

Benzimidazole Derivatives and their Complexes as Accelerators for Curing of Epoxy Resin

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ABSTRACT: Bisphenol-A-based epoxy resin was cured with an anhydride hardener in the presence of benzimidazoles and their complexes as accelerators. Investigations have revealed an appreciable reduction in the cure and gel times. The kinetic studies based on DSC showed that the rate of curing increases with enhanced concentration of accelerators. The coefficient of thermal expansion has been reduced considerably in the presence of the benzimidazole. The electrical properties of the cured epoxy resin system were unaffected

by lower concentrations of benzimidazoles. A mechanism for curing has been proposed with 1,3-bis(2-benzimidazolyl)benzene as accelerator based on IR studies, which indicate the involvement of the secondary and tertiary nitrogen of the benzimidazole in the crosslinking of the resin system. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2101–2106, 2008

Key words: curing; epoxy resins; benzimidazole derivatives

INTRODUCTION

Epoxy resins owing to their remarkable chemical resistance, good adhesion, extraordinary toughness, high mechanical strength, and good heat resistance are extensively used as electrical insulators. When properly cured, they yield tough materials, which find application in industrial flooring, foam, and electrical insulation. The applications of epoxy resins depend on the nature of curing. Generally curing takes place in the presence of a hardener or a curing agent. Anhydrides are used as curing agents for epoxy resins, and the latter are used in casting and lamination. Bases such as tertiary amines are commonly used to accelerate the curing process. Chemical reactions that take place during the period of curing determine the properties of the cured thermoset. Organometallic compounds are known to act as curing agents for various epoxy resin systems.^{1–3} Several acetyl acetonates act as latent accelerators for anhydride cure of bisphenol-A-based resins.^{4–8}

In this work, an attempt has been made to use benzimidazoles and their complexes as accelerators for curing epoxy–anhydride systems. 2-Phenyl benzimidazole, 1,3-bis(2-benzimidazolyl)benzene, dichloroquo[1,3-bis(2-benzimidazolyl)benzene]copper(II), dichloroquo[1,3-bis(2-benzimidazolyl)benzene]zinc-

(II), dichloroquo[1,3-bis(2-benzimidazolyl)benzene]cobalt(II), dichloroquo[1,3-bis(2-benzimidazolyl)benzene]nickel(II), 1,2,4-tri(2-benzimidazolyl)benzene, and 1,2,4,5-tetra(2-benzimidazolyl)benzene were prepared^{9–16} and used as accelerators. The cure and kinetic aspects of the resin and the anhydride in the presence of these compounds have been studied. Gel time and storage life studies have also been carried out. Thermomechanical properties for 1,3-bis(2-benzimidazolyl)benzene has been carried out and compared with that of the blank and the commercially available accelerator. Electrical properties such as loss factor and capacitance of the resin–anhydride system have been investigated. A cure mechanism has been suggested for the epoxy resin with carboxylic anhydride in the presence of 1,3-bis(2-benzimidazolyl)benzene involving tertiary and secondary nitrogen atoms.^{17–25}

EXPERIMENTAL

Materials and methods

Bisphenol-A-based epoxy resin, Lapox C-17 with an epoxy content of 5.2–5.5 equiv/kg, K-12 hardener (anhydride content of about 94%), and commercial accelerator K-112 were procured from Cibatul, India, and were used as such. Silica flour (w-12 grade) of 300-mesh was also procured from Cibatul, and it was dried at 110°C for 3 h and then used as filler.

2-Phenyl benzimidazole (2phBz), 1,3-bis(2-benzimidazolyl)benzene (1,3Bz), dichloroquo[1,3-bis(2-

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benzimidazolyl)benzene]copper(II) (CuBz), dichloro-aquo[1,3bis(2-benzimidazolyl)benzene]zinc(II) (ZnBz), dichloro-aquo[1,3-bis(2-benzimidazolyl)benzene] cobalt(II) (CoBz), dichloro-aquo[1,3-bis(2-benzimidazolyl)benzene]nickel(II) (NiBz), 1,2,4-tri(2-benzimidazolyl)benzene, and 1,2,4,5-tetra(2-benzimidazolyl)benzene were prepared and characterized using the procedures described elsewhere.^{9–16}

The gel time characteristics of the resin system were determined using Gel norm Gel timer (Switzerland). Differential scanning calorimeter (DSC) with data station DSC-2C of M/s. Perkin Elmer, was used for cure kinetic studies. The viscosity measurements were made using Model-RVT viscometer of M/s. Brookfield Instruments. The thermomechanical analysis was carried out using TMA 400Q of TA Instruments. The capacitance and loss factor values were determined as per ASTM D 150 specifications using Tettex bridge of M/s. Tettex Instruments, Switzerland AG. The cure process was followed using FTIR spectra. The spectra of the samples as KBr pellets were recorded using FTIR spectrometer 2000 of M/s. Perkin Elmer.

To measure the gel time characteristics of the resin system, about 5–10 g of the resin mix was taken in a tube provided with a spiral wire for agitation. This was introduced into a bath maintained at a particular temperature. The mixture was allowed to attain thermal equilibrium and then the spiral wire was mechanically moved up and down. The viscosity of the resin system gradually increased and a rubbery mass was formed. At this stage the movement of the wire gets arrested. The time taken for the mixture to become a rubbery mass from the free-flowing stage was noted as gel time. The viscosity measurements were made for the resin system in presence of 0.5 phr (parts per hundred) of benzimidazoles, and the number of days taken for a 10-fold increase in viscosity was recorded and tabulated as the storage life.

Dynamic DSC scans of the epoxy systems were carried out in the temperature range 40–400°C at varying heating rates in the range of 5–40°C/min. The temperature corresponding to the T_m of the curing exotherm was determined at various concentrations of the benzimidazoles and their complexes.

The thermomechanical analysis was done by placing the required size of the cured resin–hardener system and the sample containing 0.5 phr of 1,3-bis(2-benzimidazolyl)benzene and heating it from ambient to 200°C under inert atmosphere.

The electrical and thermal measurements were carried out as per IS: 1998 specifications. To find the possible cure mechanism of the epoxy resin system with 1,3-bis(2-benzimidazolyl)benzene, equal quantities of the resin and the hardener were accurately weighed and treated with a known quantity of 1,3-bis(2-benzimidazolyl)benzene. The mixture was stirred

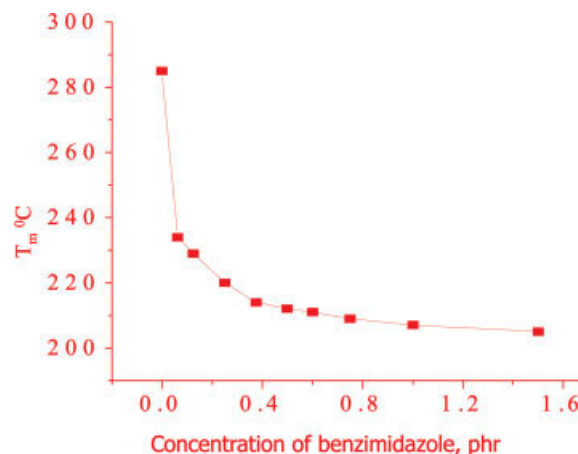


Figure 1 Effect of 1,3-bis-(benzimidazolyl)benzene on T_m cure exotherm of resin–hardener system. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

well. A portion of this was spread as a film between two KBr pellets and cured at 100°C. Infrared spectra were recorded periodically for 15 min.

RESULTS AND DISCUSSION

Resin–hardener stoichiometry

The resin–hardener stoichiometry was determined using dynamic DSC runs by plotting enthalpy change ΔH against the amount of hardener used, and the stoichiometry was found to be 1 : 1.⁶ For commercial applications the epoxy system is generally associated with suitable filler. In this study, silica flour was added as filler in such a way that the control system had the formulation of resin, hardener, and filler in the ratio of 1 : 1 : 3.

The observed temperature minimum (T_m) value of the cure exotherm was plotted against concentration of the benzimidazole. Such a plot is shown in Figure 1. The rate of decrease in the T_m value was appreciable upto 0.5 phr of 1,3-bis(2-benzimidazolyl)benzene, and thereafter it remained almost constant. A similar trend was found in the case of the other benzimidazoles. In view of this, studies on the gel time, storage life, cure kinetics, thermal and electrical properties were carried out for the resin–hardener system containing benzimidazoles and their complexes (upto 0.5 phr).

Effect of the benzimidazoles and their complexes on resin–hardener system

Gel time and storage life

The effect of benzimidazoles and their complexes on the gel time and storage life of the epoxy resin system at different temperatures was monitored. The

TABLE I
Gel Time and Storage Life of Resin System with 0.25 phr of Benzimidazole and their Complexes

Sample	Gel time (min) at temperature (°C)				Storage life (days at room temperature)
	120	140	160	180	
Control system	690	257	114	43	46
2-Phenyl benzimidazole	43	14	8	5	10
1,3-Bis(2-benzimidazolyl)benzene	55	15	14	8	27
1,2,4-Tri(2-benzimidazolyl)benzene	110	65	33	23	23
1,2,4,5-Tetrakis(2-benzimidazolyl)benzene	497	265	76	20	45
Dichloroquo[1,3-bis(2-benzimidazolyl)benzene]copper(II)	108	42	17	7	29
Dichloroquo[1,3-bis(2-benzimidazolyl)benzene]zinc(II)	209	56	27	14	33
Dichloroquo[1,3-bis(2-benzimidazolyl)benzene]cobalt(II)	164	65	30	15	42
Dichloroquo[1,3-bis(2-benzimidazolyl)benzene]nickel(II)	145	46	23	11	43
K-112 (commercial accelerator)	47	13	12	8	18

values obtained at 0.25 phr of the heterocycles are listed in Table I. The results indicate that the gel times for the resin system in the presence of benzimidazoles are lower when compared with the control system and the values decrease with increase in temperature. At a given concentration and temperature, 2-phenyl benzimidazole showed the lowest gel time followed by 1,3-bis(2-benzimidazolyl)benzene. The derivatives of benzimidazoles showed comparatively higher values indicating a decrease in the cure activity. It is observed that the addition of 1,2,4-tri(2-benzimidazolyl)benzene and 1,2,4,5-tetra(2-benzimidazolyl)benzene to the resin system further enhances the gel time values indicating a further reduction in the cure activity. This may be due to the larger number of substituents in the heterocycle, wherein the availability of lone pair of electrons on the nitrogen has been restricted due to steric effect. The storage life of the epoxy system was monitored with 0.25 phr of benzimidazoles and the results obtained are given in Table I. Apparently on storage, 1,2,4,5-tetra(2-benzimidazolyl)benzene has showed no curing property at room temperature and the value obtained is the same as that of the control system. 2-Phenyl benzimidazole shows the lowest storage life

but its curing is being present even at room temperature. The gel time and storage life data of 1,3-bis(2-benzimidazolyl)benzene are comparable with that of the commercial accelerator (K-112).

Kinetic studies

Dynamic DSC scans of the epoxy systems were carried out in the temperature range 40–400°C at varying heating rates in the range of 5–40°C/min. The temperatures corresponding to the peak minimum (T_m) of the curing exotherm were determined at various phr of the benzimidazoles. The order of the curing reaction “ n ” was calculated using a single DSC profile at a constant heating rate by plotting $\log k$ against $1/T_m$ and the best linear regression fit was observed when $n = 1$ for varied heating rates. The energy of activation (E_a) for the curing reaction was calculated²⁶ by plotting \log (heating rate) versus $(1/T_m)$. Using these values, the pre-exponential factor (Z) and also the rate constant (k) were evaluated^{27,28} at 140°C. The E_a values for the curing of epoxy system in presence of various benzimidazoles have been found to be in the range of 15–21 kcal/mol (Table II). Generally the rate constant was found to

TABLE II
Kinetic Data and Cure Schedules of the Epoxy System with Benzimidazoles and their Complexes (0.25 phr)

Accelerator	E_a (kcal/mol)	$k \times 10^{-3}$ min at 140°C	$Z \times 10^6$	Cure time (min) at 140°C
Control system resin + hardener	19.24	21.00	27.80	293
2-Phenyl benzimidazole	19.26	42.00	66.30	21
1,3-Bis(2-benzimidazolyl)benzene	15.86	42.60	0.60	16
1,2,4-Tri(2-benzimidazolyl)benzene	19.26	46.00	7.80	69
1,2,4,5-Tetra(2-benzimidazolyl)benzene	21.46	4.30	96.00	134
Dichloroquo[1,3-bis(2-benzimidazolyl)benzene]copper(II)	15.10	39.10	3.50	45
Dichloroquo[1,3-bis(2-benzimidazolyl)benzene]zinc(II)	13.53	26.50	0.40	65
Dichloroquo[1,3-bis(2-benzimidazolyl)benzene]cobalt(II)	12.20	39.30	1.10	70
Dichloroquo[1,3-bis(2-benzimidazolyl)benzene]nickel(II)	17.45	10.40	62.40	52
K-112 (commercial accelerator)	16.1	45.2	1.3	15

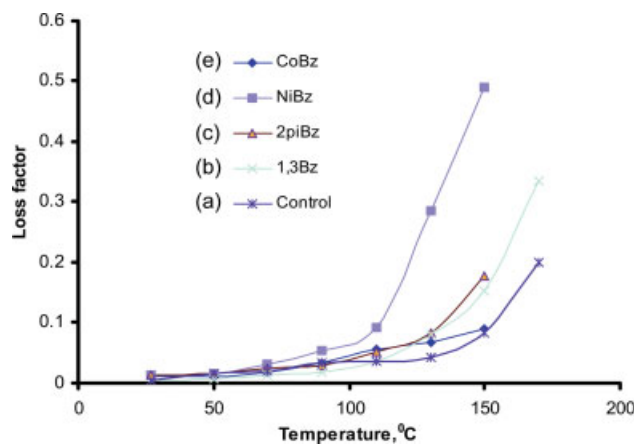


Figure 2 Plot of loss factor data against temperature for epoxy resin system in the presence of (a) control, (b) 1,3 Bz, (c) 2piBz, (d) NiBz, and (e) CoBz at 0.25 phr. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

increase with enhanced concentrations of the benzimidazoles and their complexes.

Cure studies

By considering the degradation process as a simple chemical reaction, Toop²⁹ has derived an expression to evaluate the thermal life of wire enamels. Also, several reports are available based on thermal analytical techniques. This concept has been used for the purpose of finding out the cure schedules³⁰ using the cure kinetics, which is based on the data obtained from DSC. The data obtained for benzimidazoles and their complexes are recorded in Table II. The data show comparatively lower values of cure schedule for benzimidazoles than the control system. The cure time values of 2-phenyl benzimidazole and 1,3-bis(2-benzimidazolyl)benzene have been found to be nearly 16 min at 140°C which is much lower than that of the control system (290 min). This clearly suggests that these two heterocycles are effective in the curing process of the epoxy resin system. The cure time values of 1,2,4-tri(2-benzimidazolyl)benzene and 1,2,4,5-tetra(2-benzimidazolyl)benzene are higher than those of the others, but lower than that of the control system. The transition metal complexes show a lower cure activity, probably because the metal coordinates to the ligand in the complex making the lone pair of electron on the ligand unavailable for curing the resin system.

Electrical properties

For applications in high-voltage insulation involving generators, transformers, and a.c motors, the highest voltages used usually dictate the limitations. Hence,

the present epoxy samples were subjected to variations of voltage. The capacitance and the loss factor of the cured epoxy resin system at different concentrations of the ligands and their complexes have been studied both at room temperature as well as at higher temperatures. Usually, the addition of an ionic additive or the presence of water can increase the loss factor at higher temperatures. In this study, it seems that at room temperature there is no difference in terms of the loss factor of the cured system. The loss factor data obtained for the epoxy system with variation of temperature is shown in Figure 2. The plots indicate that the trend in loss factor values is the same up to 90°C for all the systems, and thereafter the increase in loss factor values is more predominant for the epoxy system in presence of the nickel complex at lower temperatures when compared with that for control system. However, the increase in loss factor for the other accelerator systems is almost comparable with that of the control system.

Thermomechanical property

The extent of crosslinking of a cured resin system has been measured in terms of measuring the coefficient of thermal expansion of the system using thermomechanical analyzer. The coefficient of thermal expansion for the control (blank) system was found to be 133.1 $\mu\text{m}/(\text{m } ^\circ\text{C})$ and that of the resin-hardener system with 0.5 phr of 1,3-bis(2-benzimidazolyl)benzene was found to be 108.5 $\mu\text{m}/(\text{m } ^\circ\text{C})$ when measured up to a temperature of 190°C. These values indicate more compactness of the cured sample in the presence of the accelerator because of enhanced crosslinking of the resin system.

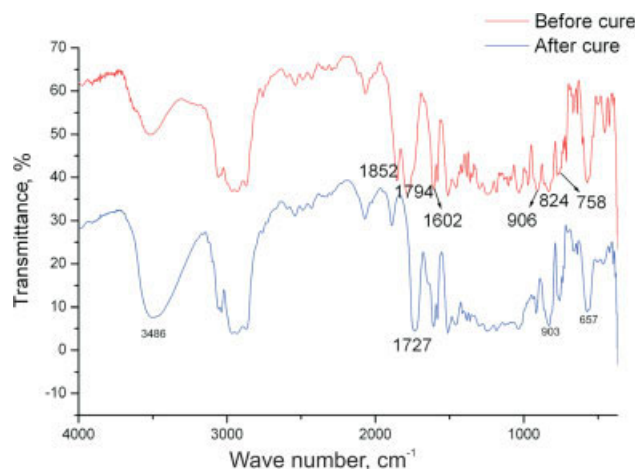
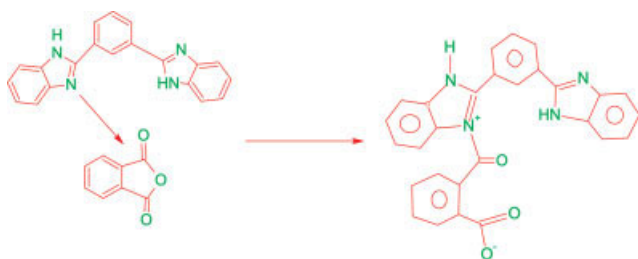


Figure 3 Infrared spectra of resin-hardener with 1,3-bis(2-benzimidazolyl)benzene before and after curing. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

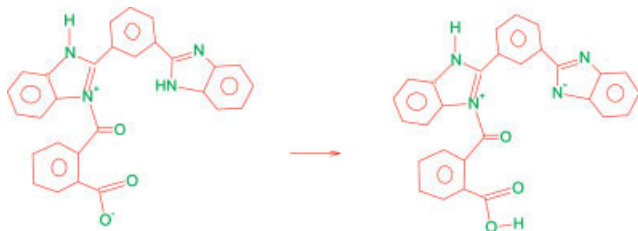


Scheme 1 Opening of the anhydride ring by tertiary nitrogen. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

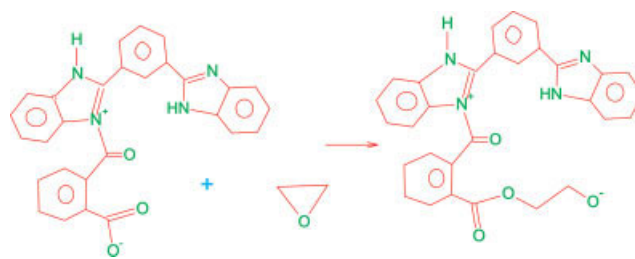
Cure mechanism

It has been observed in the IR spectra (Fig. 3) of the resin-hardener system that the intensity of the band at 3486 cm^{-1} (which is characteristic of hydrogen bonded OH group), has increased as the cure reaction proceeded. A peak at 1534 cm^{-1} because of C=C stretching and CH bending of the benzimidazole has shifted and merged with the band at 1495 cm^{-1} band due to the hardener. Both the hardener and 1,3-bis(2-benzimidazolyl)benzene exhibited a peak at 975 cm^{-1} , and this band has been attributed to the ring breathing vibration. Another band at 824 cm^{-1} of 1,3-bis(2-benzimidazolyl)benzene ring vibration has merged with a peak at 888 cm^{-1} of the hardener. The 758 cm^{-1} band because of the out-of-plane CH deformation vibration of benzimidazole and benzene ring has shifted to 713 cm^{-1} . It has been observed that the intensities of these bands have decreased as the curing of the resin-hardener system progressed. This suggests an increase in the extent of crosslinking.

A band at 1512 cm^{-1} because of coupled C—N stretching and NH bending mode of 1,3-bis(2-benzimidazolyl)benzene has overlapped with the band at 1329 cm^{-1} of the hardener. This band has decreased in intensity but has broadened as the reaction progressed. The bands at 1623 and 1602 cm^{-1} because of C=C and C=N stretching modes showed marginal change in intensity. The peaks at 1852 and 1794 cm^{-1} because of the anhydride are affected as the cure reaction proceeded. The former decreased



Scheme 2 Carbonyl group interact with imine hydrogen of the ligand to form O—H bond. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Scheme 3 Carbonyl group open up the epoxy ring facilitating curing. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

in intensity, whereas the latter has shifted to 1732 cm^{-1} without appreciable change in its intensity. This is indicative of the two carbonyl groups reacting in different ways, and this is evident by the gradual disappearance of the epoxy peak at 906 cm^{-1} . This suggests that the epoxy ring opens up during the reaction (Schemes 1–3).

The following mechanism may be proposed for the hardener reacting with the tertiary nitrogen of 1,3-bis(2-benzimidazolyl)benzene.

The tertiary nitrogen would open up the anhydride ring through coulombic interaction with one of the carbonyl groups (Scheme 1). Subsequently, the carbonyl group may interact covalently with the imine hydrogen of 1,3-bis(2-benzimidazolyl)benzene resulting in a covalent O—H bond as shown in Scheme 2.

Alternatively, in the presence of epoxide, the carbonyl group would open up the epoxy ring, facilitating the curing of resin-hardener system. The reaction is depicted in Scheme 3.

CONCLUSIONS

Epoxy resins can be converted to thermosetting materials by the action of curing agents, which are either Lewis acids or Lewis bases or reagents containing NH hydrogen. The addition of accelerators such as benzimidazole derivatives and their complexes to the resin system decreases the cure time. 2-Phenyl(2-benzimidazolyl)benzene enhances the curing activity of bisphenol-A-based resin, and its activity is comparable with that of the commercial accelerator. The cure activity decreases when benzimidazoles are complexed with divalent metal ions such as cobalt, nickel, copper, and zinc. The kinetic data indicate that the rate of curing is enhanced in the presence of the 1,3-bis(2-benzimidazolyl)benzene. The storage life of the catalyzed system is also affected in the presence of some of the heterocycles. The thermomechanical property has improved with the addition of a benzimidazole to the resin system. Electrical properties remain unaltered at ambient temperature.

In the epoxy-anhydride system, 1,3-bis(2-benzimidazolyl)benzene enhances the rate of curing. The anhydride hardener reacts with the tertiary nitrogen of 1,3-bis(2-benzimidazolyl)benzene and disrupts the anhydride ring. Further, the opening up of the epoxy ring leads to gelation and polymerization with enhanced crosslinking.

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