

## ABSTRACT

Epoxy resins have been used successfully in a wide range of applications spanning from electronic products to advanced aerospace structures. Photoreactive epoxy materials have recently gained a remarkable interest, since the photochemical reactions in organic materials can induce many changes in physico-chemical properties. Epoxy resins are widely used in industries as protective coatings. The ability of the epoxy resin to react with a variety of substrates gives versatility to the epoxy resins.

In the present study, photosensitive aromatic diol monomers were initially prepared. The aromatic diols, 2,6-bis(4-hydroxy-3-methoxybenzylidene) cyclohexanone (BHMBCH) and 2,5-bis(4-hydroxy-3-methoxybenzylidene) cyclopentanone (BHMBCP) were synthesized by reacting 4-hydroxy-3-methoxybenzaldehyde with cyclohexanone and cyclopentanone respectively in presence of borontrifluoride diethyletherate as a catalyst in ethanol medium. The monomers 2,6-bis(4-hydroxybenzylidene) cyclohexanone (BHBCH) and 2,5-bis(4-hydroxybenzylidene)cyclopentanone (BHBCP) were then synthesized by refluxing 4-hydroxybenzaldehyde with cyclohexanone and cyclopentanone respectively in ethanol medium and in the presence of the borontrifluoride diethyletherate as catalyst.

The epoxy resins were synthesized by a solution of aromatic diols with epichlorohydrin in presence of base catalyst. The effect of the diol monomer and epichlorohydrin ratio plays a major role in the properties of epoxy resins. To study this effect all the epoxy resins were synthesized by

varying epichlorohydrin-diol monomer ratio. Bisphenol-A based epoxy resin was synthesized by adopting the above said method to compare the properties with BHMBCH / BHMBCP / BHBCH / BHBCP based epoxy resins. The copolymers of bisphenol-A and BHMBCH / BHMBCP were also synthesized by adopting the same procedure. The reaction conditions were optimized to synthesize the epoxy resins.

All the monomers and epoxy resins were synthesized in good yield and the molecular structure was confirmed by elemental analysis, UV-Visible, FTIR,  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectroscopic techniques.

The epoxy equivalent, determined using pyridinium hydrochloride method, showed that the epoxy equivalent decreases with increase in epichlorohydrin ratio. This may be due to the formation of diglycidyl structure at higher ratio of epichlorohydrin. The gel permeation chromatography results revealed that the synthesized epoxy resins are of low molecular weight.

The synthesized oligomers were subjected to thermogravimetric analysis and found that the oligomers containing cyclopentanone moiety exhibited higher thermal stability than the cyclohexanone containing oligomers. This may be due to the fact that the heat of combustion per methylene unit of cyclopentanone is higher than that of cyclohexanone. The thermal stability of methoxy substituted epoxy resins was found to be more than the unsubstituted counterparts. This may be due to the excess energy needed to break the methoxy pendant group.

Differential scanning calorimetric analysis results showed that the cyclopentanone containing epoxy oligomers possess higher melting temperature than the cyclohexanone containing oligomers. This may be due to higher degree of crystallinity in cyclopentanone containing epoxy resins, which is in good agreement with X-ray diffraction studies. Further, it was also found that the transition temperature was inversely proportional to the size of the cycloalkanone ring. As the ring size increases, the hard segments start losing their linear rigid structure, which reduced the transition temperature of the epoxy resins.

The synthesized epoxy resins showed absorption maximum at around 350nm due to  $\pi \rightarrow \pi^*$  transition of the olefinic double bond present in the main chain of oligomers. A decrease in the intensity of absorbance was observed in all oligomers during the successive irradiation with regular time intervals. This may be attributed to the disappearance of double bond leading to the formation of a cyclobutane ring by the  $2\pi + 2\pi$  cycloaddition reaction of the olefinic double bond. Further, it was noticed that the rate of photocrosslinking of epoxy resins in solution state was higher than that in the film state. This could be due to the ease of orientation of chromophoric olefinic groups in solution phase for photocrosslinking.

The photoreactive nature of the epoxy group present in the main chain of the oligomers was studied by making a thin film from epoxy resin with photoacid generator (PAG) and subjected to UV irradiation. The FTIR and DSC studies revealed that the epoxy resin with photoacid generator can undergo photopolymerization. These results substantiated that the synthesized

epoxy resins can undergo both photocrosslinking reaction between the  $-C=C-$  olefinic bonds and photopolymerization by epoxy rings. This study confirmed the presence of dual functionality in the synthesized epoxy resins.

The thermal degradation kinetics of synthesized epoxy resins was also carried out using thermogravimetric analysis. The order of thermal stability was UV unexposed > UV exposed without PAG > UV exposed with PAG.

The corrosion inhibition property of the synthesized epoxy resin was studied over aluminium substrates in 3.5% NaCl solution. The synthesized epoxy resin was mixed with DDM, coated over the substrate and cured. Corrosion inhibition efficiency was measured by electrochemical impedance spectroscopy (EIS). The SEM images of the substrates were taken after the corrosion experiment. The SEM and EIS results indicated that the epoxy resin forms a passive oxide film on the aluminium substrate and acts as corrosion resistance layer.

The results of this investigation indicate that synthesized epoxy resins can be used in photolithographic and coating applications.