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Metals and coordination compounds as modifiers for epoxy resins

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Contents

Abstract

This review concentrates on the use of metals in the formulation of epoxy resin systems and the effect that this has on the physical and mechanical properties of the polymer system. Epoxy resins are one of the most important higher performance polymer systems in use today, ranging from simple two-part adhesives and sports equipment to high-tech applications such as formula one racing cars and the aerospace industry. Epoxy resins are capable of undergoing homopolymerisation, although this process generally yields products with inadequate properties for high-tech applications. Consequently, in many cases catalysts, additives and co-curing-agents are formulated with the epoxy resin to significantly increase the storage stability, decrease the cure time and improve the final properties. The use of metals to formulate resin systems with excellent storage stability is discussed, along with the use of coordination compounds to improve cured resin properties such as fracture toughness, thermal stability and water absorption, etc. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Metals; Coordination complexes; Epoxy resins; Modifiers; Additives; Resin properties

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1. Introduction

The market for thermoset polymers is substantially smaller than the demand for thermoplastics, e.g. in 1993 the total consumption of thermoplastics in Western Europe was 25 214 072 tonnes, compared with 5 026 152 tonnes of thermosets [1]. Despite this, epoxy resins still form a substantial market. In 1991 the total world consumption of epoxy resins was reportedly 516 000 tonnes [2] with the USA, Europe and Japan taking the largest shares. In general 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.

In order to convert epoxy resins from liquid or semi-solid monomers into hard, infusible thermoset networks it is necessary to use cross-linking agents. These cross-linkers, 'hardeners' or curing agents as they are variously known, promote cross-linking, or curing, of the monomer or prepolymer (depending on the degree of polymerisation which already exists). Epoxy resins, once cured, are thermoset polymers and tend to be both stiff and brittle and require some degree of modification (e.g. by the incorporation of elastomers or thermoplastics) to achieve acceptable physical properties in the processed resin. This might also entail the incorporation of non-reactive modifiers such as fillers and fire retardants [3].

To date, many materials have been used as fillers in epoxy compounds and these are generally a means of modifying the properties and characteristics of the epoxy resin, but also more importantly as a means of reducing the cost. For example, particulate fillers are very common and have included metals such as aluminium [4] and silver [5], glass micro-balloons [6] or silica [7]. However, these are relatively crude modifications to an epoxy system which may not only effect an increase in viscosity (and perhaps have important processing implications), but also lead to an increase in resin density and hence weight. While acetylacetonate (acac — see Appendix A for abbreviations) based complexes will be discussed in detail later, it is worth noting that Lin et al. [8] have reported a more subtle form of epoxy modification. The addition of metal–acac counter-ions are believed to interact with the hydroxyl groups of the BADGE oligomers via hydrogen bonding, thus resulting in an increase in the bulk viscosity of the BADGE resin (see Appendix B for epoxy structures). They observed that the increase in viscosity of the BADGE resin only occurred with the $Cr(acac)_3$ and not the $Co(acac)_3$ complex, and postulated that this was due to the higher positive charge density of the Co^{3+}, drawing the acac ligands closer towards the metal.

Aside from this rather passive employment, since the 1970s transition metal complexes have also been added to catalyse the reaction between curing agents and epoxy resins. A cursory glance at the periodic table reveals the number of different groups of metals that have potential as modifiers in the formulation epoxy resin systems. Of course, some of these metals (e.g. cadmium, mercury or lead) may be unacceptable in an industrial context on toxicological grounds or difficulties associated with handling and will not be covered in this review. Again, it should be borne in mind that the latter category might become acceptable in some, more exotic applications where the high end-value or stringent performance requirements may reduce the importance of reagent cost in materials selection criteria. Extensive work has been carried out, over the last thirty years, into the use of metals and their salts in the formulation of epoxy resin systems and this has included the use of organo-transition metal complexes as catalysts for epoxy resins when co-cured with amines, anhydrides, and phenolics. Organo-transition metal complexes have also been added to improve physical properties such as adhesion, flexural strength, fracture toughness, water adsorption and heat resistance and this will be covered later. While much of the published work concentrates on the benefits imparted by the incorporation of metal salts in epoxy resin and polymer networks it should be mentioned that there may also be drawbacks associated with the use of metal salts. For example, their presence can inflate the density of the resin (if used in sufficient quantity) or adversely affect the conductivity of the cured resin and therefore render them of little use in certain electronic applications. This review will concentrate largely on the use of transition metal salts (and their complexes) to modify the chemical, physical and mechanical properties of epoxy resins for technological application.

2. Epoxy resin cure chemistry

Structurally, epoxy resins contain at least two epoxy (or oxirane) groups within their structure; a planar, three-membered ring comprising two carbon atoms and one oxygen atom. There is substantial ring strain in the epoxy group, due to angular distortion from the tetrahedral carbon angle and the electronegativity of the oxygen atom. Consequently, the group is more reactive than non-cyclic ethers and those reactions involving either electrophilic attack (on the oxygen atom) or nucleophilic attack (on the more highly substituted carbon in the ring) are the most important routes for the synthesis and cure of epoxy resins. This enhanced reactivity towards a variety of reagents makes the epoxy very versatile in its cure chemistry. A wide variety of compounds will initiate the opening of the oxirane ring, leading to polymerisation and a full review is outside of the scope of this paper. Instead, the reader is directed to the following for a fuller discussion of this aspect [3,9–12]. This wide variety naturally includes metal coordination complexes and specific examples of these are given below.

3. Coordination compounds containing amino ligands

Curing agents based on polyamines are among the most commonly used in epoxy resin systems and make up around 22% of the commercial reagents that are used [13]. Both primary and secondary amines may be used to initiate cure in epoxy systems and are generally employed in stoichiometric amounts (as the amine becomes incorporated within the epoxy polymer network). Tertiary amines also find applications as catalysts, rather than curing agents, and are used in somewhat smaller quantities to initiate the ring-opening reaction of the oxirane group, prior to polymerisation taking place. This has serious implications for the application to which the cured resin is put, since the type of polymer networks formed via the two polymerisation routes differ in a number of ways (e.g. cross-link density). Owing to the differences in the electronic environments of the electrons on the nitrogen atoms, aliphatic and aromatic amines cure epoxy resins at different rates (the delocalisation of the lone pair into the π cloud of the phenyl group reduces the reactivity of the amine significantly). This determines the conditions required to effect cure (e.g. a higher temperature and longer cure time is often required to achieve optimum properties).

3.1. Aliphatic amino ligands

The principal use of metal–amine complexes has been to introduce the metal into the epoxy resin network, rather than e.g. utilising the complexes as latent accelerators for the epoxy resin. The largest single body of work in this area appears to have been carried out by Kurnoskin [14–25]. He has focused on the use of polyamine-based complexes as a method of introducing metal ions into an epoxy resin structure (BADGE in this case) to enhance the thermal, physical and mechanical properties of the cured resin (Table 1).

From these studies, Kurnoskin reported that the gel and cure times were dependent on the nature of the chelate. From these data, the following reactivity series were formulated. In general, in terms of their reactivity towards epoxy polymerisation, the metals were ranked: $Mn^{4+} > Ni^{2+} > Fe^{3+} > Zn^{2+} > Cu^{2+} > Co^{2+} \sim Cd^{2}$. Of the aliphatic polyamines studied, the following order was observed: trien > cydien > dien > en. While the remaining ligands fell into the following series:

$$\begin{aligned}&CH{=}N(CH_2)C_6H_4COO^- > H_2NC_6H_4COO^-\\&\quad > CH_3COO^- > CH_2{=}C(CH_3)COO^-\\&\quad > C_6H_4COO^- > HOC_6H_4COO^-\end{aligned}$$

Kurnoskin [16–22] has also correlated the effects of changing the metal, the ligand and the counter-ion on the neat resin characteristics. For example, the moisture absorption of the cured resin is an important parameter in the case of epoxy resins as the T_g of the cured resin may be dramatically reduced by the presence of sorbed moisture. Wright [26,27] correlated water absorption and T_g data for a number of commercial epoxy resins and found that the addition of 1 wt% water could reduce the T_g of the resin by up to 20 K. Kurnoskin reported [23] that for the polyamine ligands the lowest moisture absorption was recorded for cydien and that the trend cydien < trien < dien < en was observed where metal and counter-ion were held equal (Table 1). Similarly, the greatest mechanical strength was obtained when 1 mol of BADGE was cured with 0.14 mol of hardener.

3.2. Aromatic and heterocyclic amino ligands

Kurnoskin [25] has also examined the use of aromatic and heterocyclic amine complexes as curing agents for epoxy resins and found that, for a given loading of curing agent, the gel time was related to the aromatic ring substitution/catenation of the diamine. For the simple diamines he reported that the gel times (at 120 °C) fell into the order (*o*-phenylene diamine > *m*-phenylene diamine > *p*-phenylene diamine). However, when using zinc as the metal centre and acetate as the counter-ion, the corresponding coordination compounds now fell into the series *o*-phenylene diamine > *p*-phenylene diamine > *m*-phenylene diamine.

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. Hamerton et al. [28] have examined the influence of forming copper(II) complexes of common aromatic amines: *o*-phenylene diamine (OPD), *p*-phenylene diamine (PPD), DDM and DDS on the cure chemistry of MY750 (a BADGE system). An analysis of the rheological behaviour of the $[Cu(o\text{-}C_6H_4(NH_2))_2Cl_2]$/MY750 and $[Cu(p\text{-}C_6H_4(NH_2))_2Cl_2]$/MY750 mixtures suggested that the two appeared to undergo different forms of network growth. The inclusion of OPD appeared to favour more branching in the network, while PPD favoured more chain extension prior to cross-linking.

However, in a subsequent study [29] nickel complexes containing OPD ligands, such as $[Ni(o\text{-}C_6H_4(NH_2))_3$-

Cl_2], were difficult to prepare in a highly complexed form. Rather, microanlytical and IR data suggested that a single OPD molecule might become trapped in the lattice as $[Ni(o\text{-}C_6H_4(NH_2))_3Cl_2]_4{\cdot}o\text{-}C_6H_4(NH_2)$, yielding 'free' amine groups (which would initiate cure over a period of storage). 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 counter-ion 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–equatorial positions. Furthermore, a study of the formulation of OPD complexes in commercial epoxy systems demonstrated some shortcomings in their solubility, possibly due to the stability of the complex preventing solvation in non-polar solvents, coupled with the ligands forming a hydrophobic casing around the metal further preventing solvation in polar solvents. As a result, Hamerton et al. [29] examined the effects of substituting 2-aminobenzylamine (2-ABA) for OPD to produce both nickel and copper complexes incorporating chloro or acetato counter-ions (Fig. 1). 2-ABA was chosen in order to retain the latent properties of the OPD, but with improved solubility properties in the bulk epoxy.

Characteristic bands in the infrared spectra at between 3500 and 3000 cm^{-1} (corresponding to NH_2 asymmetric and symmetric stretch), 1650–1590 cm^{-1} (NH_2 deformation), $\delta(NH_2)$ and 1290–1220 cm^{-1} region (C–N stretch) showed that complexation of the amino nitrogen atoms occurred to a high degree (Fig. 2). Magnetic susceptibility data were obtained for four of the complexes: $[Cu(o\text{-}(NH_2)C_6H_4CH_2NH_2)_2(Cl)_2]$ or $[Cu(2\text{-}ABA)_2Cl_2]$ yielded a μ_{eff} value of 1.82 μ_B, whereas $Cu(2\text{-}ABA)_2(ac)_2$ yielded a μ_{eff} value of 1.84 μ_B. Measurements for $Ni(2\text{-}ABA)_3Cl_2$ and $Ni(2\text{-}ABA)_3(ac)_2$ gave values of 2.90 and 3.07 μ_B, respectively. Values for $Cu(2\text{-}ABA)_2Cl_2$ and $Ni(2\text{-}ABA)_3Cl_2$ showed close agreement with the literature values of 1.84 and 2.91 μ_B, respectively [30]. This supports the formation of

Table 1
Properties of metal–amine chelate curing agents (adapted from Refs. [14,15,23])

Curing agent	M.p. (°C)	t_{gel} in BADGE at 95 °C [a] (min)	t_{cure} in BADGE at 120 °C [b] (min)	HDT (°C)	σ_t (MPa)	E_t (MPa)	ε_c (%)	Water absorption (%)	
								20 °C [c]	100 °C [d]
$Fe(trien)(HOC_6H_4COO)_3$	65	205	90	92	63	3.9	1.8	0.02	0.07
$Fe(cydien)(HOC_6H_4COO)_3$	47	428	186	120	74	3.0	2.2	0.01	0.001
$MnO(trien)(HOC_6H_4COO)_2$	117	148	65	110	53	3.1	1.3	0.04	0.03
$Co(dien)(CH{=}N(CH_2)C_6H_4COO)_2$	228	35	15	105	65	3.6	2.3	0.06	0.10
$Co(dien)(HOC_6H_4COO)_2$	153	726	316	115	91	3.2	4.8	0.03	0.14
$Co(trien)(HOC_6H_4COO)_2$	112	451	196	108	79	3.4	3.8	0.05	0.04
$Co(cydien)(HOC_6H_4COO)_2$	90	942	410	100	53	4.0	3.5	0.04	0.01
$Ni(trien)(HOC_6H_4COO)_2$	113	180	80	95	55	4.4	2.1	0.08	0.04
$Ni(cydien)(HOC_6H_4COO)_2$	68	376	160	92	68	4.4	2.7	0.01	0.01
$Cu(en)_2(HOC_6H_4COO)_2$	142	645	280	110	97	3.1	5.0	0.10	0.15
$Cu(dien)(HOC_6H_4COO)_2$	192	555	241	100	89	3.3	5.0	0.11	0.17
$Cu(trien)(HOC_6H_4COO)_2$	139	230	100	130	65	3.1	3.5	0.05	0.08
$Cu(trien)_2(HOC_6H_4COO)_2$	97	45	60	–	–				
$Cu(trien)(CH{=}NHC_6H_4COO)_2$	80	70	31	163	39	3.5	1.3	0.02	0.03
$Cu(trien)(CH_3COO)_2$	55	215	93	102	77	3.4	4.0	0.05	0.11
$Cu(trien)(H_2NC_6H_4COO)_2$	123	213	93	134	88	3.0	2.5	0.05	0.11
$Cu(cydien)(HOC_6H_4COO)_2$	125	492	214	115	90	7.6	5.0	0.01	0.07
$Zn(trien)(HOC_6H_4COO)_2$	117	221	96	130	92	3.7	4.6	0.03	0.07
$Zn(cydien)(HOC_6H_4COO)_2$	35	451	196	130	91	3.4	5.0	0.03	0.09
$Zn(cydien)(C_6H_4COO)_2$	94	433	188	97	87	4.0	2.7	0.03	0.10
$Zn(cydien)(CH_3COO)_2$	<20	410	178	100	77	3.9	2.8	0.02	0.14
$Zn(cydien)(CH_2{=}C(CH_3)COO)_2$	<20	415	180	102	55	4.0	2.1	0.03	0.11
$Cd(en)_2(H_2NC_6H_4COO)_2$	135	1500	650	70	68	3.4	1.8	0.03	0.23
$Cd(dien)(H_2NC_6H_4COO)_2$	113	1200	520	103	96	4.2	3.4	0.01	0.10
$Cd(dien)_2(H_2NC_6H_4COO)_2$	92	200	385	–	–				
$Cd(trien)(H_2NC_6H_4COO)_2$	125	450	196	134	88	3.0	2.5	0.05	0.11
$Cd(cydien)(H_2NC_6H_4COO)_2$	92	525	228	100	100	4.4	5.0	0.03	0.03

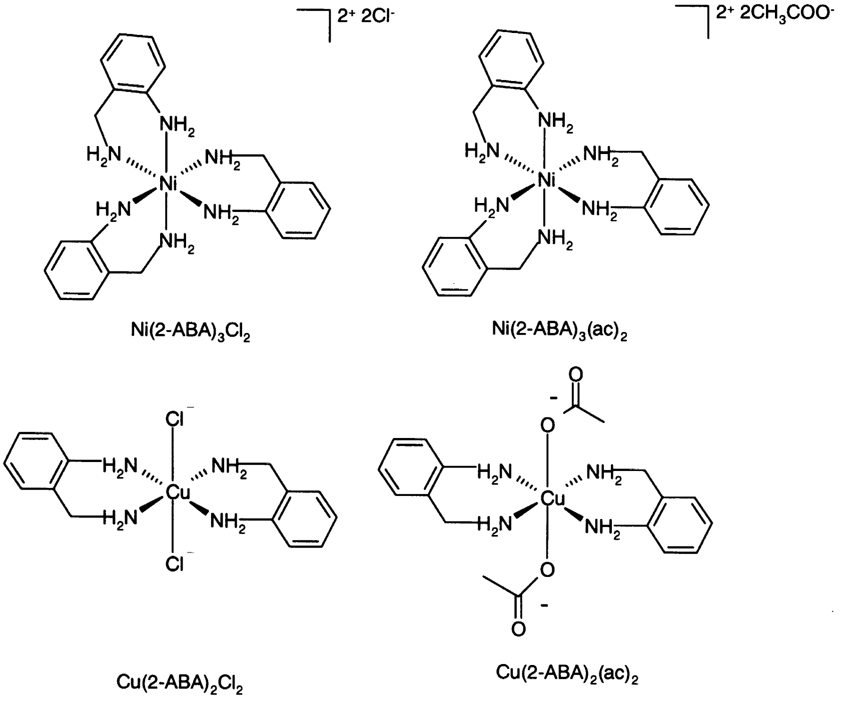
M.p. = melting point.

[a] Accelerated ageing schedule for the epoxy resin.

[b] Typical cure temperature for BADGE systems.

[c] Submerged for 24 h.

[d] Submerged for 30 min.



$Ni(2\text{-}ABA)_3Cl_2$ $Ni(2\text{-}ABA)_3(ac)_2$

$Cu(2\text{-}ABA)_2Cl_2$ $Cu(2\text{-}ABA)_2(ac)_2$

Fig. 1. Proposed structures of selected M(2-ABA)$_m$L$_2$ complexes after Ref. [29] (where M = Ni or Cu, $m = 3$ or 2, L = Cl$^-$ or CH$_3$COO$_2^-$).

discrete complexes rather than associated 'polymeric' (i.e. Cu–Cu interactions) due to simple Cu(II) complexes generally exhibiting magnetic moments in the region of 1.75–2.20 μ_B regardless of symmetry and at normal temperature. The same curing agents were incorporated into two commercial epoxy resins (MY721-a TGDDM system and MY750) and their cure properties and shelf life assessed alongside DDS and DiCy. In general, the 2-ABA based complexes dispersed well within the commercial epoxy systems and displayed good storage stability over a storage period of ca. 14 days, although some advancement of cure was evident over a much longer storage period (67 days).

It is known that the addition of metal compounds to accelerate the cure of epoxy resins does not always have the desired effect, and this has been observed when some amines are the curing agents. Nazarova et al. [31] studied the rates at which amines cured epoxy resins (by observing the gel-point, Table 2) in the presence of M–acac compounds. They observed a reduction in the cure rate as a result and postulated that this reduction in reactivity was due to the formation of dative covalent bonds between the M–acac and the amine, thus hindering the attack of the nitrogen lone pair on the oxirane ring.

Matsuda et al. [32] have reported the use of divalent metal salts of *p*-aminobenzoic acid (*p*-ABAcid) (Fig. 3) as cross-linking agents for BADGE with a diamine such as DDS or 4,4′-methylenediamine (MDA) (and also, incidentally, for polyureas as well).

The authors reported that these compounds were not soluble in BADGE and needed to be dissolved in DMF prior to mixing. Once the M(*p*-ABAcid) was fully mixed, the DMF was removed and the M(*p*-ABAcid) precipitated. The latter can be a problem, due to heterogeneity resulting in uneven curing of the resin. However, this was prevented by heating the BADGE/DMF/M(*p*-ABAcid) solution for an hour at 100 °C thereby enabling the amine groups to react with the epoxy resin and hence increasing their solubility. The incorporation of M(*p*-ABAcid) into the BADGE/MDA resin system was found to reduce the gel time significantly (Table 3).

Overall, the physical properties of the cured epoxy resin appeared to be little affected by the presence of the M(*p*-ABAcid) although the heat deflection temperature (HDT) showed a tendency to decrease with increasing metal content. In the case of the calcium analogue, the impact strength was increased significantly with increased metal content, but at the expense of HDT.

4. Coordination compounds containing acetylacetonate ligands

The introduction of metal salts into epoxy resin systems to improve physical properties has been well documented, with a large body of work involving the use of M–acac complexes to enhance the properties (e.g. electrical, thermal and chemical properties, etc.) of

BADGE and TGDDM resin systems. Consequently, complexes based on oxygen donors have also been widely studied. Markovitz [33] described the use of coordination compounds containing acac ligands as catalysts in the cure of the commercial epoxy ERL 4221 (3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate). He reported that the epoxy formulations, containing the acac complexes, displayed good storage stability and observed little or no change in the viscosity of the system (a good indication of the progress of a network forming reaction) over a period of months at room temperature. The same author [32] also described the use of the same coordination compounds as catalysts in the cure of epoxy resins with phenolic accelerators (a compound added to enhance the rate of the cure reaction). He described that low levels of the coordination compounds (0.025–5 wt% in the epoxy) were sufficient to catalyse the cure. In the absence of a phenolic accelerator, only catalytic levels of the complexes (below 1 wt%) catalysed the polymerisation of ERL 4221 (Appendix B). He also reported that the rate of reaction was increased as the concentration of com-

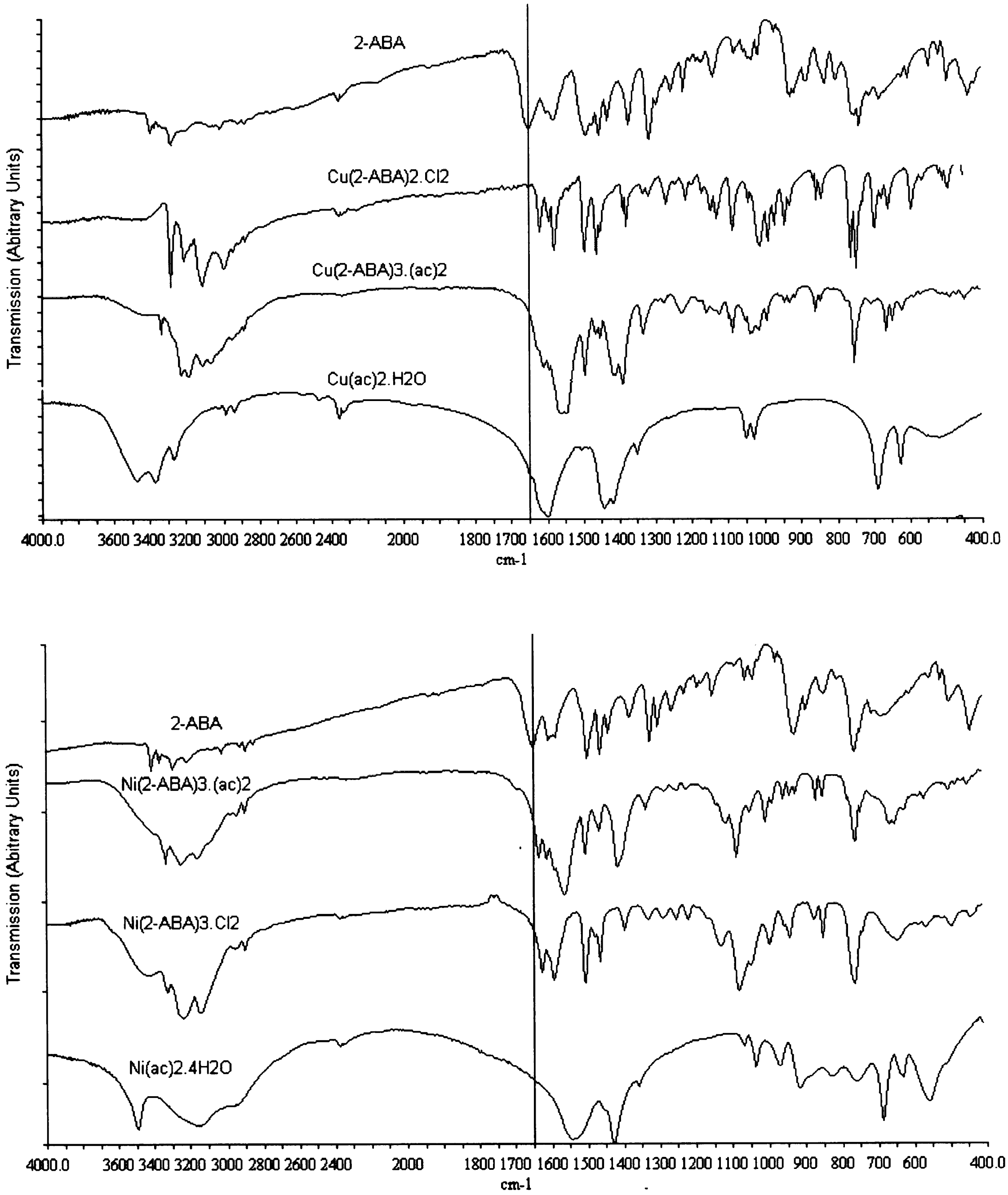


Fig. 2. IR transmission spectra of selected complexes and ligands. The $\delta(NH_2)$ (scissoring) band is indicated with a solid line at 1652 cm^{-1}.

Table 2
Gel times for selected BADGE/amine and M–acac systems

System	Curing agent (phr)	Amine: M–acac (molar ratio)	t_{gel} (min)			
			70 °C	100 °C	120 °C	20 °C
UP-606/2	2.0	–	45	30	20	3720
Fe–(acac)$_3$	2.7	1:1	115	55	22	7800
Fe–(acac)$_3$	5.4	1:2	300	115	65	20160
Fe–(acac)$_3$	8.1	1:3	400	180	120	28800
Co–(acac)$_2$	5.85	1:3	140	50	34	8400
Co–(acac)$_2$	7.8	1:4	190	65	50	12960
Ni–(acac)$_2$	5.85	1:3	160	80	42	12360
Ni–(acac)$_2$	7.8	1:4	215	94	52	19800

UP-606/2 = tris(dimethyl-*p*-aminoethyl) phenol.

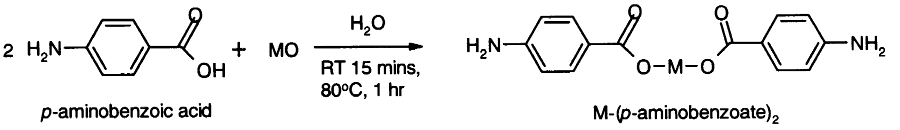


Fig. 3. Formation of coordination compounds with *p*-aminobenzoate ligands and divalent metals (M = Mg or Ca).

Table 3
Effects of M(*p*-ABAcid/MDA) incorporation in BADGE systems (adapted from Ref. [31])

Composition	Molar ratio	Metal content (%)	Gel time [a] (min)	Conversion [b] (%)	HDT (°C)	Impact strength (kg cm cm^{-1})
MDA–BADGE	1:2	–	70	95	153	1.29
Mg(*p*-ABAcid)–MDA–BADGE	1:19:40	0.13	40	97	153	1.20
	1:9:20	0.26	40	93	145	1.30
Ca(*p*-ABAcid)–MDA–BADGE	1:19:40	0.21	33	98	151	0.40
	1:9:20	0.43	30	99	132	1.32

[a] Cured at 80 °C for 16 h and 150 °C for 5 h.
[b] Determined at 80 °C.

plex was decreased (or as the phenolic accelerator concentration was increased).

Frankel [34] also reported the use of chelated coordination complexes containing acac ligands in the acceleration of acid copolymers/polyepoxy resin systems, but limited his study to mainly first row transition metals-particularly manganese, chromium or zinc. He did, however, state that any metal salt of any acetylacetonate might also be employed. The quantity of catalyst used in the blends were typically of the order of 0.025–6.0% by weight of the resin mixture though optimum results were achieved with 0.05–4.0% (Table 4).

Reddy et al. [35,36] found that the incorporation of coordination compounds containing acac ligands affected the storage times of the unmodified epoxy monomer (which was typically around 80 days). For example, addition of the Co(III) analogue (at levels of between 0.5 and 1.5 phr) reduced the storage time to between 70 and 55 days, respectively. The incorporation of coordination compounds containing Ni(II) fared worse with storage times of between 60 and 38 days in the same formulation. However, the Cu(II) analogue produced the most impressive performance by increasing the storage time to between 90 to 83 days, surprisingly little variation with respect to additive content (Table 5). For the purposes of comparison, in their studies, the end of storage life was deemed to be the time at which the viscosity of the formulation exceeded 1500 cP.

Smith [37] carried out an extensive study on 22 candidate latent accelerators, based on coordination compounds containing acac ligands, for solventless epoxy-anhydride resins. The formulations comprised BADGE and 1-methyltetrahydrophthalic anhydride with 0.1% accelerator (the complex). Of those studied, the most encouraging results for storage lifetimes (at 25 °C) were obtained for Cr(III)–acac and Co(III)–acac (both greater than 200 days) (Table 6). Of the remainder both Fe(III)–acac (< 10 days) and U–acac (< 4 days) were particularly ineffective. For the purposes of their study, the lifetime was determined by the time taken for the viscosity to reach 1000 cP.

Table 4
Effect of catalyst on stability of Epon 828 and Epon 828/acrylic systems

Catalyst	Catalyst [a] (wt%)	Tukon hardness 15 min cure at 177 °C	Relative stability [b] (days)				
			0	3	7	14	28
Control	0.0	$\ll 0.1$	1.00	0.60	0.65	0.65	0.60
DMP-30 [c]	1.2	1.2	1.00	0.23	<0.10	Gel	Gel
DMP-30 [c]	0.4	0.8	1.00	0.38	0.27	<0.10	Gel
Pyridine	1.2	1.2	1.00	<0.10	Gel	Gel	Gel
Pyridine	0.4	0.6	1.00	0.10	Gel	Gel	Gel
$Cu(pyridine)_4 \cdot (NO_3)_2$	2.0	1.8	1.00	0.40	0.10	Gel	Gel
$(CH_3)_3NHCl$	1.2	0.8	1.00	0.60	0.22	0.10	<0.10
$NaOCH_3$ [d]	–	–	1.00	0.38	0.10	<0.10	Gel
$Cr(acac)_3$	4.0	1.3	1.00	0.60	0.67	0.65	0.50
$Cr(acac)_3$	1.2	0.9	1.00	0.60	0.67	0.65	0.52
Zn(acac)	4.0	4.7	1.00		0.63	0.17	<0.10
Zn(acac)	1.2	2.1	1.00	0.71	0.64	0.29	0.10
$Mn(acac)_2$	4.0	4.3	1.00	1.00	0.76	0.45	0.26
$Mn(acac)_3$	4.0	30	1.00	1.00	0.90	0.51	0.20

[a] Based on the total weight of a polymer blend of 60 parts acrylic and 40 parts Epon 828.
[b] Stability was measured by extrudability (consistency) test.
[c] DMP-30 is tris(dimethylaminoethyl)phenol.
[d] Formulated as 25% w/v methanol solution.

Colborn et al. [38] studied the solubility of a range of coordination compounds in BADGE/dianhydride resin systems, using $Co(acac)_2$ as a standard for comparison. The latter was found to display acceptable solubility in BADGE and exhibited gel times of 2306 min (at 90 °C) and 25 min (at 120 °C). The series was based on $[Co(acac)_2(A)]$, where A represented both aliphatic and aromatic polyamines (several heterocyclic ligands were also included for comparison). Of the 13 coordination compounds tested, several were deemed to be either poorly (or slightly) soluble and these might cause precipitation problems during longer-term storage. The remaining compounds were found to have acceptable levels of solubility at an addition level of 1 wt% and showed varying degrees of promise. For example, gel times at 90 °C ranged from 73 min for $Co(acac)_2$[1,2-bis(diphenylphosphinoethane] to 1703 min for $Co(acac)_2$(*N*,*N*-di-*tert*-butylethylenediamine) (Table 7). Interestingly, there were some instances where the behaviour at 90 °C was not reflected in the performance at the higher temperature. For example, the BADGE formulation containing $Co(acac)_2$(*N*,*N*-dimethylethylenediamine) gelled after 223 min at 90 °C, placing it towards the middle of the ranking order, but after 8 min at 120 °C (one of the shorter gel times at this cure temperature). This may indicate that a change occurred in the cure mechanism at the higher temperature or that the dissociation of the coordination compound was reached, although this was not addressed within the study.

In their study, Colborn et al. utilised a combination of both aliphatic and aromatic amine ligands and the acac counter-ion to provide a substantial increase in the solubility in epoxy resins over their halogen counterparts (Table 7). The addition of metal compounds to an

Table 5
Cure characteristic of BADGE/anhydride system with $M(acac)_x$ at 40 K min^{-1} (data adapted from Refs. [35,36])

Cure time (min) [a] at 180 °C	Concentrations of $M(acac)_x$ (phr)			
	0.0	0.5	1.0	1.5
Dynamic method (Co)	110–150	90–120	70–110	60–90
Isothermal method (Co)	140	92	75	69
Cobalt (Co^{III})				
Storage stability (days) [b]	80	70	60	55
Gel time at 125 °C (min)	625–630	450	315	230
Gel time at 135 °C (min)	300–305	270	240	200
Gel time at 155 °C (min)	145–155	152	110	100
Gel time at 175 °C (min)	70–75	60	55	50
Nickel (Ni^{II})				
Storage stability (days) [b]	–	60	48	38
Gel time at 125 °C (min)	–	410	290	240
Gel time at 135 °C (min)	–	240	155	122
Gel time at 155 °C (min)	–	110	55	48
Gel time at 175 °C (min)	–	40	25	20
Copper (Cu^{II})				
Storage stability (days) [b]	–	90	85	83
Gel time at 125 °C (min)	–	520	480	450
Gel time at 135 °C (min)	–	290	250	225
Gel time at 155 °C (min)	–	145	115	112
Gel time at 175 °C (min)	–	69	48	40

[a] Time taken for the thermal peak to form.
[b] Time at which sample viscosity exceeds 1500 cP.

Table 6
Gel and lifetime study for BADGE/1-methyltetrahydrophthalic anhydride M–acac system

M–acac (0.1% in resin)	Gel-time (min)		Storage-lifetime (days) [a], 25 °C
	150 °C	175 °C	
Titanium-oxy–acac	35–40	30–35	110
Aluminium–acac	35–40	30–35	95
Cerous–acac [b]	–	50–55	–
Manganese(II)–acac [b]	–	50–65	–
Iron(III)–acac	–	<15	<10
Magnesium–acac [b]	–	50–55	–
Manganese(III)–acac	80–90	40–45	160
Cobalt(II)–acac	50–55	35–40	130
Copper(II)–acac [b]	–	90–100	–
Chromium(III)–acac	40–50	30–40	>200
Nickel–acac	–	45–50	>90
Zinc–acac [b]	–	20–25	50
Cobalt(III)–acac	80–90	25–35	>200
Vanadium(III)–acac	70–80	40–45	>90
Uranyl–acac	<10	<10	<4
Zirconium–acac	50–55	30–35	>90
Thorium–acac [b]	60–65	50–55	–
Strontium–acac [b]	100–110	60–65	–
Sodium–acac	35–40	20–25	>90
Potassium–acac	25–30	15–20	>90
Lead–acac [b]	100–110	70–80	–
Beryllium–acac	100–110	60–65	>90

[a] Indicates the point at which the viscosity has reached 1000 cP.
[b] Indicates a poor solubility ($<50\%$) in resin.

Table 7
Gel times and solubility of coordination compounds containing cobalt in BADGE

	Solubility	Gel time (min)	
		90 °C	120 °C
$Co(acac)_2$	Good	2306	25
$Co(acac)_2$(*N*,*N*′-di-*tert*-butylethylenediamine)	Good	1703	42
$Co(acac)_2$(1,2-diaminopropane)	Poor	1172	35
$Co(acac)_2$(1,2-diaminobenzene)	Slight	626	21
$Co(acac)_2$(2-amino-6-methylpyridine)	Good	494	24
$Co(acac)_2$(2,2′-dipyridine)	Good	242	25
$Co(acac)_2$(*N*,*N*′-dimethylethylenediamine)	Good	223	8
$Co(acac)_2$(1,3-dimethypropanediamine)	Slight	219	12
$Co(acac)_2$(2-aminopyridine)	Good	179	50
$Co(acac)_2$(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine	Good	157	7
$Co(acac)_2$(*N*,*N*,*N*′,*N*′-tetraethylethylenediamine)	Good	111	9
$Co(acac)_2$[1,2-bis(diphenylphosphinoethane)]	Good	73	5
$CoBr_2$(triphenylphosphene)$_2$	Poor	–	6.5
$Co(acac)_2$(1,3-diaminopropane)	Slight	–	11

epoxy system was also found to promote an increase in the rate at which the curing agents, such as anhydrides, react with the strained oxirane ring. This is the typical role that an accelerator performs. In order to formulate a curative system with a long shelf life (to enable storage 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. Similarly, if a resin system requires the action of an accelerator compound to improve the cure profile, then this also needs to have a low reactivity at the storage temperature. Typically, the $Co(acac)_2$ compounds have the advantage over conventional curing agents for thermosetting resin systems in that they have latent cure properties, whereas a range of conventional accelerators may show only a limited degree of latency in epoxy systems.

Colborn et al. [38] also studied the changes on the thermo-mechanical properties recorded for the cured BADGE epoxy resin (Table 8) when using the latent $Co(acac)_3$ complexes mentioned previously. They found that the heat deflection temperature (HDT) for the $Co(acac)_3$ was quite low (176 °C) in comparison to a conventional triphenylphosphine catalyst (320 °C), which was considered to be the target catalyst. The HDT of the base complex was thought to increase when amino ligands formed dative covalent bonds to the metal centre. Thermal ageing studies carried out on cured resins containing 2 wt% $Co(acac)_3$ (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) as a catalyst showed that there was very little loss in flexural modulus or flexural strength of the cured resin after 200 h exposure at 299 °C.

Lin et al. [39] reported that the incorporation of Cr(III)–acac or Co(III)–acac into BADGE/DETA and TGDDM/DDS resin systems improved the toughness

Table 8
Heat deflection temperatures (°C) for BADGE/ADD system[a]

Conventional catalysts	
Triphenylphosphine	320
2-Methylimidazole	262 ± 13
Adogen 464 (tetraalkylammonium salt)	226 ± 16
Tetrabutylphosphonium acetate	309 ± 26
2-Amino-6-methylpyridine	303 ± 15
4-*tert*-Butylpyridine	263 ± 60
Cobalt catalysts	
$Co(acac)_2$	176 ± 13
$Co(acac)_2$(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)	247 ± 38
$Co(acac)_2$(*N*,*N*,*N*′,*N*′-tetraethylethylenediamine)	244
$Co(acac)_2$(*N*,*N*′-di-*tert*-butylethylenediamine)	202 ± 11
$Co(acac)_2$(*N*,*N*′-di-*n*-butylethylenediamine)	267 ± 48
$Co(acac)_2$(dipentylamine)$_2$	263 ± 26
$Co(acac)_2$(*N*,*N*,*N*′,*N*′-tetraethylethylenediamine)[b]	245

[a] Post-cured at 180 °C for 6 h before testing.
[b] Resin mix of 0.8 ADD: 1.0 BADGE (all others are 1:1).

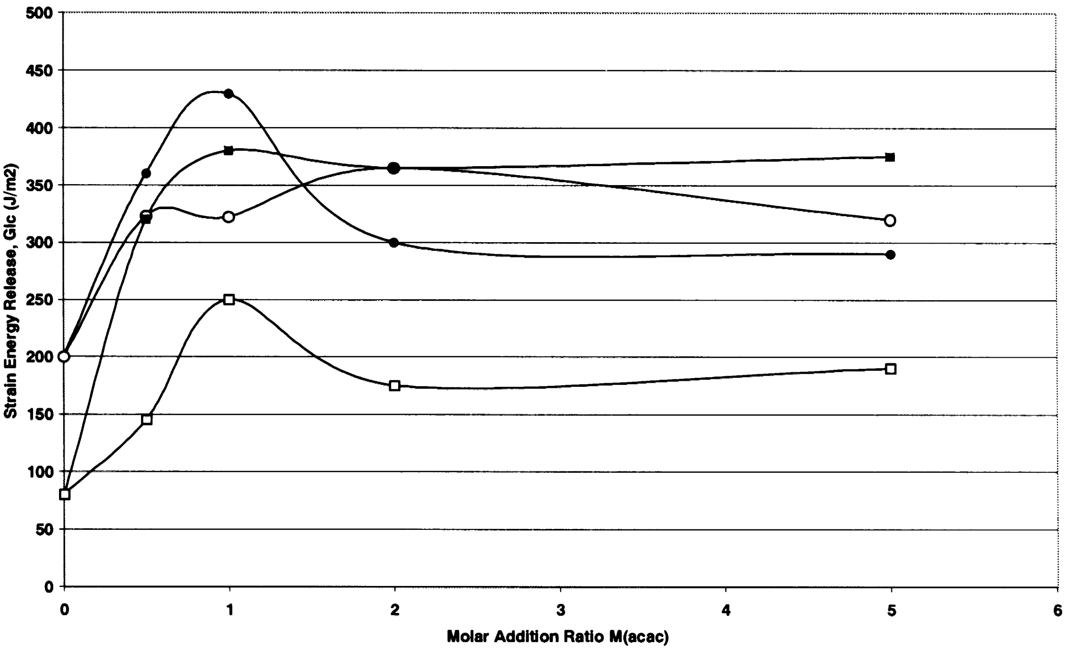


Fig. 4. Effect of M(acac)$_3$ on epoxy resin fracture toughness: ●, BADGE/DETA + Cr(acac)$_3$; ○, BADGE/DETA + Co(acac)$_3$; ■, TGDDM/DDS + Cr(acac)$_3$; and □, TGDDM/DDS + Co(acac)$_3$.

Table 9
Fracture data for cured neat resin and laminates

Formulation	G_{IC} of neat resin (J m^{-2})	G_{IC} of laminates (J m^{-2})	ΔG_{IC} (J m^{-2})	Plastic zone diameter (μm)
TGDDM/DDS/BF$_3$MEA	55 ± 5	270 ± 7	215 ± 12	6.3
TGDDM/DDS/C$_{11}$Z	128 ± 44	392 ± 22	264 ± 36	9.6
TGDDM/DDS/C$_{11}$Z/Cr(acac)$_3$	369 ± 17	560 ± 22	191 ± 39	16.3

of the overall system and it was found that the Cr(acac)$_3$ had a greater toughening effect than the Co(acac)$_3$ complex for both systems (Fig. 4).

The same group has also examined [40] the effects of M(acac)$_3$ additives, such as Cr(acac)$_3$, in combination with imidazoles such as 2-unidecyl-imidazole (C$_{11}$Z), to replace conventional BF$_3$MEA accelerators due to the occurrence of unexpected chemical reactions between Cr(acac)$_3$ and DDS/BF$_3$MEA. This led, in turn, to significant reductions in the toughening effect conferred by the Cr(acac)$_3$ on the cured resin. In this study, the fracture toughness of TGDDM/DDS resin systems increased 6–7 fold over the typical TGDDM/DDS/BF$_3$MEA epoxy system when a TGDDM/DDS/(C$_{11}$Z)/Cr(acac)$_3$ system was used, but that only a two-fold increase was obtained when the TGDDM/DDS/(C$_{11}$Z) system was used. Unfortunately, the impressive modification in the mechanical properties of TGDDM/DDS/(C$_{11}$Z)/Cr(acac)$_3$ was not realised in the formation of the corresponding laminate (which exhibited a two-fold increase in fracture toughness over the unmodified resin) (Table 9).

5. Coordination compounds containing acrylate ligands

The introduction of metal salts into the resin systems has been attempted both before and after the addition of the curing agent. For example, Srivastava and Anand [41–44] have reported the use of a series of coordination compounds containing acrylate ligands in the production of BADGE resins and their effects on the EEW, electrical properties, thermal and chemical resistance. In their studies, the coordination compound was pre-reacted with bisphenol A and an excess of epichlorohydrin (1:10 molar ratio) to yield polymers bearing complexes bound into the backbones of the resulting oligomers. There were some small increases in specific viscosity observed for the modified oligomers over the base resin (Table 10). Of potentially greater concern, however, was the substantial increase in chlorine content associated with the introduction of the metal species in this manner. The presence of residual halide species (arising from the preparative route) does preclude the use of BADGE-based resins in many microelectronics applications and so an increase in the chlorine content (presumably as chloride) would be undesirable. Indeed, while a figure of 1.50×10^{-13} $\Omega^{-1}\,\mathrm{cm}^{-1}$ was recorded for the conductivity of BADGE, the modified resins yielded substantially higher conductivities. Values ranged from 8.75×10^{-13}–3.88×10^{-12} $\Omega^{-1}\,\mathrm{cm}^{-1}$ for the copper derivative, depending on concentration; 4.55×10^{-10}–6.10×10^{-12} $\Omega^{-1}\,\mathrm{cm}^{-1}$ for the chromium analogue and 5.45×10^{-10} $\Omega^{-1}\,\mathrm{cm}^{-1}$ for a copolymer involving copper, chromium and zinc.

The epoxy resins developed by Srivastava et al. appeared to show reasonably good resistance to a wide variety of common chemicals (including mineral acids, methanol, aromatics, heterocyclics and halogenated solvents). Srivastava and Anand prepared 0.1 mm thick resin films and submerged them in different chemicals for a period of 7 days. The base resin (BADGE) was resistant to all of the chemicals tested with the exception of sulphuric and nitric acids. The resin modified with copper acrylate was generally only susceptible (i.e. sparingly soluble) to attack by methanol. The zinc analogue was slightly more susceptible, being soluble in sulphuric acid and sparingly soluble in pyridine. The chromium analogue was the least resilient of those tested as it was shown to be soluble in the mineral acids and sparingly soluble in methanol and toluene.

The activation energy for the polymerisation of the base epoxy was reported as 34 $\mathrm{kJ\,mol^{-1}}$ and the presence of the metal raised this figure in the case of the chromium (47 $\mathrm{kJ\,mol^{-1}}$) and zinc (61–86 $\mathrm{kJ\,mol^{-1}}$) acrylates. In the cured resins, the scratch hardness was improved over the base resin (ca. 1100–1800 g cf. 1000 g for BADGE) and thermal stability raised. The onset of thermal degradation for BADGE was quoted as 130 °C, whereas the modified resins underwent initial weight loss above 150 °C (and 215 °C in the case of the resin modified with zinc). The onset of the main weight loss was recorded as 275–310 °C — presumably in air, since no atmosphere was specified.

6. Coordination compounds containing imidazole ligands

Coordination compounds containing imidazoles were apparently first reported in the early 1970s for the use in the formulation of latent curing agents for epoxy resins by Dowbenko et al. [45,46]. These patents, and a subsequent paper [47], described the use of a large number of metal salts forming coordination compounds with a variety of imidazoles. The authors reported that there was a significant improvement in the storage stability (at 38 °C) of imidazole accelerators over the parent imidazoles, when the latter were complexed to transition metals. The group carried out extensive studies into twelve different imidazoles complexed to eight different transition metal salts, characterising their stability in a commercial BADGE epoxy resin (Epon 828). However, this study was only carried out over a relatively short period of time (8 days) and, as one-pot systems are expected to have shelf lives in excess of one month, the characterisation of the shelf life should reflect this requirement.

Following the work of Dowbenko et al. some 15 years earlier, Barton [48] discussed the use of differential scanning calorimetry (DSC) as a method for evaluating the shelf life, gel-point, and cure characteristics of an imidazole-based epoxy curative system. One of the problems with the metal–imidazole curing agents developed by Dowbenko et al. was the comparatively poor solubility in the epoxy resin. Prior to complexation, Barton [48] pre-reacted the 2-ethyl-4-methylimidazole

Table 10
Physical properties of M-acrylate/epoxy resin blends

Resin system	M-acrylate concentration ($\times 10^{-3}$ mol)	Epoxide equivalent (eq/100 g)	Viscosity (η_{sp}) (at 30 °C)	Specific gravity (at 30 °C)	Chlorine content (wt%)	Hydroxyl content (eq/100 g)
BADGE	0.00	194	1.58	1.173	0.50	0.12
Copper acrylate	4.20	245	1.66	1.180	0.70	0.15
	12.60	290	1.82	1.193	0.90	0.17
	21.09	338	1.92	1.203	1.00	0.17
Chromium acrylate	3.20	270	1.71	1.190	1.86	0.15
	9.79	403	1.78	1.221	2.90	0.16
	16.31	587	1.84	1.340	3.40	0.17
Zinc acrylate	4.78	234	1.63	1.185	1.83	0.13
	12.53	294	1.82	1.194	3.06	0.13
	20.89	335	1.90	1.202	3.86	0.13
Cr/Cu/Zn acrylates	3.26					
	4.21	280	2.18	1.189	0.60	0.15
	4.17					

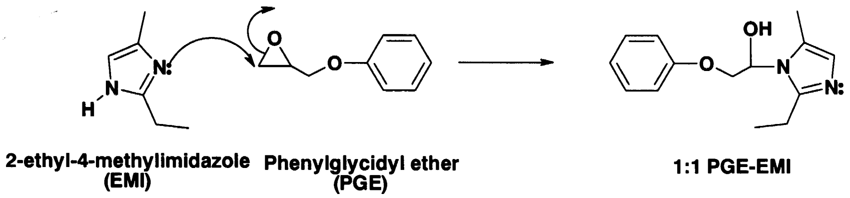


Fig. 5. Reaction of 2-ethyl-4-methylimidazle with phenylglycidylether.

Table 11
Gel times for coordination compounds containing imidazole ligands in selected epoxy resins at 176 °C

Salt	Molar ratio	Ligand	Molar ratio	Gel time (min)			
				Epon 828	Epon 871	Cy179	ECN 1280
$CuCl_2$	0.100	Imidazole	0.400	2	170	140	315
CuF_2	0.100	1-Methylimidazole	0.400	3	70	16	4
$CuCl_2$	0.100	2-Methylimidazole	0.400	210	130	60	170
$NiCl_2$	0.100	1,2-Methylimidazole	0.400	36	50	345	6
$CuBr_2$	0.150	2-Ethylimidazole	0.675	330	170	75	170
$NiCl_2$	0.050	1-Ethylmethylimidazole	0.300	4	110	310	210
CuF_2	0.050	1-(2-Carbamylethyl)imidazole	0.200	7	170	25	5
$CuCl_2$	0.050	Benzimidazole	0.200	40	70	200	315
$CuSO_4$	0.055	1-Benzyl-2-methylimidazole	0.220	13	173	240	255
$CuCl_2$	0.05	1-Allyl-2-ethyl-4-methylimidazole	0.210	7	130	345	95
CuCl	0.06	1-Imidazolecarboxanilide	0.240	4	70	60	210

Epon 828 = bisphenol A diglycidyl ether (BADGE); Epon 871 = dimer fatty acid diglycidyl ester; Cy179 = cycloaliphatic epoxide (*ex* Ciba); and ECN 1280 = epoxidised novolac resin (*ex* Ciba).

with phenylglycidylether (Fig. 5). This had the effect of modifying the structure of the ligand (and hence the catalyst) to resemble the oligomeric epoxy (and consequently improved their compatibility).

Hamerton et al. [49–55] have examined in greater detail this series of latent catalysts. An initial study of the storage stability of MY750 containing PGE–EMI and the corresponding Cu(II) complex Cu(PGE–EMI)$_4$Cl$_2$ revealed that, over a period of 850 h, the mixture containing the complex exhibited a much lower increase in its glass transition temperature (and hence its degree of polymerisation) than the mixture containing the parent imidazole. These compounds displayed excellent storage stability with the viscosity of the Cu(PGE–EMI)$_4$Cl$_2$/MY750 combination remaining relatively low (3000 Pa s) after a period of 2600 h while the corresponding PGE–EMI (containing no metal salt) had a viscosity of 8000 Pa s after only 430 h at ambient temperature. The tetrafunctional epoxy MY721 (a TGDDM epoxy), while more reactive than BADGE, also displayed significant improvements in the storage stability using the same coordination compounds.

Dowbenko et al. [47] studied the time taken for one-pot epoxy systems (containing one of several commercial epoxy prepolymers and various coordination compounds containing imidazole ligands) to reach gelation at 176 °C. While the experimental design was somewhat crude, they found that at relatively low levels of addition (metal salt, 0.05–0.1 mol and imidazole, 0.2–0.4 mol), it was possible to alter significantly the gel times of the epoxy systems (Table 11).

Dowbenko et al. postulated that there were several possible routes by which the cure of the epoxy resins using the complexed imidazoles might proceed [47]. They stated that the active species initiating the polymerisation was the imidazole itself and the problem was one of establishing the mode by which the imidazole was released from the complex. Dowbenko et al. recognised that there was a relationship between the dissociation temperature and the gel time of the epoxy system, but believed that the stability of the complex was not believed to be a significant factor in the degree or effectiveness of the cure. Poncipe [56] has also reported that coordination compounds of PGE–imidazole adducts displayed a temperature-dependent induction period and that the nature of the metal ion was important in determining the length of this period. He found that the order of stability of the transition metals followed the order of stability predicted by the spectrochemical series (i.e. $Cu^{II} > Ni^{II} > Co^{II}$) and therefore that complexes of copper had a higher dissociation temperature than the equivalent cobalt complexes.

The polymerisation kinetics of MY750 containing the PGE–EMI systems have been studied [51] using both thermal and spectroscopic methods. The first order rate constant (k_1) for the ring-opening step (of the epoxide group) was found to be 4.05×10^{-6} s^{-1} at 140 °C from fused state ^{1}H-NMR measurements. Furthermore, very good agreement was obtained for the first order rate constant (k_2) for the second (oligomerisation) step from both fused state ^{1}H-NMR (1.85×10^{-5} s^{-1} at 140 °C) and FTIR (1.88×10^{-5} s^{-1} at 140 °C). It was also found [50] that was possible to partially cure MY750 containing Cu(PGE–EMI)$_4$.Cl$_2$ for a period of ca. 5 min at 120–140 °C and then quench it to room temperature with little or no cure occurring thereafter until the cure temperature was raised once again. FTIR was used to monitor changes in the oxirane ring breathing vibration at 917 cm^{-1} and subsequent measurements revealed little progression in the cure after 6 h. This unexpected finding could be utilised to facilitate complex cure schedules requiring a B-stage (partial cure) during processing. The inclusion of 5–7 wt% Cu(PGE–EMI)$_4$·Cl$_2$ in MY750 was found to have no discernible detrimental effects on the thermal stability, dielectric properties or water absorption in the cured MY750 epoxy resin [52]. After a period of 14 h immersion in boiling water, an equilibrium value of ca. 2.5% water uptake was recorded.

An extensive series of complexes incorporating PGE–EMI was also prepared with the acetates and chlorides of Mn, Co, Ni, Cu, Zn and Ag [55]. The 23 complexes in this study were characterised extensively using spectroscopy (IR, UV–vis, ^{1}H- and ^{13}C-NMR), magnetochemistry and elemental analysis. Kinetic parameters were obtained for the polymerisation of MY750 using several complexes and the parent imidazole adduct (Table 12). ^{1}H-NMR spectroscopy was also employed to examine the thermal dissociation of the complexes. While a simple treatment of the data was not possible (due to the differences in oxidation, spin states and coordination geometries involved), it was possible to note several trends. The presence of substituents on the imidazole ring affects the reactivity of the lone pair of electrons on the nitrogen. By increasing the steric hindrance around the imido nitrogen the stability of the complex (and the dissociation temperature) was reduced. This can also take effect through simple steric effects, or inductive effects to alter the ligand's reactivity towards the oxirane ring. Furthermore, by substituting the chloride by nitrate increased the dissociation temperature by 10 °C (consistent with the anion's position in the spectrochemical series).

Table 12
Kinetic data (from ^{1}H-NMR measurements) for selected BADGE/curing agent blends cured at 120 °C (in the absence of solvent)

Curing agent (3 mol% incorporation)	k_1 rate (10^{-3} s^{-1}) (propagation)	k_2 rate (10^{-5} s^{-1}) (polyetherification)
Cu(CH$_3$COO$^-$)$_2$(PGE–EMI)$_4$	5.82	10.80
Ni(CH$_3$COO$^-$)$_2$(PGE–EMI)$_4$ [a]	5.95	14.50
Co(CH$_3$COO$^-$)$_2$(PGE–EMI)$_4$	4.97	5.67
PGE–EMI	5.18	1.88

[a] Kinetic parameters calculated on data collected at 100 °C.

Kaplan et al. [57] reported a series of coordination compounds, derived from lanthanide metal salts, of the form [M(THD)$_3$–IM] where M = Eu, Ho, Pr, Dy, Yb and Gd; THD = 2,2,6,6-tetramethyl-3,5-heptanedione; and IM = imidazole mixed with BADGE (EEW = 195). It was reported that the curing agents employing rare earth elements exhibited shelf lives in excess of one week, in comparison to the two-day shelf life of the parent imidazole/epoxy mixture. Some variations in melting point and cure temperature were related to the ionic radius of the rare earth metal series (Fig. 6); the cure temperature was reduced with increasing ionic radius.

The storage stability was also reduced with ionic radius, leading to the hypothesis that the ligands on the larger ion compounds are either sterically more accessible to reaction with the epoxy resin or less stable than the smaller ions, leading to them being lost more readily at lower temperatures. By changing the nature of the imidazole ligand (and in particular bulkier groups adjacent to the imido nitrogen), it was also possible for Kaplan et al. to effect a reduction in the cure temperature by reducing the strength of the lanthanide–nitrogen bond. Hence, for imidazole a cure temperature of 162 °C was observed, but that this could be reduced by increasing the degree of substitution around the site of complexation (e.g. 2-ethyl-4-methylimidazole, 160 °C, 2-methylimidazole, 149 °C, and 2-ethylimidazole, 148 °C). However, it was noted that the T_g of the cured resin was also progressively reduced from 120 °C (imidazole) to 108 °C (2-ethylimidazole).

7. Coordination compounds containing imidazolium ligands

Dowbenko and Anderson [58] used the information gained from experiments with the imidazole complexes discussed above and applied it to alkyl- and aryl-substituted imidazolium salts (either halides, sulphates or phosphates). They reported that after the complexes had been mixed with the epoxy resin they displayed relatively long shelf lives at room temperature, typically in the order of 4–6 months. However, once these complexes are heated to the cure temperatures 122 °C (BADGE) and 170 °C (TGDDM) they required long cure schedules and a nitrogenous based accelerator (e.g. dicyandiamide, DiCy) to reduce the cure time (Table 13).

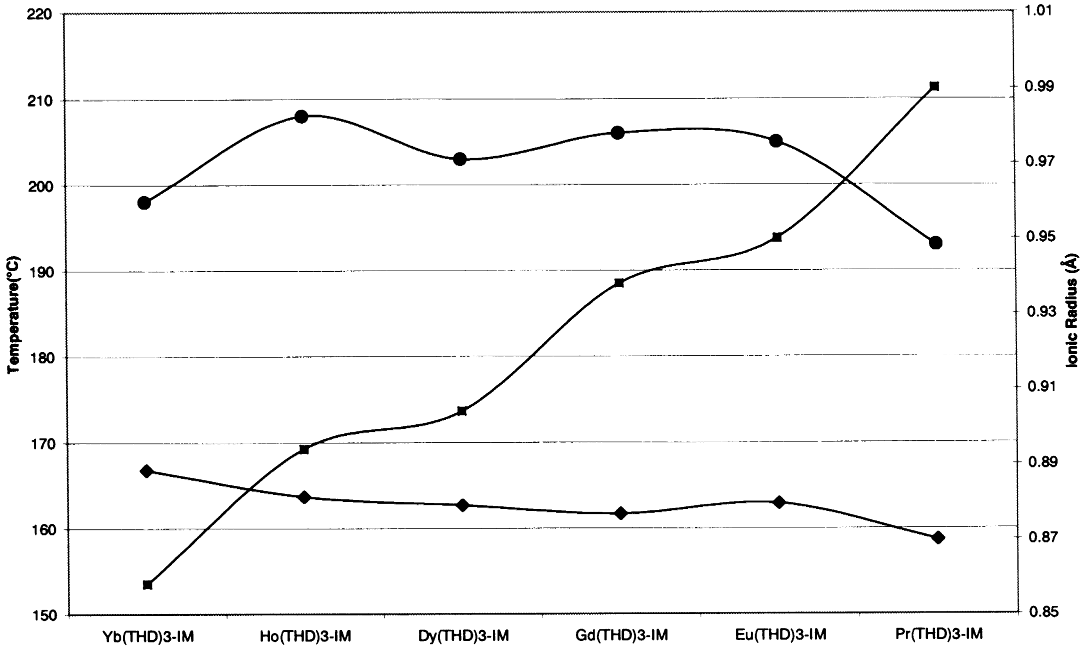


Fig. 6. Effect of ionic radius (■) of M(THD)$_3$-imidazole complexes on melting point (●) and BADGE cure temperature (◆).

Table 13
Effect of DiCy on curing times for selected BADGE/imidazolium complex blends

Imidazolium salt	Metal salt	Cure time (min)		
		DiCy (20 phr), Im. (0 phr)	DiCy (20 phr), Im. (5 phr)	DiCy (20 phr), Im. (10 phr)
2-Dimethyl-3-benzylimidazolium chloride	$CuCl_2$	270	9	5
1-Benzyl-2-ethyl-3-methyl-imidazolium chloride	$CoCl_2$	24	6	–
1-(2-Carbamylethyl)-3-hexyl-imidazolium bromide	$CuBr_2$	570	40	18
1,3-Dibenzylbenzimidazolium chloride	$CuBr_2$	900–1380	7.5	10.5
1,3-Dibenzylbenzimidazolium chloride	$Cu(NO_3)_2$	738	7	5

Im. = imidazolium complex.

8. Coordination compounds containing phthalocyanine ligands

Parry [59] reported the use of phthalocyanine compounds to cure epoxy-novolac resins to yield polymers with excellent thermal- and chemical resistance and good resistance to water absorption. Copper complexes of phthalocyanine, phthalocyanine tetra- and octa-carboxylic acids and phthalocyanine tetraanhydride were prepared and incorporated into the base resin. The tensile shear strength was measured both before and after ageing at elevated temperature (e.g. 260 °C) and Parry found that while the length of the ageing period did reduce the property somewhat. The presence of triphenylphosphine (1.5 wt%) was found to have a beneficial effect on the tensile shear strength measured.

The substituents (R in Fig. 7) could be varied as carboxylic acid, carboxylic ester, metal carboxylates, or amides, etc.

Achar et al. [60–62] have also examined phthalocyanines and have developed a series of metal(II) 4,4′,4″,4‴-phthalocyanine tetramine (MPTA) complexes

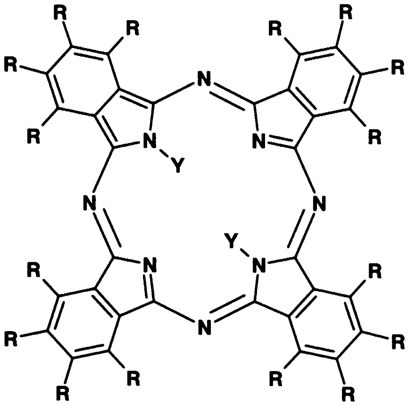


Fig. 7. Phthalocyanine ligand (Y = H atom).

Table 14
Effects of M-PTA complexes on the physico-mechanical behaviour of DEN 438

Material	Specific gravity	Resin content (wt%)	Moisture absorption (%)	Tensile strength (MPa)	Flexural strength (MPa)	Short-beam shear strength (GPa)	Dynamic modulus (GPa)
DEN 438 + CuPTA + BF_3MEA	1.46	34.6	1.51	402.39	424.04	475.76	–
DEN 438 + CuPTA + BF_3MEA + CTBN	1.47	35.2	1.65	482.44	517.81	490.23	–
DEN 438 + CoPTA + BF_3MEA	1.50	32.3	1.89	415.63	408.18	459.90	5.999
DEN 438 + CoPTA + BF_3MEA + CTBN	1.51	38.2	1.82	472.45	505.40	504.71	15.996
DEN 438 + NiPTA + BF_3MEA	1.46	35.8	1.88	400.53	444.04	484.03	–
DEN 438 + NiPTA + BF_3MEA + CTBN	1.49	39.2	1.90	456.45	513.68	539.19	–

CTBN = hycar carboxy-terminated butadiene–acrylonitrile.

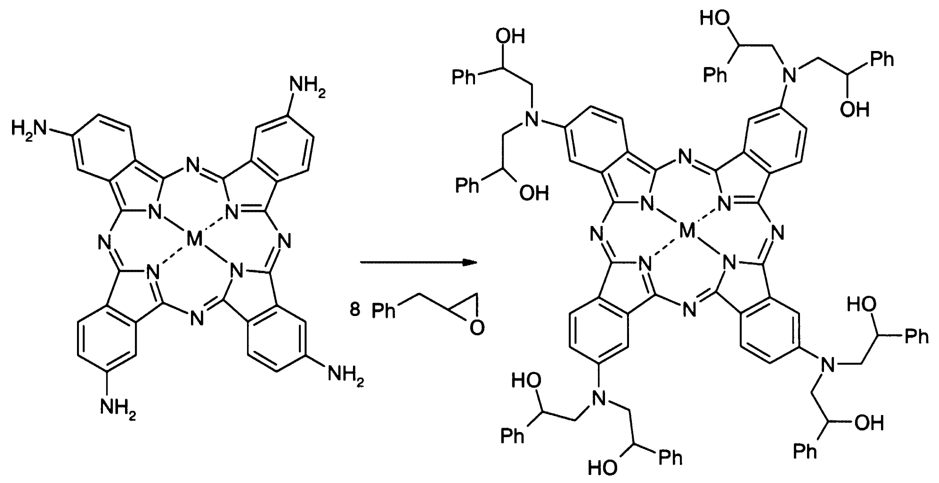


Fig. 8. Proposed addition reaction of MPTA with epoxy resins (shown as monofunctional form Ph represents aromatic moiety (M = Cu, Co, and Ni).

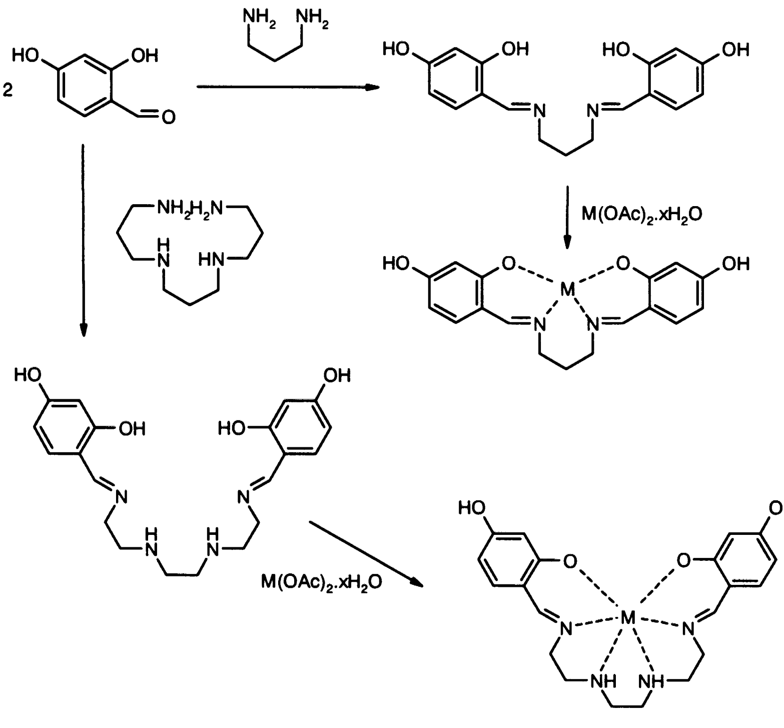


Fig. 9. Formation of tetradentate (M = Cu^{2+}, Co^{2+} and Ni^{2+}) and hexadentate (M = Ni^{2+} and Zn^{2+}) Schiff’s base complexes.

as curing agents for heat resistant epoxy resin formulations (Fig. 8).

In one study Achar et al. [60] formulated different resin systems using the epoxy novolac DEN 438 (Fig. 8). They found the complexes to be soluble in aprotic solvents (e.g. dimethyl sulphoxide, dimethyl acetamide and dimethyl formamide), allowing the introduction of the stable phthalocyanine into the epoxy resin via a solution route. Good physical properties were obtained using the complexes as curing agents (Table 14), while it was reported that the toughness of the end-cured resin could be further improved with the introduction of 3–5 phr of CTBN elastomer (presumably at the expense of some of the thermal stability).

9. Coordination compounds containing Schiff’s base ligands

Epoxy resins can be cured not only by amine based curing agents, but also by hydroxyl based curing agents such as bisphenols. Consequently, Chantarasiri et al.

have developed epoxy curing agents that possess a bisphenol-type structure. Their tetradentate [63] and hexadentate [64] Schiff base metal complexes that act as cross-linking agents for BADGE-type epoxy resins (Fig. 9) were prepared in a two-step preparation. Like many phenolic-cured epoxy resins, these epoxy systems need additional accelerators/catalysts to improve the cure profile of the resin system and tetrabutylammonium hydroxide (Bu_4NOH) was selected as the accelerator for the BADGE. The addition of modest amounts of Bu_4NOH (20 mol%) significantly reduced the DSC peak maximum by up to 62 °C for the copper complex, 36 °C for the cobalt complex and 116 °C for the nickel analogue. This, in turn, reduced the cure time of the reaction. The introduction of the Schiff base metal complexes into the BADGE network gave good thermal stability and tensile strengths when compared to epoxies cured with anhydride and a triamine. The T_g of the cured resin was consistently found to increase in the presence of Bu_4NOH.

10. Conclusions

The use of metal salts in the production and formulation of epoxy resins for use in composite materials has been widely studied since the 1960s. This review demonstrates that the use of coordination compounds in this fashion is of major commercial interest, and that their presence can significantly improve selected physical properties such as viscosity or fracture toughness, and electrical, thermal and chemical properties of epoxy resins. They have also found application as catalysts and curing agents and also as cure accelerators to modify the cure profile of commercial resin systems.

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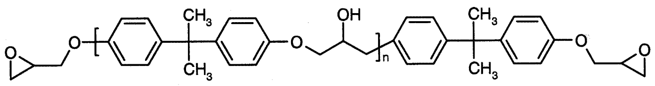
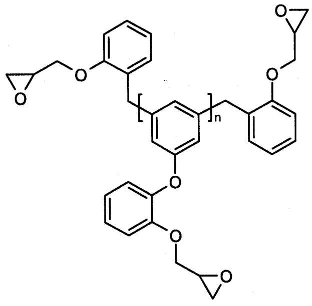
Appendix A. Abbreviations

Chemical	
Acac	acetylacetonate
BADGE	bisphenol A diglycidyl ether
BF_3MEA	boron trifluoride monoethylamine
Bu_4NOH	tetrabutylammoniumhydroxide
cydien	cyanoethylated diethylenetriamine
CY179	cycloaliphatic epoxide
$C_{11}Z$	2-unidecylimidazole
DAM	4,4′-diaminodiphenylmethane
DDM	diaminodiphenylmethane
DDS	4,4′-diaminodiphenylsulphone
DEN-438	phenol–formaldehyde novolac epoxy resin
DER-542	tetrabromobisphenol A diglycidyl ether
DETA	diethylenetriamine
DiCy	dicyandiamide
dien	diethylenediamine
DMF	*N*,*N*-dimethylformamide
ECN12	phenol–formaldehyde novolac epoxy resin
en	ethylenediamine
Epi-Rez SU-8	bisphenol A formaldehyde novolac
Epon 828	see BADGE
Epon 852	see BADGE
Epon 871	dimeric fatty acid diglycidyl ester
MDA	4,4′-methylenediamine
MPTA	metal(II)4,4′,4″,4‴-phthalocyanine tetramine
MY720/ MY721	see TGDDM
MY750	see BADGE
OPD	*o*-phenylenediamine
p-ABAcid	*p*-aminobenzoic acid
PPD	*p*-phenylenediamine
TGDDM	4,4′-tetraglycidyldiaminodiphenylmethane
THD	2,2′,6,6′-tetramethyl-3,5-heptanedione
trien	triethylenediamine
UP-606/2	*tris*(dimethyl-*p*-aminoethyl)phenol
General	
DSC	differential scanning calorimetry
ΔH	heat of reaction (enthalpy)
EEW	Eepoxy equivalent weight
E_c	compressive modulus
E_f	flexural modulus
E_t	tensile modulus
G_{Ic}	mode I strain energy release
HDT	heat deflection temperature
M	metal
Phr	parts per hundred parts resin
RT	room temperature
σ_c	compressive strength
σ_f	flexural strength
σ_t	tensile strength
TGA	thermogravimetric analysis
T_g	glass transition temperature
WA	water absorption
wt%	weight percent

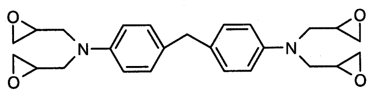
Appendix B. Structures of selected commercial epoxy resins



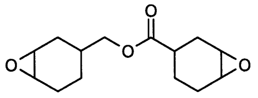
BADGE (Epon 828, MY750, *etc.*)



Epoxy novolac
(DEN 438, n = *ca.* 1.6) or ECN 1280



TGDDM (MY721)



ERL 4221 or CY-179

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