

P.A. Nommensen
M.H.G. Duits
J.S. Lopulissa
D. van den Ende
J. Mellema

Rheology of suspensions stabilized by long grafted polymers

P.A. Nommensen · M.H.G. Duits (✉)
J.S. Lopulissa · D. van den Ende · J. Mellema
University of Twente
Department of Applied Physics
Rheology Group
P. O. Box 217
7500 AE Enschede
The Netherlands

Abstract The synthesis of colloidal silica spheres grafted with long poly(dimethyl siloxane) chains as described in literature has been successfully reproduced. The particles have been elaborately characterized, using different techniques and taking advantage of the availability of the unreacted bare particles and free polymer. Rheological measurements were performed on dispersions in heptane, all made from a single stock. An effective volume fraction was defined, based on the viscosity at low concentrations. Low shear viscosities

and linear viscoelastic properties were measured at effective volume fractions up to 0.81. A transition from liquid-like to solid-like behavior is observed at $\phi \cong 0.60$. Up to this volume fraction, the particles behave much like Brownian hard spheres. At higher concentrations, softness effects become noticeable. Here, also differences from otherwise comparable soft spheres become pronounced.

Key words Dispersions–silica particle–polymer brush – characterization–rheology – hard spheres

Introduction

Since the first experimental results on the rheological behavior of sterically stabilized colloidal hard spheres were published about a decade ago, there has been a growing interest in the dispersion rheology of particles stabilized by longer chains. D’Haene et al. [1] performed an interesting set of experiments with poly(methyl methacrylate) (PMMA) particles of different sizes, coated with (end-grafted) poly(hydroxy stearic acid) (PHS) chains of the same length. In this way, the deviations from hard sphere behavior were systematically varied. Another example is the work of Buitenhuis and Förster [2], who investigated a series of block-copolymer micellar systems, with the molar mass of the outside block as a variable.

In most systems, the (grafted) chains have a “brush-like” character, i.e. the lateral dimensions are (much) smaller than the layer thickness. With this characteristic, a hairy

particle system can still be anything between “nearly hard spheres” and “nearly star polymers”. To classify a particle between these two extremes, a softness parameter can be invoked. However, different softness parameters are used in literature. For instance, D’Haene et al. use δ/a with δ the thickness of the outer layer and a the particle radius, whereas Buitenhuis and Förster also suggest the use of ε/a with ε based on the blob size of the polymer. For monodisperse systems, the volume fraction where the low shear viscosity diverges has also been used as a measure for the softness. Comparisons between the rheology of different polymerically stabilized systems have hardly been made yet.

In this paper we present a rheological study of hairy spheres consisting of silica cores coated with end-grafted poly(dimethyl siloxane) (PDMS) chains. This particle system is relatively new and was selected for a number of reasons. The size distribution for the silica cores can be kept narrow with an appropriate synthesis route. For the

grafting of PDMS chains a promising recipe has appeared in the literature. In addition, since the grafting is performed in a separate procedure, a more elaborate characterization of the particle is possible via separate analysis of the core and the free polymer. The mentioned characteristics of the silica–PDMS system should allow for meaningful comparisons with other (model) systems, as well as with theory. In this paper, the emphasis will be on the characterization as well as on the first rheological results. A comparison with other systems will be made.

Preparation

Silica seed particles having a radius of approximately 50 nm were synthesized according to the method of Stöber et al. [3] and grown out to a final radius of about 80 nm by the addition of TEOS (TetraEthylOrthoSilicate, Merck) in four steps. Next, H₂O and NH₃ were removed from the suspending medium by repeated careful rotatory evaporation at 50 °C and slightly reduced pressure. Subsequently, ethanol was replaced by DEK (DiEthylKetone, Merck) using the same technique. GLC-analysis was used to confirm that all H₂O, NH₃ and ethanol had been removed. The PDMS (ABCR, code PS347.5) used had a M_w of 110.000 g/mol with $M_w/M_n = 1.4$, and was silanol terminated at both ends.

For the grafting of PDMS onto silica, different methods have been presented in the literature [4–8]. However, we and others [6] have observed that reproducing these recipes can be difficult. We have essentially followed the method of Auroy [4] in which the grafting is effected by a condensation reaction between the silanol groups of the PDMS and the silica surface. (Differences in the details will be outlined below.

The silica dispersion was diluted with DEK plus an amount of freshly distilled DIEA (DiIsopropylEthyl Amine, Merck) to obtain weight fractions of 5% for the silica and 4% for DIEA. The function of the amine is to increase the nucleophilicity of the silica surface [5]: 1500 g of this solution were mixed with an equal amount of a 20% (by weight) PDMS-solution in DEK in a 4 L round-bottom flask placed in an oil bath. A first grafting was carried out by maintaining the mixture temperature at 100 °C for 16 h while gently stirring. In a second step, more PDMS was added (now in pure form) to increase its weight percentage in the mixture from 10 to 30%, followed by equilibration overnight, after which the reaction was continued for another 16 h at 100 °C.

The resulting particles were purified from unreacted PDMS by repeated centrifugation/redispersion in heptane. Here the speed was set not higher than 3000 rpm (corresponding to 8500 m/s²) since otherwise the sedi-

mented particles could not be redispersed anymore. The presence of free PDMS in the product was monitored by drying the supernatant, redissolving it in toluene and shaking to see if any foam could be produced. Four centrifugation steps were necessary to obtain a supernatant “free of PDMS” (containing less than 0.005%). The final yield amounted 60 g of PDMS-grafted silica particles.

All sample dispersions were made from a single stock (in heptane). Concentrated samples were made by centrifuging a weighed amount of stock in a glass tube at 8500 m/s² (3000 rpm), pipetting off the calculated weight of heptane and subsequently vigorous shaking of the tube for 5–10 min in a whirl mixer. From the weight fractions w , weight concentrations c were calculated according to $1/c = (v_p - v_s) + v_s/w$ with v_p and v_s the specific volumes of the particles and the solvent, respectively. This equation implies a zero excess mixing volume. For v_s , 1.472 ml/g was used, whereas the value of v_p was determined from mass-density measurements of a concentration series with a density meter (Mettler KEM DA-200) and was found to be 0.526 ± 0.006 ml/g. From the weight concentrations, particle volume fractions can be calculated using the relation $\phi = q*c$ where q is the appropriate specific volume.

Particle characterization

The PDMS content was determined in two ways, after drying the particles overnight at 100 °C. Using solid-state ²⁹Si-NMR, the number of Si-atoms present in PDMS was found to be 0.10 ± 0.02 times the total number of silicons belonging to the silica (as either Q^4 or Q^3); this corresponds to a PDMS content of 0.11 ± 0.02 by weight. Elemental analysis (EA) was also used to estimate the PDMS content of the particles. Here the weight percentages C, H and N of the bare and the grafted particles were compared. Assuming that the compositional changes are due to PDMS only, the weight fraction of the PDMS was estimated to be 0.12 ± 0.02 . Infrared spectroscopy was also done, but for our particles the PDMS absorption bands at 1259 or 814 cm⁻¹ were rather difficult to distinguish from the strong signal caused by the silica.

Transmission Electron Microscopy was used to determine the size distribution of the silica cores. The average radius amounted 80 nm with a standard deviation of 8%. Static and dynamic lightscattering (SLS and DLS) measurements were performed on dilute dispersions. The optical radius found with SLS was 82 ± 5 nm, in agreement with the TEM result. The hydrodynamic radius of the grafted particle in heptane was found to be 140 ± 5 nm, indicating a layer thickness of 58 ± 7 nm.

The hydrodynamic specific volume q_h was determined via intrinsic viscosity measurements using an automated

(Schott) Ubbelohde capillary viscometer. Eleven data points at relative viscosities up to 1.08 were plotted as $(\eta_r - 1)/c$ versus c , and fitted with a straight line. Using Einstein's equation, a q_h of 2.23 ml/g was found from the intercept. Comparing this number with the specific volume of 0.449 ml/g found for the bare particles, the ratio a_H/a_c between the hydrodynamic and the core radius can be calculated. We obtained a value of 1.77 ± 0.1 , in good agreement with the 1.7 ± 0.1 found with light scattering.

From the above results, a number of derived quantities can be calculated. Using a radius of 82 nm and a mass density of 2.2 g/ml for the core, and assuming for the polymer a (monodisperse) molar mass of 110.000 g/mol, a layer thickness of 58 nm (i.e. $a_H/a_c = 1.7$) and a weight fraction of 0.11, the average area per polymer chain is found to be 25 nm² at the silica surface and 72 nm² at the periphery. These calculated estimates show that the lateral dimension of the polymer chains is much smaller than their extension normal to the silica surface, and hence the polymers can be considered as "brush-like".

We have also calculated some other derived quantities, in order to allow a comparison with the work of others. The grafting density expressed in mg/m² amounts 8 ± 1 in our case, which is of the same order of magnitude as the values found for other stable silica-PDMS systems: 4.65 [4], 6.2, 7.7 [5] and 9.8, 14.3 [8]. The number of arms per particle amounts about 3000, which is well above the predicted critical value that allows crystallization of the particles [9]. Indeed crystallization under gravity has been observed.

Rheological experiments

Flow curves were measured with a Contraves Low Shear 40 rheometer equipped with a homemade vapourlock, using a Couette geometry with inner and outer radii of, respectively, 5.5 and 6.0 mm. The particle concentration was varied between 0.076 and 0.40 (weight fractions). The corresponding range for the hydrodynamic volume fraction $\phi_h (= q_h * c)$ is 0.12 to 0.81. Temperature was 25.0 °C for all measurements. The shear rate was varied between 2×10^{-4} and 80 s⁻¹. Reproducibility was checked by probing the same set of shear rates at least twice.

Linear viscoelastic properties were measured with a Bohlin VOR rheometer also equipped with a homemade vapourlock, using a cone-plate geometry. Ten samples with hydrodynamic volume fractions ϕ_h from 0.43 to 0.81 were measured, all at 25.0 °C. Prior to the measurements, all samples were presheared at 81 s⁻¹, with short test-measurements in between to monitor the time dependence of G' at 1 Hz. Measurements were started as soon as this quantity became stable: this could take 30 min for concen-

trated samples. Frequency sweeps were carried out after the critical shear amplitude marking the end of the linear regime had been determined at 1 Hz.

Results and discussion

An overview of our results is given in Fig. 1 (low shear plateau viscosity) and Fig. 2 (frequency-dependent linear viscoelasticity). From both figures it can be seen that a drastic change in the rheological behavior occurs around $\phi_h (= q_h * c) = 0.6$. The low-shear viscosity diverges at $\phi_h = 0.60$. Above this volume fraction, a low-shear Newtonian plateau is no longer observed. In the linear viscoelastic behavior, a transition from a fluid-like to a mainly elastic behavior is observed at $\phi_h = 0.61$. The data at this volume fraction showed a poor reproducibility which appeared to be inherent to the transition.

It is interesting to note that our rheological data show a remarkable resemblance to those obtained by D'Haene et al. [1] for a particular colloidal soft sphere system: PMMA particles with a diameter of 129 nm coated with a PHS-layer of 9 nm thickness and dispersed in decalin. The polydispersity of this system is 12%.

Since the two systems are chemically rather different, the resemblance of their rheological behavior poses the question, under which conditions the specific properties of the polymer layer become important to the rheology. For this reason, a comparison with the mentioned system of D'Haene will be made in the following. First, a comparison with the rheology of hard spheres will be made for both systems.

Rheological behavior for $\phi_h < 0.6$

Fitting the data in Fig. 1 to Quemada's expression [10],

$$\eta_r = (1 - \phi/\phi_m)^{-2}, \quad (1)$$

a "maximum" volume fraction $\phi_m (= q_h c_m)$ of 0.60 ± 0.02 was obtained. This value is within the range of values obtained for other systems of spherical particles with a very short-ranged repulsive ("hard sphere") potential. We have also compared the low shear viscosities themselves with the various "hard spheres" data compiled by Phan et al. [11]: the viscosities for the silica-PDMS system are slightly higher than the compiled data, but still agree within their error ranges. For D'Haene's 129 nm particles, ϕ_m was found to be 0.60 as well.

Next, we will compare the linear viscoelastic behavior of our particles with that of the hard spheres of Van der Werff et al. [12], and D'Haene's 129 nm particles. Assuming that hairy particles behave like hard spheres, it should

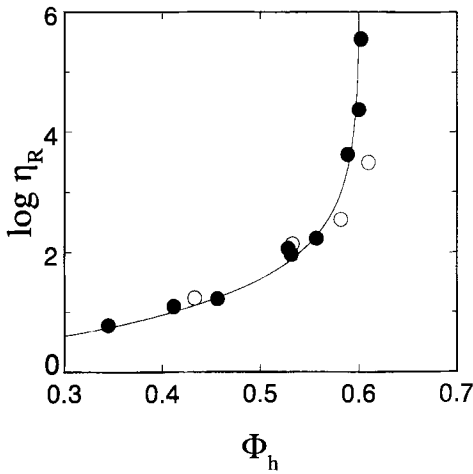


Fig. 1 Relative low shear (●) and low-frequency (○) limiting viscosity versus volume fraction. The drawn line represents the fit to Eq. (1)

be possible to scale out the hydrodynamic particle radius a_h and solvent viscosity η_s . This scaling should lead to a collapse of all data onto master curves, though it should be mentioned that some differences between presumed hard sphere systems have been observed [13]. Below we will analyze the three quantities most characteristic for hard sphere behavior: the low-frequency limit of the real part of the complex viscosity η' ($\omega \rightarrow 0$), and the dominant relaxation time (τ) and strength (G) for low frequencies.

The $\eta'(\omega \rightarrow 0)$ data are incorporated in Fig. 1 since on theoretical grounds, $\eta'(\omega \rightarrow 0)$ should be equal to $\eta(\dot{\gamma} \rightarrow 0)$. Obviously, the agreement with the low-shear data is good. The dominant relaxation time and strength for low frequencies were obtained from a fit to $G'(\omega)$ and $G''(\omega)$ using

the relaxation spectrum description [14]:

$$G'(\omega) = \sum_k G_k \frac{\omega^2}{\omega^2 + 1/\tau_k^2} (+ G_0), \quad (2)$$

$$G''(\omega) = \sum_k G_k \frac{\omega/\tau_k}{\omega^2 + 1/\tau_k^2} (+ \omega\eta'_\infty), \quad (3)$$

where k designates a relaxation, characterized with a strength G_k and a time τ_k . Like for the other two systems, we have not observed any G_0 . The contribution of η'_∞ has been neglected because of the low frequencies involved.

Some differences exist between the types of spectra that have been used by the different authors to describe $G'(\omega)$ and $G''(\omega)$. This is partly due to the different (normalized) frequency ranges used in the different studies. In addition, there are some differences in the precise shapes of $G'(\omega)$ and $G''(\omega)$, but these are not too important for the estimation of the typical relaxation time and strength.

D'Haene reported a “nearly Maxwellian” behavior (only one relaxation): hence G and τ can be directly obtained from the cross-over point between $G'(\omega)$ and $G''(\omega)$. Van der Werff et al. used a *spectrum* of coupled relaxations to describe the behavior at very high frequencies. To characterize the behavior at low frequencies, it is justified to use only the slowest relaxation, characterized by G_1 and τ_1 .

For our particle system, a fit with two relaxations gave the best description of $G'(\omega)$ and $G''(\omega)$. In that case, the mean relaxation time is the most appropriate characteristic time:

$$\tau_M = \frac{\sum_k G_k \tau_k^2}{\sum_k G_k \tau_k}. \quad (4)$$

Figure 3 shows the volume fraction dependence of the relaxation time after multiplication with $k_B T / (6\pi\eta_s a_h^3)$.

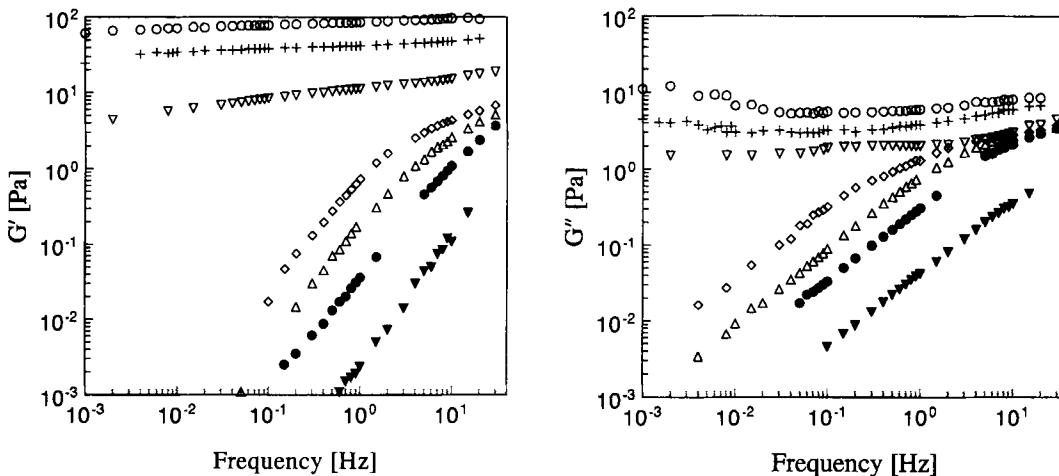


Fig. 2 Linear viscoelastic moduli versus the oscillation frequency. Volume fractions are: ▽: 0.430, ●: 0.533, △: 0.582, ◇: 0.584, ▽: 0.615, +: 0.746, ○: 0.813

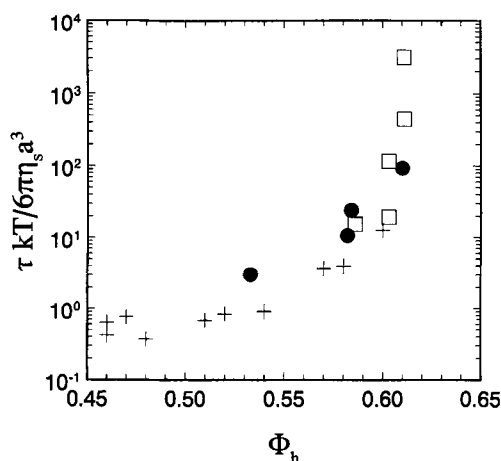


Fig. 3 Normalized relaxation time versus volume fraction: +: hard spheres, ●: silica-PDMS, □: PMMA-PHS

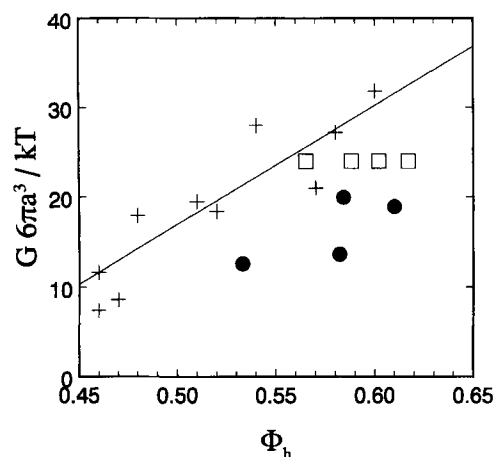


Fig. 4 Normalized relaxation strength versus volume fraction: +: hard spheres, ●: silica-PDMS, □: PMMA-PHS

Here η_s is the solvent viscosity. The background of this scaling is that the relaxation is related to a restoration of the equilibrium pair distribution function via Brownian motion. Considering that rather different systems are compared in the figure, our normalized data are in reasonable agreement with those of the other two systems.

To obtain the typical relaxation strength for the silica-PDMS particles, we have fitted our data with the spectrum as used by Van der Werff, using τ_M for τ_1 and fitting for G_1 . Figure 4 shows the volume fraction dependence of the relaxation strength after multiplication with $6\pi a_h^3/k_B T$. Clearly, the volume fraction dependence of the relaxation strength is much weaker than that of the relaxation time, for all three systems. In addition, the magnitudes of the normalized G values are roughly comparable. As evidenced both by our own data and by those of

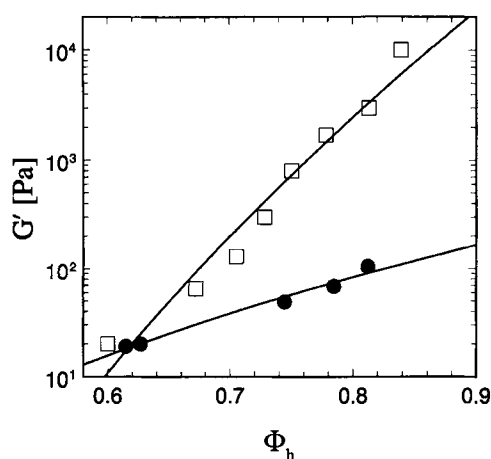


Fig. 5 Plateau value of G' versus volume fraction. ●: silica-PDMS, □: PMMA-PHS

Van der Werff, the uncertainties in the G values are large: this appears to be inherent to their extraction from G' and G'' functions that vary over three or more orders of magnitude.

Considering all foregoing observations, it appears that the different soft-sphere systems can be considered to behave much like hard spheres up to high volume fractions. Apparently, the hairy spheres have to approach each other very closely (or even be compressed slightly) before the deviations from hard sphere behavior (i.e. the detailed interactions between the polymer chains belonging to different particles) become important.

Rheological behavior for $\phi_h > 0.6$

In Fig. 5 the plateau values for G' in the elastic regime are presented as a function of ϕ_h . Fitting the data with a power law yields a power of 6. For D'Haene's particles [15], a much stronger concentration dependence of the G' plateau was found. Fitting their data we found a power of 18. Bearing in mind the relation between G' (plateau) and the particle pair potential [16], this finding indicates that our particles show more softness, when compressed.

Conclusions

The synthesis of monodisperse silica spheres coated with end-grafted PDMS, as developed by Auroy, was successfully reproduced. Working on a 4 L scale, a yield of 60 g particles was obtained. The grafting densities as determined with Si-NMR and Elemental Analysis are in good agreement with each other, as well as comparable to the results obtained by others. The thicknesses of the PDMS

layer as measured with lightscattering and as calculated from the intrinsic viscosity compare favourably with each other. The microscopic picture that emerges from these results is a layer of stretched (i.e. brush-like) polymers with a thickness of 0.7 times the particle radius.

When dispersed in heptane, the particles repel each other via a soft potential as evidenced by ordering phenomena, and long-term colloidal stability. Using a volume fraction definition based on the intrinsic viscosity, volume fractions of 0.8 (and possibly higher) can be obtained. At $\cong 0.60$ on this scale, a transition from a liquid-like to a solid-like behaviour is observed. Comparison with the

rheological behaviour of hard spheres reveals that up to a (hydrodynamic) volume fraction of 0.60, our particles behave much like hard spheres. A comparison with data for a PMMA–PHS soft-sphere reference system shows that the rheological behaviour is very comparable up to $\phi = 0.60$, but above this volume fraction our particles turn out to be softer.

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