

Tuning Mass Transport in Magnetic Nanoparticle-filled Viscoelastic Hydrogels using Low-Frequency Rotating Magnetic Fields

Shahab Boroun, Faiçal Larachi*

Department of Chemical Engineering, Laval University, Québec, QC, Canada G1V 0A6

SUPPORTING INFORMATION

Synthesis of Cobalt-Ferrite Nanoparticles

Cobalt-ferrite nanoparticles were synthesized by moderate temperature coprecipitation of Fe^{3+} and Co^{2+} ions in an alkaline solution. For this purpose, an aqueous solution of FeCl_3 (0.02 mM) and CoCl_2 (0.04 mM) was prepared and heated up to 55°C . After temperature stabilization, 2 M NaOH solution was added dropwise to the vigorously stirred solution at constant rate of 1 mL/min. The volumetric ratio of metal-bearing solution to caustic solution was 1.5. After formation of a brown precipitate, the temperature of suspension was raised to 85°C and the suspension was stirred for 30 min under reflux conditions at constant temperature. Afterwards, the black precipitate as final product was magnetically separated and washed several times with deionized water and dried 24 h at 80°C . The density of dried MNPs was 4.547 g/cm^3 measured by an Ultrapyc 1200e gas pycnometer (Quatachrome Instruments) where nitrogen was the gas phase. Finally, water at pH 9 adjusted by NaOH was added to a weighed amount of dried powder and the suspension was sonicated by means of an ultrasonic bath for 15 min. The resultant colloidal dispersion is denoted as ferrofluid. The prepared stock ferrofluid was diluted to the desired levels of MNPs mass fraction (φ) for preparation of ferrogels.

Synthesis of Hydrogels

Hydrogel samples were prepared by free radical polymerization of AM monomers using N,N'-methylenebisacrylamide (MBAA) as cross-linker, ammonium persulfate (APS) as initiator and

tetramethylethylenediamine (TEMED) as catalyst. The pregel solution containing 6 wt% AM, cross-linker and catalyst was bubbled with argon while under vigorous mixing. Afterward, solution of 1 wt% APS was added to the pregel solution to initiate the polymerization. The volumetric ratio of TEMED, APS solution and monomer solution was kept 1/10/100, accordingly. By adjusting the concentration of MBAA, the molar cross-linking ratio, defined as the molar concentration of MBAA to that of AM, was varied.

Synthesis of Ferrogels

The procedure for preparation of ferrogel samples is the same as hydrogels but the monomer, cross-linker and TEMED were initially dissolved in a ferrofluid with adjusted ϕ . Sonication in the ultrasonic bath was utilized as a mixing means to prevent aggregation of MNPs in the magnetic stirrer. The pregel solutions of hydrogels and ferrogels were poured into plastic tubes 4 mm in inner diameter and 50 mm in length right after addition of the initiator, so that obtaining the final gel in the form of cylinders. All the samples were subsequently immersed in deionized water for 4 days and the supernatant water was replaced every 12 h to remove the unreacted chemicals.

Determination of Swelling Ratio

In order to obtain the swelling ratios (*SR*), the cylindrically shaped samples were immersed in water at pH 9 for 10 days and their final weights at equilibrium swelling were recorded. The amount of water in swollen state is calculated by subtracting the PA and MNPs weights from the final weight. The samples were subsequently dried for 24 h at 80°C and then weighed again. *SR* was calculated by dividing the calculated weight of total absorbed water to the weight of the dried sample.

Determination of Effective Diffusion Coefficient from Release Kinetics

The receiver solution used in the release experiments was water at pH 9, circulated with a peristaltic pump at constant rate of 10 mL/min within a closed loop. The cylindrical shaped samples were

previously equilibrated with imbibition solution of 50 mM rhodamine B for 4 days. The concentration of solute in sample was assumed 50 mM since the volume of imbibition solution was much larger than the sample volume. Afterwards, the imbibed sample was placed in the central axis of a plastic tube with inner diameter of 22 mm and the tube was connected to the closed loop of the circulating solution. The space between the sample and inner wall of plastic tube was filled with glass beads of 1 mm in diameter, holding the sample in vertical position. The glass beads also help to eliminate radial concentration profiles that might establish in the space between the inner wall of plastic tube and peripheral surface of the sample. The concentration of released rhodamine B into the circulating solution was continuously measured by a UV-Vis spectrophotometer (Stellarnet Inc, model Black Comet) equipped with an optical cell designed for in-flow measurements. A vigorously stirred container with ventilation to atmosphere was placed prior to the optical cell to remove bubbles and possible concentration gradients in the outlet stream of the plastic tube. For determination of D , the analytical solution to the problem of solute diffusion from infinite circular cylinder to a well stirred solution of finite volume was utilized. The concentration of solute in the solution is expressed according to:¹

$$\frac{C(t)}{C_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{4\alpha(1 + \alpha)}{4 + 4\alpha + \alpha^2 q_n^2} \exp\left(-Dtq_n^2/r^2\right) \quad (\text{S.1})$$

Where t is time, r is the radius of the sample, $C(t)$ is the concentration in the solution and C_{∞} is the final concentration in the solution, q_n are the positive roots of equation:

$$2J_1(q) + \alpha q J_0(q) = 0 \quad (\text{S.2})$$

and α is defined as

$$\alpha = \frac{\text{solution volume}}{\text{sample volume}} \times K \quad (\text{S.3})$$

K is the partition coefficient defined as the ratio of equilibrium concentration of rhodamine B solution in contact with the sample (C_{∞}^s). The K values were determined by immersing the imbibed samples in water at pH 9 until the concentration of solute in water reaches a constant value. The equilibrium concentration inside the sample was simply calculated from the known mass of water in the sample. C_{∞} was also calculated according to the obtained K values.

After swelling, sample expansion in the axial direction was negligible, so that the radius of sample was calculated assuming sample expansion only in radial direction. The initial radius was set to 2 mm equal to the inner radius of the plastic tube. The Diffusion coefficients were estimated by plotting $C(t)$ as the function of t and minimizing the root-mean squares error between experimental and theoretical data by iterating on the values of D .

Procedure of Vibrating Sample Magnetometry

Magnetic characterization was carried out in a vibrating sample magnetometer (VSM) from Princeton Instrument (MicroMag model 2900) at 298 K for determining magnetizations of MNPs and ferrogels. The external magnetic field (H) applied from the instrument had a maximum value of 14 kOe. Swollen samples were weighed and then put into a hollow cylinder made of silicone rubber mounted and fixed on the VSM vibrating probe by means of silicon grease. The cylinder was capped with a plastic sheet to prevent evaporation of water during the experiment. The magnetization (M) of each sample was calculated by dividing the measured magnetic moments by the mass of magnetic nanoparticles in the sample, determined from the known initial amount of MNPs in the pregel solution. The amount of MNPs in the pregel solution and swollen samples are identical since the nanoparticles did not diffuse out of the ferrogel samples during the swelling process as verified by magnetometry of supernatant liquids during swelling process.

References

1. L. Haggerty, J. H. Sugarman, R. K. Prudhomme, *Polymer*, 1988, **29**, 1058-1063.