

COLLOID SCIENCE

Frequency dependent linear viscoelastic properties of ordered polystyrene latices

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Abstract: An experimental investigation of linear rheological properties of monodisperse ordered latex dispersions has been carried out. Measurements of the dynamic shear modulus and the dynamic viscosity in the frequency range between 0.04 Hz and 2500 Hz are reported. The volume fraction and the electrolyte concentration were variables in the experiment. The results show that a description of the rheological behaviour with a simple linear phenomenological equation is not possible. The measured dynamic moduli can only be described with a great number of relaxation times.

Key words: ordered polystyrene latex, viscoelastic properties

1. Introduction

A monodisperse latex dispersion is a frequently used model system for the investigation of electrostatic interacting forces between colloidal particles. The present study is confined to linear viscoelastic properties of ordered polystyrene latices. As such it is connected to other investigations on the rheological properties of polystyrene latex dispersions reported in the past years [1–10]. In these studies one relates the viscoelastic properties of the latex dispersions to the interparticle forces, which are dependent on parameters such as particle diameter, electrolyte concentration and surface potential. The viscoelastic properties derived in these studies are only valid in a very small frequency range. One group has measured the dynamic shear modulus at about 5 Hz. [9]. A few groups have measured the complex dynamic modulus at one frequency between 185 and 350 Hz [1, 6, 7], another group at 40 kHz [4] and 70 kHz [2]. Basic for their analysis is the question if the measured shear modulus can be compared with the theoretical shear modulus they derived. Russel and Benzing [5, 6] state that their theory (based on a cell model) and measurements at about 300 Hz give the low frequency plateau value of the dynamic shear modulus. Buscall et al. [7, 8] indicate the shear modulus calculated by considering pair wise added particle interactions as the high frequency limit. They conclude to have measured it between 185 and 225 Hz for $\phi > 0.14$. Mitaku et al. [3, 4] also used a cell

model but reason to have measured the high frequency limit at 40 kHz ("glass-like state"). In the present study the dynamic moduli of monodisperse polystyrene latices are measured between 0.04 Hz to 2500 Hz. Its aim is to show that the knowledge of this dynamic behaviour in a large frequency range can give more insight in the number and nature of the relaxation mechanisms that play a role in these systems with strongly interacting particles.

2. Experimental

2.1 Latex preparation

The polystyrene latex was prepared by polymerization of styrene in aqueous potassium hydrogen carbonate (KHCO_3) at 70 °C, using potassium persulphate ($\text{K}_2\text{S}_2\text{O}_8$) as initiator. The used method has been described in detail by Norde [11]. The water was deionised, bidistilled and saturated with N_2 . The styrene (Baker grade) was distilled under reduced N_2 pressure. The potassium persulphate (Merck p. a.) was recrystallized, washed with cold water and dried. The potassium hydrogen carbonate (Merck p. a.) was used without further purification. The concentrations of the components were KHCO_3 : 10^{-3} mol/dm³, $\text{K}_2\text{S}_2\text{O}_8$: $18.5 \cdot 10^{-3}$ mol/dm³ and 65.6 cm³ styrene on a total of 4 dm³ mixture. The polymerization time was 24 hrs. The concentration and cleaning of the latex was performed with a diafiltration system (Amicon TCF 10). The diafiltration of the latex under N_2 atmosphere was repeated until the conductivity of the filtrate was less than 2 μmho . The conductivity of the used wash water, with quality as given above, was less than 1 μmho . The volume fraction of the latex after purification was about 0.25.

The latex volume fractions were determined gravimetrically, by drying a sample to constant weight at 60 °C. The volume fraction

was calculated by taking the density of polystyrene to be $1.05 \cdot 10^3 \text{ kg/m}^3$. Three sample with volume fractions of 0.25, 0.21 and 0.10 were prepared from the same batch of material.

The mean diameter of the latex particles, as determined with electron microscopy was 330 nm, with a standard deviation of 3%.

2.2 Rheological measurements

The dynamic moduli were determined with four single torsion pendula operating in the frequency range of 80 Hz to 2500 Hz and with a dynamic viscometer operating in the frequency range of 0.04 Hz to 1 Hz. A detailed description of the torsion pendula is given by Blom and Mellema [12]. The measuring method is based on the determination of the resonance frequencies and bandwidths of the pendula immersed in the liquid under investigation and in air. From the frequency and bandwidth difference between the measurements in the two media, the dynamic moduli can be deduced.

A condition to be met for this method is that the amplitude of the induced shear wave is almost damped out when it reaches the wall of the sample holder. The penetration distance i. e. the distance over which the amplitude is damped out by a factor or $1/e$ is given by [13]:

$$\delta = \frac{1}{\omega} \sqrt{\frac{2}{\rho} \left(\frac{G'^2 + G''^2}{\sqrt{G'^2 + G''^2} - G'} \right)}, \quad (1)$$

where ρ is the sample density and ω is the angular frequency.

The form of this formula differs appreciably from the one given by Benzing and Russel [6], but they are identical apart from a typographical error.

The dynamic viscometer used in an apparatus similar to the one described by Te Nijenhuis [14]. This apparatus consists of a cylinder suspended by a torsion wire. The torsion wire is given a sinusoidal oscillation. When the cylinder is immersed in the sample it will oscillate with the same frequency but with a different amplitude and out of phase. From the phase lag and the amplitude ratio of the top of the torsion wire and the cylinder, the dynamic moduli can be calculated. For this method a condition to be met is that the wavelength of the induced shear wave is much larger than the gap between the measuring cylinder and the surrounding cylindrical sample holder. The expression for the wavelength λ is given by [13]:

$$\lambda = \frac{2\pi}{\omega} \sqrt{\frac{2}{\rho} \left(\frac{G'^2 + G''^2}{\sqrt{G'^2 + G''^2} + G'} \right)}. \quad (2)$$

The steady state viscosities were determined with a Couette viscometer (Contraves LS 30).

All measurements were performed at a temperature of $10.0 \pm 0.5^\circ\text{C}$.

Except for the steady state measurements, the measurements were performed under a N_2 atmosphere. When an ordered latex is exposed to air, the ordering will disappear within a few days (see also [15]). Then the latex changes from bright iridescence to milky white.

3. Results

3.1 Steady state measurements

Due to the fact that the steady state measurements could not be performed under a N_2 atmosphere, these

measurements gave no reproducible results for the steady state viscosity. The magnitude of the measured viscosities is of the order of the measured dynamic viscosities at the lowest frequency. All the steady state measurements showed the same phenomenon: with increasing strain a sudden drastic lowering of the viscosity occurred at a strain of about 0.25.

3.2 Frequency dependence of G^*

A. Influence of the volume fraction on G^*

Of the prepared samples, with volume fraction $\Phi = 0.25$, $\Phi = 0.21$ and $\Phi = 0.10$ the dynamic modulus

$$G^* \equiv G' + iG'' \equiv \omega(\eta'' + i\eta') \equiv i\omega\eta^*, \quad (3)$$

was measured.

In figure 1 the dynamic shear modulus G' is given as function of the frequency.

In figure 2 the relative dynamic viscosity, defined by

$$\eta'_{\text{rel}} = \eta'/\eta \quad (4)$$

is given. Here η is the viscosity of the continuous phase.

In these and the following figures the lines are drawn tentatively. Both conditions mentioned in section 2 for the damping and the wavelength are met for the results given here.

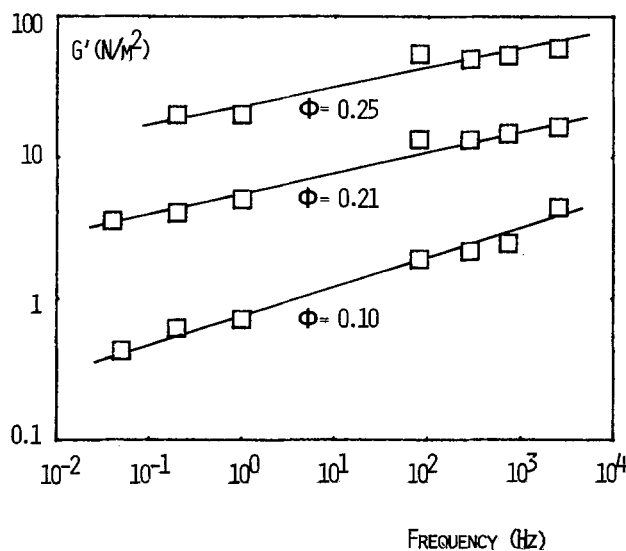


Fig. 1. The dynamic shear modulus as function of the frequency; the indicated parameter is the volume fraction Φ of the latex

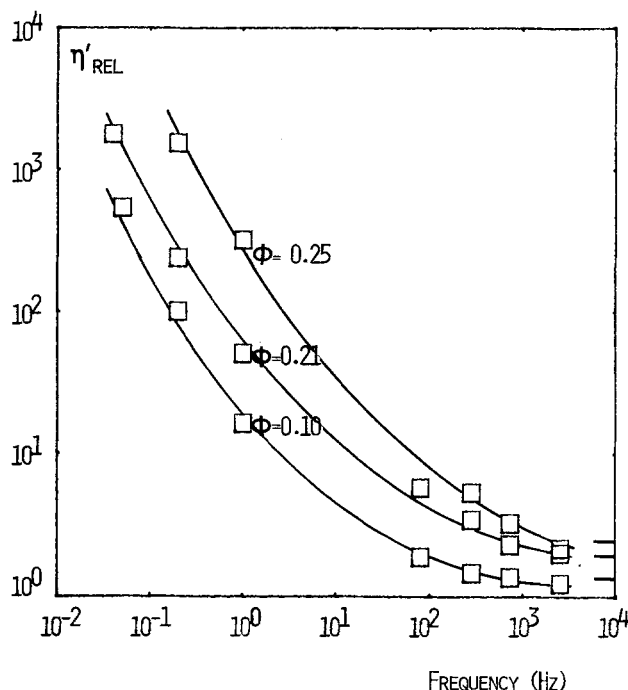


Fig. 2. The relative dynamic viscosity as function of the frequency; the indicated parameter is the volume fraction Φ of the latex. The calculated high frequency limits are indicated with bars

The dynamic viscometer measurements were performed with a maximum strain $\gamma_{\max} < 0.1$ and for the torsion pendula measurements $\gamma_{\max} < 0.01$. Linearity was checked by changing γ_{\max} by a factor 2 and 10 respectively below these upper limits. No deviation from linearity has been demonstrated.

The estimated uncertainties in the dynamic measurements are summarized below. For the dynamic viscometer the uncertainty in η' is 10 % with a bound of 10^{-3} Pa s and the uncertainty in G' is 10 % with a bound of $2 \cdot 10^{-2} \text{ N/m}^2$. For the torsion pendula the uncertainty in η' is 5 % with a bound of $5 \cdot 10^{-5} \text{ Pa s}$ and the uncertainty in G' is 5 % with a bound of $5 \cdot 10^{-2} \text{ Nm}^2$.

The maximum feasible frequency is related to the ratio of the wavelength λ of the shear waves and the interparticle distance a . To provide that macroscopically the latex can be considered as homogeneous in good approximation, this ratio λ/a should be much larger than unit. For example for $\Phi = 0.1$ (for this value the interparticle distance is about equal to the particle diameter) and frequency $F = 2500 \text{ Hz}$, The values for G' and G'' are about $3,5 \text{ N/m}^2$ and 25 N/m^2 respectively. From (2), using $\rho = 10^3 \text{ kg/m}^3$ it follows that $\lambda \approx 10^{-4} \text{ m}$, which means that there are about 150 particles over one wavelength. For higher frequencies this

number will become smaller which means that macroscopically the latex behaves less and less as a continuum. The measurements give the impression that the ratio λ/a is large enough, as no anomalies at the highest frequencies are observed. Figures 1 and 2 show, as observed by others [4, 6, 7], that at a fixed frequency G' and η' increase as function of the volume fraction. New is that it appears that G' is increasing with frequency. Further η'_{rel} is strongly decreasing with frequency.

Noteworthy is that $\frac{\partial \log G'}{\partial \log F}$ is almost independent of the latex volume fraction.

B. Influence of the electrolyte concentration on G^*

To the sample with volume fraction $\Phi = 0.21$, KCl has been added such that the overall KCl concentrations in the sample were about 10^{-5} , 10^{-4} and 10^{-3} mol/dm^3 respectively. In figures 3 and 4 the influence of the added electrolyte on the dynamic shear modulus and the relative dynamic viscosity as function of the frequency is demonstrated. The upper curve in both figures represents the measurements with no electrolyte added to the sample. The gradual destruction of the lattice with increasing electrolyte concentration displays it-

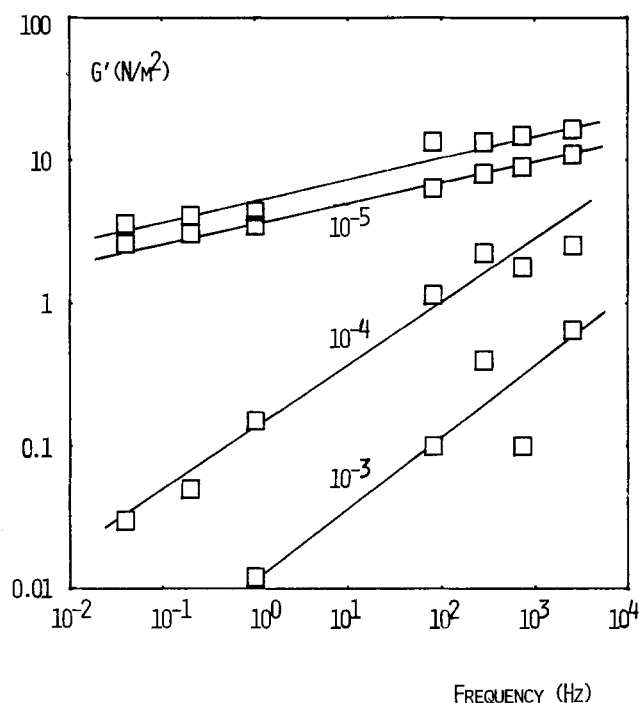


Fig. 3. Influence of the added electrolyte on the dynamic shear modulus, $\Phi = 0.21$; indicated parameter is the (added) electrolyte concentration in mol/dm^3 .

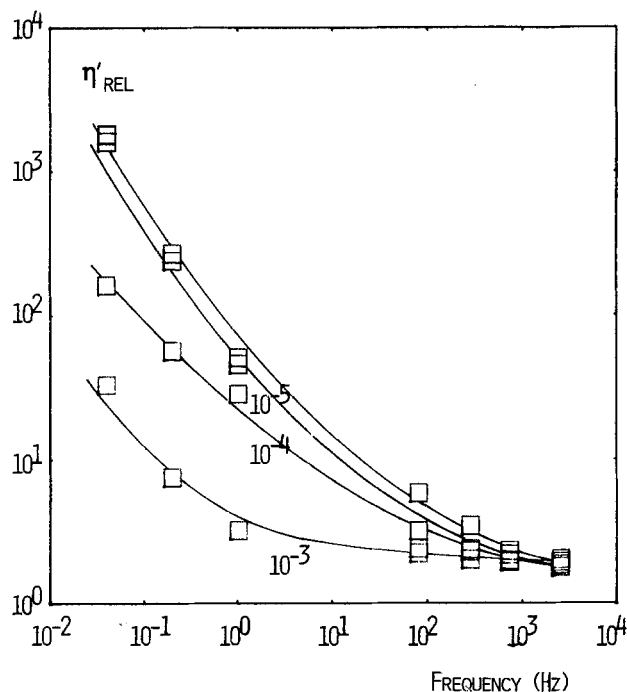


Fig. 4. Influence of the added electrolyte on the relative dynamic viscosity; $\Phi = 0.21$; indicated parameter is the (added) electrolyte concentration in mol/dm³

self in the decreasing values of G' and η'_{rel} at fixed frequencies. It is interesting to observe that $\frac{\partial \log G'}{\partial \log F}$ and $\frac{\partial \log \eta'_{rel}}{\partial \log F}$ change appreciably by addition of electrolyte.

4. Discussion

4.1. Linearity

The measurements of the steady state viscosity made clear that the strain range in which linear behaviour is observed is small ($\gamma < 0.25$). Obviously this is related to the interparticle distance in the lattice and one should expect deviations from linear behaviour above an upper limit of γ which will be less than 0.5. The dynamic measurements have been performed such that $\gamma_{max} < 0.1$ for all frequencies and below this upper limit no deviation from linearity was demonstrated.

4.2. Phenomenological equation

Given the linear viscoelastic behaviour, the scope of the analysis is restricted to the general linear viscoelastic constitutive equation (see e. g. [16]):

$$\sum_{k=0}^m p_k \frac{d^k}{dt^k} \sigma = \sum_{k=0}^n q_k \frac{d^k}{dt^k} \dot{\epsilon} + q \epsilon. \quad (5)$$

Here σ is the shear stress, ϵ is the strain, $\dot{\epsilon} = \frac{d\epsilon}{dt}$, p_k , q_k , and q are parameter, and t is the time. Four categories of materials can be identified. Two of them are called solids because $q \neq 0$. For the other two $q = 0$ and these are therefore called fluids. For both categories, solids and fluids, two relationships are allowed between m and n ($m = n + 1$ and $m = n$). For harmonically oscillating shear experiments with angular frequency ω , the stress and strain can be written as $\sigma = \sigma_0 e^{i\omega t + \phi}$ and $\epsilon = \epsilon_0 e^{i\omega t}$, where ϕ is a phase shift. In this case relation (5) transforms into

$$\sum_{k=0}^m p_k (i\omega)^k \sigma = \sum_{k=0}^n q_k (i\omega)^k \dot{\epsilon} + q \epsilon. \quad (6)$$

The dynamic modulus defined by

$$G^* \equiv \frac{\sigma}{\epsilon} \quad (7)$$

is given by

$$G^*(i\omega) = \frac{q + \sum_{k=0}^n q_k (i\omega)^{k+1}}{\sum_{k=0}^m p_k (i\omega)^k} \quad (8)$$

Relevant to the analysis is the behaviour of G^* (c. q. η^*) for $\omega \rightarrow 0$ and for $\omega \rightarrow \infty$. In Table 1 a survey is given of the presence (indicated by a plus sign) or the absence (indicated by a naught) of some quantities.

Considering the behaviour for $\omega \rightarrow 0$ one realizes that the lattice of the latex particles is temporary, i. e. due to the thermal motion there is a finite chance that a

Table 1. Survey of some properties of the four different types of linear viscoelastic materials

	q	$\omega \rightarrow 0$ η'	G'	$\omega \rightarrow \infty$ η'	G'
fluid $m = n + 1$	0	+	0	0	+
fluid $m = n$	0	+	0	+	+
solid $m = n + 1$	+	+	+	0	+
solid $m = n$	+	+	+	+	+

particle leaves its place, so that $\lim_{\omega \rightarrow 0} G'_{\omega \rightarrow 0} = 0$. For $\omega \rightarrow \infty$ there is always dissipation in the system, e. g. by the liquid between the particles, so that $\lim_{\omega \rightarrow \infty} \eta'_{\omega \rightarrow \infty} \neq 0$. It can be concluded (see table 1) that the valid constitutive equations is given by

$$\sum_{k=0}^n p_k \frac{d^k}{dt^k} \sigma = \sum_{k=0}^n q_k \frac{d^k}{dt^k} \dot{\epsilon} \quad (9)$$

This conclusion differs from that of Buscall et al. [7] who deduced from their measurements a fluid type behaviour with $m = n + 1$ and one retardation time and two relaxation times. Since their model is not compatible with $\lim_{\omega \rightarrow \infty} \eta'_{\omega \rightarrow \infty} \neq 0$ we think that even the fluid type with $m = n + 1$ is not relevant for (ordered) latices. In addition our measurements show that a great number of relaxation times is necessary to describe the viscoelastic behaviour.

4.3. Possible relaxation mechanisms

At low electrolyte concentrations, the latex particles order in a lattice. Assuming the sample not to be one single crystal, ordering exists over some characteristic length which probably decreases with increasing electrolyte concentration. There is no reason to expect the ordering to be perfect, so that dislocations, vacancies and interstitials will be present. Calculation of a shear modulus by means of pair wise added neighbour interactions for these different kind of configurations would give a range of G' -values with pertinent relaxation times and strengths. This would partly explain the presence of many relaxation times. The actual situation, however, incorporates mechanisms which can not be accounted for by pair wise added particle interactions or the used cell models. In some cases the collective motion of a group of interacting particles can, for small deformations, be decomposed in a number of normal modes of motion. This is probably also the case for ordered latices. To each normal mode of motion a relaxation time can be assigned. The number of modes will be high considering the number of particles involved. The longer relaxation times are pertinent to relaxation of coherent mode of motion of particles over a long distance and the shorter times are pertinent to those over short distances. The shortest being those of pairs of particles. This qualitative picture allow a few predictions. For sufficient high frequency the shear forces dominate any finite restoring force.

Consequently one expects that at high frequency G' and η' levels off as function of the frequency, because

of the finite number of relaxation times. The $\lim_{\omega \rightarrow \infty} G'_{\omega \rightarrow \infty}$ is the sum of contributions of all the relaxation mechanisms including those belonging to independent pair interactions.

The viscosity $\lim_{\omega \rightarrow \infty} \eta'_{\omega \rightarrow \infty}$ is equal to the viscosity of only hydrodynamically interacting particles. For hard spheres this limit is in good approximation given by the semi-empirical formula of Simha [17]:

$$\eta'_{\text{rel}} = \frac{10 \Phi R^3 (R^7 - 1)}{4 (R^{10} + 1) - 25 (R^7 + R^3) + 42 R^5} \quad (10)$$

where

$$R = f \Phi^{-1/3}. \quad (11)$$

Empirically it is found that the hydrodynamic interaction factor $f = 1.11$ for electrical neutral particles and $\Phi < 0.15$ [18]. This value of f is used to calculate the in figure 2 indicated limits. According to Simha [17] the value of f will be higher for a system with electrostatic interaction, which results in lower values of η'_{rel} . This explains probably the difference between the measured and calculated limit values of η'_{rel} for $\omega \rightarrow \infty$ (see figure 2). Another prediction which can be made is that at a fixed frequency one expects G' and η' to decrease with increasing electrolyte concentration, because the characteristic length of long distance ordering gradually decreases by the addition of electrolyte so that the longest relaxation mechanisms are annihilated. This can be observed in figure 3 and 4. Summarizing we conclude that G^* of (partly) ordered latex is strongly frequency dependent and can only be described with a great number of relaxation times. There is an indication that long range ordering is broken down by adding of electrolyte. It seems necessary to develop temporary network theories to analyse the observed phenomena adequately.

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