Study of phthalic anhydride and glycerol polycondensation

E.A. Prudnikova and P.P. Maksimov

Abstract. In the article, the basic physical and chemical properties of polymers based on glyphthalic resin are considered. The main advantages and disadvantages are revealed. The areas of application and the main methods for obtaining glyphthalic resins are considered. The research studying the course of the polycondensation process on the change of acid number during the reaction of obtaining glyphthalic resin of polyatomic alcohol of glycerol and phthalic acid anhydride is carried out. It is revealed that the results of acid number determination during polycondensation can be used for directed regulation of synthesis of alkyd oligomers and their subsequent curing to obtain a polymer with specified properties. The data was obtained that the polymer under study can be further modified to give special properties that extend the area of its application, as well as to ensure the environmental safety of the waste generated during its use. On the basis of the available data, it is concluded that further research of glyphthalic resin is necessary.

Key words: glyphal resin, glycerin, phthalic anhydride, acid number.

1 Introduction

Currently, the main direction of fundamental research in the polymer field, especially physical and physicochemical research, is the study of various structures and regularities of their formation in multicomponent polymer systems, the study of the properties of such systems in relationship to their morphology, as well as the development of chemical and physical approaches to optimise these properties.

Glyptal resins — are the most common types of polyester (alkyd) resins and are polycondensation products of glycerol and phthalic anhydride. For various needs resins are produced in pure and modified form.

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The process of resin formation proceeds according to the scheme (Fig. 1, 2):

Fig. 1. Chain of soluble glyptal resin, linear structure

Fig. 2. Form of insoluble glyptal resin, three-dimensional structure

The industry produces unmodified (in the form of powder and solution) and modified glyphthalic resins. Modification of resin is carried out in the process of its synthesis by adding modifying reagents that form cross-links between macromolecules. Modification of glyphthalic resins allows to use them for production of hot and cold drying varnishes and enamels, as well as adhesives. Lacquers based on modified glyphthalic resins are used for insulation of electrical machines operating at high temperatures (150 °C and above).

The technological process of production of resin № GF consists of the following:

glycerine is loaded into the boiler, which is heated to 120 °C. Then phthalic anhydride is added and melted under stirring. After the phthalic anhydride is melted the mass in the boiler is heated to 190-200 °C and kept at this temperature until the finished resin is obtained, which is drained into trays through the bottom drain cock. After cooling, the resin is crushed into a fine powder on a crusher.

Unmodified resin has a hard and brittle structure, transparent in a thin layer. The colour ranges from yellow to dark brown. The physical properties of the powder depend on the degree of polymerisation. The softening point of this substance should lie within the range of 80-95 °C.

There are three stages of polymerisation: stage A — melting resin, soluble in acetone and unstable to water; stage B — melting resin, insoluble in acetone and stable to water; stage C — unmelting resin, insoluble in water and stable to its action. Under strong heating glyphthalic resin decomposes, forming a white deposit of phthalic anhydride.

The resin must be hard, mirror smooth in the fracture, homogeneous in colour and must not contain any extraneous impurities. Resin of the third group may have a spongy structure.

If the mesh frequency index is high, the products are characterised by hardness, non-smoothness and resistance to swelling.

Unmodified glyphthalic resins have good electrical insulating ability and therefore are used for production of electrical insulating varnishes at that they are dissolved in alcohol or in water depending on the degree of polycondensation. After applying the varnish, the resin...
2 Materials and methods

3 Results and discussion
Acid number determined by titration.

Acid number — number of milligrams of potassium hydroxide (KOH), required to neutralise all the acidic components contained in 1 g of the substance under test. The acid number is a measure of the sum of carboxylic acids in an organic compound, such as fatty acids, or in a mixture of compounds. Usually, a known amount of sample dissolved in an organic solvent (most often a mixture of polar and nonpolar solvents) is titrated with a potassium hydroxide solution of known concentration and phenolphthalein as an indicator [32,33]. In general, the titration proceeds by the following reaction:

\[ \text{R−COOH} + \text{KOH} \rightarrow \text{R−COOK} + \text{H}_2\text{O} \]

For this purpose, a sample of the substance is dissolved in acetone, phenolphthalein is added and titrated with alcoholic KOH solution until a light pink colour appears.

All the obtained data are placed in Table 1.

Table 1. Dependence of acid number on synthesis time

<table>
<thead>
<tr>
<th>Time from the start of synthesis, min</th>
<th>Empty cup weight, g</th>
<th>The mass of the cup with a sample, g</th>
<th>Sample weight, g</th>
<th>Volume of KOH used for titration, ml</th>
<th>Acid number</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>28.33</td>
<td>28.84</td>
<td>0.51</td>
<td>12.5</td>
<td>675.3</td>
</tr>
<tr>
<td>45</td>
<td>31.32</td>
<td>31.83</td>
<td>0.51</td>
<td>12.5</td>
<td>620.4</td>
</tr>
<tr>
<td>60</td>
<td>33.45</td>
<td>33.92</td>
<td>0.47</td>
<td>9.8</td>
<td>571.9</td>
</tr>
<tr>
<td>75</td>
<td>33.29</td>
<td>33.79</td>
<td>0.46</td>
<td>9.4</td>
<td>560</td>
</tr>
<tr>
<td>90</td>
<td>33.28</td>
<td>33.78</td>
<td>0.53</td>
<td>9.0</td>
<td>548</td>
</tr>
<tr>
<td>120</td>
<td>31.34</td>
<td>31.87</td>
<td>0.53</td>
<td>7.5</td>
<td>448</td>
</tr>
<tr>
<td>150</td>
<td>28.28</td>
<td>28.79</td>
<td>0.51</td>
<td>4.5</td>
<td>386</td>
</tr>
<tr>
<td>165</td>
<td>28.28</td>
<td>28.79</td>
<td>0.51</td>
<td>3.0</td>
<td>236.1</td>
</tr>
<tr>
<td>180</td>
<td>28.28</td>
<td>28.79</td>
<td>0.51</td>
<td>1.5</td>
<td>148</td>
</tr>
</tbody>
</table>

Based on the data presented in Table 1, figure 3 has been constructed.
4 Conclusions

After synthesis of one of the common polyesters - glyphaltalic resin by polycondensation of polyatomic alcohol glycerol and phthalic acid anhydride, new possibilities of its application were revealed. While investigating the course of the polycondensation process, a change in the acid number during the reaction was observed. The results of acid number determination during polycondensation can be used for directed control of alkyd oligomer synthesis and their subsequent curing to obtain a polymer with desired properties. The obtained polymer can be further modified to give special properties that extend the scope of its application, as well as to ensure the environmental safety of waste generated during its use.

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