

**Anna KRZTOŃ-MAZIOPA, Marta SUKIENNIK, Adam BAŃKOWSKI,
Janusz PŁOCHARSKI**
Warsaw University of Technology, Warsaw

ELECTRORHEOLOGICAL FLUIDS CONTAINING POLYELECTROLYTES

Key words

Electrorheological effect, yield stress, ER fluid, electrorheological suspension.

Summary

Electrorheological (ER) fluids belong to the broadly studied class of so called “intelligent materials” whose properties are sensitive to external stimuli. The ER fluids increase their viscosity upon application of an electric field. This paper reports the results of electrorheological experiments and describes a synthetic procedure leading to an ER suspension exhibiting predetermined characteristics. The fluid was designed for application in a prototype ER clutch.

Introduction

Electrorheological (ER) fluids are usually suspensions of fine, polarisable solid particles dispersed in a non-polar liquid of low viscosity. Under an external electric field, these fluids significantly change their viscosity by even a few orders of magnitude in a millisecond time scale. This fast and reversible increase of the fluid’s viscosity resulting from a change of a suspension structure is called the electrorheological effect. In an electrified ER suspension, initially, randomly distributed particles form columns or fibres spanning the inter-electrode gap. Morphology of the aggregates created under an electric field has been widely studied and extensively described in the literature. In most cases,

when the field is applied to the suspensions comprising uniform spherical particles, the quasi-crystalline phases are formed. However, if a polydisperse material is used, the field-induced structures are not so well organised, but it is usually more stable due to the higher packing density of the particles [1, 2]. The electrorheological activity is generally attributed to electrostatic interactions between the polarised solid particles leading to a conclusion that the solid particles play a more important role, whereas the liquid serves rather as a carrier. After a few decades from the discovery of the ER effect, it has been revealed that large number of different material combinations of solid particles and liquid phases exhibit ER activity; but only a few of them manifest really high ER effect necessary for practical applications. The materials utilised as the solid phases can be roughly divided into three main groups: inorganic (metal salts, oxides, hydroxides), organic (containing polar functional groups) and conductive polymers (having conjugated system of multiple bonds).

The ER activity originally has been assigned to the mismatch between the dielectric constants of the solid and liquid phase in the suspension [3]. Then much work has been done on the role of conductivity in ER effect [4]. The most recent concept, called the dielectric loss mechanism, involves elements coming both from the polarisation and conduction models [5]. According to this model, the ER effect can be mainly related to the interfacial polarisation of solid particles, because the solidification of the ER suspension under an electric field results from the charge carriers' movement along the fibrous structures formed between electrodes. This charge transport takes place in the bulk and/or on the surface of the contacting aggregates and in single grains between these structures. It is also known that the increase in viscosity of an ER fluid is always accompanied by the passage of electric current through the suspension.

ER fluids without an electric field behave like Newtonian fluids, and the application of the field transforms its rheological characteristics into the one that can be approximated by the Bingham model. According to this model, the relation between shear stress and shear rate can be approximated by the following equation: $\tau = \tau_0(E) + \eta(\dot{\gamma})$ where τ – shear stress [Pa], $\tau_0(E)$ – yield stress [Pa] (depending on the electric field strength), E – electric field strength [V/m], η – plastic viscosity of ER fluid [Pa s], $\dot{\gamma}$ – shear rate [s^{-1}]. The τ_0 parameter is the limiting shear stress above which the ER fluid begins to flow. Below this characteristic value, it behaves like a solid. Yield stress is the basic parameter that characterises the ER effect in a given system. It also permits a comparison between different ER fluids. Although the Bingham model is the most popular description for ER systems, because of its simplicity (it can be applied to most ER systems), there are also fluids that cannot be approximated with it, for example, fluids containing polyelectrolytes or solid electrolytes as dispersed phases. For these systems, the Casson's model is usually applied.

In the case of heterogeneous ER fluids, the yield stress is a function of electric field strength and can reach kPa values can exceed multiples of ten (presently, the scientific literature reports about suspensions that exhibit very high yield stress reaching 200 kPa [6]). An ideal ER fluid is a fluid, which contains small amount of dispersed phase and exhibits a high ER effect without a current consumption that is too high. Moreover, it should not settle, and its components should be non-toxic and easily available. Although many compositions of commercial ER fluids have been developed, there is still no ideal ER fluid. Most of commercial fluids show good practical properties and are utilised in prototype devices. A practical ER fluid should have high yield stress at electric fields of reasonable strength, low current density – preferably below 20 $\mu\text{A}/\text{cm}^2$ at 2kV/mm, a broad working temperature range (-20–120°C), a short response time (few milliseconds), a low viscosity without the field (about 100 mPas or lower), and a high viscosity when the field is applied as well as a high chemical and physical stability.

The typical ER fluid usually contains three main components: dispersed phase, which in most cases is solid (ER emulsions being mixtures of only liquid components are also known), a carrier fluid and additives. Homogeneous ER fluids, which are solutions or melts of liquid crystalline substances, have also found some areas of application. Typical heterogeneous fluids comprise polarisable substances of the previously mentioned composition. As dispersing agents, insulating fluids are usually used like silicones, mineral oils, paraffin and chlorinated hydrocarbon oils to give a few examples. These oils must have a low conductivity and a high electric breakdown strength. Most ER fluids also contain various additives at concentrations below 5% by weight. The most common are water, inorganic and organic acids, alkali, salts or surfactants. Any polar substance that enhances the ER effect and/or the stability of the suspension can be applied as the additive.

Electrorheological fluids react fast and reversibly in the presence of an electric field, which enables the design of many devices utilising this property. Among them the most important are controllable shock absorbers, valves, clutches, and brakes [7]. During the last decade, other applications have also appeared like rehabilitation or telesurgery systems [8], medical sensors [9], tactile panels [10], artificial muscles [11], intelligent inks [12] and others. Although many prototype ER appliances and ER fluids recipes have been created, there still are technological difficulties in designing the ER fluid composition.

Among materials that can be applied in ER fluids synthesis, the polyelectrolytes, better known as ion-exchange resins, look very promising. In the literature concerning the ER effect, information about such systems can be found. Most of these articles describe the electrorheological effect in suspensions of sulphonated polystyrene-*co*-divinylbenzene (SPS). The ER effect of the reported fluids was related to the humidity of the dispersed material [13], solid phase

content [14], grain size [15], electric field strength and frequency [16]. The information coming from these publications and the parameters of investigated ER fluids were interesting, but some discrepancies between the published results were evident. For example, the results concerning the influence of solid phase concentration, moisture content and grain size distribution on the ER effect magnitude were inconsistent in a few cases.

The aim of our work was to prepare a practical ER suspension that could be used in a prototype ER clutch [17]. The synthesised fluid should have a yield stress of about 2 kPa at 3 kV/mm, a current density not higher than $15 \mu\text{A}/\text{cm}^2$ for 2 kV/mm at 20°C and a low off-field viscosity – 0,25 Pas or lower.

We have assumed that the ER fluid containing a solid ion-exchange resin as a dispersed phase should fulfil the above requirements.

Experimental

At the initial stage of this project, some work has been done on the ER fluids containing sulphonated polystyrene. The solid phases were prepared by milling the commercial cationite-type resins (Amberlite 200C or IR120 in Na^+ form). The schematic chemical structure of this resin is shown in Fig.1a. It was found that the prepared ER suspensions exhibited a high ER effect, as Fig. 1b shows, and good rheological properties. However, the zero-field viscosity of this fluid was about 300 mPas, which exceeded the requirements of the specification.

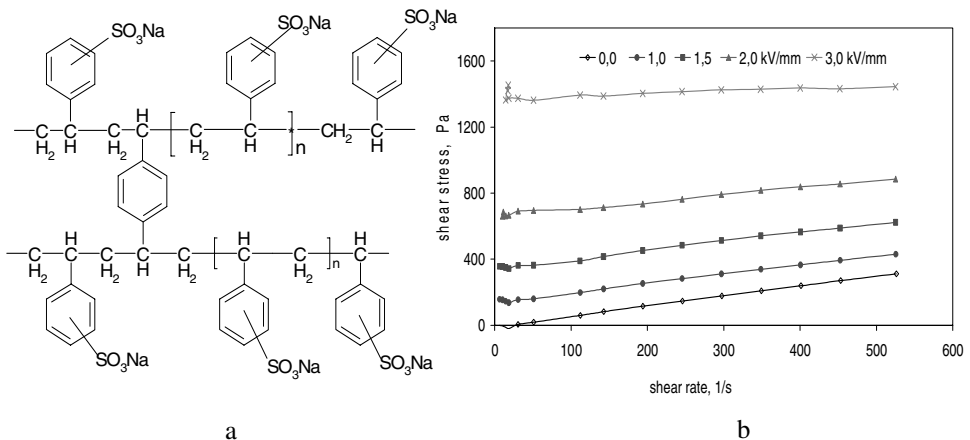


Fig. 1. a) Schematic representation of chemical structure of sodium salt of sulphonated polystyrene-co-divinylbenzene (SPS-Na), b) flow curves of wt.30% of Amberlite 200C in silicone oil

The way to decrease the zero field viscosity, which was too high, as confirmed in our initial experiments, was to change the shape of the dispersed solid grains from irregular, being the result of mechanical pulverising, to spherical – obtained by a dedicated polymerisation method. The spherical grains can be obtained by the suspension or emulsion polymerisation method [18]. In our case, the styrene-divinylbenzene copolymer was prepared according to the suspension polymerisation method, because the product is less contaminated in comparison to the emulsion polymerisation and the size of particles can be controlled by adjusting pH, the type and quantity of a protective colloid, and the rate of stirring. The synthetic procedure applied was as follows: the mixture of styrene and divinylbenzene monomers with dissolved initiator of radical polymerization (benzoyl peroxide) was added as drops to the reactor containing acidified aqueous solution of polyvinyl alcohol. The acidity of the reaction environment was adjusted by the addition of oxalic acid. The mixture of monomers contained not more than 10wt% divinylbenzene, because the higher crosslinking degree of the raw copolymer resulted in a lower efficiency of the consecutive sulphonation process. The reactor was equipped with a high-speed mechanical agitator and a reflux condenser. After the addition of monomers, the reaction mixture was heated to 85°C and intensively stirred for 6 hours. Afterward, the temperature was increased to 100°C and the reaction was carried out over 1 hour. Then the product was filtered, washed with distilled water and dried in a dryer over 24 hours at 80°C.

Then the prepared copolymer was sulphonated with concentrated sulfuric acid at 95–100°C in the presence of cobalt (II) and/or silver salts as catalyzers. The precipitate was filtered out and the sulphonation was repeated twice to increase the concentration of sulphonic groups in the polymer backbone. The obtained polystyrenesulphonic acid was washed with distilled water and then protons were replaced by sodium cations using 5% aqueous solution of sodium hydroxide. The suspension was stirred for 24 hours. Then the ionite was filtered out and the precipitate was washed with distilled water to pH = 7. The prepared materials were dried to a constant mass at 120°C.

Before the ER fluids synthesis, the obtained materials were additionally dried in a vacuum of about 10^{-5} Tr over a period of 12 hours. Then the aliquots of the powders were dispersed in dry silicone oil – polydimethylsiloxane (PDMS) to obtain ER fluids containing 40% by weight of the solid phase. The viscosity of the silicone oil used in the ER fluids preparation was about 16 mPas. The prepared suspensions were additionally dried in a vacuum at an elevated temperature over a period of 10 hours. The ER effect of the prepared fluids was measured using a rotational viscometer Bohlin Visco 88 equipped with a modified measuring tool, operating in a concentric cylinders geometry with a 1 mm gap between electrodes, under dc electric fields up to 3 kV/mm. Leak currents drawn through the studied suspensions were also measured and recorded. All rheological measurements were carried out at ambient temperature.

Results

As mentioned earlier, the polarisation processes are responsible for the magnitude of the ER response of heterogeneous ER fluids. The electrified particles transform into dipoles that interact with each other and form the characteristic structures within the electrode gap. It suggests that, not only the dipole size, but also its shape influence the formation of the structures responsible for the increase in suspension viscosity. Sancho and Sanchis [19] proved that the attraction forces between adjacent polarised grains depended on their shape. According to their investigations, the attraction force between spherical particles is much higher than in the case of ellipsoidal, cylindrical or rod-like grains. The higher attraction force is a result of the charge distribution on the grain surface, which is more uniform in the case of spherical particles. Our studies on irregular and spherical particles also showed a similar dependence. The fluids comprising irregular particles showed lower yield stresses in comparison to the suspensions with the same content of spherical grains. It should also be mentioned that the zero field viscosity of the ER fluid containing spherical grains was about five times lower in comparison to the suspension with irregular particles. Fig. 2 illustrates the results obtained for fluids with 40% (wt.) of the dispersed phases.

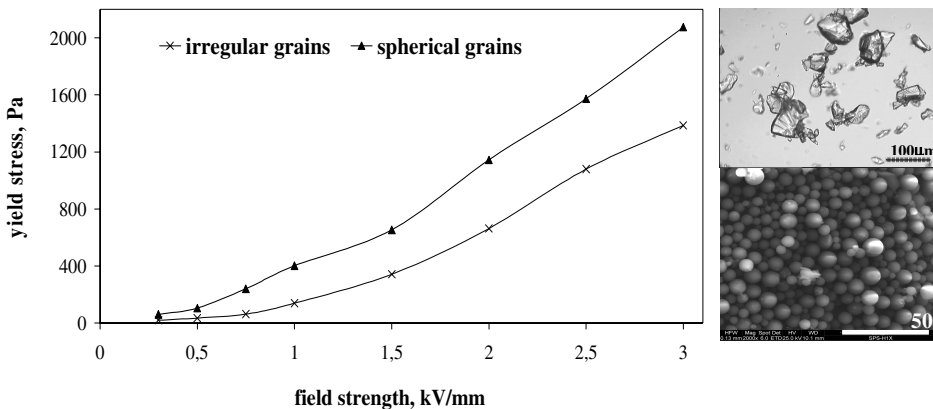


Fig. 2. Yield stress dependence on electric field for suspensions containing 40% wt.) SPS-Na with irregular and spherical grains, (moisture content $\sim 1.4\%$)

According to the literature, the spherical shape of grains assures the highest packing density of adjacent spheres in the fibrous aggregates formed upon the electric field, which results in a higher ER effect in comparison to fluids containing non-spherical particles. The formed aggregates are much stronger when they are composed of particles of different sizes [13]. In the case of our polymerisation method, the solid spherical particles were of average diameter within 2 and 18 μm with most of them below 12 microns as shown in Fig. 3.

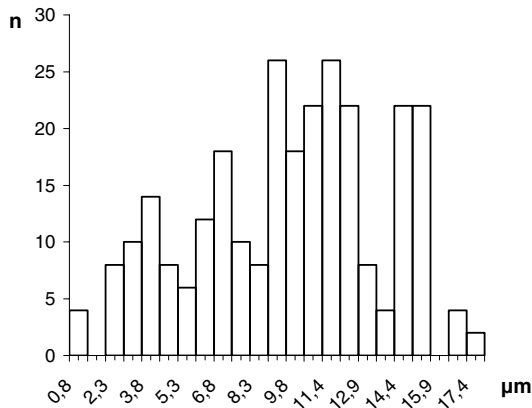


Fig. 3. Grain size distribution of synthesised resin

In polyelectrolyte-based fluids, the ionic groups are responsible for the polarisation processes resulting in the ER effect, and attention should be paid to maintain the concentration of these groups in the solid phase at the appropriate level. The higher concentration of ionic groups, the higher ER effect; because, the polarised particles form more stable aggregates under field. When the concentration of ionic species per monomer unit is too low, the ER effect decreases as Table.1 shows. The concentration of sulphonic groups in the solid materials were calculated on the basis of sulfur content in the cationite samples determined by scanning electron microscopy with X-ray microanalysis (SEM/EDS) method. The measurements were made on pellets pressed out of the prepared powders.

Table 1. ER effect dependence on multiplicity of sulphonation process

Multiplicity of sulphonation process	Average number of sulphonic groups per one monomer unit (by SEM/EDS method)	Yield stress at 3 kV/mm for 40% suspensions, Pa
1	0.22	~1000
2	0.81	~1500
3	1.3	~2000

The other typical problem related to ER fluids is their tendency to sedimentation that results in worsening the ER fluid parameters. A lot of work has been done to impede the sedimentation rate. The typical way to do that is by using antisedimentation additives, e.g. fumed silica or others. We have also carried out a series of experiments with fumed silica as an additive for improving the stability of an ER fluid. The results obtained for different silica concentration are shown in

Fig. 4. It was found that the addition of silica improves the stability of suspension, but it is accompanied with a strong reduction in the ER effect, even at small concentrations of the additive. The concentrations of SiO_2 below 0.1% (wt.) does not improve the stability of ER suspensions at all. The suspension becomes stable at a silica concentration above 0.5% (wt.), but its ER effect is considerably lower. These observations proved that the fumed silica should not be applied for the stability improvement of ER suspensions based on polyelectrolytes.

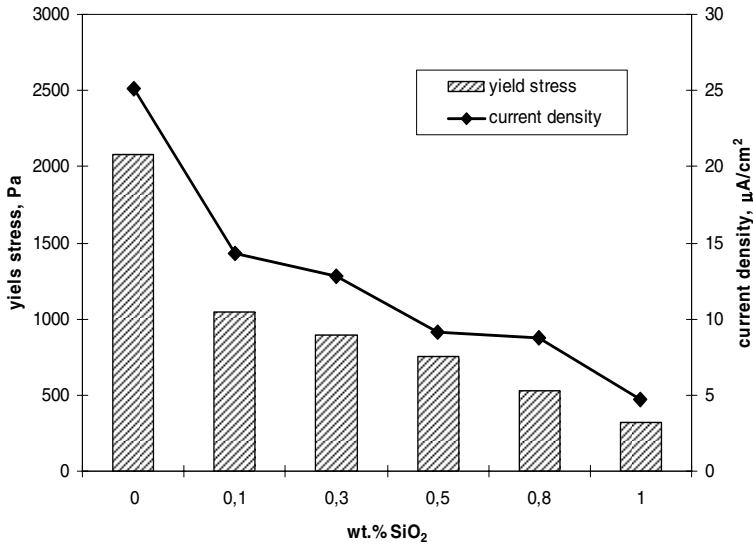


Fig. 4. Change of yield stress of 40% (wt.) suspensions of SPS-Na with SiO_2 concentration

Another method leading to the improvement of the ER suspension's stability is the application of surfactants. For this purpose, different surfactants are usually applied, but the problem is to find a surfactant that does not increase the current drawn by the electrified suspension too much. In our studies, the following surfactants were applied: sodium dodecylsulfate (ionic, well soluble in water, high polarity), Pluronic® PE10100 (copolymer of ethylene oxide and propylene oxide, insoluble in water, nonpolar), Brij® 30 (polyoxyethylene lauryl ether, nonionic, soluble in water, polar), Rokwin® 80K (the mixture of esters of sorbitol and stearic and oleic acids, poorly soluble in water, low polarity). The measurements were done at the following concentrations of surfactants: 0.1; 0.2; 0.3; 0.5; 0.7 and 1% (wt.). The presence of surfactants influenced the shear stress magnitude, current density and the stability of suspensions. At surfactant concentrations above 0.7% (wt.) the suspensions were stable but their ER effect decreased. The best results were obtained by addition of 0.2% (wt.) of Rokwin® 80K. Fig. 5 indicates how the addition of the surfactant influences the ER response of the investigated fluid.

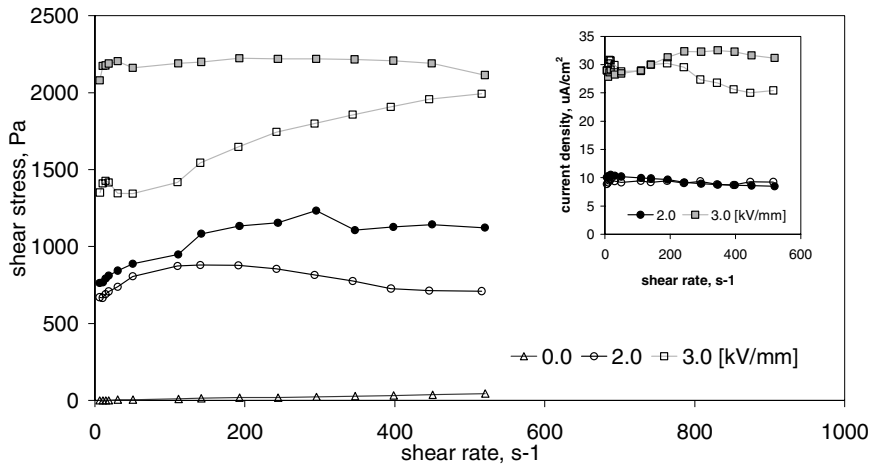


Fig. 5. Flow curves and current densities of 40% (wt.) suspensions of SPS-Na with (filled symbols) and without (open symbols) surfactant (0.2% (wt.) of Rokwin@ 80K)

The other parameter that is closely related with the ER activity of the polyelectrolyte-based ER fluids is the type of cation connected with an ionic group. In the case of the investigated materials, we checked if the change of Na^+ into a spatial organic cation having siloxane groups in its structure can improve the stability of suspension or lower the currents drawn by the suspension. For this purpose, the samples with the N-trimethoxysilylpropyl-N,N,N-trimethylammonium cation (the structure of this cation is shown in Fig. 6a) were prepared and their ER effect was measured. The flow curves of 40% suspension of this material are shown in Fig. 6b.

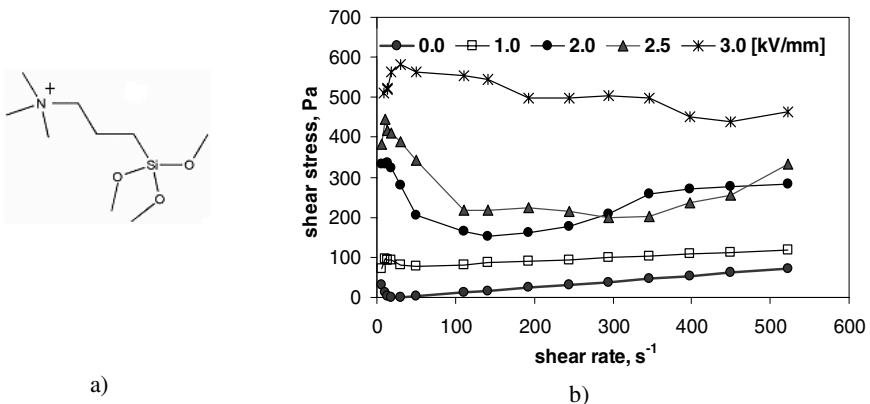


Fig. 6. a) Structure of N-trimethoxysilylpropyl-N,N,N-trimethylammonium cation, b) flow curves of 40% (wt.) suspensions

The presence of the large organic cation in the resin resulted in the decrease of current densities and the ER effect was comparable to the fluids stabilised with fumed silica. The current density did not exceed a few $\mu\text{A}/\text{cm}^2$ at 3 kV/mm, which was beneficial from the practical point of view. ER fluids usually work at an elevated temperature, and it is important to know the temperature dependence of the ER effect for a given ER fluid. For chosen samples of investigated fluids, the ER effect was recorded at 20, 40, 60, 80°C. It was found that the suspensions containing resins with the N-trimethoxysilylpropyl-N,N,N-trimethylammonium cation were less sensitive to the elevated temperature – the ER effect was almost unchanged and the current density increased only slightly with temperature. Additionally the introduction of the spatial cation to the polymer matrix improved significantly the stability of suspensions.

Similar experiments were made with zinc cation. In this case, the observed ER effect was low (about 100 Pa at 3 kV/mm) and the current density was below 1 $\mu\text{A}/\text{cm}^2$. With the temperature increase from 20 to 80°C, the ER effect increased threefold that was accompanied with the two orders of magnitude increase of the current density.

Another parameter affecting the ER effect of the studied suspensions was the presence of water or other polar substance, which activated the ER suspension under field. When a polyelectrolyte polymer is used as a solid phase, water is supposed to be the activator. We found out that there was an optimal range of water content that enabled it to fulfil the required parameters of the ER fluid. The water content in the ER fluid is particularly important in case of currents drawn by the suspension when the electric field is applied. Fig. 7 indicates the yield stress and current density dependence on the water content in the investigated fluids.

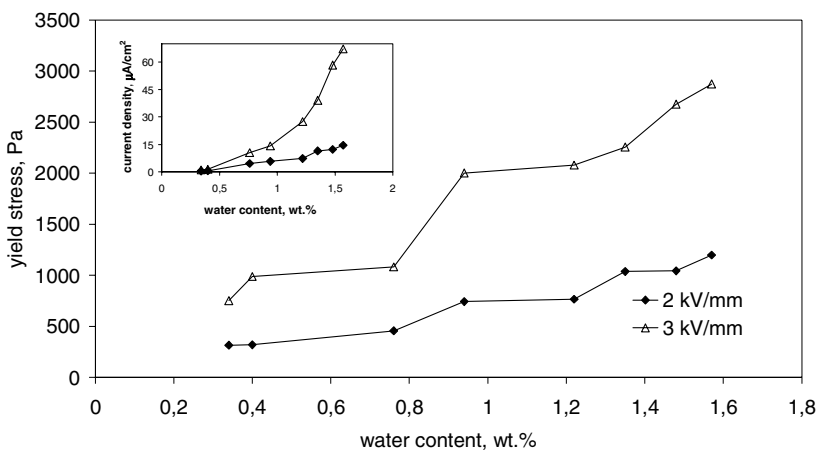


Fig. 7. Influence of the water concentrations on the ER effect and current density of 40% (wt.) suspensions of SPS-Na

The yield stress of the investigated fluids increased with water concentration, and the limiting value in the case of SPS-Na based suspensions was 1.6% (wt). Above this concentration of water, the ER effect is higher but the current density exceeds $15 \mu\text{A}/\text{cm}^2$ for 2 kV/mm, which was assumed to be the limit. The prepared ER fluid works properly when the water concentration is within the range of 0.9 to 1.6% (wt). As a result of the above investigations, the synthetic route for the ER fluid exhibiting good rheological characteristics was developed. The flow curves and current densities of the prepared material are shown in Fig. 8. The uncertainty bars of the measurements were indicated in the figures.

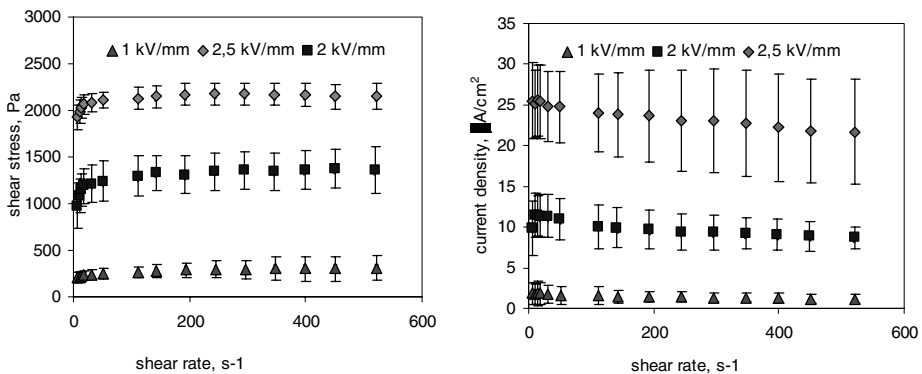


Fig. 8. Flow curves and current densities of 40% (wt.) suspensions of SPS-Na (moisture content ~1.6%)

Conclusions

The presented results show that the prepared electrorheological suspension had the following parameters:

- yield stress: 2 kPa at 3 kV/mm;
- power consumption: below $15 \mu\text{A}/\text{cm}^2$ for 2 kV/mm at 20°C;
- viscosity: 0.06 Pas for 0 kV/mm at 20°C.

This fulfils the specified requirements, and the suspension can be applied in an ER device. It was also found that there are some opportunities resulting in the improvement of the polyelectrolyte-based ER fluid properties. The ER fluid power consumption can be easily tailored by the change of the counter ion in the cationite. The prepared ER suspension has very good rheological characteristics as shown above, but the problem of sedimentation is still open. The rate of sedimentation was lowered significantly by the application of surfactants but not excluded definitely. Therefore, much more work should be done on the long-term stability of ER fluids.

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Reviewer:

Dariusz BIELIŃSKI

Ciecze elektroteologiczne zawierające polielektrolity

Słowa kluczowe

Efekt elektroteologiczny, granica płynięcia, ciecz ER, zawiesina elektroteologiczna.

Streszczenie

Ciecze elektroteologiczne (ER) należą do intensywnie badanej grupy tak zwanych inteligentnych materiałów, których właściwości można modyfikować za pomocą czynników zewnętrznych. Cechą charakterystyczną cieczy ER jest gwałtowny i odwracalny wzrost lepkości pod wpływem przyłożonego pola elektrycznego. Niniejsza praca zawiera wyniki eksperymentów elektroteologicznych i opis syntezy prowadzącej do otrzymania zawiesiny elektroteologicznej spełniającej określone parametry użytkowe. Ciecz została sporządzona w celu zastosowania w prototypowym sprzęgle elektroteologicznym.