

## **UV-Curing of Heat and Corrosion Resistant Siliconized Epoxy Resin**

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## Abstract

Polymeric materials are exposed to high temperatures that results in lowering of the film integrity. A blend of an epoxy resin with the silicone acrylate resin was developed to provide high heat resistance UV cured coatings. Earlier siliconized epoxy coatings had been developed by conventional curing. But due to environmental awareness, high productivity rate, low process costs and energy saving UV curable coatings are enjoying considerable growth. Thermally stable UV cured coatings used in the present study was developed from silicone acrylate and epoxy acrylate resin with different diluents and photoinitiator. Such coatings provide higher thermal stability (420<sup>0</sup>C). In addition, such coatings can also be obtained by using functional amino silanes. The resin developed provides a simple and practical solution to improve heat resistance along with physical and chemical corrosion resistance of the UV cured coatings. The purpose of this research paper is to develop UV curable heat resistant coatings by the combination of inorganic and organic polymer, taking epoxy acrylate as a base resin.

**Key Words:** - Novolac Epoxy, Epoxy Acrylate, Acrylation, Silicone Acrylate, UV-Curing

**Paper Type** - Research Paper

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## 1. Introduction

Epoxy resin belongs to second group or thermosetting family. Epoxy resin holds pride position among the resins used in coating industry. They may be used for coating without modification or they may be esterified with acrylic acid or methacrylic acid [1,2]. Epoxy resins are characterised by low shrinkage, ease of cure and processing, excellent moisture, solvent and chemical resistance and good adhesive strength. However their shortcomings are low fracture energy, low thermal stability, low pigment holding ability, poor hydrophobicity, weathering and impact strength which restrict their wide application in the field of coatings and paints. To improve these properties a second component such as rubber, amino terminated butadiene nitrile rubber, polyurethane, silicone and some other thermoplastics are added as modifiers for epoxy resin. Silicone is considered to be one of the suitable modifiers for epoxy resin, owing to its superior thermal and thermo-oxidative stability, excellent moisture resistance, partial ionic nature, low surface energy, good flame retardancy and free rotations of chains about Si-O bonds, good hydrophobicity, compressivity and doping action [3-5].

Structural materials have limitations for use at high temperature due to oxidation chemical reaction and corrosion therefore to provide improved reliability at high operating temperature, high heat and corrosion-resistant protective coatings are used. Epoxy silicone based coatings have high thermal stability, excellent adhesion, good flexibility and improved acid and solvent

resistance compared to conventional epoxy coatings. In past heat resistant siliconized epoxy coating had been developed by conventional curing.

Conventional organic protective coatings fail due to carbonization and evolution of aggressive gases. Such films age rapidly at elevated temperature ( $>100^{\circ}\text{C}$ ) and exhibits loss of flexibility, elasticity, adhesion and protective value. In general, physical properties of highly desirable heat resistant coatings have a high glass transition temperature ( $>250^{\circ}\text{C}$ ) and a high decomposition temperature ( $>400^{\circ}\text{C}$ ) [6]. Recently heat resistant UV-curable coatings have enjoyed considerable growth due to environmental awareness and increased productivity compared to traditional method of curing [7,8]. In contrast the usage of UV curing can cut process costs, decrease pollution and save energy [9-14]. Novolac acrylate provides a higher aromatic content and more crosslink sites in the pendent positions along the backbone of molecules than conventional epoxies [15]. Further its blending with silicone acrylate enhances the thermal stability thus giving high heat resistance coating. The utility of silicon-based coatings has evolved from specialty high performance applications into broad usage throughout the coatings industry.

In the present study a thermally stable, UV curable, epoxy coating has been developed by the combination of silicone based inorganic and organic polymer. It has been observed that use of silicone invariably enhances the thermal stability, resistance towards chemical corrosion of the epoxy coating. Besides thermal stability silicone provides better flexibility and gloss to coatings.

## 2. Experimental

### 2.1 Materials

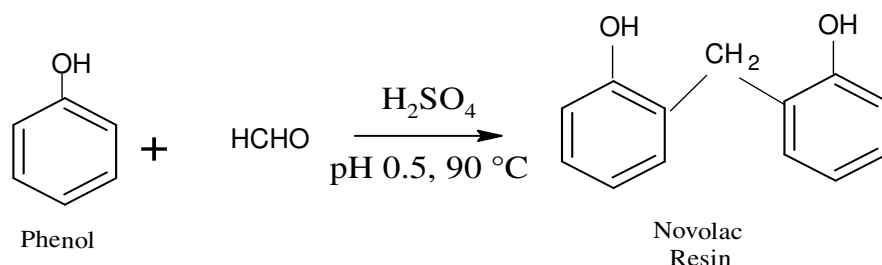
### Make

Epoxy novolac/cresol resin	Synthesized in Laboratory
Acrylate novolac/cresol resin	Synthesized in Laboratory
Acrylated Silicone Resin	Synthesized in Laboratory
Epichlorohydrin (ECH)	E. Merck
Acrylic Acid	E. Merck
Hydroquinone (HQ)	E. Merck
Trimethylolpropane triacrylate (TMPTA)	Aldrich
Pentaerythritol triacrylate (PETA)	Aldrich
1,6 Hexanediol diacrylate (HDDA)	Flucka
2,2-Diethoxyacetophenon	Flucka

### 2.2. Method

#### 2.2.1 Synthesis of novolac/cresol resin

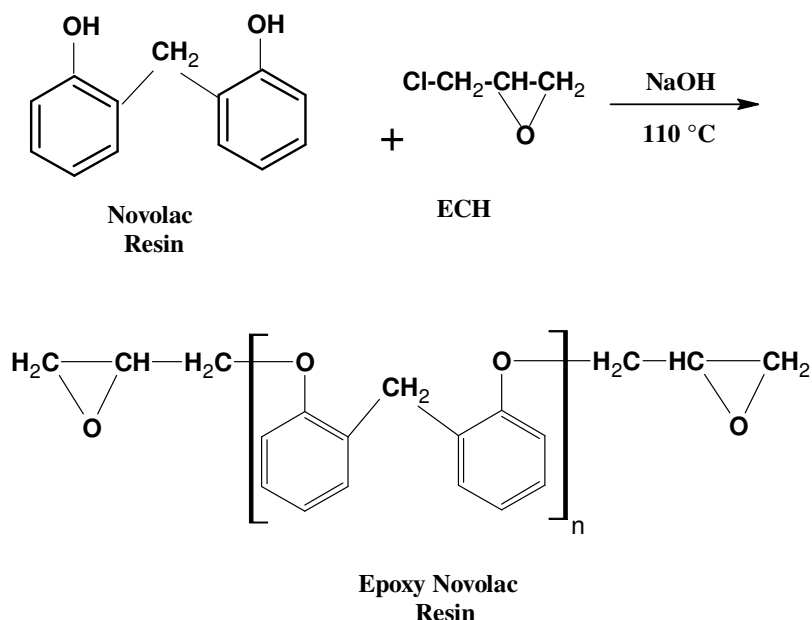
Novolac resin was prepared by condensation reaction between phenol / cresol and formaldehyde in acidic condition. Initially phenol / cresol (1 mole) with some quantity of water was taken in three neck flask. The pH was adjusted to 0.5 with sulphuric acid (used as catalyst) and the contents were heated to 90°C with constant stirring. The required amount (0.5mole) 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.(Figure.1)



**Figure. 1** Synthesis of novolac resin

### 2.2.2 Synthesis of epoxy novolac/cresol resin

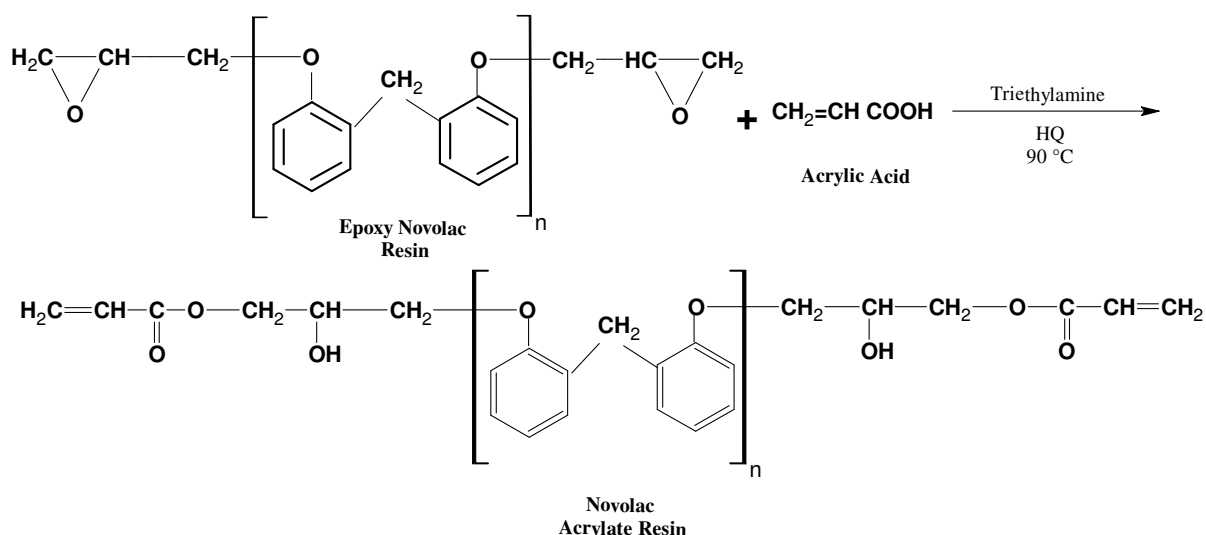
Laboratory prepared epoxy novolac / cresol resin (1 mole) was reacted with epichlorohydrine (10 mole) at 110<sup>0</sup>C and 40% sodium hydroxide solution was added gradually to the reactants over a period of 3 hours through a dropping funnel. After completion of reaction, salt (NaCl) was removed by washing with hot water and then water was removed through vacuum distillation.(Figure.2)



**Figure. 2.** Synthesis of epoxy novolac resin

### 2.2.3. Synthesis of novolac/cresol acrylate resin

Acrylation of above prepared epoxy resin was carried out by using 1:0.9 molar ratios of epoxide and acrylic acid in presence of triethylamine as catalyst (1 Phr) and hydroquinone (200 ppm) as inhibitor. The extent of reaction was determined by calculating the acid value [16] at definite time intervals.(Figure.3)

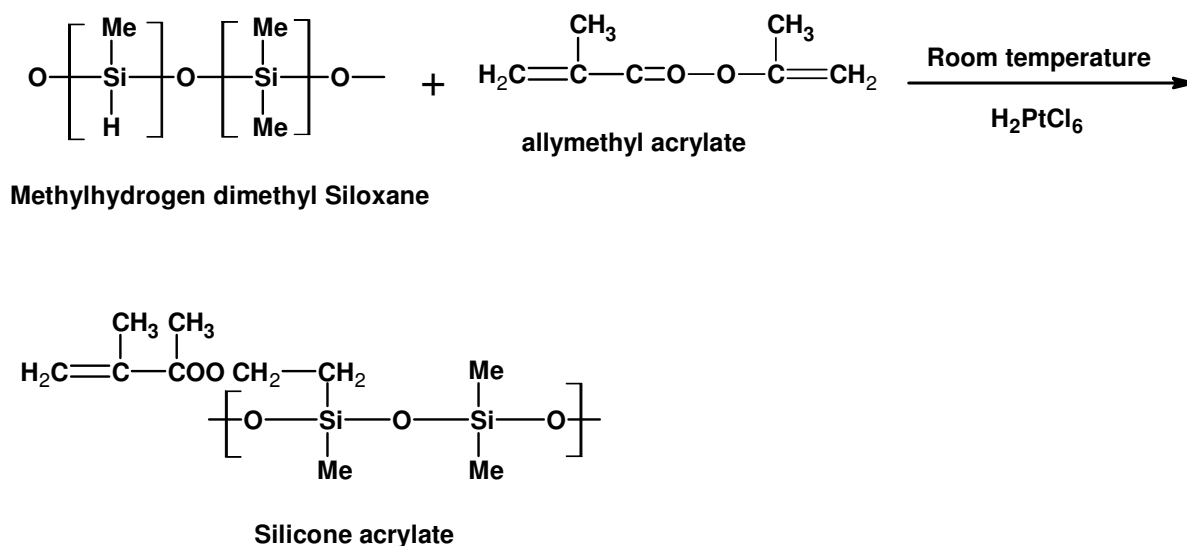


**Figure. 3. Synthesis of novolac acrylate resin**

### 2.2.4. Synthesis of silicone acrylate resin

Acrylated silicone resin was prepared by the reaction of methylhydrogendimethyl siloxane with allyl methyl acrylate in presence of H<sub>2</sub>PtCl<sub>6</sub> (catalyst) at room temperature. Prepared resin was characterised by IR. (Si O Si, 1040-1070cm<sup>-1</sup>, Si Me, 1261 cm<sup>-1</sup>) (Figure.4)





**Figure. 4. Synthesis of silicone acrylate resin**

#### 2.2.5. Characteristics of epoxy novolac/cresol resin

The epoxide equivalent weight of the prepared epoxy novolac resin (NE) was determined by pyridinium chloride method. Spectral analysis of this resin was done by IR to confirm the presence of epoxy group. Specific gravity was determined by hydrometer while viscosity of the epoxy novolac resin was determined by Brookfield Viscometer (ASTM-1824-66) in methyl ethyl ketone. (Table I).



Resin	Code	Sp.Gravity @25 <sup>0</sup> C	Viscosity @ 25 <sup>0</sup> C	Epoxide eq. Wt.	Solubility
Epoxy Novolac Resin	NE	1.148	11500	185	Alcohols, dioxane, ketone, ester
Cresol Epoxy Resin	CE	1.142	10500	180	Alcohols, dioxane, ketone, ester

NE- Epoxy novolac resin

CE- Cresol epoxy resin

**Table I. Coding and characterization of epoxy novolac resin**

#### 2.2.6. Characterization of acrylated resin

Prepared acrylate resins i.e. novolac acrylate (NA) and cresol acrylate (CA) were analyzed by IR spectroscopy to confirm the acrylation process of the epoxy which is due to the carbonyl group of ester formed during the acrylation of epoxy resin. Viscosity of resin is determined by brookfield viscometer (ASTM-D1824-66). The color of the resin was determined by gardener color standard using ASTM-D 1544. While the refractive index was determined by abbe – refractometer. (Table II).

Resin	Code	Refractive index	Viscosity @ 60°C	Color (Gardner)
Novolac Acrylate Resin	NA	1.534	18000	3G
Cresol Acrylate Resin	CA	1.521	16000	2G

NA- Novolac acrylate resin

CA- Cresol acrylate resin

**Table II. Coding and characterization of epoxy acrylate resin**

#### 2.2.7. Determination of acid value

The acid value of the prepared acrylate resin was determined with respect to time until the resin had an acid value of about 6 mg KOH/g resin [17] (Table III).

S.No	Reaction Time	Acid Value (mgKOH/g solid)	
		CA	NA
1	0	120.0	120.0
2	30	84.0	92.0
3	60	66.4	78.2
4	90	50.9	65.0
5	120	38.0	53.6
6	150	28.7	44.02
7	180	21.6	35.5
8	210	14.0	28.1
9	240	9.1	22.9
10	270	6.0	16.6
11	300	-	6.2

**Table III. Acid value and reaction time of different acrylate resin**

### 2.2.8. Determination of degree of polymerization

The number average degree of polymerization  $X_n$  is the total number of molecules initially present divided by the total number of polymer molecules and was calculated (Table IV) using following expression,

$$X_n = \frac{1+r}{1+r-2rp}$$

Where  $r$  is the stoichiometric imbalance ratio and  $p$  the extent of reaction.

S.No	Reaction Time (min.)	Degree Of Polymerization ( $X_n$ )	
		CA	NA
1	30	1.27	1.39
2	60	1.49	1.74
3	90	1.77	2.20
4	120	2.13	2.80
5	150	2.48	3.50
6	180	3.05	4.48
7	210	3.69	6.00
8	240	4.48	7.78
9	270	5.39	10.00
10	300	6.78	-

**Table IV. Degree of polymerization with time for different epoxy acrylates**

### 2.2.9. Preparation of test samples

The prepared acrylate resins (NA and CA) were mixed with calculated amount of reactive diluents (Table V) i.e. TMPTA, DETA, and HDDA, along with silicone acrylate resin and photoinitiators. The films were applied on the mild steel and glass panels with the film applicator of approximate 15µm film, the coated panels were then exposed to UV-lamp of 80 W/cm for curing. The panels were evaluated for various film characteristics.

S.No.	Ingredients	Samples (by part)					
		I	II	III	IV	V	VI
1.	NA	4	4	4	-	-	-
2.	CA	-	-	-	4	4	4
3.	SA	0.5	0.7	0.9	0.5	0.7	0.9
4.	TMPTA	1.7	1.7	1.7	1.7	1.7	1.7
5.	HDDA	1.7	1.7	1.7	1.7	1.7	1.7
6.	PETA	1.9	1.7	1.5	1.9	1.7	1.5
7.	DEAP	.2	.2	.2	.2	.2	.2

NA = Novolac Acrylate Resin

CA = Cresol acrylate Resin

SA = Silicone Acrylate Resin

TMPTA = Trimethylolpropane triacrylate

HDDA = 1,6- Hexane diol diacrylate

PETA = Pentaerythritol triacrylate

DEAP = 2,2- Diethoxyacetophenone

**Table V. Formulation of coatings with silicone compound**

### 2.2.10. *Thermogravimetric analysis*

Thermogravimetric analysis of the samples were carried out (on TGA V5.1A DuPont 2100 by heating at the rate of 20<sup>0</sup>C)/min) to study the thermal behavior of the coatings.

## 3. Results and discussion

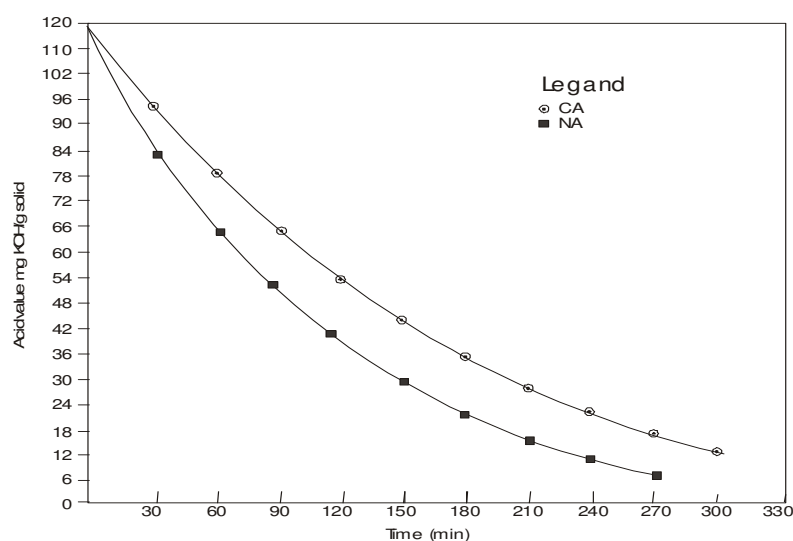
Table I. shows the coding and characterization of different epoxy resins. The resin epoxy novolac (NE) has epoxide equivalent weight 185, highly viscous and pale yellow in color. Cresol epoxy novolac resin (CE) has epoxide equivalent weight of 180, is highly viscous but slightly less than NE and light yellow in color.

Table II. shows the coding and characterization of different acrylate resin. The novolac acrylate resin (NA) is highly viscous and yellow in color as compared to cresol acrylate resin (CA), which is slightly less viscous and yellow in color.

Table III. shows the change in acid value of different acrylate resin with the reaction time. It is apparent from the table that the acid value decreases with the reaction time. The time required for product having desired acid value ( $\leq 6.0$  KOH/gm. solid) was 270 and 300 min. for CA and NA respectively.

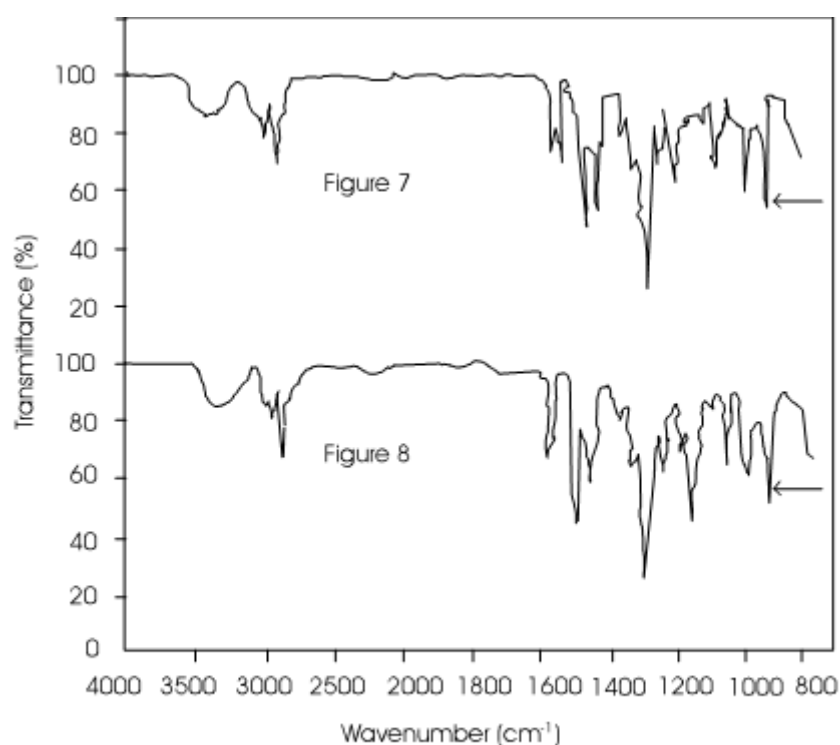
Table IV. gives data showing the change in number average degree polymerization ( $X_n$ ) with time for different acrylate resins CA and NA. It can be seen from the table that the degree of polymerization was low at the initial stage of reaction (<50 per cent conversion), whereas sharp increase is observed above 85 percent conversion.

Figure.6 illustrates the change in acid value with reaction time for all the samples. It is apparent from the plot that the decrease in acid value in the initial stages of reaction is not linear. This is because of the higher concentration of reactive sites and greater possibility of association of acid and epoxide groups. The linearity of the plot in higher conversion region is 70% and above (taking the decrease in acid value from the initial value as a measure of conversion) reveals that the reactivity of functional group is independent of molecular size which is characteristic of such esterification reaction.



**Figure 6. Drop in acid value with time**

Figure 7 & 8 shows the I.R. graph of epoxy novolac resin and cresol epoxy resin NE and CE. A prominent band is observed at  $940\text{ cm}^{-1}$ ,  $933\text{ cm}^{-1}$  in NE and CE which shows the presence of oxirane rings in all epoxy resins.

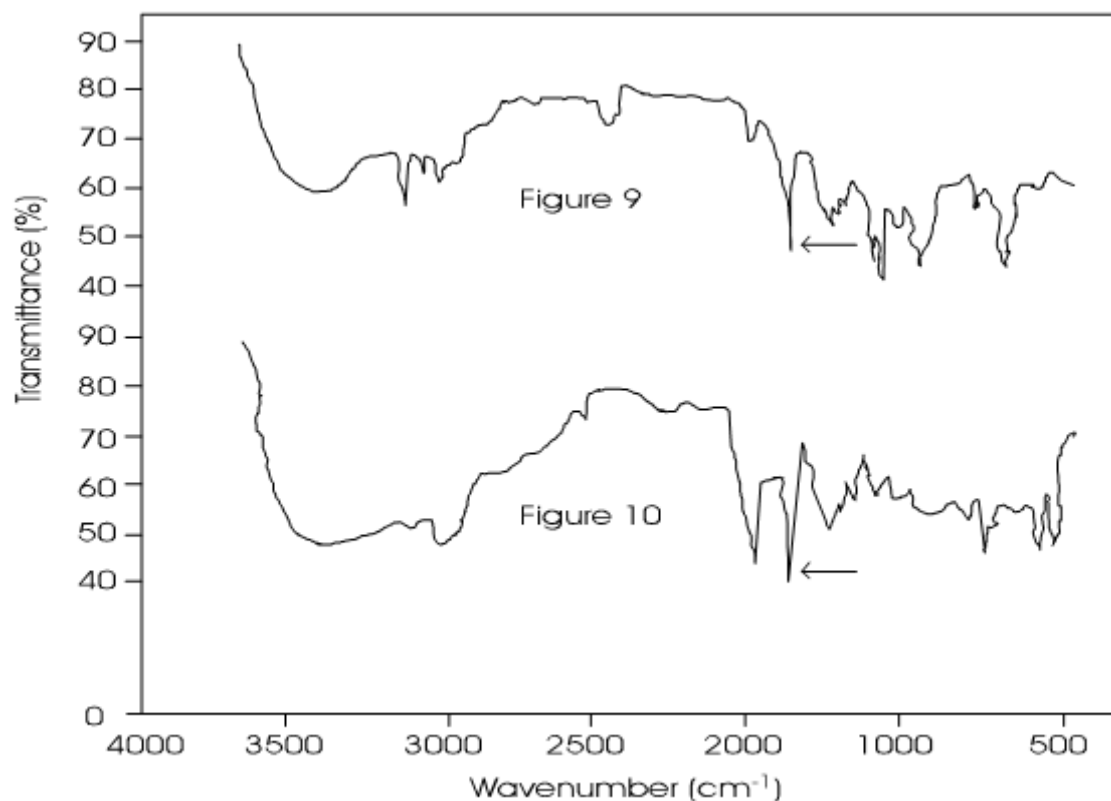


**Figure 7. IR Spectrum of epoxy novolac resin (NE)**

**Figure 8. IR Spectrum of cresol epoxy resin (CE)**

The I.R. graph of epoxy acrylates shown in figure 9&10 of NA and CA exhibits band in the region of  $1775\text{ cm}^{-1}$  and  $1750\text{ cm}^{-1}$  which confirms the presence of ester linkages. The epoxy bands are not so prominent in these graphs due to the opening of oxirane ring during the process of acrylation. A band corresponding to acryl double bond appeared at  $1610\text{ cm}^{-1}$  and  $1615\text{ cm}^{-1}$  for acrylate resin NA and CA and a broad band near  $3454\text{ cm}^{-1}$  shows the presence of  $-\text{OH}$  group.





**Figure 9. IR graph of novolac acrylate resin (NA)**

**Figure 10. IR graph of cresol acrylate resin (CA)**

### *3.1. Coating composition*

Table V shows coating composition of different acrylate resin with acrylated silicone resin having same photoinitiator (2,2-diethoxy acetophenone) and reactive diluents and all films are cured within 20 seconds by UV radiation.

### *3.2. Mechanical properties of cured films*

The coated tin, mild steel and glass panels were subjected to following performance test by BIS-101 specifications.

### 3.3. *Flexibility*

The flexibility of the coated films was determined with the help of ¼” mandrel. The coated tin panels were bend to 180<sup>0</sup> by using mandrel (Sheen Instrument Limited, England) all the samples passed flexibility test, sample no. III and VI exhibit highest flexibility because they contain higher percentage of silicon compounds as compared to others (Table VI).

### 3.4. *Scratch hardness*

Hardness is the resistance of a material to indentation of scratching. The most widely used hardness test for coatings are scratch hardness. Load bearing capacity of the films was measured by using scratch hardness tester (ASTM D 5178, Sheen Instrument Limited, England). The panels were loaded with different weights until a clear scratch showing the bare metal surface was seen, scratch hardness of sample no. III and VI with higher percentage of silicon compound were higher. (Table VI).

### 3.5. *Gloss*

After watching the sample from different angles it has been observed that all the samples possess excellent gloss. (Table VI)

### 3.6. *Pencil hardness*

In this test sample strip is drawn under a pencil (for example one with changeable 0.5 mm flattened leads) until a hardness grade is reached which will scratch the surface. The hardness value of coating is then assigned as H, 2H, 3H etc. which therefore signifies the hardness grade. Different pencils of different

grades have been used and found that samples III and VI passes maximum extent of hardness due to higher percentage of silicone (Table VI)

S.No	Sample No.	Scratch Hardness (gm)	Pencil Hardness	Flexibility (1/4" Mandrel)	Gloss (%)
1	I	1,700	4h	Pass	92-95
2	II	1,750	4h	Pass	92-97
3	III	1,800	5h	Pass	100
4	IV	1,700	4h	Pass	92-95
5	V	1,750	4h	Pass	92-97
6	VI	1,800	5h	Pass	100

**Table VI. Mechanical properties of UV cured siliconized epoxy resin**

#### **4. Corrosion resistance properties of cured films against various chemicals**

To evaluate the overall performance of the coatings, the coated films were exposed to various acids, alkalis and water. The coated panels were sealed from three sides by using molten paraffin wax before dipping in various chemicals.

##### *4.1. Resistance to acids*

Sulfuric acid, hydrochloric acid and acetic acid were dissolved in water to make solution of 5 % and 10% concentration on a weight per volume basis. The coated panels were then dipped in these acid solutions for 108 hours to check their corrosion against various acids. Samples which possess high percentage of silicone compound show better resistance against the acid corrosion. (Table VII).

S.No	Sample No.	Acetic acid		Sulfuric acid		Hydrochloric acid	
		5%	10%	5%	10%	5%	10%
1	I	5	4	4	3	5	5
2	II	5	5	5	4	5	4
3	III	5	5	5	5	5	5
4	IV	5	5	5	4	5	4
5	V	5	5	4	5	4	4
6	VI	5	5	5	5	5	5

5- Film Unaffected

4= Loss in Gloss

3= Blistering in films

**Table VII. Resistance of UV cured siliconized epoxy resin towards acids**

#### *4.2. Resistance to distilled water and saline water*

Coated cured panels were dipped in distill water and saline water at ambient temperature for 108 hours. The panels were observed for a visible change in the same condition. All the samples exhibit excellent corrosion resistance against distilled and saline water. (Table VIII).

S.No	Sample No.	Distilled Water	Saline Water
1	I	5	5
2	II	5	5
3	III	5	5
4	IV	5	5
5	V	5	5
6	VI	5	5

5 = Film unaffected

**Table VIII. Resistance of UV cured siliconized epoxy resin towards distilled and saline water**

*4.3. Resistance to alkali*

To check the alkali resistance of the samples coated glass panels were placed in 5% and 10% solution of NaOH and  $\text{NH}_4\text{OH}$  for 108 hrs on a weight per volume basis. All the samples exhibit good corrosion resistance towards the alkali except few showing loss in gloss in NaOH solution. (Table IX).

S.No	Sample No.	Sodium Hydroxide		Ammonium Hydroxide	
		5%	10%	5%	10%
1	I	5	4	5	5
2	II	5	5	5	5
3	III	5	5	5	5
4	IV	5	5	5	5
5	V	5	4	5	5
6	VI	5	5	5	5

5- Film Unaffected

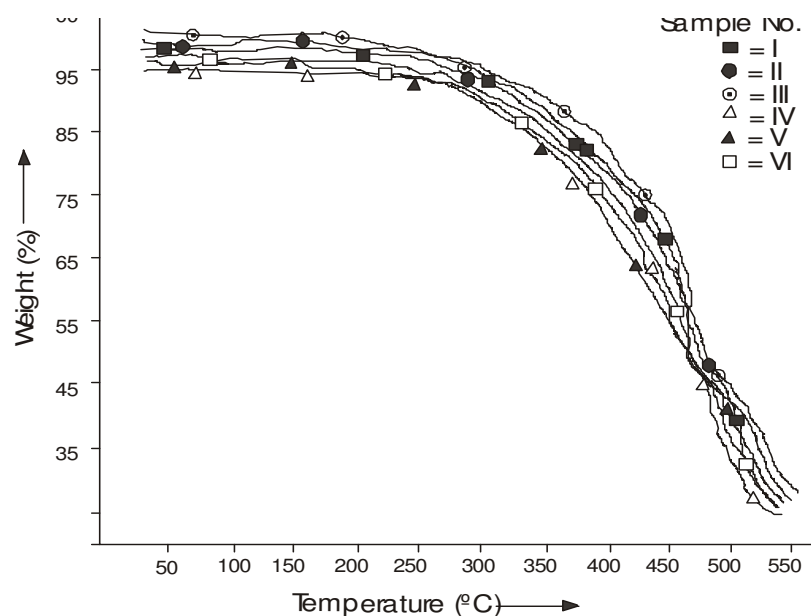
4= Loss in Gloss

3= Blistering in films

**Table IX. Resistance of UV cured siliconized epoxy resin towards alkali**

## 5. TGA analysis

Activation energy ( $E$ ) for the thermal decomposition of the UV-cured epoxy has been evaluated from the dynamic thermograms. The fractional decomposition ( $\alpha$ ) for the respective temperature has been calculated from TGA graph (Figure. 11). Higher value of activation energy in the system may be due to the presence of (silicon in the resin) polynuclearity in the resin. High activation energy for the decomposition of system leads to better thermal stability of the compounds [18,19].



**Figure 11. Thermogravimetric graph**

## 6. CONCLUSION

The thermal stability of the epoxy resin increases i.e. to about 420<sup>0</sup>C with the higher content of silicone. The increased activation energy with respect to increase in silicon compound up to certain level indicates a more thermally stable cresol novolac epoxy resin system. Chemical corrosion resistance of the composition has also shown improvement while mechanical properties like scratch hardness and flexibility have given satisfactory results. This type of UV cured coatings may be recommended for their applications in moderately stringent environment and under moderately high temperature applications where thermal stability is the main concern.



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