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Dynamics of nanocomposites

Gerald J Schneider

The results on the dynamics of the polymer chains in classical nanocomposites of hard nanoparticles in a soft matrix are summarized. The molecular motion depends on the interactions of the chains with the nanoparticle surfaces and concentration. Addition of nanoparticles reduces the diffusion of chains and changes the entanglement density. Even strongly adsorbed chain segments seem to be highly mobile. The mode spectrum of the large-scale segmental chain relaxation is strongly affected by adsorption, while the relaxation time is lesser or not affected. Substantial progress has been achieved in understanding and producing materials with unparalleled properties. Especially grafting chains that are chemically dissimilar to the matrix chains can use the dynamic asymmetry and have the capability to manipulate and produce materials for future applications.

Address
Department of Chemistry and Department of Physics, Louisiana State University, Baton Rouge, LA 70803, USA

Corresponding author: Schneider, Gerald J (gjschneider@lsu.edu)

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Introduction and background

Adding fillers to polymer melts changes the macroscopic properties. These materials are very useful for automotive structural components [1], such as car tires, but also electromagnetic conductivity, shielding, and resistance to high voltages [2]. All these materials have in common that a 'hard' filler is added to a soft matrix, and the properties of the composite are more favorable than those of the pure constituents. In the classical definition, the term soft refers to a material with a low modulus, such as a polymer, and the notion hard to high modulus fillers like silica, carbon black, or carbon nanotubes [3]. More recent results increased the awareness on the importance of 'soft' fillers, like in all-polymer nanocomposites [4,5,6••,7] or stimuli responsive materials [8••]. Hereafter the focus is on blends of hard particles with a soft matrix.

In classical composite materials, the desire to increase the stiffness, modulus or viscosity by a 'hard' filler added to a soft matrix is associated with the so-called dispersion of the fillers, that is, their spatial distribution in the sample [9] and the specific surface area of the smallest unit, the so-called primary particles [3]. In a standard definition, the material is called nanocomposite when at least one component has a size lesser than 100 nm [10]. Many examples suggest a more accurate definition, like the challenges associated with hierarchically structured particles in composites [11•,12–19]. In such systems, the primary particles usually assemble into aggregates and the latter eventually form larger structures [3]. Hereafter, we concentrate exclusively on those nanocomposites in which nanoparticles do not assemble into clusters.

Many authors have demonstrated that stable colloidal dispersions of hard particles in a soft matrix can be produced [20••,21–26,27••,28,29••,30,31•,32,33•]. A variety of techniques permit to characterize the morphology and the dynamics of such systems, including the structure of the particles, the conformation of the polymer chains, and dynamics of the particles and the chains. Hereafter, the scope is on the dynamics of the polymer chains and those changes caused by the addition of nanoparticles.

The viscosity of polymer chains is an easily accessible parameter that represents the motion of the chains. A first theoretical attempt was developed by Einstein [34–36]. In his Ph.D. thesis, he calculated the viscosity η as a function of the volume fraction of spheres and the viscosity, $\eta_{\Phi=0} = \eta(\Phi = 0)$, of the solvent [34–36]. He limited his calculations to low sphere concentrations and a repulsive hard-sphere potential and derived a clear and well-proven result $\eta = \eta_{\Phi=0}(1 + 2.5\Phi)$. Guth and Gold extended this equation in the 1950s to the case of composites [37]. In order to account for the strong increase of the viscosity by adding carbon black to rubber materials an additional non-linear (empirical) term was introduced $\eta = \eta_{\phi=0}\left(1 + 2.5\Phi + 14.1\Phi^2\right)$ [37,38]. The authors associated this additional term with previously neglected particle–particle interactions. Despite the missing theoretical justification this equation has been frequently used in the literature [38]. Even in up-to-date text books this or similar equations can be found [3]. It shows (i) rheology experiments at high concentrations are influenced by the polymer dynamics, by particle–particle and particle–polymer interactions, but also that (ii) this model does not capture the viscosity decrease that has been reported [3] or the strong changes in nanocomposites [39,40•], as exemplified later.

Nevertheless, the theoretical treatment enhances our awareness on two important challenges, multiple constituents contribute to the signal, and the perturbation, for example, caused by a shear stress, or induced by different techniques needs to be considered, as in the application of shear force. To understand the experiments Einstein concentrated on the solvent viscosity (dynamics), whereas effective medium theories try to account for all the effects, but as a drawback *average over all contributions*, thus considerably simplifying systems and allowing for a reasonable agreement with experimental data [3]. Hereafter we summarize a variety of results and try to emphasize on those results that enhance our fundamental understanding.

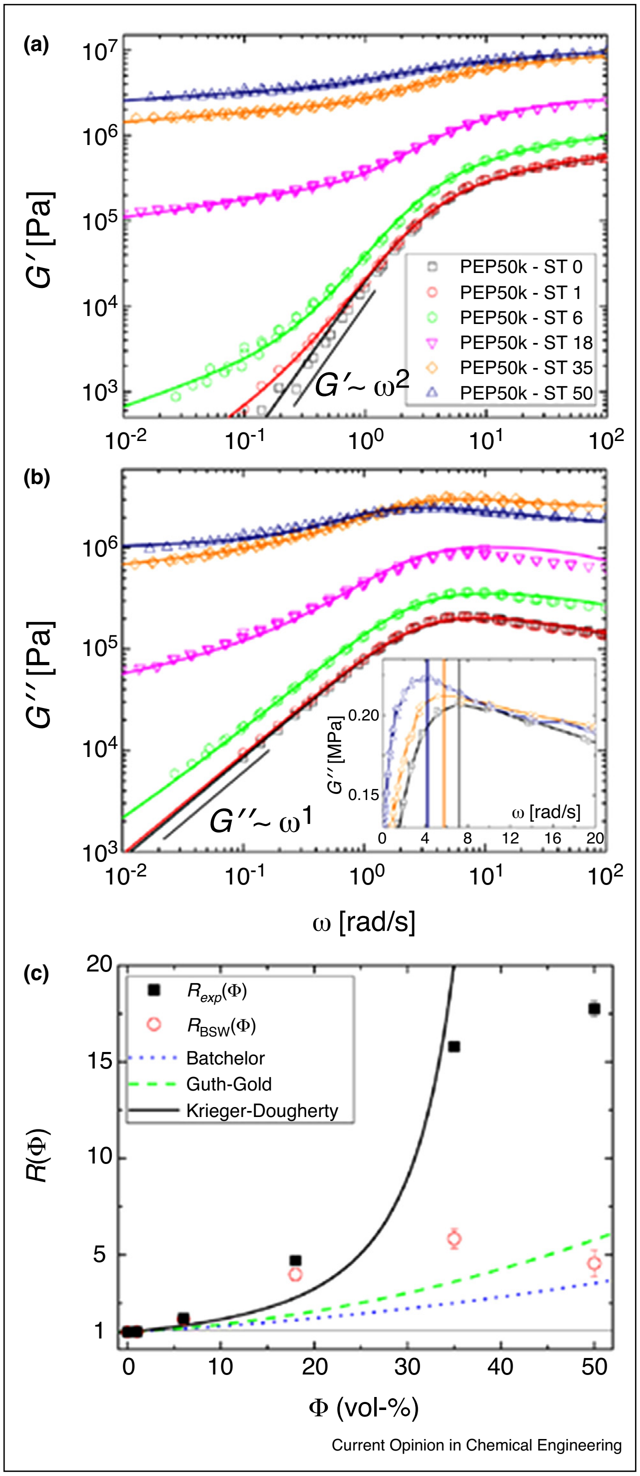
Macroscopic response of nanocomposites

Notable advances have been made in the field of nanocomposite physics in the last few decades using a variety of different experimental techniques and very sophisticated samples or sample preparation techniques. The literature reflects multiple exceptional number of effects that can be generated and may be useful for our future advancement.

There are many dynamical mechanical studies in the literature evidencing the broad variations that can be achieved with different mixtures [25,39,41–43,44•]. Both reinforcement [3,25,39,41,45–47] as well as viscosity reduction [25,48,49,50•] are observed. Besides topological filler–filler effects, sometimes referred to as gelation and caused by deformation of the polymer [42,51,52], additional mechanisms are discussed. When chains adsorb on surfaces, they form essentially irreversibly adsorbed layers, frequently referred to as a bound layer, which is accompanied by dangling ends and chains forming loops [44•,52–55]. Even in the case of weak adsorption of monomers, the entire chain could be strongly adsorbed due to many monomers contacting the surface [56]. In case of strong adsorption, flattened chain conformation and a lengthening of the relaxation time is observed [52,54,56–59]. Because each component and their mutual interactions can contribute, interpreting the results of rheology experiments is challenging and relies on assumptions.

Figure 1 displays a typical result of rheology experiments in the linear region by Nusser *et al.* [40•]. For this study a mixture of a polymer with linear architecture, poly(ethylene-*alt*-propylene) (PEP), and silica particles were used. The particles carried a short organic layer, to avoid adsorption of PEP, and as described later also important to reduce or avoid agglomeration [26]. Here the storage G' and loss modulus G' as a function of the frequency, ω, are used, while many studies concentrate on the energy dissipation of the material ascribed to $\tan \delta = G''/G'$ [3]. The data presentation concentrates on the very important frequency region associated with the large-scale slow

Figure 1



Experimental results on the viscoelasticity of PEP-silica PNCs [40•]. The molecular weight of PEP is 50 kg/mol. The number after ST indicates the volume fraction of silica nanoparticles. Reproduced from Nusser *et al.* [40•].