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Magnetization measurements reveal the local shear stiffness of hydrogels probed by ferromagnetic nanorods

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ABSTRACT

The local mechanical coupling of ferromagnetic nanorods in hydrogels was characterized by magnetization measurements. Nickel nanorods were synthesized by the AAO-template method and embedded in gelatine hydrogels with mechanically soft or hard matrix properties determined by the gelatine weight fraction. By applying a homogeneous magnetic field during gelation the nanorods were aligned along the field resulting in uniaxially textured ferrogels. The magnetization curves of the soft ferrogel exhibited not only important similarities but also characteristic differences as compared to the hard ferrogel. The hystereses measured in a field parallel to the texture axis were almost identical for both samples indicating effective coupling of the nanorods with the polymer network. By contrast, measurements in a magnetic field perpendicular to the texture axis revealed a much higher initial susceptibility of the soft as compared to the hard ferrogel. This difference was attributed to the additional rotation of the nanorods allowed by the reduced shear modulus in the soft ferrogel matrix. Two methods for data analysis were presented which enabled us to determine the shear modulus of the gelatine matrix which was interpreted as a local rather than macroscopic quantity in consideration of the nanoscale of the probe particles.

1. Introduction

Hydrogels constitute an important class of soft elastic materials which is widely used in medical, pharmaceutical, cosmetic and food industries [1,2]. The mechanical properties of such low modulus materials can be investigated by conventional shear rheometry or using several microrheological approaches which have been developed in recent years [3–6]. The general concept of microrheology is to deduce the viscoelastic properties of soft materials from the thermal fluctuations [7–9] or an actively driven motion of colloidal particles embedded inside the sample [10–12]. External mechanical force and torque can be applied by optical tweezers [13–15] or using magnetic beads [10,16,17]. Chippada et al. [18] used ferromagnetic microcylinders with diameters of about 1 μm as probes and exerted a magnetic torque by applying a homogeneous magnetic field. With lengths in the range of 10 μm the corresponding torque-dependent rotation could be detected optically and the shear modulus be calculated [18]. In what follows, we argue that the size of the probe particles is an important parameter for several reasons.

The mechanical properties of polymer hydrogels depend on their molecular structure such as the number density and functionality of elastically active cross-links and the resulting mesh size [19,20]. The relationship between the molecular structure of the polymer network and the hydrogel physical properties on the macroscopic level is provided by rubber elasticity theory [21–26]. The mechanical viscoelasticity deduced from microrheology experiments reflects the macroscopic properties if the size of the probe particle is much larger than the characteristic length scale of the molecular microstructure [11]. By contrast, particles much smaller than the mesh size experience the local restoring forces of stretched polymer chains provided both particle and polymer are firmly bonded together. Furthermore, the contribution of interphases in which the network structure is modified by chemical interaction between the particle surfaces and the polymer increases with decreasing particle size. Direct covalent bonding of the polymer to the surface enables significant reinforcement of inorganic particle/polymer nanocomposites [27,28]. In order to investigate the mechanical coupling of nanoparticles in soft elastic materials on the molecular level several approaches have been developed in recent years in which ferromagnetic nanoparticles have been applied as nanoprobes [29–33]. These experiments

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utilize the concept of microrheology not focussing on the macroscopic properties but to explore the mechanical interaction of the probe particles with their matrix on a local scale.

In two previous studies [34,35] we used single-domain nickel nanocylinders with an average diameter of 17.7 nm and an average length of 151.2 nm as probe particles to estimate the local shear modulus of a gelatine hydrogel. The sizes of these nanorods are of the same order of magnitude as the medium mesh sizes of about 100 nm typical for gelatine concentrations of 2 wt% [36]. The Ni nanorods of this size are ferromagnetic uniaxial single domain particles with a permanent magnetization along the long rod axes due to shape anisotropy [37–40]. The rotation of such magnetic nanoparticles in an elastic matrix leads to characteristic changes in the macroscopic magnetization behavior which could be analyzed using two different approaches. In [35] the Ni nanorods were aligned during the ferrogel synthesis and the soft and hard ferrogels were magnetically characterized in this uniaxial state. Data analysis was presented which enabled us to determine the rotation angle of the rods in the soft gel matrix as a function of the applied magnetic torque and finally allowed to determine the local shear modulus. Application of this analysis on time-dependent magnetization curves revealed a logarithmic increase of the local shear modulus with increasing gelation time which is a characteristic of the macroscopic properties of the physical gelation process [41]. This method, however, required a series of angular-dependent magnetization curves of the hard ferrogel for reference. A second approach was presented in [34] which required only two measurements of the soft and hard ferrogels in the isotropic state. Applying an extension of the Stoner–Wohlfarth (SW) model [42] enabled the estimation of the local shear modulus of the soft ferrogel from the coercivity of the magnetization curve relative to the reference value of the hard ferrogel. However, it is known that Ni nanorods do not comply with the assumption in the SW-model of a coherent rotation during irreversible magnetization changes so that the reliability of this approach has yet to be evaluated.

In the present study two alternative methods are presented to estimate the local shear modulus of soft materials. Both approaches require two magnetization measurements only, the magnetization of a textured soft ferrogel and of a mechanically rigid reference sample. In method 1, the rotation angle of the nanorods is obtained as a function of the magnetic torque and the local shear modulus retrieved from the linear elastic model for the rotation of a rigid inclusion [18]. If the details of the rotation process are not requested, method 2 provides a direct analysis based on the initial susceptibilities of the soft elastic ferrogel and the rigid reference sample. The experiments are performed using gelatine hydrogels as matrix. The temporal evolution of the local shear modulus is investigated and the results are compared among the different methods as well as with the macroscopic shear modulus of gelatine hydrogels of the same composition.

2. Methods

2.1. Synthesis of the ferrogels

The synthesis of the Ni nanorod ferrogels involves several steps which have been described in detail in [35]. Briefly, an alumina layer with a thickness of $\sim$800 nm was produced via twofold anodization of high purity aluminium foils (Goodfellow, 99.999%) in 2 M sulphuric acid at 0 °C and a constant voltage of 15 V [43]. After electrolytical thinning of the barrier oxide at the pore bottom and an additional pore widening in 0.1 M phosphoric acid for 10 min, Ni was deposited into the pore channels by current-pulsed electrodeposition from a Watts-bath [44]. The nanorods were released from the template by dissolving the alumina in 250 ml of 20 mM sodium hydroxide solution to which $\sim$5 g polyvinylpyrrolidone (PVP) [45] was added for steric stabilization of the nanorods. After several washing, centrifugation and separation steps the nanorods were dispersed in bidistilled water using an ultrasonic bath resulting in a stable colloidal dispersion.

The nanorods were incorporated into physical hydrogel matrices of different mechanical stiffnesses. A mechanically hard ferrogel with 10 wt% gelatine as well as a mechanically soft ferrogel with 2.5 wt% gelatine was prepared by mixing the colloid at 60 °C with a gelatine sol of the appropriate concentration and crossing the sol–gel transition upon cooling to room temperature.

2.2. Characterization

The structural characterization of the bare nanorods and the nanorods embedded in the gelatine matrix was performed using scanning electron microscopy (SEM, JEOL JSM-7000F) and transmission electron microscopy (TEM, JEOL JEM-2011). A small droplet of the aqueous colloid was deposited onto a TEM grid or a silicon wafer for SEM. For analysis of the nanorods dispersion in the hydrogel matrix the ferrogels were melted at 60 °C and a small droplet of the sol was deposited on a TEM grid. A particular TEM specimen was prepared by applying a homogeneous magnetic field of $\mu_0 H = 500$ mT during gelation in order to evaluate the impact of the magnetic field on the alignment of the nanorods and possible field induced chain formation. During evacuation of the specimen in the microscope vacuum lock the water evaporates leaving the Ni nanorods attached to the gelatine network.

Magnetic characterization of the ferrogels was employed using a vibrating sample magnetometer (VSM, Lakeshore Model 7400) and 180–200 µl teflon cylinders as sample holders. Uniaxial ferrogels were prepared by heating the filled sample capsules to 60 °C and subsequent cooling to room temperature in the presence of a homogeneous magnetic field of $\mu_0 H = 500$ mT. Hysteresis loops were measured at room temperature ($\sim 21 \pm 0.2$ °C) starting at a maximum field of $\mu_0 H = 700$ mT which proved to be highly enough to achieve saturation into field direction and thus to determine the saturation moment m_s of the sample. Assuming homogeneous magnetization of the nanoparticles the normalized field-dependent magnetic moment $m_H/m_S = \cos \Phi$, where Φ is the angle between the total magnetic moment and the applied field. To analyze the orientation-dependent magnetization of the ferrogels, the angle Θ between the magnetic field and the induced anisotropy axis was varied between $\Theta = 0°$ ($\vec{H} \parallel$ anisotropy axis) and $\Theta = 90°$ ($\vec{H} \perp$ anisotropy axis).

The macroscopic complex shear modulus $G^*(\omega) = G' + iG''$ of gelatine hydrogels was determined by applying a Small-Amplitude-Oscillatory-Shear-Rheometer (Thermo Fisher Scientific, HAAKE MARS II). The measurements were performed at a frequency of 0.1 Hz which was sufficiently low to associate the obtained storage modulus G' of the hydrogels with their static shear modulus G.

3. Results

3.1. Structural characterization

In Fig. 1a TEM-image of the Ni nanorods embedded in a thin gelatine film and a SEM-image of the bare Ni nanorods on a silicon wafer is shown. In TEM the gelatine matrix and the PVP layer do not generate any contrast and thus allow structural characterization of the Ni nanorods. The nanorods are linear in shape with minor diameter fluctuations and the contrast fluctuations in the bright-field image indicate a nanocrystalline substructure. By measuring >100 nanorods the average length and diameter