Synthesis and characterization of epoxy resin in the presence of \( p \)-acetylbenzylidene triphenylarsoniumylide-mercuric chloride complex

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\( p \)-Acetylbenzylidene triphenylarsoniumylide mercuric chloride complex modifies and also has autocatalytic curing properties for epoxy resin. The degree of cure \( (\alpha') \), percentage crystallinity and glass transition temperature \( (T_g) \) of the modified resin, investigated by differential scanning calorimetry, are 1.03, 91% and 298°C respectively. The TGA technique has been used to calculate the activation energy and the order of reaction, which are 97 kJ/mol and one respectively. The SEM analysis shows presence of Hg (40%) in the epoxy resin.

Amongst versatile thermosetting polymers, epoxy resin has assumed a more important role by virtue of the greater flexibility in tailoring for desired ultimate properties. As a result, the epoxy resin has been subjected to modification using different additives (metal acrylate\(^1\)) or modification of monomers like quinoline\(^4\), thiocarbonhydrazone\(^5\), etc. The acetylbenzylidene triphenylarsoniumylide-mercuric chloride complex seems to be a strong candidate for modification of epoxy resins; but publications in this area are still scarce\(^6\). The present work shows that the complex has autocatalytic curing properties at room temperature (within 17 hr). It is, therefore, worthwhile to examine the effect of complex on the properties of epoxy resin.

**Experimental**

Bromine (Fluka), bisphenol-A (Robert Johnson), triphenylarsine (Merck) and epichlorohydrin (Ranbaxy) were used as received. The rest of chemicals, i.e., toluene, methanol, pyridine and dioxane were purified according to standard methods\(^8\).

**Synthesis of ylide:** \( p \)-Acetylbenzylidene triphenylarsonium ylide was prepared by the method of Singhal et al.\(^7\). Briefly, a solution of 0.04 mol of triphenylarsine and 0.04 mol of \( p \)-bromomethylacetophenone in benzene was refluxed for 72 hr. Excess of solvent was removed under vacuum and 12.0 ml ethyl acetate was added to the residue. The precipitate was isolated by filtration and recrystallised twice from chloroform-benzene mixture (v/v) to get colourless microcrystals of \( p \)-acetylbenzylidene triphenylarsinium bromide. Then 2.0 g of \( p \)-acetylbenzylidene triphenylarsinium bromide, in 100 ml benzene was treated with sodium ethoxide in methanol, where by ylide was obtained, m.p. 250°C.

**Synthesis of metal-ylide complex**

The complex was prepared by the method\(^6\) exactly similar to that for phenacyldimethylsulphonium ylide-mercuric chloride complex. A methanolic solution (25 ml) of mercuric chloride (1.0 m mol) was added dropwise to a solution of \( p \)-acetylbenzylidene triphenylarsonium ylide (2.0 mmol) in methanol (20 ml), stirred for 2 hr at room temperature and then isolated by suction filtration. It was then washed with methanol followed by diethyl ether.

It was insoluble in non-polar solvents like benzene and carbon tetrachloride but partially soluble (<10%) in polar solvents like as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).

**IR data**

1734 cm\(^{-1}\) (\( > \)C = O); 2853 cm\(^{-1}\); (C-H, aliphatic); 1375 cm\(^{-1}\) (\( > \)C-H\(_2\)); 750 cm\(^{-1}\) (C-H, aromatic); 1600 cm\(^{-1}\) (C = C; aromatic).
Preparation of epoxy resin

It was prepared according to the method of Lee and Neville. The epoxidation was carried out by refluxing bisphenol-A and epichlorohydrin in 1:10 mole ratio, in a three-necked flask followed by gradual addition of sodium hydroxide over a period of 3.5 hr. The content was dissolved in toluene and the solution was filtered to remove the salt. The excess epichlorohydrin and toluene were removed by distillation under reduced pressure (400 mm). The resulting viscous product epoxy resin (A) was stored in an air-tight container. Epoxy resin B was prepared by reacting bisphenol-A and epichlorohydrin, in 1:10 mole ratio, in the presence of 3.2x10⁻⁴, 7.2x10⁻⁴ and 11.2x10⁻⁴ molar equivalent of metal-ylide complex, in a similar manner to epoxy resin A.

Characterization

Epoxide equivalent weight (EEW): 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 0.2 N pyridinium chloride in pyridine. The solution was warmed to dissolve the sample and then heated under reflux for 0.5 h. The solution was cooled to room temperature and diluted with methanol (50 cm³), was titrated against methanolic NaOH (0.5/N). The epoxide equivalent was calculated from the titer value.

Hydroxyl equivalent

This was determined by acetylation with acetylchloride in pyridine solution. The excess chlorine was decomposed with water and the resulting acetic acid, formed both in hydrolysis and in the acetylation process, was titrated with standard alkali solution. The value was calculated using following equation:

\[
\text{Hydroxyl content} = \frac{\text{Weight of sample}}{\text{Normality of alkali} \times \text{V₁} - \text{V₂} \times 170}
\]

V₁ = volume of alkali used for blank
V₂ = volume of alkali used for sample

Hydrolyzable chlorine content

It was determined by treating the resin solution with alcoholic KOH and titrating it against standard HCl.

Viscosity

Viscosity of the resins was determined in dimethylformamide at various temperatures (25 to 80°C) using an Ubbelohde viscometer.

Infrared analysis

The infrared spectra were recorded using a Perkin-Elmer spectrophotometer (Model 377).

Scanning electron microscopy (SEM)

Scanning electron micrographs were obtained using a JEOL JSM 840A scanning electron microscope. This film was mounted vertically on an SEM stub using a silver adhesive paste.

Thermal analysis

Differential scanning calorimetry

The measurements of heat of reaction were conducted using a Dupont 2100 differential scanning calorimeter with nitrogen as purge, 40 ml/min. All the experiments were carried out under typical scan conditions (at 156° and 419°C) to obtain the heat flow curve. The weight of the sample was between 2 and 5 mg. The glass transition temperature (Tg) of the cured sample after the typical scan runs was determined in dynamic region at 10°C/min.

Thermogravimetric analysis (TGA)

It was carried out on a TGA/5 1A Dupont 2100 apparatus at 10°C/min, under a nitrogen atmosphere.

Results and discussion

An examination of Table 1 reveals that the values of epoxide equivalent, chlorine content and specific gravity increase as functions of the molar equivalent.
of metal-ylide complex in epoxy resin. Lifeline, the value of hydroxy increase and then decrease are the least affected. It is further noted that the value of specific viscosity (η) increases with increases in the molar equivalent of metal-ylide complex.

**IR analysis**

The IR spectra of modified epoxy resin (ER₉) show a band at 910 cm⁻¹ in the IR spectrum which confirms the presence of an epoxy resin group. The band at around 1060 cm⁻¹ is due to stretching vibration of –C–O–C– group and a band around 2910 cm⁻¹ is due to phenyl group. The broadened band around 3320 cm⁻¹ indicates the presence of –OH group, possibly due to oligomerization. However, there are additional bands at 780 cm⁻¹ and 1760 cm⁻¹ which confirm the presence of the metal-ylide complex in the epoxy resin B. Morphology of resin has been studied with the help of SEM. The unmodified epoxy resin (A) has only one phase, and the fracture surface is smooth and featureless as reported previously¹⁵-¹⁶. The modified resin has two phase morphology, first phase shows mercury (Hg) as white portion present in the dark region due to the epoxy region.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Properties</th>
<th>ER₉ (O.OM)</th>
<th>ER₉ (3.2M)</th>
<th>ER₉ (7.2M)</th>
<th>ER₉ (11.2M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Epoxide equivalent (eq./100 g.)</td>
<td>194</td>
<td>608</td>
<td>1104</td>
<td>3342</td>
</tr>
<tr>
<td>2.</td>
<td>Hydroxyl content (eq./100 g.)</td>
<td>0.12</td>
<td>0.041</td>
<td>0.046</td>
<td>0.071</td>
</tr>
<tr>
<td>3.</td>
<td>% Crystallinity</td>
<td>30%¹⁵</td>
<td>—</td>
<td>91%</td>
<td>—</td>
</tr>
<tr>
<td>4.</td>
<td>Degree of cure (%)</td>
<td>070¹⁵</td>
<td>—</td>
<td>1.03</td>
<td>—</td>
</tr>
<tr>
<td>5.</td>
<td>Glass transition temperature (Tg)°C</td>
<td>130°C</td>
<td>—</td>
<td>298.25°C</td>
<td>295.71°C</td>
</tr>
<tr>
<td>6.</td>
<td>Chlorine content (in %)</td>
<td>0.56</td>
<td>1.6</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td>7.</td>
<td>Viscosity (at 25°C)</td>
<td>1.58</td>
<td>1.17</td>
<td>1.19</td>
<td>1.27</td>
</tr>
<tr>
<td>8.</td>
<td>Specific gravity (at 25°C)</td>
<td>1.173</td>
<td>1.6552</td>
<td>1.7038</td>
<td>1.7048</td>
</tr>
<tr>
<td>9.</td>
<td>Refractive indices (at 25°C)</td>
<td>1.5695</td>
<td>1.425</td>
<td>1.422</td>
<td>1.421</td>
</tr>
<tr>
<td>10.</td>
<td>Physical state</td>
<td>Viscous</td>
<td>Viscous</td>
<td>Viscous</td>
<td>Highly viscous</td>
</tr>
<tr>
<td>11.</td>
<td>Colour</td>
<td>Whitish yellow</td>
<td>Yellow</td>
<td>Yellow</td>
<td>Dark yellow</td>
</tr>
</tbody>
</table>

**Element Line | Weight% | K-Ratio | Cnts/s**
| S   | Ka | 1.08 | 0.0019 | 5.06 |
| Cl  | Ka | 0.19 | 0.3610 | 139.90 |
| Ca  | Ka | 0.81 | 0.0645 | 17.56 |
| Fe  | Ka | 11.28 | 0.1153 | 11.90 |
| As  | La | 0.00 | 0.0000 | 0.00 |
| Hg  | La | 40.65 | 0.2979 | 1.16 |
| Total | | 100.01 |

**Fig. 1 — SEM of ER₉ (Analysis)**
Fig. 1 shows that 40% (weight %) mercury is incorporated in the epoxy resin. DSC heat flow curve is used to obtain the residual heat of reaction with the help of following equation\(^{17,18}\):

\[
(\alpha') = \text{H}/\text{Hult}, \quad \text{Hult} = \text{Ht} + \text{Hr} \quad \ldots (1)
\]

where \(H\) = instantaneous heat of reaction, \(Ht\)=total heat of reaction, \(Hr\) = residual heat of reaction and \(\alpha'\) = degree of curve.

Percentage crystallinity was also calculated by using following formula\(^9\):

\[
\text{Percentage crystallinity} = \frac{\text{Ha}-\text{Hc}}{\text{Ha}-\text{Hc}} \quad \ldots (2)
\]

where \(\text{Ha}\) = amorphous enthalpy; \(\text{Hc}\) = crystalline enthalpy, and \(\text{H}\) = sample enthalpy

The values of \(\text{Ha}\) and \(\text{Hc}\) were calculated from DSC curves [Fig. 2(ii)]. The values of degree of cure and percent crystallinity for modified epoxy resin (C) were higher than those for control epoxy resin, and increase as a function of concentration of metal-ylide complex. The glass transition temperature (Tg) values for the modified epoxy resin C and D were higher than those for the control epoxy resin (A). [Fig. 2(i), (ii) & (iii)].

The effect of the structure of metal-ylide complex on the thermal stability of the epoxy resin resin was studied by thermogravimetric analysis (TGA) (Fig.3).
A resin sample (B) containing metal-ylide complex was stable up to 280°C and started losing weight above this temperature. However, the control epoxy resin (A) was stable up to 130°C (ref. 10). In modified epoxy resin, containing metal-ylide complex, a rapid decomposition was observed at 400-600°C and was almost total volatilization of the polymer (at 800°C), which confirms that incorporation of metal-ylide complex increases the thermal stability of the polymer.

**Kinetics**

The activation energy corresponding to the decomposition process and order of reaction, was
calculated using Coats and Redfern equation from dynamic experiment.

$$\log (\alpha)/T^2 = E_a/2.3RT + \log ZA/BE \times (1-2RT/E_a) \ldots (3)$$

$Z$ = pre-exponential factor, $T$ = temperature, $R$ = gas constant, $B$ = linear heating rate and $E_a$ = activation energy.

The activation energy, calculated from the slope of linear graph, between $\log g (\alpha)$ vs. $(1/T) \times 10^3$ is 97 kJ/mol, which is higher compared to that for control epoxy resin (34 kJ/mol). This overall order of reaction follows a first order kinetics.

**Conclusion**

A comparison of IR spectrum of complex with epichlorohydrin shows, shifting of band 910-930 cm$^{-1}$ due to epoxy ring, hence it is concluded that mercury (Hg), being transition element, forms a complex with epichlorohydrin but not with bisphenol—A, according to (Structure I).

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**References**