Cholesteryl-coated carbonyl iron particles with improved anti-corrosion stability and their viscoelastic behaviour under magnetic field

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ABSTRACT

In principle, bare particles used in magnetorheological suspensions exhibit apparent corrosion instability. To suppress substantially this adverse phenomenon, the carbonyl iron particles modified with cholesteryl group (CI-chol) were suspended in silicone oil. There was found a deterioration of magnetorheological efficiency in comparison when only bare carbonyl iron (CI) particles are used; nevertheless, from the viewpoint of applicability this change is fully acceptable. However, an anti-corrosion stability was significantly improved. Furthermore, dynamic oscillatory measurements and other characterizations were carried out and analyzed when both CI and CI-chol particles are applied.

Keywords: Carbonyl iron, cholesteryl chloroformate, silicone oil suspensions, viscoelasticity, magnetorheology.

1 Introduction

Magnetorheological (MR) suspensions generally represent a two-phase system consisting of liquid phase, in most cases silicone or mineral oil and solid phase, particles able to be magnetized under external magnetic field [1-4]. Solid phase is commonly represented by ferro- or ferri-magnetic particles as reviewed in several studies [5-10]. Ferro-magnetic (carbonyl iron) particles exhibit higher magnetization saturation in comparison with ferri-magnetic (ferric oxides) ones [11-13]. That is why the carbonyl iron (CI) particles are frequently used as a solid phase in the MR suspensions [14-17]. On the other hand, this is connected with several disadvantages appearing when the CI particles are dispersed in the liquid medium and exposed to the real-life application conditions. The most significant problems are represented in poor long-term sedimentation and thermo-oxidation stability. Various techniques such as preparation of bidispersed or dimorphic particle-based suspensions [18-21], application of coatings of the CI particles with various materials (polyaniline, polysiloxane, MWCNT etc.) [22-26] or inorganic-inorganic core-shell [27] are commonly used to prevent or suppress those drawbacks. Furthermore, poor stability of the bare CI particles under acidic conditions represents another well known disadvantage requiring a corresponding attention. Suspensions with enhanced stability properties are much closer to the real-life applications.

In the preceding paper [28], we showed that the modification of carbonyl iron particles surface with cholesteryl groups (CI-chol) improved both sedimentation and thermo-oxidation stability. Moreover, facile redispersibility of the suspensions was achieved. Investigation under steady shear conditions provides the promising results of MR efficiency for CI-chol particle-based suspensions. Nevertheless, in potential real-life applications, the properties of suspensions characterized by dynamic oscillatory tests play a dominant role. Therefore, the present study was carried out in two steps. Firstly, an attention is paid to the investigation of dynamic oscillatory behaviour of the modified carbonyl iron particles in silicone oil suspensions under both an absence and a presence of an external magnetic field. Secondly, the suspension behaviour at elevated temperatures and stability under acidic conditions are analyzed and quantified.

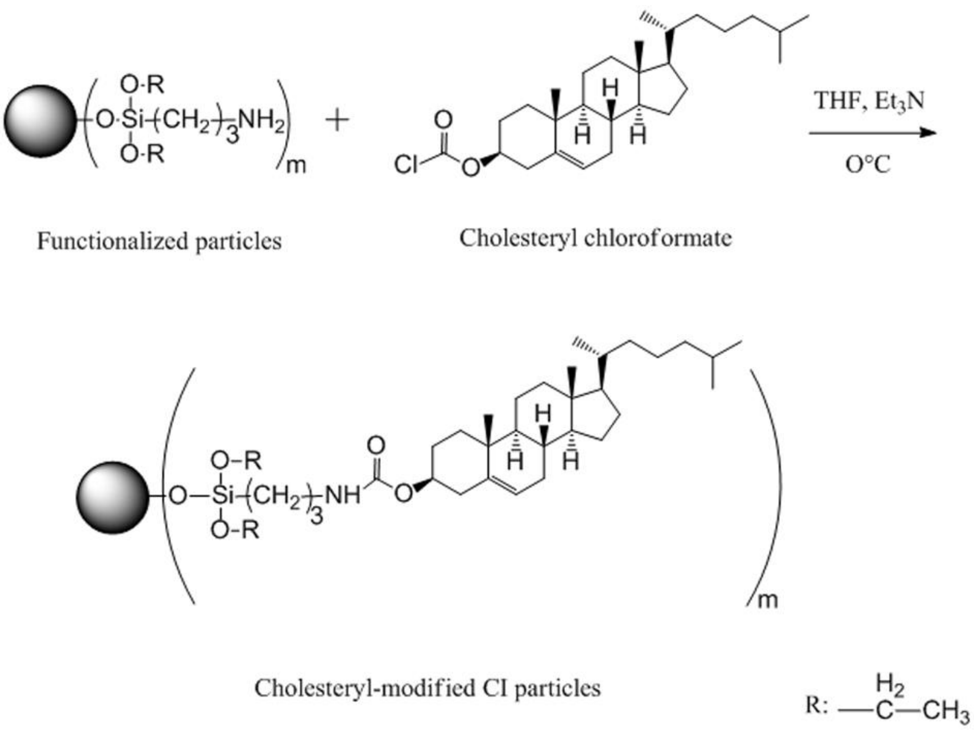
2 Experimental

2.1 Materials

Carbonyl iron microparticles (ES grade) consisting of > 97% of iron particles produced by BASF (Germany), solvent tetrahydrofurane (THF) by POCH (Poland), (3-aminopropyl) triethoxy silane, cholesteryl chloroformate (both Sigma Aldrich, USA), and triethylamine (Fluka, Switzerland) were used as received.

2.2 Preparation of cholesteryl-coated CI particles

The CI-chol particles were prepared as described in [28], where first the CI particles were treated under acidic conditions to obtain reactive groups on their surface. Then the particles were functionalized with 3-aminopropyltriethoxy silane and this was utilized as a coupling agent. Finally, amidation reaction (Scheme 1) was used to coat the surface of CI particles with cholesteryl groups.



Scheme 1: Modification of the functionalized particles with cholesteryl chloroformate by amidation reaction.

2.3 Characterization of the prepared particles

Synthesized particles were characterized using Fourier transform infrared spectroscopy (FTIR) (Nicolet Magna-550 Spectrometer, USA) in the region of 4000-600 cm^{-1} to verify uniform functionalization and coating of CI surface.

The magnetic properties of both coated and uncoated particles were determined using a vibration sample magnetometer (VSM) (EG&G PARC 704, Lake Shore, USA) at room temperature. Furthermore, the magnetic spectra were evaluated by means of the Langevin model [29]

$$M(H)=\left[\frac{1}{\tanh\left(\frac{m\cdot\mu_0\cdot H}{k\cdot T}\right)}-\frac{1}{\frac{m\cdot\mu_0\cdot H}{k\cdot T}}\right]\cdot M_S \qquad (1)$$

where m is the magnetic moment, μ_0 is the magnetic permeability of free space (4π x 10^{-7} H m^{-1}), H is the magnetic field, k is the Boltzmann constant (1.38 x 10^{-23} J K^{-1}), T is the temperature in Kelvin, and M_s is saturation magnetization.

Under the assumption of the spherical shape of particles, the diameter, d, **of magnetic core** was determined by the following relation **formulate by Shliomis [30]**

$$d=\left(\frac{6\cdot m}{\pi\cdot M_S}\right)^{\frac{1}{3}} \qquad (2)$$

Calculations of the particles magnetic core to estimate the shell thickness of the prepared core-shell particles were used also by other authors [21].

2.5 Rheological measurements

Bare CI and CI-chol particles were mechanically dispersed in silicone oil (Lukosiol M 200, viscosity η_c = 194 mPa·s, density d_c = 0.970 g.cm^{-3}, relative permittivity ε' = 2.89, loss factor tan δ = 0.0001, Chemical Works Kolín, Czech Republic) to obtain 40 and 60 wt. % particle concentrations. The suspensions were mechanically stirred before each measurement. The rheological properties under an external magnetic field in the range 0-300 mT were investigated using a rotational rheometer Physica MCR 501 (Anton Paar GmbH, Austria) equipped with the Physica MRD 180/1T magneto-cell. The true magnetic flux density was measured using a Hall probe, and the temperature was checked with the help of an inserted thermocouple [30]. Temperatures 25, 45 and 65 °C used for rheological measurements were performed and stabilized using an Anton Paar Viscotherm VT2 circulator with a temperature inaccuracy ±0.02 °C.

2.6 Anti-corrosion stability

The stability of the particles against corrosion was elucidated after immersion of the same amount of bare CI and CI-chol particles into the 0.05 mol L^{-1} HCl (Penta, Czech Republic). Change in pH values due to reaction of CI with HCl was detected for 70 minutes using a pH meter (GLH 014, Germany).

3 Results and discussion

3.1 Modification of CI particles

To modify CI particles, their surface was first activated by acid treatment. The treated particles contained hydroxyl groups on their surface, which were further used for reaction with 3-aminopropyltriethoxy silane. The triethoxy silane part serves for reaction with hydroxyl groups at the CI surface and simultaneously it reacts with other triethoxy silane groups to form crosslinked siloxane layer on the CI surface. The amino groups can be then used for modification of the particles surface to obtain the required properties. In our case the amine groups reacted with cholesteryl chloroformate to introduce nonpolar cholesteryl moieties on the CI surface.

The process of modification of the CI particles was followed by FTIR spectroscopy. Bare CI particles, consisting of ~97% of iron, did not exhibit any visible characteristic peak. After modification with 3-aminopropyltriethoxy silane the peaks at 1072, 1212, 1285, 1388 and 1441 cm^{-1} characteristic for O-Si vibrations, C-O stretching vibrations from triethoxy groups, $Si-CH_2$ vibrations, aliphatic C-H vibrations and C-N vibrations, respectively, were observed [26].

Surface modification of the functionalized CI particles was also determined using FTIR. After subsequent modification with cholesteryl group new peaks appeared at 1258, 1818, and within 2800-3000 cm^{-1} corresponding to C-O-C, C=O, and C-H stretching vibration bands, respectively.

3.2 Magnetic Properties

Magnetic properties of both bare CI particles and CI-chol ones are shown in Fig. 1. As can be seen cholesteryl-coated particles exhibit **decreased** values of the magnetization saturation **(app. 3.5%)** in comparison to the bare CI ones, because substantial coating shields the activity of magnetic dipoles in the presence of the magnetic field. Furthermore, VSM spectra were fitted using the Langevin model **[29]** whose parameters are presented in Table 1. Calculated magnetization saturation was slightly higher in comparison with the measured data due to the unsaturated state of samples at measured magnetic fields.

Moreover, the thickness of the cholesteryl coating was calculated using eq. 2 **[30]** as a difference between diameter of the **magnetic cores** of bare CI particles (6.49×10^{-7} m) and CI-chol ones (6.41×10^{-7} m); the thickness of the coating was estimated to be 4 nm.

Table 1: Parameters of the Langevin model fit.

Sample	M_s	m
bare CI	216.4	3.1×10^{-17}
CI-chol	208.9	2.8×10^{-17}

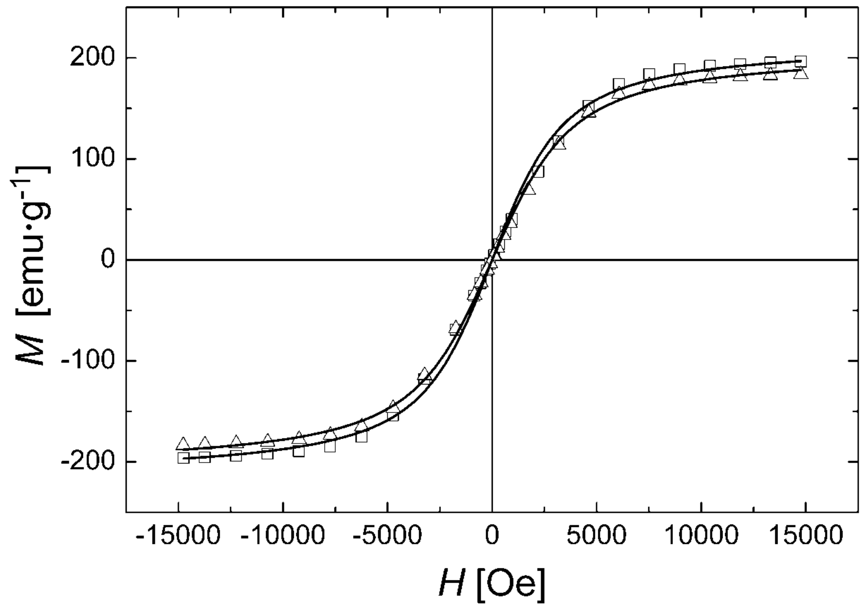


Figure 1: VSM spectra of bare carbonyl iron particles (□) and carbonyl iron particles modified with cholesteryl groups (△); solid lines represent the Langevin model fits.

3.3 Anti-corrosion stability

In the case of practical applications, the stability against corrosion represents very important property usually not taken into account in the case of magnetorheological suspensions. Only few articles **[21, 24]** has been devoted to this phenomena.

Commonly the bare CI particles undergo corrosion after relatively short time (in order of hours) of exposure to the acidic conditions. To check the anticorrosion stability, the bare CI and CI-chol particles were dispersed in 0.05 M HCl. As can be seen from Fig. 2, the p*H* in the case of bare CI rapidly increased in time, implying that reaction between CI and HCl was present to cause oxidation of bare CI particles surface. On the other hand, in the case of the CI-chol particles the p*H* of the dispersion was stable during the same time of exposure. Thus the cholesteryl layer present on the surface of the CI can significantly suppress the corrosion of the CI surface.

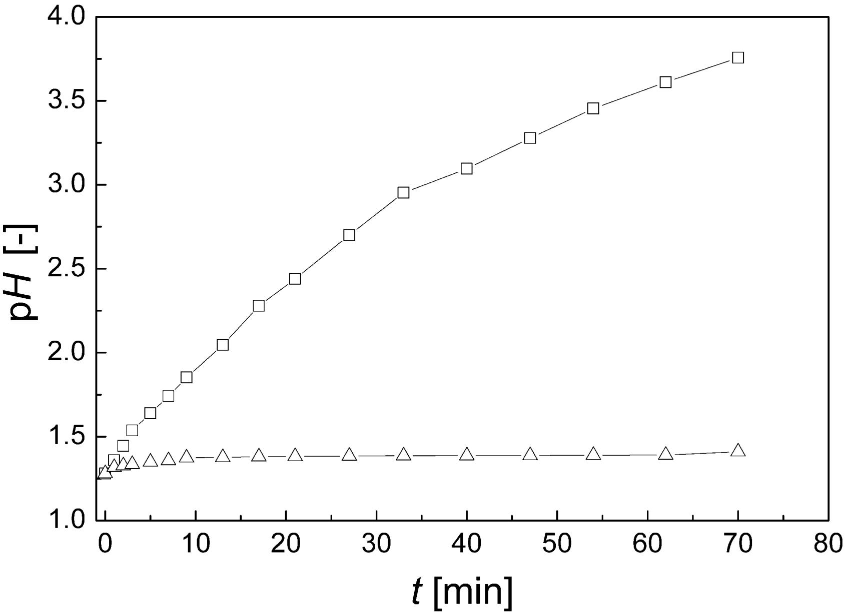


Figure 2: Anti-corrosion stability of the bare carbonyl iron particles (□) and carbonyl iron particles modified with cholesteryl groups (△).

3.4 Dynamic oscillatory measurements

The MR suspensions repeatedly change the state from liquid-like to solid-like upon application of the external magnetic field. In the real life applications (as e.g. **dampers** and shock absorbers), the dynamic oscillation mode is usually applied to the material, therefore the performance of the novel suspensions should be tested in the oscillatory mode rather than in the steady state.

In the oscillatory mode the viscoelastic quantities such as elastic modulus (G'), viscous modulus (G''), and complex viscosity (η^*) are employed to describe behaviour of the suspensions in the presence and absence of the external magnetic field strength.

All measured viscoelastic quantities should be obtained in the linear viscoelastic region (LVR). Therefore, first the LVR was determined from the dependence of the viscoelastic moduli (G', G'') on the strain γ, as a region where the moduli were strain independent (Fig. 3). In the case of CI-chol the LVR exists for strains below 2 x 10^{-2}. Within the LVR the elastic modulus was higher than the viscous one, proving the presence of the internal structures under application of the external field. Opposite behaviour was observed in the absence of the external field when the particles were randomly dispersed in the silicone oil and the viscous modulus exceeded the elastic one. Finally, it can be seen that with the increasing external magnetic field strength the LVR expands to the higher strain deformations due to the formation of tougher internal structures.

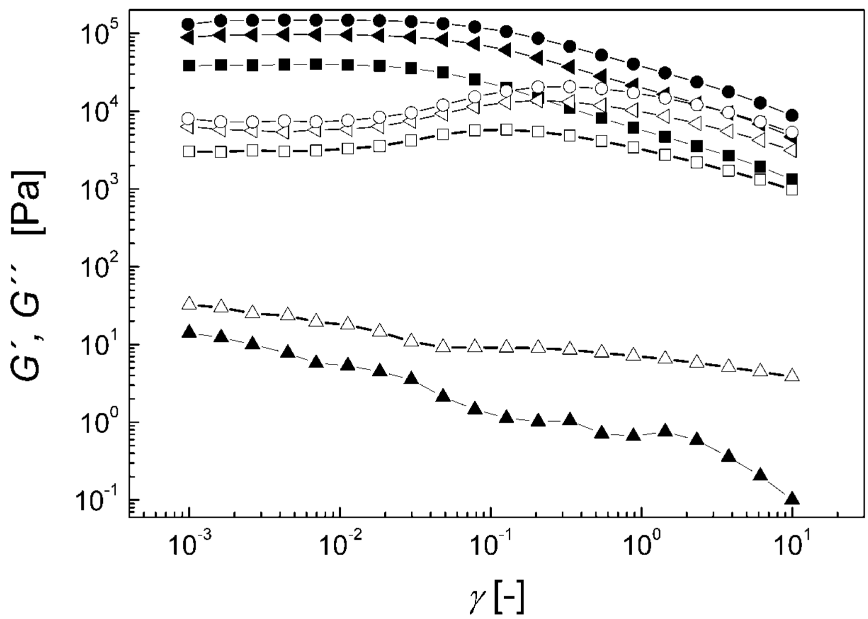


Figure 3: Dependence of elastic modulus , *G´*, (solid symbols) and loss modulus, *G´´*, (open symbols) on the strain, *γ*, for 40 wt.% suspensions of carbonyl iron particles modified with cholesteryl groups in silicone oil, at temperature 25 °C, under various magnetic flux densities (mT): (△, ▲) 0, (□, ■) 87, (◁, ◀) 178, (○●) 267.

To investigate the viscoelastic properties of the prepared suspensions containing bare CI or CI-chol particles, the frequency dependences of both elastic and viscous moduli were measured. As follows from Fig. 4, in the absence of the external magnetic field both suspensions exhibited the liquid-like behaviour since the *G´´* was higher than *G´* throughout the whole measured frequency range. Both moduli were slightly frequency dependent presenting typical low-viscous flow of such systems. On the other hand, after application of the external magnetic field the dispersed particles were oriented and created relatively stiff internal structures. *G´* exceeded the *G´´* and solid-like behaviour of suspensions appeared. Moreover, the *G´* was nearly independent at whole measured frequency range confirming the creation of highly elastic internal structures. Fig.4a documents that the suspension based on bare CI reached the values of *G´* close to 3 x 10^5 Pa confirming sufficient MR performance reported also by other authors [28-30]. In the case of cholesteryl-coated CI-based suspension (Fig. 4b) the modulus *G´* attained slightly lower values, around 1 x 10^5 Pa, but still sufficiently high for adequate MR performance in potential applications.

Industrial applications of the MR suspensions are tightly adhered with their utilization under elevated temperatures. Due to the restriction of the MR measuring cell to be used above 70 °C, the MR performance, namely frequency dependence of complex viscosity of the suspensions containing CI-chol particles, was examined at three different temperatures of 25, 45 and 65 °C (Fig. 5). In the absence of the external magnetic field the suspension exhibited slightly pseudoplastic behaviour at all temperatures and the complex viscosity was highest at the lowest temperature (Fig. 5a). With increasing temperature, the viscosity of the silicone oil decreases, therefore the viscosity of the CI-chol suspensions decreased as well. On the other hand, after an application of the external magnetic field, suspensions exhibited purely pseudoplastic behaviour. The highest values of complex viscosity were observed for the highest temperature. The reason is that due to the intensified Brownian motion and decreased viscosity at elevated temperatures the particles can be easier oriented forming the stiffer internal structures (Fig. 5b). Finally, the shear thinning behaviour was observed. With increasing frequency, representing intensified deformation, viscosity of the suspensions decreased, indicating the partial destruction of the formed internal structures.

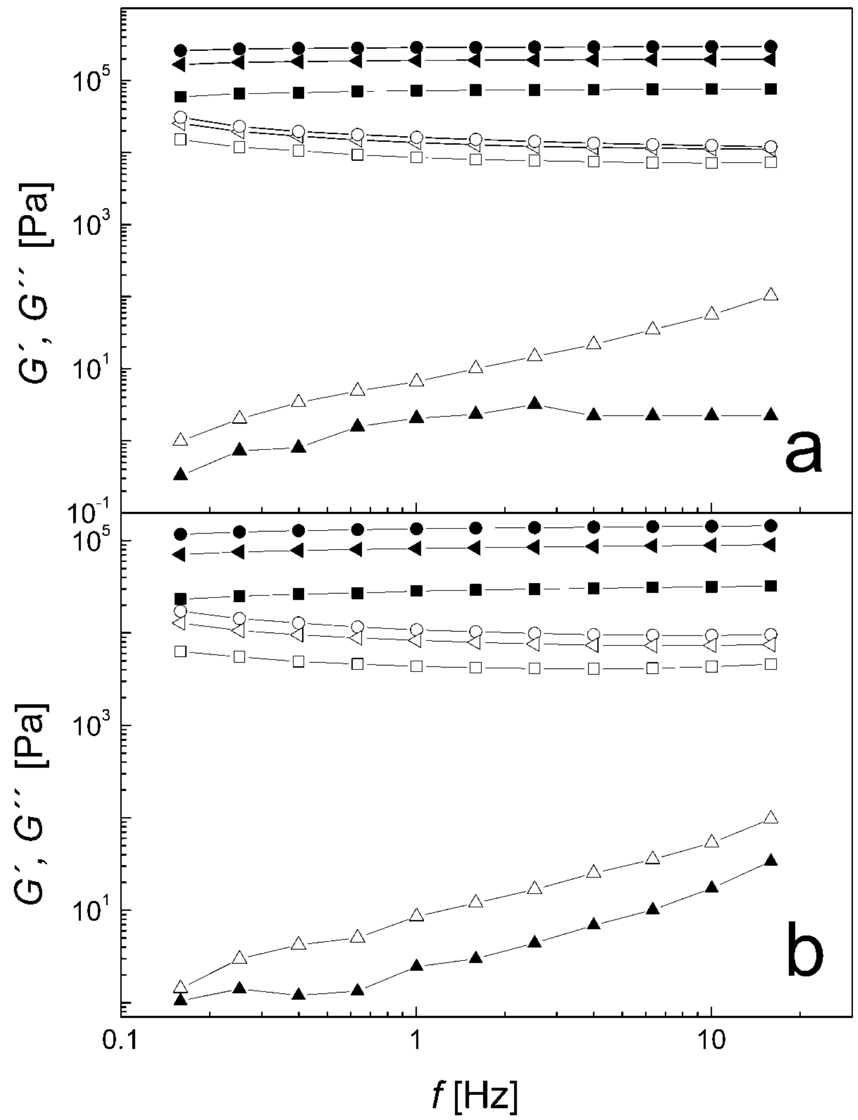


Figure 4: Dependence of elastic modulus, *G´*, (solid symbols) and loss modulus, *G´´*, (open symbols) on the frenquency, *f*, for 40 wt.% suspensions of bare carbonyl iron particles (a) and carbonyl iron particles modified with cholesteryl groups (b) in silicone oil, at temperature 25 °C, under various magnetic flux densities (mT): (△, ▲) 0, (□, ■) 87, (◁, ◀) 178, (○●) 267.

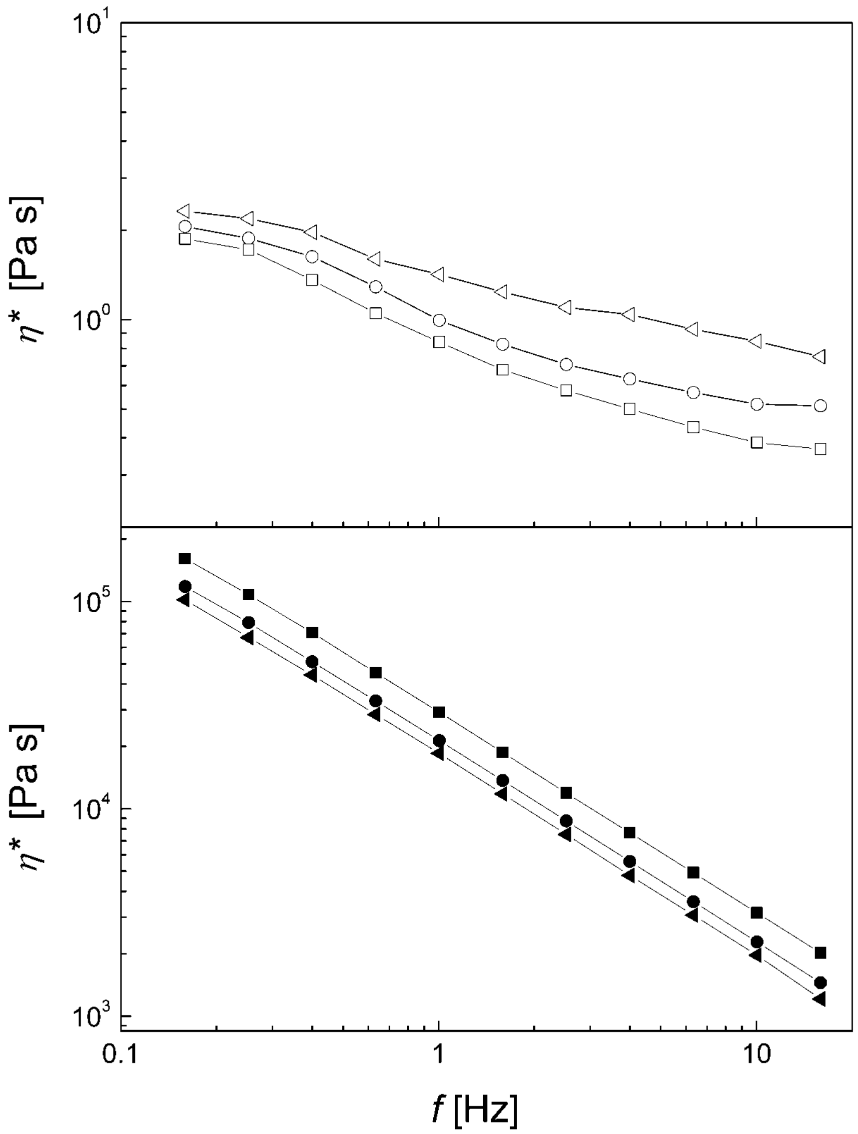


Figure 5: Dependence of the complex viscosity, η*, on frequency, *f*, for 40 wt. % suspension of carbonyl iron particles modified with cholesteryl groups in silicone oil in the absence (open symbols) and presence (solid symbols) magnetic flux density (267 mT) at various temperatures (°C): (◁, ◀) 25, (○, ●) 45, (□, ■) 65.

In order to evaluate the effect of CI-chol particle concentration on the MR performance, the elastic modulus obtained at low frequency (*f* = 1 Hz) was plotted against magnetic flux density (Fig. 6). From here it follows that for the low magnetic field strengths the elastic modulus increased with the higher slope and this slope decreased with increasing particles concentration. This behaviour could be caused by the local saturation of the magnetic dipoles of the spherical CI-chol particles in the suspension. The slope also decreased with increasing magnetic flux density. This behaviour was observable for all measured suspensions and could be again related to the local magnetic saturation of the particles due to relatively high magnetic field applied to the measured suspensions.

Finally, it can be concluded that the elastic modulus could be enhanced approximately by one order of magnitude with increasing particle concentrations, although the differences decreased with increasing magnetic field.

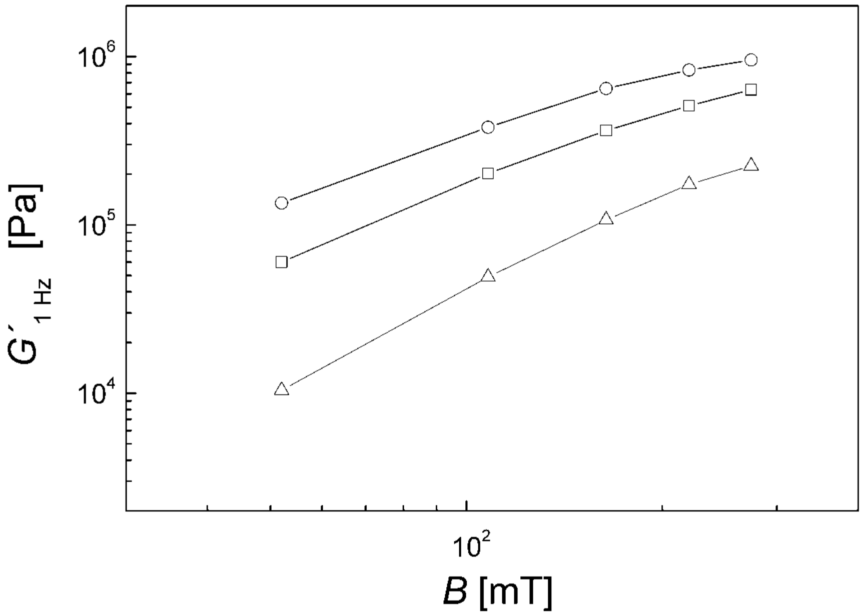


Figure 6: Dependence of the elastic modulus *G*′, at *f* = 1 Hz, on the magnetic flux density for silicon oil suspensions with various concentrations of carbonyl iron particles modified with cholesteryl groups (wt. %): (△) 40, (☐) 60, and (○) 80.

4 Conclusions

This article deals with the investigation of magnetorheological behaviour of CI particles covalently coated with cholesteryl groups (CI-chol) under oscillatory conditions. Due to the substantial coating with cholesteryl groups, modified carbonyl iron exhibited only slightly lower MR efficiency under dynamic oscillatory conditions in comparison to bare carbonyl iron particles. The crucial point is that the CI-chol particles exhibited significantly higher stability against corrosion. It was shown that coating of the CI particles with low molecular weight substances, such as cholesteryl groups, is a perspective method for obtaining particles with good MR performance and considerably enhanced stability under acidic conditions.

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