IMPACT MODIFIER OF EPOXY RESIN WITH CITRACONICATED POLYBUTADIENE AS TOUGHENING AGENT

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ABSTRACT:

The impact strength of epoxy resin based on diglycidyl ether of bis phenol-A- with citraconicitated polybutadiene were investigated. The polybutadiene citraconicitated by reaction with citraconic anhydride and benzoyl peroxide as initiator. The percent citraconicitation was 10%.

In the present work citraconicitated polybutadiene was used as impact modifier for epoxy resin. The percentage of the blend between citraconicitated polybutadiene and epoxy resin was (5, 7.5, 12.5, and 20%) while the amine hardener of the epoxy resin was added at a ratio of 1 part amine to 3 part epoxy.

Keywords: epoxy resin citraconicitated polybutadiene, impact strength

1- INTRODUCTION:

Epoxy resins are widely used as high-performance thermosetting resins for many industrial applications , but unfortunately some are characterized by a relatively low toughness. Many efforts have been made to improve the toughness of cured epoxy resins by the introduction of rigid particles , reactive rubbers , interpenetrating polymer networks , and thermoplastics within the matrix (Sumeera Ikram et al., 2003). The great majority of the studies involves the chemical modification with reactive liquid rubbers such as carboxy terminated polybutadiene co-acrylonitrile (CTBN). The microstructure formed consists of an elastomeric phase finely dispersed in the epoxy matrix and the impact behavior of the final material is highly dependent on the size of the elastomeric particles produced. Other studies involve modification of epoxy resin with kaolin as a toughening agent (S. Fellahi et al., 2001) and with hydroxy terminated polybutadiene (Payam Saadati et al., 2005). In the present work, a citraconicitated polybutadiene used as impact modifier to improve the toughness of epoxy resin with different percentage of citraconicitated polybutadiene. The infrared spectra of the polybutadiene and citraconicitated polybutadiene were measured and impact strength of modified epoxy resins was evaluated in terms of the Izod impact strength.
2- EXPERIMENTAL
2,1- Materials:
Polybutadiene a commercial adhesive material, liquid free epoxy resin and triethylene tetramine as hardener supplied from Ciba-Geigy corporation, citraconic anhydride, and supplied from Fluka company, used without purification, acetone, and citric acid from Merck company, Benzoyl peroxide supplied from BDH company.
2,2- Preparation:
2,2,1- Preparation of Citraconiciated Polybutadiene
The citraconic anhydride was added and mixed with polybutadiene as a ratio of 10% from citraconic to polybutadiene in the presence of 0.5% benzoyl peroxide as initiator at 110°C for 15 min (A. Benny Cherian and Eby T. Thachil, 2003). With vigorous stirring, then the product was washed with a large quantity of acetone and dried at vacuum oven at 50°C for 2 hrs. The grafting reaction was confirmed by FTIR spectroscopy and chemical testing.
2,2,2- Determination of the Degree of Citraconiciation
Standard procedure was adopted thus samples from the citraconiciated polybutadiene was dissolved under reflux in xylene at a concentration of (1% wt/vol), followed by the addition of an excess amount of (0.3 M) trichloroacetic acid solution in xylene. The mixture was reflux for (90 min) to drive the ring opening reaction of epoxy (with the acid) to complete. The hot solution was titrated immediately with (0.05 N) ethanolic KOH using three to four drops of (1%) thymol blue in DMF was added and the deep blue colour was back-titrated to a yellow end point against (0.05 N) isopropanolic HCl in the hot solution (A. A. Sultan 2007, Yasuharu Nakayama, 1973; Takayuki Okamura and Shobu Maitono, 1975). The acid number and the percent grafted citraconated anhydride content was determined from the following relationships (Payam Saadati et al. 2005).

\[
\text{ml KOH} \times N \text{ KOH} \times 56.1 \]
\[
\text{Acid Number ( mg KOH / g Polymer )} = \frac{\text{ml KOH} \times N \text{ KOH} \times 56.1 }{ \text{Polymer ( g )} }
\]

Therefore
\[
\text{Acid no. } \times 98
\]
\[
\text{Cit – anhydride \%} = \frac{\text{Acid no. } \times 98 }{2 \times 56.1}
\]

2,2,3- Preparation of Blends
The blends were prepared by mixed the citraconiciated polybutadiene with epoxy resin at a ratio (5, 7.5, 12.5, 20%) respectively, then the curing was done at room temperature for 24 hrs, followed by post curing at 120°C for 3 hrs.
2,3- Characterization Methods
Infrared Spectroscopy (FTIR)
FTIR Spectroscopy was used to characterized the polybutadiene Fig. 1 and the citraconic polybutadiene.

2,4- Impact Strength Evaluation
Izod Impact Strength
The Izod impact strength was evaluated according to ASTM D256 using a standard notched specimen. Five samples from each formulation were broken. Average impact strength values were reported and their Izod values are calculated in (J/cm²) as follows:
The value Izod impact strength was measured of samples (epoxy alone and blends).

3- RESULTS AND DISCUSSION:

The grafting of citraconic anhydride onto polybutadiene characterized by FTIR spectra Fig. 1 which show the band at a region 1780, 1856 cm\(^{-1}\) represents the symmetric and asymmetric stretching, 1140 cm\(^{-1}\) represent the C---O of anhydride (A. A. Sultan, 2007; Moayad N. Khalaf, 2005). The above bands are indicating the grafting of anhydride to the backbone of polybutadiene. Table 1 represent the wave number data of polybutadiene and citraconiclated polybutadiene.

\[
IS = \frac{U_1 - U_2}{(W - a) t}
\]  

(W/cm\(^{-1}\))

Fig. 1. FTIR of a) PB and b) Citraconiciated PB
Table 1. Characteristic Infrared Bands of Polybutadiene and Citraconiciated Polybutadiene

<table>
<thead>
<tr>
<th>Band number</th>
<th>Band intensity</th>
<th>Wave number cm(^{-1})</th>
<th>Absorption</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybutadiene 1 and 2</td>
<td>Strong</td>
<td>2950, 2850</td>
<td>CH</td>
<td>Stretching vibration</td>
</tr>
<tr>
<td>3</td>
<td>Medium</td>
<td>1650</td>
<td>C==C</td>
<td>Stretching vibration</td>
</tr>
<tr>
<td>Citraconiciated Polybutadiene 1 and 2</td>
<td>Strong</td>
<td>2950, 2850</td>
<td>CH</td>
<td>Stretching vibration</td>
</tr>
<tr>
<td>3</td>
<td>Medium</td>
<td>1856</td>
<td>C==O</td>
<td>Asymmetrical stretching</td>
</tr>
<tr>
<td>4</td>
<td>Strong</td>
<td>1780</td>
<td>C==O</td>
<td>Symmetrical stretching</td>
</tr>
<tr>
<td>5</td>
<td>Low</td>
<td>1707</td>
<td>C==O</td>
<td>Symmetrical stretching *</td>
</tr>
<tr>
<td>6</td>
<td>Strong</td>
<td>1140</td>
<td>C---O</td>
<td>Asymmetrical stretching</td>
</tr>
</tbody>
</table>

* due to acid form

The Izod impact strength results show increasing in the value of impact strength of epoxy resin with increased percentage of citraconic polybutadiene due to the increasing in the elastic behavior of epoxy resin. The funcatinilization of polybutadiene with citraconic increases compatibility between the citraconic polybutadiene and the epoxy resin, while the unfactinilized polybutadiene will not be compatible with epoxy and the impact strength of the epoxy will not improve as shown in the results. Table 2 and Fig. 2 show the value of impact strength.

Table 2. The Values of Izod Impact Strength Versus Percentage of Citraconic Polybutadiene to Epoxy Resin

<table>
<thead>
<tr>
<th>Percentage of Citraconic Polybutadiene to Epoxy Resin</th>
<th>Izod Impact Strength for Notch Specimens (J/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.35</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>7.5</td>
<td>0.6</td>
</tr>
<tr>
<td>12.5</td>
<td>1.05</td>
</tr>
<tr>
<td>20</td>
<td>1.25</td>
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CONCLUSIONS:
In the present work the fictionalization of polybutadiene with citraconic will increased the compatibility of the polybutadiene with the epoxy resin. The impact strength of modified epoxy resin was increased with the increased percent of citraconiated polybutadiene.

REFERENCES:

**Nomenclature**

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Description</th>
<th>Unit</th>
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<tbody>
<tr>
<td>a</td>
<td>The notch length</td>
<td>cm</td>
</tr>
<tr>
<td>t</td>
<td>The specimen thickness</td>
<td>cm</td>
</tr>
<tr>
<td>U₁</td>
<td>The impact energy</td>
<td>J</td>
</tr>
<tr>
<td>U₂</td>
<td>Residual energy</td>
<td>J</td>
</tr>
<tr>
<td>W</td>
<td>The specimen width</td>
<td>cm</td>
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