Tomas Bata University in Zlín
Faculty of Technology

*Doctoral thesis*

# Surface modification of particles for preparation of ER and MR suspensions

# Povrchová modifikace částic pro přípravu ER a MR suspenzí

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# CONTENT

# ABSTRACT

Nowadays, many scientists are focused on the development of the special types of materials, whose properties could be reversibly controlled by an external stimulus. In 1948 Winslow found out phenomenon when suspensions of particles dispersed in liquid medium were able to create internal structures after application of the external electric field. Similar observations were published by Rabinow in 1953 for suspensions sensitive to application of magnetic field. Development of internal structures results in the change of rheological properties, in some cases in several orders of magnitude. Furthermore, such changes (viscosity or viscoelastic moduli) are reversible and when the external field is switched-off they revert to their original values. Such infinitely reversible change from liquid-like to solid-like state within the few milliseconds falls under interest of both academics and engineers.

The systems able to react on the external electric field are called electrorheological (ER) suspensions and those sensitive to the external magnetic field magnetorheological (MR) suspensions. Basically, suspensions are two-phase systems including polarizable particles in case of ER fluids and magnetic particles in case of MR fluids randomly dispersed in a liquid medium.

Although, both phenomena were found approximately 60 years ago, the first real applications for such materials have been realized since 1990s. While MR suspensions are widely used in dumping systems or shock absorbers, real application of ER suspension are still limited due to their lower efficiency. Although, such suspensions can be found in various application, there are still some limitations, which should be taken into account i.e. sedimentation of the particles, thermal and corrosion instability, etc. All these disadvantages influence potential applicability of ER or MR suspensions. In the case of ER suspensions the priority is in improvement of their efficiency, which is considerably lower in comparison to MR ones.

Therefore, the aim of this study is to prepare novel ER and MR suspensions providing solution of some of above mentioned problems. One part is dealing with synthesis and preparation of novel materials based on core-shell, rod-like particles and aniline oligomers, both exhibiting enhanced ER efficiency of suspensions under applied external electric field. In the case of core-shell particles the influence of the rod-like shape as well as the effect of the conducting polymer polypyrrole on the ER efficiency was investigated. In case of novel ER material aniline oligomers, the impact of the one-step synthesis conditions on the ER efficiency was elucidated. The other part is concentrated on the surface modification of the carbonyl iron particles, in order to enhance the sedimentation, thermooxidation stability and suspensions redispersibility, while the MR efficiency remains in level enabling their usage in the real applications.

Keywords: Electrorheology, magnetorheology, conducting polymers, polypyr-

role, titanates, carbonyl iron, core-shell, dielectrics, steady shear, oscillatory shear, sedimentation and thermooxidation stability.

# ABSTRAKT

V současnosti se řada výzkumníků zaměřuje na vývoj speciálních typů materiálů, jejichž vlastnosti lze vratně řídit vnějším podnětem. V roce 1948 Winslow [1] objevil, že částice dispergované v kapalném médiu po aplikaci vnějšího elektrického pole vytvářejí vnitřní organizované struktury. Podobné pozorování publikoval v roce 1953 Rabinow [2] při aplikaci vnějšího magnetického pole. Změna vnitřní struktury suspenzí se odráží ve změně reologických vlastností (viskozita nebo viskoelastické moduly), v některých případech až o několik řádů. Dále je pak tato změna viskozity vratná a v případě, že je elektrické pole vypnuto hodnota viskozity se během smýkání vrátí na původní hodnotu. Schopnost suspenzí měnit charakter z kapalného do téměř tuhého skupenství během několika milisekund, poutá zájem vědecké i aplikační sféry.

Systémy schopné reagovat na vnější elektrické pole se nazývají elektroreologické (ER) kapaliny a na vnější magnetické pole pak magnetoreologické (MR) kapaliny. V podstatě jsou tyto suspenze dvou-fázovými systémy obsahující polarizovatelné částice v případě ER a magnetické částice v případě MR dispergované v kapalném médiu.

Ačkoliv, byly oba jevy známé již přibližně 60 let, první skutečné aplikace takovýchto materiálů se objevily až v devadesátých letech. Zatímco MR suspenze jsou široce používané v tlumících systémech, nebo jako absorbéry nárazů, ER suspenzím brání v jejich širším uplatnění nižší ER účinnost. Ačkoliv jsou ER a MR suspenze využívány v praktických aplikacích, stále mají svá omezení, se kterými je třeba počítat, jako jsou sedimentace částic, tepelná a korozní nestabilita a pod.

Cílem této práce je příprava nových ER a MR suspenzí, které přinesou odstranění některých ze zmiňovaných nevýhod. Jedna část práce je zaměřena na syntézu materiálů na bázi částic typu jádro-slupka (core-shell) ve tvaru tyčinek a částic anilinových oligomerů, které přináší zvýšenou ER účinnost jejich suspenzí pod vlivem vnějšího elektrického pole. Dále bude hodnocen vliv tvaru částic stejně tak jako vliv vodivého polymeru tvořícího povrchovou vrstvu částic typu jádro-slupka. V případě nového ER materiálu na bázi anilinových oligomerů bude hodnocen vliv podmínek jednokrokové polymerační reakce na účinnost ER suspenzí. Druhá část práce se zabývá povrchovou úpravou v současnosti široce používaných částic karbonylového železa, která přinese zlepšení sedimentační, termooxidační stability, redispegovatelnosti suspenzí, při zachování dostatečné MR účinnosti.



Klíčová slova: Elektroreologie, magnetoreologie, vodivé polymery, polypyrol, titanáty, karbonylové železo, jádro-slupka, dielektrika, ustálený smyk, oscilační smyk, sedimentační a termooxidační stabilita.

# FUNDAMENTAL THEORY

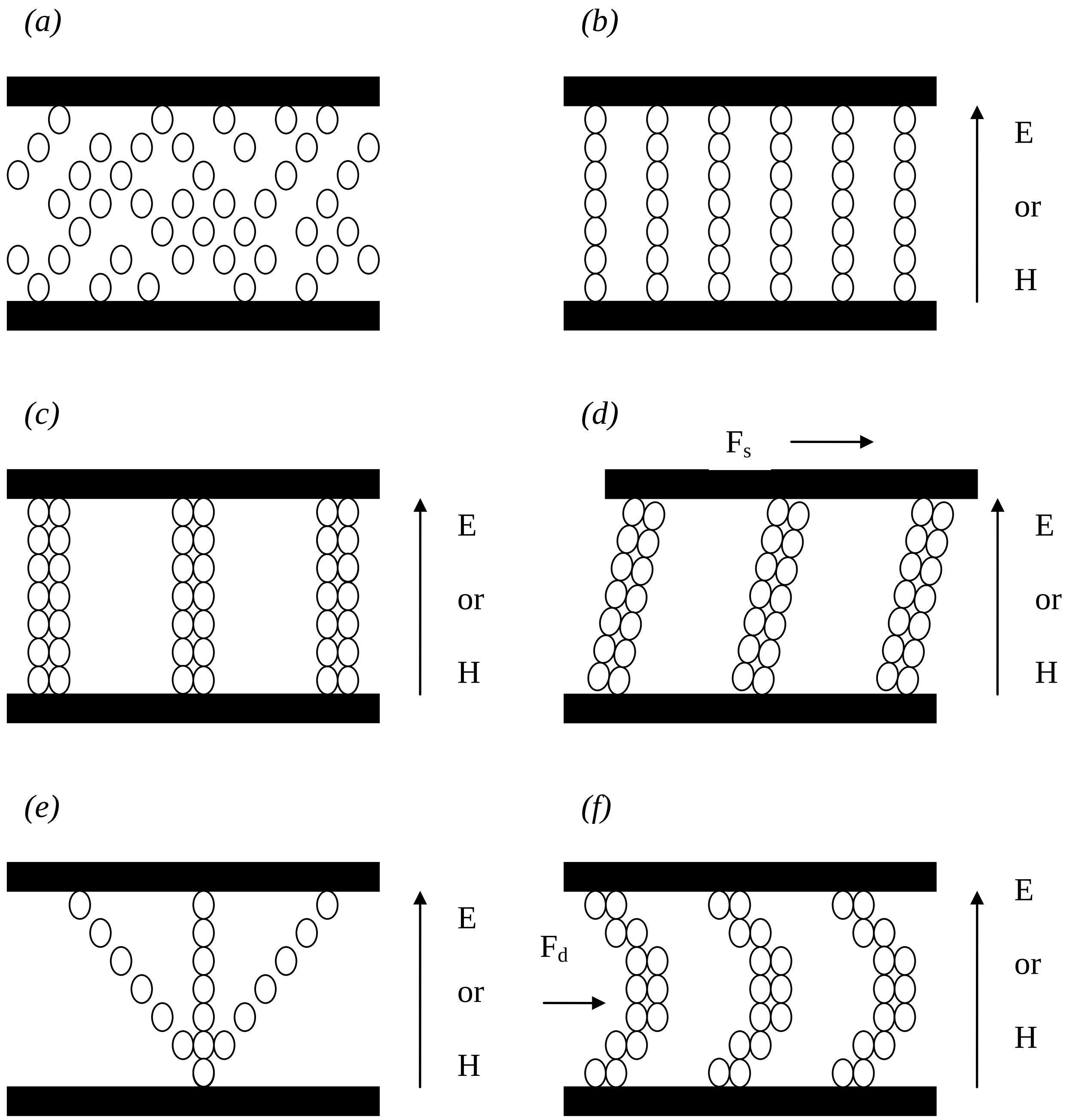
## 1. ER and MR suspensions under external static fields

ER and MR suspensions are from the rheological point of view two-phase systems consisting of the electro- or magneto-responsive particles dispersed in the liquid medium. Depending on the external field application as well as on the nature of the particles, the suspensions can be reversibly changed from their liquid-like to solid-like state within the several miliseconds. This behaviour is induced by dipolar electric and magnetic attractive forces causing creation of the field-induced chain like structures in the streamlines direction of the external field strength [3, 4].

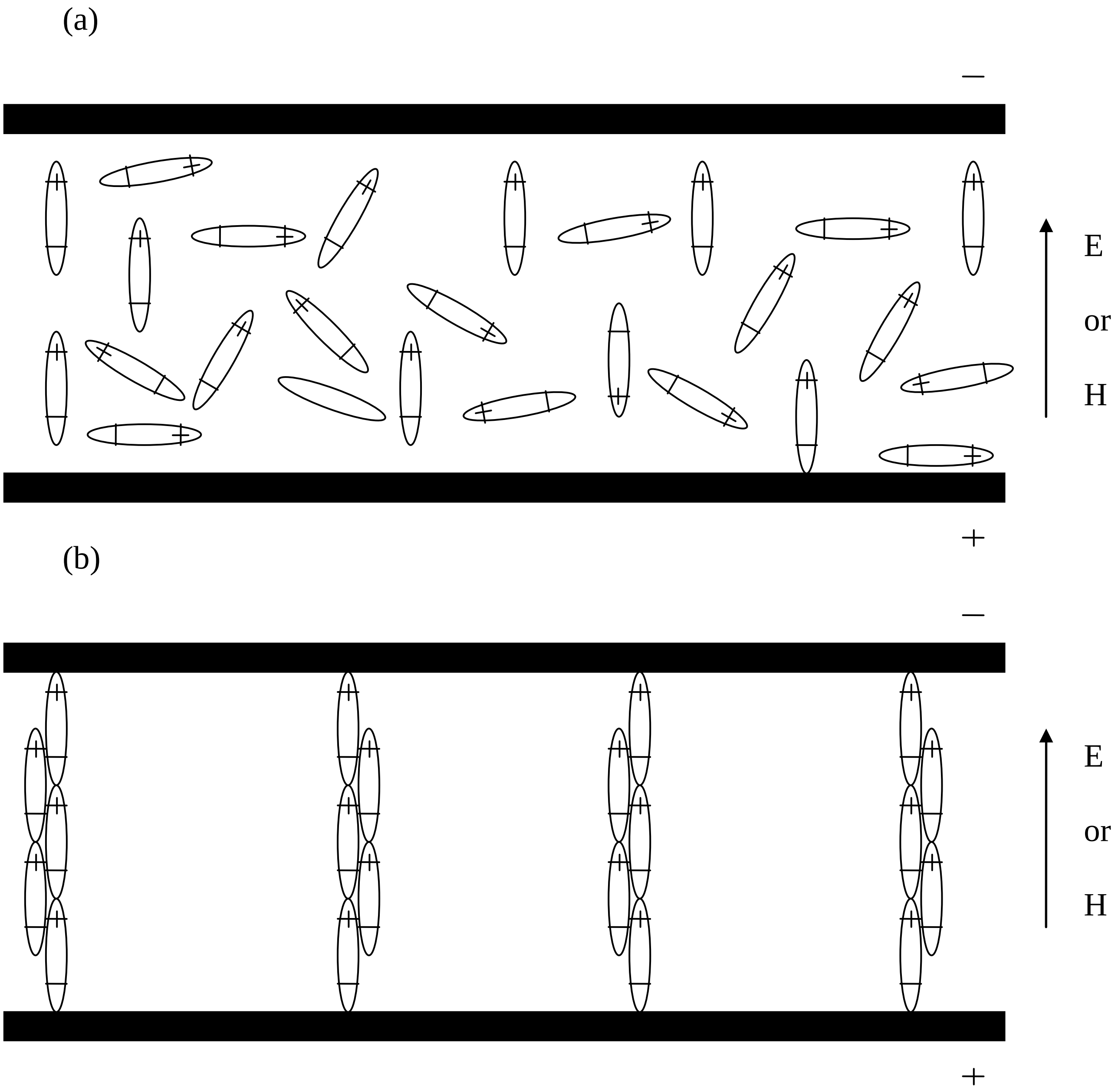
## 2. ER and MR structures

Although, the composition of the ER and MR suspensions might be slightly different, the principal of the phenomenon affecting their rheological properties is similar. In both cases, ER or MR suspensions are placed between two electrodes (Scheme 1a) and particles are randomly dispersed in the liquid medium. Further, in the absence of the external field the suspensions exhibit nearly Newtonian behaviour. However, after the application of the external electric field strength $E$ (kV.mm$^{-1}$) for ER systems or the magnetic field strength $H$ (kA.m$^{-1}$) for MR systems, the particles become polarized or magnetized (dielectric or magnetic dipoles are induced) and create chain-like structures perpendicular to the electrodes (Scheme 1b). Such structure formation causes change of the rheological properties (i.e. viscosity and viscoelastic moduli) of suspensions and shear-thinning behaviour appears with semi-elastic character. Increase of the external field strength contributes to the stiffer column-like structures formation (Scheme 1) resulting in the considerable enhancement of the viscosity [5]. In the case of potential applications suspensions are usually stressed by shear, oscillatory or pressure driven forces (Scheme 1d-f) while the external field is applied [6]. In all cases, competition between electro- or magneto-static and hydrodynamic forces appears (further described in the section 3) [7]. When the electro- or magneto-static forces are higher than that of hydrodynamic ones considerable yield stress, $\tau_y$, can be observed. This can be expressed as a minimum energy required to the field-induced structure destruction and flow beginning [8].

Stronger ER and MR behaviour of the one-dimensional particles based silicone oil suspensions was observed (Scheme 2). In the absence of the external field particles are randomly located. After application of the electric as well as magnetic field, dipoles on the particles are induced and particles orient along their longer axis. Kuzhir *et.al* observed that one-dimensional particles based suspensions exhibit enhanced yield stress in comparison to spherical ones, due to higher interparticle attractive forces mostly connected side-by-side and consequently due to the higher solid friction between particles. [9]




*Scheme 1: Microstructure of ER or MR suspension before (a), and after (b, c) application of an external electric or magnetic field, E or H. Furthermore, simultaneous application of shear force, $F_s$, (d), dynamic shear force, $\omega$, (e) and pressure force, $F_p$, (f) on formed structure. Redrawn from Ref. [7, 8].*




*Scheme 2: Microstructure of ER or MR one-dimensional particles based suspension before (a), and after (b) application of an external electric or magnetic field, E or H. Redrawn from ref. [9].*

# 3. Rheological properties

Investigation of the rheological properties of ER and MR suspensions is a useful tool how to classify their behaviour in the absence as well as in the presence of the external fields. Such classification can elucidate the suitability of these suspensions for potential applications. Moreover, using various rheological models, yield stress as a measure of the rigidity of the internal structures created after application of the external field can be estimated.
However, steady shear measurements represent potential application of devices when the control of torque is important (valves or brakes), oscillatory shear measurements represent dynamic behaviour of suspensions, when the control of damping force is necessary. Hence, both kinds of experiments provide information of suspension behaviour with connection to the potential application [10].

## 3.1 Steady shear behaviour

In the absence of the external field, both ER an MR particle based suspensions exhibit nearly Newtonian behaviour in the steady shear flow following Newton model [11] Eq. 1:

$$\tau = \eta \cdot \dot{\gamma} \tag{1}$$

Where, $\tau$, is shear stress linearly proportional to the shear rate, $g$, and, $\eta$, is shear viscosity.
Considerably different behaviour can be observed after application of the external field when suspension is transformed from liquid-like to solid-like state (Fig.1).

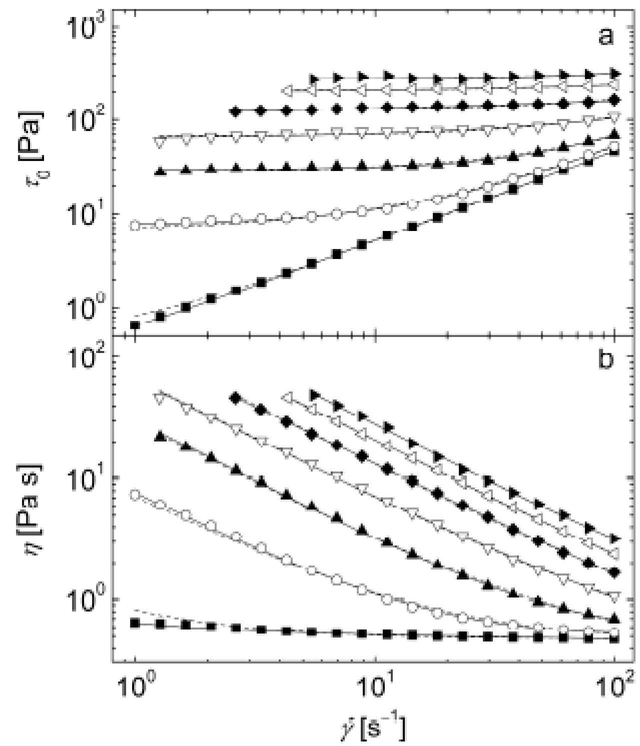



*Figure 1: Dependence of the shear stress, $\tau$, and shear viscosity, $\eta$, on the shear rate, g, for typical suspension of PANI particles in silicone oil at various external electric field strengths, E (kV.mm$^{-1}$): (■) 0, (○) 0.5, (▲) 1, (▽) 1.5, (◆) 2,(◁) 2.5, (◀) 3. Reprinted from ref. [15].*

In the presence of external field, suspensions exhibit pseudoplastic behaviour with the certain level of the yield stress, $\tau_y$ (Fig. 1a). Value of the yield stress is proportional to the rigidity of the internal structures developed in the presence of external field. For the evaluation of $\tau_y$ of both electro- and magneto-rheological suspensions different mathematical models can be applied.

The first one and the simplest is Bingham model Eq. 2 frequently used [12-15]

$$\tau = \tau_y + \eta_{pl} \cdot \dot{\gamma} \tag{2}$$

Where, $\tau_y$, is yield stress and, $\eta_{pl}$, is plastic viscosity.

However, Bingham model does not take into account common shear thinning behaviour above, $\tau_y$, while the suspension is exposed to the electric field.

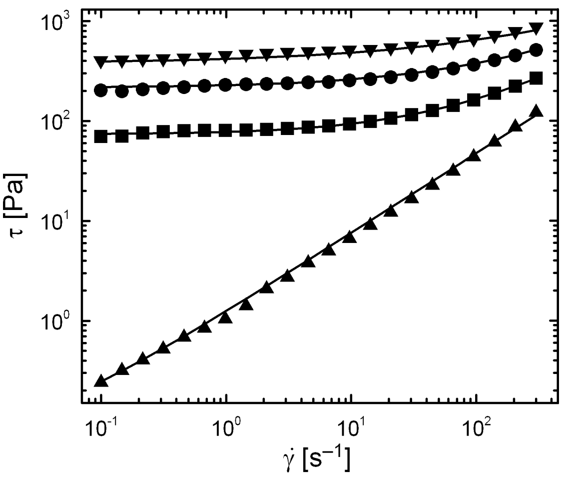



*Figure 2: Dependence of the shear stress, τ, on the shear rate, g, for 5. wt. % CI/PPy ribbon-like particles silicone oil suspensions at various magnetic flux densities, B (mT): (▲) 0, (■) 87, (●) 177, (▼) 268. Solid lines represent Herschel-Bulkley model fit. Adopted from ref. [16].*

Therefore, the Herschel-Bulkley model Eq. 3 was applied by other authors from the field of electro- and magneto-rheology [17-19]

$$\tau = \tau_y + \eta_{pl} \cdot \dot{\gamma}^n \tag{3}$$

Where, $\tau_y$,, is yield stress, $\eta_{pl}$, is plastic viscosity and, *n*, is Herschel-Bulkley index, for ER and MR suspension is accepted condition that n<1.

In some cases ER suspensions does not exhibit the classical shear stress plateau at low shear rates, but shear stress decrease up to critical shear rate $g_c$ (Fig. 3). For such systems Cho *et al.* developed a novel six-parameters mathematical model Cho-Choi-Jhon Eq. 4 [20]

$$\tau = \frac{\tau_y}{1+(t_2 \cdot \dot{\gamma})^{\alpha}} + \eta_\infty \cdot \left(1 + \frac{1}{(t_3 \cdot \dot{\gamma})^{\beta}}\right) \cdot \dot{\gamma} \tag{4}$$

Where, $\tau_y$, is yield stress defined as the extrapolated stress from low shear rate region, exponent, $\alpha$, is related to the decrease in the stress, $t_2$, and, $t_3$, are time constants and, $\eta_\infty$, is the viscosity at high shear rates and corresponds to viscosity of the suspension in the absence of the electric field. Further, the exponent, $\beta$, is in the range $0>\beta>1$ since $d\tau/dg >0$.

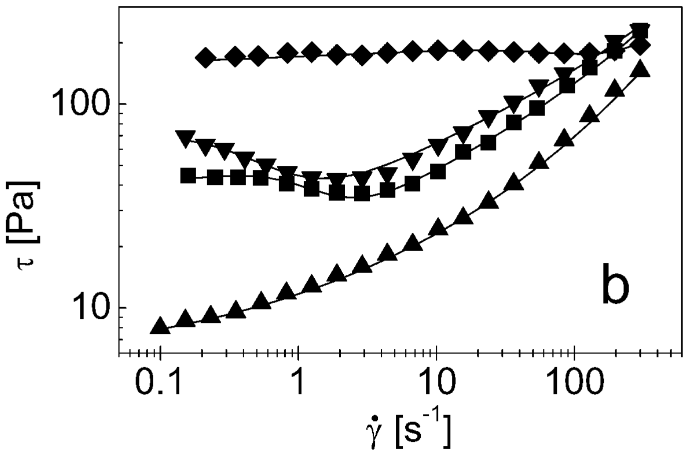



*Figure 3: Dependence of the shear stress, τ, on the shear rate, g, for 5. wt. % particle silicone oil suspensions at electric field strength of 3 kV.mm$^{-1}$ where are (▲) neat titanate, (■) 1 ml of pyrrole, (▼) 2 ml of pyrrole, (◆) 4 ml of pyrrole used for polymerization on the surface of the titanate rods. Solid lines represent Cho-Choi-Jhon model fit. Adopted from ref. [21].*

As was mentioned in the previous section determination of the yield stress was found as a key factor reflecting the toughness of the internal structures after application of the external electric or magnetic field. Generally, two basic principles can be utilized to obtain a value of the yield stress. The first one is rheological measurement in the controlled shear rate (CSR) mode, where shear rate is applied to the material and shear stress necessary to make material flow is measured. From such CSR measurement the dynamic yield stress can be obtained by extrapolation of the shear stress to zero shear rate. The second procedure involves measurement in the controlled shear stress (CSS) mode, where the stress required for the shear flow initiation (static yield stress) is determined at test.

### 3.2 Viscoelastic properties

Mostly dynamic behaviour is utilized in the real industrial applications e.g. in damping systems, shock absorbers etc. [22, 23]. Hence, investigation of viscoelastic properties in various modes (amplitude sweep and frequency sweep) represents suitable method characterizing dynamic behaviour [24-26].

Basic difference between steady shear and oscillatory shear mode inhere in fact that former measuring mode is destructive, while later mode has rather deformation character. Dynamic behaviour can be evaluated using complex shear modulus Eq. 5.

$$G^*{}_{(\omega)} = G'_{(\omega)} + iG''_{(\omega)} \tag{5}$$

Here the real part, $G'$, is storage modulus reflecting reversibly stored energy and imaginary part, $G''$, is loss modulus reflecting energy dissipated per cycle of deformation. For the investigation of the dynamic behaviour, firstly the linear viscoelastic region (LVR), where both moduli are independent of the applied strain deformation should be determined (Fig. 4). As can be seen from this figure, the LVR is shifted to the lower strain deformations with increasing external field strengths connected to the internal structure development. Later the frequency dependence of both viscoelastic moduli is evaluated for different fields with accurate strain deformation (Fig. 5).

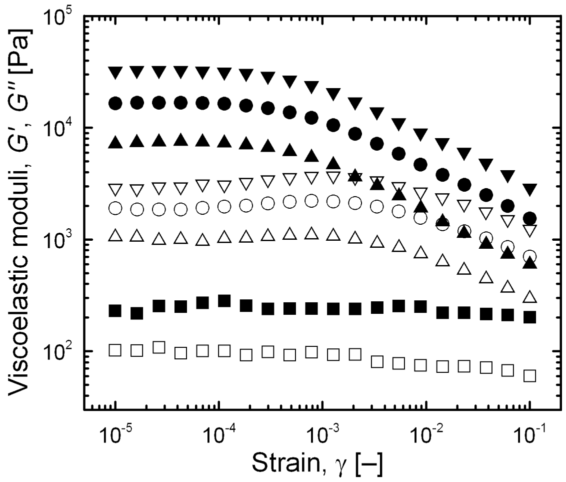



*Figure 4: Dependence of storage modulus, G′, (solid symbols) and loss modulus, G′′, (open symbols) on the strain, γ, for 40 wt. % suspensions of CI/PPy ribbon-like particles in silicone oil, at temperature 25 °C, under various magnetic flux densities B, (mT): (□,■)0, (△, ▲) 84, (○,●) 174, (▽,▼) 263. Reprinted from ref. [10].*

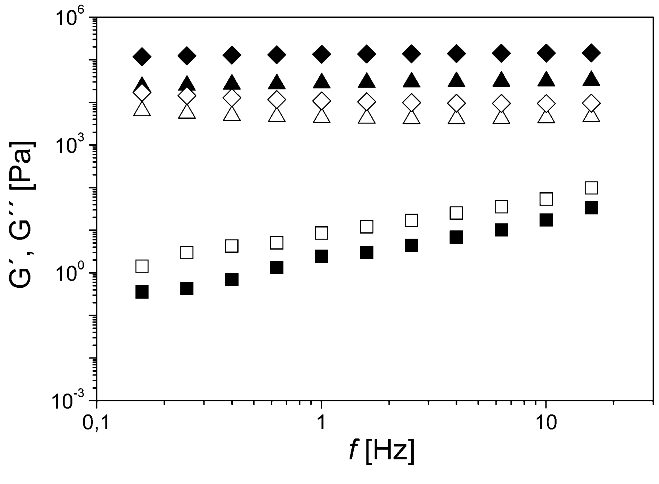



*Figure 5: Dependence of, G′, (solid symbols) and G′′, (open symbols) on the frequency, f, for suspensions of CI particles modified with cholesteryl chloroformate under various magnetic flux densities, B (mT), 0 (■,□), 86 (▲,△), 266 (◆,◇). Adopted from ref. [27].*

In the absence of the external field ER or MR suspensions exhibit liquid-like behaviour, thus loss modulus $G''$ dominates over storage modulus $G'$. On the other hand, after the application of the external field, developed field-induced internal structures result in the transition from liquid-like to solid-like state of the suspension and thus storage modulus $G'$ becomes dominating over loss modulus $G''$ Further both moduli are nearly independent of frequency as is characteristic for stiff gel-like structures [28].

## 4. Dispersed phase for ER suspensions

For application as a dispersed phase in ER suspensions, particles have to be polarizable, and able to develop internal structures in suspensions in the presence of the external electric field. Further, long-term and thermal stability is important.

First, the materials based on natural polymers (potato starch, crystalline cellulose) [29, 30] were used as a dispersed phase due to their ability to form internal structures in ER suspensions. However, in these types of material usually a small amount of water is responsible for ER effect, thus at higher temperature around water boiling point, water evaporates and suspensions based on these materials lose their ER properties. Narrow working temperature range, possible device corrosion forced the aim of the researches to the anhydrous materials [31].

Therefore, another possible group of materials was introduced including inorganic particles. Among the most investigated belong silica ($SiO_2$) [32-34], titanium dioxide ($TiO_2$) [35-37], titanates [78, 39], talc [40] or zeolites [41]. Advantage of all these materials is in relatively high relative permittivity that contributes to enhanced ER performance together with the nanoparticle-sized particles provide systems exhibiting enormous yield stresses [42, 43]. Unfortunately, some disadvantages were observed for these materials such as, high off-state viscosity in case of nanoparticles, high abrasion and fast sedimentation due to considerably higher particle density. Moreover, such particles also contain the small amount of water, responsible for the enhanced ER efficiency. However, if the particles are sufficiently dried such ER inorganic water-free particle based suspensions exhibit only moderate ER effect.

Conducting polymers have suitable chemical structure and include conjugated system of double bonds, which is responsible for charge transport and contributes to appropriate electrical properties. Conducting polymers based on polypyrrole [44, 45], polyaniline [46, 47], poly-*p*-phenylene [48] and polythiophene [49] can be used in ER suspensions. The possibility to control conductivity by another reaction step using doping or de-doping agents provides the materials with tuneable ER performance. Density of these polymers is comparable to the liquid medium, thus long-term sedimentation stability is assured.

Furthermore, there is a group of materials with several aniline constitutive units bonded together called aniline oligomers (Scheme 3). This kind of material is very promising in the case of ER suspensions due to its semiconducting character [53, 54]. Moreover, only one-step synthesis provides materials with controllable conductivity, which can be directly used as a dispersed phase in ER suspensions [55] in comparison to common already mentioned conducting polymers [56]

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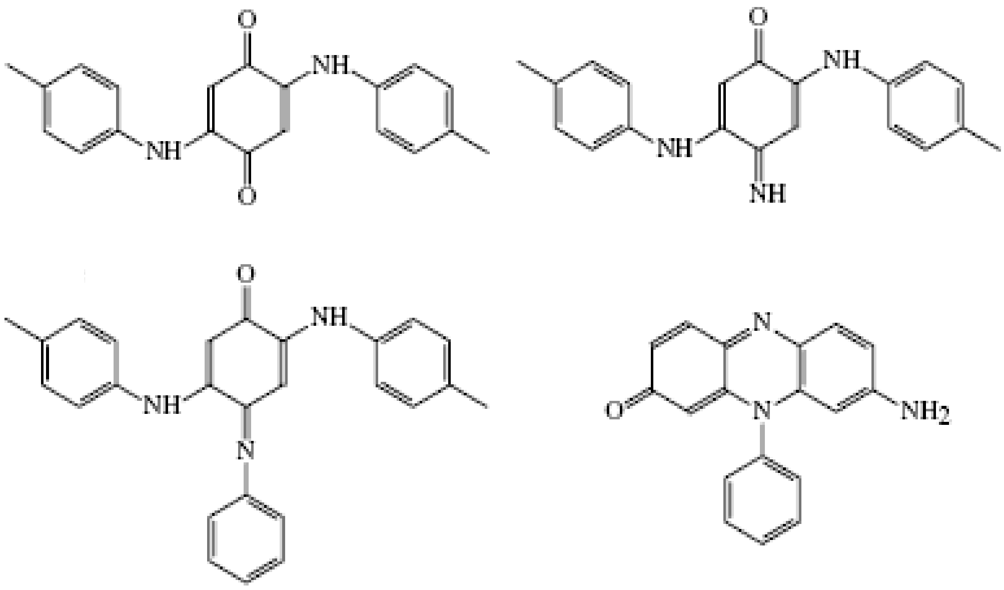


*Scheme 3: Possible oligoaniline structure formation. Redrawn from ref. [9].*

Core-shell particles can combine benefits of core material which can be prepared in various shapes and shell material having suitable dielectric properties and thus they provide enhanced ER efficiency of their suspensions in comparison to the both individual components based suspensions. While core is mostly represented by inorganic material, shell is preferably based on conducting polymers, hence the suitable core and non-abrasive and highly polarizable shell, finally provides systems with improved ER behaviour [50-52].

# 5. Factors influencing the ER effect

## 5.1 Dielectric properties of suspensions

As was already mentioned the ER suspension are consisting of the particles including dipoles, which are able to become polarized after application of the external electric field. Because the ER suspensions are two phase system mostly interfacial polarization is presented and this kind of polarization is responsible for the ER effect. The evaluation of the dielectric properties is therefore very important for analysis of ER performance of investigated suspensions [57-59].

In dielectric spectroscopy behaviour of ER suspensions is usually characterized using complex permittivity Eq. 6:

$$\varepsilon^*_{(\omega)} = \varepsilon'_{(\omega)} + i\varepsilon''_{(\omega)} \tag{6}$$

Where, $\varepsilon'$, is relative permittivity and, $\varepsilon''$, is dielectric loss factor.

Investigation of the dielectric spectra, frequency dependence of the relative permittivity and dielectric loss factor (Fig. 6) enables to obtain two crucial parameters influencing the ER performance. The first one is dielectric relaxation strength, $\Delta\varepsilon' = \varepsilon'_s - \varepsilon'_\infty$, representing the degree of polarization induced by electric field. Parameters, $\varepsilon'_s$, and $\varepsilon'_\infty$ represent relative permittivity extrapolated to the zero frequency and relative permittivity extrapolated to the infinite frequency [60-62]. Higher the dielectric relaxation strength, higher ER performance is achieved. The second parameter is relaxation time, $t_{rel}$, reflecting the polarization rate as well as strength of interparticle interactions [63-65]. In this case, shorter relaxation time reflects higher ER efficiency of the suspensions.

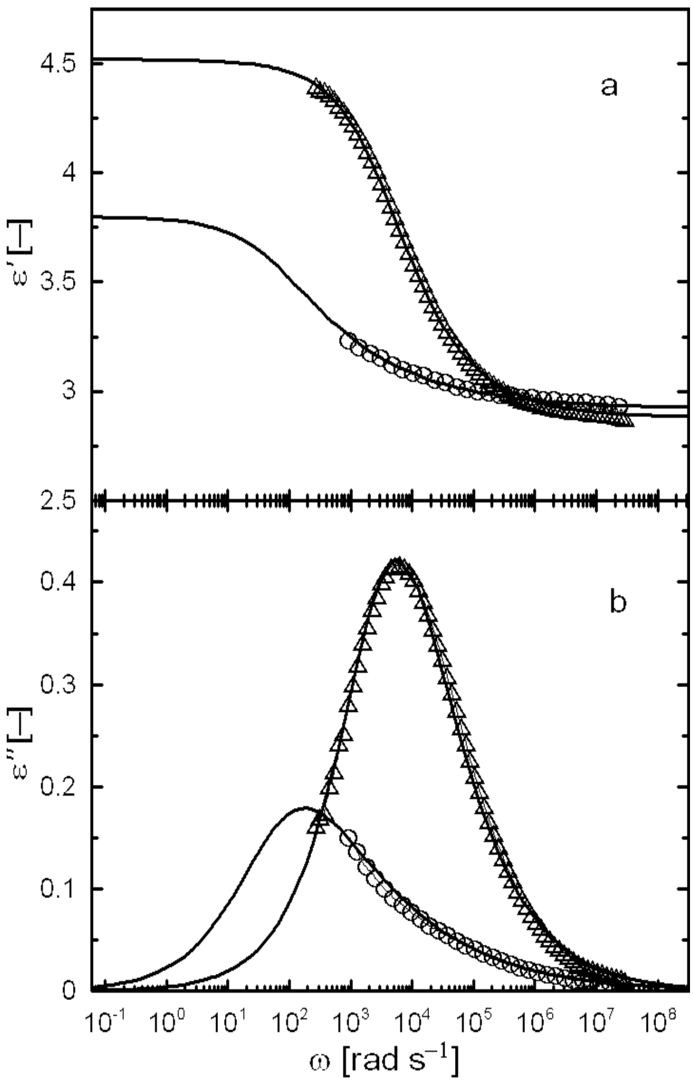

*Figure 6: Dependence of relative permittivity, ε′, and dielectric loss factor, ε′′, on frequency for 5 wt. % suspension of hollow globular clusters (○) and-TiO$_2$/PPy particles (△). Reprinted from ref. [66].*

In order to analyze dielectric spectra to obtain dielectric parameters the Cole-Cole model was introduced Eq. 7

$$\varepsilon^*(\omega) = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{1 + (i\omega \cdot t_{rel})^{1-\alpha}} \tag{7}$$

where $\varepsilon'_s$, is relative permittivity at zero frequency, $\varepsilon'_\infty$, is relative permittivity at infinite frequency, $\omega$, is angular frequency, $t_{rel}$, is relaxation time and parameter, $\alpha$, usually lies between 0 and 1 and allows to describe different spectral shapes.

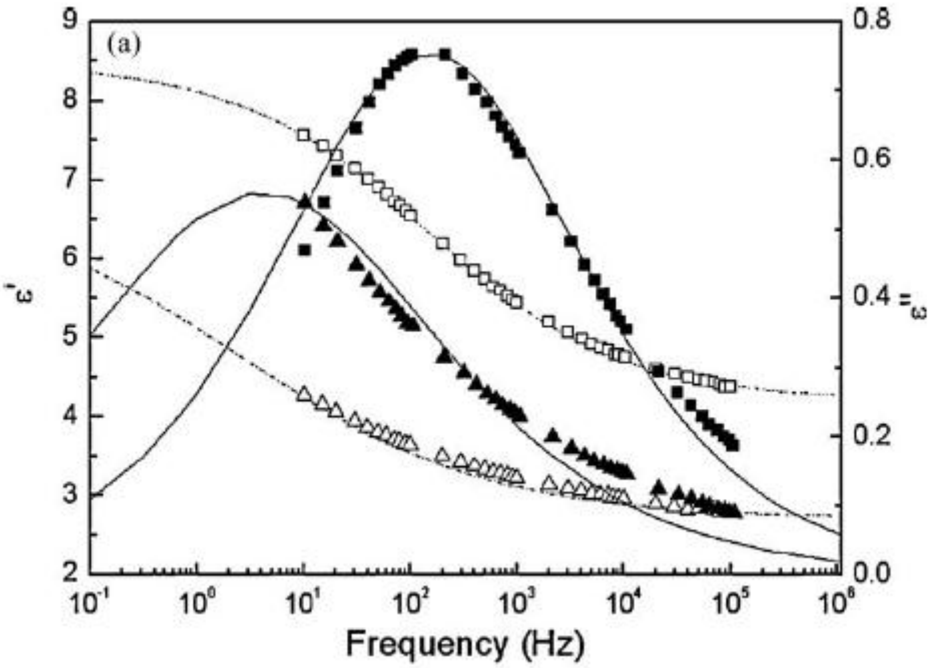


*Figure 7: Dependence of relative permittivity, ε′, and dielectric loss factor, ε′′, on frequency for (■, □) TNTs and (▲, △) P25. Reprinted from ref. [67].*

However, this model can be used, when the relaxation peak is symmetric (Fig. 7). In other cases this model provides inaccurate results. Hence, the model including another parameter, describing relaxation peak asymmetry has to be employed. Thus, Stenicka *et. al*. applied Havriliak-Negami model Eq. 8 and properly fit the dielectric spectra of polyaniline suspensions (Fig. 8) [40].

$$\varepsilon^*(\omega) = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{(1 + (i\omega \cdot t_{rel})^\alpha)^\beta} \tag{8}$$

Here, $\varepsilon'_s$, is relative permittivity at zero frequency, $\varepsilon'_\infty$, is relative permittivity at infinite frequency, $\omega$, is angular frequency, $t_{rel}$, is relaxation time and parameter, $\alpha$, usually lies between 0 and 1 and, $\beta$, is parameter representing the asymmetry of the relaxation peak and further including condition when $\alpha \,.\, \beta < 1$.

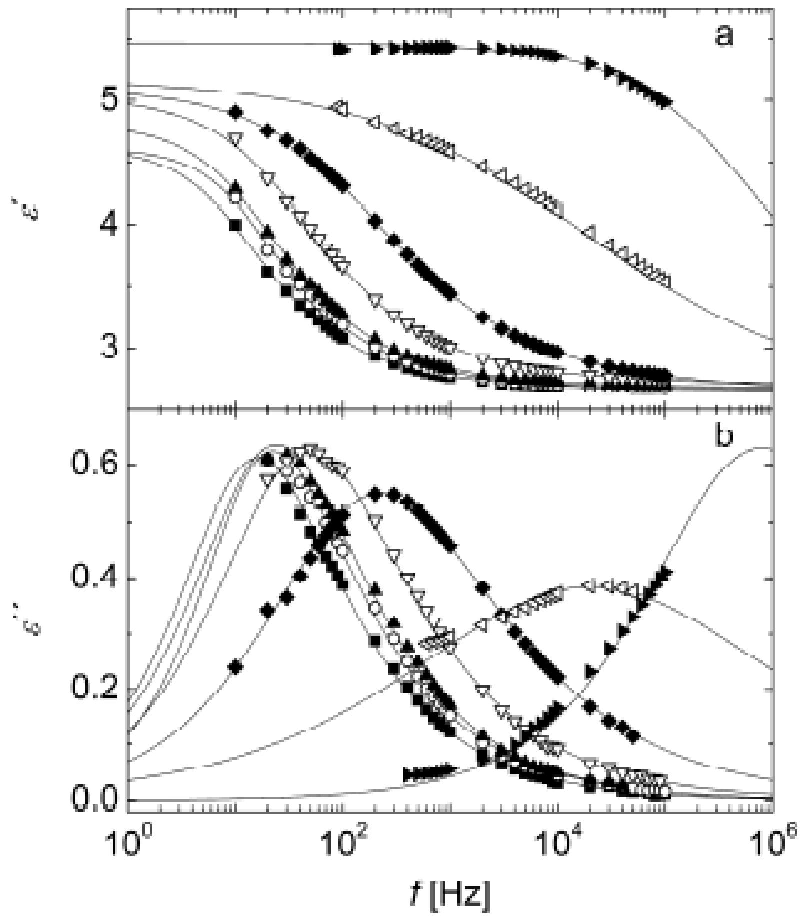


*Figure 8: Dependence of relative permittivity, $\varepsilon'$, and dielectric loss factor, $\varepsilon''$, on frequency for variously protonated PANI based suspensions. Reprinted from ref. [68].*

### 5.2 External electric field strength

Formation of the internal structures in ER suspensions is caused by an external field. Generally, toughness of the internal structures, which are represented by yield stress increases with increasing external field strength.

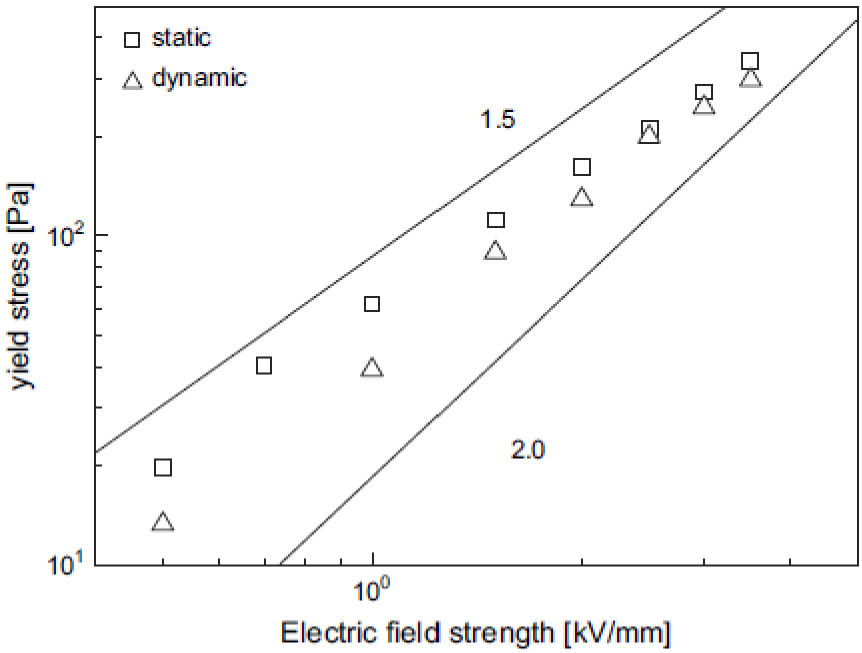


*Figure 9: Static and dynamic yield stresses vs. electric field strength for 1.5 DBSA-doped PANI based suspensions bounded by two slopes of 1.5 and 2. Reprinted from ref. [69].*

In case of ER suspensions, dependence of the yield stress on the electric field strength has two boundary conditions (Fig. 9). Yield stress, $\tau_y$, increases with $E^2$ and this is connected to the polarization mechanism, indicating that relative permittivity mismatch between particles and medium is essential to the interparticle forces and strengthen the internal structures [70, 71]. Thus, particles with high relative permittivity should provide suspensions with strong ER effect [72]. When the, $\tau_y$, increases with $E^{1.5}$ toughness of the internal structures is connected to the conductivity mechanism, where conductivity mismatch between particles and medium is responsible for the ER effect [73, 74].

## 6. Dispersed phase for MR suspensions

Materials used as dispersed phase in MR suspensions are limited on the ferro- or ferri-magnetic particles. Presence of the magnetic domains in the particles is necessary for formation of the internal structures in the suspensions after application of the external magnetic field.

The iron particles, mostly formed by carbonyl iron are used as a dispersed phase in MR suspensions [42, 75-77] due to their shape, wide size range from 1 to 10 $\mu$m and also suitable magnetic properties already described in section 5. Cobalt-ferrite, magnetite and maghemite particles can also used for preparation of MR suspensions, however their considerable lower magnetization saturation reduces MR effect. All mentioned materials based on iron, provide particles with relatively high density. Hence, fast sedimentation appears in the iron-based

MR suspensions. Moreover, iron particles exhibit also low thermal stability resulting in the considerable decrease in MR performance.

These disadvantages can be solved with the coating of the magnetic core, with usually polymer shell, when core-shell particles provide slightly reduced magnetic properties, while the sedimentation and thermal stability is significantly enhanced [77-80]. While the former types of coatings were based mainly on the physical bonding, covalent modification seems to be very promising, due to the good interaction between core and shell material and thus increased stability under high shear deformations [81].

Sedimentation stability can be further improved using small amount nanoparticles even non-magnetic, with negligible impact on the MR performance [38, 41]. Also new types of MR systems based on bidispersed or dimorphic particle suspensions with enhanced sedimentation stability were investigated [82, 83].

# 7. Factors influencing MR effect

## 7.1 Magnetic properties

Particles usually utilized as a dispersed phase in MR suspensions are mostly feromagnetic or ferimagnetic. The former is consisting of magnetic dipole moments in the magnetic domain of the same values and orientation (Fig. 10a). Such materials are iron (Fe), cobalt (Co) or nickel (Ni). On the other hand, the latter one includes the magnetic dipole moments in the magnetic domain of various values as well as orientation (Fig. 10b). These materials are usually iron oxides or oxides of other mentioned metals. The behaviour of the presented materials under magnetic field is very similar as can be seen in the (Fig. 10c and 10d) [84].

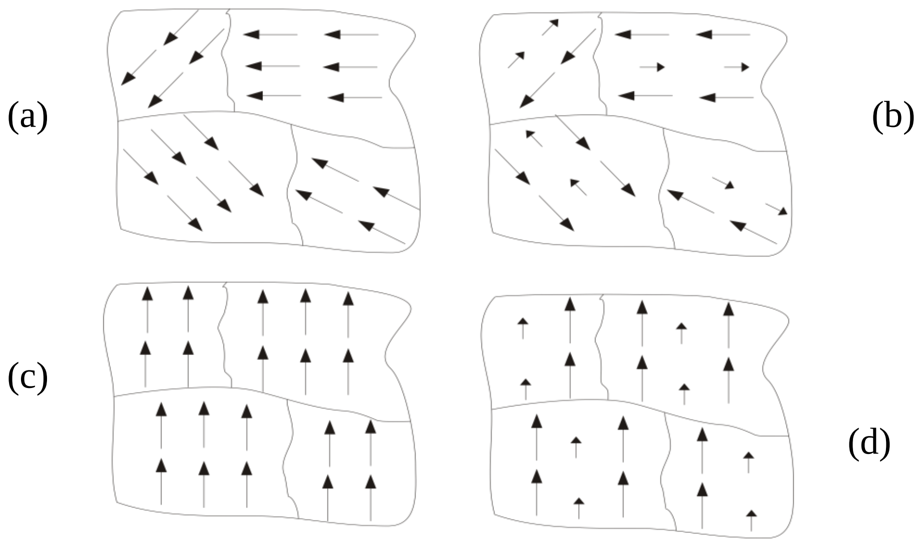


*Figure 10: Magnetic domain structure of ferro- (a), ferrimagnetic (b) material in the absence of external field, and ferro- (c), ferrimagnetic (d) material under external field applied Reprinted from ref. [84].*

Therefore, their magnetic properties of particles are very important for design of effective MR suspensions. Magnetization saturation, $M_s$, should be high because higher the magnetization saturation tougher the internal structures developed under external magnetic field. Further, low value of coercivity, $H_c$, is preferable for MR suspensions indicating value of residual magnetization after demagnetization [85, 86].

Magnetization saturation and other magnetic properties can be obtained from Langevin model Eq. 9 (Fig. 11a) [87].

$$M(H) = M_s \cdot \left[ \frac{1}{\tanh\left(\frac{m \cdot \mu_0 \cdot H}{k \cdot T}\right)} - \frac{1}{\left(\frac{m \cdot \mu_0 \cdot H}{k \cdot T}\right)} \right] \qquad (9)$$

Where, *M*s, is the magnetization saturation, *m*, is the magnetic moment, $\mu_0$, is magnetic permeability of free space ($4\pi.\ 10^{-7}$ Henry.m$^{-1}$), *H*, is magnetic field strength, *k*, is the Boltzmann constant ($1.38\ .10^{-23}$ J.K$^{-1}$) and, *T*, is temperature.

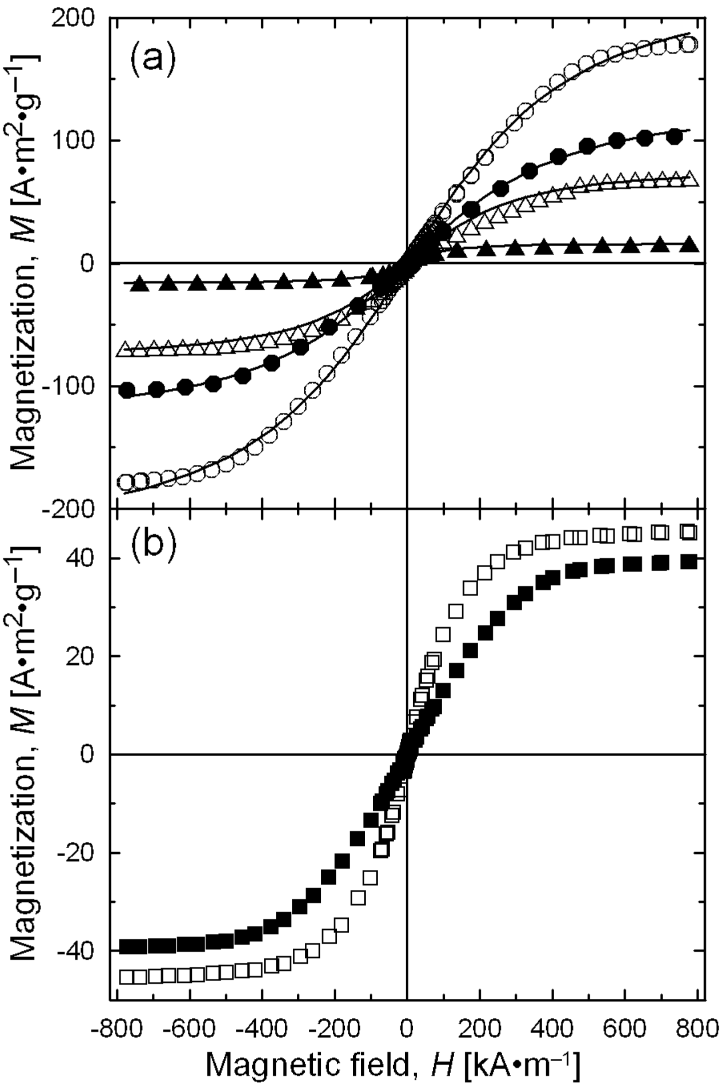


*Figure 11: Magnetization curve of uncoated (○) and coated (●) CI particles, uncoated (△) and coated (▲) Fe rod-like particles (a), and uncoated (□) and polysiloxane-coated (■) particles based dimorphic MR fluids (b). Solid lines are application of Langevin equation. Reprinted from ref. [82].*

### 7.2 External magnetic field strength

For the MR suspensions the yield stress, $\tau_y$, also increases with increasing external magnetic field strength. However, the increase is not linear in whole range of the applied magnetic field (Fig. 12). At low magnetic field strengths, $\tau_y$, increases with $H^2$, thus particles form the internal structures according to the dipole mechanism. On the other hand, at higher magnetic field strengths the contact regions between particles are magnetically saturated and thus, $\tau_y$, increases in the range $H^{1.5}$- $H^1$. Internal structure formation is therefore followed by magnetization saturation mechanism [65, 88-91].

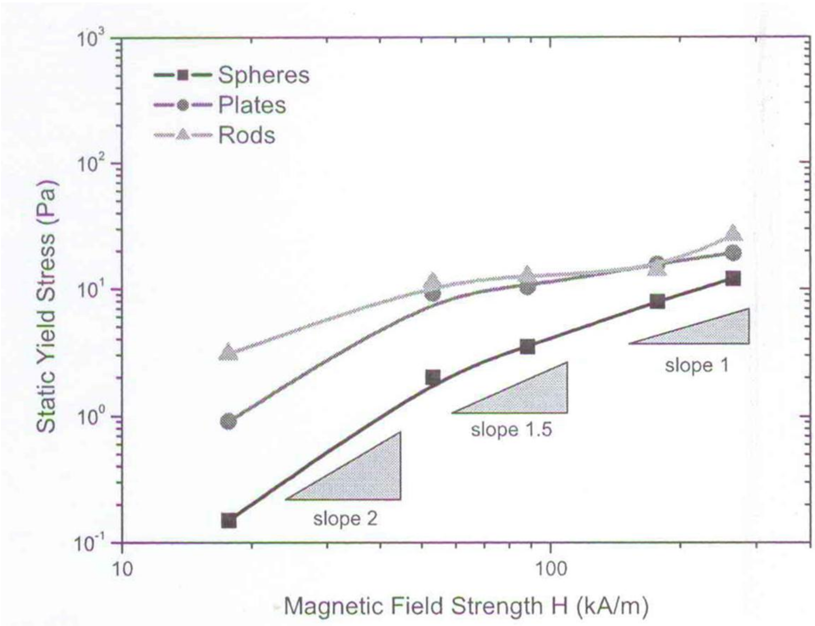


*Figure 12: Dependence of the static yield stress of MR fluids at different magnetic field strengths. Reprinted from ref. [91].*

### 7.3 Redispersibility

In the common MR suspensions there is a considerable difference in densities between dispersed phase and liquid medium and sedimentation takes place very quickly. When particles settle after certain time period, they may form a hard cake consisting of tightly bounded primary particles [92]. Therefore, the redispersibility of particles is very important and further dictates the rheological properties of MR suspension under applied field and thus their potential applicability in the real life [83]. Method for the redispersibility measurement is based on the penetration of the standard needle according to the (ASTM-D5-05a) connected to the device able to record force, *F*, necessary to be applied for penetration to the column of suspension (Fig. 13). Suspensions exhibiting lower penetration force will show easier redispersibility during long-term use.

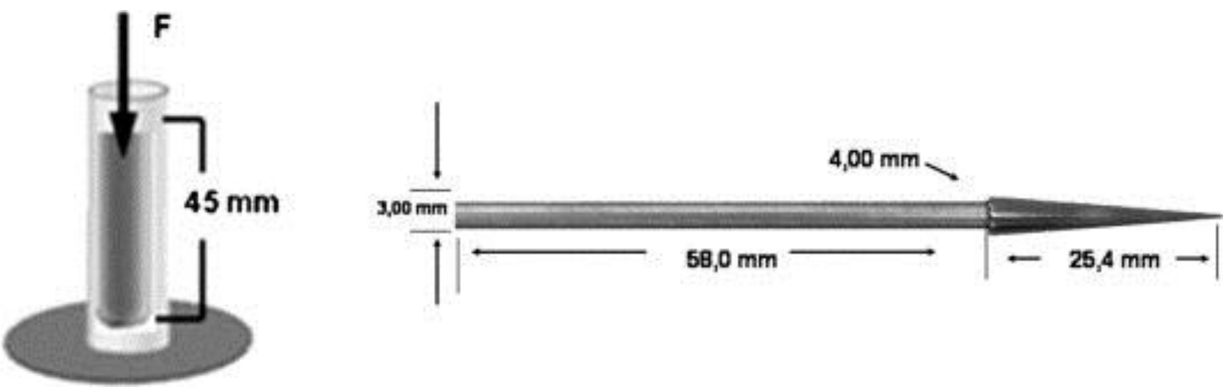


*Figure 13: Schematic illustration of the redispersibility measurement. Right: ATSM-D5-05a standard needle. Reprinted from ref. [83].*

# 8. Further factors influencing ER and MR effects

## 8.1 Temperature

Temperature is parameter limiting the use of both ER and MR suspensions. In the case of ER suspensions, the ER activity is more influenced by temperature, than that of MR ones because the magnetic properties are not so sensitive to temperature. Increased temperature intensifies the charge transport (conductivity) and also contributes to enhanced value of relative permittivity. Hence, usually with increasing temperature improved ER effect is observed [69, 75]. On the other hand, when the temperature is too high the structure formation is disturbed by intensified thermal Brownian motion and ER effect is weakened [93].

Temperature influences the liquid medium viscosity in the suspensions. With increasing temperature viscosity of the medium decreases and particles easily form internal structures under applied external fields [94]. However, the sedimentation rate could be increased, because lower viscosity enables easier sedimentation of dispersed particles.

## 8.2 Particle concentration, size and shape

There exists a minimal threshold concentration of the particles below which only small amount of weak internal structures can be created in the suspension. The optimal concentration, when the ER or MR effect is the highest, depends on the responsive particles used, but usually lies in the range from 15-40 vol. %. Higher concentration significantly increases field-off viscosity and thus ER efficiency, *e*, Eq. 10 decreases.

$$e = \frac{(\eta_E - \eta_0)}{\eta_0} \tag{10}$$

Where, $\eta_E$, is viscosity of suspension in the presence and, $\eta_0$, is viscosity in the absence of external electric field.

The optimal concentration of the particles is also connected to the size of the primary particles. In the case of ER suspensions the highest ER effect was observed for the nanoparticle-sized based suspension [31]. However, the off-state viscosity was relatively high and thus efficiency was comparable to those obtained for microparticles-sized based suspensions [95].

On the other hand, completely different situation was observed for MR suspensions. Here, the MR effect depends on the magnetic properties, more specifically on the value of magnetization saturation $M_s$ [96]. As was developed by many research groups, microparticle-sized magnetic particles exhibit higher values of $M_s$ than those of nanoparticles sized and thus enhance MR efficiency [76, 97, 98]. However, here should be taken into account that, magnetic particles usually have density around 7 and thus sedimentation appears very quickly in the liquid medium with density around 1. Hence, the size of the particles should be chosen with the respect to the sedimentation stability as well as to the MR performance.

Particle shape significantly influences intensity of ER and MR effects. While in the absence of the external field, suspensions of globular particles exhibit lower values of viscosity in comparison to the one dimensional particles. In the presence of the external field the globular particles have not that strong particle-particle interaction as was observed for the one dimensional ones. Here the one dimensional particles mostly represented by rods exhibit considerably enhanced interactions between particles under applied external fields and thus the toughness of internal structures is higher in comparison to globular ones.

Also the impact of the particle-size distribution influences suspension behaviour in the absence as well as in the presence of the external field While in the absence of the external field, suspensions with narrow particle-size distribution exhibit lower values of the viscosity in comparison to the suspensions with wide particles-size distribution, in the presence of the external field, the researchers found out that situation is vice versa [9, 82, 83].

## 9. Liquid medium for ER and MR suspensions

Liquid medium used in ER suspensions, due to the application of the high voltages in order of kV mm$^{-1}$, is preferably non-conducting usually based on water-free substances usually silicone [80], mineral [77] or vegetable [99] oils with low density, large variety of viscosities, low relative permittivity and negligible value of dielectric loss factor. For the purpose of potential applications the thermal and chemical stability of the medium is also very important. In case of MR suspensions much greater freedom is possible in the medium selection. Here, also silicone and mineral oils are frequently used [79, 82, 83] but glycol [100] and water based media [101] are effectively applied in MR suspensions as well. However, as was already mentioned, sedimentation of the particles is unfavourable in case of MR suspensions and thus the draft of suitable medium with connection to the potential applications, plays an important role. Generally, there are some methods how to solve the suspension stabilization. The first one is based on the steric stabilization, where the surface of the particles is coated with relatively thick and compact polymer layer. The second is electrostatic stabilization based on creation of the double layer on the surface leading to the enhanced suspensions stabilization [102, 103]. Unfortunately, both of these methods are not that effective especially in the case of ER suspension. The former one utilizing the thick polymer layer suppresses the ability of the particles to move freely and create internal structures in the presence of external field. The latter one, due to the change of the electrical properties of the particles negatively influences polarizability of the particles on the particles-silicone oil interface, resulting in the decrease of the ER efficiency.

# AIMS OF THE DOCTORAL STUDY

The aim of the doctoral study research can be divided into two main parts.

First part is concentrated on the synthesis of ER active materials based on one dimensional core-shell particles and investigation of ER properties of their suspensions under external electric field. Here, titanate rods are used as a core material and different amount of conducting polymer is forming its shell. Improved efficiency of ER suspensions based on one dimensional core-shell particles is expected. Furthermore, the novel ER material based on aniline oligomers prepared in one-step synthesis with controllable conductivity depending on the reaction procedure is prepared. Due to the adjustable conductivity of the particles the enhanced ER behaviour of their suspensions is also predicted.

Second part is concentrated on the synthesis of MR active materials based on core-shell particles and further on MR behaviour of their suspensions under external magnetic field. In this case the carbonyl iron particles are coated with polypyrrole ribbons, in order to improve long-term stability of their suspension, while MR efficiency is not going to be dramatically decreased. Similar approach is selected in the case of second synthesised material only instead of conducting polymer surface modification via two-step covalent synthesis is performed using low molecular substance cholesteryl chloroformate. Here, sedimentation, thermo-oxidation as well as good redispersibility is expected.

# SUMMARY OF THE PAPERS

In the following, summaries of the more important results from already published papers.

## 10. Enhanced ER efficiency

To investigate the influence of the shape as well as impact of the polymer coating to the ER efficiency, titanate/polypyrrole core-shell rod-like particles were synthesized. The core material (titanate rods) was prepared using solvothermal synthesis of titanium dioxide particles in concentrated solution of NaOH. After 24 hours the rod-like titanates particles were obtained by filtration of the white precipitate. Further, the particles were dispersed into surfactant cetyltrimethylammonium bromide solution, then the monomer pyrrole and oxidizing agent ammoniumpersulfate was introduced and reaction was carried out for 6 hours at 0°C and another 18 hours at room temperature. Further, the final core-shell particles were collected on the filter and dried at 60°C over vacuum.

Suspension including as prepared particles were compared with suspensions including both individual components.

From the investigation of the rheological properties (Figure 14) enhanced ER efficiency of the core-shell rod-like particle based suspensions was observed. Here it can be concluded, that one-dimesional particle based suspensions provide systems with enhanced ER efficiency in comparison to globular ones and further core-shell particle based suspension exhibit higher ER effect than those observed for both individual components [102].

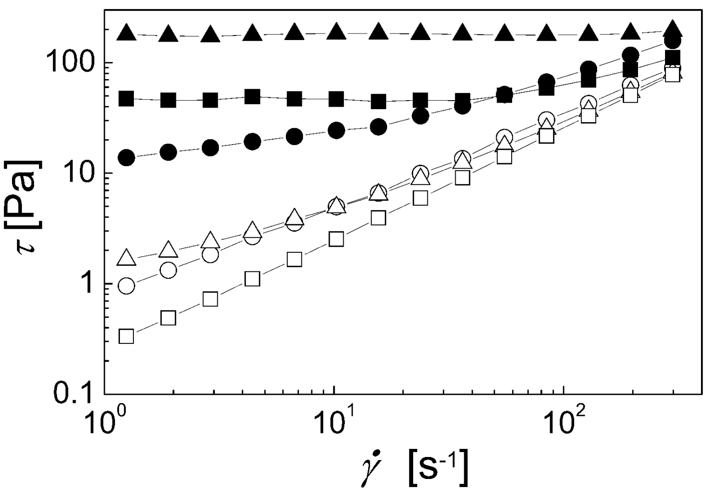


*Figure 14: Dependence of the shear stress, τ, on the shear rate, γ, for 5. wt. % various particles silicone oil suspensions at various external field strengths, E (kV.mm$^{-1}$): 0 (open symbols) 3 (solid symbols), where (□,■) – polypyrrole globular particles, (○,●) - neat titanate rods and (▲,△) – core-shell titanate/polypyrrole rod-like particles [104].*

## 11. Effect of conducting polymer polypyrrole on ER efficiency

Different amount of monomer pyrrole used for preparation of titanate/polypyrrole core-shell particles significantly influenced dielectric properties of final products. From the dielectric investigation of the suspensions (Figure 15) can be clearly seen that with increasing amount of the monomer used for polymerization, enhanced dielectric relaxation strength and shorter relaxation time was observed. Thus compact coating of the titanates particles with conducting polymer (polypyrrole) contributes to enhancement of ER efficiency of the core-shell particles suspensions [21].

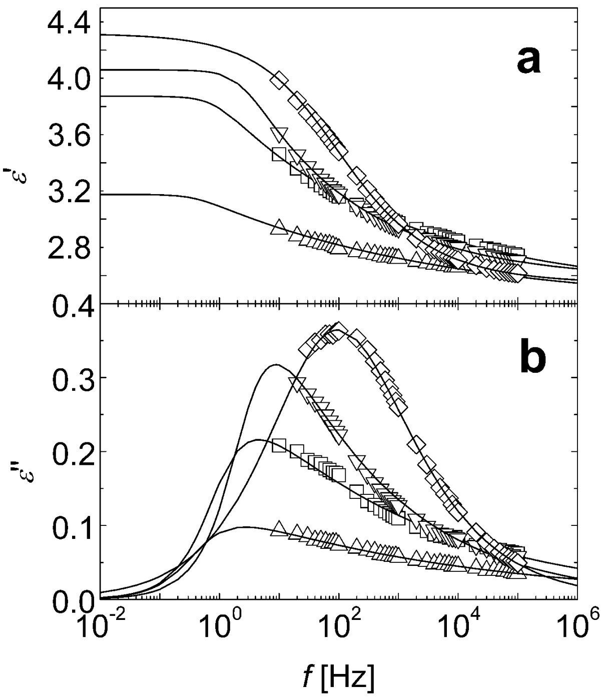


*Figure 15: Relative permittivity, ε′, (a) and dielectric loss factor, ε″, (b) as a function of the frequency, f, for 5 wt.% particle silicone oil suspensions for (△) - neat titanate, (□) - 1ml of pyrrole,(▽) – 2 ml of pyrrole, (◇) – 4 ml of pyrrole. Solid lines represent Havriliak-Negami model fit [21].*

## 12. ER material prepared in one-step synthesis

The novel material was synthesized via oxidative reaction of aniline with p-benzoquinone in the presence of various molar concentrated methanesulfonic acid (MSA). Depending on the molar concentration materials with oligoaniline structures with different conductivity were synthesized. Rheological properties of suspensions of such materials were investigated in the absence as well as in the presence of external electric field. Furthermore, aniline oligomer-based suspensions were compared to the standard suspensions including polyaniline base particles (Fig. 16). Here it was observed that aniline oligomer based suspension prepared by one step synthesis exhibited higher ER activity in comparison to suspension consisting of polyaniline base particles needed two-step reaction to provide  material with suitable ER activity [55].

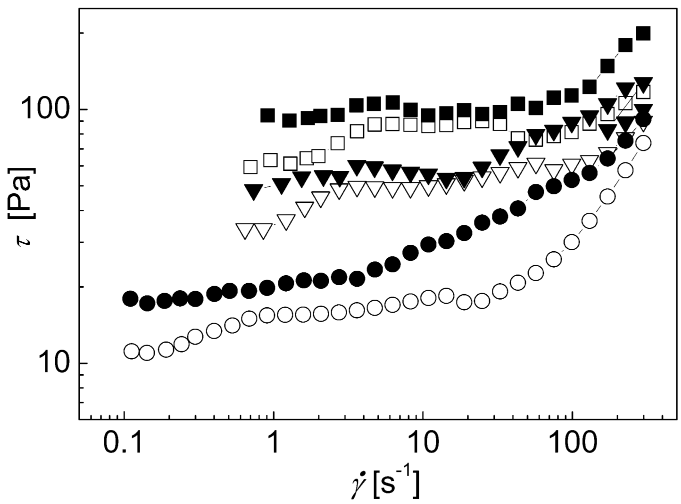


*Figure 16: Dependence of the shear stress, τ, on the shear rate, g, for 10 vol. % aniline oligomer (solid) and polyaniline base (open) particles silicone oil suspensions at various external electric field strengths, E (kV mm$^{-3}$): (●, ○) 0, (▼, ▽) 1, (■, □) 2. Adopted from ref. [55]*

## 13. Improvement of the sedimentation stability

Commercially available carbonyl iron particles were modified with conducting polymer (polypyrrole) layer. The carbonyl iron particles were dispersed in the distilled water and via oxidative polymerization of the pyrrole, with ammoniumpersulfate and appropriate ratio of surfactant to monomer, the surface of the carbonyl iron was coated with polypyrrole ribbon-like particles. This modification resulted in a slight reduction of the magnetic properties however they were still high enough for the use of modified particles in MR suspensions, while the sedimentation stability (Figure 17) was considerably enhanced, due to the partially decreased density of the particles and also better compatibility between modified surface and liquid medium [10].

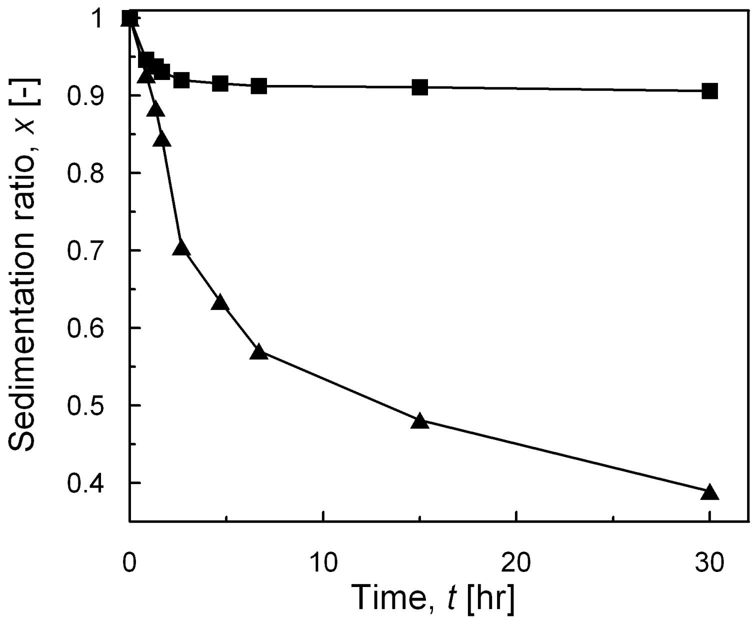

*Figure 17: Sedimentation stability test for 40 wt. % particle silicone oil suspensions for (▲) – bare carbonyl iron and (■) – coated carbonyl iron with polypyrrole ribbon-like particles [10].*

## 14. Covalently coated particles with enhanced redispersive properties

The two-step covalent modification was performed using low molecular weight substance cholesteryl chloroformate. The surface of the carbonyl iron particles was firstly activated, and then was functionalized with silane coupling agent and finally cholesteryl groups were synthesized on the surface. Such particles exhibited slightly lower value of magnetization saturation. Therefore, the MR performance of the coated particles is also slightly lower, but still on appropriate level to be utilized in the real applications. Moreover, the sedimentation and thermo-oxidation stability were improved. Because the covalent modification of the particles prevents the magnetic particle agglomeration MR suspensions exhibited better redispersibility properties in comparison to uncoated ones. Figure 18 shows higher stiffness of sedimentation cake of bare carbonyl iron particle suspensions over time as well. [105].

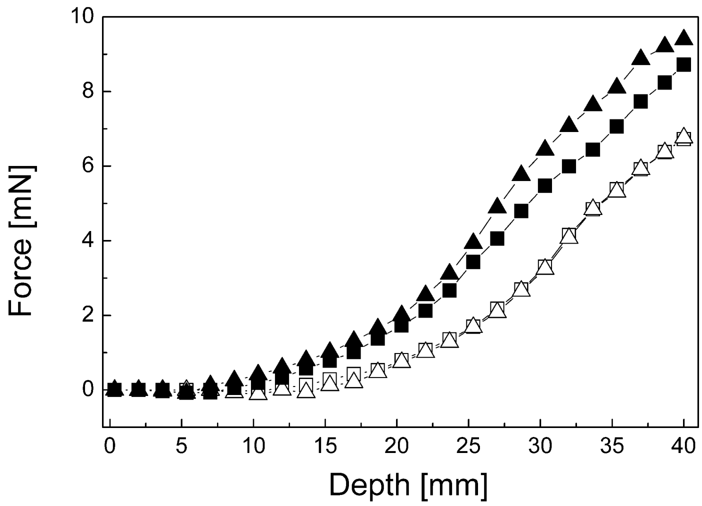


*Figure 18: Redispersibility test for 40 wt. % particle silicone oil suspensions for (▲, △) – bare carbonyl iron and (■, □) – coated carbonyl iron with cholesteryl groups, where open symbols represent suspension immediately after mixing of components and solid symbols after 5 days [105].*

# CONTRIBUTION TO THE SCIENCE

Thesis deals with ER and MR phenomenon-basic principles, role of the factors influencing the phenomenon. The main attention is paid to the preparation of the novel ER and MR suspensions based on core-shell composite particles with improved properties Benefits of this study to the field of electro and magnetorheology are as follows:

- Synthesis of novel titanate/polypyrrole core-shell particles with enhanced ER performance in comparison to the both individual components
- Novel ER core-shell composite particles with conducting shell enabling to control the performance of ER suspensions.
- Novel ER material based on aniline oligomers prepared via one-step oxidative reaction of aniline.
- Synthesis of novel carbonyl iron particles coated with polypyrrole ribbons of suitable MR performance.
- Novel MR core-shell composite particles with enhanced mutual compatibility to the silicone oil.
- Covalently bonded coating of carbonyl iron particles with improved sedimentation, thermo-oxidation stability and redispersibility of the MR suspensions.

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## LIST OF SYMBOLS AND ACRONYMS

| | | |
|---|---|---|
| $H$ | [kA m$^{-1}$] | magnetic field strength |
| $B$ | [mT] | magnetic flux density |
| CSS | | control shear stress mode |
| CSR | | control shear rate mode |
| $e$ | [–] | MR or ER efficiency |
| $E$ | [kV mm$^{-1}$] | electric field strength |
| *ER* | | electrorheological |
| $f$ | [Hz] | frequency |
| $F_p$ | [N] | pressure force |
| $F_s$ | [N] | shear force |
| $G^*$ | [Pa] | complex modulus |
| $G'$ | [Pa] | storage modulus |
| $G''$ | [Pa] | loss modulus |
| LVR | | linear viscoelastic region |
| $M_S$ | [A m$^{-1}$] | saturation magnetization |
| *MR* | | magnetorheological |
| $n$ | | Herschel-Bulkley index |
| $\Delta\varepsilon'$ | [–] | dielectric relaxation strength |
| $\varepsilon''$ | [–] | dielectric loss factor |
| $\varepsilon'_0$ | [–] | static relative permittivity |
| $\varepsilon'_\infty$ | [–] | high frequency relative permittivity |
| $t_{rel}$ | [s] | relaxation time |
| $\alpha$ | [–] | parameter characterizing broadness of the peak |
| $\beta$ | [–] | parameter characterizing the peak asymetry |
| $\gamma$ | [–] | strain amplitude |
| $\dot{\gamma}$ | [s$^{-1}$] | shear rate |
| $\eta$ | [Pa s] | shear viscosity |
| $\eta_0$ | [Pa s] | shear viscosity of Newtonian liquid |
| $\eta_{pl}$ | [Pa s$^{-1}$] | plastic viscosity |
| $\mu_0$ | [N A$^{-2}$] | magnetic permeability of vacuum |
| $m$ | [–] | magnetic moment |
| $k$ | [J.K$^{-1}$] | Boltzmann constant |
| $\rho$ | [g cm$^{-3}$] | density |
| $\tau$ | [Pa] | shear stress |
| $\tau_y$ | [Pa] | yield stress |
| $\omega$ | [rad s$^{-1}$] | angular frequency |
| $F$ | [mN] | penetration force |

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