

Rheological behaviour of polystyrene latex near the maximum packing fraction of particles

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Abstract

Additional developments in the comprehension of the rheological behaviour of polymer latices, especially near the high critical concentration ϕ_c , are presented for two polystyrene latices of average particle diameters close to 200 nm with different electrostatic properties. Not surprisingly, there is a rapid transition in the rheological characteristics over a narrow range of polymer volume fractions as the concentration of the disperse phase increases. By examining twelve different polymer volume fractions a unique value of the critical volume concentration, ϕ_c , was found for each latex. At this point, the steady shear viscosity, dynamic modulus, and dynamic shear viscosity change dramatically. Furthermore, these critical concentrations are well confirmed by the percolation theory for the dynamic zero shear viscosity as a function of volume fraction. The Cox–Merz rule is not obeyed by these dispersions at the concentrations greater than ϕ_c . By using a controlled strain Couette rheometer with a gap of 1.2 mm, shear thickening limits were also observed for both latices. The concentration dependence of the onset shear rate for shear thickening changes near ϕ_c for each of the two latices.

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1. Introduction

The rheological properties of suspensions of non-deformable particles with relatively narrow distribution have been described in the recent literature by many researchers. The volume fraction dependence viscosity of a wide variety of these dispersions is well described by the Krieger–Dougherty [1] equation, originally introduced to describe hard sphere suspensions. More recently, the rheological properties of aqueous polyurethane dispersions were reported by Flickinger et al. [2,3], who observed the development of an apparent yield stress at the highest concentrations considered (~ 44 vol%). It has also been shown that the rheological character of a dispersion changes from a primarily viscous response at low particle concentrations, to an elastic response at high particle

concentrations. This was demonstrated by measuring the viscoelastic properties of many polymeric latices [4–9].

As the effective volume of the particle becomes more deformable, e.g. when there is a thick layer of stabilizer surrounding a hard particle, Mewis et al. [10] showed that the Krieger–Dougherty equation becomes less effective in describing the variation of the zero shear viscosity data as a function of particle concentration. For hard particles, this expression also underestimates the low shear rate relative viscosity (η_{0r}) as the maximum packing volume fraction (ϕ_m) is approached [11,12]. Under these conditions, the dispersions approach a glass transition and the Doolittle [13] equation often captures the volume fraction dependencies of η_{0r} better than that of Krieger and Dougherty equation.

Horn et al. [14] prepared dispersions of concentrated charge-stabilized polystyrene using the potassium salt of styrene-sulfonate as co-monomer. They investigated the shear rheology of this latex and demonstrated that both high frequency and high shear viscosity were dominated by hydrodynamic interactions, and were independent of the

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ionic strength. They also showed that these two quantities were not identical due to the micro-structural distortion resulting from high shear.

On the other hand, the zero-shear viscosity (η_0) tends to infinity at volume fractions denoted as ϕ_m , which are well below values of 0.58–0.63 (upper limit for the volume fraction of randomly packed spheres). This range is typical for mono-dispersed dispersions of hard spheres. Furthermore at low shear, ϕ_m strongly depends on the ionic strength, which determines the range of electrostatic interactions. Rescaling the volume fraction by ϕ/ϕ_m allows one to obtain a master curve (i.e. independent of size of particles and salt concentrations) for zero-shear viscosity versus volume fraction. The same dispersions of charged stabilized polystyrene have been used for preparation of bimodal dispersion by Horn and Richtering [15]. In addition, the Cox–Merz rule, i.e. the correlation between the dynamic shear viscosity $|\eta^*(\omega)|$ and the steady shear viscosity $\eta(\dot{\gamma})$ with $\omega \equiv \dot{\gamma}$, is obeyed by solid dispersions only at strains in the linear viscoelastic region and at concentrations below the gel point where the system can obtain a Newtonian shear plateau or the onset of an apparent yield point for the system [2,3,16]. In the regions of shear thinning, the dynamic viscosity is always greater than the shear viscosity.

Another important phenomenon in highly concentrated latices is shear thickening behaviour. For example, Laun et al. [17] investigated shear thickening in non-aqueous dispersions using various types of rheometers, and concluded that the apparent critical shear rate for the onset of shear thickening depended on the rheometer geometry, but also that the viscosity change of this phenomena can be traced continuously by using a stress-controlled rheometer. Viscosities of concentrated shear thickening dispersions were measured as a function of shear rate, Couette cylinder size, and time by Boersma et al. [18,19]. At shear rates above the onset of shear thickening for $\phi > 0.57$, strong viscosity instabilities were detected, together with a dependence on cylinder size. The instabilities are attributed to reversible order–disorder transitions, e.g., from strings to clusters. This dependence on cylinder size is due to wall slip, slipping planes in this dispersion, and even plug flow in the gap. With less concentrated, or polydisperse dispersions the effects are much less severe, but thixotropic behaviour was observed nevertheless, probably due to a reordering of the dispersion. Laun [20] also measured the first and second normal stress differences for a strongly shear thickening nonaqueous polymer dispersion of 58.7 vol% of styrene and acrylate copolymer.

The rheological and microstructural properties of dense suspensions of uniform, charge-stabilized colloidal spheres were investigated by Chow and Zukoski [21,22]. Thickening was only observed above a volume fraction of 0.4–0.5, depending on particle size and the shear rates. Xu et al. [23] observed a time-dependent shear thickening phenomenon in a commercial aqueous poly(acrylic ester) dispersion. The critical shear rate for the shear thickening transition varied

as a function of the volume fraction, temperature, pH, and particle size distribution, in a manner which indicates that the phenomenon is associated with a reversible shear-induced colloidal order–disorder transition. It is possible that the time-dependence is caused by the temporary formation of particle clusters at high shear rates. The authors measured the critical shear rate at which shear thickening begins for four concentrations above 57%. It has been shown that this shear rate is a strongly decreasing function of solid concentration.

Melrose et al. [24] and Catherall [25] studied the shear thickening of systems stabilized by charges and/or polymer layers using Stokesian dynamics at core volume fractions $> 40\%$ (the core volume fraction refers to the fraction occupied by the particle alone, and does not include the volume of the stabilisation layer). Strong thickening behaviour was only observed in the case where a polymeric stabilizer was used. However, there remains a lack of studies on the non-Newtonian phenomena common to almost all of dense suspensions as shear thickening.

The objective of the present work is to investigate the rheological properties of concentrated polystyrene latices with different electrostatic properties around the high critical concentration. Linear viscoelasticity experiments were used to study the transition from viscous to elastic flow, and the variation of the dynamic zero shear viscosity at the gel point is discussed in terms of the percolation theory. Additionally, the critical exponent on the dynamic zero shear viscosity at the percolation threshold will be correlated with the Krieger–Dougherty equation. Furthermore, the zero shear viscosity of PS latices is discussed in terms of effective volume fraction, and the applicability of the Cox–Merz rule is examined. Finally, the shear-thickening behaviour of the two different latices is studied in terms of the critical shear rate in order to identify the shear thickening transition as a function of the volume fraction.

2. Experimental

2.1. Material preparation

The two latices were made by emulsion polymerisation using ammonium persulphate (APS) as the free radical initiator. The first latex of polystyrene homopolymer (PS) was produced in a semibatch reaction that lasted for 12 h, using Disponil[®] 3065 (mixture of linear ethoxylated fatty acids) as the non-ionic surfactant. The second latex (PSS) is a copolymer of styrene plus 13% by weight (with respect to total polymer) of the potassium salt of styrene sulphonate. PSS was produced directly in a batch reaction using Triton 405X as the non-ionic surfactant. The major difference between the two latices is the presence of strong acid groups on the surface of PSS with a dissociation constant similar to that of the initiator. These acid groups will change the degree of the hydrophilicity of the particle surface.

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