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## Rheology of Polymer Suspensions in Electric Fields

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The effect of electric field on room temperature mechanical properties of cellulose-based polymer suspensions are reviewed.

KEY WORDS Rheology, electric fields, polymer suspensions, cellulotics.

### RESULTS AND DISCUSSION

A classic technique to evaluate relaxation phenomena in different media is the measurement of a number of their properties, such as physico-mechanical and dielectric ones etc. as a function of temperature. We have evaluated the response of mechanical properties of cellulose-based polymer suspensions in the electric field intensity at room temperature.

As is known, relaxation transitions as a function of temperature are associated with variations of molecular mobility in different fragments of the polymeric matrix, resulting in higher polarization in the electric field or in a variation of mechanical deformation values, and influencing the temperature dependences. Beginning from certain values of the threshold intensity, the electric field may apparently influence the system of polymer hydrogen bonds and the polarization process. More recently, we have made a detailed study into the influence of the static and variable electric field on materials in the form of paper and film based on different cellulose derivatives. In particular, we have found a considerable dependence of their dielectric properties ( $\tan \sigma$ ,  $\epsilon$ ) on the intensity of the polarizing field for samples containing acid groups: carboxyl, phosphate, sulphate and others. In this case, a dependence is observed for the type of groups, their content, and the moisture content of the polymers. Higher moisture content, in particular, markedly decreases the activation polarization barrier in the electric field intensity.

It was found by the IR spectroscopy technique that an electric field has an influence on the system of hydrogen bonds in polymers with ionogenic groups. This is shown by an increase of molecular mobility and polarization process with the field intensity.<sup>1</sup>

We believe that the results obtained testify to a possible relaxation process taking place, the polymers are not only heated but also under the action of the electric field, beginning from its intensity level at room temperature.

By using an electrorheology technique during a study of the electrosensitivity of cellulose ion exchangers, we have evaluated their response to the electric field. Polymer filler powder was placed in an inert binder (oil). This technique (the technique of immersion media<sup>2</sup>) is widely used for evaluating electrophysical and optical properties of different materials, polymeric materials included. The test substances used as active fillers were various commercial cellulose materials in powder form: both non-modified cellulose and its derivatives—carboxymethylcellulose, cellulose phosphate, aminoethylcellulose, methyl-, ethyl- and oxypropylcellulose. Also used were a number of derivatives, particularly cellulose citrates and tartrates, which were synthesized under laboratory conditions.

Electrorheological properties of polymer suspension-based compositions were studied in different oils as well as in the medium of non-polar solvents, solutions of cellulose ethers in dioxane:cellulose diacetate, acetophthalate, acetosuccinate, oxyethylcellulose, water-soluble carboxymethylcellulose and also polyvinyl alcohol. The rheological properties were evaluated by the technique presented<sup>3</sup> with the help of a Reotest-2 rotational viscosimeter. To characterize the influence of the field, the relative viscosity was evaluated ( $\Delta\eta/\eta$ ,  $\Delta\eta = \eta_1 - \eta$ , where  $\eta_1$  is the viscosity of the suspension with the field applied,  $\eta$  is the viscosity with no field).

The electrorheological effect of cellulose suspension-based compositions was known before, but in fact it was non-modified cellulose that was well-studied.<sup>4</sup> We have found that the introduction of ionogenic acid groups by chemical modification results in a considerable increase of the electrorheological effect. Electrorheological suspensions (ERS) may be thus prepared on the basis of cellulose phosphate, different types of carboxymethylcellulose and cellulose citrate and tartrate. Polymers with no ionogenic groups, methyl-, ethyl- and oxypropylcellulose and non-modified cellulose, possess a lower electrosensitivity or do not possess it at all. Cellulose aminoderivatives (aminoethylcellulose, diethylaminoethylcellulose) can also be used for the ERS preparation.

It was established that higher electrosensitivity, which is evaluated by the relative viscosity value, is attributable to cellulose derivatives with a more voluminous substitute. Thus, these groups are listed in decreasing electrosensitivity: cellulose tartrate and citrate, carboxymethylcellulose, and cellulose phosphate. Aminoderivatives are still less active. The threshold intensity also depends on the type of cellulose modification (Figure 1) and lies in the range of 0.5 to 1.5 KV/mm. Dielectric characteristics ( $\text{tg } \sigma$ ,  $\epsilon$ ) of the material under study also depend on the content and type of ionogenic groups introduced and the electric field intensity (Figure 2). Relying on the IR spectrography, we associate a change in dielectric characteristics under the influence of the field of a certain intensity on the system of hydrogen bonds and on molecular mobility of cellulose derivatives. This enhances the polarization process and leads to an increase of the dielectric permittivity values. Apparently, the behavior observed may be associated with the relaxation transition already taking place in the field at room temperature. The analogy of  $\text{tg } \sigma$ ,  $\epsilon$  and relative viscosity allows a supposition that the limiting stage which influences the relative viscosity values is also the influence

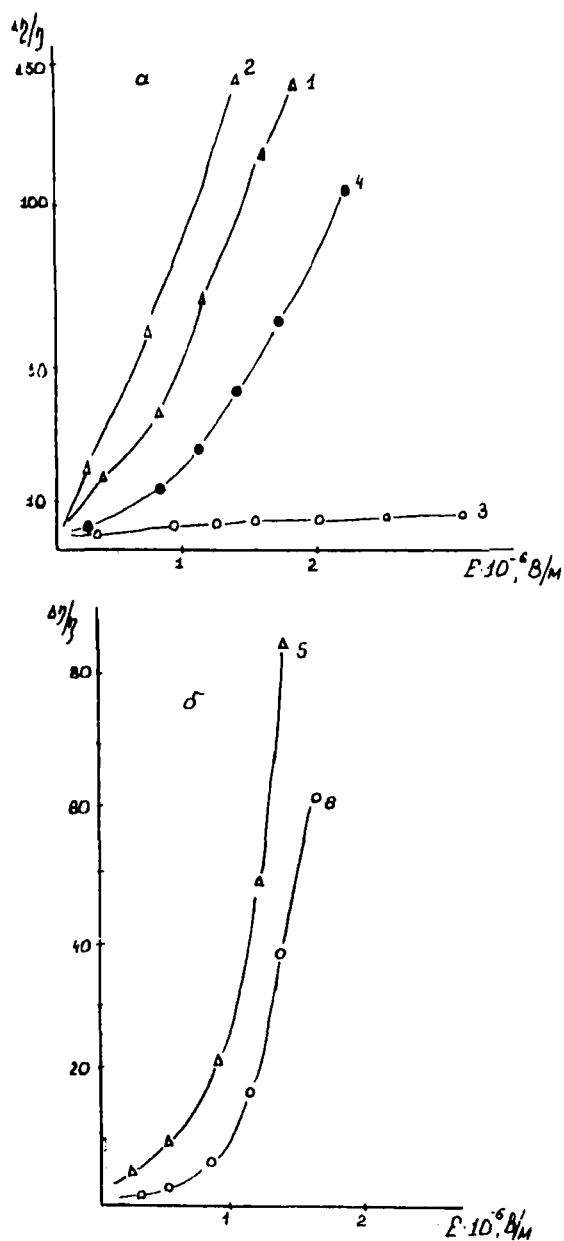


FIGURE 1 Relative viscosity of suspensions based on cellulose citrate (1), cellulose tartrate (2), non-modified cellulose (3) (Sps. 6-09-10-18-18-87), carboxymethylcellulose (Sps. 6-09-10-1814-87) (4), cellulose phosphate (6-09-10-99-73 no. 71015083, product of Bulgaria) (5, 6) as a function of static electric field intensity.

of the field on molecular mobility and, at the cost of this, an enhancement of the dipole polarization process: orientation of certain macromolecule units of the composition-filler polymer. This enables us to consider the changes of this type as structure-sensitive evaluation techniques which characterize the structure of field-active polymers.

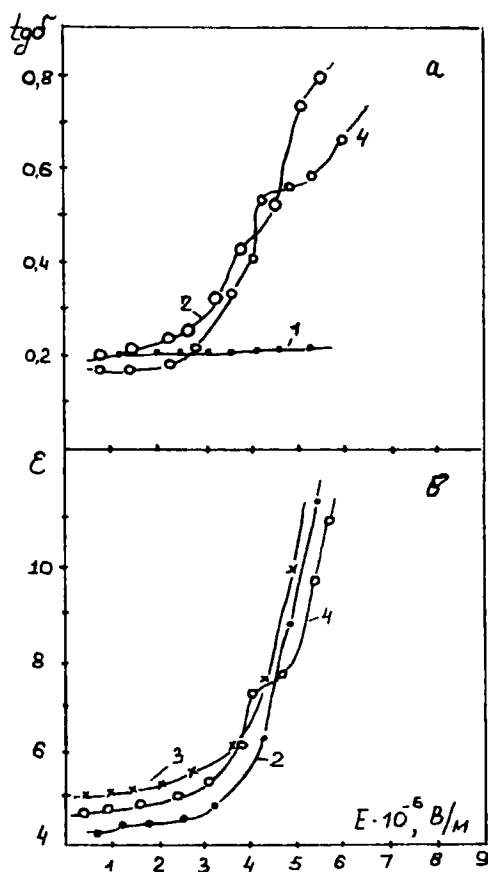


FIGURE 2 The influence of 50 Hz variable electric field intensity on the values of dielectric loss tangent (a) and dielectric permittivity (b), measured on air-dry carboxymethylcellulose samples in the form of paper with the COOH group content of 0.8 (2), 1.4 (3), 2.6 (4) as well as on nonmodified paper (1).

It has been found that the electrorheological effect of cellulose derivative-based compositions depends on the polymer-sorbed water. An increase of relative viscosity and decrease of the threshold field intensity are observed with moisture content increasing up to a certain level above which (more than 20%) a decrease of electrosensitivity is observed. It is known<sup>5</sup> that water changes the cellulose physical structure significantly, increases the molecular mobility and, at a certain moisture content, promotes the transition of polymers from a glass-like to a highly elastic state which is characterized by a higher mobility of different structural elements of the polymeric matrix: both of the segments and the macromolecule as a whole. This apparently results in lower threshold intensity of the electric field, which is evaluated by both dielectric characteristics and viscosity values.

The electrorheological effect of cellulose derivatives is observed not only in oils but also in the medium of non-polar solvents. In hexane and dioxane the overall relationship and threshold intensity values are affected (Figure 3a). For polymer

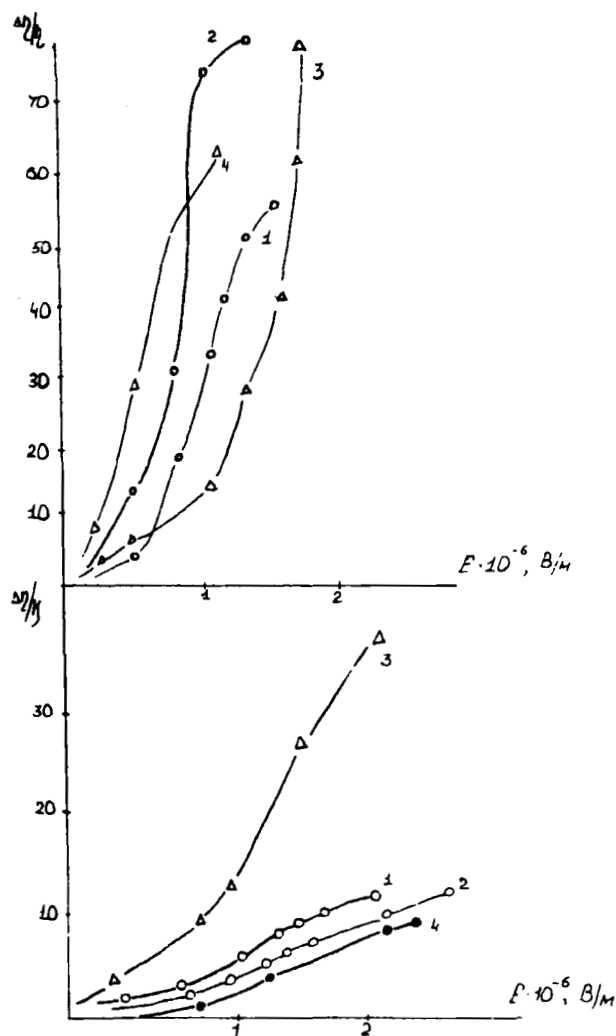


FIGURE 3 Relative viscosity of the 10% cellulose phosphate-based suspension (Sps. 99-67) in transformer oil, dioxane, hexane, heptane (a, 1-4) as well as in 10% cellulose acetophthalate solutions in dioxane with the phthalyl group content of 9.7, 24.3, 31.0 mass %; cellulose diacetate solutions (b, 1-4) as a function of static electric field intensity. Displacement rate with the measurement is  $16.2 \text{ s}^{-1}$ .

solvent-based compositions, and particularly for cellulose acetophthalate and acetosuccinate, this process is more marked. By introducing a polymer with active groups (phthalyl, succinyl and carboxyl groups), the response of the system to the electric field is increased considerably.

Figure 3b shows the changes in relative viscosity as a function of the electric field intensity for cellulose phosphate suspensions (Sps. 9-67) with 10% cellulose diacetate and acetophthalate solutions in dioxane (phthalyl group contents 9.7, 24.3 and 31.0 mass %) used as binders. These results show that optimum electrosensitivity is characteristic of polymers based on cellulose acetophthalate with a maximum

content of phthalyl groups. Compounds based on this example show an effect to a smaller electric field intensity and achieve a variation of viscosity in the field.

Suspensions in polyvinyl alcohol and oxypropylcellulose solutions are also electrosensitive, although their electrosensitivity is several times lower than it is when cellulose acetophthalate-based compounds are used as a binder. Compounds which contain water-soluble carboxymethylcellulose and oxypropylcellulose showed no substantial effect to the applied static electric field under the conditions of this study.

Thus, the electrorheological effect depends to a large degree on the binder type. It is more pronounced in polymer solutions containing ionogenic acid groups, and varies with the concentration of these groups in the polymer. This effect seems to be associated with a peculiarity of the physical interaction between the binder particles and the solution.<sup>6</sup>

The electrosensitivity of these suspensions also depends on the binder concentration and polymer solution. Thus, for example, for carboxymethylcellulose suspension (Sps. 6-09-10-1874-87) in the cellulose acetophthalate solution, the composition is optimal at the concentration (mass %): carboxymethylcellulose—1-20; 2–15% cellulose acetophthalate solution—99-80.

The influence of surface effects at the solid body—liquid interface testifies to the fact that the electrorheological effect is associated with the solid-phase surface structure, which changes as a result of various actions and treatments. This permits us to postulate that the electrorheological technique generally characterizes relaxation processes in the surface layers on binder particles, in this case, a polymeric one based on cellulose derivatives.

The ERS formulations developed here may be recommended for moulding film materials with preset properties in fields and for their subsequent use as working fluids of power units in electrohydroluminomatics.

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