Characterization of magnetite nanoparticle / polymer nanocomposite materials in gel and dry state

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***Abstract*— We present the characterization of nanocomposite materials made from functionalized magnetite nanoparticles and HEUR amphiphilic polymers in the gel and dry states. The hydrophobically modified particles are mainly associated with the two hydrophobic end-groups of the polymer. One part of this study focuses on the polymeric state and dynamics, that are governed by the polymeric network through amphiphilic interactions forming a gel in the wet state and microphase separated system in the dry state. Apart from the network, the particles seem to be well distributed at concentrations below 1%wt, while strong clustering is observed at higher concentrations. The magnetic response of the dry nanocomposite shows super-paramagnetic behavior with a blocking temperature of ca. 25K.**

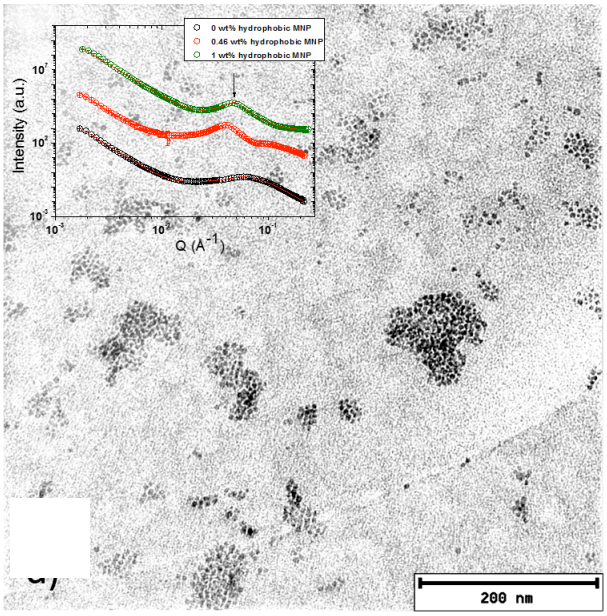
I. Introduction

Nanocomposites of magnetic nanoparticles and polymers are possible candidates for responsive materials in cancer treatment, separation devices, sensors and for electro-magnetic wave absorbers. One crucial task in the construction of such materials is the dispersion of the particles in the polymer matrix that would serve for a homogenous response of the material to magnetic fields. Thus, a good characterization of the composite material is needed aiming at the polymeric structure and dynamics in concert with the macroscopic magnetic behavior [1-3]. Apart from the characterization, an emphasis was placed on simple nanoparticle chemistry with commercially available polymers.

II. Polymer Structure

The polymeric network in the wet and dry state is governed by hydrophobic domains that form crosslinks for the longer polymeric hydrophilic segments in between the crosslinks. Using small angle neutron scattering experiments [1], this network is characterized in terms of the network-strength on long length scales, and of the domain spacing between the hydrophobic units. The network-strength is lower at polymer concentrations below ca. 7%wt, indicating that some polymers still form loop structures around the hydrophobic domains. Above ca. 10%wt, basically all polymers contribute to the strong network, and the network tends to expel excess water. Adding nanoparticles to polymer-rich gels increases the domain spacing. Higher nanoparticle concentrations above 1%wt result in coexisting dense particles clusters that are not embedded in the polymer matrix anymore, while below 1% the particles seem to be well embedded. This finding is confirmed by transmission electron micrographs (Fig. 1).

Figure 1. Transmission electron micrograph of a 1%wt nanoparticle loading to a dried HEUR polymer gel.



The inset shows the small angle neutron scattering curves of the nanocomposite gels, where the correlation peak indicates the domain spacing.

III. Polymer Dynamics

The polymer dynamics have been studied in the gel and dry state. The magnetic particle concentration was rendered below the cluster formation – so the particles were well embedded. The most important characterization methods were dielectric spectroscopy, differential scanning calorimetry, and neutron spin echo spectroscopy.

For the gels, a temperature range from ca. 120K to 298K was covered, and different relaxations were identified: the polymer α- and β-relaxation, and the water α-relaxation (Fig.2). The polymer relaxations showed a dependence on the particle loading: The β-relaxation was mainly dependent on the near particle segment (or blob) movements, where due to nearly the same functionality (number of anchored polymers)

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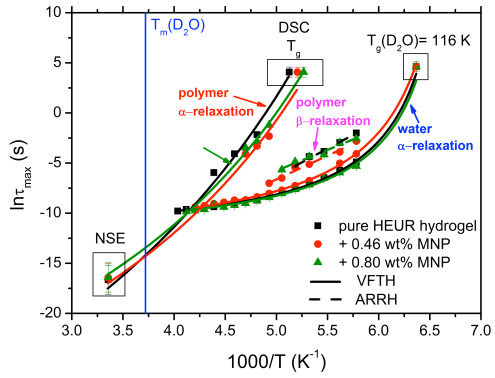
the monomer density was lower for magnetic particle loadings, which was connected to slower relaxations. Neutron spin echo spectroscopy mainly observed the largest blobs, i.e. the middle part of the polymers between the crosslinks. Here, the particle loading leads to larger blobs with slower relaxations. Also, at lower temperatures, the α-relaxation slows down with nanoparticles. The electric conductivity could be connected to two counteracting trends: Higher conductivity mechanism for particle loadings, and slower relaxation mechanism at highest particle loadings.

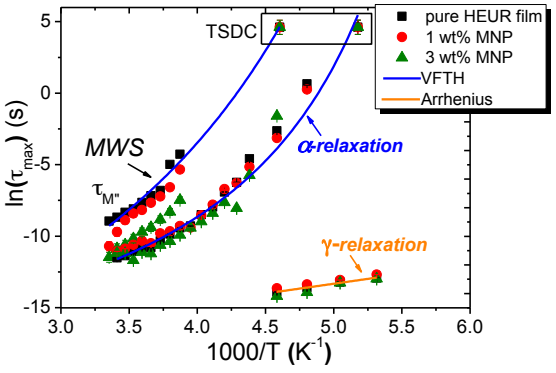
Figure 2. Arrhenius map of the gels with nanoparticles



The α-process of the polymer, including the NSE, dielectric spectroscopy and DSC measurements; the β-process of the polymer and the α-process of water. The curved lines correspond to the Vogel-Fulcher theory (VFTH), and the dashed straights to Arrhenius (ARRH) behavior. Melting of D_2O is indicated in blue.

The dry films display an unchanged glass transition (and α-relaxations, Fig. 3) when nanoparticles are added, while the conductivity is increased. This increase is explained by the middle block micro-domain formation from the two different monomers: close to the hydrophobic domains, the mid-block is confined, and the micro-domain formation is confined stronger for the small hydrophobic crosslinks without magnetic particles. This conductivity is described by the Maxwell-Wagner-Sillars process.

Figure 3. Arrhenius maps of the dry films with nanoparticles.

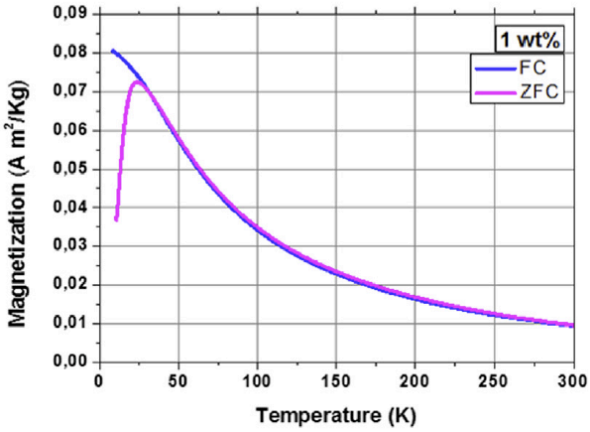


Vogel-Fulcher theory curves to the Maxwell-Wagner-Sillars (MWS) process and the α-relaxation. Arrhenius lines for the γ-relaxation.

IV. Magnetic Behavior

Further information about the magnetic properties and about the size of the magnetic nanoparticles embedded in the polymer matrix are achievable by recording the zero-field cooling (ZFC) and the field-cooling (FC) magnetization curves. The applied magnetic field is 0.01 T. The curves we obtained for the nanocomposites as thin dry film with different hydrophobic MNp loadings are shown in Fig. 4. From the shape of the ZFC and FC curves one can extract several characteristics of the sample. The general shape of the ZFC curves is typical for a superparamagnetic system. The maximum in the ZFC curves marks the blocking temperature, T_B of the system. The high-temperature branches of both ZFC and FC above T_B display a typical 1/T Curie behavior. The FC curve splits from the ZFC curve near the blocking temperature indicating a narrow particle size distribution. The blocking temperature of all the investigated samples is found to be (24.5 ± 3.1) K from which we calculate a nanoparticle radius of (3.1 ± 1.1) nm. It seems that the separation of the nanoparticles is enough to reach superparamagnetism.

Figure 4. Magnetization measurements of the dry films.



Zero field cooling (ZFC) and field cooling (FC) measurements of the dry nanocomposites with 1%wt particle content.

V. Conclusion

We characterized nanocomposites consisting of magnetite particles and HEUR polymers with respect to structure, polymer dynamics and magnetic response. Below a particle concentration of 1%wt the formed gels and dry film display a homogenous particle distribution, while larger loadings lead to cluster formation.

References

[1] A. Campanella, Z. Di, A. Luchini, L. Paduano, A. Klapper, M. Herlitschke, O. Petracic, M.S. Appavou, P. Müller-Buschbaum, H. Frielinghaus, D. Richter, *Polymer* **60**, 176-185 (2015)

[2] A. Campanella, O. Holderer, K. N. Raftopoulos, C. M. Papadakis, M. P. Staropoli, M. S. Appavou, P. Müller-Buschbaum, H. Frielinghaus, *Soft Matter* **12**, 3214-3225 (2016)

[3] A. Campanella, A. Brás, K.N. Raftopoulos, C.M. Papadakis, O. Vassiliadou, A. Kyritsis, M.S. Appavou, P. Müller-Buschbaum, H. Frielinghaus, Polymer **96**, 70-80 (2016)