Ionically conductive polymers for ER fluid preparation

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Abstract. Two groups of electrorheological (ER) suspensions containing polyelectrolytes and solid polymer electrolytes as dispersed phases of ionic conductivity were synthesized and their ER effect at elevated temperatures was studied. Polymers were carefully characterised and detailed analysis of their ionic conductivity change with temperature was performed. It was found that in suspensions comprising both types of materials ER effect and current density were closely related to cation type presented in resin and in salt added to solid electrolyte. If small monovalent cations of high mobility were present in the solid phase the ER effect of suspensions as well as their current densities increased strongly with temperature both for polyelectrolytes and solid electrolytes. Presence of spatial cations resulted in lower power consumption and reasonable ER effect within wide temperature range.

1. Introduction

Over the last years a lot attention has been paid to materials being a dispersed phase in ER suspensions. Although a lot of work has been done on ER fluid preparation there are still problems with their usage in practical devices. The main drawback here is their susceptibility to overheating during the prolonged work, which results in strong current density increase [1]. Among the materials used in ER fluid synthesis the most promising for ER fluids synthesis are polymers with ionic conductivity like: polyelectrolytes with different counterions and solid polymer electrolytes – complexes of polymers with various salts. In both cases conductivity of the solid phase and its electrorheological behavior can be relatively easy controlled by the change of counterion in polyelectrolyte or the salt type and concentration in polymer electrolyte. In the scientific literature there are publications concerning ER fluids based on polyelectrolytes like sulphonated polystyrene-co-divinylbenzene (SPS), phosphorylated cellulose [2], polymer electrolytes based on polyacrylate copolymers [3] and polyurethane polymer electrolytes [1]. ER effect of the reported fluids was related to the humidity of the dispersed material [4], solid phase content [5], grain size [6], electric field strength and frequency [7] but the information about their temperature characteristics are still unsatisfactory. It is necessary therefore to shed more light to this matter.

The aim of our work was a synthesis and investigation of an ionically conductive polymer with good ER response for application in ER devices working at room and elevated temperature without significant current density increase. To this end detailed analysis of rheological and electric properties of ER fluids with different solid phases of ionic conductivity were performed. Measurements were carried out on six suspensions containing: sulphonated polystyrene-co-divinylbenzene with sodium cation (SPS-Na), sulphonated polystyrene-co-divinylbenzene with N-trimethoxysilylpropyl-N,N,N-trimethylammonium cation (SPS-NTSi), aminofunctional polystyrene-co-divinylbenzene resin neutralized with sulfuric acid (PS-A) and polycrylonitrile-co-methylmethacrylate (PAN) complexes
with lithium trifluoromethanesulfonate (LiTF), zinc chloride (ZnCl$_2$), N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride (NTSi).

### 2. Experimental

Polystyrene-co-divinylbenzene (PS) was prepared from monomers by the well known suspension polymerization method in a presence of benzoyl peroxide as initiator and aqueous solution of polyvinylalcohol as a protective colloid then washed with water and dried at 80°C over 24h. Product containing not more than 10wt.% of divinylbenzene, was sulphonated at elevated temperature with concentrated H$_2$SO$_4$ in the presence of CoCl$_2$. Then obtained acidic resin was filtered under reduced pressure, washed with diluted H$_2$SO$_4$ and distilled water. Next protons were replaced to sodium and NTSi cations and two cationites were obtained: SPS-Na and SPS-NTSi. Anionite (PS-A) was prepared by chloromethylation of the initial PS copolymer followed by amination of the chloromethylated product with triethylamine. The preparation method was adopted from [8]. The alkaline resin was then filtered, washed with distilled water and neutralized with diluted H$_2$SO$_4$. Final product was filtered and washed with distilled water to neutrality. After synthesis all ionomers were dried in a dryer at 120°C to constant mass. Polymer electrolytes were prepared from polycrylonitrile/methylmethacrylate copolymer (Dralon®, Bayer AG). Polymer was dissolved in dimethylformamide solutions of LiTF, ZnCl$_2$ and NTSi. Then solutions were poured into Petri dishes and the solvent was evacuated in vacuum at 80°C. The obtained thin foils of PAN-LiTF, PAN-ZnCl2 and PAN-NTSi were powdered with impact mill, sieved and dried again in high vacuum about 10$^{-5}$ Tr at 80°C over 24 hours. Salts concentrations in prepared samples were constant and amounted 0.2 mol/kg of polymer. Electrorheological suspensions were prepared by dispersing the weighted amounts of prepared samples in silicone oil (PDMS) of 0.01Pa·s viscosity to obtain 40wt.% suspensions.

Conductivities of samples were calculated from impedance spectra recorded with PARSTAT 2263 system equipped with PowerSuite software at frequencies 100mHz - 100kHz and temperatures from 20 to 80°C. Impedance spectra were analyzed with Equivalent Circuit v.455. Morphology of grains was determined by scanning electron microscope FEI Quanta 200. Quantitative data on grain size distribution of the solid phase were taken from optical images recorded with Nikon Alphaphoto-2 YS-2 microscope with CCD camera. Images were analysed with the MicroScan v.1.3. ER effect of the prepared fluids at temperatures from 20 to 70°C was measured with a rotational rheometer Physica MCR301 (Anton Paar) with ER cell operating in a coaxial cylinders geometry, under dc electric fields up to 3 kV/mm. Leak currents drawn through the studied suspensions were also measured and recorded. Yield stresses were calculated from flow curves using Herschel-Bulkley extrapolation.

### 3. Results

Ion-exchange resins were prepared from polymer obtained by suspension polymerization and have spherical shape of grains as figure 1a shows.

**Figure 1.** SEM image and grain size distribution of SPS-Na (a) and PAN-LiTF (b).

Grain size distributions of the prepared polyelectrolytes were identical as for the resin presented in figure 1a with the average diameters of particles within 2 to 18 µm with most of them below 12
microns. Solid electrolyte materials were in a form of polyhedral particles with smooth surface as the example SEM image in figure 1b shows. In this case the average particle diameter was taken into account for determination of grain size distribution.

ER effect is related to polarization processes coming from ionic polarization governed by ionic conductivity of dispersed solid phase [9]. Ionic conductivity increases with temperature even a few orders of magnitude that is rather unfavorable because this growth is related to higher power consumption and usually with ER effect drop. In practical applications, especially in shock absorbers and brakes ER suspensions work at elevated temperature and detailed knowledge about temperature characteristic of working fluid is indispensable. ER suspension is a multicomponent system and studying the temperature dependence of solid phase only is not sufficient. Full information can be obtained from direct measurements taken on samples simulating the aggregates formed in ER fluid upon field, where solid phase is densely packed, grains touch each other and small empty spaces between them are filled with carrier fluid. Taking the above into account dense (85%) pastes made out of solid phase and small amount of silicone oil are good objects for carrying such experiments. Results were plotted in the Arrhenius type coordinates shown in figure 2a.

**Figure 2.** (a) Arrhenius plots of investigated materials, (b) relation between conductivity and yield stress of suspensions for different temperatures

The conductivity values were calculated from total resistance (bulk + intergranular) together with geometry of a particular sample. Activation energies (Ea) of ionic conductivities for all materials were also determined. Ionic conductivities at 20ºC calculated for the investigated samples ranged from $1.20 \times 10^{-9}$ S/m (SPS-NTSi) to $4.8 \times 10^{-8}$ S/m (SPS-Na). After heating to 80ºC the conductivity values increased significantly and were within $1.60 \times 10^{-7}$ S/m (for PS-A) to $2.10 \times 10^{-4}$ S/m (PAN-LiTf). Comparing the two cationites (SPS-Na and SPS-NTSi) we can see that introduction of spatial organic cation instead of Na$^+$ resulted in flattened conductivity-temperature characteristics. Similar relation was observed for polymer electrolytes where the samples can be set up in a series of decreasing conductivity: PAN-LiTf > PAN-ZnCl2 > PAN-NTSi.

Figure 3a illustrates the increase of yield stresses of investigated suspensions with electric field strength. The corresponding change of the yield stress with temperature and conductivity is shown in figure 2b. The changes of current densities at 2kV with temperature are shown in figure 3b.
Suspensions of SPS-Na and SPS-NTSi exhibited a strong ER effect while the PAN complexes as well as PS-A were less active. PAN-NTSi suspension had an ER effect comparable to PS-A. In PAN-complexes the ER effect can be related to the cation type of salt applied as an ionic dopant. If the salt comprised a big organic cation (NTSi+) the ER effect of the suspension was rather low although the conductivity measured for this sample was higher in comparison to cationite-based suspension with the same cation (SPS-NTSi). The strongest temperature dependences were observed for ion exchange-based suspensions where current density increased even three orders of magnitude. In the case of solid electrolyte samples this growth was significantly lower.

4. Conclusions
The above-mentioned results proved that all investigated materials of ionic conductivity can be easily modified and applied as solid phases in ER fluids. It means that ER effect in suspensions of solid electrolytes can be tuned by introduction of spatial cations of limited mobility. It was found that ER effect of suspensions of polyelectrolytes and solid electrolytes can be related with the type of cation present in a given system. When small monovalent cations of high mobility were present in the solid phase the ER effect of suspension as well as current density of suspensions increased strongly with temperature both for polyelectrolytes and solid electrolytes. Application of spatial cations resulted in lower power consumption and reasonable ER effect within wide temperature range. Suspension of PAN-complexes with different salts are good candidates for practical application within wide temperature range.

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