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Viscosity of Melts of H Complexes Based on Acidic Diesters of Benzophenonetetracarboxylic Acid and Diaminodiphenylmethane or \textit{m}-Phenylenediamine

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Abstract—The time dependences of the viscosity of melts of H complexes formed by dimethyl or diethyl dihydrogen \textit{3,3},\textit{4,4}'-benzophenonetetracarboxylate and \textit{4,4}'-diaminodiphenylmethane, \textit{m}-phenylenediamine, or equimolar mixture of these diamines at 95 and 105°C were studied.

It is known that thermal imidization of H complexes formed by dimethyl dihydrogen \textit{3,3},\textit{4,4}'-benzophenonetetracarboxylate and aromatic diamines is the key step in preparation of light-weight polyimide foam composites containing felts and fabrics based on organic thermally stable fibers (including polyimide felt) as a reinforcing filler. Due to their low density along with high cryo- and thermal stability, refractoriness, and high thermal and sound insulation properties, these composites show promise for ship-building and aircraft industry [1].

In preparation of polyimide foam composites H complexes are used as prepolymer of polyimide binders. In the process, relatively low melting point (mp) of H complexes (from 70 to 130°C depending on the composition [2]) is a decisive factor. However, thermal imidization of H complexes also starts at low temperatures (100–120°C [3]). Thus, separation of melting and further intensive imidization of H complexes during prepreg preparation is of particular importance. This problem can be solved by preparing the prepreg at lower temperature (95–105°C) when the required H complexes occur in the molten state, but imidization is yet very slow.

To optimize the prepreg preparation the viscosity of the melt of the H complex (binder) and the kinetics of its variation should be determined. In this work we studied H complexes of dimethyl or diethyl dihydrogen benzophenonetetracarboxylate with aromatic diamine (diaminodiphenylmethane, \textit{m}-phenylenediamine, or their mixture) under various preparation conditions.

EXPERIMENTAL

The initial H complexes were prepared as follows. \textit{3,3},\textit{4,4}'-Benzophenonetetracarboxylic dianhydride (0.03 mol) was dissolved with stirring in 15 ml of boiling methanol or ethanol (absolute or with addition 10 vol % water). The solution of dialkyl dihydrogen benzophenonetetracarboxylate was cooled to room temperature and the equimolar amount of the corresponding diamine (or diamines) was added dropwise with stirring. After solution homogenization the resulting solid H complexes were recovered by removing the solvent in a vacuum at room temperature. The abbreviations of the H complexes studied (depending on diamine and esterifying agent) are presented in the table.

Before use \textit{3,3},\textit{4,4}'-benzophenonetetracarboxylic dianhydride [BZP; TU (Technical Specifications) TSR 2159–69] was purified by refluxing in acetone (mp 225°C); \textit{4,4}'-diaminodiphenylmethane (DADPM) was distilled in a vacuum (1–3 mm Hg, mp 90–92°C); and \textit{m}-phenylenediamine (\textit{m}-PDA) was sublimed from zinc dust in a vacuum (mp 63°C).

The viscosity of the melts of H complexes was measured at 95 and 105°C on a PIRSP rheometer with a cone–plane working unit (1° angle at the cone apex, 40 mm cone diameter) [4].

The kinetic dependences of the viscosity of the melts of H complexes based on dimethyl dihydrogen benzophenonetetracarboxylates (BZPMe) prepared under various conditions are shown in Figs. 1a and 1b (in absolute methanol and in the mixture of methanol...
H Complexes based on dialkyl dihydrogen benzophenonetetracarboxylates

<table>
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<tr>
<th>Esterifying agent</th>
<th>H complexes with diamine</th>
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<tr>
<td></td>
<td>DADPM</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>BZPMe · DADPM</td>
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<tr>
<td>CH₃OH + 10%H₂O</td>
<td>BZPMe · DADPM(H₂O)</td>
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<tr>
<td>C₂H₅OH</td>
<td>BZPEt · DADPM</td>
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<tr>
<td>C₂H₅OH + 10%H₂O</td>
<td>BZPEt · DADPM(H₂O)</td>
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with 10 vol % water, respectively. As expected, with increasing temperature from 95 to 105°C the viscosity of melts increases more rapidly. The decrease in the viscosity, most pronounced at 105°C (Fig. 1a, curves 2, 3; Fig. 1b, curve 3), is probably due to foaming of the molten sample and weight loss occurring in this case, because the foaming melt partially escapes from the rheometer cell (observed visually). The viscosity decrease is the more pronounced, the greater the melt foaming.

The time dependences of the viscosity of the melts of H complexes based on diethyl dihydrogen benzophenonetetracarboxylate (BZPEt) prepared under various experimental conditions are shown in Figs. 1c and 1d. With substitution of BZPEt for BZPMe in the H complex the life period of the melt increases,

![Fig. 1. Viscosity \( \eta \) of the melts of H complexes as a function of time \( t \). (a): (1) BZPMe-DADPM, (2, 2') BZPMe-m-PDA, and (3, 3') BZPMe-(DADPM + m-PDA); (b): (1, 1') BZPMe-DADPM(H₂O), (2) BZPMe-m-PDA(H₂O), and (3, 3') BZPMe-(DADPM + m-PDA)(H₂O); (c) (1, 1') BZPEt-DADPM, (2, 2') BZPEt-m-PDA, and (3, 3') BZPEt-(DADPM-m-PDA); (d) (1, 1') BZPEt-DADPM(H₂O), (2, 2') BZPEt-m-PDA(H₂O), and (3, 3') BZPEt-(DADPM + m-PDA)(H₂O).]
whereas the intensity of foaming significantly decreases.

Now, we consider the effect of the diamine nature in the H complex on the melt viscosity. As seen from Figs. 1a–1d, H complexes based on DADPM possess the greatest viscosity (curves 1, 1'). It should be noted that the temperature of 95°C is insufficient to melt the BZPMe-DADPM H complex prepared in absolute methanol (curve 1' in Fig. 1a is absent). As a rule, H complexes based on m-PDA exhibit the lowest viscosity (Figs. 1a–1d, curves 2, 2'). The melts of H complexes based on the mixture of diamines (curves 3, 3') exhibit the intermediate viscosities.

Next, we analyze the effect of water present in the solvent used for esterification of BZP dianhydride and preparation of H complex on the melt viscosity. At 95°C the life period of the melts of H complexes prepared in aqueous alcohol (Figs. 1b, 1d, curves 1–3') is greater as compared with H complexes prepared in absolute solvents (Figs. 1a, 1b, curves 1–3'). However, at 105°C the relation is reverse: the life period of the melts of H complexes prepared in absolute alcohols (Figs. 1a, 1c, curves 1–3) is greater than that of the complexes prepared in aqueous solvents (Figs. 1b, 1d, curves 1–3).

Let us analyze how the structure of the H complex and the temperature of the experiment affect the rate of the increase in the melt viscosity at the final stage of the process, which is usually regarded as cross-linking and polymerization [5]. In our case it involves thermal imidization of H complexes. In all the cases the rate of the increase in the viscosity of the melt of the H complex based on BZPEt is significantly lower as compared with the H complex based on BZPMe. The rate constant of the increase of the melt viscosity of the H complex based on BZPMe-DADPM at 105°C is two times lower as compared with the H complex based on BZPMe-DADPM (2.7 × 10^{-3} and 5.2 × 10^{-3} s^{-1}, respectively). For H complexes based on the mixture of the diamines this difference is still greater (2.0 × 10^{-3} and 9.0 × 10^{-3} s^{-1}, respectively). Actually, the rate constant of imidization of the H complexes based on BZPEt is several times lower as compared with the H complexes based on BZPMe [3].

As for water present in the solvent during preparation of H complexes, it decelerates or accelerates the growth of the melt viscosity for H complexes based on BZPMe and BZPEt, respectively.

The dependence of the melt viscosity η on the shear rate γ was studied for the H complex based on BZPEt–(DADPM–m-PDA) (Fig. 2). This dependence can be approximated by the following expression:

\[ η \sim \gamma^{-n}. \]

For high-molecular-weight flexible-chain polymers n varies within 0.5–0.7 [5, 6]. In the case of structural ordering of the melt, e.g., typical for liquid-crystalline polymers, application of the shear stress breaks the melt structure and, as a result, n increases. In our case n = 0.8 (Fig. 2), which suggests formation of the mesomorphic rather than the liquid-crystalline structure in the melts of H complexes.

Our data allow some conclusions on the selection of the chemical composition of the binder for polyimide foam composites and conditions for preparing the corresponding precursors.

**CONCLUSIONS**

(1) Taking into account high viscosity of H complexes based on 4,4'-diaminodiphenylmethane, the use of binders based on the mixture of two diamines (4,4'-diaminodiphenylmethane and m-phenylenediamine) is the most promising.

(2) Preparation of binders in aqueous alcohols is advisable.

(3) Since curing of H complexes based on diethyl dihydrogen benzophenonetetra-carboxylate at 95°C to prepare precursors is very slow, higher temperatures are recommended as compared with curing of H complexes based on dimethyl dihydrogen benzophenonetetra-carboxylate.
REFERENCES

1. RF Patent 2081134.