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# Field-induced motion of ferrofluids through immiscible viscous media: Testbed for restorative treatment of retinal detachment

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#### Abstract

Biocompatible, hydrophobic ferrofluids comprised of magnetite nanoparticles dispersed in polydimethylsiloxane show promise as materials for the treatment of retinal detachment. This paper focuses on the motion of hydrophobic ferrofluid droplets traveling through viscous aqueous media, whereby the movement is induced by gradients in external fields generated by small permanent magnets. A numerical method was utilized to predict the force on a spherical droplet, and then the calculated force was used to estimate the time required for the droplet to reach the permanent magnet. The calculated forces and travel times were verified experimentally. © 2006 Elsevier B.V. All rights reserved.

Keywords: Ferrofluid; Magnetite; Polydimethylsiloxane; Retina; Ferrohydrodynamics; Nanoparticle; Retinal detachment

#### 1. Introduction

We worked for several years to develop biocompatible polysiloxane ferrofluids for treating retinal detachments [1–5]. Retinal detachment is a leading cause of blindness, and currently available treatments fail in as many as 1/3 of complicated retinal detachment patients, resulting in partial or complete loss of vision for several million people worldwide. A retinal tear provides a pathway for vitreous fluid to pass through and underneath the retina, thus detaching the retina from the choroid. The goal of surgery is to close any holes in the retina, preventing further fluid flow into the subretinal space, allowing for reattachment of the retina.

The proposed treatment (Fig. 1) requires synthesizing magnetic nanoparticles and complexing them with a functionalized polysiloxane, then dispersing the complex in a non-functional polysiloxane oligomer to form the ferrofluid. The fluid can be injected through a fine needle into the vitreous cavity of the eye in apposition to a tiny permanent magnet inserted beneath Tenon's capsule on the outside of the scleral wall of the eye. The polysiloxane fluid is hydrophobic and has a high interfacial tension against the vitreous gel, and thus a stable spherical ferrofluid droplet forms within the aqueous environment. The permanent magnet attracts the ferrofluid droplet toward the side of the eye, and it is anticipated that the droplet can then seal a retinal hole.

Understanding the motion of a ferrofluid droplet as it travels in the eye is important for the success of this procedure. The permanent magnet on the exterior of the eye should generate a magnetic field of sufficient strength to pull the ferrofluid droplet to the retinal tear in a reasonable amount of time. The droplet volume must also be considered, as it will likely affect the size of the hole that can be sealed, as well as the overall motion of the droplet. Mathematical models for the motion of ferrofluids were described by Shliomis [6–11] and Felderhof [12–14]. Others investigated the use of gradient fields for positioning ferrofluids in microfluidic [15], capillary [16], and controlled rheological systems [17–19]. Rinaldi et al. [20] published an excellent review on this subject.

The intention of this research was to demonstrate the control of polysiloxane ferrofluid motion through a viscous

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Fig. 1. Proposed procedure for treating a retinal detachment: (1) A permanent magnet (a) with a pre-aligned magnetic field is placed in the conjunctiva proximal to the site of the retinal detachment (b), (2) a ferrofluid droplet (c) is injected into the vitreous humor, (3) attracted to the permanent magnet, the ferrofluid closes the hole in the retina, and (4) the body absorbs the liquid that has accumulated underneath the retina.

aqueous medium. Fundamental magnetic properties of the ferrofluid, mathematical calculations of the forces applied to ferrofluid droplets by an external permanent magnet, and simulations of the mobility of a ferrofluid droplet as it travels through the medium will be described.

# 2. Experimental

### 2.1. Materials

Hexamethylcyclotrisiloxane (D<sub>3</sub>, Gelest) was dried over calcium hydride and sublimed under vacuum into preweighed, flame dried, roundbottom flasks, each containing a magnetic stirring bar. The flasks were purged with argon and re-weighed to determine the amount of  $D_3$  in each flask. Cyclohexane (EM Science, 99%) was stirred with concentrated sulfuric acid for 1 week, washed with deionized water until neutral, stirred over calcium hydride, distilled, stored over sodium under a nitrogen atmosphere, and distilled before use. Tetrahydrofuran (THF) (EM Science, 99.5%) was dried over calcium hydride, distilled, stored as the purple sodium/benzophenone dispersion under nitrogen, and distilled just before use. Toluene (Burdick and Jackson, 99.9%) was distilled from calcium hydride and deoxygenated by purging with dry nitrogen before use. Hydrochloric acid solution was prepared by adding 5 mL of concentrated hydrochloric acid (37 wt% in water, EM Science) to 5 mL of deionized water. Ferric chloride hexahydrate (FeCl<sub>3</sub> $\cdot$  6H<sub>2</sub>O) and ferrous chloride tetrahydrate (FeCl<sub>2</sub> $\cdot$ 4H<sub>2</sub>O), both from Aldrich, were stored under nitrogen in a desiccator and used as received. Ammonium hydroxide (Alfa Aesar, 50% v/v aqueous), mercaptoacetic acid (97%, Aldrich), 2,2'-azobisisobutyronitrile (AIBN, 98%, Aldrich), n-butyllithium (2.0 M, Aldrich), trivinylchlorosilane (Gelest), trimethylchlorosilane (Gelest), MQP-B NdFeB powder (kindly donated by Magnequench, Toronto, Canada), Provisc<sup>TM</sup> solution (Alcon Inc., generously supplied by the Lion's Eye Institute, Nedlands, WA, Australia), and Tarzan's Grip<sup>®</sup> (Selleys Pty Ltd.) general purpose clear cyanoacrylate adhesive were used as received.

# 2.2. Ferrofluid synthesis

The methods for synthesizing the ferrofluid components were previously reported [5]. The ferrofluid utilized in the present work was comprised of magnetite nanoparticles complexed with a carboxylate-functional polydimethylsiloxane (PDMS) (Fig. 2), and this complex was dispersed in a 5000 g mol<sup>-1</sup> PDMS carrier fluid. The complex contained 50 wt% of magnetite and 50 wt% of the PDMS dispersant, and this complex was combined with the carrier fluid (50 wt% complex: 50 wt% carrier fluid), yielding a ferrofluid that contained 25 wt% magnetite. A brief synthetic procedure is described.

The PDMS dispersion stabilizer having three carboxylic acid groups at one end was prepared by first subliming  $D_3$ (27.44 g) into a septum sealed, flame dried, roundbottom flask. The flask was purged with nitrogen, and cyclohexane (30 mL) was added via a syringe to dissolve the D<sub>3</sub>. The n-butyllithium initiator (3.5 mL of a 2.5 M solution,  $8.75 \times 10^{-3}$  mol) was added to the reaction, and the solution was stirred at 25 °C for 1 h. THF (10 mL) was charged to the solution as a reaction promoter, and the polymerization was conducted at 25 °C. <sup>1</sup>H NMR was utilized to monitor the progress of the living anionic polymerization. The polymer was terminated by adding excess trivinylchlorosilane (2.2 mL, 0.0142 mol) at  $\sim$ 70–80% conversion and allowing the mixture to stir overnight. The excess trivinylchlorosilane was removed under vacuum, then the product was precipitated by pouring into methanol. The PDMS oligomer was diluted with chloroform, washed three times with deionized water, the chloroform was removed, and the polymer was dried under vacuum at 80 °C overnight. The synthetic procedure for the 5000 g mol<sup>-1</sup> PDMS carrier fluid was similar to the one outlined above, except the living anionic polymerization was terminated with trimethylchlorosilane.

The thiolene addition of mercaptoacetic acid to the trivinyl-terminated PDMS oligomer was as follows. A 2500 g/mol trivinylsiloxy terminated PDMS (12.3 g, 0.0148 equiv vinyl) was added into a flame dried, roundbottom flask and dissolved in toluene (60 mL). Argon was bubbled

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