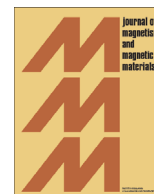




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Assessing magnetic nanoparticle aggregation in polymer melts by dynamic magnetic susceptibility measurements



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ABSTRACT

Aggregation of magnetic nanoparticles in polymer melts was assessed using dynamic magnetic susceptibility measurements. Magnetic nanocomposites consisting of polybutadiene/CoFe₂O₄ and polystyrene/CoFe₂O₄ mixtures were prepared using different techniques and characterized using dynamic magnetic susceptibility measurements. The presence of nanoparticle aggregates determined using magnetic measurements was confirmed with transmission electron microscopy examinations. The results were in good agreement with predictions from the Flory–Huggins interaction parameters.

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1. Introduction

The addition of nanoparticles (NPs) to a polymer matrix may significantly improve their properties such as their electrical conductivity, heat and chemical resistance, and mechanical strength [1–7]. The extent of these property enhancements is usually affected by the presence of NP aggregates in the polymer. Unfortunately, controlling the dispersion of NPs in polymers remains a challenge [1]. In order to prevent particle agglomeration and accomplish homogeneous dispersion, NPs are often coated with surfactants [8–10] or polymers [4,11–15]. These molecules stabilize the NP by adding steric repulsion that prevents aggregation [16]. Even so, if there is incompatibility between the NP surface and the polymer, dewetting may occur, leading to phase segregation and NP agglomeration. Significant efforts are dedicated to understanding and predicting miscibility of NPs in polymers, both theoretically [17–23] and experimentally [4,11,12,15,24–27].

From a thermodynamic point of view, the miscibility of NPs in polymers is dictated by enthalpic and entropic contributions. For

the case of low molecular weight surfactants, enthalpic contributions dominate over entropic contributions, and the interaction energy between the particle surface and the matrix plays a critical role [28]. Several methods and strategies have been developed to create homogeneous dispersions in polymer matrices, such as sonication, melt shear, solid-state pulverization, and rapid precipitation [24,29].

Commonly used techniques to evaluate the presence of NP aggregates in nanocomposites include atomic force microscopy (AFM), small angle x-ray scattering (SAXS), small angle neutron scattering (SANS), chemical spectroscopic methods, electrical and dielectric characterization, mechanical spectroscopy, and transmission electron microscopy (TEM), the latter being the most widely used technique [29]. Each one of those techniques has its own limitations. For example, AFM only probes the surface of the materials. Also, TEM requires the preparation of ultrathin sections out of bulk samples, and, in some cases, chemical fixation. For low viscosity polymers, the preparation of TEM samples can be very delicate. SAXS measurements require complex equipment calibration [30–32], especially for liquids and low viscosity melts. Access to SANS is limited and experiments often require deuterium labels to achieve good contrast. Thus, although a variety of techniques are available to characterize NPs dispersion in polymer

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melts there is still a need for complementary characterization techniques.

Magnetic nanoparticles (MNPs) have been used as fillers in polymer nanocomposites in order to imbue the polymers with properties such as for electromagnetic interference shielding [33–36], for triggered drug release [37,38], and to enable magnetothermal repair of the damaged composite [39–41], among other applications [42–45]. For many of these applications it is ideal that the MNPs be well dispersed as single entities throughout the polymer matrix, such that their properties are predictable and such that their enhancement is uniform throughout the material. As such, techniques to assess the presence of MNP aggregates in polymer nanocomposites are of interest for the evaluation of preparation and processing strategies.

For nanocomposites containing MNPs, unique techniques to characterize their dispersion can be developed by taking advantage of the magnetic properties of the NPs. One such technique is the measurement of MNP response to an applied low amplitude alternating magnetic field, through so-called dynamic magnetic susceptibility (DMS) measurements (also known as ac magnetic susceptibility measurements). We have previously shown that quantitative nanoscale viscosity measurements can be obtained from DMS measurements [46]. We have also used this technique to monitor phase transitions in the surrounding media, colloidal stability of MNPs in simple fluids, and adsorption of proteins to MNPs [47–49]. Others have also applied this technique to evaluate the mobility of nanoparticles in polymer hydrogels [50] and to evaluate the rheological properties of the suspending fluid [51]. Here we show that dynamic magnetic susceptibility measurements can be used to evaluate the presence of MNP aggregates in polymer matrices.

Controlling the spatial distribution and aggregation of NPs in polymers remains a challenge [1]. Various theoretical approaches have been introduced to predict NP miscibility and behavior in polymers, such as the Polymer Reference Interaction Site Model (PRISM) [18,19], application of Density Functional Theory (DFT) [20], and Self-Consistent Mean Field Theory (SCMFT) [21–23]. However, developing simpler so-called rules-of-thumb to predict and understand NP dispersion in polymers would be desirable. The Flory–Huggins interaction parameter χ has proven useful in predicting the miscibility of polymer blends [52,53]. Recently, the Flory–Huggins interaction parameter, calculated from the so-called solubility parameters δ , has been used to interpret the dispersion of NPs in polymers [28]. Even though estimating χ from δ and predicting the dispersion state based on the value of χ may not be as accurate as the computational methods listed above, the ease with which the Flory–Huggins parameter can be estimated could facilitate exploratory studies in new polymer–MNPs systems.

In this article, we use DMS measurements to assess if MNPs are well dispersed or aggregated in polymer melts. The experimental observations are then interpreted with the use of Flory–Huggins interaction parameter.

2. Use of DMS measurements to study nanoparticle dispersion in polymers

Magnetic nanoparticles subjected to time-varying magnetic fields may have their magnetic dipoles track the applied magnetic field through the so-called Brownian or Néel relaxation mechanisms [54]. In Brownian relaxation, the magnetic moments of the NPs are “locked” to a crystal direction (so-called thermally blocked NPs). Therefore, the magnetic dipole tracks the applied time-varying magnetic field by physical particle rotation, with a characteristic response time that is a function of the rotational

diffusivity of the particles. In Néel relaxation, the magnetic moment rotates within the particle, opposed by internal energetic constraints represented by the magnetocrystalline anisotropy of the material. In this case, the magnetic dipole can track the time-varying magnetic field without any rotational movement of the particle. The characteristic times for these two mechanisms are given by the equations

$$\tau = \frac{\tau_B \tau_N}{\tau_B + \tau_N}; \tau_B = \frac{\pi D_h^3 \eta_0}{2k_B T}; \tau_N = \tau_0 \exp\left(\frac{\pi K D_m^3}{6k_B T}\right) \quad (1)$$

after reference [54], where τ is the effective magnetic relaxation time of the particles, τ_B is the Brownian relaxation time, τ_N is the Néel relaxation time, D_h is the particle hydrodynamic diameter, η_0 is the suspending medium viscosity, k_B is Boltzmann's constant, T is the absolute temperature, τ_0 is a characteristic time, K is the particle magnetocrystalline anisotropy constant and D_m is the diameter of the magnetic core. For particles that relax through the Brownian relaxation mechanism, the magnetic relaxation time will depend, at a given temperature, on the hydrodynamic diameter of the particles and the viscosity of the surrounding medium, as long as the assumptions inherent in Eq. (1) apply. This will be the case when the particles are well dispersed, such that there are no particle–particle magnetic or hydrodynamic interactions. When MNPs aggregate one would expect an increase in resistance to particle rotation and hence an increase in the effective magnetic relaxation time, as demonstrated previously for aggregation of magnetic particles in simple fluids [48]. In this case, we assume that there may be a change in effective magnetic relaxation time when there is particle aggregation, which would correspond to an increase in the effective hydrodynamic diameter of the particles.

The mechanism of magnetic relaxation for suspended MNPs, and the corresponding relaxation times can be studied using a variety of methods, including DMS measurements [55,56]. DMS measurements do not require optic access and require small sample volumes. DMS measurements consist of measuring the magnetization of a sample subjected to an applied, low amplitude alternating magnetic field of selected frequency. For the case of a sinusoidal applied field of low enough amplitude, such that the magnetization response is linear with the field, the dynamic magnetization of a suspension of MNPs is described by the Debye model [57], which relates the components of the dynamic or complex susceptibility $\hat{\chi}$ to the applied field frequency Ω and the effective magnetic relaxation time according to

$$\hat{\chi} = \chi' - j\chi''; \chi' = \chi_\infty + \frac{\chi_0 - \chi_\infty}{1 + \Omega^2 \tau^2}; \chi'' = \frac{(\chi_0 - \chi_\infty) \Omega \tau}{1 + \Omega^2 \tau^2} \quad (2)$$

where χ' and χ'' are the real (in-phase) and imaginary (out-of-phase) components of the dynamic susceptibility, respectively; χ_0 is the initial susceptibility, and χ_∞ is the high frequency susceptibility.

According to the Debye model, a plot of the dynamic susceptibility spectrum as a function of applied field frequency should show an in-phase susceptibility with plateaus at low and high frequencies and an out-of-phase susceptibility with a peak corresponding to the condition $\Omega_{peak} \tau = 1$. Thus, measurements of the dynamic magnetic susceptibility can be used to verify Debye behavior in MNP suspensions and to determine the effective magnetic relaxation time, either from determination the peak frequency Ω_{peak} or from fitting Eq. (2) to the measured in-phase and out-of-phase susceptibility.

Because DMS measurements allow for accurate determination of the relaxation time of suspended MNPs, such measurements using particles relaxing by the Brownian mechanism have been proposed for applications such as biosensors [58–61] and

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