Electrorheological fluids based on the modified aromatic polyimides

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Abstract. Fine-dispersed particles of aromatic polyimides, modified by cobalt acetylacetonate, are synthesised. The electrorheological activity of the dispersed systems, based on mineral oil and such particles, is investigated. It is shown, that polyimides and polyamide acids are perspective to be used as dispersed phase in electrorheological compositions.

1. Introduction
Electrorheological fluids (ERF) are complex fluids consisting of micron-sized or, rarely, nano-sized dielectric particles (so-called filler) dispersed in a nonconducting fluid [1]. As fillers, various oxides, silica modifications, silica gels, aerosil, diatomite, and also calcium titanates, aluminosilicates, metallic oxides in the form of a single dispersed powder with a particle size from 1 to 10 µm are widely used [2]. However, many well-known compositions have a number of disadvantages, such as: a rather low stability in time, a limitation in the temperature stability range, a limitation in the chemical stability of the dispersion medium, and a rather low electrostructural response to the electric impact. Recently, a number of new organic compositions [3], natural and synthetic polymers [4], namely, cellulosic materials and polypyrroles [5] have been regarded as potential candidates for ERF fillers. Since such kinds of the organic fillers are of a key interest nowadays, we have developed a new type of the composition for ERF based on the aromatic polyimides [6], and investigated the electrorheological properties of it.

Aromatic polyimides are a class of polymers obtained by the interaction of aromatic diamines with dianhydrides of aromatic tetra carbon acids according to the so-called two-stage scheme. They have a unique complex of properties, including high dielectric and mechanical properties in the temperature range of −200 — +350°C, and good chemical and radiation stability. The first stage of the synthesis includes the interaction of diamines and dianhydrides in the medium of aprotic amide solvents [6]:

\[
\text{O=C=O} + n\text{H}_2\text{N}^\cdot\text{R}^\cdot\text{NH}_2 \rightarrow \left[\text{\begin{tabular}{c}
\text{HN-C-O-C=O} \\
\text{HO-C-C-NH-R} \\
\end{tabular}}\right]_n
\]

where
As the result, a prepolymer — polyamide acid (PAA) is obtained, and the final product is received by the reaction of the solid phase thermal dehydrocyclization by means of a step by step heating up to 300–320 °C or by a so-called chemical imidization, consisting in the treatment of PAA by hydro retaining reagents and carried according to the scheme [6]:

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{C} \\
\text{N} \\
\text{N} \\
\text{O} \\
\text{O} \\
\text{H} \\
\text{H}
\end{array}
\xrightarrow{-2\text{H}_2\text{O}}
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{C} \\
\text{N} \\
\text{N} \\
\text{O} \\
\text{O} \\
\text{H} \\
\text{H}
\end{array}
\]

The structure of the polymers of this class allows us to give them peculiar properties, needed for the certain areas of application, while the complex of main properties is retained. Therefore a particular interest as dispersed phase of ERF presents the class of modified aromatic polyimides. The use of aromatic polyimides is perspective in the enhancement of sedimentation stability of composition because of substantially low density of material (1.1 – 1.2 g/cm³) in comparison with the dispersed phases of an inorganic nature, and the decrease of the particle aggregation will make easier the process of dispersion of the particles up to the needed sizes.

High sorption capacity of polymeric materials allows us to carry out a wide range of possibilities of controlling the electrorheological properties of the dispersed medium by the introduction of activators. The most important is the implementation of the purposed formation of the electrosensitivity for the filler by the aid of different types of modifies due to the creation of optimum quantity of active groups (hydroxyl-carboxyl containing), responsible for effective surface polarization of the particles in the electric field, and also their mobility, that regulates the kinetics of structural processes.

2. Experimental

As dispersed phase we have chosen polyimides, based on the pyromellitic dianhydrides and dianinodiphenyloxide, modified by cobalt acetonate. Aromatic polyimides we obtained by the above described two-step synthesis process, in which at the first stage a prepolymer — poliamidacid (PAA) is formed by the interaction of equimolecular quantity of pyromellitic dianhydride and dianinodiphenyloxide in dimethylformamide. The final polymer — polyimide (PI) is formed at the second stage of the synthesis — by the solid phase high temperature or low temperature chemical dehydrocyclization of a prepolymer [5]. A modifier – cobalt acetylacetonate was introduced by two methods:

- by the introduction of its calculated quantity in PAA solution, mixing during 30-40 min, sedimentation of the solvent in acetone, separation of its solid polymeric precipitatives and its drying, and solid phase dehydrocyclization (imidization) by means of smooth temperature elevation up to 300 °C in the ambient of nitrogen;
- by the introduction of its calculated quantity in solid PAA, obtained by the sedimentation of its solution of dimethylformamide in acetone, separation of its solid polymeric precipitation by filtering, and solid phase dehydrocyclization (imidization) by means of smooth temperature elevation up to 300 °C in the ambient of nitrogen;

Polymeric dispersed phases based on the modified polyimide compositions were prepared by attrition in an agate mortar until a high dispersion powder was obtained. Thermal properties of the samples were investigated by means of thermograph device Paulik-Paulik-Erdei, the degree of the transition of the prepolymer into polyimide — by means of IR spectroscopy, using IR-Furier spectrometer FT-IR «Thermo Nicolet». Suspensions were prepared by accurate mixing of the calculated quantity of the milled polymeric dispersed phase with mineral oil in a ceramic mortar.
Electrorheological characteristics of compositions were tested in a coaxial cylindrical unit of a rotational viscometer.

3. Results and discussion

Thermographic investigation of the PI samples, modified by cobalt acetylacetonate has shown that the losses of 5% of mass are reached only at approximately 300 °C. It means that the chosen thermal treatment conditions of the modified polyimide provide its rather high thermal stability.

As IR spectra of the modified polyimide have shown (not presented in paper), the process of imidization runs rather deep in the obtained modified polymer under thermal treatment, which is indicated by the intensive absorption bands at 1780, 1720, 1380 and 720 cm\(^{-1}\). They are due to the valence and deformational vibrations of the five termed imide cycle, the formation of which occurs at PAA transition to PI. However, in the IR-spectrum it is impossible to identify absorption bands of modified macromolecules that have fragments of a modifier, which is due to the low concentration of the modifier.

The results of SEM measurements indicate that the polyimide, modified by cobalt acetylacetonate, is composed of uniformed particles of the size about 100 µm (Figure 1). Although it is a bigger particle size than generally used and expected in ERF composition, it did not affect the electrorheological properties of the fluid. Further improvement of the milling technique, concerning this material, should be done.

![Figure 1. SEM of polyimide dispersed phase used in electrorheological compositions.](image)

In the experiment we have used 10 wt. % suspensions of PAA in mineral oil. By preparing the sample 1, PAA was milled in the agate mortar with the periodical cooling in liquid nitrogen, and the sample 2 was prepared in the orbed ultrasound mill. Sample 1 and sample 2 were not modified by cobalt acetylacetonate. The composition of ERF containing polyimide, modified by cobalt acetylacetonate is shown in Table 1. There were prepared suspensions with a concentration of 2.6% and 5.7% based on the modified 11.5% and 32.0% cobalt acetylacetonate, differed by the way of the introduction of the modifier – in sample 4 cobalt acetonate is introduced by the reaction in solution, while in sample 5 – by the solid phase method. The results of investigation of the electrorheological activity of compositions with the use of polyamidacid and modified aromatic polyimides as dispersed phase are presented in Figures 2 and 3.

As it is seen from the Figure 2, for ERF with polyimide the process of imidization and modification by cobalt acetylacetonate does not yield any substantial enhancement of shear stress under the electric field. The current density \(j\) is changed simbate to the shear stress \(\tau\) at increasing the intensity of the electric field for samples 1 and 2 (Figure 3). The values \(j\) for the samples 4 and 5 coincide, and for the sample 3 are somewhat bigger. The use of PAA (samples 1 and 2) as dispersed phase of electrorheological compositions leads to the substantial enhancement of their shear stress in the electric field – up to 2 orders at the strength 2 kV/mm. This can be explained by the enhanced concentration of hydroxyl groups in the polymeric chain of PAA in comparison with their composition in the modified PI.
Table 1. The composition of electrorheological suspensions, based on transformer oil and polyimide.

| Indication | Sample № | 3 | 4 | 5 |
|------------|----------|---|---|---|
| Quantity of an introduced modifier in relation to dry PAS, m. % | 11.5 | 32.0 | 32.0 |
| Content of cobalt in the modified PI, % | 3.3 | 23.57 | 23.57 |
| Concentration of PI in suspension, % | 5.7 | 2.6 | 2.6 |
| The way of introduction of the modifier in PI | Reaction in solution | Reaction in solution | Solid phase reaction |

Figure 2. The dependence of shear stress of ERF (samples 1 – 5) on the electric field strength (the shear rate value is 27 s⁻¹).

Figure 3. The dependence of current density in ERF (samples 1 – 5) on the electric field strength (the shear rate value is 27 s⁻¹).

In the course of the study we have noticed that the properties of electrorheological compositions are highly dependent on the way of the preparation. Comparing the properties of the samples 1 and 2 we can conclude, that the preferential way of milling is the milling in the agate mortar with a periodical cooling by liquid nitrogen, which was used for sample 1. Milling in the orbed grinder, used for the preparation of the sample 2, results in a slight decrease of the electrosensitivity of the composition, that can be due to the imidization process occurring at such conditions and consequently with the decrease in OH-group concentration.

It is also possible that by the synthesis of PI, modified by cobalt acetylacetonate (samples 3-5), the content of cobalt was not enough for the formation of the needed quantity of the mobile charge carriers, to which electrorheological effect is due to. Nevertheless, the performed investigation has shown that modified polyimides are perspective to be used, although further investigations are needed.

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