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Characterization of Hydrogels at the Micro- and Nanoscale by FESEM and SFM

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Abstract – Structural and mechanical properties of the hydrogels poly(N-isopropylacrylamide) (PNIPAAm) and poly(venyl-methyl-ether) (PVME) were studied in different states by field emission scanning electron (FESEM) and scanning force microscopy (SFM) at the micro- and nanoscale. Using state-of-the-art cryo-preparation and thin film coating the FESEM allows for imaging of structural details as small as 5-10 nm. Imaging of the hydrogels in the wet state by SFM at high resolution is hampered by (i) their distinct softness (Young´s modulus ranges from about 1-10 kPa) and (ii) their sponge-like structure. However, the SFM is well suited for local measurement of Young´s modulus.

Soft materials like hydrogels play an important role in areas such as medical care, medicine, foods, and bioengineering. A large amount of today's research is focused on probably the most interesting hydrogels, the so-called "smart" or "intelligent" hydrogels, possessing a defined phase transition capable to abruptly swell to many times its original size or to collapse into a compact mass when stimulated externally [2]. For many new applications of hydrogels and the aim to develop tailor-made gels, there is a growing need for a detailed understanding of the properties of hydrogels at a microscopic and nanoscopic scale [1, 3].

For the studies by FESEM the hydrogels placed on supports were rapidly frozen into liquid ethane (-196 °C), subsequently freeze-dried for 6 h at ~ -80 °C and then rotationally coated with 2.5 nm Pt/C at an elevation angle of 65°. High-resolution images were recorded with the "in-lens" FESEM S-5000 (Hitachi Ltd., Japan) at low acceleration voltages (2-10 kV) utilizing secondary (SE) and back scattered electrons (BSE). The studies of the dry or wet hydrogels on supports by SFM (for imaging: Nanoscope III, Digital Instruments, for probing elasticity: Explorer, TopoMetrix, both USA) were performed at ambient conditions.

FESEM and SFM images of the air-dried PNIPAAm show in very close agreement a smooth surface with elevations up to ~25 nm within individual areas of ~4 μm^2; it is advantageous that in contrast to FESEM the SFM reveals directly quantitative data about the topography. FESEM micrographs of cryo-prepared wet PNIPAAm in the swollen or shrunk state show the fine sponge-like structure at the nanometer scale (Fig. 1) but the cavities possess a smaller mean size in the shrunk state [4]. Even if very low imaging forces were applied in SFM no usable images of the wet hydrogel could be obtained. Though the SFM allowed for local measurement of Young´s modulus with modified cantilevers using a silica sphere with a diameter of very few micrometres instead of a sharp tip. Young's moduli obtained in this manner were ~1.7 kPa for the swollen state at 10 °C, ~4.5 kPa at 30 °C, ~180 kPa for the shrunk state at 35 °C, and ~800-900 kPa for the dry hydrogel [4]. Another hydrogel called PVME was studied in the wet state without and with incorporated nanoparticles (fillers) of barium titanate, poly(vinylidene fluoride), or Ni [5]. While the SE imaging shows clearly the hydrogel structure the BSE image displays the location of nanoparticles within the hydrogel.

In conclusion, FESEM and SFM proved to be powerful tools for the characterization of the structural and micromechanical properties of hydrogels.

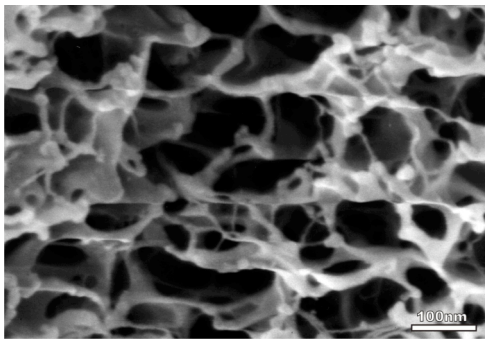

Figure 1: PNIPAAm hydrogel imaged in FESEM with SE. The bar corresponds to 100 nm.

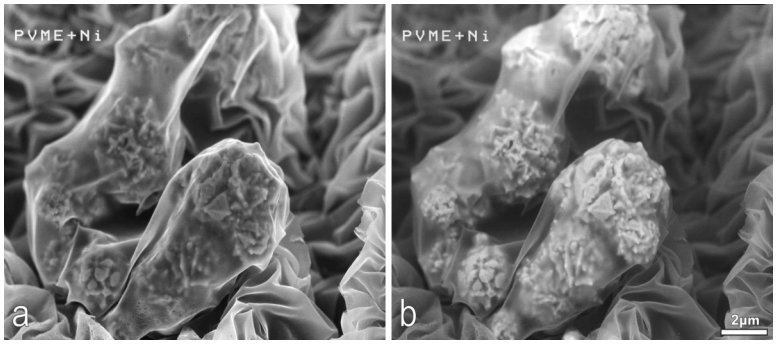

Figure 2: PVME hydrogel with incorporated Ni-particles imaged in FESEM simultaneously with SE (a) and BSE (b).

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