

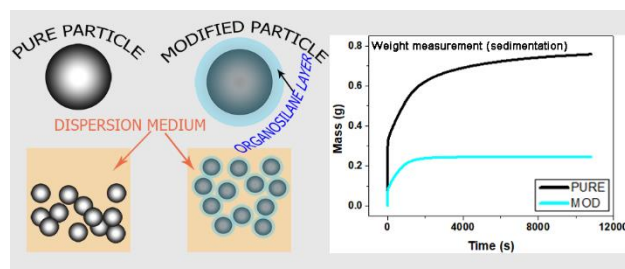
Magnetorheological fluids based on core-shell carbonyl iron particles modified by various organosilanes: Synthesis, stability and performance

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Although smart materials, specifically the magnetorheological (MR) fluids, have shown remarkable practical importance, their drawbacks such as an aggregation of magnetic filler, its insufficient compatibility with the carrier liquid, low resistance to corrosion and poor sedimentation stability still cause severe limitations for their broader utilization. To address this challenge, our study presents the



facile concept for the coating of magnetic particles, leading to their enhanced utility properties, and sufficient MR performance. It concentrates on the coating of magnetic carbonyl iron (CI) particles with a thin modifying layer as a surface shell utilizing four organosilanes; tetraethoxysilane, (3-aminopropyl)triethoxysilane, bis[3(trimethoxysilyl)propyl]amine and vinyltrimethoxysilane. Characterization of the modified particles and their suspensions was examined using various methods. The XPS analysis confirmed successful particles modification, while the surface free energy was evaluated by tensiometric measurements reflecting in better compatibility of particles with dispersing medium. The lowest surface free energy possessed particles modified with (3-aminopropyl)triethoxysilane. The magnetization of modified core-shell particles was not negatively affected by the organosilanes layer presented on the particles resulting in comparable MR performance of systems based on pure CI particles and their modified analogues as was proved by the fitting of the corresponding flow curves by the Robertson-Stiff model. Moreover, the modification of the particles improved their thermo-oxidation stability and chemical stability investigated via thermogravimetric analysis and acidic tests, respectively. Finally, sedimentation stability of modified particles-based systems expressed as a weight gain measured using tensiometer device was enhanced in comparison with pure CI particles-based system, which can be very positive in the intended applications.

Introduction

Magnetorheological (MR) fluids belong to a special group called smart materials. Smart materials can change their physicochemical properties under an external stimulus, i.e. magnetic or electric field, pH, and temperature, etc.¹⁻³ The MR fluids have been investigated since the 1940s and during the past two decades, they have found a large number of applications.¹⁻³ They are able to reversibly transform within milliseconds from a liquid-like state to a semi/solid-like state under the actions of the magnetic field. They are basically two-phase systems consisting of micrometer-sized magnetic filler and a non-magnetic dispersion medium.⁴ If dimensions of magnetic particles

are in nanometer scale, the system is called ferrofluid.⁵ The most commonly used filler of the MR fluids is the carbonyl iron (CI) due to its superior magnetic properties, however, other magnetic metals such as cobalt ferrites could be also used.⁶ The dispersion medium is usually selected from mineral and silicone oils, or polyesters. Additionally, in a non-active state, i.e. without the presence of a magnetic field, the MR suspensions behave as non-Newtonian fluid because of randomly oriented magnetic particles within the dispersing medium. On the other hand, the imposed magnetic field arranges magnetic dipoles of particles into chain-like structures oriented along the magnetic field streamlines.^{7,8} As a result, a complex structure is developed, the viscosity of the MR fluid appreciably grows (several orders of magnitude) and this system can resist a certain loading. Moreover, with a higher magnetic field, the viscosity increases following the Jolly's dipole-interaction model.⁹

The MR fluids are applied in many sectors. For instance, they are used as car dampers,^{10,11} earthquake dampers,¹² seals,¹³ automotive clutches,¹⁴ shock-absorbers,¹⁵ brakes,¹⁶ optical filters,¹⁷ bio-signal monitoring¹⁸ and also for temporary embolization of blood vessels.¹⁹

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Even though the MR fluids have a broad utilization spectrum, they still have several drawbacks as an aggregation of magnetic particles caused by van der Waals attraction forces due to their high surface area,²⁰ insufficient compatibility between the magnetic filler and carrier liquid, the lack of corrosion and sedimentation resistance.⁶ Therefore, it is necessary to avoid critical problems in all sectors of utilization caused by these liabilities and to find the best technique for the improvement.

Because of these drawbacks, certain enhancement methods have been applied. The first option is the utilization of various types of additives or applying special surfactants.²¹ The main advantage of this method is that magnetization is not diminished. On the other hand, the particles may not have primary protection, which can limit their corrosion resistance. The second method is the various uncontrollable coating of magnetic particles,^{22,23} for example creating a silica layer.²⁴ These coatings of magnetic particles might cause a perceptible decrease of magnetization of the particles and also irregularities in the polymeric shell, which slightly overlooks the conservation of basic MR fluids properties for the long-term utilization. The third method is the controllable coating of magnetic particles via living radical polymerizations.^{25,26} Although the controllable coating does not highly affect the magnetization, which is very positive, the synthesis route requires special chemicals, might be time-consuming and difficult to scale-up.

Indeed, magnetic particles should be protected by the layer which withstands the corrosion agents and improves compatibility between the carrier liquid and the particles, thereby decreasing the sedimentation rate. Further, the layer should not negatively affect the magnetization of the particles and should preserve the typical rheological traits of the MR fluids. The modification of magnetic particles should not be very laborious, preferably with a scale-up potential, because of its possible application in various utilization directions. As is done in this paper, these goals can be achieved by facile uncontrollable, yet compact, coating by various organosilanes, called also silane surface treatment.

Organosilanes are widely applied as coupling agents for various surfaces as glass or metal oxides to polymers.²⁷ It has been studied, that surface coating by some organosilanes may protect metals against corrosion agents.²⁸ There are two groups of silanes, "mono-silanes" and "bis-silanes". Mono-silane has only 3 hydrolyzable –OR groups attached to the silicon (Si), on the other hand, bis-silane has 6 hydrolyzable –OR groups because of two Si atoms at the end of the molecule. In this work, three mono-silanes (Tetraethoxysilane, (3-aminopropyl)triethoxysilane, vinyltrimethoxy silane) and one bis-silane (bis[3(trimethoxysilyl)propyl]amine) have been used. It has been discovered that the corrosion protection of "bis" silanes is higher in comparison with "mono" silanes.²⁸

This study was designed to improve the interaction between magnetic particles and the disperse medium represented by silicone oil via particles modification with various types of organosilanes. Moreover, it was planned to preserve the magnetization of particles and improve their long-term, thermooxidation, and chemical stabilities. Furthermore, the comparison of MR performance of systems based on pure CI particles and their organosilanes-modified

analogues quantified by the relevant parameters of the Robertson-Stiff rheological model was also investigated in this study.

Experimental section

Organisation

Carbonyl iron particles were coated with four types of organosilanes. Then, the surface free energy of modified particles was examined by tensiometric analysis. Subsequently, successful particles modification by various types of organosilanes was proved by XPS analysis. Afterwards, the magnetization, thermo-oxidation, chemical and sedimentation stability of particles were evaluated. Finally, the MR fluids consisted of particles under the investigation were prepared and their MR performance and long-term stability were described.

Materials

Carbonyl iron particles (ES grade, 6 μm in diameter, spherical particles with iron purity of $\text{Fe} > 99.5\%$) supplied by BASF (Germany) were used as a magnetic filler in the MR fluids under the investigation. As a surface activator, hydrochloride acid (HCl, 35%, p.a.) was used. For the modification of the CI particles, (3-aminopropyl)triethoxysilane (APTES, $\geq 99\%$), tetraethoxysilane (TEOS, $\geq 98\%$), bis[3(trimethoxysilyl)propyl]amine (BIS, $\geq 90\%$) and vinyltrimethoxysilane (VIN, $\geq 97\%$) were used individually as a surface overlayer. Acetone, ethanol, toluene, and HCl all in p. a. quality were purchased from Penta Labs (Czech Republic). Silicone oil (Lukosiol M200) obtained from Chemical works Kolín (Czech Republic), with dynamic viscosity of $\eta = 194 \text{ mPa}\cdot\text{s}$ and a density of $0.97 \text{ g}\cdot\text{cm}^{-3}$ at 25°C was used as a dispersion medium, and the concentration of prepared MR fluids was set to 60 wt.%.

Particle surface activation

Prior to the coating, the CI surface was activated. To attach –OH groups, the CI particles (100 g) were stirred for 10 min in 0.5M HCl (250 mL). Secondly, they were collected using magnet-accelerated decantation method and purified by distilled water, ethanol, and acetone. Lastly, the particles with a residue of acetone were dried overnight at 60°C and a reduced pressure of 50 mBar.

Coating of particles

Dried activated CI particles (90 g), toluene (300 mL), and the individual volume of silane (the equimolar silane concentration was ensured, Tab. 1) were used to modify the particle surface. The process was as follows; dried activated CI particles were put into a three-necked flask, dispersed in toluene, which was used as a reaction medium, and mechanically stirred at 250 rpm. The content of the flask was heated to the temperature of 110°C and the relevant amount of the organosilane was carefully injected into the flask. The reaction was carried out at 110°C with a constant stirring for 6 hrs. Finally, the modified particles were separated, purified and dried in the same way as after the surface activation. Labeling of the samples is shown in Tab.1.

Table 1 Relevant characteristics of investigated particles.

Modification of the carbonyl iron particles	Sample ID	Amount of silane in reaction	Oxidation temperature*
without modification	PURE	0	409 °C
with TEOS	MOD1	10.0 mL	482 °C
with APTES	MOD2	10.5 mL	494 °C
with BIS	MOD3	14.7 mL	486 °C
with VIN	MOD4	6.9 mL	457 °C

*Oxidation temperature is based on the TGA points of inflexion.

Characterization of the particles

Surface free energy of pure CI and modified particles was evaluated with a tensiometer Krüss K100 (KRÜSS, Germany) by sorption measurement, which determines the surface energy of solids in a powder form (Washburn method). First, the capillary constant of the powdered samples was measured using n-hexane (Sigma Aldrich, p.a.) followed by the contact angle evaluation using water and diiodomethane (Sigma Aldrich, USA) as testing liquids. Then, the surface energy of the investigated particles was calculated using Krüss K100 software (LabDesk 3.2.2) according to the implemented Owen-Wendt-Rabel-Kaelble theory.⁶

To detailed particles surface specification the XPS analysis was done. The XPS measurements were performed using a TFA XPS device from Physical Electronics. The base pressure in the XPS analysis chamber was approximately $6 \cdot 10^{-8}$ Pa. The samples were excited by X-rays over a $400 \mu\text{m}^2$ spot area with monochromatic Al $K\alpha_{1,2}$ radiation at 1486.6 eV. Photoelectrons were detected with a hemispherical analyzer positioned at an angle of 45° with respect to the normal to the sample surface. The energy resolution was approximately 0.5 eV. Survey-scan spectra were acquired at pass energy of 187.85 eV, whereas for Fe 2p, O 1s, Si 2p, N 1s and C 1s. All the spectra were referenced to the main C 1s peak of the carbon atoms, which was assigned a value of 284.8 eV. The spectra were analyzed using MultiPak v8.1c software (Ulvac-Phi Inc., Kanagawa, Japan, 2006) from Physical Electronics, which was supplied with the spectrometer.

The magnetic properties of all samples under the investigation were measured by the vibrating-sample magnetometer (VSM 7407, Lakeshore, USA) in a magnetic field up to $1200 \text{ kA} \cdot \text{m}^{-1}$ at room temperature.

In order to estimate the resistance to thermal oxidation, the thermogravimetric analysis (TGA; TA Instruments Q500, USA) was done. Measurements were carried out under the air purge of $50 \text{ mL} \cdot \text{min}^{-1}$ at a controlled heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$.

To determine the chemical stability the acidic test was carried out. The pH meter Senso direct 150 (Lovibond, Germany) was used to record pH evolution in time. Prior to each measurement, the pH meter probe was calibrated with two standard buffer solutions. The difference between pure and modified particles was specified by simulated aging by HCl. Aging in the real conditions was stimulated by the effect of 0.05M HCl. Firstly, the pH of 0.05M HCl was measured independently. Briefly, 10 g of the CI particles were poured over with

100 mL HCl in a flask under mechanical stirring (100 rpm) and the pH of flask content was determined.

Characterization of the suspensions

Firstly, the sedimentation measurement was performed. This test was done using the tensiometer with a specially designed conical shape probe (Krüss SH0640) for trapping the sediment particles. To ensure the repeatability, the MR fluids were prepared and dosed identically. The suspensions, all of the same volume, were firstly manually mixed and then dispersed using a sonoprobe (UP400S, Hielscher, Germany) applying 1 min. After the sonification, the special conical shape probe was attached into the balance of the tensiometer (zeroed out) and the samples were placed underneath the probe. The probe was moving with a speed of $7 \text{ mm} \cdot \text{min}^{-1}$ until the contact with the MR fluid was achieved. Subsequently, the conical-shaped probe was immersed 10 mm under the surface of the MR fluid with a controlled speed of $50 \text{ mm} \cdot \text{min}^{-1}$. The probe recorded the weight gain of settling particles for 2 hours.

The rheological characteristics of the MR fluids were examined by the rotational rheometer Physica MCR 502 (Anton Paar, Austria) equipped with the MRD 170/1 magneto-cell and PP20/MRD/TI geometry at a constant temperature of 25°C (Julabo FS18, Germany). The cell generated a coil current up to 1.5 A; thereby it ensured a stable uniform magnetic field in the sample.²⁹ A parallel-plate measuring system (20 mm in diameter) and the gap of 0.5 mm were used. For each rheological measurement, 60 wt.% suspension was prepared. The samples were studied both, in the off-stated (random particles distribution) and the on-state (chain-like structures presented within the system). In the typical measurement, 0.25 mL of a well-dispersed system (mixed similarly as in the sedimentation test) was placed into a cleaned lower-plate center. The MR experiment was measured under the steady shear mode in the interval of $10^{-2} - 2.5 \cdot 10^2 \text{ s}^{-1}$.

Briefly, the suspension was pre-sheared for 1 min at the shear rate of 50 s^{-1} to impose the same initial conditions before each measurement. Second, the rheological behavior of the suspension was measured in the off-state. Third, the application of the appropriate value of the magnetic field for each measurement for 1 min was used in order to eliminate the slip wall. It arises due to the creation of the columnar structure of particles in the MR fluid, which increases the contact between the walls of the geometry and the suspension.⁶ Rheological measurement itself and subsequent data summarization followed.

Results and discussion

Surface free energy

To characterize the surface properties of the CI particles and interactions between them and silicone oil, the surface free energy of each type of particles was determined. It is generally known that polymers have lower surface energy than metals.⁶ Therefore, to confirm a successful coating of the particles and verify the reduction of the surface energy of the coated particles, the tensiometric measurement was performed. Figure 1 shows the data from surface free energy evaluation. As seen in the figure, pure particles have the highest surface free energy ($65.44 \text{ mN} \cdot \text{m}^{-1}$). According to our

expectations, surface free energy was significantly lower for the modified samples. As has been proved, the modification with MOD2 had almost exactly twice lower surface free energy than that of the pure particles. Due to their high surface energy, the CI particles are certainly formed into aggregates and succumb the sedimentation. Moreover, the decreased surface free energy after the modifications can be attributed to the organosilane layer on the surface of the CI particles.

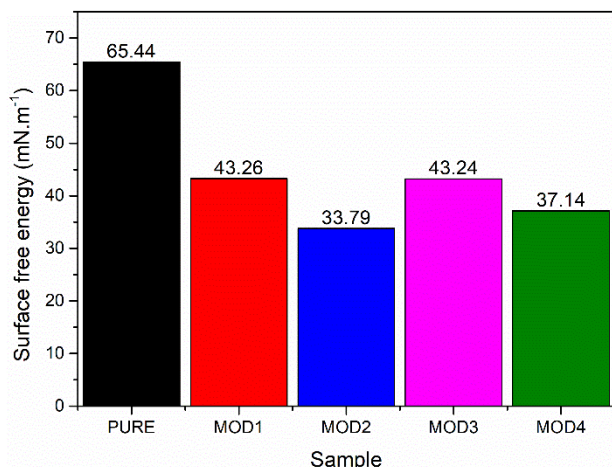


Figure 1 Surface energy for modified and non-modified samples.

Finally, the results of tensiometric measurements validate the successful particle modification and prove a decrease of the surface free energy of the magnetic particles. There is a strong possibility that the compatibility between modified particles and silicone oil will result in better utility properties of prepared MR fluids, due to a closer surface free energy between them. There is high possibility, that reason of higher surface free energy of MOD1 and MOD3 compared with MOD2 and MOD4 is the presence of functional (hydrophobic) groups.

XPS characterization

All samples that were modified contain a substantial amount of silicon which is an indicator of successful "silanization" of all samples. The values given in Tab.2 are the averages of three spot measurements. On some samples (MOD2 and MOD3) also nitrogen was found which is in agreement with the composition of the deposited molecules APTES and BIS. The deposited coating is the thickest in the case of the sample MOD2 (APTES) because this sample has the lowest intensity of Fe peak (Fig. S1) and thus a very small concentration of Fe which is shielded with the deposited layer of APTES.

Table 2 Surface composition (average of three measurements) of the samples as determined from XPS survey spectra which are shown in Fig. S1 (in atomic %).

	C	O	Fe	Si	N
PURE	45.4	42.2	12.4	–	–
MOD1	26.3	54.5	7.4	11.8	–
MOD2	54.4	26.7	1.6	9.5	7.8
MOD3	38.1	41.7	5.0	9.4	5.7
MOD4	30.6	49.2	7.3	13.0	–

Magnetic properties

Generally, any non-magnetic layer on the surface of the CI particles reduces their magnetization. Therefore, it is necessary to encapsulate magnetic particles with a layer having a negligible effect on their magnetization. Figure 2 depicts the hysteresis curves of the pure CI-particles and their organosilanes-modified analogues. As can be seen, the magnetization curves are very similar in their initial magnetization (Fig. 2b) and only a small difference can be detected close to the saturation magnetization. In fact, the curve of pure CI particles lies in the middle of modified samples as revealed in Fig. 2.

In Fig. 2 can be also seen, that MOD1 has the lowest magnetization, which is by 4 emu.g⁻¹ lower than that of the PURE sample. It would seem a negligible difference compared with the research of Zhang and Dong,²³ where the magnetization decrease of the modified sample was exactly by 36 emu.g⁻¹ compared to the pure magnetic particles, or in research by Chuah et al.²² where the value for pure particles was 184 emu.g⁻¹ at 63 kA.m⁻¹ and it collapsed to only 112 emu.g⁻¹ for wrapped CI particles with a polystyrene foam layer samples. It can be concluded that in our research the coating of CI particles with an organosilane layer did not significantly affect their magnetic properties and the modification was optimally performed.

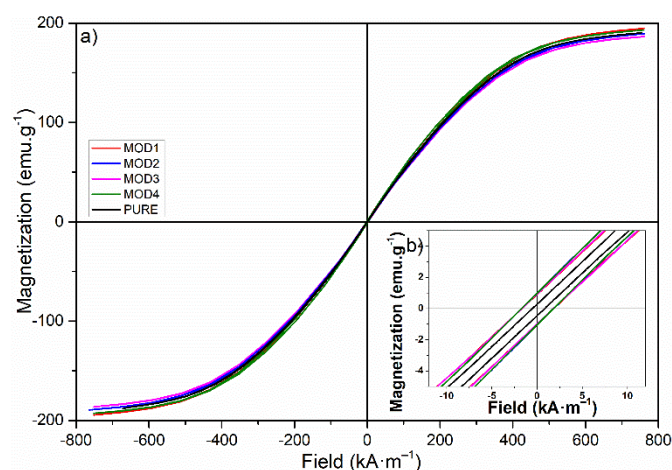


Figure 2 Dependence of magnetization curves on the magnetic field for measured samples; b) Detail of the dependence of magnetization curves between $-12 - 12$ kA.m⁻¹.

Thermogravimetric analysis

The improved thermo-oxidation stability by the organosilane layer on the surface of CI particles is usually investigated by TGA; the results are given in Fig. 3. Evidently, the weight of pure particles grows slowly to 350 °C and then dramatically shoots up as a result of the iron oxides formation on the particles surface.³⁰ The lower weight gain is observed for all the organosilane-modified particles confirming the protecting ability of the surface layer against the thermo-oxidation of the iron core. In addition, MOD1, MOD2 and MOD3 proved similar weight gain trend within the temperature range used, which could be caused e.g. for MOD3 by its theoretical attachment to the CI particles theoretically via 6 bonds (bis[3(trimethoxysilyl)propyl]amine) or by the thicker layer of MOD2 onto the CI particles as could be expected from the XPS results as this modification possesses the lowest amount of Fe in the surface layer.

Furthermore, the thermo-oxidation stability of the samples was compared based on the TGA points of inflexion (Tab. 1), which unambiguously confirmed the above-mentioned positive effect of organosilane layer onto the CI particle. These improvements will be beneficial in real applications.

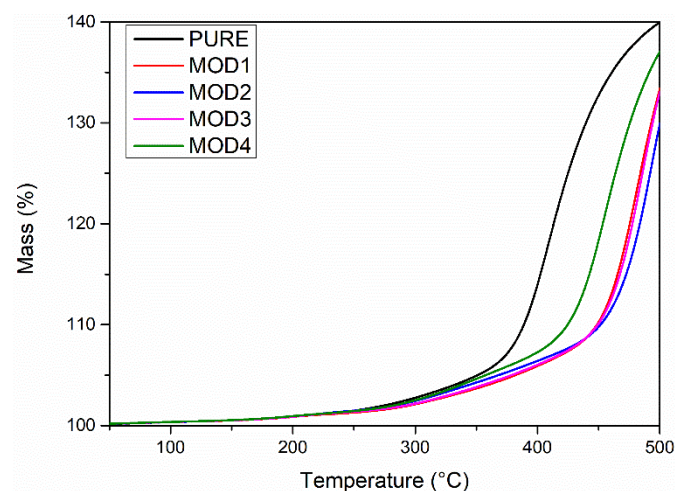


Figure 3 Dependence of the weight of the samples on temperature loading.

Chemical stability

Anti-acid corrosion stability of the particles is an important factor for their successful utilization in the MR fluids. Corrosion of the particles used in smart systems leads to lower magnetic performance.^{30,31} The acid corrosion resistance can be expressed by pH values evolution in time. As revealed in Fig. 4, the CI particles react with the acid, therefore pH values start growing from acidic to neutral region. It can be seen that particles with the MOD2 resist the 0.05M HCl better than other samples within the interval 0–25 min due to the thickest layer of this coating as proved via XPS analysis (Table 2). On the other hand, the MOD1 layer resists under the same conditions better than other samples in longer time period (30–60 min) as reflected in lower reached pH value in Fig. 4 probably due to the most inert structure of this organosilane. The results of the improvement of the CI particles chemical stability can be thus attributed to the organosilane layer on the particle surface.

Next, the correlation between the molecular structure of the organosilanes and the chemical stability of the modified particles was evaluated. Bis-silanes generally exhibit a superior corrosion protection, when compared to mono-silanes.²⁸ Therefore, the best anti-acid resistance was expected for the MOD3. Nevertheless, as said, the best chemical stability was attained for the MOD2, which is the most probably a consequence of its higher shell thickness as evidenced by XPS data. We tend to believe that the overall behavior of silane-modified particles is a combination of the following factors: synthesis efficiency/layer thickness, shell density, the surface free energy, shell porosity, besides the molecular structure and other factors.

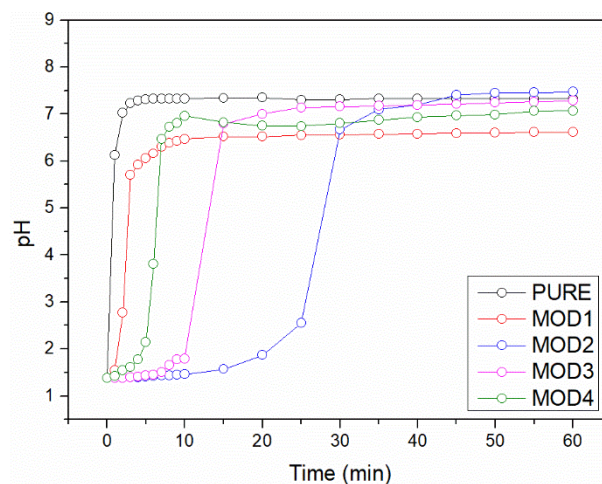


Figure 4 Acidic test for CI particles under investigation.

Sedimentation test

For all types of MR fluids, the sedimentation stability was analyzed. Figure 5 provides the weight gain relevant to settling particles as a function of time. As can be seen, MOD4 proves the best sedimentation stability, however, MOD1 and MOD3 prove enhancement sedimentation stability compared to PURE particles too. It could be claimed that the organosilane layer onto the particle surface leads to better wetting with non-polar silicone oil, and remarkable non-aggregating nature. These phenomena result in an enhanced compatibility between components in the created MR fluids.

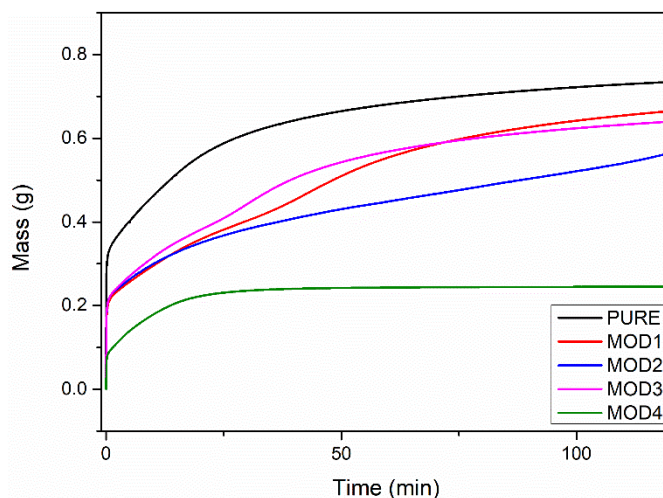


Figure 5 Sedimentation of prepared MR fluids expressed as a weight gain in time.

Rheological measurements

Magnetorheological behavior of the MR fluids is the most important feature affecting their practical applicability.⁷ Considering the negligible effect of the silanization process on the magnetization of the particles (Fig. 2), it can be suggested that the resulting MR fluids should exhibit almost identical MR performances. However, changing the surface chemistry of the particles may influence, besides the other characteristics, the compatibility with silicone oil and consequently the MR flow. Figure 6 shows the flow properties, which are represented as the dependence of shear stress on the

shear rate for the prepared MR fluids under various magnetic field strengths.

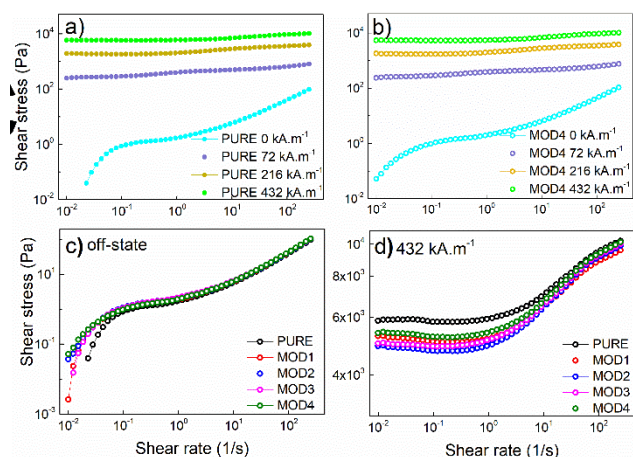


Figure 6 Dependences of the shear stress on shear rate; a) the MR fluid containing pure CI particles; b) the MR fluids containing MOD4 particles; both at different magnetic field strengths; c) the off-state behavior for all the investigated MR fluids; d) the on-state behavior for all the investigated MR fluids collected under $432 \text{ kA}\cdot\text{m}^{-1}$.

For brevity, we present the entire dataset for the reference materials (PURE, Fig. 6a) and one analogue suspension containing the modified particles (MOD4, Fig. 6b). As can be seen from Fig. 6 (a–c), at a low shear rate the MR fluids generally exhibited almost Newtonian/slightly pseudoplastic behavior in the absence of a magnetic field. In contrast, in the presence of a magnetic field at low shear rate the MR fluids behaved as a solid material and beyond a critical shear loading, they behaved as highly-viscous liquids. This behavior is typical for the Bingham fluids showing that the magnetic particles are ordered into chain-like internal structures that are able to resist certain deformation strain without liquid-like behavior.^{32,33} As expected, the rheological data, depicted in Fig. 6, shows that all samples exhibited apparently similar rheological traits.

To identify the differences, the rheological data was fitted using the appropriate rheological model. The Robertson-Stiff (RS) model is currently considered as the most suitable three-parameter viscoplastic equation to predict the flow behavior of the MR fluids.³⁴

$$\tau = \left[K \frac{1}{n} |\dot{\gamma}|^{\frac{n-1}{n}} + \left(\frac{\tau_0}{|\dot{\gamma}|} \right)^{\frac{1}{n}} \right]^n \dot{\gamma} \quad (1)$$

The RS equation contains the yield stress, τ_0 , consistency index, K , and the non-Newtonian index, n , as the fitting parameters. The numerical values of the parameters are presented in Tab. S1 for the best model predictions. Overall, the predictions of the RS model correlated well with the data ($R^2 > 0.988$ in all the cases). The extracted τ_0 was further plotted as a function of the applied magnetic field (Fig. 7). As seen, the MR fluids containing pure CI particles exhibited the highest values of τ_0 . The presence of organosilanes resulted to slightly lower τ_0 due to weaker local saturation zones for the modified particles, and hence a lower permeability of the MR fluid.³⁵ It worth mentioning that the dependence of τ_0 on magnetic field strength is usually plotted in log-log scaling,³⁶ but we decided to use linear scaling to better illustrate almost negligible difference

between MR fluid containing pure CI particles and those based on polysiloxane-modified CI particles. It is important to mention that the most significant decrease was recorded for the MOD2-based MR fluid. This result correlates well with the XPS data (Tab. 2), which proved the thickest organosilane layer for these particles.

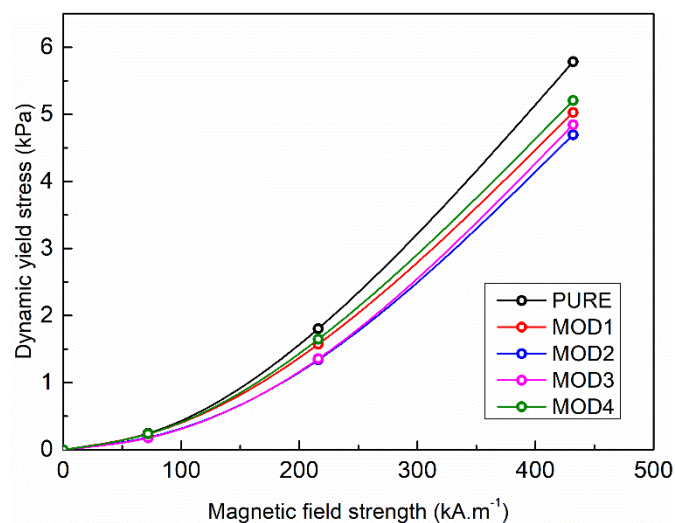


Figure 7 The dynamic yield stress as a function of the applied magnetic field strength for all the investigated MR suspensions. The solid lines represent the spline function as a guide for the eye.

Thus, it can be claimed that the coating thicknesses are reflected in τ_0 decrease. In parallel, these observations were evidenced by analogous decrease in K parameter, which represents the toughness of the particle chain structures.³⁴ Finally, the behavior of the n index was addressed; this parameter was slightly below one ($n < 1$) in the absence of magnetic field suggesting close-to-Newtonian behavior. Once the magnetic field was applied, the n parameter dropped to 0.116–0.154 indicating severe pseudoplasticity. The MR fluid containing pure CI particles exhibited the highest non-linearity response proving its dominating MR performance. To conclude, the reduction in the MR parameters was identified due to the organosilane coating of the particles. This reduction correlated well with the coating thickness and was relatively small in the low-to-moderate magnetic fields, which predetermines reasonable applicability of as-treated MR fluids.

Dynamic characteristics of microstructures formed within the MR fluids were investigated by oscillatory tests. Figure 8 shows the dependence of the storage modulus, G' , symbolizing elastic behavior of the system, and the loss modulus, G'' , representing the viscous behavior component, on the frequency for the prepared MR fluids. As shown by the graphs, the fluidity of the MR fluids in the absence of a magnetic field is confirmed by slightly larger G'' than G' in the frequency range 1.5–60 Hz. After the application of an external magnetic field, G' and G'' increase by three and two orders of magnitude, respectively. Furthermore, G' values are constant or slightly grow, and lie higher than G'' values, which is an indication of a developed stiff three-dimensional network that can resist certain loading.

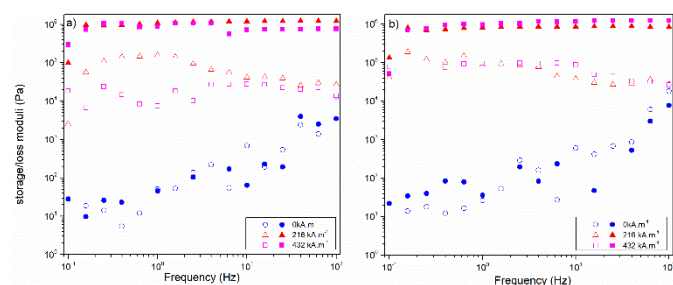


Figure 8 Dependence of storage, G' (solid symbols) and loss, G'' (open symbols) moduli on frequency, f , for a) PURE and b) MOD4 particles-based MR fluids (60 wt.%) under various magnetic field strengths.

Conclusions

In our research, four various types of organosilanes were used to form a compact coating shell applied onto the CI particles. The successful core-shell formation was confirmed using the tensiometric technique and XPS analysis. Modified particles have better wetting with a non-polar silicone oil used as a carrier liquid for MR fluids in this study due to the decreased surface free energy of particles. The magnetization curves were almost the same irrespectively the particles modification. On the other hand, the organosilane coating markedly improves thermo-oxidation stability and chemical stability of magnetic particles and long-term stability of their MR systems, therefore there is a definite contribution in its utilization. Finally, MR fluids based on organosilane-modified particles exhibited similar MR performances as their pure analog as was proved also by comparison of relevant parameters from the Robertson-Stiff model.

The prepared MR fluids containing core-shell particles with organosilane surface layer and CI core can find applications in many sectors as dampers, seals or clutches, in which low sedimentation, high thermo-oxidation stability and anticorrosion properties are required.

Conflicts of interest

There are no conflicts to declare.

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