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Electrorheological response of modified silica suspensions

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Abstract

Electrorheological (ER) properties of colloidal suspensions composed of silica particles in different type of oils were investigated under DC electric field. Silica particles were prepared through the sol–gel method by hydrolyze of tetraethylorthosilicate (TEOS). Different silica powders were prepared by adding metallic cations (Co^{2+}or Zr^{4+}) in order to study their effect on the ER behaviour. The powders microstructures were characterized by XRD, FT-IR, TGA and SEM. The suspension with higher ER response was tested in an automotive damper instead of classic hydraulic oil.

Keywords: Silica; Suspension; Electrical properties; Electrorheology

1. Introduction

Electrorheological fluids are dispersions of polarisable or semi conducting micron-sized particles in insulating liquid medium, this effect was first observed by Winslow.[1] They represent a unique class of electro active materials that exhibit drastic changes in their viscosity under an applied electric field. This reversible change is due to the particle migration and formation of a chainlike or columnar structure oriented along the electric field direction.[2–5] Suspensions showing this effect rank among the smart systems, whose properties can be adjusted and controlled by external factors. The significant change in rheological properties, coupled with extremely short response time, offers a variety of applications, including electrical clutches or brakes, torque transducer, shock absorber, hydraulic valves, dampers and other tunable control and servo devices.

Many parameters affect the ER response such as dielectric properties of the powder and the dispersing media, volume fraction of the powder, its water content, grain size and morphology.

The ER effect has been observed for suspensions of both inorganic and organic powdered materials. Among them silica particles dispersed in silicon oil.[6–8] In this paper, we are investigating the effect of some metallic cations on the silica structure and its ER behaviour when mixed with silicone or organic oil.

2. Materials and methods

Silica particles were synthesized through the sol–gel method. Tetraethylorthosilicate (TEOS) (Fluka > 99%) was hydrolyzed in a mix of ultrapure water and ethanol (95%) with hydrochloric acid catalyst.

A 1 M hydrochloric acid solution was added to TEOS previously dissolved in ethanol ratio $a = (n_{EtOH}/n_{TEOS}) = 5$, the catalyst ratio $a = (n_{HCl}/n_{TEOS}) = 10$. Then, water was added to reach a hydrolyze ratio $h = (n_{H_2O}/n_{TEOS}) = 10$. The mixture was left standing for 24 h at 40 °C under stirring until complete gel formation. The silica was then roughly crashed, washed several times with ultrapure water to remove Cl^-, dried at 70 °C for 48 h and finally grounded in a planetary grinder at 600 rpm for 1 h to reach a micron size.

The procedure of producing modified silica is almost as same as producing pure silica, but chloride solution of metallic cations (Co^{2+} or Zr^{4+}) was added before hydrolyze of TEOS by water addition. The molar ratio of Co/Si and Zr/Si were both equal to 0.03. The aim was to trap these cations into the silica network.

For all powders, the host insulating oil used in the ER fluids was silicon oil (47V300 from prolabo) with a dielectric constant of 2.68, density of 0.97, viscosity of 300 mPa s at 25 °C. The silica concentration was fixed to 20 wt% for all suspensions based on previous investigations. Each suspension was well mixed using ultrasonic dispersion prior ER measurements. For the best responding powder, an ER suspension with Vaseline oil (Chemi-Pharma, Tunisia) with a dielectric constant of

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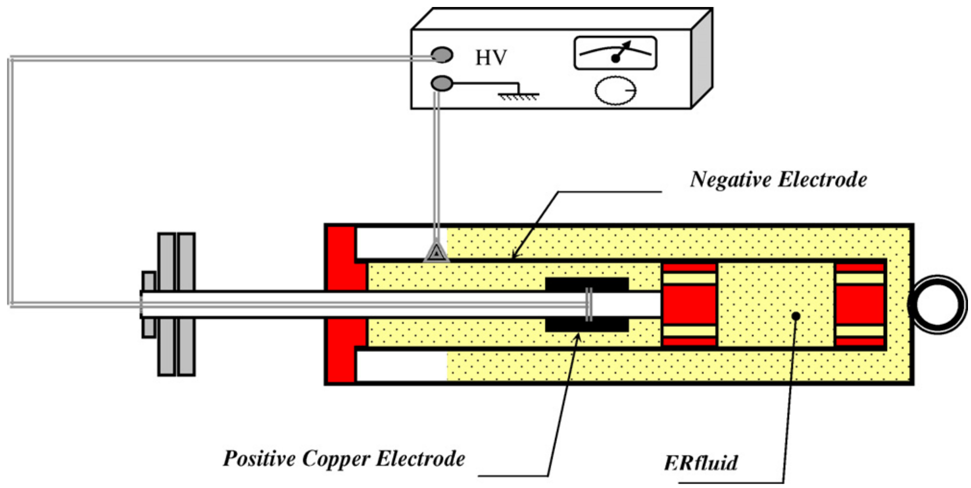

Fig. 1. Electrorheological Bi-tube hydraulic damper.

2.32, density of 0.87, viscosity of 289 mPa s at 25 °C instead of silicone oil was prepared in order to investigate the oil effect. Rheological behaviour (shear stress–shear rate) of the ER suspensions was measured with a viscotester (Haake VT550) equipped with coaxial cylinders. The gap between the inner and the outer cylinder was 1 mm. The DC electric field was varied from 0 to 4 kV using a TREK 610D high voltage supplier.

XRD analyses of the powders were performed on a Philips (XpertPro) X-ray diffraction system. Specific surface areas were measured by multipoint BET and grain size was determined by a laser diffraction particle size analyser (coulter LS230). The morphology was observed with a Philips ESEM (Quanta 200) while chemical analyses were performed by an EDX analyser. Thermal analyses were performed on a Setaram TGA/DTA (SetSys1750) system.

The dielectric constant ε_r of the ER mixture was measured through the assumption that the impedance of the suspension can be expressed as a parallel resistance–capacitance (RC) circuit connected to a sinusoidal voltage.[8] The dielectric constant of the particle ε_p was estimated from that of the suspension by a volume average calculation[9] given by equation $\varepsilon_r = \varepsilon_p\phi + (1-\phi)\varepsilon_L$ where ϕ and ε_L are the volume fraction of the powder in the suspension and the dielectric constant of the fluid (silicone oil).

The suspension with higher ER response was tested in an especially designed ER automotive damper[10] instead of classic hydraulic oil (Fig. 1).

3. Results and discussion

3.1. Characterisation of samples

Microscopic observations of modified silica powders coupled with EDX analysis on particles indicated that modifying cations were present in the silica network (Fig. 2). The X-ray diffraction patterns presented on Fig. 3 showed that pure silica was roughly crystallised. However, the addition of cobalt or zirconium ions

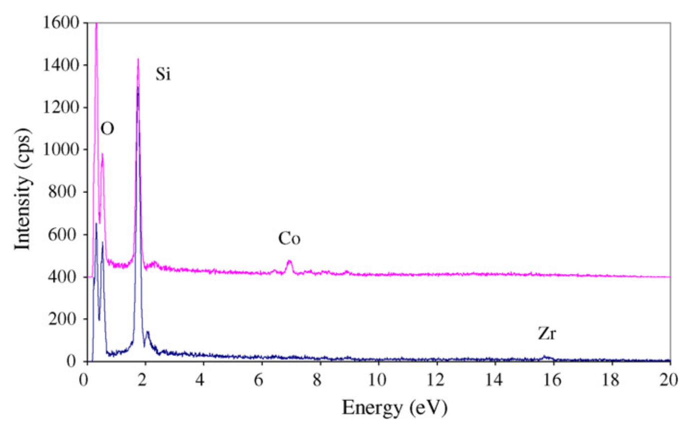

Fig. 2. EDX analyses of modified silica powders.

in the structure prevents crystallisation and the resulting powder was completely amorphous. Hydroxide groups on the silica powders were identified by FT-IR, two types of adsorbed water exist at the silica surface and pores; free water and bound water. Thermal analyses showed that free water responsible of higher ER effect[6] was removed at nearly 130 °C while bonded water was removed at much higher temperature (360–480 °C). Some of the physical properties of silica powders used as electrorheological materials are listed in Table 1.

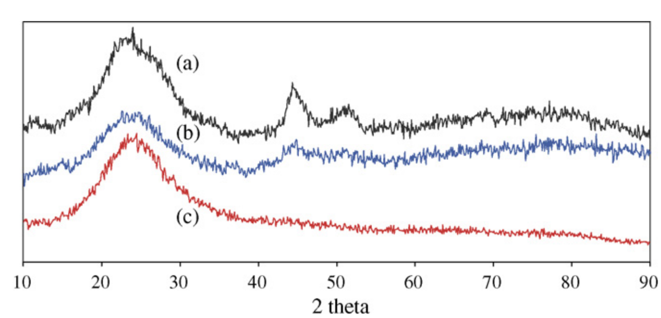

Fig. 3. X-ray diffraction pattern of (a) pure silica, (b) Co-silica and (c) Zr-silica powders.

Table 1
Some physical properties of silica powders

Powder	Grain size (μm)	Specific area (m^2/g)	Micropore area (m^2/g)	Density (g/cm^3)	Water content (%wt)
SiO_2	1.2	426	245	1.587	10.2
SiO_2 (Co)	1.15	573	173	1.712	10.6
SiO_2 (Zr)	1.35	544	258	1.784	11.7

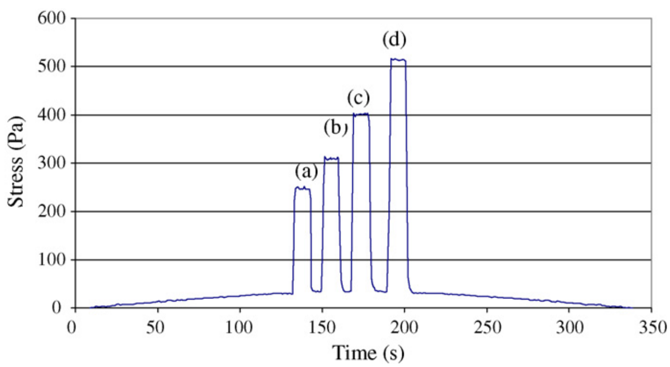

Fig. 4. ER response of SiO_2–Zr in Vaseline oil at (a) 1 kV/mm, (b) 2 kV/mm, (c) 3 kV/mm and (d) 4 kV/mm. Flow curve was a ramp up of the shear rate from 0 to 25 s^{-1} in 120 s, stay 90 s at 25 s^{-1} then ramp down to 0 s^{-1} in 120 s. Shear rate was 25 s^{-1} during ER measurements.

3.2. ER effect

Electrorheological measurements of all silica suspensions showed a positive behaviour in terms of shear stress (τ), the suspensions presented a Newtonian behaviour before applying electric field as shows Fig. 4 for zirconium modified silica. Among the tested powders, silica modified with zirconium showed the highest ER response behaviour compared to pure silica or Co doped silica. All results concerning ER characterisation are summarised on Table 2. According to physical properties listed on Table 1, specific area and grain size could not be the major reason for this behaviour since all powders have comparable characteristics. The difference in specific surface areas may be due to the particle surface morphology. We have then measured the dielectric constant ε_r for the different suspensions since this parameter was reported to be very important in terms of polarisation of particles under an external electric field effect.[11,12]

The zirconium doped silica showed a higher dielectric constant value (16.64) compared to the other powders which have very close values (3.32 for SiO_2 and 4.45 for SiO_2–Co). This explains the higher ER response of the fluid prepared with this powder. The increase of dielectric constant may be due to the zirconium cation structure which has high electric charge compared to Co^{2+} but not more investigation were done on the reasons of this change. Similar effects of dielectric constant increase were observed with modified TiO_2, SiO_2 and ZrO_2 powders.[13–15]

A Zr-silica based fluid with Vaseline oil was tested in order to study the effect of dispersing media. The ER response was higher than silicone oil fluid although the dielectric constants of the two oils were very close. FT-IR of the Vaseline oil revealed a linear saturated hydrocarbon chains structure. This compact structure compared to that of silicone oil $-(O-Si(CH_3)_2)_n-$ may facilitate the particle chain formation during electric field application.

ER measurements with suspension of pure silica dehydrated 24 h at 200 °C in silicone oil confirmed the hypothesis that free water plays an essential role in the charge formation on the particle surface[16] since almost no ER response was observed.

Table 2
ER response of silica based fluid in terms of τ_x/τ_0 (x is the electric field value) at a shear rate of 25 s^{-1}, S for silicone oil and V for Vaseline oil

	τ_0 (Pa)	τ_1/τ_0	τ_2/τ_0	τ_3/τ_0	τ_4/τ_0
SiO_2 + S	32.3	2.7	3.2	4.1	4.7
SiO_2–Co + S	31.7	3.2	3.9	4.7	5.1
SiO_2–Zr + S	33.5	5.5	6.1	7.2	8.5
SiO_2–Zr + V	30.0	8.2	10.4	13.4	17.1

3.3. ER fluid application

The damper was characterised by measuring the force function of the applied velocity. Zr-silica–Vaseline oil fluid was used since it gave best ER performance. On Fig. 5, the upper part of the curve, corresponding to positive speeds, is related to the expansion while the lower part, corresponding to negative speeds, is related to the compression. Using this plot, the damping coefficient C was obtained from the slope of the best linear curve fitting the experimental points, with $E = 0$, 1, 2 and 3 kV/mm. The electric field was limited to 3 kV/mm in order to prevent perturbation of electronics in the measuring devices (sensors, computer, ...) close to the damper. When the generator is turned on, the effect of the applied high voltage is readily observed as represented on Fig. 6. It can be observed that the rebound damping coefficient is related to the applied voltage by a relationship of the form: $C = 278E + 3110$. For an electric field of

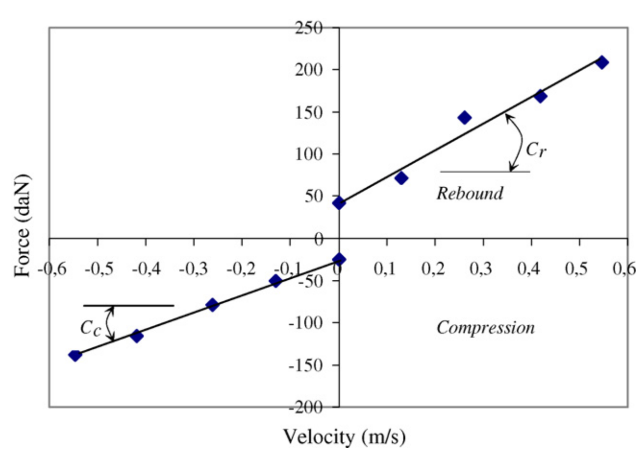

Fig. 5. Experimentally measured force vs. velocity, without high voltage.

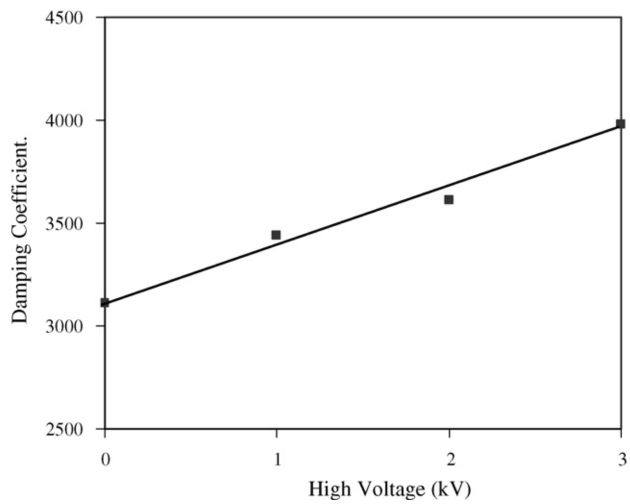

Fig. 6. Measured Rebound damping coefficient vs. applied electric field.

3 kV/mm, the damping coefficient presents an improvement rate of 28%.

4. Conclusion

Silica obtained by sol–gel method was successfully modified with metallic cation in order to improve its ER response.

Silica with zirconium cation trapped into its network showed the best ER behaviour due to the increase of its dielectric constant. This may be due to the Zr^{4+} cation structure in the silica network.

Vaseline oil had a better ER behaviour compared to silicon oil probably due to its linear hydrocarbon structure which may make easier the formation of a chainlike or structure oriented along the electric field direction.

The ER suspension with the best ER behaviour has been tested in an ER automotive damper and ensured a 28% increase of the damper performance.

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