Electrorheological fluids containing phosphorylated polystyrene-co-divinylbenzene

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Abstract. Electrorheological fluids based on ion-exchange resins were thoroughly described in literature. Most of the papers reported on application of sulphonated polystyrene-co-divinylbenzene as a dispersed solid phase. The aim of the presented work was to synthesise phosphorylated polystyrene-co-divinylbenzene (PPS/DVB) and compare properties of the obtained suspensions with a sulphonated polystyrene-co-divinylbenzene based fluid. PCl$_3$ was used as the phosphorylating agent. The prepared PPS/DVB resin powders were dispersed in a silicone oil and flow curves were recorded under DC electric field up to 3 kV/mm. It was found that yield stress values depended on the cation type in PPS/DVB: Na$^+$ containing resins exhibited the highest ER effect, and on the water content with the optimum concentration depending on the cation type.

1. Introduction
Electrorheological (ER) fluids comprising micron sized polarisable particles dispersed in non-polar liquids of low viscosity have been intensively investigated for a few decades. Among them a particular attention was paid to polyelectrolyte polymers, better known as ion-exchange resins [1]. Most of the performed work was, however, dedicated to electrorheological effect in suspensions of only one kind of these resins – sulphonated polystyrene-co-divinylbenzene (SPS/DVB). The ER effect observed in these fluids was related to humidity [2], solid phase content [3], grain size [4] as well as electric field strength and frequency [5]. One of obvious objectives of designing electrorheological fluids for practical applications is to maximize the magnitude of polarization forces within dispersed solid particles under external electric field what can be possibly achieved by modification of a kind and concentration of polar groups attached to a polymer backbone. The aim of the present work was to check whether replacing the sulphonic groups in a SPS/DVB resin by their phosphorus analogues would result in any improvement of ER properties of the related fluids.

2. Experimental
The polystyrene-co-divinylbenzene was synthesized using a suspension polymerisation method [6] and then polymer was phosphorylated with PCl$_3$ at the presence of AlCl$_3$ as a Lewis acid-type catalyst [7]. PCl$_3$ (188 ml) and PPS/DVB (30 g) were introduced into a three-necked flask equipped with a reflux condenser, a high speed homogeniser and a thermometer. The content was stirred at ambient temperature for 1h and AlCl$_3$ (15 g) was subsequently added. The mixture was intensively stirred at 75°C for 3 hours. Then the suspension was cooled to ambient temperature and stirred for further 24
hours. The obtained precipitate was filtered out and first washed with dioxane and then hydrolysed with water at 4°C. Acid protons in phosphinic groups were replaced by potassium, sodium or lithium cations using 10% aqueous solutions of appropriate hydroxides. The cation substituted PPS/DVB powders were filtered out and washed with distilled water to pH = 7. Then they were dried in an air drier at 80°C and/or in vacuum of approximately 10⁻⁵ mbar for 8 hours. For comparative reasons a sulphonated copolymer was also prepared according to well known method described in literature [8].

A few methods were applied to characterise the obtained resins. FT-IR spectroscopy was used to identify functional groups in PPS/DVB. SEM/EDS (Scanning Electron Microscopy/Energy Dispersive Spectroscopy) was used to reveal the morphology of the prepared powders and to determine concentrations of phosphorus, sulphur, carbon and oxygen in the samples. We have also examined the ionic capacity of the obtained resins with a classic titration method. Water content was determined by the Karl Fisher method directly before each ER measurement.

Aliquots of powders were dispersed in a dry silicone oil (polydimethylsiloxane) of 0.1 Pa·s viscosity. ER fluids containing 30 and 40 wt.% of solid phase were prepared. Flow curves of ER fluids were recorded using a rotational viscometer Bohlin Visco 88 equipped with a concentric cylinder geometry of 1 mm gap. The measurements were recorded under DC electric field up to 3 kV/mm. Currents drawn by the ER fluids were measured simultaneously. All measurements were taken at ambient temperature of about 23°C.

3. Results and Discussion

3.1. Characterisation of materials

Figure 1 shows the FT-IR spectrum of the raw PS/DVB and the copolymer phosphorylated with PCl₃. The band at 2326-2275 cm⁻¹ is due to –P–H vibration. The absorption bands at 1402 and 1344 cm⁻¹ are typical of –P–C and –P=O vibrations, respectively. The ester bands are visible at 1150-970 cm⁻¹. The wide band at 3680-3300 cm⁻¹ was assigned to –OH groups. These data show that a considerable amount of phosphinic groups were attached to the polystyrene backbone.

Figure 1. FT-IR spectra of raw polystyrene-co-divinylbenzene and the copolymer after phosphorylation.

We attempted also to determine the concentration of the polar groups in the ion-exchange resin. The EDS analysis of phosphorus showed that approximately 0.4 phosphinic group is attached to each aromatic ring. A different result was obtained from a classic titration giving only 0.19 phosphinic per one ring. This discrepancy can be easily understood after assumption that the phosphorylation process of the polymer took place mostly in a surface layer of each grain and not within a whole volume.

The EDS analysis of oxygen showed that the O/P ratio in surface layers was 2.44 suggesting that not only phosphinic but also phosphonic groups were present in the studied material. Since the phosphorylation reaction was performed in a presence of air it was possible that a simultaneous oxidation reaction took place. It seems that the concentration of the two phosphorus containing functional groups is almost equal.
A morphology of PPS/DVB-Na particles was investigated by SEM. Figure 2 shows that the obtained grains were regular and spherical in shape. Diameters of most of the particles were between 10 and 20 µm. Some small spheres – significantly below 10 µm – could be also found.

3.2. Electrorheological measurements
A set of flow curves of 40 wt.% suspensions of PPS/DVB substituted with Na⁺ is presented in figure 3. The observed ER effect is strong since the yield stress amounts to about 2.6 kPa at 3 kV/mm with a reasonably low current not exceeding 6 µA/cm².

![Flow curves and current densities of 40 wt.% PPS/DVB-Na. Water content is 1.6%](image)

Figure 3. Flow curves and current densities of 40 wt.% PPS/DVB-Na. Water content is 1.6%.

In the case of suspensions containing sulphonated polystyrene we observed a dependence of ER properties on the cation type. We performed similar experiments for fluids based on PPS/DVB. The fluids taken for comparison had the same content of water (1.6%). High yield stresses were recorded for potassium containing fluids (2070 Pa at 3 kV/mm for 30 wt.%), but in the case of 40 wt.% suspension accompanying currents were unacceptably high and exceeding in some cases the capacity of the high voltage supply. The yield stresses of sodium containing fluids were only slightly lower (2600 Pa for 40 wt.% at 3 kV/mm) with a very acceptable level of current consumption (6 µA/cm²). In the case of lithium based fluids both yield stresses and the currents were much lower (600 Pa and 5 µA/cm² at 3 kV/mm). We believe that the sodium based fluids show optimum properties.

One of typical features of SPS/DVB based ER fluids is that their properties depend on water content [9]. Apparently this was also the case of the studied PPS/DVB based fluids (figure 4). With the exception of PPS/DVB-Li the yield stress increased with water concentration, reached the maximum value and then decreased. Possibly the PPS/DVB-Li fluids behave also in a similar way, but the eventual maximum appeared at higher concentrations of water which were not studied. The optimal values of humidity were different for K⁺ and Na⁺ and amounted to 1.75%, 1.6% respectively.

![Dependence of yield stresses a) and current densities b) of 30 wt.% PPS/DVB suspensions on water content at 1 kV/mm. Data given for K⁺, Na⁺ and Li⁺ substituted resins](image)

Figure 4. Dependence of yield stresses a) and current densities b) of 30 wt.% PPS/DVB suspensions on water content at 1 kV/mm. Data given for K⁺, Na⁺ and Li⁺ substituted resins.

The results obtained for the PPS/DVB based fluids were compared with ER activity of their sulphonated analogues. The results depicted in figure 5 clearly show that the yield stress of the
phosphorus fluids was almost two times higher with a significantly lower current consumption proving its higher ER activity. It is worth to note that the number of sulphur atoms per one aromatic ring (according to EDS) in the SPS/DVB resin was about 0.81 while the number of phosphorus atoms per one aromatic ring in the PPS/DVB resin was only 0.4. It means that phosphinic/phosphonic groups are considerably more effective in evoking ER activity than the sulphonic ones used to date. If we manage to obtain PPS/DVB with increased number of functional groups it will be probably possible to get ER suspensions of even higher activity.

![Flow curves and current densities of 40 wt.% PPS/DVB-Na and SPS/DVB-Na suspensions at 3 kV/mm. Water content 1.6%.

4. Conclusions
The presented findings suggest that PCl$_3$ is a suitable phosphorylating agent. The presence of polar groups in the product obtained by phosphorylation with phosphorus chloride(III) was confirmed by EDS and FTIR methods. The phosphorylation process takes place mostly at the surface of grains because of the high cross-linking level of the copolymer and limited diffusion of the phosphorylating agent into a bulk of a grain.

It seems most likely that suspensions of PPS/DVB can exhibit much higher ER effect provided the phosphorylation reaction efficiency is improved. We had also showed that suspension of PPS/DVB needs lower current densities in comparison to the sulphur analogue.

Summing up – suspensions of PPS/DVB exemplify new, promising materials characterized by high electrorheological activity. Prepared materials are described by following parameters: the yield stress about 2.6 kPa at 3 kV/mm, viscosity below 0.3 Pa·s (at 23°C and 0 kV/mm) and the current consumption below 10 µA/cm$^2$ (at 3 kV/mm). The investigated fluid can be used as a new material in ER technology.

Acknowledgments
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