Synthesis and characterization of epoxy resins containing zinc chloride

Saurabh Pandey & A K Srivastava*
Department of Science, H B Technological Institute, Kanpur 208002, India

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As evidenced from IR spectroscopy, ZnCl₂ forms a complex with oxygen atom of epichlorohydrin and thus cures the epoxy resins simultaneously. Differential Scanning Calorimetry (DSC) studies show that the properties, like degree of cure, percent crystallinity, glass transition temperature of the epoxy resin improved significantly. The Scanning Electron Microscopy (SEM) studies confirms the presence of zinc metal in the epoxy resin. The activation energy is 95 KJ/mol and order of reaction is first.

Epoxy resins, having good mechanical, thermal and electrical properties are widely used as engineering materials. A search of literature reveals that there have been a number of efforts to improve some of the properties of the epoxy resins. Toughness of the epoxy resins has been enhanced by blending with reactive liquid rubbers or terminally functionalized engineering thermoplastics. Enhancement in electrical conductivity has been observed by using metal acrylate. However, there is no report to improve glass transition temperature, percent crystallinity & degree of cure using Lewis acids. The present work reports the use of ZnCl₂ as modifier as well as curing agent to enhance the above properties.

Experimental Procedure

Preparation of epoxy resin A—Epoxy resin A was prepared according to method of Lee and Neville. Preparation of 0.018 mol bisphenol-A and 0.18 mol epichlorohydrin in a three-necked flask under reflux at 110°C over a period of 3.5 hr followed by a gradual addition of sodium hydroxide (5.4 M). Heating was continued for an additional 15 min, after which the content was dissolved in toluene (Ranbaxy) (80 mL) and the solution was filtered to remove the sodium chloride salt. The excess of epichlorohydrin (unreacted) and toluene was removed by distillation under reduced pressure (400 mm). The resulting viscous product was stored in an air-tight container.

Epoxy resins ER₁₋₆ were prepared following the same procedure in the presence of requisite equivalent of zinc chloride (S.d fine) (Table 1). The self life of epoxy resin at room temperature is six months.

The epoxy resins were characterized as—Epoxide equivalent (EE): The epoxide equivalent of various resins was obtained using the pyridinium chloride method. A weighed sample of epoxy resin (2-4 meq.) was treated with 25 cm³ of 0.2M pyridinium chloride in pyridine. The solution was warmed to dissolve the sample and heated under reflux for 0.5 hr. Then it was cooled to room temperature and diluted with methanol (50 cm³) and titrated with standard methanolic sodium hydroxide. The epoxide equivalent was calculated from the titer value.

Hydroxyl content—This was determined by acetyl chloride method.

Hydrolysable chlorine content—This was determined by heating the resin solution with alcoholic potassium hydroxide and titrating it with standard hydrochloric acid.

Results and Discussion

Table 1 & 2 report some characteristic properties of cured epoxy resins, ER₁ to ER₆. The values for refractive indices, viscosity, hydroxyl content are lower for epoxy resins prepared in the presence of zinc chloride (sample ER₁ to ER₆) as compared to sample ER₁ (without ZnCl₂). However, the epoxide equivalent, chlorine content, % crystallinity, degree of cure (α') and glass transition temperature show higher trend.

The measurement of the heat of reaction were conducted using the Du Pont 2100 differential scanning calorimetry with nitrogen as purge gas at the
In order to examine the role of the zinc chloride on properties of the epoxy resins, a comparison of IR spectra of epichlorohydrin containing ZnCl₂ and pure epichlorohydrin was made on Perkin-Elmer spectrophotometer Model 377 (Figs 1a & 1b). From this study it is clear that there is a shifting of band from 910 to 930 cm⁻¹ of epoxy group confirming a complex formation between the zinc chloride and epoxy oxygen of the epichlorohydrin. The ZnCl₂ and epichlorohydrin complex has 1:1 stoichiometry.

DSC heat flow curve (Fig. 2) was used to obtain the residual heat of reaction because the heat capacity
of the resin sample changed with temperature. Pasatioglu and Han showed that the degree of cure \( \alpha' \) can be expressed as:

\[
(\alpha') = \frac{H}{H_t} + H_r
\]

where \( H \) = instantaneous heat of reaction, \( H_t \) = total heat of reaction, \( H_r \) = residual heat of reaction and \( \alpha' \) = degree of cure.

Degree of cure \( \alpha' \) of modified epoxy resin is higher than for control epoxy resin and increases as a function of concentration of ZnCl\(_2\). The percent crystallinity is calculated by using the following formula:

\[
\text{Percent crystallinity} = \frac{H_a - H_c}{H_a - H_c}
\]

where \( H_a \) = amorphous enthalpy, \( H_c \) = crystalline enthalpy and \( H \) = sample enthalpy.

The percent crystallinity of modified epoxy resin (B & E) is more than that of the control (unmodified resin).

**Thermogravimetric Analysis**—The effect of ZnCl\(_2\) on the thermal stability of the epoxy resin was studied by thermogravimetric analysis (TGA of Du Pont 2100) at heating rate of 10°C/min under nitrogen atmosphere. A resin sample ER\(_a\) containing ZnCl\(_2\) was stable up to 275°C and started losing weight above this temperature (Fig. 3), however, control epoxy resin ER\(_a\) is stable up to 130°C. In epoxy resin containing ZnCl\(_2\), rapid decomposition was observed around 350-400°C. In case of control epoxy resin rapid decomposition observed at 200-250°C and almost total volatilization occurred around ~350°C (ER\(_a\))

Percent crystallinity is at or above 500°C. The enhanced thermal stability of epoxy resin may be attributed to the incorporation of zinc into the resin.

**Kinetics of epoxide reaction**—The activation energy \( E_a \) and order of reaction have been calculated from Coats and Redfern equation from dynamic thermogram (Fig. 5).

\[
\log_{10} \left[ g / T^2 \right] = \frac{E_a}{2.3RT} + \log_{10} \left( \frac{ZR}{BE} \left( 1 - 2RT / E_a \right) \right)
\]

\[
g = [- \log (1 - \alpha') / \alpha']
\]

The plot of \( \log \left[ g / T^2 \right] \) versus \( (1/T)x10^3 \) gives a linear curve. Its slope is equal to \( E_a / 2.3RT \) and its intercept gives

\[
\log_{10} \left( \frac{ZR}{BE} \left( 1 - 2RT / E_a \right) \right)
\]

where \( Z \) = pre-exponential factor, \( E \) = Activation energy (KJ/mol), \( T \) = Temperature (in °K), \( R \) = Gas constant (J/°K), \( B \) = Linear heating rate (°C/S) and \( n \) = order of reaction.

The activation energy, calculated from the slope of a linear graph plotted between \( \log g / (\alpha') \) versus \( (1/T)x10^3 \), is 95 KJ/mol (Fig. 5). The straight line (Fig. 5)
confirms the order of reaction as one, which matches well this will those reported earlier\textsuperscript{22,21}. Thus, it is clear that zinc chloride forms a complex with epichlorohydrin that acts as a acidic curing agent. The enhanced degree of cure explains the change in properties of the epoxy resin (Table 2).

Mechanism—A comparison of IR spectrum of complex with epichlorohydrin (Fig.1b) shows, shifting of band from 910 to 930 cm\(^{-1}\) of epoxy group, hence it is concluded that zinc, being transition element, forms a complex with epichlorohydrin but not with bisphenol-A, according to structure (1).

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Reference