Synthesis and Characterisation Studies of Phenolic Resin Modifications on Epoxy Systems

Najuma AbdulRazack and Lity Alen Varghese

Abstract--- In the present study, various modifications for epoxy resin system were done for metal to metal bonding. Epoxy adhesives were synthesized from epichlorohydrin and bisphenol-A and the mole ratio of reactants (BPA/ECH) were optimized to be 1:3 from various shear and peel strength experimentations. In the first part modification was done by blending epoxy with phenol formaldehyde (PF) resole resin and later, the epoxy was further modified by replacing it partially with hyperbranched structures like epoxidised phenolic novolacs (EPN) and epoxidised cresol novolacs (ECN). Phenol and cresol novolacs were prepared by the reaction of phenol and cresol respectively with formaldehyde. The results indicated that EPN/PF and ECN/PF blends gave better strength properties when compared to EPN/PF and Epoxy/PF blends. Morphological analysis using SEM gives an idea on the energy absorption during failure for the Epoxy/PF blend.

Keywords--- Adhesive; Epoxy; Novolac; Blends; Hyperbranched

I. INTRODUCTION

Epoxies are probably the most versatile family of adhesives because they bond well to many substrates and can be easily modified to achieve widely varying properties[1]. The most common epoxies used in adhesives are derived from bisphenol-A and epichlorohydrin and are usually cured with reactive hardeners containing primary and/ or secondary amine groups[2]. In general, epoxy resins are prepared by the reaction of compounds containing an active hydrogen group with epichlorohydrin followed by dehydrohalogenation. Epoxies dominate the field of structural adhesives due to their better wetting ability, excellent mechanical properties and high chemical and thermal resistance [3]. Because of the normally brittle nature, epoxy adhesives have been toughened with many different resins including thermoplastic particles, nylon and various elastomers.

Combinations of epoxy and phenolic resins provide structural adhesives with superior high temperature resistance. Both novolac and resole type phenolics may be used. The blends cure through reaction of the epoxy groups with the phenolic hydroxyl groups. When resoles are used, the epoxy may also react with the methyol groups. Adhesives based on epoxy-phenolic blends are good for continuous high temperature service in the 350°F range or intermittent service as high as 500°F. They retain their properties over a very high temperature range[4]. Resistance to weathering, oil, solvents and moisture is very good. Because of the rigid nature of the constituent materials, epoxy-phenolic adhesives have low peel and impact strength and limited thermal-shock resistance. These were developed primarily for bonding metal joints in high temperature applications. Usually the phenolics used are the resole type and often the epoxy is a minor component[5].

In this paper, we are reporting the adhesive properties of epoxy resin, epoxidised phenol novolacs (EPN) and epoxidised cresol novolacs (ECN) in blend with phenol formaldehyde for metal to metal (Al-Al) bonding. Novolac epoxy resin, being multifunctional, can produce a more tightly crosslinked three dimensional network and hence give better adhesive strength. Also, they combine the reactivity of the epoxy group and the thermal resistance of the phenolic backbone.

II. EXPERIMENTAL

A. Materials

Phenol, m-cresol, formaldehyde (40% solution), sodium hydroxide (All from Merck India Ltd.), Epichlorohydrin (Sisco Research laboratories Pvt. Ltd., Mumbai, India) and Bisphenol A (Loba Chemie Pvt. Ltd., Mumbai, India) was used in this investigation.

B. Synthesis of Epoxy resin

Bisphenol A (1 mole) was dissolved in a mixture of an excess of epichlorohydrin (6 moles) and 50 cc water in a one litre three necked flask. The flask was equipped with a mechanical stirrer, thermometer and a Liebig's condenser. The mixture was heated gently over a water bath till the epichlorohydrin began to boil. Heating was stopped and caustic soda (2 moles) was added in two pellets at a time down the condenser. The reaction was allowed to subside before more alkali was added. When all the caustic soda pellets had been added, the reaction mixture was boiled gently for 45 minutes. Heating was stopped as the reaction mixture turned viscous. The excess epichlorohydrin was removed by vacuum distillation. The remaining mixture was extracted with benzene to precipitate sodium chloride which was removed by filtration under vacuum. The filtrate was distilled in vacuum to remove benzene and dried in vacuum for about 3 hours.

C. Synthesis of novolac resins

The novolacs were prepared by reacting phenol with formaldehyde in the molar ratio 1:0.8 in presence of oxalic acid catalyst in a 3-necked flask fitted with a mechanical stirrer, water condenser and thermometer. The reaction mixture was heated and allowed to reflux at about 100°C for 2-3 hours. When the resin separated from the aqueous phase the reaction was stopped. The resin was neutralised with sodium
hydroxide, filtered, washed with water and vacuum dried. The novolac resin contains 4-6 benzene rings per molecule. The same procedure was used to synthesise novolac resin from m-creosol (ECN)[6].

D. Synthesis of Epoxidised phenolic novolacs (EPNs)

1 mole of the novolac resin (1:0.8) was dissolved in 6 moles of epichlorohydrin and the mixture heated in a boiling water bath. The reaction mixture was stirred continuously for 4 hours while 1 mole of sodium hydroxide in the form of 30% aqueous solution was added drop wise. The rate of addition was maintained such that the reaction mixture remains at a pH insufficient to colour phenolphthalein. The resulting organic layer was separated and then fractionally distilled under vacuum. Epoxidised novolac resin was similarly prepared from m-creosol novolac (ECN) using the same procedure.

E. Synthesis of Phenol formaldehyde (PF) resole resins

The resole resin were prepared by reacting phenol with formaldehyde in the molar ratio 1:1.7 in presence of 33% NaOH solution in a 3-necked flask fitted with a mechanical stirrer, condenser and thermometer. The reaction mixture was heated and allowed to reflux at about 100°C for 1 hour. The resin was further neutralised with oxalic acid in minimum amount of water, washed with water and vacuum dried.

F. Bonding and adhesive performance

Aluminium strips of size 100x25 mm were machined from 0.8 mm thick sheets to serve as metal substrates for peel studies on metal-to-metal bonds. Strips of 100x25x1 mm were used for shear strength. Surface preparation is necessary before the application of adhesive. Solvent degreasing was done with trichloroethylene, to remove dust and traces of oily impurities on the surface. Following the solvent wiping, the surface was abraded with emery paper (P 100) and is again wiped with solvent to remove completely the debris of abrasion. An even contact pressure is applied throughout the joining surface after the application of the adhesive and it is then kept in the oven at the required temperature for the specified time.

Peel strength and lap shear strength of metal-to-metal specimens were determined on a universal testing machine as per ASTM D903[7] and ASTM D1002[8] respectively with a grip separation rate of 50 mm/min at room temperature.

G. Formulation of adhesive blends

Epoxy resin were synthesized in varying molar ratios of Epichlorohydrin (ECH) to Bisphenol-A (BPA) viz. 1.57:1, 3:1, 3.5:1 and 4:1 and the mole ratio were optimised based on lap shear and peel strength experimentations. The epoxy was further modified by replacing it with epoxy/PF blend in varying ratios. The same procedure is repeated for EPN/PF and ECN/PF. All the blends were tested for lap shear and peel strength in the Universal testing machine.

H. Resin Characterisation

Epoxide Equivalent weight (EEW): The epoxy content of epoxy resins is an important variable in determining their reactivity and the properties of coatings made from them. Knowing the EEW, the required amount of the crosslinking agent can be calculated. EEW is usually defined as the weight of resin in grams, which contains 1 g of the equivalent. The epoxy content of liquid resins is frequently expressed as weight per epoxide (wpe) or equivalent/kg of the resin. A common method of analysis of epoxide content of liquid resins involves the opening of the epoxy ring by hydrogen halides (hydrohalogenation). Weight per epoxide values of the synthesised epoxy, EPN and ECN resins were determined by the pyridinium chloride method as per ASTM D 1652-73.

0.1 to 0.2 gm of the epoxy resin was mixed with 2 ml HCl in 25 ml pyridine. The mixture was heated to reflux on a water bath for 45 minutes. The solution was cooled to room temperature and the unreacted acid present was estimated by back titration with standard NaOH solution (0.1 N) using Phenolphthalein indicator. A blank was also carried out under same reaction conditions.

Epoxide equivalent = NxV/w, where N is the strength of alkali, V is the volume of alkali used up and w is the weight of the resin. Epoxide equivalent can be obtained as eq/kg from which wpe value of the resin can be calculated.

Gel time determination of blends: About 2 gm of the sample is filled into a test tube and dipped into a water bath at 100°C. The increase in viscosity is monitored with a glass rod used roughly like a reciprocating piston. As soon as the gel point is reached the glass rod gets trapped in the resin. This period of time is recorded as the gel time. The test is done as per DIN16945.

Spectroscopic analysis Fourier transform infra-red (FTIR) spectra are generated by the absorption of electromagnetic radiation in the frequency range 400 to 4000 cm⁻¹ by organic molecules. Different functional groups and structural features in the molecule absorb at characteristic frequencies. The frequency and intensity of absorption are indicative of the bond strengths and structural geometry in the molecule. FTIR spectra of the samples were recorded on a Shimadzu, IR Prestige 21 Spectrometer by KBr pellet method.

Nuclear magnetic resonance (NMR) spectroscopic method has been used to good effect by authors investigating the structure of phenol-formaldehyde resins. Here ¹H NMR spectroscopy is used for the characterization of the synthesized resins (EPN, ECN and PF). The spectra were recorded on a 500 MHz Bruker Avance DPX spectrometer using acetone as solvent.

I. Morphological studies

Scanning electron microscope (SEM) is a very useful tool in polymer research for studying morphology and microstructure. Hitachi SU6600 Variable pressure field emission SEM (FESEM) was used to investigate the morphology of the failed adhesive surfaces. In this technique, an electron beam is scanned across the specimen resulting in back scattering of electrons of high energy, secondary electrons of low energy and X-rays. These signals are monitored by detectors (photo multiplier tube) and magnified. An image of the investigated microscopic region of the specimen is thus observed in a cathode ray tube and
photographed using black and white film. The SEM observations reported in the present study were made on the fracture surfaces of failed peel specimens.

III. RESULTS AND DISCUSSION

A. Mechanical properties

The average lap shear and peel strengths of epoxy resins synthesized in varying molar ratios of BPA/ECH is given in Table 1.

Table 1: Variation of lap shears and peel strengths with bpa/ech molar ratio

<table>
<thead>
<tr>
<th>Sample(BPA/ECH)</th>
<th>Average lap shear strength(N/mm²)</th>
<th>Average peel strength (N/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 1.57</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1 : 3</td>
<td>4.402</td>
<td>0.550</td>
</tr>
<tr>
<td>1 : 3.5</td>
<td>1.412</td>
<td>0.513</td>
</tr>
<tr>
<td>1 : 4</td>
<td>0.627</td>
<td>0.497</td>
</tr>
</tbody>
</table>

In the case of 1:1.57, the glycidyl ether formation is less than 10% and the resin formed is in solid form which is uncoatable. On increasing the ratio beyond 1:4, the viscosity of the resin formed was found to decrease considerably. Consequently, the more viscous liquid epoxides are usually preferred to the less viscous members of the series for adhesive applications. According to the experimental data, a relatively good adhesion property is achieved by replacing epoxy with EPN and ECN in the same ratios as above. The variations in lap shear and Peel strengths of these systems can be observed from Tables 2 and 3.

Table 2: Variation of Lap Shear Strengths of Various Systems

<table>
<thead>
<tr>
<th>PF content (phr)</th>
<th>Epoxy/PF</th>
<th>EPN/PF</th>
<th>ECN/PF</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.92</td>
<td>2.08</td>
<td>2.72</td>
</tr>
<tr>
<td>20</td>
<td>2.12</td>
<td>2.35</td>
<td>2.88</td>
</tr>
<tr>
<td>40</td>
<td>3.02</td>
<td>3.15</td>
<td>3.84</td>
</tr>
<tr>
<td>60</td>
<td>3.36</td>
<td>3.54</td>
<td>4.02</td>
</tr>
<tr>
<td>80</td>
<td>4.01</td>
<td>4.07</td>
<td>4.35</td>
</tr>
<tr>
<td>100</td>
<td>4.6</td>
<td>4.6</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Table 3: Variation of Peel Strengths of Various Systems

<table>
<thead>
<tr>
<th>PF content (phr)</th>
<th>Epoxy/PF</th>
<th>EPN/PF</th>
<th>ECN/PF</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.13</td>
<td>0.15</td>
<td>0.18</td>
</tr>
<tr>
<td>30</td>
<td>0.18</td>
<td>0.22</td>
<td>0.24</td>
</tr>
<tr>
<td>50</td>
<td>0.22</td>
<td>0.29</td>
<td>0.31</td>
</tr>
<tr>
<td>70</td>
<td>0.31</td>
<td>0.34</td>
<td>0.46</td>
</tr>
<tr>
<td>80</td>
<td>0.36</td>
<td>0.41</td>
<td>0.59</td>
</tr>
<tr>
<td>100</td>
<td>0.61</td>
<td>0.61</td>
<td>0.61</td>
</tr>
</tbody>
</table>

It was observed that the lap shear and peel strengths of almost all the systems increased with PF content. The results indicated that ECN/PF blends gave better strength characteristics when compared to EPN/PF and Epoxy/PF. Phenol formaldehyde, due to its brittle nature, increases the cross linking sites in the system, thereby increasing the flexibility and lap shear strength. m-cresol, has 3 reactive positions, which can react with PF, to give a cross linked structure, resulting in an increase in strength.

B. Resin Characterisation

Epoxide Equivalent weight (EEW): The epoxide equivalents of the synthesized resins were determined by the titration method. The epoxy equivalents for Epoxy, EPN and ECN resins were found to be 4.2, 2.6 and 3.1 eq/kg respectively. Epoxidised cresol novolac was found to have greater epoxide content than epoxidised phenol novolac. The high epoxide functionality, results in a higher density of crosslinks and hence improved heat resistance.

Gel time determination of blends: From the experiment, it was found that the gel time for Epoxy/PF blend was 40 min, while the EPN/PF and ECN/PF blends were stable after 1 hr. ie, the gel time was found to increase when the epoxy was replaced with novolac resin in the blend. Also, it is evident that Epoxy/PF blend have a short gel time and often a short shelf life compared to the other blends. This is attributed to the low reactivity of novolac based blends.

Spectroscopic data FTIR: The FTIR spectrum of epoxy resin is given in Figure 1. The C-H stretching in epoxies is at 3250-3500 cm⁻¹ range indicates the phenolic hydroxyl group, 2964 cm⁻¹ is typical of the C-H stretching of methylene groups. The less intense broad band at 3080-3120 cm⁻¹ and 2931 cm⁻¹ are typical of the epoxy group [9]. The band at 915 cm⁻¹ (asymmetric ring stretching in which C-C stretches during contraction of C-O bond), 829 cm⁻¹ and 750 cm⁻¹ are typical of the epoxy group [9].

Figure 1: FTIR Spectra of Epoxy Resin

Figure 2: FTIR Spectra of Epoxidised Phenol novolac Resin

The Figure 4 shows the FTIR spectra of synthesised EPN resin. Similar to Figure 3, here also we can see peaks which show the epoxide functionality. The band at 1242 cm⁻¹ denotes symmetrical C-O stretching (ring breathing frequency) in epoxides. Further, the bands at 2931 cm⁻¹, 815 cm⁻¹ and 748 cm⁻¹ are also typical of epoxides. The less intense broad band at 3250-3500 cm⁻¹ range indicates the phenol hydroxyl group, which also has a considerable involvement in epoxidation.
**NMR:** Figures 3, 4, and 5 show the $^1$HNMR spectra of PF, EPN, and ECN resins respectively. In the proton NMR for PF resin, the spectra displayed peaks of aromatic protons ($\delta$ 7.2), methoxy protons ($\delta$ 3.7), -CH=CH- protons ($\delta$ 5.35), -CH$_2$-Ar protons ($\delta$ 2.55) and -CH$_2$-CH=CH- protons ($\delta$ 2.01).

The proton NMR of EPN displayed strong peaks of Aryl protons ($\delta$ 2.1, $\delta$ 2.45) and –CH$_3$- protons ($\delta$ 0.98). Peaks for aromatic protons ($\delta$ 6.8- $\delta$ 7.3) and –CH$_2$ protons are also evident. In proton NMR of ECN, the doublet signal at 6.8 ppm is for aromatic protons. The spectra also displayed peaks of Aryl protons($\delta$ 2.3), CH-X protons ($\delta$ 2.9), Alkenyl H ($\delta$ 4.1) and -CH$_3$- protons ($\delta$ 0.95). The weak singlet at 3.8 ppm is for –CH$_2$.

**C. Morphological studies**

Fracture surfaces of the failed adhesive bonds were subjected to Scanning electron microscopy (SEM) to observe morphological features. Figure 6 is a view of the fracture surface of an Epoxy/PF blend after the peel test.

**IV. Conclusions**

Adhesive behaviour of different epoxy/phenolic blends has been investigated by lap shear test using aluminium substrates. All the synthesised resins were characterised using FTIR and NMR spectroscopic analysis. It is observed from the results that, the modifications by phenolic resin systems are very effective for improving the strength properties of epoxy resins. The 3:1 ratio of ECH/BPA is found to give optimum lap shear and peel strengths. The shear strengths of various systems were found to increase by increasing the incorporation of PF. Further modifications for this system to obtain comparable shear strengths with the other systems are possible by trying with various adhesion promoters. The fracture mechanisms were also studied using FESEM.

**References**