

Synthesis of high purity o-cresol formaldehyde novolac epoxy resins

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Summary

The content of total chlorine in o-cresol formaldehyde novolac epoxy resin (CNE), the main resin component for encapsulation formulation, affects the reliability of semi-conductor device greatly and it is one of the major criteria used by the electronic industry in measuring the quality of resins. A new process which synthesizes a high purity CNE with less than 300 ppm total chlorine content has been developed. This high purity resin has provided an extended device life under the accelerated stress test condition.

Introduction

One of the most frequent failures encountered in the encapsulated micro devices is the so-called open circuit, which results from a break of bonding wire between circuitry. This breakage is primarily caused by corrosion. It is initiated by the impurities in epoxy resins such as halogen, which upon exposure to heat and moisture generate a corrosive acid. With the consistent increase in computer memory capacity (from 16K to 4 MM) the requirement of higher purity epoxy resins becomes essential since the circuitry of high capacity memory chips has to be much denser and finer which will render it more susceptible to corrosion failure. This paper will discuss an in-depth examination of the chemical dehalogenation methods for CNE and also establish a definite relationship between device reliability and total chlorine content in the encapsulating resin.

Experimental

Eighty (80) g of a CNE resin having an average epoxide equivalent weight (EEW) as indicated and containing the indicated amounts of bound chlorine content is dissolved in 100g of 50/50 by weight mixture of methyl ethyl ketone (MEK) and toluene. Varying amounts of dimethylsulfoxide (DMSO) is added to the solution and the solution is heated to reflux (90°C) with stirring. Varying amounts of 45% aqueous potassium hydroxide (1.8 eq. KOH to 1 eq. of total chlorine in the resin) is then added all at once and the reaction mixture is maintained at this temperature for three hours with good agitation. The reaction mixture is diluted to 20% resin concentration with MEK/toluene solvent mix, neutralized with CO₂ and then washed with water three to four times to remove KCl. The organic phase from the water washes is placed on a rotary evaporator under a full vacuum and 170°C to remove the solvent completely. A purified CNE resin with a total chlorine content of less than 300 ppm and an EEW of 195 is obtained.

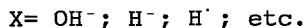
Three types of chlorines are differentiated as follow: Easily hydrolyzable chlorine (I) is saponified by refluxing a resin-methyl ethyl ketone solution with 0.1 N ethanolic KOH. Both easily and hardly hydrolyzable chlorines, (I) and (II), are determined by refluxing the resin-dioxane solution with 1.0 N ethanolic KOH. Total chlorines, (I), (II) and (III) are determined by refluxing the resin-dimethylformamide solution with 3.0 N ethanolic KOH. The resulted chlorides from saponification are then titrated with standard silver nitrate solution. From the volumes of titrant consumed, three types of chlorines are calculated.

Since easily hydrolyzable chlorine (I) can be dechlorinated very easily without affecting the oxiranyl ring, the starting CNE resin has been pretreated with 0.1 N KOH to remove (I) completely (less than 10 ppm). The total chlorine number described below is just the indication of analytical method used (3 N KOH-DMF reflux) and it actually describes the content of type (II) and (III) chlorine.

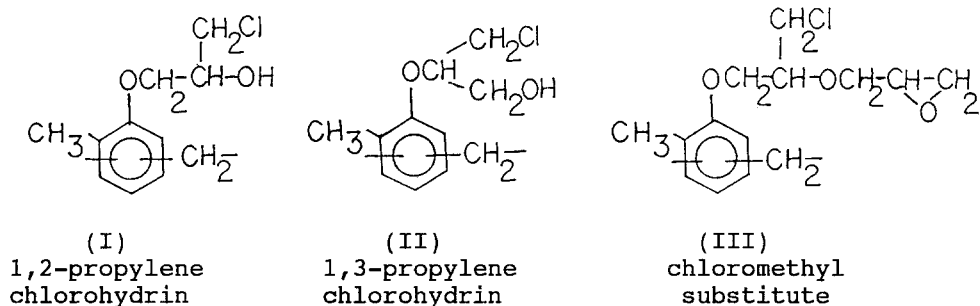
Result and Discussion

General Scope of Chemical Dehalogenation

Chemical dehalogenation generally refers to the cleavage of carbon-halogen bond and replaces the halogen atom with hydrogen or other group.



O-cresol formaldehyde novolac epoxy resin (CNE) contains three types of organic chlorine, i.e., easily hydrolyzable chlorine(I), hardly hydrolyzable chlorine(II) and bound chlorine(III):



The difference in reactivity of three types of chlorine (I), (II) and (III) is determined by the strength of saponifying agent and refluxing solvents as described in the experimental portion. Severe dechlorination conditions will always lead to the partial cleavage of oxiranyl rings. In order to obtain CNE with low total chlorine while maintaining high epoxide content, various types of chemical dehalogenation methods commonly seen in organic synthesis were studied. The term "selectivity" and "efficiency" are used here to describe the results. Reagents with high selectivity only attack carbon-chlorine bond without affecting oxiranyl rings. Reagents with high efficiency will reduce total bound chlorine greatly and they may or may not be selective.

Free Radical Dehalogenation [1-4]

The total chlorine content of CNE can be substantially reduced by using a free radical dehalogenation method without affecting the oxiranyl ring when treating CNE with organotin compounds, such as tributyltin hydride in the presence of catalytic amounts of free radical initiators in inert, halogen-free solvents such as toluene, etc. (Table 1). However, the unstable nature of the tin free radical species resulted in consumption of excess organotin reagents in order to achieve the high transformation. The separation of tributyltin chloride by-product from CNE product was difficult and hence CNE resin was contaminated with organotin residue. The tin content in CNE resin ranged from 300 ppm to 1500 ppm depending on the purification methods (Table 2). This made the CNE unsuitable for microelectronic encapsulation. The starting CNE resin used for dehalogenation study contains 21.0% epoxide and 866 ppm total chlorine. The supported tin hydride, di-n-butyltin hydride bound on alumina (supplied by Alpha products), was studied. However, its efficiency was very low.

Table 1. Free Radical Dehalogenation

Lot No.	Reagent	Initiator	Eq.	Deg. °C/Hrs	Epoxide %	Total Cl
A	Bu ₃ SnH	AIBN	X2	65/2	20.87	635 ppm
B	Bu ₃ SnH	AIBN	X4	95/1	20.97	598 ppm
C	Bu ₃ SnH	AIBN	X8	80/5	20.45	176 ppm
D	Bu ₃ SnH	AIBN	X8	80/3	20.74	189 ppm

Table 2. Residual Tin Content in CNE After Purification

Purification method	Tin Residual Content
High temperature stripping	>1500 ppm
Caustic Hydrolysis	1000-2000 ppm
Hot n-hexane extraction	300-1000 ppm

Dehydrohalogenation by Elimination Reaction [5-8]

It was reported that tetraethylammonium fluoride is about 800 times as effective as sodium ethoxide in ethanol in assisting the E2 elimination from phenylethylchloride. In this study, tetrabutylammonium fluoride and potassium fluoride were compared. Potassium fluoride is not efficient while tetrabutylammonium fluoride is not a selective reagent. Substantial loss in epoxide percentage occurred when excess amount of tetrabutylammonium fluoride was used (Table 3).

Table 3. Dehydrohalogenation Induced by Fluoride Anion

Lot No.	Reagent	Eq.	Solvent	Temp. °C/Hr	Epoxide %	Total Cl
E	KF + PE-400	x6	MIBK/tol.	95/15	20.68	814 ppm
F	KF + PE-400	x6	CH ₃ CN/ tol.	95/12	20.86	802 ppm
G	KF + Crownether	x2	dioxane	100/42	19.72	800 ppm
H	Bu ₄ NF	x2	MEK/tol.	60/8	20.80	712 ppm
I	Bu ₄ NF	x2	MEK/tol.	80/4	19.67	548 ppm
J	Bu ₄ NF	x2	MEK/DMF	50/5.5	20.80	760 ppm
K	Bu ₄ NF	x4	MEK/tol.	60/12	19.96	575 ppm
L	Bu ₄ NF	x4	MEK/tol.	75/3	20.52	653 ppm
M	Bu ₄ NF	x8	toluene	55/7.5	20.50	753 ppm
N	Bu ₄ NF	x8	tol./DMF	60/8	20.10	596 ppm

Dehalogenation by Aliphatic Nucleophilic Substitution [9-15]

Chlorines in 1,3-chlorohydrin (II) and chlormethyl group in structure (III) can be displaced by certain Lewis base having an unshared pair of electrons, such nucleophiles as OH⁻, H⁻, CN⁻,

SCN⁻, etc. Since chlorine atom is not a good leaving group, therefore, the most possible mechanism for this type of aliphatic nucleophilic substitution would be SN2 type version.



[X=Cl; Y= OH, H, CN, SCN, etc.]

Of the reagents investigated, NaBH₄, NaBH₃CN, KCN, KSCN, and K₂CO₃ were neither efficient nor selective (Table 4).

Table 4. Dehalogenation by Aliphatic Nucleophilic Substitution

Lot No.	Reagent	Eq.	Solvent	Temp. °C/Hr	Epoxide %	Total Cl
O	NaBH ₄	x 3	toluene	65/8	20.85	830 ppm
P	NaBH ₄	x10	toluene	80/16	20.72	757 ppm
Q	NaBH ₄	x10	DMF	80/4	gelled	
R	NaBH ₄	x20	DOWANOL-PM	65/14	17.40	631 ppm
S	NaBH ₃ CN	x 5	DOWANOL-PM	100/6	18.01	778 ppm
T	KCN	x30	toluene	r.t./20	20.70	742 ppm
U	KCN	x80	dioxane	r.t./48	19.90	792 ppm
V	KSCN	x30	toluene	r.t./20	20.68	622 ppm
W	KSCN	x 5	toluene/ MEK	80/2	20.18	821 ppm
X	K ₂ CO ₃	x 6	MEK/toluene	75/4	20.54	782 ppm

KOH treatment with a polar aprotic solvent DMSO, so far, is the most effective and practical method for the production of high purity CNE having total chlorine content of less than 300 ppm without excessive loss in epoxide (Table 5).

Table 5. KOH Treatment of CNE

Lots	Y-1	Y-2	Y-3	Y-4	Y-5	Y-6	Y-7
CNE	80g	80g	80g	80g	80g	80g	80g
MEK/ toluene	100g	100g	100g	100g	100g	100g	100g
DMSO	10g	10g	10g	5g	0	0	0
45% KOH (eq./ eq.Cl)	0.413g (1.8)	0.376g (1.8)	0.471g (2.0)	0.589g (3.0)	0.585g (3.0)	0.418g (2.0)	0.310g (1.6)
Epoxide Content							
Before (%)	23.22	23.10	23.22	23.05	23.04	23.01	22.88
After (%)	21.77	22.16	21.83	21.44	22.88	22.36	22.34
Bound Chlorine							
Before (ppm)	695	691	692	662	639	641	644
After (ppm)	206	283	276	266	427	383	442

Device Reliability vs. Total Chlorine Content

CNE resins containing three levels of total chlorine, 1800 ppm, 1000 ppm and 250 ppm, are formulated into an electrical encapsulating formulation. The formulations are each cured at 175°C for 4 hours. The encapsulation formulation is given below (Table 6). The curing agent is a phenol-formaldehyde novolac with an average hydroxyl functionality of 6 and a phenolic hydroxyl equivalent weight of 104. The mold releasing agent is a refined Montan Wax. The device testing is determined by a highly accelerated stress test, which involves the following conditions : 110°C, 100% relative humidity and 20 volts bias. The device is a 14-pin LM 324 quad operational amplifier with a single passivation layer. The percentage of device that fail as a function of time are given in Figure 1. It demonstrates the relationship between resin purity and device reliability; the higher the purity the longer the expected device life. Inorganic chloride of resins are less than 5 ppm.

Table 6. Encapsulation Formulation

CNE	Curing agent	Ph ₃ P	Mold release	Epoxy silane	Fused silica	Sb ₂ O ₃	Carbon black
200.2	90.0	2.25	4.0	4.0	685.0	10.0	4.0

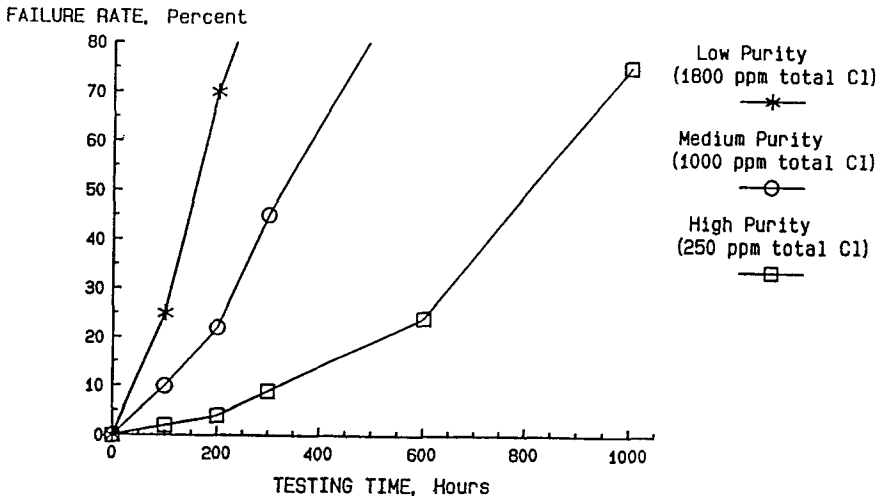


Figure 1. Bias Pressure Cooker-Device Reliability Test

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