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N Heterocycles in Electrical Applications

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Abstract: **In order to boost sustainable growth in industries, formulating and implementing safe and effective productivity schemes is essential. Economic growth and national transformation would naturally follow. Risks to industries has been a potential hazard many times. Fires caused by faulty insulation systems have affected the safety in homes and in industries. Anhydride cured epoxy resins have been extensively used in the past for electrical insulation. The cure was accelerated with commercial accelerators which were known to be toxic and had a short shelf life. An effort is made in this paper to substitute the commercial accelerator with a suitable and safer alternate. A few N-heterocycles are prepared and they are used as the substitutes. They have a longer shelf life and have no known adverse physiological effects. They liberate nitrogen on heating providing an inert atmosphere in times of fire. Thus minimizing the damage. Various studies including kinetic, mechanical and electrical properties of these cured resins reveal that the results are comparable and at times better than those cured with commercial accelerator.**

Keywords: **Insulation, epoxy resins, N- heterocycles.**

I INTRODUCTION

The International Monetary Fund has projected slow growth in the advanced economies between 2012-17. In such a scenario, risks to business establishments can prove to be a serious obstacle to development. In order to stimulate growth, we need a risk free environment. It is important to analyse and quantify potentially destructive risks to industries so that sustainable growth can be assured. Risk surveys in industries show that almost 10% of the risk factor points to fire accidents [1].26% of industrial fires are attributed to faulty electrical circuits [2]. Electrical fires are mainly caused due to short circuiting. The smoke that evolves due to the incomplete combustion chokes and causes breathlessness and most deaths are due to this cause. Smoke kills faster than fire. An effort is made to substitute carbon atoms with nitrogen atoms in electrical insulation material to check if its properties can be improved.

Polymer materials like epoxy resin systems, have been associated with electrical applications since the early days of the electrical industry. 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, epoxy resins 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 laminations. Bases such as tertiary amines are commonly used to accelerate the curing process. Evaluation studies of cured epoxy resin systems are of considerable importance in understanding their electrical insulating behavior.

The perfection of cures depend on the nature of curing and accelerator. Material degradation may arise due to the formation of voids or cracks and these would promote the formation of destructive ionisation even under normal rated voltage of the equipment. A US patent [3] has revealed the use of 0.1 – 0.25 parts per hundred of an imidazole as curing agent in epoxy system. The infusible product obtained has been found to have excellent electrical properties. A Dutch patent [4] has revealed the use of amines and imidazoles in curing poly-epoxides and the product is reported to have outstanding electrical properties. Hardening of epoxy resins in the presence of benzimidazoles has been reported by Chernobai [5]. The samples obtained have retained longer shelf life and have had higher heat resistance and dielectric loss tangent. Beck Hans et al [6] have reported the use of heterocyclic compounds as reactive diluents and viscosity depressant for thermosetting epoxy resins. The product has been found to maintain a low dielectric loss factor.

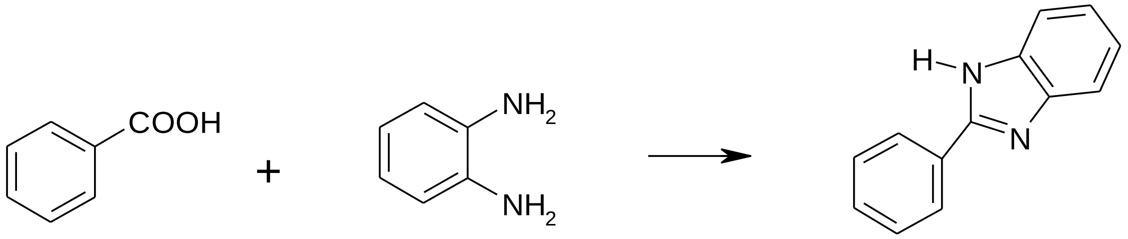
A Japanese patent [7] has revealed the use of benzimidazoles in curing epoxidized resins for good electrical and mechanical properties. Glass and quartz fabric – reinforced polymers including epoxy – poly benzimidazole laminating systems have been evaluated for application in high temperature microwave systems [8].

In this paper an attempt has been made to study the effect of different benzimidazolyl benzene and a commercial accelerator (K112) on the thermal and electrical properties of the cured resin- hardener system. The Gel time has been carried out. Thermal properties and electrical properties such as loss factor 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(benzimidazolyl)benzene [1,3Bz}involving tertiary and secondary nitrogen atoms.

II PREPARATION OF BENZIMIDAZOLES

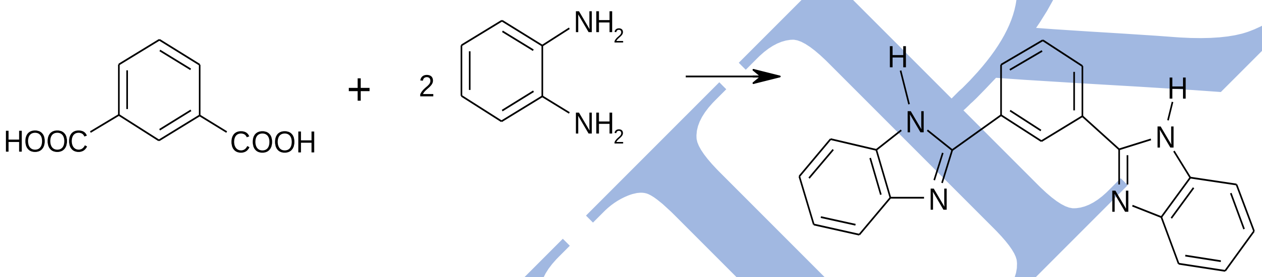
1.Preparation of 2-phenyl benzimidazole [9]

Benzoic acid (0.1 m mole) was added to a mixture of o-phenylene diammine (0.1 m mole) in syrupy phosphoric acid (50 ml) and stirred for 4 hours in a sand bath at 240^{0}C. The greenish blue melt that was obtained was poured into cold water and subsequently neutralized with 10% sodium carbonate solution. The pink coloured solid separated was recrystallised from ethanol and the resultant white needles was checked for its melting point (m.p.294^{0}C ; yield 88%.)



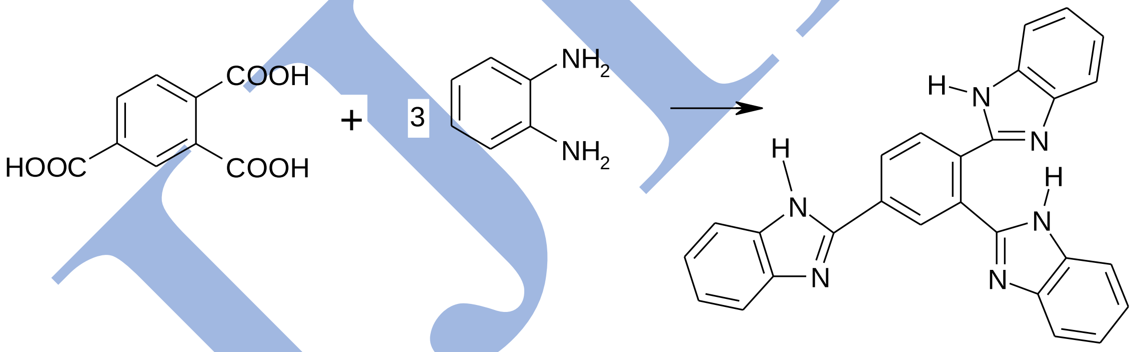
2. Preparation of 1,3-bis(benzimidazolyl) benzene [10]

Isophthalic acid (8.3 g, 0.05 m mole) was added to a mixture of o-phenylene diamine (10.8 g, 0.1 m mole) in syrupy phosphoric acid (50 ml) and stirred for 4 hours in a sand bath at 240^{0}C. The greenish blue melt that was obtained was poured into cold water and subsequently neutralized with 10% sodium carbonate solution. The pink colored solid separated was recrystallised from ethanol and the resultant white needles was checked for its melting point. (m.p. 185^{0}C; yield 85%)



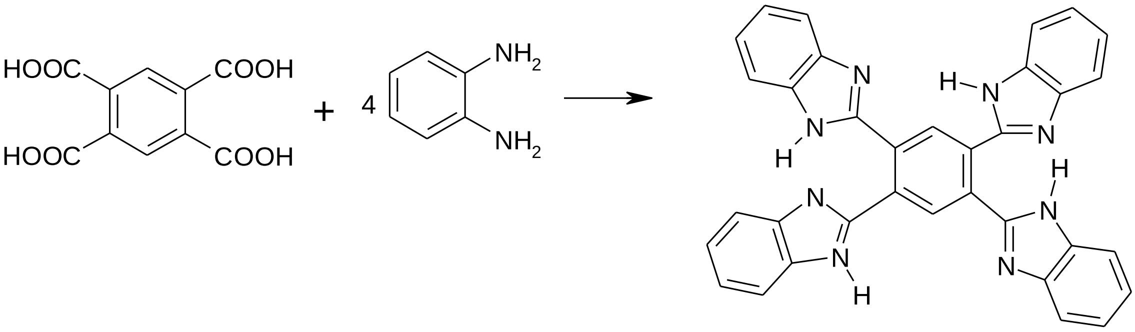
3 Preparation of 1,2,4-tris(benzimidazolyl)benzene

1,2,4 benzene tricarboxylic acid (1m mole) was added to a mixture of o-phenylene diamine (3m mole) in syrupy phosphoric acid (50 ml) and stirred for 4 hours in a sand bath at 240^{0}C. The greenish blue melt that was obtained was poured into cold water and subsequently neutralized with 10% sodium carbonate solution. The pink colored solid separated was recrystallised from ethanol and the resultant white needles was checked for its melting point.(m.p. ; yield 75%)



4. Preparation of 1,2,4,5-tetrakis(benzimidazolyl)benzene

Pyromellitic acid (1 m mole) was added to a mixture of o-phenylene diamine (4 m mole) in syrupy phosphoric acid (50 ml) and stirred for 4 hours in sand bath at 240^{0}C. The greenish blue melt that was obtained was poured into cold water and subsequently neutralized with 10% sodium carbonate solution. The pink colored solid separate was recrystallised from ethanol and the resultant white needles was checked for its melting point (m.p. <450^{0}C; yield 85%)



III METHODOLOGY

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. 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.

Gel time of the benzimidazoles on resin-hardener system

The effect of benzimidazoles and their complexes on the gel time of the epoxy resin system at different temperatures was monitored. The values obtained at 0.125 – 0.5 phr of the accelerators are tabulated in Table 1

Thermal properties of the cured system

Thermal properties are measured and tabulated in Table 2

(i) Heat distortion temperature (HDT):

The degree of cure of a resin material is reflected in the magnitude of its heat distortion temperature (HDT) and it is usually measured according to ASTMD 648-56 method. HDT specimens are subjected to an arbitrary set of testing conditions at a specified heating rate of 2^0/min. The data could be used to predict the behavior of the test material at elevated temperature.

(ii) Glass Transition Temperature (T_g):

It provides a means of characterizing the cure and often defines the optimum temperature of use. Enthalpy relaxation accompanying the glass transition would give information about the thermal history or physical aging of thermosets [11]. According to Fava [12] the glass transition temperature of an epoxy system increases smoothly as the reaction proceeds to completion. An empirical correlation between relative degree of cure and glass transition temperature has been established by Gray [13].

(iii) Thermo-Gravimetric Analysis (TGA):

This is a technique that measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. A sensitive balance is used to follow the weight change of the sample as a function of temperature. The temperature is increased at a constant rate for a known initial weight of a substance and changes in weight are accurately recorded at different times.

Electrical properties:

The power factor or the dielectric loss factor or the tan delta property of a material is required to be known in order to find its suitability to any electrical application. 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 subject to variations of voltage. The loss factor of the cured epoxy resin system at 0.5phr (parts per hundred) of the ligand and K112 have been studied both at room temperature as well as at higher temperatures at 500V. They are recorded in Figure 1.

Cure mechanism:

IR spectra before and after cure is shown in Figure 2

IV RESULTS AND DISCUSSION

Gel time studies

The results indicate that the gel times of the resin system in the presence of benzimidazole are lower when compared with the blank system which does not have any accelerator. The values decrease with increase in temperature. The gel time data of 2-phenyl benzimidazole and 1,3-bis(benzimidazolyl)benzene are comparable with that of the commercial accelerator (K-112).

Table 1 Effect of gel time on cured epoxy system

System	Concentration of accelerators (phr by weight)	Gel Time (mins) at temperature (K)				
		373	393	413	433	453
Blank System	--------------	**1110**	690	257	114	43
2-phenyl benzimidazole	0.5	73	22	12	06	03
	0.375	89	32	13	08	05
	0.25	96	43	15	08	05
	0.125	140	61	30	16	10
1,3-bis(benzimidazolyl)benzene	**0.5**	**111**	32	08	07	04
	0.375	**125**	45	11	08	05
	0.25	**140**	55	15	14	08
	0.125	**180**	80	25	18	10
1,2,4-tris(benzimidazolyl)benzene	0.5	113	37	19	12	11
	0.375	160	90	55	28	20
	0.25	179	110	65	33	23
	0.125	186	450	225	66	47

1,2,4,5-tetrakis(benzimidazolyl)benzene	0.5	800	352	157	50	31
	0.375	870	473	213	52	17
	0.25	912	598	252	63	20
	0.125	960	612	257	76	28
K-112	**0.5**	**70**	19	06	05	03
	0.375	85	32	08	07	05
	0.25	101	47	13	12	18
	0.125	135	60	16	15	09

Thermal Properties

Table 2 Thermal properties of the blank, and the systems cured with 1,3 Bz and K112

Accelerator	HDT (K)	Transition temperature (K)	TGA (K)
Blank	349	380	350
K112	358	386	356
1,3 Bz	365	392	379

(i) Heat distortion temperature (HDT):

Higher values of HDT correspond to higher degree of cross-linking of the cured system. This test could be used as a rough guide to a range of temperatures over which the physical and electrical property would remain almost constant. The system cured with 1,3 Bz seems to be superior compared to the one cured with commercial accelerator.

(ii) Glass Transition Temperature (T_g):

The glass transition temperature is the temperature at which the molecular rotation about single bonds becomes restricted. It is the temperature at which transition from the glassy to the high elastic state or vice versa occurs. The results show that the system with 1,3 Bz is superior compared to other systems.

(iii) Thermo-Gravimetric Analysis (TGA):

The system cured with 1,3 Bz showed a very high level of stability since its value is 379K.

Effect of Electrical properties of the benzimidazoles on resin-hardener system

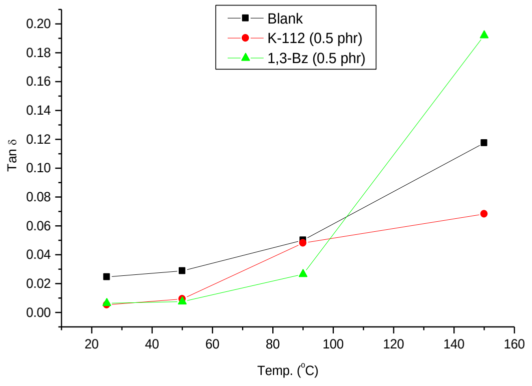


Figure 1: Tan ∂ values with respective to temperature for cured systems

It has been observed that at room temperature, the presence of accelerators have not altered the tan ∂ value. With increase in temperature the plot indicates that the trend in loss values is almost equal to the blank. Thus, this electrical property is not deteriorated by the addition of an accelerator.

Cure mechanism:

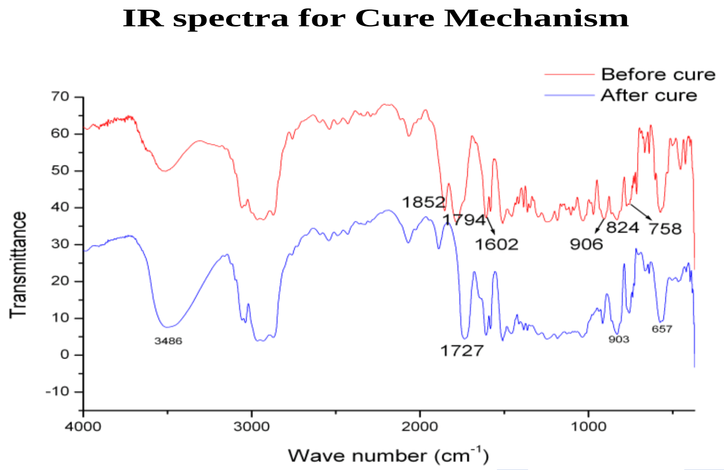
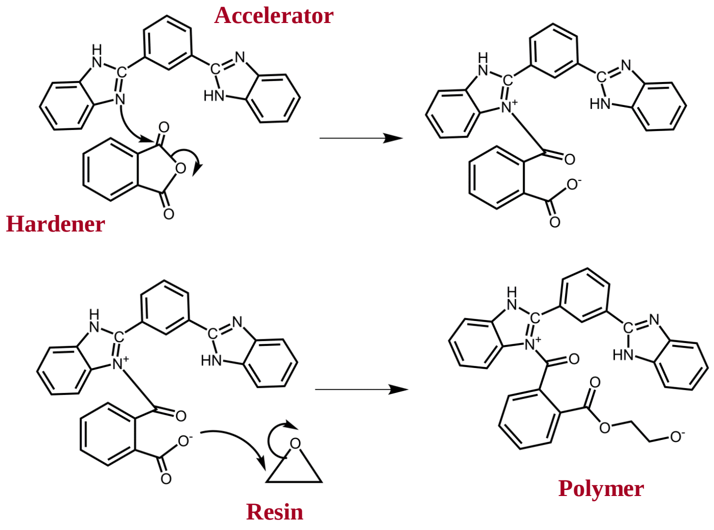


Figure 2 : IR Spectra before and after curing

It has been observed in the IR spectra 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 progresses. This suggests an increase in the extent of cross linking.

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 in intensity, where 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.

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



The tertiary nitrogen would open up the anhydride ring through coulombic interaction with one of the carbonyl groups. Subsequently, the carbonyl group may interact covalently with the imine hydrogen of 1,3-

bis(benzimidazolyl)benzene resulting in a covalent O-H bond as shown. Alternatively, in the presence of epoxide, the carbonyl group would open up the epoxy ring, facilitating the curing of resin-hardener system.

V 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 accelerator to the resin system decreases the cure time. 1,3 (benzimidazolyl)benzene enhances the curing activity of bisphenol-A-based resin, and its activity is comparable with that of the commercial accelerators.. The thermal property has improved with the addition of benzimidazoles to the resin system. Electrical properties remain unaltered at ambient temperature.

Since then other N heterocycles and their complexes have also been prepared and their properties evaluated.

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