

2,6-Dibromo-3,5-dimethyl-4-hydroxybenzyl ether and epoxy systems

Their application in electronic packaging

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Summary

Meta-halogenated phenols are generally known to be more chemically and thermally stable than their ortho- or para-halogenated counterparts. A novel compound, 2,6-dibromo-3,5-dimethyl-4-hydroxybenzyl ether, is synthesized and is being used to incorporate this stable meta-bromo-phenol moiety into epoxy resins. In electronic encapsulation applications, epoxy derivatives of novolacs containing meta-bromo-phenol have exhibited exceptional hydrolytic and thermal stability compared to the conventional tetrabromobisphenol-A epoxies which are ortho-brominated phenolics. The meta-bromo-phenol moiety contributes to the extended device reliability life while providing fire retardancy property.

Introduction

Cresol novolac epoxy resin and the epoxy derivatives of tetrabromobisphenol-A (TBBA) are the resins typically employed to encapsulate microelectronic devices in molding compounds. The brominated resin, which is utilized as a flame-retardant additive to impart a degree of ignition resistance to the encapsulant, contains many unstable hydrolyzable bromides. These bromides, along with the presence of chloride impurities, are detrimental to the life of the electronic component. Since the introduction of the low chloride epoxy resins, the wire bond failure due to the chloride impurities in the resin has become much less prominent than that due to the bromine from the fire retardant in the encapsulation formulation.¹⁻⁵

Brominated compounds, where the bromine is in the meta position to the phenolic hydroxyl, have been shown to be more hydrolytically and thermally stable than ortho-brominated compounds such as TBBA,⁶⁻⁸

Unfortunately, only a few meta-brominated bisphenols have been known in the literature. The aim of the present paper is to describe synthesis of a novel compound which is being used to incorporate this stable meta-bromo-phenol moiety into epoxy resins in order to extend the device reliability life of electronic components.

Experimental

Preparation of 2,6-dibromo-3,5-dimethyl-4-hydroxybenzyl ether

A 373 g (1.0 mole) portion of 4-bromomethyl-3,5-dibromo-2,6-dimethylphenol is dissolved in 750 ml of acetone. The solution is heated to reflux and 250 ml of water is added. A clear solution is obtained. The solution is refluxed for five hours. A white precipitate forms during the refluxing period. The hot slurry is filtered to afford 184 g of white solid containing 97% ether and 3% 3,5-dibromo-2,6-dimethyl-4-hydroxymethylphenol by liquid chromatography. The solid is further purified by slurrying in 800 ml of acetone and 200 ml of water and refluxing for one-half hour. Hot filtration of the slurry produces a solid of 98+% purity with a melting point of 240°-241°C. The proton nuclear magnetic resonance spectrum has the following signals: (DMSO d_6) δ ; 2.26(s,12H), 4.75(s,4H), 7.5(s,2H). Anal. Calcd. for $C_{18}H_{18}Br_4O_3$: C,35.88; H,2.99; Br,53.16; O,7.97. Found: C,35.96; H,3.01; Br,53.03; O,8.00.

Alkylation and Epoxidation of Cresol Formaldehyde Novolac Resin

(A) Alkylation

To a one-liter reaction vessel equipped with temperature control and indicating means and reflux condenser, are added 292.6 g (2.52 eq.) of cresol formaldehyde novolac resin (softening point= 94.3°C. and average phenolic hydroxyl functionality= 5), 65.4g (0.217 eq.) of 2,6-dibromo-3,5-dimethyl-4-hydroxybenzyl ether and 80 g of methyl ethyl ketone. Upon stirring at room temperature and atmospheric pressure to thoroughly mix the contents, the temperature is raised to 80°C. and 2.0g of p-toluenesulfonic acid is added as a catalyst. The mixture is allowed to stir at 80°C until the slurry reaction mixture turns clear indicating all 2,6-dibromo-3,5-dimethyl-4-hydroxybenzyl ether is reacted.

(B) Epoxidation

The epoxidation procedure⁹ of o-cresol formaldehyde novolac is used to prepare this epoxy resin which contains meta-bromophenol moiety. The resulting polyglycidyl ether has an epoxide content of 20.83% and contains 7.28% bromine and has a softening point of 80°C.

Advancement of Cresol Formaldehyde Epoxy Novolac Resin With 2,6-dibromo-3,5-dimethyl-4-hydroxybenzyl ether

500g (2.5 eq.) of cresol formaldehyde novolac epoxy resin having a EEW of 183 and an average epoxide functionality of 6, a Kinematic viscosity of 125 centistokes ($125 \times 10^{-6} \text{ m}^2/\text{s}$) at 150°C. and containing 975 ppm total aliphatic chloride is dissolved in 500g of a 75/25 percent by weight mixture of methyl ethyl ketone and toluene in a 2-liter flask equipped with thermowell, reflux condenser and stirrer. 83.6g (0.287 eq.) of 2,6-dibromo-3,5-dimethyl-4-hydroxybenzyl ether is added to the epoxy resin solution and the resultant solution is heated to 85°C with stirring. 2.1g (1.2 eq. per eq. of total aliphatic chloride contained in the epoxy resin) of 45% aqueous potassium hydroxide is added all at once and the reaction mixture is maintained at 85°C for 3 hours. The reaction mixture is diluted to 20% solids concentration with a 75/25 percent by weight methyl ethyl ketone-toluene solvent mixture, neutralized with carbon dioxide and washed with deionized water several times to remove the residual potassium chloride. The organic phase from the water washes is placed on a rotary evaporator under a full vacuum at 160°C to remove the solvent. A yellow, solid resin having a Mettler softening point of 79°C, an EEW of 242, a viscosity of 227 centistokes ($227 \times 10^{-6} \text{ m}^2/\text{s}$) at 150°C containing 642 ppm of total aliphatic chloride and 7.5% bromine is obtained.

Epoxidation of 2,6-dibromo-3,5-dimethyl-4-hydroxybenzyl ether and its Blending with Cresol Formaldehyde Novolac Epoxy Resin

(A) Epoxidation

To a 2-liter reaction vessel equipped with a temperature and pressure control and indicating means, means for continuous addition of aqueous sodium hydroxide, a means for condensing and separating water from a codistillate mixture of water, solvent and epichlorohydrin and means for returning the solvent and epichlorohydrin to the reaction vessels is added 190.6 g (0.634 eq.) of 2,6-dibromo-3,5-dimethyl-4-hydroxybenzyl ether, 586.1 g (6.34 eq.) of epichlorohydrin and 103.4 g of the methyl ether of propylene glycol (1-methoxy-2-hydroxypropane) as a solvent. After stirring at room temperature ($\sim 25^\circ\text{C}$) and atmospheric pressure to thoroughly mix the contents, the temperature is raised to 45°C and the pressure is reduced to 65 mm Hg absolute. To the resulting solution is continuously added 50.7 g (0.634 eq.) of 50% aqueous sodium hydroxide solution at a constant rate over a period of 7 hours. During the addition of the sodium hydroxide, the water is removed by codistillation with epichlorohydrin and solvent. The distillate is condensed thereby forming two distinct phases, an aqueous phase (top) and an organic epichlorohydrin-solvent phase (bottom). The organic phase is continuously returned to the reactor. After completion of the sodium hydroxide addition, the reaction mixture is maintained at temperature of 45°C and a pressure of 65 mm Hg absolute for an additional one hour. The diglycidyl ether of 2,6-dibromo-3,5-dimethyl-4-hydroxybenzyl ether is not soluble in the organic

solvent and precipitated from the reaction mixture. It is filtered from the reaction mixture and redissolved in methylene chloride. The methylene chloride solution is washed several times with deionized water to remove the residual sodium chloride. The organic phase from the water washes is placed in a vacuum oven under a vacuum at 160°C to remove solvent completely. 210 g of yellowish white solid is obtained.

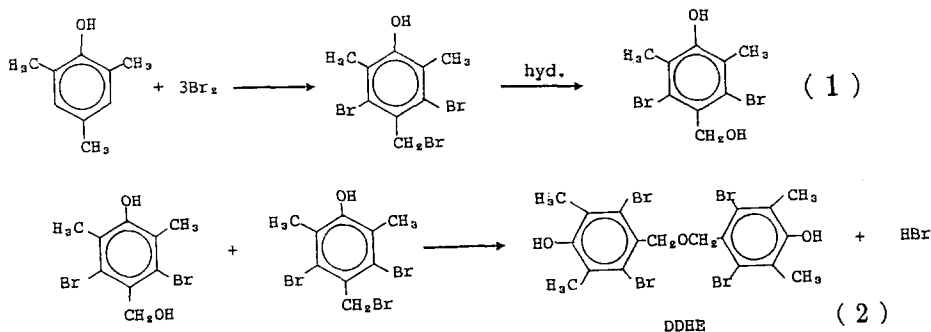
(B) Blending

73 g (0.207 eq.) of the diglycidyl ether of 3,5-dimethyl-4-hydroxybenzyl ether prepared in A above and 346 g (1.725 eq.) of a cresol formaldehyde novolac epoxy resin having a EEW of 191, an average epoxide functionality of 6, a Kinematic viscosity of 313 centistokes ($313 \times 10^{-6} \text{ m}^2/\text{s}$) at 150°C and containing 622 ppm total aliphatic chloride are placed in a 1-liter flask on a rotary evaporator at 160°C and a full vacuum until the two epoxy resins are completely mixed. The resultant mixture, 420 g of product, has an EEW of 211, a viscosity of 292 centistokes ($292 \times 10^{-6} \text{ m}^2/\text{s}$) at 150°C and contains 7.5% bromine by weight.

Result and Discussion

Synthesis of 2,6-Dibromo-3,5-Dimethyl-4-Hydroxybenzyl Ether (DDHE)

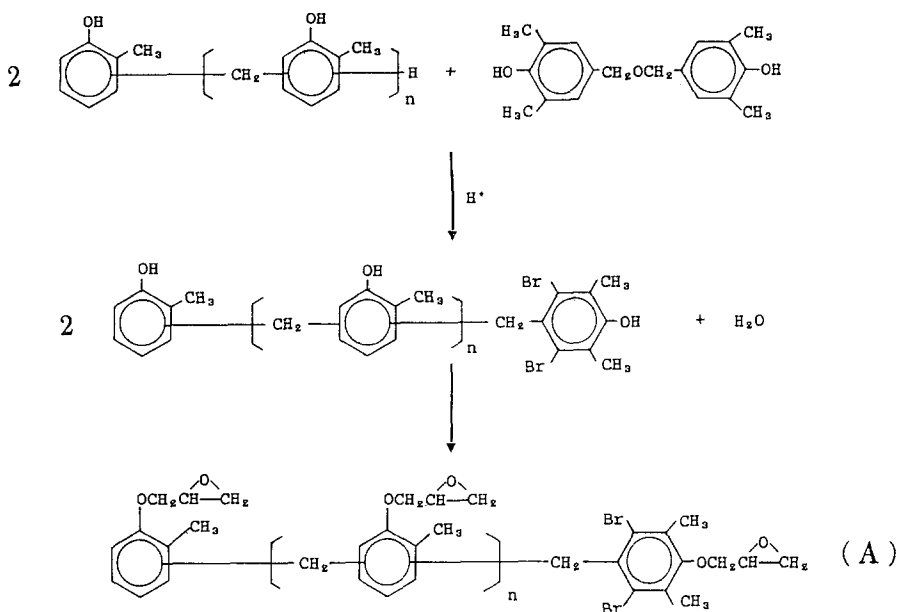
Bromination of 2,4,6-trimethylphenol with excess bromine produced 4-bromomethyl-3,5-dibromo-2,6-dimethylphenol¹⁰ as a major product which on hydrolysis produced 4-hydroxymethyl-3,5-dibromo-2,6-dimethylphenol. Dehydrobromination by the condensation of 4-hydroxymethyl-3,5-dibromo-2,6-dimethylphenol with 4-bromomethyl-3,5-dibromo-2,6-dimethylphenol produces the product 2,6-dibromo-3,5-dimethyl-4-hydroxybenzyl ether. A simplified synthesis method which consists of a partial hydrolysis of 4-bromomethyl-3,5-dibromo-2,6-dimethylphenol to 4-hydroxymethyl derivative which then reacts with starting 4-bromomethyl compound in situ to form the desired product DDHE in one step is developed.



Incorporation of Meta-bromophenol Moiety into Epoxy Resins.

The incorporation of meta-bromophenol moiety into the cresol formaldehyde novolac epoxy resin (CNE) can be achieved by the following three routes:

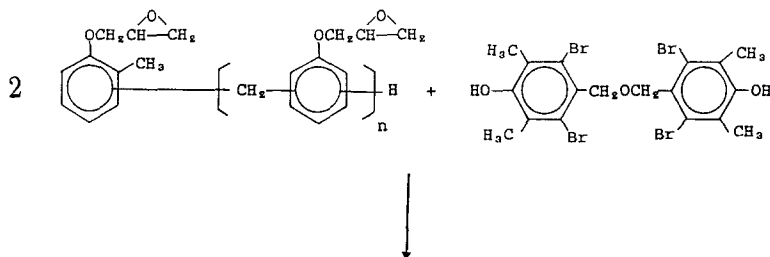
- A). Incorporation into cresol novolac followed by epoxidation. Alkylation of cresol formaldehyde novolac with DDHE using p-toluenesulfonic acid as a catalyst produces m-bromophenol containing cresol formaldehyde novolac which upon epoxidation produces the desired product.

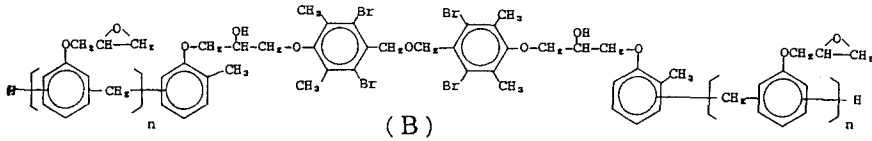


The m-bromophenol containing novolac and epoxy resin are identical to the reported products¹¹ using 4-bromomethyl-3,5-dibromo-2,6-dimethylphenol as an alkylating agent.

- B). Advancement of CNE with DDHE

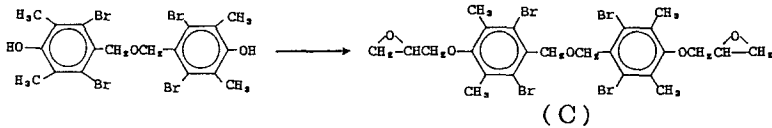
The opening of epoxy ring in CNE by a dihydric phenol, DDHE, produces the advancement product of CNE.





C). Epoxidation of DDHE and its blending with CNE

Epoxidation of DDHE followed by blending it with CNE in a certain ratio produces an epoxy resin mixture (C) which contains desired amount of bromine.



The performance of meta-bromophenol containing epoxy resins (A,B, and C) are compared with a standard encapsulation resin as a control. The control resin consists of a mixture of Quatrex 3430 (a CNE by the Dow Chemical Company) and Quatrex 6410 (ortho-brominated epoxy of tetrabromobisphenol-A by the Dow Chemical Company) adjusted to have a bromine content of 7.5 percent.

Hydrolytic Stability

The sample is dissolved in 1,4-dioxane and saponified by refluxing with 3N ethanoic KOH solution. The resulting halides are titrated with standard silver nitrate solution. From the volume of titrant used, hydrolyzable chloride and hydrolyzable bromide are calculated. The results on Table 1. demonstrate the superior hydrolytic stability of meta-brominated epoxy resins over the ortho-brominated epoxy resin.

Table 1. Total Hydrolyzable Halide Analysis

Sample number	Hydrolyzable chloride, ppm	Hydrolyzable bromide, ppm
A	115	0
B	132	25
C	130	0
control	125	181

Encapsulation Formulation

A, B, C, and control resin are formulated into electrical encapsulating formulations. The formulations are each cured at 175°C for 4 hours. The encapsulating formulations are given in Table 2. The curing agent is a phenol-formaldehyde novolac with an average hydroxyl functionality of 6 and phenolic hydroxyl equivalent weight of 104. The mold releasing agent is a refined Montan wax.

Table 2. Encapsulation Formulation

Component	A	B	C	Control
Epoxy Resins, g	200.5	195.1	195.1	195.1
Curing Agent, g	97.9	89.9	96.8	95.5
Triphenyl- phosphine, g	2.0	2.0	2.0	2.0
Mold release Agent, g	4.0	4.0	4.0	4.0
Epoxy silane, g	4.0	4.0	4.0	4.0
Fused silica, g	685.5	685.0	685.0	685.0
Antimony oxide, g	10.0	10.0	10.0	10.0
Carbon Black, g	4.0	4.0	4.0	4.0
% Bromine in Formulation, g	1.46	1.46	1.46	1.46

Flame Retardancy Test

Above formulations all passed UL-94 VO flame retardancy test using castings of 1/16 inch thickness.

Device Reliability Test

The device testing is determined by a highly accelerated stress test, which involves the following conditions: 121°C, 15 psig steam, and 25 volts bias. The device is a 14-pin LM 324 quad operational amplifier with a single passivation layer. The percentage of devices that fail as a function of time are given in Table 3. Failure: each device is electrically tested for the necessary output voltage and currents as well as power dissipation. Any device which fails to meet these electrical parameters is considered a failure.

Results in Table 3. demonstrate these stable meta-bromine containing formulations give substantially better performance than the conventional system while providing the required fire retardancy property.

Table 3. Device Reliability

Sample Number	% Device Failure		
	400 hours	600 hours	800 hours
A	3	7	28
B	5	10	40
C	2	6	21
Control	25	75	100

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