



Feature article

Linear viscoelasticity and dynamics of suspensions and molten polymers filled with nanoparticles of different aspect ratios



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ABSTRACT

In the present review, we report the linear viscoelasticity of suspensions and polymers filled with nano-size particles of different aspect ratios and structuration. The viscoelastic behaviour of liquid suspension filled with well-dispersed and stabilised particles proves that the Brownian motion is the dominant mechanism of relaxation. Accordingly, dilute and semi-dilute suspensions of stabilised carbon nanotubes, cellulose whisker and PS nanofibres obey a universal diffusion process according to the Doi–Edwards theory. Regarding spherical particles, the Krieger–Dougherty equation is generally successfully used to predict the zero shear viscosity of these suspensions. Regarding fractal fillers, two categories can be considered: nanofillers such as fumed silica and carbon black due to their native structure; and secondly exfoliated fillers such as organoclays, carbon nanotubes, graphite oxide and graphene. The particular rheological behaviour of these suspensions arises from the presence of the network structure (interparticle interaction), which leads to a drastic decrease in the percolation threshold at which the zero shear viscosity diverges to infinity. Fractal exponents are then derived from scaling concepts and related to the structure of the aggregate clusters. In the case of melt-filled polymers, the viscous forces are obviously the dominant ones and the nanofillers are submitted to strong orientation under flow. It is generally observed from linear viscoelastic measurements that the network structure is broken up under flow and rebuilt upon the cessation of flow under static conditions (annealing or rest time experiments). In the case of platelet nanocomposites (organoclays, graphite oxide), a two-step process of recovery is generally reported: disorientation of the fillers followed by re-aggregation. Disorientation can be assumed to be governed by the Brownian motion; however, other mechanisms are responsible for the re-aggregation process.

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1. Introduction

The rheology of the suspensions started with the famous work of Einstein in 1905 and 1911 on the prediction of the viscosity of hard-sphere suspensions at low particle concentrations. In this dilute regime, the hydrodynamic disturbance of the flow field induced by the particles in the suspending liquid leads to an increase in the energy dissipation and an increase in the relative viscosity, η_r , according to the equation (1):

$$\eta_r = \frac{\eta}{\eta_s} = 1 + 2.5\phi \quad (1)$$

where η is the viscosity of the suspension, η_s the viscosity of the suspending liquid and ϕ the volume fraction of particles. In fact, the

constant 2.5 is the intrinsic viscosity ($[\eta] = \lim_{\phi \rightarrow 0} (\eta - \eta_s / \phi \eta_s)$), and theoretically for rigid spheres $[\eta] = 2.5$.

In the dilute regime of hard particles, the interparticle forces are negligible compared with hydrodynamic forces and Brownian diffusion. In other words, there are no attractions between the particles but only an excluded volume effect. At higher concentrations the probability of particle collisions increases so that the hydrodynamic interactions become the dominant ones. As a result the Einstein law fails since a significant positive deviation of the relative viscosity is observed. Furthermore, a shear thinning behaviour of the viscosity is observed with increasing volume fraction of particles. There are numerous models available for the description of the rheology of suspensions of spherical spheres, which is still an open domain of theoretical investigations [1]. However, the semi-empirical equation of Krieger and Dougherty [2] for mono-dispersed suspensions is one of the most used and developed in the literature. The concentration dependence of the zero shear viscosity is expressed as:

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$$\eta_0 = \eta_s \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \quad (2)$$

Where ϕ_m is the maximum packing fraction of particles. At this concentration, the zero shear viscosity rises to infinity and the suspension exhibits a yield stress behaviour. The Krieger–Dougherty equation can be simplified to the Quemada equation [3] $\eta_0 = \eta_s(1 - (\phi/\phi_m))^{-2}$ since it generally observed that $[\eta]\phi_m = 2$ in most usual suspensions.

In model systems of monodispersed hard spheres, the critical volume fraction ($\phi_m \approx 0.63$) reported by Bicerano et al. [4] and Smith and Zukoski [5] for the approach of the zero shear viscosity to infinity is near the random close packing value of 0.64. The right particle fraction at which the zero shear viscosity diverges to infinity is still an open debate as most of the experimental results are far below the theoretical packing value. The Krieger–Dougherty model is generally used as a mathematical equation, where ϕ_m and $[\eta]$ are two fitting parameters, to numerically fit the concentration dependence of the zero shear viscosity. To give a physical meaning to both parameters, a common way is to derive ϕ_m as an effective maximum packing fraction $\phi_{m,eff}$ and $[\eta]$ is related to the deviation from ideal spheres in terms of aspect ratio of the particles. The value of $\phi_{m,eff}$ is no more a universal value as it has to be determined for each suspension. In fact, $\phi_{m,eff}$ includes deviation from ideal particles, as deformable spheres for example. On the other hand, aggregate particles can be expressed from an effective volume fraction ϕ_{eff} . Regarding the particle aspect ratio, Barnes [6] proposed the following formula for the intrinsic viscosity $[\eta] = 0.07(L/d)^{5/3}$ and $[\eta] = 0.3(L/d)$ for rod-like and disc-like particles respectively (L : longest length and d = diameter or thickness respectively). Even without any physical meaning, the Krieger–Dougherty equation is a useful tool to visualise at a glance the rheological trend of suspensions. In some cases (latex for example), it is of importance for useful development from the point view of process-engineering applications to have the lowest viscosity for the highest solid content. From equation (2) and keeping constant the viscosity of the suspending liquid, the only way is to increase the packing fraction ϕ_m . This is generally achieved by using a bi-modal distribution of particles [7]. In contrast, in some applications like suspensions filled with conductive fillers, the lowest percolation threshold is required in terms of formulation costs and weight saving. The Krieger–Dougherty equation shows that particles with high aspect ratio (an increase of $[\eta]$ and/or with aggregation ($\phi_{eff} > \phi$) including fractal particles) are required for such applications. Consequently, the physic of suspensions and its extension to molten filled polymers is extremely complicated as the simple case of inert and rigid spheres at low concentration is generally far from real life. The suspensions and filled polymers are the world of colloidal particles as they offer many possibilities of material developments. In the colloidal size domain, the Brownian forces, direct interparticle forces and viscous hydrodynamic forces are all of comparable magnitude. In some cases, the particle–particle interactions play a dominant role in these systems and results in aggregation or flocculation with possible fractal organisation of such clusters. In fact, the balance of the different interaction can be tuned from a judicious chemical modification of the filler surface and then open a marvellous world for the control of the target rheological behaviours. Therefore, the rheology of colloidal dispersions exhibits a rare diversity and has been the subject of several publications and reviews. The last one of greatest and practical interest was published by Genovese [8]. This paper reviews the shear rheology of suspensions and matrix polymers filled with microscopic and colloid particles. The shear rheology of the suspensions has been discussed from the Krieger–Dougherty equation as it is well known, with some simple modifications taking into account the deviation from ideal cases, to

effectively predict the concentration dependence of many types of suspensions. In the case of aggregated suspensions, the authors demonstrated the analogy between several theoretical models devoted to yield stress and elastic modulus of these gels.

If the shear rheology (steady shear flow experiments) is well described in the literature for suspensions, the linear viscoelasticity under oscillatory measurements is more limited in terms of publications. However, the linear viscoelasticity has been extremely used to characterise the viscoelastic properties of polymer melts filled with nano-sized fillers (nanocomposites). A direct consequence of filler incorporation in molten polymers is the significant change in viscoelastic behaviour as they are sensitive to the structure, concentration, particle size, shape (aspect ratio) and surface modification of the fillers. As a result, rheological methods are useful and suitable to assess the quality of filler dispersion [9]. In recent years, nearly all types of nano-fillers have been used for the preparation of nanocomposites: organoclays, carbon black, fumed and colloid silica, carbon nanotubes, cellulose whiskers, metallic oxide, etc. and more recently graphite oxide and graphene. From a literature survey, thousands of papers and reviews have been published in this broad scientific area and consequently we can only cite the most recent reviews [10–14]. From a physical point of view, nanoparticles in suspending fluid are submitted to particle–particle forces, particle–fluid interactions, viscous forces under flow and finally Brownian forces. The Brownian motion arises from thermal randomising forces that lead to the dispersion of the nanoparticles. Consequently, Brownian motion is ever present even in highly viscous systems (entangled polymer melts). The aim of the present paper is to review some linear viscoelastic behaviours of suspensions and molten polymer filled with nanoparticles of different aspect ratios such as spheres, platelets and nanotubes (or nanofibres). Actually, the viscoelastic and dynamic behaviours have been discussed for each system taking into account the dispersion at different scales of nanoparticles as it was reported in the corresponding papers. Finally, this review is addressed in terms of a comprehensive study of the viscoelastic behaviour and modelling from the Brownian diffusion of nanoparticles.

2. Particle diffusivity

In the dilute regime of suspensions, the particles can rotate about their centre of mass. The particles are then able to rotate freely without any interference interaction with neighbouring ones. The particle diffusivity in this dilute regime is controlled by the Brownian forces ($\sim k_B T$, k_B is the Boltzmann constant) in the suspending liquid (viscosity η_s), which exerts the Stokes friction ($\sim 6\pi\eta_s R$) on the particle (radius of the particle R) and is written as:

$$D_0 = \frac{k_B T}{6\pi\eta_s R} \quad (\text{m}^2\text{s}^{-1}) \quad (3)$$

This equation is also known as the Stokes–Einstein law. The rotary particle diffusivity (Unity: s^{-1}) has been derived for non-spherical particles as following [15]:

Particles of nearly spherical shape (diameter d):

$$D_{r0} = \frac{k_B T}{\pi\eta_s d^3} \quad (4)$$

Spheroid particles of the longest length L :

$$D_{r0} = \frac{3k_B T \left(\ln\left(2\frac{L}{d}\right) - 0.5 \right)}{\pi\eta_s L^3} \quad (5)$$

Platelet or circular disc-like particle of diameter d :

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