

Development and characterization of Flame retardant epoxy resin for battery terminal sealing application

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ABSTRACT : *The present objective of the study is to develop and characterize the Flame retardant epoxy resin for the battery terminal sealing application. The major use of this sealing application is to identify the positive and negative terminals of the battery and to avoid acid leaks. Different types of epoxy resins and hardeners are explored and different mixing ratios were tried to finalize the optimum composition. Also identified vital test methods for the characterization of cured flame retardant resin and hardener.*

KEYWORDS: *Flammability, Epoxy Resin, Hardener, Battery terminal sealing*

Date of Submission: 11-01-2019

Date of acceptance: 26-01-2019

I. INTRODUCTION

Epoxy resins may be higher or lower molecular weight polymers with at least two epoxide groups. Sometimes, the epoxide group is either a glycidyl or oxirane. A wide range of epoxy resins are produced industrially. Petroleum derivatives are used as raw materials for epoxy resin production which are commercially available. Epoxy resins are pure materials which contains polymeric or semi-polymeric materials. An important criterion for epoxy resins is the epoxide content. It is commonly expressed as the epoxy equivalent weight, which is the number of epoxide equivalents in 1 kg of resin (Eq./kg), or as the equivalent weight, which is the weight in grams of resin containing 1 mole equivalent of epoxide (g/mol). To achieve maximum physical properties, epoxies are typically cured with stoichiometric or near-stoichiometric quantities which are curative. Blending different grades of epoxy resin, as well as use of additives, plasticizers or fillers is common to achieve the desired processing or final properties, or to reduce cost. Use of blending, additives and fillers is often referred to as formulating.

II. MATERIALS AND METHODS

Epoxy resins consist of two components that react with each other forming a hard, inert material. Part A consists of an epoxy resin and Part B is the epoxy curing agent, sometimes called hardener. In order to discuss the more specific classifications of epoxy resins we must dive into some technical info.

A. TYPES OF RESIN MATERIAL

A. Bisphenol A epoxy resin

Bisphenol A diglycidyl ether is commonly abbreviated as DGEBA which is used as constituent of epoxy resins. It is unstable and cost-effective, which demonstrates excellent alkali resistance, good acid resistance and fair-to-good solvent resistance (1) (2).

B. Bisphenol F epoxy resin

Bisphenol F may also undergo epoxidation in a similar fashion to Bisphenol A. It contains higher mean epoxy content per gram. It is a low-viscosity material which provides excellent alkali resistance, improved acid and solvent resistance compared to Bisphenol A (2).

C. Novolac epoxy resin

Novolac epoxy resins are synthesised by reacting phenolic novolac resin with epichlorohydrin in the presence of sodium hydroxide as a catalyst. These polymer network exhibits high temperature and chemical resistance, but low flexibility (3). Novolac epoxy resins are highly recommended in formulations for high-performance applications requiring excellent chemical resistance, solvent resistance and exceptional high temperature resistance than the standard Bisphenol A epoxy resins.

Based on the literature survey and the available data, Bisphenol F is chosen for the study as it possess good chemical and thermal resistance and stable in nature.

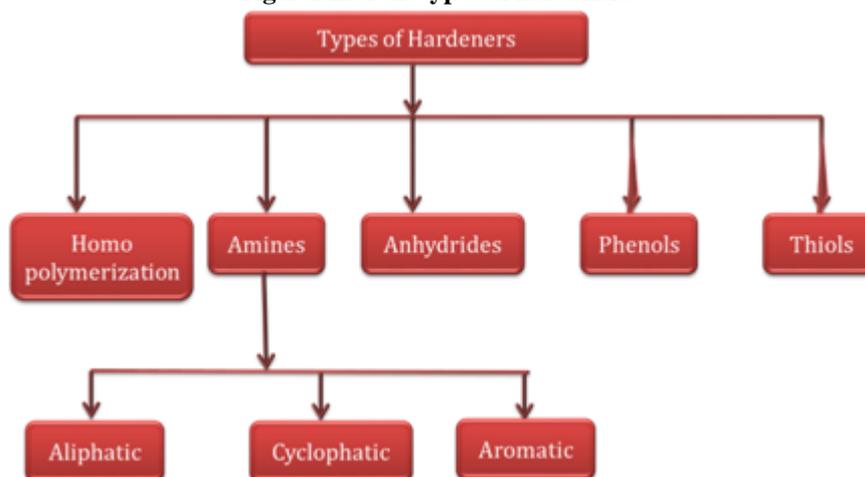
B. TYPES OF HARDENERS

At their most basic, epoxy curing involves combining an epoxy resin with a hardening agent, which are then allowed to react with one another before being applied. Depending on the specific system used, the epoxy base resin may be clear or pre-pigmented. In general, uncured epoxy resins have only poor mechanical, chemical and heat resistance properties. However, good properties are obtained by reacting the linear epoxy resin with suitable curatives to form three-dimensional cross-linked thermoset structures. This process is commonly referred to as curing process. Exothermic reaction occurs during the curing process.

In principle, any molecule containing a reactive hydrogen may react with the epoxide groups of the epoxy resin. Common classes of hardeners for epoxy resins include amines, acids, acid anhydrides, phenols, alcohols and thiols. Relative reactivity (lowest first) is approximately in the order: phenol < anhydride < aromatic amine < cycloaliphatic amine < aliphatic amine < thiol.

The epoxy curing reaction may be accelerated by addition of small quantities of accelerators. Tertiary amines, carboxylic acids and alcohols (especially phenols) are effective accelerators. Bisphenol A is a highly effective and widely used as accelerator, but is now increasingly replaced with Bisphenol-F due to its health concerns with this substance (2).

Fig.1. Different types of hardeners



A. Homopolymerisation

Epoxy resins are reacted themselves in the presence of an anionic or cationic catalyst for curing. This process is called as catalytic homopolymerisation. High temperature is required for curing and the cured component is brittle even though it exhibits high thermal and chemical resistance (4).

B. Amines

Ammonia with organic groups in place of hydrogen atoms are called as Amines. These are used as epoxy hardeners and are classified as aliphatic- having only aliphatic groups attached, aromatic- having one or more aryl groups attached and open-chain, in which the nitrogen is not part of a ring, or cyclic, in which it is a member of a ring (generally cycloaliphatic). The reactivity order of these amines is aliphatic amines > cycloaliphatic amines > aromatic amines respectively. Temperature resistance is as of same reactivity order. Handling issues are present with aromatic hardeners there by aliphatic and cyclo aliphatic are safer to use. The resins that cured with aliphatic are shown excellent thermal and mechanical properties. General properties of aliphatic amines are high reactivity, fast cure at ambient or low temperatures, Reasonable color retention and high chemical resistance(4).

C. Anhydrides

One of the most widely used curing agents for epoxy resins is anhydrides. Anhydride curing agents are derived from the diacids by eliminating water molecule. Most of the anhydrides used for curing epoxy resins are liquids. The low viscosity and high latency of anhydride hardeners makes them suitable for processing systems which require addition of mineral fillers prior to curing. The reactivity of liquid anhydride curing agents are very slow even at high temperature (5, 6).

D. Phenols

In organic chemistry, phenols are a class of chemical compounds consisting of a hydroxyl group (—OH) bonded directly to an aromatic hydrocarbon group. They are similar to alcohols but forms stronger hydrogen bond and are highly reactive toward electrophilic aromatic substitution and participates in the reaction at elevated temperatures in presence of catalyst. The cured material contains ether linkages which will exhibit higher oxidation and chemical resistance(7).

E.Thiols

Thiols are a class of organic chemical compounds varied with alcohols and phenols by containing a sulfur atom in place of the oxygen atom. They are highly reactive with the epoxide group, even at ambient or sub-ambient temperatures. High reactivity of the thiol group makes it useful for natural curing applications .Thiols have a characteristic odour, and are toxic in nature (8).

By reviewing the different hardeners, aliphaticamines are chosen due the following benefits.

- No handling issues
- Fast curable at low temperature
- Compatible with bisphenols
- Good mechanical /thermal properties

C. TYPES OF FLAME RETARDANT MATERIALS:

There are vast types of flame retardant materials comprising of eco-friendly and non-ecofriendly. These are the fillers of epoxy resin that imparting flame retardant property to the base resin. Explored different flame retardant materials for the study.

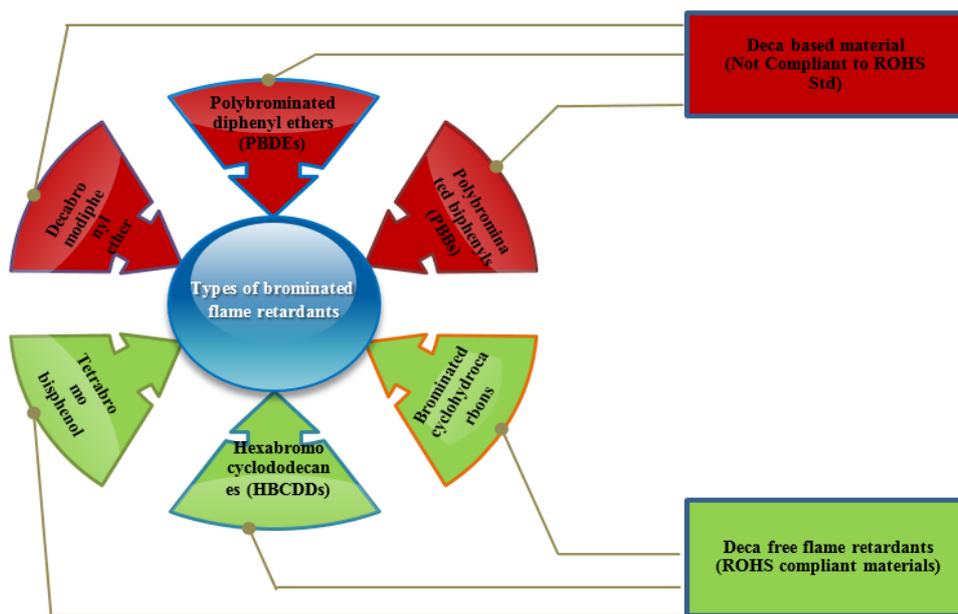


Fig.2. Flame retardant Materials

As the classification clearly explains, the RoHS compliant material falls under eco-friendly category. Hence, eco- friendly category materials are chosen for the epoxy resin material as a filler. Based on the application, Tetrabromobisphenol A material is shortlisted for our application purpose (9).

Table.1. FR Material applications

Material	UL rating	Applications
TBBPA	UL V0	Thermo Plastics, Electronic equipment, circuit boards
HBCDD	UL – V0	Insulation for building industry, Textiles industry
BCHC	UL- V2	Textiles, plastics

All the materials were mixed at the manufacturer's location and provided as Resin and Hardener materials with two different colors i.e. Post office Red and Black. The colors were achieved with epoxy compatible pigments. The mixing and characterization trials were done at our end.

III. EXPERIMENTAL DATA

The following parameters were explored to finalize the suitable composition of Resin and Hardener for Battery terminal sealing application

- Mixing time
- Mixing ratio (Resin : Hardener)
- Pot life
- Curing time
- Hardness (Shore D)

a. Mixing time

Mixing time of the resin and hardeners is an important process. It is the initiation phase of exothermic reaction which is necessary for the curing of resin and hardener. By providing proper mixing time, the air bubbles, pot life and color deviations can be optimized. For verifying the mixing time, different mixing ratios (100:20 to 100:60) are investigated.

Table. 2. Mixing time

S. No	Mixing time (minutes)	Observations
1	2	The homogeneous solution wasn't formed
2	3	Slight hardener color shades after curing are observed
3	4	No abnormalities are observed Homogeneous solution is formed
4	5	Small air bubbles after mixing the solution are observed
5	6	More air bubbles after mixing are observed

The inference from the experiment carried out is 4 minutes of mixing time exhibited with good results.

b. Pot life

Pot life and curing times are the outcomes of the mixing time and mixing ratio. Pot life is defined as the time between mixing the resin and hardener & the initiation of curing process. The product gets unusable (becomes highly viscous) at the end of the pot life. The total time taken from mixing to complete curing is considered as curing time. Higher the better for pot life where as lower the best for curing time.

Table. 3. Pot life

S. No	Mixing Composition		Pot life (minutes)	Observations
	Resin	Hardener		
1	100	20	25	No abnormalities are observed
2	100	30	20	No abnormalities are observed
3	100	40	15	No abnormalities are observed
4	100	50	10	Pungent smell, high temperature and fumes while pouring are observed
5	100	60	6	High fumes & high temperature while pouring are observed. High viscous solution is formed within less time

The inference from the experiment is the pot life is inversely proportional to the hardener content is observed.

The optimum ratio should result in low curing time and high pot life, here can identify 100:40 only suppresses that requirement.

c. Curing time

Epoxy resin and hardener are mixed for uniformity and in the due course, exothermic reaction is initiated and then material starts curing with an increasing temperature up to 50°C. There should not be any stress marks on the cured material to treat this as a complete curing.

Table. 4. Curing time

S. No	Mixing Composition		Curing time (minutes)	Observations
	Resin	Hardener		
1	100	20	>360	No abnormalities are observed
2	100	30	270	No abnormalities are observed
3	100	40	180	No abnormalities are observed
4	100	50	120	No abnormalities are observed
5	100	60	60	Air bubbles and physical distortion after curing are observed

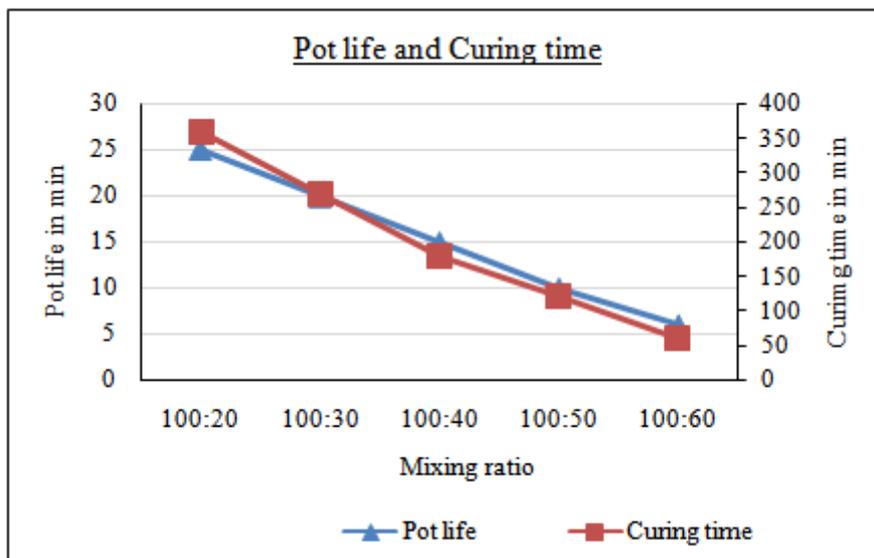


Fig.3. Pot life and Curing time Vs. Mixing ratio

d. Hardness (Shore D)

Shore D hardness is measured for the different composition after complete curing and as listed below..

Table .5. Hardness (Shore D)

S. No	Mixing Composition		Hardness (Shore D)	Observations
	Resin	Hardener		
1	100	20	36	Low hardness and high curing time are observed
2	100	30	58	Moderate hardness and high curing time are observed
3	100	40	75	No abnormalities are observed
4	100	50	85	No abnormalities are observed
5	100	60	-	Air bubbles and physical distortion after curing are observed

The inference from the experiments carried out, 100:40 ratio exhibited good results in terms of Pot life, Curing time and Hardness (Shore D). Finalized this mixing ratio and conducted different characterization tests on this ratio cured materials.

IV. CHARACTERIZATION OF CURED RESIN

The main objective of this study is to identify the resin and hardener for Battery terminal sealing application. The cured resin should be resistant to acids and chemicals, shouldn't deform under high thermal conditions. The cured resin should be flame retardant i.e. fire proof. In view of these requirements, identified some vital analysis that are required for the Cured Resin as listed below:

- i. Acid resistance
- ii. Flammability (as per UL 94)
- iii. Thermal test (as per JIS)

i. Acid resistance

Acid resistance test is done based on IS: 1146 – 1981. Initially, the test sample is washed with Dil.HCL and then thoroughly cleaned with double distilled water. The sample is dried in ambient condition and the initial weight is measured. Then the sample is immersed in a 1000 ml beaker containing 1.245 specific gravity of Sulphuric Acid at 60 ± 2.5 °C for 28 days. At the end of test period, the sample is removed and cleaned with distilled water. The sample is dried in a hot air oven at a temperature of 105 ± 5 °C for 60 minutes and then cooled at ambient conditions. Then the final weight is measured and the percentage of weight loss is calculated(10)

The test carried for both the red and black cured resins which represents positive and negative terminals of the battery. The observed weight loss is very minimal i.e. 0.05 %. The cured resin exhibits good chemical resistance.

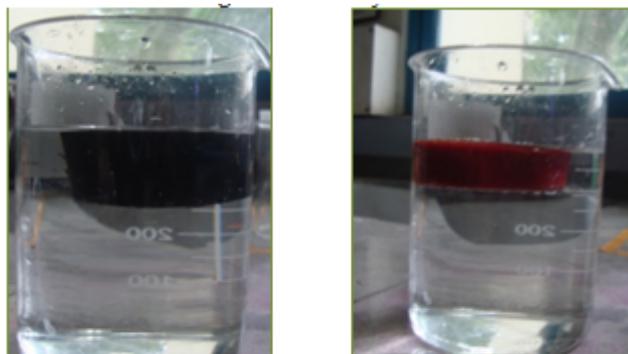


Fig 4. Acid resistance of cured resin

ii. Flammability as per UL 94

UL94 is the finest standard to check the flammability properties of poly material. Cured resin considered as the specimen and is used to identify the UL 94 V0, V1 and V2 flammability ratings. It evaluates both the burning, afterglow times and dripping of test specimen. Before performing the test, the test specimens are pre-treated at 23 ± 2 °C and 50% relative humidity for a period of 48 hours. In vertical position, the specimens are subjected to a defined flame ignition source with a flame height of 20mm for a specific time period. The specimens prepared and conducted the analysis as per the standard. The notable observations are given below(11).



Fig 5. Flammability test as per UL94

The cured material has met the requirements of V0 grade as per UL94. The dripping particle doesn't ignite the cotton and the afterglow time is less than 10 sec.

iii. Thermal test as per JIS

Thermal test carried out as per the JIS standard to check the contraction and expansion of the cured resin from the post. The battery covers with cured resin were kept in heating and cooling cycles simultaneously for 48 hrs at 60 °C & -40 °C (12). The covers were examined after 48 hours for aesthetic issues. There is no discoloration and no expansion/ contraction are observed.

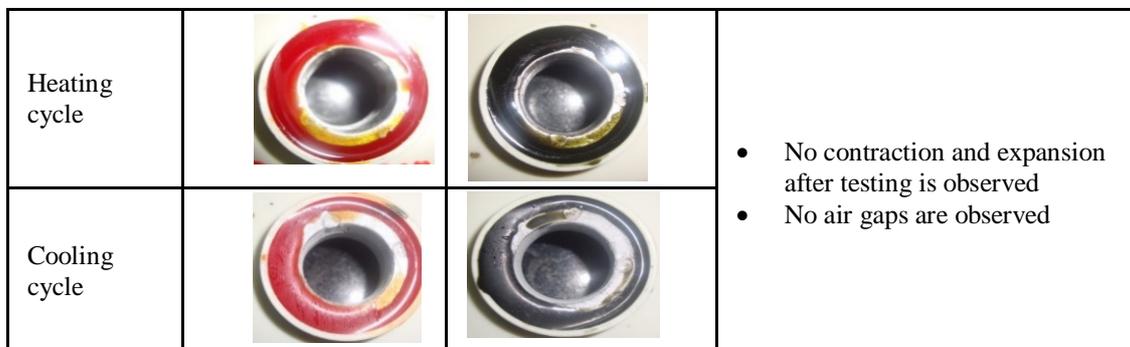


Fig. 6. Thermal cycling test

V. CONCLUSION:

By verifying the different types of resin and hardeners material, finalized the bisphenol F resin and aliphatic amines. The compatibility of these two materials are really good and exhibited excellent thermal, chemical and acid resistance. Based on the results of different experiments conducted, 100:40 mixing ratio is finalized. The characterization techniques were taken from different standards in the view of battery applications. The flammability property is achieved and confirmed that the material is complied with V0 ratings. The FR reagent used in this combination is ROHS compliance and eco-friendly material. The formulated cured resin both red and black are proven without any acid leaks at terminal.

VI. ACKNOWLEDGEMENT

The authors acknowledge with gratitude the resources and support provided by the Management of Amara Raja to carry out this study. Thanks to Roto polymers, Chennai for providing technical details and materials for the trials. Special thanks to Shyam for his support in the theoretical work.

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Madhava Rao. B" Development and characterization of Flame retardant epoxy resin for battery terminal sealing application" American Journal of Engineering Research (AJER), vol.8, no.01, 2019, pp.260-266