



SYNTHESIS, CHARACTERIZATION AND MODIFICATION OF M-CRESOL-ANISALDEHYDE AND M-CRESOL – 2-METHYL BENZALDEHYDE NOVOLAC RESINS WITH EPOXY

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ABSTRACT

Novolac phenolic resins were synthesized by the condensation reaction between phenol derivatives and different aldehyde with a stoichiometric ratio in acidic medium has been studied. The modified phenolic novolac resins composition depends on monomeric ratio, catalyst, reaction conditions, and residual free monomers. The modification has been recognized with modifier (epichlorohydrin) in basic medium. These modified epoxy novolac phenolic resins are characterized by FTIR spectroscopy.

Keywords : Phenolic novolac resins, epoxide, synthesis and FTIR spectroscopic studies.

INTRODUCTION

A variety of difunctional and multifunctional epoxy reagents can be used to generate network with excellent dielectric properties were studied by Knop and Coworkers ^[1]. Hasegawa and Coworkers ^[2] prepared epoxy resin from o-cresol novolacs and studied the structure and viscoelastic properties of epoxy resin. Epoxy modified novolac resins are commonly used as high performance protective coating, object adhesives and matrix resins for composites. The epoxy resin gets thermoset during the cross-linking or curing reaction using a wide variety of curing agents like anhydrides³, acids⁴ and HMTA⁵. This epoxy resin has been widely used as

engineering plastics. Recently, high performance epoxy resin are subject to strict requirements. o-cresol novolac-type epoxy resins have been used as encapsulation materials for semiconductor for their good heat resistance. The epoxy modified novolac resins possess excellent mechanical properties, water resistance, chemical resistance, heat resistance, time electrical properties and so on. They are widely used as encapsulating and packing materials in the electronic industry as the matrix of high performance, fiber reinforced composites in the aerospace and automotive industries.

The reaction between hydroxyl groups and epoxides have been catalyzed by a variety of acid and base catalysts most commonly used reagent Soane and Coworkers^[6] with thermosetting resins such as epoxy resins crosslinking density is an important factor governing the physical properties of cured resin. Ogata and Coworkers^[7] investigated the effect of crosslinking on physical properties of cured resins, particularly focusing on amine or anhydride cured epoxy resin. As a result, the scientists observed that the cross linking density increased, the whole free volume contributed to a fluidity decreases. In the glossy region, highly cross-linked resin had a large specific volume, coefficient of linear thermal expansion, water absorption, diffusion coefficient and permeability and small elastic modulus. Oyanguren and Williams^[8] cured epoxy novolac. They used aromatic diamines like 4,4-diamino diphenyl sulfone (DDS) used in high Tg formulation. To improve the thermal and mechanical properties of epoxy resin, the modification of molecular back bone or increase in the number of epoxide group functionalities are the generally employed methods^[9]. The effect of prereaction of the epoxy groups in the resins and carboxyl group in the elastomer on curing parameters, such as the cure reaction conversions, processing parameters, such as gel times, initial cure temperatures and activation energy values were studied by Padma and Coworkers^[10]. Jeevananda and Coworkers^[11] studied the spectral and thermal studies on polyaniline epoxy novolac resin composite materials. They suggested that it may be used for antistatic floor applications because of polyaniline is electrically conductive and possesses good environmental stability. Whan Gunkim and Coworker studied curing characteristics of o-cresol novolac epoxy resin modified by bismaleimide^[12]. The main drawback of epoxy resins is their flammability. A flame retarding additive may be lost in processing and during use of the polymer and this may mean that high loadings are initially required. Another way in which to reduce the flammability of polymer is to use a reactive flame retardant. Jeng-Yueh and Chun-Shan Wang^[13] used novel-phosphorus containing hardener for epoxy resin. The influence of the side groups on the water absorption behaviour of the cured

epoxy resins were studied by Yifu Ding and Coworkers^[14]. The cure reaction of commercial epoxidized with 4,4-diaminodiphenylsulfone (DDS) was studied at constant cure temperatures in the range 120 – 270°C as well as constant heating rates by P.A. Oyanguren and Coworkers^[15]. A vinyl siloxane – modified cresol novolac epoxy/cresol novolac hardener (CNH) molding compound with both siloxane and epoxy components capable of further crosslinking were synthesized by Horeng-Jer and Coworkers^[16]. Curing kinetics of o-cresol formaldehyde epoxy resin and its blends with a liquid crystalline block copolymer cured with linear phenol-formaldehyde resin were studied by Song Ting Tan and Coworkers^[17]. Water absorption and thermomechanical properties of epoxy systems based on multifunctional dicyclopentadiene epoxy novolac resin cured with 4,4-diaminodiphenylsulfone (4, 4' DDS) as curing agent has been studied by Blanco and Coworkers^[18]. Yang fong Liu and Coworkers^[19] prepared and cured Bisphenol- A type novolac epoxy resin.

EXPERIMENTAL ANALYSIS

Raw Materials

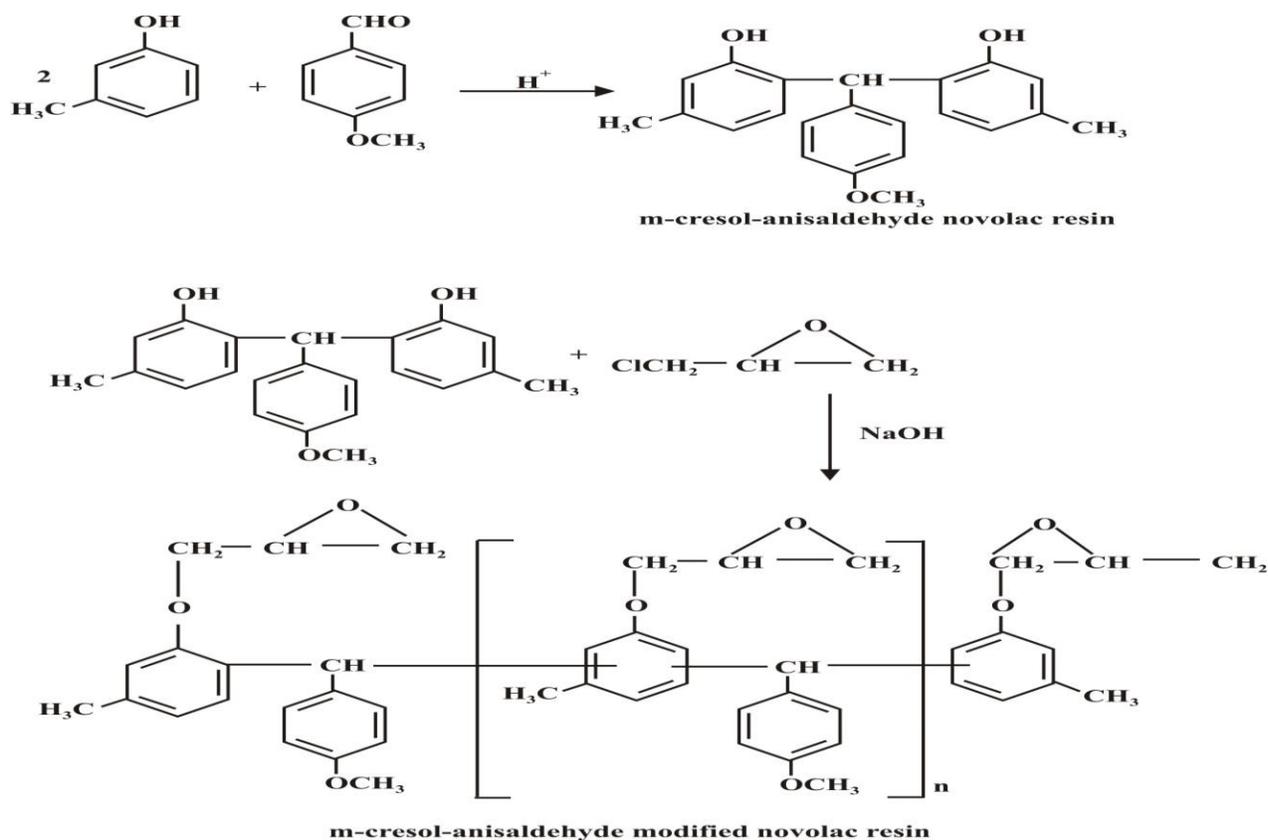
All the monomers were of good quality and analytical grade most of them purified by vacuum distillation. The catalyst used were purified by usual methods. The catalyst is acid calculated amount used accurately during condensation reaction.

Synthesis and modification of m-cresol-anisaldehyde novolac resin with Epoxy (Epichlorohydrin)

6.0 g m-cresol-anisaldehyde novolac resin and 24 ml epichlorohydrin were taken in a 100 ml three necked round bottom flask and mixed. Reflex condenser was connected with R.B. flask. The reaction mixture was heated on water bath at 55°C and then from the side tube by dropping funnel 10% solution of NaOH (10 ml) was added with stirring over 1h. After the addition of NaOH, the reaction was continued for 3.5 – 4h. At this point there emerged two layer which were separated by decandation. The resin was washed with 100 ml hot water in three times, whole resin is poured into a porcelain dish, dried in the oven till it got constant weight. This modified novolac resin was soluble in acetone, alcohol, carbon disulphide, toluene, but insoluble in chloroform, carbon tetrachloride and water. The melting point of modified novolac resin was 95°C. The colour of the modified resin was yellow. The yield of the modified resin was 65%.

Reaction of m-cresol-anisaldehyde novolac resin with Epoxy (Epichlorohydrin)

When m-cresol reacts with anisaldehyde in presence of dil. HCl, gives a condensation product, m-cresol-anisaldehyde novolac resin. The modified novolac resin was formed by the reaction of epichlorohydrin and phenolic group of m-cresol-anisaldehyde novolac resin in presence of sodium hydroxide. The reaction is as follows –



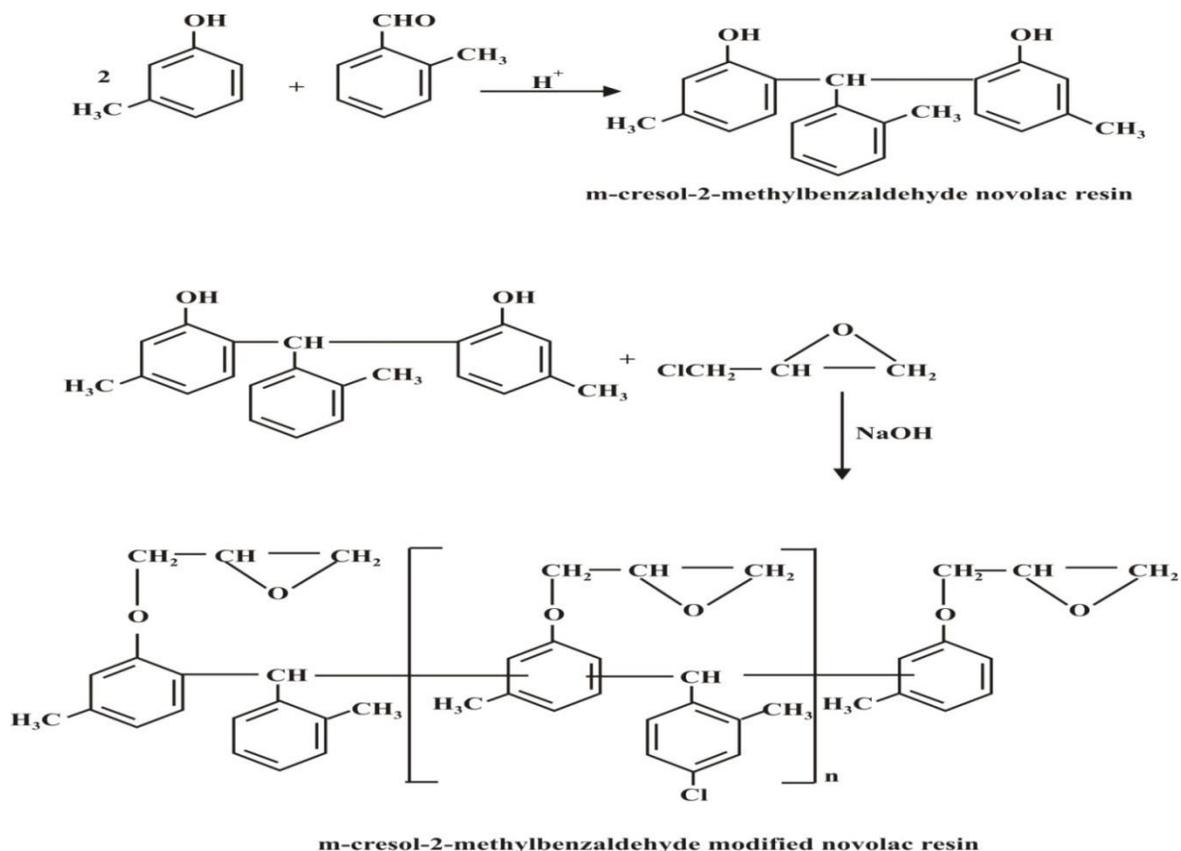
Scheme:1

Synthesis and modification of m-cresol – 2-methyl benzaldehyde novolac resin with Epoxy(Epichlorohydrin)

7g m-cresol-2-methylbenzaldehyde and 25 ml epichlorohydrin taken in a three necked round bottom flask were mixed. The reaction mixture was heated on water bath at 55°C under stirring and then from the side tube by dropping funnel 10% solution of NaOH (10ml) was added with stirring over 1h. After the addition of NaOH, the reaction was continued for 3.5 – 4h. At this point there emerged two layer which were separated by decandation. The modified resin was washed with 100 ml hot water three times to remove chloride ions and NaOH. Finally the whole resin was poured in to a porcelain dish, dried in the oven at 100°C till it got constant weight. This modified resin was soluble in chloroform, acetone, alcohol, toluene and insoluble in carbontetrachloride and water. The melting point of the modified resin was 100°C and colour of the modified resin was orange. The yield of modified resin was 83%.

Reaction of m-cresol – 2-methyl benzaldehyde novolac resin with Epoxy(Epichlorohydrin)

When m-cresol reacts with 2-methylbenzaldehyde in the presence of H₂SO₄ it gives a condensation product, m-cresol–2-methylbenzaldehyde novolac resin. The modified novolac resin is formed when epichlorohydrin reacts with phenolic group of this novolac in presence of alkali. The reaction involved is as follows:



Scheme:2

CHARACTERISATION

FTIR spectrum Interpretation of m-cresol-anisaldehyde epoxy modified novolac resin :

The infrared spectra of synthesized m-cresol-anisaldehyde epoxy modified novolac resin are shown in figure 1. The broad and strong band situated at 3418 cm^{-1} can be attributed to overlapping of $-\text{OH}$ stretching. The band from the range $2835 - 2928\text{ cm}^{-1}$ is attributed to the C-H stretching vibrations of methylene groups. The peak for monosubstitution in phenyl ring at 692 cm^{-1} and the carbon-oxygen stretch at 1108 cm^{-1} . The chloromethylen groups of epoxy were incorporated predominately at the *p*-positions of novolac resin as indicated from the newly formed carbon-carbon stretch at 1509 cm^{-1} .

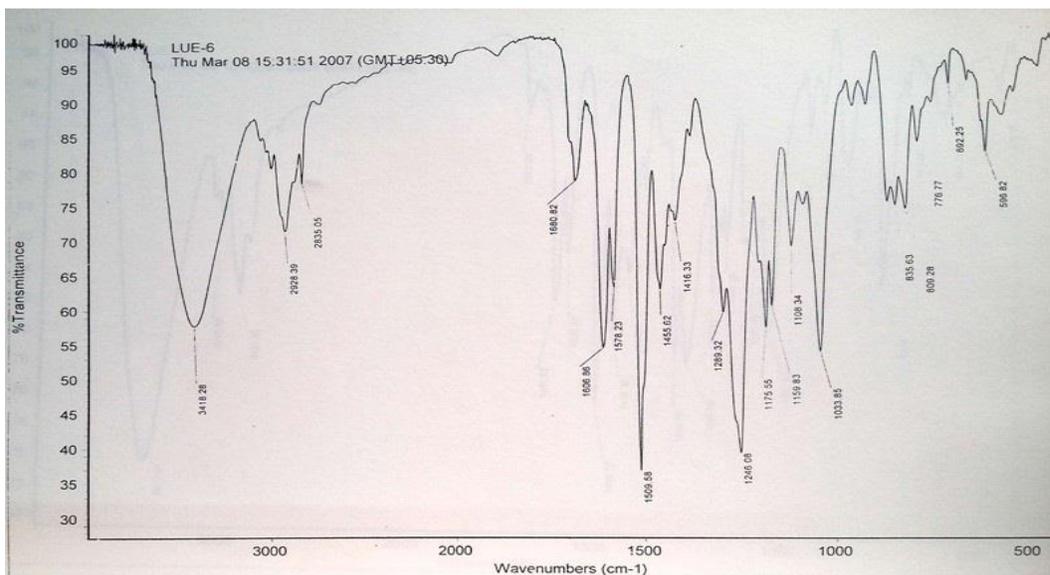


Figure : 1

FTIR spectrum Interpretation of m-cresol-2-methyl benzyldehyde epoxy modified novolac resin:

The infrared spectra of synthesized m-cresol- 2-methyl benzyldehyde epoxy modified novolac resin are shown in figure 2. The broad and strong band situated at 3417 cm^{-1} can be attributed to overlapping of -OH stretching, 3015 cm^{-1} CH unsaturated stretch. The band at 2921 cm^{-1} is attributed to the C-H stretching vibrations of methylene groups. The peak for monosubstitution in phenyl ring at 690 cm^{-1} and the carbon-oxygen stretch at 1192 cm^{-1} . The chloromethylen groups of epoxy were incorporated predominately at the *p*-positions of novolac resin as indicated from the newly formed carbon-carbon stretch at 1580 cm^{-1} , 1499 cm^{-1} $\text{C}=\text{C}$ aromatic ring, 1378 cm^{-1} OH in-plane bend and 1045 cm^{-1} single bond C-O stretching.

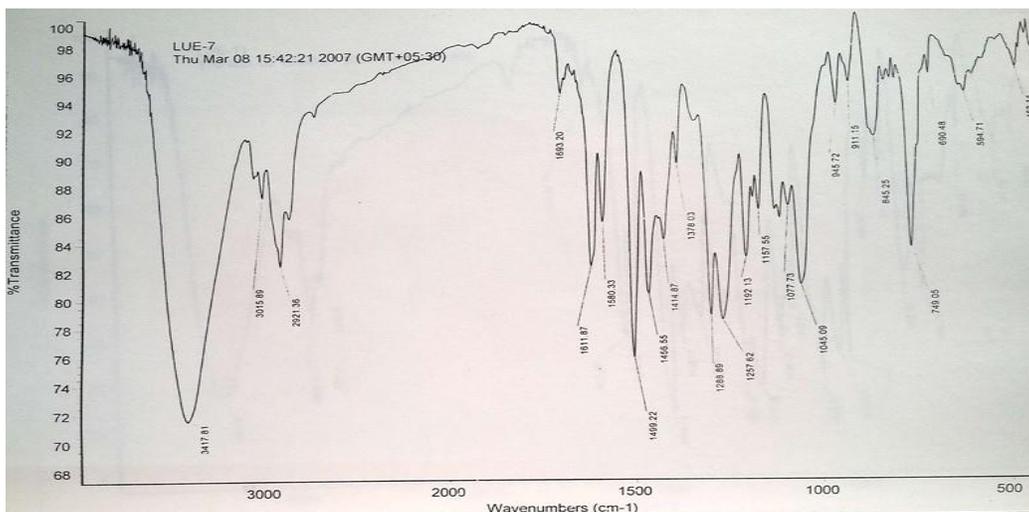


Figure: 2

CONCLUSIONS

In the present experimental study modification of phenolic novolac resin for increases the thermal properties. The optimal quantity of epoxy has been taken for the modification of phenolic resins. Thermal and impact strength values of modified phenolic resins also indicate the positive result comparatively unmodified phenolic resin. They were then investigated for spectroscopic studies.

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