

Development of Siliconized Epoxy Resins and Their Application as Anticorrosive Coatings

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Received March 31, 2011; revised May 17, 2011; accepted July 3, 2011

Abstract

The present work involves the development of siliconized epoxy resin to overcome the drawback of epoxy resin like poor impact strength, high rigidity and moisture absorbing nature because of which they are not applied as corrosion resistant coating. By embedding silicone into the back bone of polymeric resin the above drawback can be reduced to substantial level. For achieving this, siliconised epoxy resins were prepared by reacting amine terminated silicone resin with novolac epoxy resin and meta-phenylenediamine was used as curing agent. The applied films of coating were baked at 150°C. Cured films were evaluated for their thermal, mechanical, chemical and corrosion resistance properties to ascertain the commercial utility of these eco-friendly resins for use in anti corrosive formulations. The siliconized epoxy resins system was found to exhibit good thermal and anticorrosive properties.

Keywords: Epoxy Resin, Silicone Resin, Anticorrosive Coatings

1. Introduction

A novel coating of high performance polymeric material is a need of today. These polymeric materials have superior mechanical, thermal and anticorrosive characteristics ideally suitable for adverse environmental conditions [1]. Inorganic-organic hybrid resins have become a creative polymer with unique combination of distinctive properties of both constituents for applications in various industries.

Epoxy resins are widely used in protective coatings, adhesives, sealant, fiber reinforced composites and electronic industry due to their outstanding surface properties like low shrinkage, ease of cure and possessing good moisture, solvent and chemical resistance, and excellent adhesion performances [2,3]. They lack fracture resistance, impact strength, low thermal stability, low pigment holding ability, flexibility and poor hydrophobicity, which restrict their wide application in the field of coatings and paints [4,5]. To improve these properties the component like rubber, polyurethane silicone are added as modifier to the epoxy resins [6-8].

Silicones are used in coating materials because of the following properties:

- improved water repellency
- improved thermal stability; resistance to oxidation
- they retain physical properties over a wide range of

temperature

- low toxicity
- they impart unique flexibility to the backbone chain and intrinsic surface active property.

Silicone is suitable modifier for epoxy resins. The modified resin has superior thermal and thermo-oxidative stability, fracture energy, excellent moisture resistance, partial ionic nature, low surface energy and good hydrophobicity [9].

Aliphatic epoxy modified polysiloxane coatings can be prepared by the combination of aliphatic epoxy resins, polysiloxane, organo oxysilane and difunctional aminosilanes hardeners which provide highly improved resistance to ultraviolet and weathering in sunlight and improved chemical and corrosion resistance.

In practical applications, amine-based hardeners hold the largest share in epoxy hardener markets. Aromatic amine cured epoxy resin systems have excellent resistance to water, solvents and alkaline solutions as well as a range of good to excellent dilute acid resistance [10,11].

Generally, the incorporation of siloxane into polymer has been carried out through physical blending methods [12,13]. The blending of siloxane and epoxy causes an increase in viscosity, phase separation and bleeding of siloxane component of the blended system.

In the present work an attempt has been made to im-

prove the shortcomings of siloxane epoxy blended coating. The properties of novolac epoxy resin are enhanced by embedding the amine terminated silicone into the backbone of polymeric resin. As silicone is chemically bonded to epoxy resin, the resulting materials have desired properties and with more consistent results.

2. Experimental

2.1. Materials

Phenol novolac epoxy resin, Synthesized in laboratory, Epichlorohydrin, EMerck, Diethoxydimethyl silane, Aldrich γ -aminopropyl diethoxy methyl silane, Lancaster.

2.2. Methods

2.2.1. Synthesis of Novolac Resin

Novolac Resin was prepared by condensation reaction between phenol and formaldehyde in acidic medium. Initially, phenol (1 mole) with some quantity of water was taken in three neck flask. The pH was adjusted to 0.5 with sulphuric acid (used as catalyst) and the contents were heated to 90°C with constant stirring. The required amount (0.5 mole) of formaldehyde (37% formaline solution) was added over a period of 3 hours through a dropping funnel, and stirring was continued for an additional 30 minutes, water was then removed under vacuum.

2.2.2. Synthesis of Epoxy Novolac Resin

Laboratory prepared Novolac Novolac Resin (1 mole) was reacted with Epichlorohydrin (10 mole) at 110°C and 40% Sodium hydroxide solution was added gradually to the reactants over a period of 3 hours through a dropping funnel. After completion of reaction, salt (NaCl) was removed by washing with hot water and then water was removed through vacuum distillation.

2.2.3. Determination of Epoxide Equivalent Weight (EEW)

Epoxide equivalent weight was determined by standard BIS method.

2.2.4. Cohydrolysis of Diethoxydimethyl Silane and γ -Aminopropyl diethoxy Methyl Silane

Calculated amount of Diethoxydimethyl silane and γ -

aminopropyl diethoxy methyl silane in 97:3 ratio were taken in three-necked flask, 50 ml aq. alcohol (50:50) was added dropwise. The reaction was continued at 0°C with constant stirring. After complete addition of aqueous alcohol, the reaction was further continued for half an hour. The mixture was separated and distilled to make it solvent free. The resin was dried.

2.3. Characterization of Resins

The characterization of synthesized resins like epoxide equivalent and texture appearance are shown in **Table 1**.

2.4. Coating Composition and Film Preparation

The coating compositions were prepared by incorporation of amino terminated silicone resin in the ratio of 1.5 to 7.5 with curing agent (conventional amine).

Simultaneously a standard was also prepared by reacting epoxy resin with conventional amine.

The samples EA, EAS₁, EAS₂, EAS₃, EAS₄ and EAS₅ of different molar ratio (as shown in **Table 2**) were applied on steel and glass panels with the help of 100a film applicator. All efforts were made to maintain a uniform film thickness of 100 μ for the general mechanical and chemical resistance properties. The films were cured at 150°C till becomes tack free.

2.5. Curing of Epoxy Resin

The curing of the above prepared resin was carried out by using different curing agent under varying conditions:

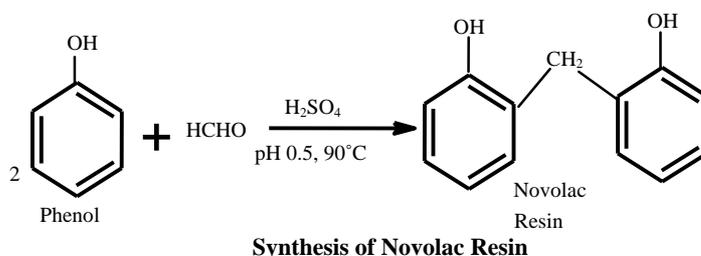
a) Curing of epoxy resin with aromatic amine: The epoxy resin was melted and mixed with stoichiometric amount of curing agent, *i.e.* m-phenylenediamine (MPDA) at a temperature 80°C.

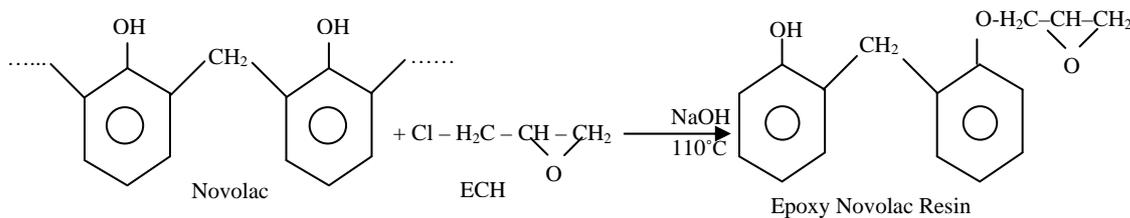
b) Curing of epoxy resin with mpda and amino terminated silicone resin in different ratios at 150°C.

3. Results and Discussion

3.1. Spectral Analysis

Figure 1 shows the I.R. spectra of novolac epoxy resin. A prominent band is observed at 940 cm^{-1} , which shows





Reactions

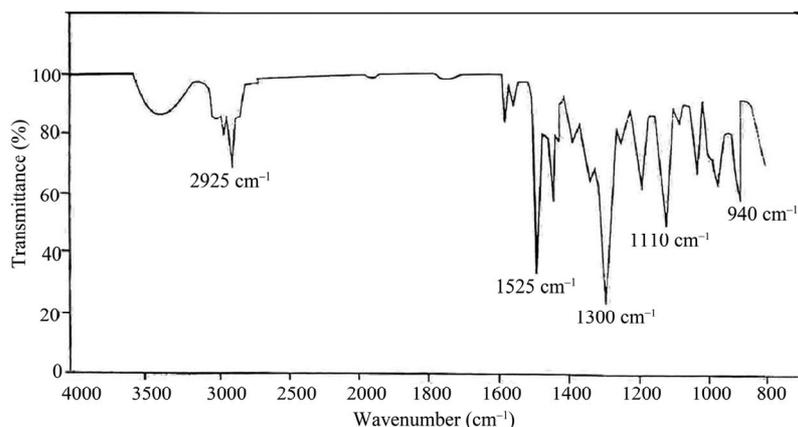
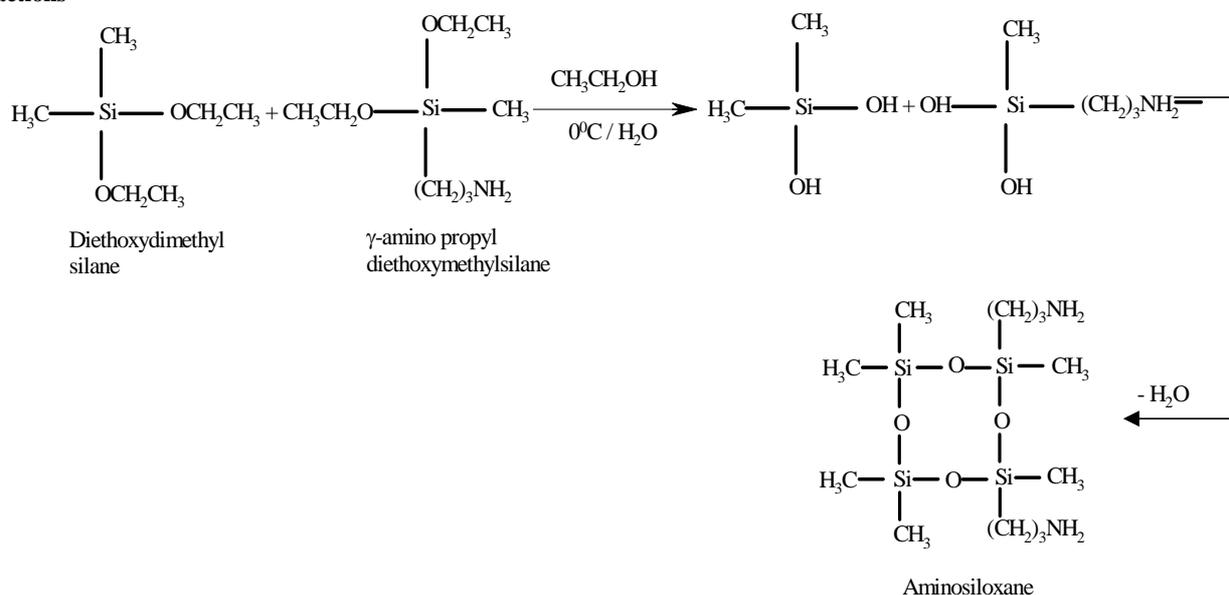


Figure 1. I.R. spectra of novolac epoxy resin.

the presence of oxirane ring in epoxy resin.

The formation of amino silicone resin was also con-

Table 1. Characteristics of epoxy and silicone resins.

S.No.	Sample	Texture appearance
1.	Novolac based epoxy resin (epoxide equivalent= 190)	Highly viscous, water white in colour.
2.	Amino silicone resin	Viscous, pale yellow

Table 2. Formulation of coating samples.

Sample	Epoxy resin	MPDA	Amino terminated silicone resin (w/w)
EA	100	15.0	--
EAS ₁	100	13.5	1.5
EAS ₂	100	12.0	3.0
EAS ₃	100	10.5	4.5
EAS ₄	100	9.0	6.0
EAS ₅	100	7.5	7.5

firmed by the I.R. spectral analysis. A peak was observed at 1021 cm^{-1} referred as Si-O-Si linkage and a peak near 3369 cm^{-1} showed the presence of $-\text{NH}_2$ group. The spectrum is presented in **Figure 2**.

3.2. Evaluation of Film Properties

The cured films were evaluated for their optical, mechanical, chemical resistance and anticorrosive properties as per the standard test methods viz. gloss at 60° (ASTM: D523-99), scratch hardness (ASTM: D 5178), pencil hardness (ASTM: D 3363-00), chemical resistance (ASTM:D 1308-87) and solvent resistance (ASTM:D 5402).

3.3. Mechanical Properties

The results of evaluation of various mechanical properties have been shown in **Table 3**.

a) Scratch hardness:

It was determined by using an automatic scratch hardness tester (Sheen U.K.). The scratch hardness varies from 1700 - 2000 g. It is clear from the data that as we increase the silicone percentage the scratch hardness of the film goes on increasing.

b) Pencil hardness:

It was measured by using pencil hardness tester (Sheen U.K.). The coating films showed that it varies from 3H-5H. Higher pencil hardness is due to higher silicone content.

c) Cross-hatch adhesion:

It was measured by using crosscut adhesion tester (Sheen U.K.). All the coating films demonstrated good cross-hatch adhesion.

d) Flexibility:

Flexibility was determined by using $\frac{1}{4}$ inch Mandrel Bend tester (Sheen U.K.). Films of all the coating compositions passed $\frac{1}{4}$ inch mandrel bend test. Based on this qualitative measurement, it can be said that all the films had reasonably good flexibility.

e) Gloss:

It was measured by using triglossometer (Sheen U.K.). On watching the films at 60° angle, it was observed that all coating films had good gloss.

3.4. Chemical Resistance

The cured films of coating samples were tested for their chemical resistance. The codified results of the chemical resistance have been presented in **Table 4**.

a) Acid resistance:

To examine the acid resistance, coated films were immersed in 1.0 N aqueous solution of sulfuric acid. Results showed that all the samples exhibit from good to very good resistance against acid.

b) Alkali resistance:

To examine the alkali resistance, coated films were immersed in 1.0 N aqueous solution of sodium hydroxide. These films showed good to excellent resistance against alkali. It was observed that sample with higher ratio of silicone were found to be excellent.

c) Water resistance:

All the coated films exhibited very good to excellent resistance against distilled water when they were exposed to it.

d) Solvents resistance:

All the coated films exhibited very good to excellent solvent resistance when they were exposed to non polar solvents like xylene and mineral turpentine oil. Resistance against MEK was fair to good because MEK is very polar solvent. Samples with high silicone content showed better performance than those having low content of silicone.

3.5. Salt-Spray Test Results

No visible corrosion products were seen on the surface of the unscratched area of the coated panels at the end of the salt-spray test. Corrosion products were seen mainly on scratched area of the coated panels. Corrosion is lower in the case of siliconized epoxy coated panels than in epoxy. Siliconized epoxy coated panels show excellent corrosion resistance in salt-spray test. The superior corrosion resistance showed by coating systems may be due to the inherent water repelling nature of silicone.

3.6. TGA Analysis

Figure 3 shows the TGA graph of the samples. Activation energy (E) for the thermal decomposition of siliconized epoxy has been evaluated from the dynamic thermograms. The fractional decomposition for the respective temperature has been evaluated from TGA graph. Higher value of activation energy (see **Table 5**) may be due to the presence of silicon in the resin. High activation energy for the decomposition of system leads to better thermal stability of the compound [14,15].

4. Conclusions

Amino containing siliconised epoxy resin was synthesized. The spectral analysis, thermal stability, mechanical and chemical resistance properties of siliconised epoxy resins were studied using FTIR, TGA and standard methods respectively. It was found that on increasing the ratio of silicone resin, the thermal stability was increased and the effect of amino silicone resin on epoxy resin im-

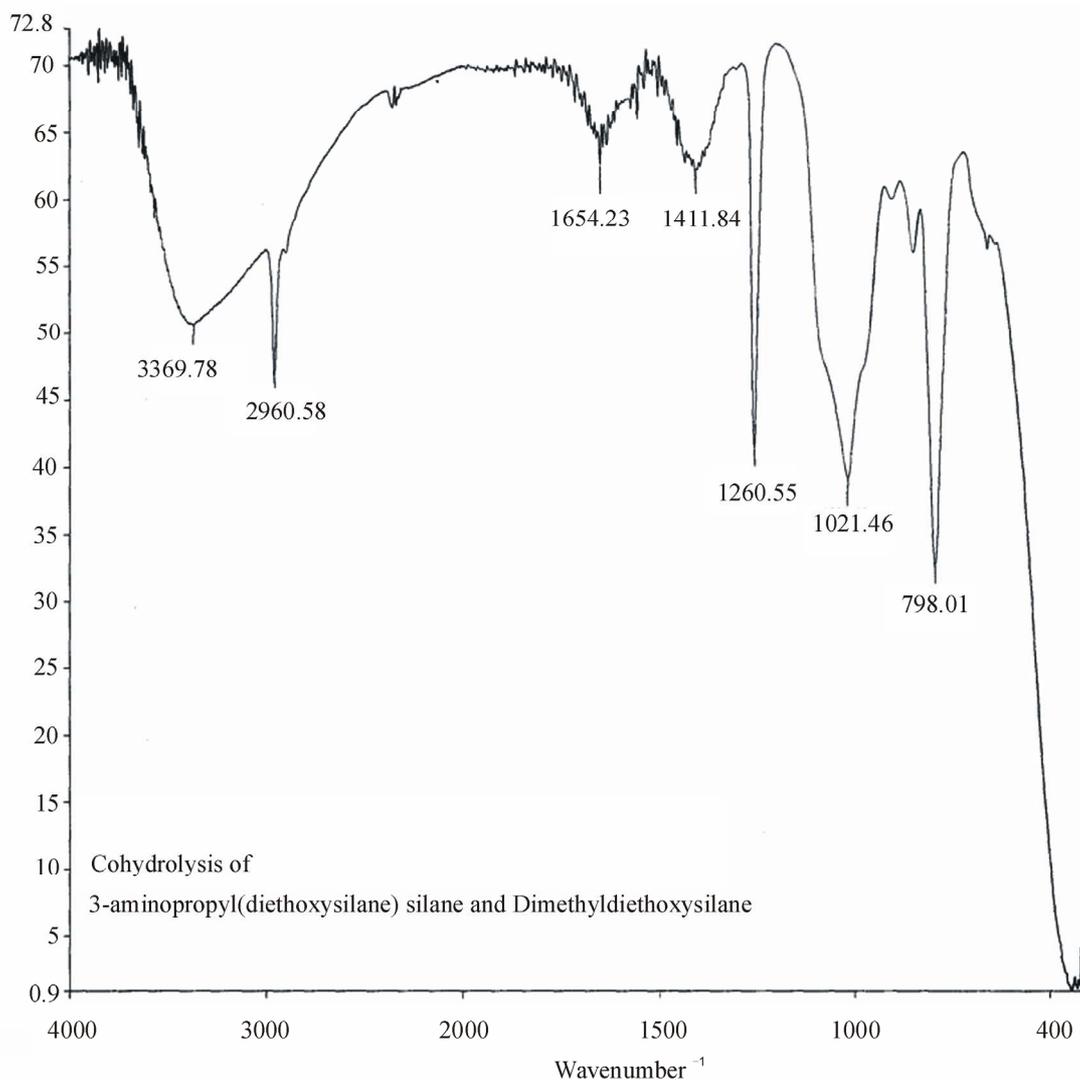


Figure 2. I.R. spectra of aminosilicone resin.

Table 3. Mechanical properties of cured films.

S.No.	Property	Results					
		EA	EAS ₁	EAS ₂	EAS ₃	EAS ₄	EAS ₅
1.	Scratch hardness (g)	1700	1750	1800	1850	1900	2000
2.	Pencil hardness	3H	3H	4H	4H	4H	5H
3.	Cross-hatch adhesion (%)	100	100	100	100	100	100
4.	Flexibility (1/4" Mandrel)	pass	pass	pass	pass	pass	Pass
5.	Gloss at 60° (%)	85	90	92 - 95	92 - 97	92 - 97	95 - 99

Table 4. Chemical resistance of cured films.

S.No.	Property	Results					
		EA	EAS ₁	EAS ₂	EAS ₃	EAS ₄	EAS ₅
1.	1.0 N H ₂ SO ₄	G	G	G	VG	VG	VG
2.	1.0 N NaOH	G	G	VG	VG	VG	E
3.	Distilled water	VG	VG	E	E	E	E
4.	Mineral turpentine oil	VG	VG	VG	E	E	E
5.	Methyl ethyl ketone	F	F	F	F	G	G
6.	Xylene	VG	VG	VG	E	E	E

P: poor; F: fair; G: good; VG: very good; E: excellent.

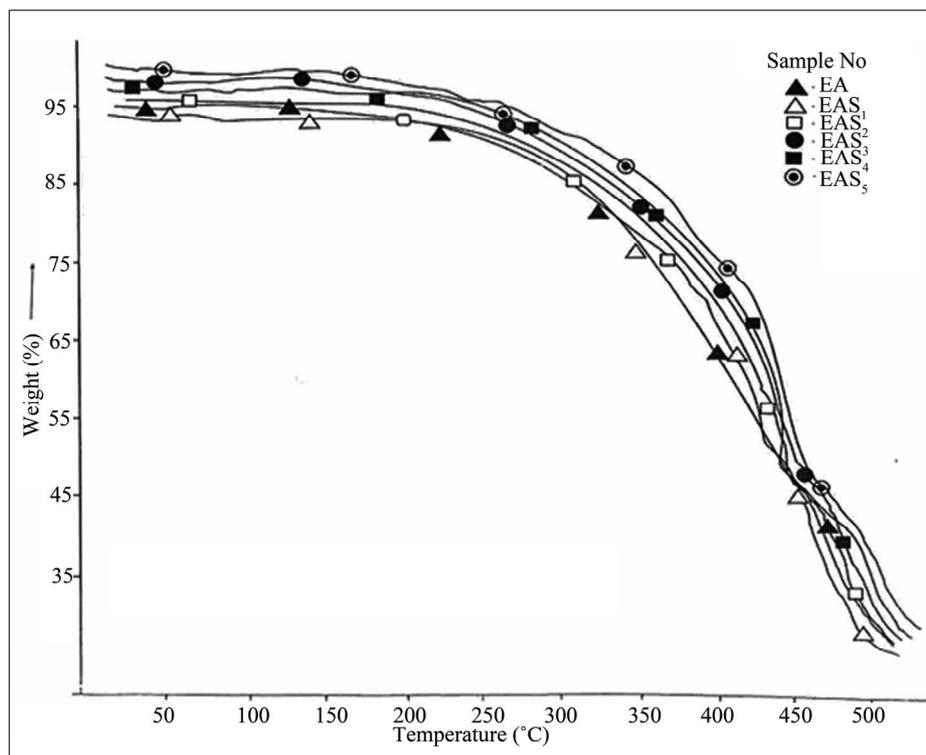


Figure 3. TGA graph.

Table 5. Activation energy of samples.

S.No.	Sample	Activation energy (j/mole)
1	EA	18.2
2	EAS ₁	20.1
3	EAS ₂	22.3
4	EAS ₃	22.5
5	EAS ₄	23.1
6	EAS ₅	24.2

proved anticorrosive properties.

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