Modification of epoxy–bisphenol A resin with tetrachlorinated bicyclic compounds containing dicarbonyl bridges

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As is known, polychlorinated bicyclic compounds are widely used as monomers and modifiers for the production of heat and fire-resistant polymeric materials and elastomers, and also fireproofing additives to flammable thermoplastic materials. The fireproofing action of polychlorinated compounds is connected with the fact that, during heating, they split off atomic chlorine, which is an effective fire retardant. Their introduction into epoxy resins makes it possible to produce heat-resistant composites [1–5].

The large scales of production of organochlorine products are due to their combination of physical, physicochemical, and chemical properties, on account of which they are used in practically all sectors of the national economy. Their range is extremely great and varied. The users of organochlorine products are the plastic and resin, synthetic fibre, and varnish industries, general chemistry, the chemico-pharmaceutical industry, and so on [4, 5].

It must be pointed out that epoxy polymers possess a combination of valuable properties (adhesion, mechanical, electrical, etc.) that in many cases make them irreplaceable in developing the base materials for adhesives, paint and varnish coatings, compounds, and reinforced plastics [1–3]. Epoxy resins, in particular ED-20, possess good compatibility with other oligomers and can be cured by compounds of different types. However, most compounds based on epoxy–bisphenol A resins have a shortcoming – comparatively low thermal properties, which makes it impossible to use them in articles operating at high temperatures. To increase the heat resistance of epoxy composites, modifiers are used, as the properties of epoxy resins can be changed by the choice of curing agent, modifier, and a number of other additives.

The synthesis of halogen-containing monomers and semiproduts used for the production of polymeric materials is of great importance to the national economy. The present work is devoted to a study of the modifying capacity of tetrachlorinated bicyclic compounds with a carbonyl bridge, with the aim of increasing the heat resistance of epoxy composites.

In this connection, tetrachlorinated bicyclic compounds with carbonyl bridges (I–IV) were tested as modifiers of epoxy resin ED-20. Compounds I–IV were obtained by a well-known procedure – diene condensation of tetrachlorobenzoquinone-1,2 with ethylene and acetylene dienophiles by Scheme 1.

Compounds I–IV, the physicochemical constants of which are given in Table 1, were produced by the procedures that we described in earlier papers [6–8].

The amount of modifier was varied from 10 to 30 parts per 100 parts resin. It must be pointed out that all modifiers, irrespective of their structure, have good compatibility with resin. PEPA was used as the curing agent. Curing was carried out on a Paulik–Paulik–Erdei derivatograph, with a specimen weight of 100 mg, a DTA channel sensitivity of 250 µV, and a DTG channel sensitivity of 1 mV, in an air flow.

The thermal properties of the cured epoxy resins were investigated using thermograms.

Thermo-oxidative degradation was assessed by activation energy parameters. The data obtained indicate that the optimum amount of modifier is 20 parts per 100
parts ED-20 resin. The thermal characteristics obtained in tests are given in Table 2.

As can be seen from Table 2, the structure of the modifier affects the heat stability of the epoxy composite material. The greatest heat resistance is achieved by introducing compound IV into the epoxy resin. This is evidently connected with the presence in compound IV of terminal acetylene bonds giving stability to the entire composite material. The presence of a branched structure in the side chain lowers not only the heat resistance of the epoxy material but also the half-life and the thermogravimetric index (TGI) of the composite.

Thus, on the basis of the conducted investigations, it can be concluded that compounds of the tetrachlorinated bicyclic series with carbonyl bridges can be used as modifiers giving the compounds heat resistance and non-flammability.

Table 1. Physicochemical characteristics of compounds I–IV

<table>
<thead>
<tr>
<th>Compound number</th>
<th>Compound</th>
<th>Yield, %</th>
<th>Tmelting, °C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td><img src="i" alt="Image" /></td>
<td>85.3</td>
<td>130–131</td>
<td>8</td>
</tr>
<tr>
<td>II</td>
<td><img src="ii" alt="Image" /></td>
<td>55.0</td>
<td>65–66</td>
<td>7</td>
</tr>
<tr>
<td>III</td>
<td><img src="iii" alt="Image" /></td>
<td>58.0</td>
<td>91–92</td>
<td>7</td>
</tr>
<tr>
<td>IV</td>
<td><img src="iv" alt="Image" /></td>
<td>80.0</td>
<td>88–89</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 2. Thermal properties of composite based on ED-20 modified with compounds I–IV

<table>
<thead>
<tr>
<th>Modifier (20 parts per 100 parts ED-20)</th>
<th>E_{decomposition}, kJ/mol</th>
<th>Half-life φ_{1/2}, min</th>
<th>Thermogravimetric index (TGI), °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>195.06</td>
<td>54.8</td>
<td>122</td>
</tr>
<tr>
<td>II</td>
<td>191.37</td>
<td>54.0</td>
<td>120</td>
</tr>
<tr>
<td>III</td>
<td>182.95</td>
<td>52.2</td>
<td>115</td>
</tr>
<tr>
<td>IV</td>
<td>218.07</td>
<td>60.8</td>
<td>127</td>
</tr>
</tbody>
</table>

where

R = –C≡CC\((CH_3)_2\)OH (I); –CH_2OH (II); –C≡CC\((CH_3)_2\)OCH_2CH–CH_2 (III); –C≡CH (IV)

Scheme 1
REFERENCES


4. N. S. Zefirov et al., Chemistry of hexachlorocyclopentadiene and related compounds. Moscow State University, 1985, 212 pp.


