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Dedicated to Academician Professor Dr. Emil Burzo on His 80th Anniversary

MAGNETIC FLUIDS AND NANOCOMPOSITES: IMPROVING THE MAGNETIC RESPONSE

**V. SOCOLIUC[1], R. TURCU[2], D. SUSAN-RESIGA[1],
T. BORBÁTH[3], L. VÉKÁS[1*]**

ABSTRACT. Magnetic nanofluids, nano-micro composite fluids and polymeric nanocomposites designed for leakage-free rotating magnetofluidic seals and for biomedicine and magnetic separation are reviewed. The synthesis procedures and the magnetic and magnetorheological properties are discussed in terms of achieving the highest volume or mass magnetization of the nanomaterials prepared for specific applications.

Keywords: *magnetic fluids, ferrofluids, magnetic nanocomposites, nano-micro composite fluids, magnetic properties, magnetorheological properties*

INTRODUCTION

Magnetic field control of the motion and positioning of magnetizable fluids (ferrofluids and magnetorheological fluids) and magnetic nanocomposite particles is highly relevant both for engineering and biomedical applications of these nanomaterials [1,2,3]. Magnetic properties, such as volume magnetization of magnetic fluids and mass magnetization or magnetic moment of nanocomposite particles, are determined by the magnetic particle content and are tailored by adequate synthesis procedures [2].

Among the engineering applications, the performances of leakage-free rotating seals with magnetic fluids are fully determined by the magnetic and flow properties of the sealing fluid [4]. The sealed pressure difference is mainly determined by the fluid

[1] *Romanian Academy-Timișoara Branch, Center for Fundamental and Advanced Technical Research, Lab. Magnetic Fluids, 24 M. Viteazu Ave., 300222 Timișoara, Romania*
[2] *National Institute R&D for Isotopic and Molecular Technologies, 67-103 Donat str., 400293 Cluj-Napoca, Romania*
[3] *ROSEAL Co., 5A Nicolae Balcescu str., Odorheiu Secuiesc, Romania*
* *Corresponding author e-mail: vekas@acad-tim.tm.edu.ro, vekas.ladislau@gmail.com*

magnetization and by the highest value of the magnetic induction in the sealing stage. To achieve high magnetization the magnetic content of the ferrofluid has to be increased as much as possible, the saturation magnetization being determined by the volume fraction of magnetic nanoparticles stably dispersed in the carrier liquid. At the same time, the particle volume fraction directly influences the flow properties of the sealing fluid and consequently, the viscous dissipation in the constitutive stages of a rotating seal. The increase of dispersed particle concentration implies an exponential increase of the dynamic viscosity, which limits the saturation magnetization of commercial sealing ferrofluids usually to approx. 600 G [5].

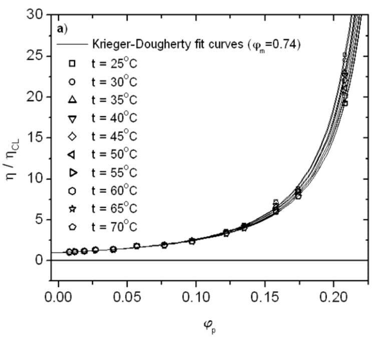
For specific applications in the field of high gradient magnetic separation of biomaterials [6] or in magnetic drug targeting and medical imagistics [7], the nanocomposite particles obtained from magnetic nanoparticle clusters of controlled shape, size, and high magnetic moment in an external magnetic field are of particular interest.

In both kinds of applications, the high magnetic response of the nanomaterials involved is the essential requirement to be considered by the specific synthesis procedures applied. In what follows, some recent results concerning high magnetization sealing fluids and polymeric nanocomposites will be reviewed.

HIGH MAGNETIZATION SEALING FLUIDS

Leakage-free dynamical sealing is among the most important and widely used applications of magnetic fluids [8]. The high vacuum ferrofluidic (FF) rotating seals (FF feedthroughs) and also pressure seals are valuable components of a lot of high-tech equipment [9].

The need to extend the applications to relatively high pressure differences, at the order of tens of bars, requires increasing the saturation magnetization M_s of ferrofluids. In case of magnetite ferrofluids, the upper limit of the solid volume fraction and its influence on the structural and flow properties were discussed in [10]. Transformer oil based magnetic nanofluid samples were prepared applying a previously developed procedure [11,12] involving chemical coprecipitation, followed by steric stabilization of magnetite nanoparticles. The basic procedure was refined and optimized for the synthesis of high concentration magnetic fluids using oleic acid, an unsaturated carboxylic acid, qualified as highly efficient in stabilizing the magnetic nanoparticles in hydrocarbon carriers [13]. Corresponding to the solid volume fraction of 21% the hydrodynamic volume fraction of the most concentrated sample is about 59%, which is close to the maximum random packing fraction of spheres (64%) [10]. This means that practically the upper limit for engineering applications was attained. Indeed, the reduced particle clustering tendency (mean number of particles per cluster estimated to be approx. 1.26) and the dependence of dynamic viscosity on the magnetic content are still adequate for sealing applications. The dynamic viscosity dependence on the magnetic solid volume fraction (**fig. 1a**) and on the hydrodynamic volume fraction (**fig. 1b**) are well described by the Krieger-Dougherty type function in the operating temperature range of interest for MF seals, up to the highest concentration of surface coated particles close to the maximum random packing. By optimizing the mean particle size (6-7 nm) and the sterical stabilization of nanoparticles by chemisorbed oleic acid monolayer, while eliminating the excess surfactant, the saturation magnetization of ferrofluids attained 1200 G (95 kA/m). The flow properties of transformer oil based ferrofluids show Newtonian behavior up to the highest volume fraction [10] which denotes excellent colloidal stability. This is a basic requirement for rotating seal applications involving long-term stability in strong and very non-uniform magnetic field (B_{max} approx. 1-1.5T; field gradient ~10^9 A/m^2).



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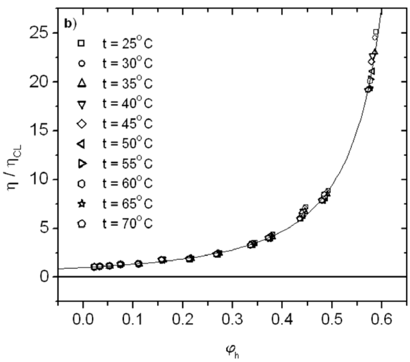

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Fig. 1. Composition and temperature dependence of dynamic viscosity a) solid volume fraction; b) hydrodynamic volume fraction (Reproduced with permission from [10], fig.6; Copyright Elsevier Publ.Co.).

A recent trend to obtain high magnetization ferrofluids involves the synthesis of Co, FeCo and Fe nanoparticles by thermal decomposition of carbonyl precursors in the presence of aluminium organics [14]. Surface coated with Korantin SH (N-oleylsarcosine, AOT (sodium dioctyl sulfosuccinate) or LP4 (fatty acid condensation polymer) after smooth surface oxidation, the procedure yields Co magnetic fluids with very high magnetization (over 1700 G (135 kA/m)) and long-term colloidal stability [14]. The saturation magnetization attained by these Co ferrofluids exceeds with about 35% the magnetization of magnetite ferrofluids discussed above. However, results concerning the behavior of Co ferrofluids in rotating seals are not available.

A possible solution to further increase the saturation magnetization is to consider extremely bidisperse magnetizable fluids, such as ferrofluid based suspensions of carbonyl iron particles of several micrometer sizes [3], i.e. nano-micro composite magnetizable fluids (CMFs). The use of CMFs in rotating seals was thoroughly examined by investigating the magnetic properties [15] and magnetorheological behavior [16,17], the sealing capacity [4,18] and the structural processes [19] involved, depending on the volume fraction of Fe particles dispersed in the concentrated ferrofluid carrier. The behavior of CMFs in non-uniform magnetic field, specific to ferrofluidic rotating seals, was investigated by X-ray microcomputed tomography (XμCT), which allows three-dimensional visualization of microstructures of particles even at a single Fe particle level [19]. In a non-uniform magnetic field the XμCT imaging technique allowed to depict not only the surface deformations of the Rosensweig instability but also the internal Fe particle structures within a nano-micro composite magnetizable fluid spike. This noninvasive technique for the microstructural investigation of magnetizable composite fluid systems evidenced the migration of Fe particles along the gradient of the non-uniform magnetic field, but no particle separation from the FF carrier was observed; this supports the use of CMFs in magnetic fluid rotating seals [4]. In **fig. 2** there are reconstructed tomography images of CMF spikes similar to those first analyzed in [4] (the light yellow–brown colour represents the iron particle and the blue–grey colour shows the magnetic nanofluid carrier liquid), which evidence the migration of Fe particles towards the top of spikes, without separation of the Fe particles from the carrier, which could occur in a conventional magnetorheological fluid.

The saturation magnetization of CMFs shows a linear increase with the volume fraction of Fe particles and attains approx. 700 kA/m for 40% Fe content [17]. However, the use of CMFs in rotating seals is strongly restricted by the orders of magnitude increase of the effective viscosity and yield stress in magnetic field. To exemplify, for sealing applications 10% Fe content gives M_s=2900 G (230 kA/m), improving 2.4 times the sealing capacity corresponding to a high magnetization ferrofluid (1200 G). Higher Fe volume fractions produce significant yield stress increase and pronounced magnetoviscous effect [17], which limit the use of CMFs to very low rotation speed MF seals. To illustrate the effect of added micrometer size multidomain ferromagnetic (Fe) particles, the dynamic (Bingham) yield stress is plotted versus magnetic flux density in **fig. 3**, for increasing values of the Fe particles volume fraction φ.

Fig. 2. Nano-micro composite fluid (CMF) in non-uniform magnetic field: formation of spikes similar to Rosensweig instabilities in case of ferrofluids

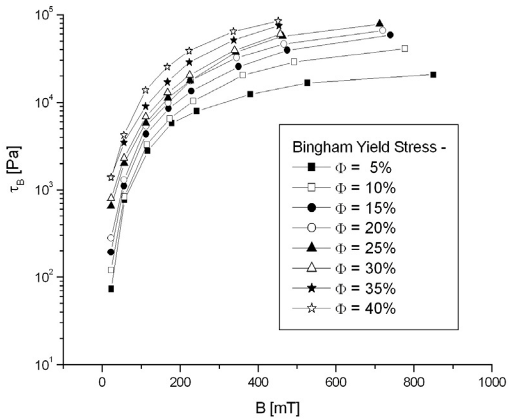

Fig. 3. Bingham yield stress versus magnetic induction-samples with various Fe particle volume fraction φ (using measured data from [17])

For the same set of samples, the magnetoviscous effect (relative increase of effective viscosity) for a moderate shear rate (100 s^{-1}) shows a significant increase due to the added Fe particles (**fig. 4**).

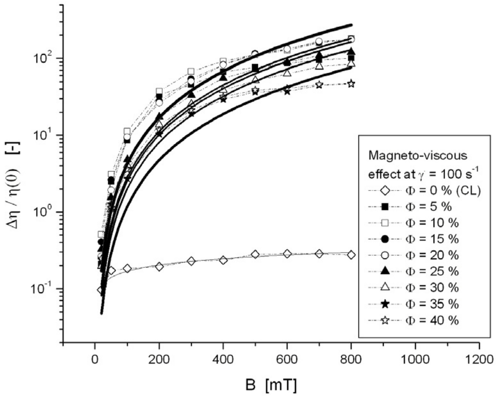

Fig. 4. Magnetoviscous effect for CMFs at 100 s^{-1} shear rate; the influence of Fe volume fraction φ (using measured data from [17])

The measured sealing capacity vs. M_s is given in **fig. 5** for a set of ferrofluids (magnetic nanofluids) and CMFs [4] with increasing saturation magnetization values, the $\Delta p \approx M_s B_{max}$ linear dependence being approximatively respected.

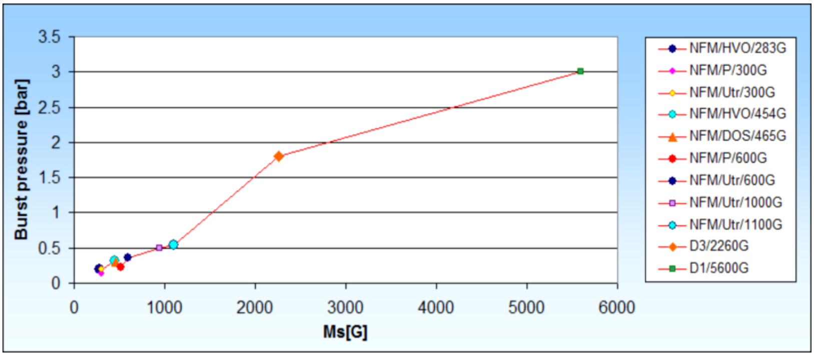

Fig. 5. The burst pressure (sealing capacity) vs. saturation magnetization measured for a single stage MF seal (Ref. [4]).

The very high magnetization nano-micro composite magnetic fluids considerably improve the sealing capacity of MF rotating seals. A 2-3 times increase of the sealed pressure difference may be achieved by using a CMF with moderate (5-15%) volume fraction of Fe particles.

MAGNETIC NANOCOMPOSITES: HIGH MAGNETIZATION CORE-SHELL PARTICLES

A wide variety of synthesis procedures have been reported which exploit the specific composition and property of both the polymeric material and the magnetic nanoparticles used as primary materials, to achieve the required functionalization, morphology and magnetic nanoparticle volume distribution in various types of magnetic beads. Superparamagnetic iron oxide - magnetite and maghemite- nanoparticles are the most used constituents of magnetoresponsive nanosystems-magnetic beads- in the rapidly expanding researches and applications in nanomedicine and biotechnology, including magnetic resonance imaging, magnetic drug delivery systems, magnetic fluid hyperthermia and HGMS separation of cells, proteins and other valuable bio-compounds [6,20,21]. The high magnetic moment of the functionalized carriers is among the most important requirements for successful applications in biomedicine and biotechnology [22,23]. To fulfil this, the optimal localization and amount of magnetic nanoparticles in the magnetic-nonmagnetic material structure, which are essential for the overall magnetic response, favour the magnetic core-organic shell type nanostructures [24]. In the ideal case, densely packed clusters of surface-coated superparamagnetic nanoparticles 5–20 nm in size form the magnetic core of polymeric particles. The requirements for the organic functional shell are determined by the particular application, such as magnetic drug targeting [21,22] or magnetic separation [6]. For both applications the resultant magnetic moment of the core-shell type magnetizable beads in an applied magnetic field is a key property, controlled by the magnetic moment density and the size of particles. Indeed, in the absence of an external magnetic field, the resultant magnetic moment of the nanocomposite particles is zero, while in a nonzero field, the permanent magnetic moments of the constituent nanoparticles align along the field direction, resulting in a net magnetic moment of the particles. Concerning the preparation of magnetic core–polymeric shell-type particles, the ferrofluid-based techniques proved to be efficient, providing a highly reproducible manufacturing procedure [25,26]. This involves controlled clusterization of surface-coated magnetic nanoparticles (MNPs) [27] of a light hydrocarbon based ferrofluid, using the oil-in-water miniemulsion method [28]. The saturation magnetization of these colloidal clusters (NPCs) is dependent on the mean size of the MNPs, packing density and organic (non-magnetic) content. The synthesis procedure for NPCs coated with the surfactants SLS or CTAB is highly reproducible and is suitable for upscaling [28]. The hydrophilic NPCs obtained (**fig. 6**) were further used for encapsulation into polymers. Such densely packed magnetic nanoparticle clusters in polymer shell (**fig. 7**) provided high magnetization spherical particles, promising for both magnetic drug delivery [29] and magnetic separation [30]. The saturation magnetization M_S of NPCs has relatively high values: M_S=63.9 A·m^2/kg for NPCs stabilized with SLS; M_S=76.7 A·m^2/kg for NPCs stabilized with CTAB (**fig. 8**). After polymer coating of NPCs stabilized with

SLS and CTAB, the magnetization of the microgels decrease: M_S=46.8 A·m^2/kg for *M1-pAAc*; M_S=43 A·m^2/kg for *M2-pNIPA-pAAc*; M_S=55 A·m^2/kg for *M3-pAPTAC* (**fig. 8**).

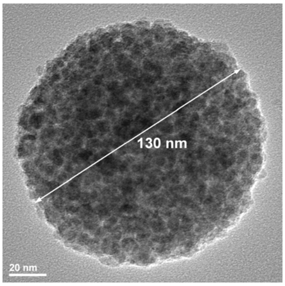

Fig. 6. Magnetic nanoparticle cluster obtained by ferrofluid miniemulsion procedure (reproduced from fig.2, Ref. [30])

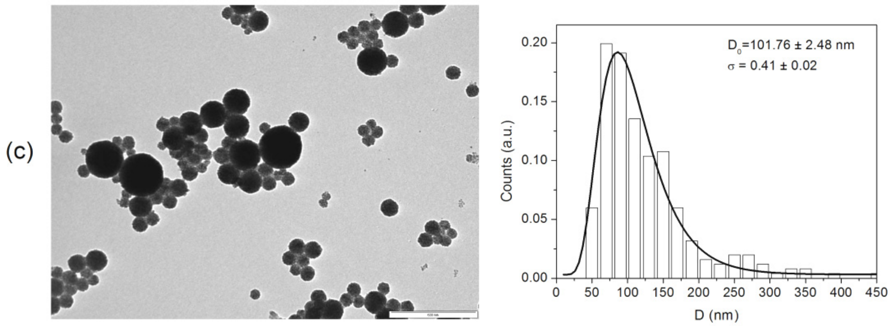

Fig. 7. TEM images of magnetic microgels and their size distributions: sample M3-pAPTAC (reproduced from fig.2, Ref. [30])

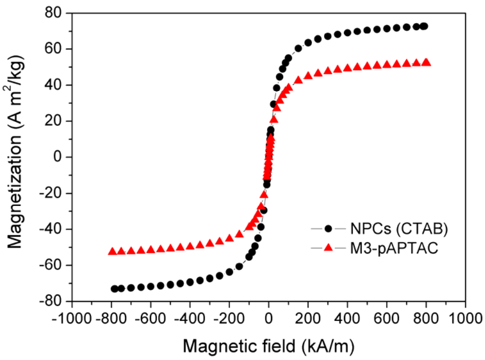

Fig. 8. Magnetization curves for magnetic nanoparticle clusters (NPC) and magnetic microgels (pAPTAC) (reproduced from fig.6, Ref. [30])

Magnetic nanoparticle clusters entrapped into nano-(or micro) gels are promising magnetic carriers in magnetic drug targeting or magnetic separation. The applicability of the aqueous dispersions of magnetic nanocomposite particles depends on their colloidal stability under the influence of various factors like temperature, external magnetic field, concentration and dispersion medium pH. Due to their high induced magnetic moment in applied magnetic field, the magnetic microgel suspensions are susceptible to magnetically induced aggregation [31], a basic process to be considered both in biomedical and biotechnology applications.

CONCLUSIONS

Optimizing the synthesis procedure of magnetite ferrofluids the saturation magnetization of sealing nanofluids attains 100 kA/m. Concentrated ferrofluid based nano-micro composite fluids further increase the saturation magnetization to 700 kA/m, implying also the order of magnitudes increase of the yield stress and magnetoviscous effect of nano-micro composite fluids, which strongly restrict their use for sealing applications. The ferrofluid based mini-emulsion procedure proved to be efficient and reproducible in manufacturing high magnetization hydrophilic nanoclusters (77 emu/g) and polymeric nanocomposites (microgels) (55 emu/g) designed for biomedical and biotechnology applications.

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