Heterogeneous electrorheological fluids with liquid crystalline matrices

M Ciszewska, T Sadoś and J Płocharski

Faculty of Chemistry, Warsaw University of Technology, ul. Noakowskiego 3, 00-664 Warszawa, Poland

E-mail: janusz@ch.pw.edu.pl

Abstract. Hybrid ER fluids comprising powders of ionic, electronic and mixed conductivity dispersed in lyotropic and thermotropic LC matrices were studied. Flow curves of the ER fluids were recorded under electric field and compared to analogous data obtained for dispersions in silicone oil. The best results were obtained for electronically conducting pyrolysed polyacrylonitrile powders dispersed in poly(n-hexyl isocyanate) solutions showing a significant enhancement of the ER effect. A qualitative model based on local electric field increase has been proposed for the enhancement phenomenon.

1. Introduction

Classic ER fluids consist of solid particles dispersed in inert liquids. Under electric fields the particles form structures giving rise to the increase of the fluid viscosity while the inert matrix does not contribute to this change. The so called homogeneous ER fluids comprise liquid crystalline (LC) solutions or emulsions whose viscosity increases upon electric field. Combination of these two phenomena leads to a concept of a hybrid ER fluid in which solid particles are dispersed in a LC matrix. Possibly, the two effects – from interactions between solid grains and from viscosity increase of the matrix itself – sum up giving an ER fluid of improved properties. Despite the apparent attractiveness of this concept it found only a limited response in literature. Its realisation was first described by Quist and Filisko [1] who dispersed an ion-exchange resin and a synthetic zeolite in a lyotropic LC solution and reported a strong ER activity of the dispersions. It was considerably higher than the expected sum of the two mechanisms. The aim of the presented study was to compare results obtained for two systems of LC matrices and three types of dispersed solids in order to reveal the nature of the extraordinary enhancement of the ER effect.

2. Experimental

Poly(n-hexyl isocyanate) (PHIC) was prepared by polymerisation of the monomer in a DMF/toluene mixture [2]. Viscosity of a xylene PHIC solution depends on molecular weight of the polymer and its concentration. To obtain the required viscosity of 0.1 Pas, the same as for the silicone oil used as the reference matrix liquid, a 15%wt. solution was prepared. The PHIC solution at this concentration is isotropic but its viscosity does increase with electric field. Application of 1.6kV/mm resulted in increase of shear rate from 20 to about 70Pa@200s\(^{-1}\). This solution was used as an active LC matrix.

LC polysiloxane (LCPSi) was prepared according to Inoue et al. [3]. 4-cyanophenyl 4-[2-(propyloxy)ethoxy]benzoate mesogenic groups were attached to a polydimethylsiloxane main chain. The mesogen was connected to every second (50%) or to every twenty fifth (4%) carbon atom in the main siloxane chain. The prepared polymers were thoroughly characterized.

Solid electrolyte (SE) samples – polyacrylonitrile complexes of KSCN, NaSCN, KClO\(_4\) and Bu\(_4\)NI were prepared by dissolving the salts and the polymer in DMF, evaporation of the solvent and mechanical grinding/screening to obtain powders within 1÷22 µm range [4].
Fine powders of poly(p-phenylene) (PPP) were obtained from benzene at 75°C [5,6] and doped in a nitromethane/FeCl₃ solution. Depending on the doping level a total conductivity was $10^{-8}$÷$10^{-7}$ S/cm with equal electronic and ionic contributions. The grains were within 1±8 µm range.

Pyrolysed polyacrylonitrile (PPAN) samples were prepared from a copolymer of acrylonitrile and methyl methacrylate that was oxidized in air (230°C, 30 min), pyrolysed in nitrogen (500°C, 10 min), then ground and screened. PPAN had a pure electronic conductivity of about $10^{-8}$S/cm with polar functional groups on a grain surface. The particle size of PPAN was in the range of 1÷36 µm.

The ER fluids were prepared by dispersing weighted amounts of the powders in dimethyl silicone oil (PDMS) of 0.1Pas viscosity and in the two LC matrices. The concentration of solids was 15%wt.

The ER experiments were performed in a concentric cylinders geometry with Bohlin Visco 88 viscometer within a shear rate range of 6÷530s⁻¹ and at DC voltages of 0-5kV/mm. Currents were recorded. The measurements were done at ambient temperature of about 23°C (if not indicated otherwise). The yield stress values given were obtained by extrapolation of the measured data to the zero shear rate. The results neglected a behaviour of the systems at shear rates below 6s⁻¹.

Raman spectra of the ER dispersions were studied with the Nicolet Almega spectrometer combined with the confocal microscope Olympus BX-50.

3. Results and Discussion

3.1. ER fluids containing PHIC based matrix

In most cases of heterogeneous ER fluids the dispersed phase has ionic conductivity, so the first experiments were with SE samples. These powders dispersed in PDMS gave stable ER fluids of moderate strength. The yield stress values reached 200Pa@3kV/mm with currents not exceeding 4µA/cm². Replacing the inert matrix with the active one based on the PHIC polymer resulted in a higher ER effect, however, only at low field strengths. The maximum recorded yield stress was about 400 Pa@1.6 kV/mm that was accompanied by high currents exceeding 60µA/cm².

Dispersions of the doped PPP in PDMS showed moderate ER activity [6]. The flow curves were smooth and of Bingham type. The yield stress reached about 100Pa@3kV/mm that was accompanied by currents in the range of 10µA/cm². Replacing the inert matrix with the active one (PHIC/xylene) resulted in poorly reproducible results caused by electrophoresis taking place during the ER experiments.

![Flow curves of PPAN dispersion in silicone oil (a) and in 15%wt. PHIC in xylene (b).](image)

Figure 1. Flow curves of PPAN dispersion in silicone oil (a) and in 15%wt. PHIC in xylene (b).

In contrast to SE and PPP the PPAN samples exhibited stable ER activity both in PDMS and PHIC/xylene as shown in Fig.1. A very strong increase of the ER activity is clearly seen exemplified by the yield stress change from 100Pa@1.6 kV/mm for PPAN/PDMS up to 2500Pa@1.6 kV/mm for PPAN/PHIC. It is worth to note that this high ER effect was obtained at relatively low voltages and low concentration of solid phase. The system, however, had a high current – about 75µA/cm².
The observed ER effect in the PPAN/PHIC system is about 18 times higher than the expected straight sum of the two mechanisms – the arrangement of PPAN grains and the increased viscosity of the PHIC matrix. The reasons causing this phenomenon have not been clearly revealed to date. Quist and Filisko suggested that some specific sorption of LC took place on the grain surface [1]. To verify this concept we measured local concentrations of PHIC in ER suspension in various conditions. The experiments were performed in a 0.5 mL quartz cuvette comprising two electrodes. A thin glass cover was used to prevent xylene evaporation. The cuvette was placed in the microscope chamber and Raman spectra were taken point by point to record maps of the PHIC concentration. The spectra of PHIC showed that its concentration was exactly the same within the whole sample – at the ER column formed from PPAN and far from it, for a pristine dispersion, for an electrified dispersion with PPAN columns formed and for samples with the voltage switched off. Considering these results we concluded that the concept of the specific sorption did not found an experimental support.

3.2. ER fluids containing LCPSi based matrix
The LCPSi with 4% of the mesogen was in a liquid form of about 1Pas viscosity that did not change upon electric field. The one with 50% of the mesogen took a form of a semi-solid paste making ER experiments difficult. Therefore, we mixed the two LCPSi’s in 9:1 proportion to get a liquid of a reasonable viscosity. Fig.2 shows the flow curves of this mixture at 60°C proving its ER activity.

Further experiments were performed with dispersions of PPAN in a LCPSi based active matrix. Following the suggestions of Inoue et al. [3] we prepared emulsions of the “9:1” mixture in PDMS having 10%wt. of LCPSi. The resulting stable emulsion had a negligible ER effect at ambient temperature that increased when heated to 60°C. The shear stress measured at 100s⁻¹ was about 20Pa@2kV/mm with a considerably high current. Finally, the PPAN powder was added to this emulsion. The flow curves were recorded and shown in Fig.3. Some enhancement of the ER effect could be observed but it was lower than for PPAN/PHIC. In addition, the ER effect was poorly reversible. Switching the voltage off resulted in a very slow decrease of the shear stress and a continuous shearing for a few minutes was necessary to reset the system to the initial state.

In order to determine the distribution of the ER dispersion components the experiments with the microscope/Raman spectrometer were performed. The results obtained for an electrified dispersion are presented in Fig.4. They clearly show that the PPAN particles were surrounded with the LCPSi polymer filling spaces between the grains. The Raman maps taken before application of electric field did not show this phenomenon. The “9:1” LCPSi mixture had a relatively high viscosity what explains the observed limited reversibility of the ER effect in this system.
3.3. Mechanism of the ER effect enhancement

Any explanation of the extraordinary enhancement of ER effect in LC matrices should account for a few important points evidenced by the presented results. First of all, the strong enhancement took place in homogeneous solutions of lyotropic LC and only when the dispersed phase had relatively high electronic conductivity, higher that the optimal for a classic ER fluid. In addition, the concept of specific sorption of LC on dispersed grains found no experimental support. The enhancement mechanisms for lyotropic LC solutions and LCPSi/PDMS emulsions were apparently different.

Considering that we propose a simple qualitative model of the enhancement. It assumes that in the case when electric conductivity of a solid phase is higher than the conductivity of a liquid carrier the main drop of an electric potential takes place within intergranular spaces. This is because the potential drop amounts to a product of current and resistance ($u_i = j \times R_i$). The current $j$ is constant in steady conditions of an ER experiment and all local potential drops must sum up to the $E$ value between electrodes ($\Sigma u_i = E$). This situation is schematically presented in Fig.5. The active matrix between grains is exposed to this high field and increases its viscosity far more than initially expected. This increase contributes to the total enhancement of the shear stress value. In case of ioniocally conductive particles DC electric field applied causes transport of ions to grain boundaries resulting in generation of additional potentials reducing the electric field intensity in intergranular spaces.

4. Conclusions

Hybrid ER fluids comprising dispersions of polarisable powders in LC matrices were studied. The experiments showed that powders of pure electronic conductivity dispersed in a homogeneous lyotropic matrix gave fluids of the best ER performance. The observed extraordinary enhancement of the ER effect was attributed to local increase of electric field in itergranular spaces.

5. Acknowledgements

The authors thank dr. G. Żukowska for her invaluable assistance during the Raman experiments. The work was supported by statutory funds of Faculty of Chemistry, WUT.

References

[1] Quist G P, Filisko F E 1999 Int. J. Mod. Phys. B 13 675
[2] Aharoni S M, Walsh E K 1979 Macromolecules 12 271
[3] Inoue A, Maniwa S, Ide Y 1997 J. Appl. Phys. Sci. 64 303
[4] Krzytoń-Maziopa A, Ciszewska M, Płocharski J 2005 J. Electrochim. Acta, 50 3838
[5] Hirai H, Toshima N, Tanaka K, 1987 Chem. Lett. 1461
[6] Krzytoń-Maziopa A, Wyciślik H, Płocharski J 2005 J. Rheol. 49 1177