)
Benzylamine	3371 (s) 3290 (s)	—	—	—
Aniline (10% in CCl_4)	3475 (s) 3392 (s)	—	—	—
$[\text{Cu}(\text{C}_7\text{H}_8\text{N}_2\text{O})_2\text{Cl}_2]^*$	3370 (s) 3317 (s)	3230 (s) 3180 (s)	—	1668 (s)
$[\text{Co}(\text{C}_7\text{H}_8\text{N}_2\text{O})_2\text{Cl}_2]^*$	3382 (s) 3306 (s)	3236 (s) 3183 (s)	—	1640 (s)
$[\text{Ni}(\text{C}_7\text{H}_8\text{N}_2\text{O})_2\text{Cl}_2]^*$	3372 (s) 3312 (s)	3220 (s) 3182 (s)	—	1642 (s)
$[\text{Cu}_2(\text{C}_7\text{H}_8\text{N}_2\text{O})_2(\text{CH}_3\text{CO}_2^-)_3]$	3479 (m) 3376 (m)	3462 (m) 3349 (m)	3437 (w/ot) 3260 (w/ot)	1659 (s)

^a s = strong, m = medium, w = weak, ot = overtone, * = data originally reported in ref. 9, — = not present in compound.

Determination of shelf life of the epoxy-complex formulation using thermal analysis

Thermal analysis can give a good indication of shelf life over an extended period of storage¹⁷ by monitoring changes in polymerisation enthalpy and indirectly the extent of reaction. A blend of MY721 with the new complex was prepared and it was noticeable that bis(acetanilido)-tris(acetato)docuprate(II) showed greater solubility in the epoxy formulations than *e.g.* OPD, presumably as a result of the interaction between the polar amine/carbonyl groups with the glycidyl amine groups; no precipitation was observed during prolonged room temperature storage. The thermal behaviour of blends of MY721 and the complex were examined using scanning DSC and the data are presented in Table 2 and Fig. 2.

The thermogram of the newly-formulated mixture (acquired at a heating rate of 10 K min⁻¹) is shown in the “Day 0” entry of Fig. 3. Over a period of 70 days, the formulated samples were stored at ambient temperature and analysed periodically *via* dynamic scan (10 K min⁻¹) between 30 °C and 300 °C to monitor the effects of storage on the magnitude and the onset temperature of the polymerisation exotherm. A plot of the variation in the polymerization enthalpy is depicted in Fig. 3 and aside from some outliers (exacerbated by a reducing enthalpy and an increasingly ‘noisy’ baseline as storage progressed), a general downward trend is observed. The prolonged storage does show evidence of increasing ambient cure, although this is not dramatic despite the length of the storage period. In comparison with OPD and 2-ABA based complexes,⁸ the presence of uncoordinated amino species in the complex reduced the overall stability of these complexes in the epoxy resins.

The spectroscopic data for the complex suggested that the two anthranilamide ligands are only monodentate within the dimeric complex, thus leaving a free amino group available on each ligand able to react with the epoxy resin. This is clearly less desirable than *e.g.* OPD or 2-ABA, in which complete association was achieved, but it was decided to assess the effect of the free amino groups on storage stability nonetheless.

Blends of bis(acetanilido)-tris(acetato)docuprate(II) and MY721 display similar thermal behaviour to that reported⁸ for [Ni(OPD)₃Cl₂] or [Cu(2-ABA)₂Cl₂]. The DSC thermogram of the complex (shown in Fig. 2a as the uppermost

Table 2 Thermal analysis of an unaged MY721/[Cu₂(C₇H₈N₂O)₂-(CH₃CO₂⁻)₃] formulation (at *t* = zero days) undertaken using DSC (at 10 K min⁻¹, under flowing nitrogen)

Heating rate/K min ⁻¹	Cure onset ^a /°C	<i>T</i> _{max} /°C ^b	Δ <i>H</i> /J g ⁻¹ ^c	<i>T</i> _g /°C ^d
20	145	158	497	128
15	140	153	523	—
10	134	146	529	—
5	123	136	508	—

^a The cure onset is quoted as the point at which the exothermic peak rises from the baseline. ^b DSC analysis reveals a large exotherm with the *T*_{max} tabulated and several less well-defined shoulders at higher temperatures. ^c The individual exothermic processes were poorly resolved and so a total value (J g⁻¹) of formulation: epoxy + curing agent) is quoted. ^d Glass transition temperature quoted as the midpoint of the transition after rescan experiment.

Fig. 2 DSC thermograms (exothermic flow upwards) obtained at 10 K min⁻¹ under flowing nitrogen during prolonged storage at ambient temperature for an MY721/[Cu₂(C₇H₈N₂O)₂(CH₃CO₂⁻)₃] blend.

thermogram) reveals one major exothermic peak, although it does have less prominent shoulders between 160 °C and 280 °C. The latter are presumably due to the reactions of the (liberated) amido nitrogen or carbonyl oxygen with the epoxy ring; the acetato ligand and the epoxy and, ultimately,

Fig. 3 Plots of polymerization enthalpy (♦) from DSC data *versus* ambient storage time for an MY721/[Cu₂(C₇H₈N₂O)₂(CH₃CO₂⁻)₃] blend.

polyetherification of the epoxy group. During the first week of the extended storage study, there was only a slight decrease (<1 K) in the temperature of the cure onset, although this is probably not significant within the somewhat limited precision of a scanning DSC experiment. In contrast, the initial cure onset temperature decreased by 4 K after 28 days and by 20 K after 64 days (although the position of the peak maximum did not change significantly over the 70-day period, with only a shift of around 2–3 K being observed). Over the same period of time the ΔH had decreased to around 25% of its initial value, but remained quite constant during the remaining 69 days.

A rescan was performed during each DSC experiment in order to determine the dry T_g . The value for MY721 cured with bis(acetanilido)-tris(acetato)dicuprate(II) was initially 128 °C and displayed an initial drop of 23 K during the first day of storage, but thereafter remained practically constant during the remaining 69-day period (the last T_g recorded was 98 °C). It should be borne in mind that this T_g represents a single scan in the DSC instrument and is not representative of a cure schedule optimised for use at elevated temperatures.

Investigating the thermal dissociation behaviour of the complex

We recognize that the use of thermogravimetry (TG) to determine the dissociation of a complex within an epoxy formulation should be treated with caution as the measurements may not represent the behaviour of the complex within an epoxy matrix. The data from the present TG experiments are presented in Table 3: bis-(acetanilido)-tris(acetato)-dicuprate(II) appeared to degrade before reaching a melting point (>230 °C). The dynamic TG data obtained showed a dissociation pattern over a large temperature range (160–1000 °C) with the initial mass loss (45%) occurring at 210 °C (24% min⁻¹). The complex was apparently stable below 160 °C with no drop in mass, indicating the absence of residual solvent in the sample. Using TG and differential thermal analysis, anthranilamide has been found¹⁰ to be thermally stable in the range 20–140 °C with pyrolytic decomposition commencing at 148 °C and total elimination of the sample occurring by 420 °C.

However, TG is only semi-quantitative, due to the lack of a coupled detection method, such as mass spectrometry, gas chromatography or infrared spectroscopy, to observe which species are being released at the specified temperature. Consequently, at an early stage it was decided to use a combination of both infrared spectroscopy and thermal methods in order to determine the dissociation temperatures for the ligands.

Table 3 TG analysis of bis(acetanilido)-tris(acetato)dicuprate(II) performed under flowing nitrogen at 10 K min⁻¹

Temperature (°C) for a given mass loss (%)										
5%	10%	15%	20%	30%	40%	50%	60%	80%	100%	
381	418	453	481	519	652	710	732	780	N/A	

^a N.B. while single temperatures are quoted this indicates the approximate temperature at which the mass loss is recorded. It should not be inferred that the precision of the measurement is ± 1 K. ^b N/A The complex did not achieve total mass loss during the course of the experiment and an approximate char yield of 20% at 1000 °C was recorded.

In a separate experiment, the complex was heated from room temperature to 150 °C and an FT-IR spectrum taken at 10 K intervals (Fig. 4). Additional information was provided by subjecting the spectral data to principal components analysis (PCA), a multivariate analysis technique,¹⁷ which utilises all the data and uses a holistic approach to determine similar and dissimilar spectra. The extraction of the principal components (PCs), which account for the variance in data, enables the particular analysis to be simplified, but makes no suppositions about the chemical meaning of the data. This technique has been shown¹⁹ to yield useful information in the correlation of infrared spectra of cyanate ester/bismaleimide blends with thermo-mechanical properties and has also been employed⁹ to probe the mechanism by which our previous complexes have undergone dissociation.

PCA was performed on the spectral data and it was found that three PCs account for 99.9% of the variation in the data (Fig. 5). A plot of PC1 (accounting for 87.1%) vs. PC2 (accounting for 7.0%) shows regular incremental changes in the data until ca. 130 °C at which point there is a large change in the plot, indicating that a significant change in the complex is occurring at this point.

Most of the spectral changes observed during the experiment occur in regions associated with both amino and amido groups (3100–3500 cm⁻¹ and 1550–1690 cm⁻¹). The main band changes, from the regression coefficient with temperature, are reductions at 3500, 3460, 3378, 1662, 1621, 1581, 1541 and 1267 cm⁻¹. The overall reduction in the intensity of the amino and amido (3100–3500 cm⁻¹) peaks upon heating is consistent with the ligands undergoing dissociation and volatilisation. To simulate the action of the complex within an epoxy formulation, a second series of spectroscopic experiments was performed using near infrared (NIR) spectroscopy on an epoxy formulation containing the complex and this is discussed later.

Kinetic analysis of the thermal polymerisation behaviour of the epoxy/curing agent formulation during ambient storage

We have previously examined the kinetics of both polymerisation and degradation processes involved with polycyanurates directly from differential equations.^{20,21} In this approach, the polymer is assumed to consist of a number of reactive species, reacting independently of each other to form a single product by simple Arrhenius kinetics with activation energies and orders of reactions of $A_1, E_1, n_1, A_2, E_2, n_2$, etc.

We can thus write the kinetic equation for the i th process as:

$$k_i = A_i e^{\frac{-E_i}{RT}} \quad (1)$$

where k_i is the rate constant at absolute temperature T and R is the universal gas constant.

The rate of reaction at temperature T is then:

$$\frac{d(\text{reactant}_i)}{dt} = k_i [\text{reactant}_i]^{n_i} \quad (2)$$

Differentiating eqn. (1) with respect to temperature gives:

$$\frac{dk_i}{dT} = \frac{E_i}{RT^2} A_i e^{\frac{-E_i}{RT}} = \frac{E_i}{RT^2} \cdot k_i \quad (3)$$

Fig. 4 Individual absorption spectra (showing selected regions) for bis(acetanilido)-tris(acetato)docuprate(II) acquired at different temperatures.

and, if we plot extent of reaction against temperature, we can use the relationship $\frac{dT}{dt} = 1$ (*i.e.* assuming a linear heating rate in the DSC) to solve eqns. (2) and (3) simultaneously for any number of concurrent processes, using numerical methods.

The formulation containing MY721 and bis(acetanilido)-tris(acetato)docuprate(II) was analyzed using DSC at a variety of heating rates and each data set was therefore treated individually to obtain the best fits to the data with the minimum number of equations, using an arbitrary linear baseline, which is reasonable in this case, since we see little evidence of baseline drift in the experimental data. The results are given in Table 4 and an example of the best fits to the DSC raw data is shown in Fig. 6.

In practice, the minimum number of processes required to fit the DSC data turned out to be four and the kinetic analysis allows these four processes to be compared with polymerizations of other epoxy formulations (Table 5). From a

comparison of the Arrhenius parameters in Table 5, it is immediately noticeable that the figures for the first process (a near second order process, with mean activation energy 370 kJ mol^{-1}) are unusually high for a typical amine-epoxy cure, suggesting that this initial step could incorporate both the dissociation of the coordinated ligand (*e.g.* the primary amido nitrogen) and the amide-epoxy co-reaction. For instance, a study²² of DER332 (a bisphenol diglycidyl ether) cured with dicyandiamide (cyanoguanidine or DICY) yielded a near first order process with an activation energy of 101 kJ mol^{-1} . Admittedly, this is a complex cure process as the DICY molecule ($\text{C}_2\text{H}_4\text{N}_4$) contains amino, amido and cyano groups and the high activation energy results partly from the requirement for the material to melt ($\text{mp} > 150^\circ\text{C}$) prior to reaction. This is analogous to the need to effect thermal dissociation of the complex before full cure can take place, again resulting in high activation energies.

Fig. 5 PCA for bis(acetanilido)-tris(acetato)docuprate(II) showing (anticlockwise, from bottom left) the two largest PCs, the third PC, the overall regression coefficient for temperature, and a plot of PC2 against PC1 showing the discontinuity at 130 °C.

Table 4 Arrhenius kinetic parameters for the thermal polymerization of an unaged MY721/[Cu₂(C₇H₈N₂O)₂(CH₃CO₂)₃] formulation (at *t* = zero days)

Parameter	DSC heating rate/K min ⁻¹					Mean value	Standard deviation
<i>A</i> ₁	5	10	15	20		9.05 × 10 ⁴⁶	1.75 × 10 ⁴⁷
<i>E</i> ₁	3.53 × 10 ⁴⁷	2.29 × 10 ⁴⁵	2.47 × 10 ⁴³	6.56 × 10 ⁴⁵		370	10
<i>n</i> ₁	1.70	1.45	1.43	1.49		1.52	0.12
<i>A</i> ₂	3.88 × 10 ¹⁸	6.83 × 10 ¹⁵	7.81 × 10 ¹⁷	1.68 × 10 ¹⁹		5.37 × 10 ¹⁸	7.80 × 10 ¹⁸
<i>E</i> ₂	150	137	155	168		153	13
<i>n</i> ₂	3.40	1.62	1.40	1.56		1.99	0.94
<i>A</i> ₃	5.22 × 10 ²⁵	4.92 × 10 ²⁷	3.49 × 10 ¹⁴	4.43 × 10 ¹⁸		1.24 × 10 ²⁷	2.45 × 10 ²⁷
<i>E</i> ₃	223	242	138	174		194	47
<i>n</i> ₃	1.70	2.53	1.19	1.54		1.74	0.57
<i>A</i> ₄	1.11 × 10 ⁹	4.10 × 10 ⁵	1.11 × 10 ⁵	3.65 × 10 ³		2.78 × 10 ⁸	5.55 × 10 ⁸
<i>E</i> ₄	100	71	68	57		74	18
<i>n</i> ₄	0.85	0.89	0.60	0.40		0.69	0.23

^a *A*_{*i*} Pre-exponential factor for the *i*th process (s⁻¹). ^b *E*_{*i*} Activation energy for the *i*th process (kJ mol⁻¹). ^c *n*_{*i*} Reaction order for the *i*th process.

In their study of the kinetics of polymerization of RTM6 (a polyfunctional epoxy resin comprising two aromatic amines), Partridge *et al.* reported²³ that in order to fit their isothermal DSC data, it was necessary to use a modified kinetic model to account for both the early (kinetically controlled) and later (diffusion controlled) stages of reaction. It is striking that the activation energy for the later stages of the RTM6 cure mechanism has both an activation energy (137 kJ mol⁻¹) and pre-exponential (collision) factor (6.487 × 10¹⁸ s⁻¹) that agree well with the parameters for the second process in the present study (153 kJ mol⁻¹, 5.37 × 10¹⁸ s⁻¹), implying that a similar mechanism might be responsible.

The Arrhenius parameters for the third (near second order) process (mean activation energy 194 kJ mol⁻¹) are also unusually high and imply dissociation of a coordinated ligand (*e.g.* the primary aromatic amino nitrogen) followed by amine-epoxy co-reaction. Finally, the highest temperature, near first order, process (*E*₄ = 74 kJ mol⁻¹, *A*₄ = 2.78 × 10⁸ s⁻¹) has parameters that are consistent with the figures recorded for a BF₃-MEA-catalysed polyetherification.²⁴

However, beyond inferring similarities on the basis of the magnitude of the parameters, it does not give a direct indication of the nature of the processes involved. Therefore, a further study of the polymerization process involving

Fig. 6 Plots of derived rate parameters and DSC data *versus* temperature (K) for an unaged ($t = \text{zero days}$) MY721/[Cu₂(C₇H₈N₂O)₂(CH₃CO₂[−])₃] blend at different heating rates (clockwise from top left: 5 K min^{−1}, 10 K min^{−1}, 15 K min^{−1}, 20 K min^{−1}).

Table 5 Comparison of activation energy for the thermal polymerization of an MY721/[Cu₂(C₇H₈N₂O)₂(CH₃CO₂[−])₃] formulation (at $t = \text{zero days}$) with other epoxy resin systems

Epoxy resin system	$E_i/\text{kJ mol}^{-1}$	A_i/s^{-1}	Reference
MY721/[Cu ₂ (C ₇ H ₈ N ₂ O) ₂ (CH ₃ CO ₂ [−]) ₃]	$E_1 = 370$ $E_2 = 153$ $E_3 = 194$ $E_4 = 74$	$A_1 = 9.15 \times 10^{46}$ $A_2 = 5.37 \times 10^{18}$ $A_3 = 1.24 \times 10^{27}$ $A_4 = 2.78 \times 10^8$	— — — —
MY720	172	—	25
MY720/DDS (100/100 pbw)	73	4×10^4	24
MY721/DDS (100/27 pbw)	75	—	26
RTM6	137 ^a	6.487×10^{18b}	22
DER332/DICY (1.0/0.9 equiv.) ^c	101	3.96×10^{9d}	22

^a Activation energy for the later, diffusion-controlled cure process(es) (kJ mol^{−1}). ^b Pre-exponential factor for the later, diffusion-controlled cure process(es) (s^{−1}). ^c DICY particle size <125 μm. ^d Reaction order, $n = 0.7\text{--}1.4$. ^e E_i Activation energy for the i th process (kJ mol^{−1}). ^f A_i Pre-exponential factor for the i th polymerization process (s^{−1}).

thermal NIR spectroscopy was carried out to verify the curing mechanism.

Spectroscopic examination of the cure mechanism of the epoxy/curing agent formulation

Variable temperature NIR spectroscopy was used to investigate the cure mechanism involving the complex, [Cu₂(C₇H₈N₂O)₂(CH₃CO₂[−])₃], and MY721 epoxy. In preparation for the experiment, individual NIR spectra were acquired for MY721, [Cu₂(C₇H₈N₂O)₂(CH₃CO₂[−])₃] and the MY721/[Cu₂(C₇H₈N₂O)₂(CH₃CO₂[−])₃] blend (Fig. 7), from which the correspondence in signals is reasonably clear. On the basis of these assignments, a scanning experiment was performed during which individual spectra were acquired initially at 60 °C and thereafter at 2.5 hourly intervals (*i.e.* 15 K increments, equating to an instrumental heating rate of 0.1 K min^{−1}) until 150 °C, followed by a dwell period of an hour. The $t = \text{zero}$ spectrum is presented at the top of Fig. 8 and spectra representing the time course are depicted descending. There are distinct changes in the spectral region

of 5500–6000 cm^{−1}: the bands associated with the first overtone of the terminal methylene and the fundamental stretching vibration of the epoxide are seen to diminish during cure. (The aromatic CH stretching first overtone bands are also observed in this region near 5980 cm^{−1}). Perhaps more notably, there is a corresponding decrease in a complex series of bands at *ca.* 5000 cm^{−1} corresponding to the amine combination bands (N–H asymmetric stretch and deformation); the prominent band at 4600 cm^{−1} also undergoes significant reduction during this period.

Examination of the thermal NIR spectral data also provided kinetic information for the process, although these are not directly comparable with the thermal analyses due to the disparity in heating rates (the spectroscopy experiments were conducted at a heating rate of 0.1 K minute^{−1} between glass microscope cover slips, whilst the slowest of the DSC experiments was conducted in sealed aluminium pans at 5 K minute^{−1}), there are obvious similarities. A comparison of the NIR transmission spectra of the pure MY721 and the cured mixture (Fig. 8) allows one to differentiate between the bands belonging to the epoxy and those arising from the

Fig. 7 Plots of near infrared transmission spectra of MY721 (green), $[\text{Cu}_2(\text{C}_7\text{H}_8\text{N}_2\text{O})_2(\text{CH}_3\text{CO}_2^-)_3]$ (blue), and MY721/ $[\text{Cu}_2(\text{C}_7\text{H}_8\text{N}_2\text{O})_2(\text{CH}_3\text{CO}_2^-)_3]$ blend (red).

incorporation of the curing agent (*i.e.* 6748, 5038, 4993 and 4947 cm^{-1}). In each case, integration of the named band was normalised to the invariant aromatic combination band observed near 4620 cm^{-1} .

It appears that different ‘populations’ are present in the spectral kinetic data: due to the epoxy and the curing agent (Fig. 9). Allowing for the fact that the oxirane intensity is presumably slightly affected by the large viscosity changes experienced during this period, the two epoxy bands appear to undergo little change until the temperature just exceeds 100 °C; the bands belonging to the curing agent behave very differently. At this stage the precise nature of the assignments is not clear from the spectra, but work is currently planned

with model compounds to investigate the dissociation and curing mechanism.

Conclusions

A copper(II) complex, containing anthranilamide ligands, has been shown to display some measure of latent behaviour over a prolonged period of storage when formulated within a commercial epoxy resin. The storage stability of the complexes is slightly poorer than 2-aminobenzylamine (2-ABA) analogues and this is attributed to the lower degree of ligand complexation (*i.e.* the presence of free amido nitrogens is still able to initiate some polymerisation at ambient temperatures).

Fig. 8 Plots of near infrared transmission spectra of MY721/[Cu₂(C₇H₈N₂O)₂(CH₃CO₂⁻)₃] blend at time zero (top spectrum). Other spectra acquired at 2.5 hourly intervals (corresponding to 15 K) starting at 60 °C and dwelling at 150 °C.

Fig. 9 Plots of selected (named) NIR bands within the MY721/[Cu₂(C₇H₈N₂O)₂(CH₃CO₂⁻)₃] blend as a function of time and temperature, normalised to the aromatic combination band at 4620 cm⁻¹.

Despite this observation, the latent storage behaviour is still impressive and the thermal dissociation of the free ligands, being less volatile than 2-ABA, no longer cause voids within the curing sample. The polymerisation of MY721 with the curing agent yields a polymer with a dry T_g of 128 °C. Kinetic analysis of the thermal polymerization of an MY721/[Cu₂(C₇H₈N₂O)₂(CH₃CO₂⁻)₃] formulation showed that four

processes were sufficient to model the behaviour and the first (*ca.* second order) process has an unusually high activation energy (*ca.* 370 kJ mol⁻¹) suggesting both ligand dissociation and epoxy-amine cure. The parameters for the second process agree well with the later stages of the cure of RTM6, a commercial epoxy used for resin transfer moulding. The third (*ca.* second order) process also has a high activation energy

(ca. 194 kJ mol⁻¹) and may also involve a second thermal dissociation step, whereas the final step appears to represent polyetherification. Work continues to examine the cure mechanism using model compounds.

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