Functionalized microfibers for field responsive materials and biological applications

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Outline

I- Use of microfibers in MR fluids: Why are they more efficient than spherical particles?

II- Fibers based on functionalization of sepiolite for ER and MR composites

Jessica Alves-Marins, Phd, Rio de Janeiro/Nice, may 2014

III- Magnetolysis of cancer cells with magnetic particles (spheres and rods)

Biran Wang, Phd, Nice, december 2012
Fiber shape prevents compaction and aggregation under sedimentation

Iron nanorods (growth in templates)

$L = 7.6 \pm 5 \mu m \quad \text{Aspect ratio} \approx 30$

Alumina template for electrodeposition of metal


Formation of a percolated network of fibers partly due to remnant magnetisation
Synthesis of magnetic wires in the presence of a magnetic field


B = 0.03 Tesla

Precursor: Co(OH)₂
Reduction agent: Ethylene glycol

Cobalt microwires
L = 60 ± 24 µm
Aspect ratio ≈ 12


B = 0.4 Tesla

Magnetite
L = 7 ± 4 µm
Aspect ratio ≈ 10
yield stress: comparison spheres/rods

Same observation for iron rods compared to iron spheres in J. De Vicente et al J. Rheol. 54, 1337 (2010)

Much larger yield stress with rods due to friction?
Yield stress and friction from magnetic torques


Macroscopic approach: \[ f_n = \frac{T_m}{2s} \]

Torque

Friction

\[ \tau = \frac{1}{V} \sum r_z f_y \]

\[ r_z = s \cos(\theta) \]

\[ f_y = f_n \cos(\theta) + \xi f_n \sin(\theta) \]

Yield stress given by the maximum of \( \tau_s(\theta) \)

Magnetic susceptibility of aggregates

Order of magnitude:

\[ \tau_Y = \chi_a(H) \Phi \mu_0 H^2 \]

Two unknowns:
- internal volume fraction of aggregates \( \Phi_a \)
- the friction coefficient \( \xi \)
Susceptibility of an aggregate of fibers/spheres

Magnetic susceptibility for pure cobalt: \( \chi_p (H) = \frac{70}{1 + \frac{70}{1370} H} \)

\( n \): demagnetisation factor \( n= \frac{1}{3} \): sphere \( n_{//}= 0 ; n_{\perp} = 0.5 \): needle

\( \Phi_a \): volume fraction inside the aggregate

Maxwell-Garnett theory:

\[
\beta_{//} = \frac{1}{3} \frac{\chi_p}{1 + n_{//} \chi_p} \quad \beta_{\perp} = \frac{1}{3} \frac{\chi_p}{1 + n_{\perp} \chi_p}
\]

Random orientation of fibers:

\[
\chi_{\text{fiber - i}} = \frac{(\beta_{//} + 2\beta_{\perp}) \Phi_a}{1 - (n_{//} \beta_{//} + 2n_{\perp} \beta_{\perp}) \Phi_a}
\]

Aligned fibers:

\[
\chi_{\text{fiber - a}} = \frac{3 \beta_{//} \Phi_a}{1 - 3n_{//} \beta_{//} \Phi_a}
\]

Suceptibility of aggregate of fibers several times higher than for aggregates of spheres
Comparison Fibers/spheres; theory/experiment

Cobalt rods (aspect ratio=10)/versus cobalt spheres

Phi=5%

$\xi=0, \Phi_a=0.64$

$\xi=0.4, \Phi_a=0.50$  { Fibers:Theory

Fibers:Experiment

Spheres:theory

Spheres:experiment
Comparison with theory for magnetite spindle

Not possible to say if friction plays a role or not because internal volume fraction of aggregates : $\Phi_a$ is unknown.
Typical aggregates of spindle like particles

Without field

H=600 Oe

The orientational order is not perfect and the internal density $\Phi_a$ depends on this order (and so on the field)

Macroscopic approach: torque on the aggregates

Microscopic approach: rupture between particles
For the same volume and aspect ratio the rupture stress is much larger for fibers than for chain of spheres.

Rupture stress: comparison sphere/fiber

Electronic balance

Nickel fibers
Conclusion about the comparison sphere/fiber for MR fluids

1) The main cause of enhancement of yield stress with fibers is the increase of the permeability of the suspension due to the elongated shape

2) Not possible to tell if friction plays a role or not due to the lack of knowledge of $\Phi_a$; may be by numerical simulation?

Keep in mind: the maximum volume fraction with fibers is lower than with spheres

II- High aspect ratio using functionalized sepiolite fibers

Aspect ratio of sepiolite: \( <r> = 25 \)

Density \( \rho = 2.3 \text{g/cm}^3 \)

Sepiolite is a fibrous clay. Silanol groups \( \text{SiOH} \) are used to graft magnetite on their surface.
Grafting magnetite on sepiolite

Reaction of sepiolite with DAPTMS in ethanol

Magnetite grafted with Glycidoxypropyltrimethoxysilane (Glymo)

Partial coverage of sepiolite by magnetite

Reaction

$T=70^\circ C$ +$H_2SO_4$
Sepiolite grafted with magnetite

Magnetisation curve

Rheogram

Use as an oriented filler in epoxy resin
Alignment of fibers inside cured Epoxy

Sepiolite and magnetite are covalently bounded to epoxy

Epoxy molecule

Curing molecule

Electromagnet

T=130°C

H
Modulus of the composite Sepiolite/epoxy matrix

\[ E = \Phi E_{\text{sepiolite}} + (1-\Phi)E_m \]

with \( E_{\text{sepiolite}} = 100 \text{GPa} \)

\[ E = 10^{-11} \text{GPa} \]

*Increase of modulus of 800 MPa in the presence of aligned fibers

* Strongly anisotropic epoxy composite
Functionalization of Sepiolite with polyaniline (PANI) for ER fluids

Aspect ratio ≈ 8

Polymerization of Aniline:

\[\text{Aniline} + 2\text{SO}_2^- + 2n\text{H} \rightarrow \text{PANI} \]

Hybrid SP fibers

Pani-Clusters

200nm

Sepiolite 50%_Pani50%

Aspect ratio ≈ 25
Comparison Sepiolite/Pani (SP) and Pani

The yield stress and especially the shear modulus are much higher for the composite than for pure PANI.

\[ \tau_y \propto E^{1.24} \]

\[ 3 < \frac{\tau_{SP}}{\tau_P} < 6 \]

\[ G'_{SP} / G'_P \approx 10 \]


The yield stress and especially the shear modulus are much higher for the composite than for pure PANI.
Possible explanation for the better performance of Sepiolite-Pani (SP)

**Dipolar force**  \( \propto m^2 \propto \beta^2 \)

Generalization to the case of ellipsoids:

\[
\beta^2 = \frac{1 + (\omega \tau_0)^2}{1 + (\omega \tau_{MW})^2} \left( \frac{\sigma_p - \sigma_f}{3(\sigma_f (1 - n_z) + \sigma_p n_z)} \right)^2
\]

\[
\tau_0 = \frac{\varepsilon_p - \varepsilon_f}{\sigma_p + \sigma_f}
\]

\[
\tau_{MW} = \frac{(1 - n_z)\varepsilon_f + n_z\varepsilon_p}{(1 - n_z)\sigma_f + n_z\sigma_p}
\]

\( \sigma_f \ll \sigma_p \quad \varepsilon_f \ll \varepsilon_p \)

**Ratio of dipolar forces**  \( \frac{\beta^2 (\sigma_{SP}, n_{zSP})}{\beta^2 (\sigma_p, n_{zp})} \approx 5 \)

**Conductivity:**  
\( \sigma_{SP} = 2 \times 10^{-7} \)  
\( \sigma_p = 7.3 \times 10^{-6} \)

**Depolarization factor**  
\( n_{zSP} = 0.005 \)  
\( n_{zp} = 0.03 \)

Still a shape effect; could be amplified by increasing the conductivity (better coating of sepiolite by PANI)
III-Biological applications of magnetic fibers

-Hyperthermia
  
  B.Wang, PhD, Nice, December 2012

Specific loss power (Watt/g):

\[ SLP = \frac{\mu_0 \nu}{1000 \rho} \int_{H_{\text{min}}}^{H_{\text{max}}} M_z(t) \frac{dH}{dt} dt \]

\( \nu = 50\text{kHz}, \quad H = 2000\text{Oe} \)

SLP = 100W/g

-Nanofibers of cobalt

-Capture of pollutants
  
  C.Magnet, PhD, Nice, December 2013

One stage without loss of specific surface

With a nanofiber (sepiolite) coated by magnetite NP

Two stages: 1) capture of pollutant on magnetite NP
  
  2) capture of NP on nickel microspheres

-Magnetolysis of cancer cells
Destruction of cancer cells with magnetic nanoparticles

Fe₃O₄ MNP (15nm sphere) in 200nm of pyrene sphere  
- Hu et Gao. JACS, 2010

Fe-Ni microdiscs (60nm thick, ~1µm diameter)  
- Kim et al. Nat Mater, 2009

Electrodeposition of Ni nanowires,  
(4.4 µm long, 200nm diameter)  
Particles used

Reduction of hematite under H$_2$ at T=400°C and coating with gold (J. Mendez-Garza et al. 2013)

SEM image of acicular Fe@Au NPs

Carbonyl iron particles

\[ \langle d \rangle = 1\mu m \]
Experimental setup

- Well defined magnetic force

Force on the particles: \[ F_H(t) = \mu_0 \chi V_p H(t) \nabla H_x \]

- Petri Dish
- Magnetic particles above cancer cells
- Feeding liquid
- Magnet
- Electromagnetic Exciter

\[ H(t) = H_{\text{min}} + \frac{\Delta H}{2} (1 + \sin \omega t) \]
Mortality test

counting of dead cells

Trypan blue
a vital stain used to selectively colour dead tissues or cells
Mortality test: Results

0.02wt% in the suspension represents 0.5% volume particles/volume of cells

Not too much difference between spindle and spherical particles

A constant applied force has no effect on the mortality
Alternating indentation by AFM tips

Need to reach an indentation depth >100nm to damage the cells
Theory of indentation by particles

\[ J(t) = \frac{1}{G_0} \left( 1 - \frac{G_1}{G_1 + G_0} e^{-t/\tau_1} \right) \]

With \( \tau = \tau_1 \left( \frac{G_1 + G_0}{G_1} \right) \) and \( \tau_1 = \frac{\eta_1}{G_1} \)

**From AFM experiments:** \( G_0 = 210 \text{Pa} \) \( G_1 = 181 \text{Pa} \) \( \tau_1 = \eta_1 / G_1 = 5.6 \text{s} \)

*B.Wang et al Micron, 44(2013), 287*

Hertz theory (static case):

\[ F = \frac{16}{3} \sqrt{R} \frac{1}{J} \delta^{3/2} \]

\( \delta \): depth of penetration \( J = 1/G \):
invert of shear modulus

For a cone of angle \( \beta \)

\[ F = \frac{8}{\pi \tan(\beta)} J \delta^2 \]

\[ \delta^2(t) \text{ or } \delta^{3/2}(t) = \frac{1}{C} \int_0^t J(t - t') \frac{dF(t')}{dt'} \, dt' \]

Time dependent Hertz model (linear theory)
Result for the alternating indentation

Comparison between theory and FEM (Abaqus) for indentation of a spherical particle under an alternating magnetic force; $f=2\text{Hz}$

Predicted indentation is an order of magnitude too small compared to indentation causing mortality with AFM.
Importance of clustering

Hertz model:

Conical tips\[ F = \frac{2}{\pi} \frac{E}{1-v^2} \frac{\delta^2}{\tan \beta} \Rightarrow \delta \propto F^2 \]

Spherical tips\[ F = \frac{4}{3} \sqrt{R} \frac{E}{1-v^2} \frac{\delta^2}{\delta^2} \Rightarrow \delta \propto F^3 \]

Before field application

![Before field application](image1)

After field application

![After field application](image2)

*Cluster formation is needed to destroy the cells
*A static force has no effect on the cell mortality
Main Conclusions

1) The better performance of rods against spheres is more related to the decrease of demagnetisation (depolarization) field than to friction.

2) Functionnalized sepiolite seem promising both for MR and ER fluid (large aspect ratio, low density).

3) Mechanical destruction of cells by submicronic magnetic particles is due to the formation of aggregates and is likely related to the time delay needed to close the pores.


Need for a better coverage.

Need to determine the relaxation time of pores.