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Determination of the shear modulus of gelatine hydrogels by magnetization measurements using dispersed nickel nanorods as mechanical probes

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ABSTRACT

Ni nanorods are dispersed into gelatine gels and used as nanoprobes to estimate the shear modulus of the surrounding gel matrix by magnetization measurements. The nanorods are synthesized via pulsed electrodeposition of Ni into porous alumina, released from the templates by dissolution of the oxide layer and after several processing steps dispersed into gelatine gels with an isotropic orientation-distribution. Magnetization measurements of the resulting gels show a significant influence of the gelatine concentration on their magnetic behavior. In particular, with decreasing gelatine concentration the measured coercivity is reduced indicating a mechanical rotation of the nanorods in the field direction. A theoretical model which relates the measured coercivity to the shear modulus of the surrounding gel matrix is introduced and applied to investigate the ageing process of gelatine gels with different gelatine concentrations at room temperature.

1. Introduction

It is a well established concept in microrheology to retrieve the viscoelastic properties of soft materials from the motion of embedded nano- or microsized probe particles subjected to either thermal energy (passive) [1–3] or an external force (active) [4–6]. A topical overview of the different techniques and theoretical background can be found in recent reviews [7,8]. Optical transparency of the matrix provided, microsized particle can be manipulated using optical tweezers with a calibrated force constant while their displacement is measured using an optical microscope [9–11]. Alternatively, the motion of magnetic beads in a static [12], oscillating [13,14] or rotating [15,16] magnetic field has been analyzed to study the mechanical properties of complex viscoelastic systems, such as mucus [16], actin solutions [13], or cytoplasm [17]. Using anisometric ferromagnetic particles, it is possible to observe not only the displacement of the probe particle as a result of a force $\vec{F}_m$ but also the rotation of the probe induced by a magnetic torque $\vec{T}_m$ [4,18–20]. Rotational relaxation of chained superparamagnetic beads in gelatine sols near the sol–gel-transition [21] and in micellar solutions [15] was measured making use of birefringence and anisotropic light scattering and analyzed to derive the rheological properties of the matrices.

A common feature in many experimental approaches is the analysis of individual probes by means of light microscopy. As a consequence, optical resolution defines a lower limit to the size of the employed particles. Chippada et al. [18] for example used microneedles of length $L\approx10$ μm and diameter $D\approx1$ μm to investigate the mechanical properties of soft hydrogels. However, nickel microneedles of this size are magnetic multidomain particles [22]. At low magnetic fields, their magnetization behavior – and hence the magnetic torque in a transversal field – depends on the stability of the domain structure which is determined by structural defects and chemical impurities and therefore ill-defined. In contrast, Ni nanorods with diameters below 42 nm are single-domain particles with high remanence and preferential magnetization along the rod axis due to the high shape anisotropy energy as compared to the magnetocrystalline anisotropy of Ni [22–26]. Thus, nickel nanorods are nearly a prime example of uniaxial ferromagnetic single-domain particles with well-defined intrinsic magnetization properties. Because of their small dimensions, light microscopy may not be feasible for the detection of particle motion and rotation. Yet, any physical quantity which reflects the mechanical response of an ensemble of nanometer-sized probe particle to the external stimulus could be used to infer the viscoelastic properties of the matrix. For instance, it is well known that the viscosity of the liquid matrix of ferrofluids can be deduced from the Debye relaxation frequency of ferromagnetic nanoparticles [27], determined by ac-magnetization measurements [28], and their hydrodynamic radius [29] using the Einstein relation [30]. In analogy, it should be possible to employ ferromagnetic nanoparticles to probe the mechanical properties of

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an elastic material. Schmidt et al. [31] for example were successful in monitoring the direct mechanical interactions of ferromagnetic $CoFe_2O_4$ nanoparticles with the surrounding polymer segments of PAAm ferrohydrogels by applying quasi-static magnetization measurements. The measured magnetization $M(H)$ reflects the alignment of the particles magnetic moments into the direction of the magnetic field. This alignment is facilitated – and hence the magnetization at a given field is increased – if the matrix is sufficiently soft to allow a significant rotation of the particles under the influence of the magnetic torque. In addition, particle rotation reduces the critical field for magnetic switching. Hence, the field-dependent magnetization of such a magnetic nanocomposite is determined by the magnetic and geometric properties of the probe particles on the one hand as well as the mechanical compliance of the matrix on the other hand.

In a previous study, we have shown that the rotation angle of nickel nanorods dispersed in a gelatin-based hydrogel can be obtained from static magnetization measurements [32]. The combination of this rotation angle and the related magnetic torque allowed the derivation of the shear modulus of the gelatin matrix. However, this particular approach required that the nanorods were aligned parallel in the sample prior to the measurement. The objective of the present study is to devise an experimental scheme that allows the determination of the shear modulus of a soft elastic material with an isotropic dispersion of nickel nanorods using static magnetization measurements. For a quantitative analysis, the well-known Stoner–Wohlfarth-model [33] is adapted to explicitly include the rotation of the uniaxial ferromagnetic particles enabled by the elastic deformation of the matrix. The results obtained from these magnetization measurements of isotropically dispersed nanorods are compared with those obtained from the analysis of the rotation angle of pre-aligned nickel nanorods in the same materials [32]. Furthermore, the presented method is employed to investigate the dependence of the shear modulus of gelatine hydrogels on time, which is supposed to exhibit a logarithmic increase, and on concentration, which has been shown to follow a c^2-dependency [34].

2. Methods

2.1. Synthesis of the ferrogels

The synthesis of Ni nanorod ferrogels involves multiple steps which are described in detail in [32] and are briefly outlined in the following. In the first step hexagonally ordered porous alumina films with a thickness of ~800 nm were produced via a twofold anodization process of high purity aluminium foils (Goodfellow, 99.999%) [35] using an electrolyte of 2 M sulphuric acid and an anodization voltage of 15 V. After thinning of the barrier oxide at the pore bottom by reducing the applied voltage in 1 V steps of 3 s duration down to 6 V and subsequent pore widening in 0.1 M phosphoric acid for 10 min, the nanorods were synthesized by current-pulsed electrodeposition [36] of nickel into the pores from a Watts-bath [37] with a nickel foil as a counter electrode.

The nanorods were then released from the templates by dissolving the alumina in 250 ml of 20 mM sodium hydroxide solution, containing ~5 g polyvinyl-pyrrolidone (PVP) as a surfactant [38]. After several washing and centrifugation steps and magnetic separation in a field gradient the nanorods were dispersed in bidistilled water resulting in a stable colloidal dispersion.

From such a colloid sample (Sample 1), two ferrogels with 10 wt% (in the following named mechanically hard ferrogel) and 2.5 wt% gelatine (mechanically soft ferrogel) were prepared by mixing the colloid at 60 °C with a gelatine sol containing the appropriate amount of gelatine and crossing the sol–gel transition upon cooling the mixture to room temperature. The same procedure was repeated to synthesize a second Ni nanorod colloid (Sample 2) from which four ferrogels with 10 wt% (hard ferrogel) and 2.5 wt%, 2 wt% and 1.5 wt% gelatine (soft ferrogels) were prepared. It is important to note that the analysis presented below relies on measurements of soft and hard ferrogels containing identical nanorods as probe particles. This condition requires that only ferrogels prepared from a specific colloid sample may be combined in a series of measurements.

2.2. Characterization

Scanning electron microscopy (SEM, JEOL JSM-7000F) was employed to characterize the structural properties of the nanorods. For this purpose a small droplet of the colloidal dispersion was applied onto a silicon wafer. For the structural characterization of the nanorods embedded in the gelatine matrix, transmission electron microscopy (TEM, JEOL JEM-2011) as well as environmental scanning electron microscopy (ESEM, FEI Quanta 400 FEG) were used. A small droplet of the nanorod gelatine–sol mixture was applied to a TEM grid and cooled down to room temperature. During evacuation of the microscope, the water in the hydrogel matrix evaporates leaving the Ni nanorods attached to the gelatine network as a residue on the TEM grid.

The magnetic characterization of the ferrogels was performed using a vibrating sample magnetometer (VSM, Lakeshore Model 7400). Teflon containers were used as sample holders providing a sample volume of 180–200 μl. After filling with the nanorod/gelatine sol, the sample holder was cooled down to room temperature upon which the sample turned into an isotropic ferrogel. The hysteresis loops were all measured at room temperature ($\sim 21 \pm 0.2$ °C) starting at a maximum field of $\mu_0 H = 700$ mT. The measured magnetization m_H was normalized to the saturation magnetization m_S of the sample.

The macroscopic complex shear modulus $G^*(\omega) = G' + iG''$ of the gelatine hydrogel was measured at a frequency of 0.1 Hz as a function of the gelation time using a Small-Amplitude-Oscillatory-Shear-Rheometer (Thermo Fisher Scientific, HAAKE MARS II). In the low frequency limit the storage modulus G' of the gelatine hydrogel is directly comparable with the static shear modulus G, as determined in the presented analysis.

3. Results

3.1. Structural characterization – Sample 1 and Sample 2

Fig. 1 shows a TEM-image of the nanorods of Sample 2, embedded in a thin ferrogel film and for comparison a SEM-image of the bare nanorods on a silicon substrate. In TEM the organic gelatine matrix as well as the PVP surfactant layer do not generate a significant contrast enabling the direct imaging of the nanorod structure. As expected, the nanorods are linear in shape and thus exhibit the distinct anisotropy necessary for steric interaction with the polymer network. From the average length and diameter of the nanorods the mean aspect ratio can be determined (Table 1). It should be noted that in both samples slight structural inhomogeneities such as diameter fluctuations and irregular rod-ends can be observed as well as a nanocrystalline substructure, evident from the bright-field contrast fluctuation within a single nanorod.

The average diameter of the nanorods of both samples determined from SEM is larger than the values obtained from TEM. This apparently larger diameter is found to be systematic and is attributed to the organic PVP-layer surrounding the nanorods which is visualized in SEM but not in TEM, Fig. 1. From the