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Characterization of polymer dispersions by Fourier transform rheology

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Abstract Fourier transform rheology is a very sensitive technique to characterize non-linear rheological fluid properties. It has been applied here for the first time to polymer dispersions in water and the results are compared to those from conventional rheology, namely steady and small amplitude oscillatory shear experiments. The investigated systems are mainly based on styrene and *n*-butylacrylate.

A first attempt was made to evaluate how far colloidal parameters like particle volume fraction and ionic strength as well as chemical composition and surface characteristics of the dispersed particles are reflected in FT-rheology spectra. Significantly different non-linearities are observed for highly concentrated dispersions of particles with different T_g . These differences are not detected in linear oscillatory shear and show up in steady shear only at significantly higher shear rates.

Particle surface characteristics influence the non-linear response in oscillatory shear significantly and the intensity of the overtones is found to be higher for a dispersion of particles with a “hairy” swollen

surface layer as compared to a system of smooth particles, although the solids content was adjusted to match the steady shear viscosity.

The intensity of the overtones in FT-rheology strongly decrease upon dilution. At a solid content below 35% no differences are observed in the FT-experiments for the systems investigated here, whereas the differences in steady shear are very pronounced in this concentration range.

A significant influence of added salt onto the non-linear response is detected for some systems, which might be correlated to the stability of these systems.

The observed phenomena certainly cannot be explained in terms of constitutive equations or microstructural statistical mechanical models at present. Thus, FT-rheology yields information complementary to classical steady or linear oscillatory shear experiments.

Key words Fourier transform rheology · FT-rheology · Dispersions · Non-linear shear · LAOS

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Introduction

Dispersion particles are used as binders in various fields of applications such as paints, adhesives and in paper coatings (Distler 1998; Hunter 1989; Ottewill and

Rennie 1998; Russel et al. 1991). These products are often applied under non-linear shear conditions that means the colloidal systems do not show a linear or Newtonian shear response (Schaller 1997). In this work the analysis of aqueous colloidal model systems under

non-linear and oscillatory shear conditions is presented. The response of the dispersion is analyzed in the frequency domain via the Fourier transform (FT) method to detect the higher harmonics (Wilhelm et al. 1998, 1999). Suitable model dispersions with large differences in their chemical composition or interaction potential have been chosen where the non-linear behavior was expected to be pronounced.

One emphasis of our experimental work was to investigate the influence of different shear conditions such as amplitude and frequency of the applied shear field. A second scope was to study the effect of colloid chemical parameters like chemical composition, T_g , packing fraction, and surface characteristics of the latex particles on FT-rheology. Similar experiments on suspensions of spherical particles showed higher overtones depending on the increase of volume fraction in FT-analysis (Heymann et al. 2000). The obtained results are compared with data from standard rheological experiments like steady shear and linear oscillatory shear. The aim of this exploratory work is not to yield a complete picture of the rheological behavior of such dispersions. Rather our aim is to demonstrate what kind of new information might be accessible using the FT-Rheology approach.

Systems and methods

Synthesis of the colloidal dispersions

Different polymer dispersions were prepared by conventional seeded semi-batch emulsion polymerization. The standard recipe (sample A, Table 1) is described below. The recipes for the variations can be found in Table 1. The reaction temperature was 358 K. The initial feed was prepared from 342 g of de-ionized water, 10% of the pre-emulsion, and polystyrene seed particles. The amount of seed particles was adjusted to give a final particle size of about 165 nm. The emulsion was prepared from 540 g *n*-butylacrylate, 360 g styrene, 48 g of a 15 wt% aqueous solution of sodium laurylsulfate ($\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4\text{Na}$), and 294 g water. As an initiator, 107 g of a 2.5 wt% aqueous solution of sodium peroxodisulfate ($\text{Na}_2\text{S}_2\text{O}_8$) was used. The emulsion and initiator were fed parallel over a period of 3 h. After the feeding time the reaction was allowed to proceed for an additional hour at 358 K. After the polymerization, the latices were neutralized with an aqueous solution of ammonium hydroxide at room temperature to pH 7.5–8. The solid content has been determined gravimetrically. Particle size was measured via dynamic light scattering using an Autosizer IIC (Malvern Instruments, UK). All particle sizes are reported as a number averaged (cumulant *z*-average) particle diameters.

Table 1 Summary of the colloidal model dispersions synthesized for this study

Sample	Styrene [wt%]	<i>n</i> -BA [wt%]	AA ^a [wt%]	AM ^a [wt%]	Solids content [wt%]	Particle diameter [nm]	T_g [K]
A	40	60	0	0	50.5	168	
C	0	100	1.5	0	51.3	155	219
D	100	0	1.5	0	51.5	159	373
E	40	60	1.5	1.5	51.0	166	

^aAcrylic acid (AA) or acrylamide (AM) according to the weight of styrene and *n*-BA monomers

Some of the samples were diluted in order to vary the particle-particle distance or the particle-particle interaction, respectively. The modifications are listed in Table 2.

Rheological measurements

Rheological experiments were mainly performed on a controlled strain rheometer (ARES, Rheometric Instruments). The instrument was equipped with two different transducers covering the torque range from 2×10^{-6} to 0.2 Nm. The frequency response of the transducers was calibrated externally, verifying a quantitative signal at the shear stress transducer up to 30 Hz. The oscillatory shear experiments in the linear region were performed with another controlled strain rheometer (Rheometric RFS) equipped with an air bedded force transducer covering the measurement range from 10^{-7} to 10^{-3} Nm. Measurements were done at ambient temperature (295 K). The samples were filled in a Couette cell with a gap width of 1 mm. Experiments performed with cone-plate and plate-plate geometry did not at first give reasonable results due to fast evaporation of water or phase separations in the sample. Therefore, prior to the experiment, the filled Couette cell was covered with a thin film of dodecane to prevent the evaporation of water during the experiment. Alternatively, water evaporation out of the Couette cell could also be delayed by a “water trap” that kept constant conditions of water vapor around the sample. Usually the oscillations were started 1 min before recording data in order to reach steady state conditions for the colloidal system. Typically, 50–100 oscillations for a 1-Hz excitation were applied, depending on the system. For high strain amplitudes it also seems possible to study shear induced transitions via the change of the relative intensity of the third harmonic as a function of time.

The fully automated data acquisition was realized by adding LabView (see below) in parallel to a LeCroy 9354A oscilloscope in the set-up described previously (Wilhelm et al. 1998, 1999). For the acquisition of the raw strain, stress, and normal force time response, a separate PC had been attached to the BNC ports of the rheometer via a 16-bit AD-converter by using double shielded BNC-type cables in order to keep the electronic noise level as low as possible.

For controlling the acquisition of the raw time data a home written program was developed by using the software package LabView of National Instruments Laboratory 5.1. With this program an automated data uptake for the signal of the excitation strain and the response signal (shear plus normal forces) was possible. A raw data file for a single FT-rheology spectra (see also below) was obtained by typically recording 50 oscillations. Depending on the oscillation frequency used the measurement time for one spectrum sampled between several seconds, for high frequencies ($\omega_1/2\pi \sim 10$ –15 Hz), and about 8 min, for the lowest frequencies ($\omega_1/2\pi \sim 0.1$ Hz) applied. Usually four to five spectra were taken in order to monitor fluctuations and reproducibility during the measurements. Typical fluctuations are in the range of $\pm 0.5\%$ for the relative intensity of the higher harmonics. To reduce experimental uncertainties, different spectra were averaged after having been Fourier transformed prior the quantitative analysis.

To obtain a FT-spectrum out of raw time data a discrete, complex, half-sided, magnitude, fast Fourier transformation was applied on the real data set of the shear response (Bracewell 1986;

Table 2 Modified samples by addition of salt or water, the first letter is according to Table 1

Sample	Solids content [vol%]	Added NaCl [vol%]
A.1	47.0	0
E.1	40.0	0
E.2	36.2	0
E.3	51.0	1.5
E.4	51.0	0.03

Ramirez 1985; Wilhelm et al. 1999). Careful shielding of any spurious signals is needed to increase sensitivity in the frequency domain. In this type of experiment we reach typically a signal-to-noise ratio in the spectra of up to 5000:1 for the signal at the fundamental frequency per single measurement. For better comparison of the results obtained for different samples the spectra were normalized by dividing the intensity value for the different harmonics $I(n\omega_1)$ by the intensity value obtained for the fundamental excitation frequency $I(\omega_1)$. This way an intensive property is obtained which is much less vulnerable to experimental uncertainties than the intensities themselves. Moreover, throughout this paper only relative, not absolute, changes are discussed. This normalization especially compensates errors due to variations of the sample volume.

General description of non-linear response under oscillatory shear

In dynamic shear experiments materials are exposed to oscillating shear fields and generally the applied strain is sinusoidal. The dynamic mechanical properties of the material determine the extent of the stored or dissipated energy within the material. In the linear regime a sinusoidal strain with frequency ω_1 leads to a sinusoidal stress response where the amplitude and phase change are then converted into the storage and loss modules G' , G'' . In case of non-linear behavior the response can still be periodic yet exhibit deviations from a plain sinusoidal shape. A typical example for a sinusoidal excitation together with its stress response signal depicted for a colloidal dispersion is shown in Fig. 1 for $\gamma_0 = 0.25$ at 1 Hz excitation.

These deviations from a sinusoidal shaped response are caused by the inherent materials properties that do not follow a linear

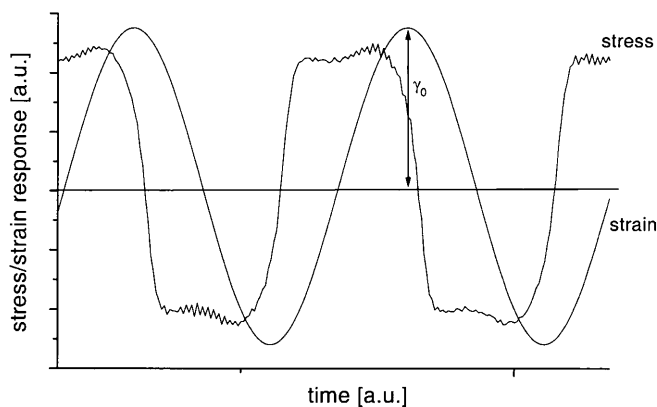


Fig. 1 Typical time data set for a colloidal system exposed to an oscillatory shear strain (sinusoidal shaped curve) together with the measured torque signal for the stress response. The excitation frequency was 1 Hz and the applied strain amplitude $\gamma_0 = 0.25$

response. The information about the non-linear behavior of a material can be extracted efficiently by Fourier transforming the time response signal into frequency space. The transition from the time domain to the frequency domain is illustrated in Fig. 2. Deviations from linearity are characterized quantitatively by the number and intensity of the higher overtones (also called harmonics) $I(n\omega_1)$ in the frequency spectra (Wilhelm et al. 1998). In addition to the quantitative description of the non-linear properties of the system the Fourier transformation itself entails the advantage of noise reduction due to the periodic analysis technique. The theoretical derivation of the Fourier analysis for oscillatory shear experiments will be outlined only briefly in this article. A more detailed description of the experimental aspects has been given by one of the authors recently (Wilhelm et al. 1999).

The generation of only odd mechanical overtones of a non-linear, viscous sample under oscillatory shear shall be explained by the following tutorial approach for a purely viscous system.

The viscous flow of a system is described by the basic equation where the force F is necessary to move the plate having an area A with the velocity v at a distance d in a viscous medium of the viscosity η :

$$F/A = \eta v/d = \eta \dot{\gamma} \quad (1)$$

The ratio between the velocity v and the distance d (between plate and bottom surface) defines the shear rate $\dot{\gamma}$. Assuming non-Newtonian viscosity, the viscosity might be described for simplicity by a Taylor series with respect to the applied shear rate. Due to the symmetry of the underlying stress-strain tensor only even terms occur with respect to the shear rate because the viscosity is independent of the direction of shear field ($\eta(\dot{\gamma}) = \eta(-\dot{\gamma})$) using a scalar notation:

$$\eta(\dot{\gamma}) = \eta_0 + a\dot{\gamma}^2 + b\dot{\gamma}^4 \dots \quad (2)$$

Equation (2) is inserted into Eq. (1) and for simplicity the shear rate is used in complex notation (Bird et al. 1971). For the viscosity η_0 , a , and b (see Eq. 2) complex numbers might also be possible. The following time-dependence results for the force, respective the torque response:

$$\begin{aligned} F(t) &\propto (\eta_0 + a\dot{\gamma}^2 + b\dot{\gamma}^4 \dots) \dot{\gamma} \\ \dot{\gamma} &\propto e^{i\omega_1 t} \\ F(t) &\propto (\eta_0 + ae^{i2\omega_1 t} + be^{i4\omega_1 t} \dots) e^{i\omega_1 t} \\ F(t) &\propto \eta_0 e^{i\omega_1 t} + ae^{i3\omega_1 t} + be^{i5\omega_1 t} \dots \end{aligned} \quad (3)$$

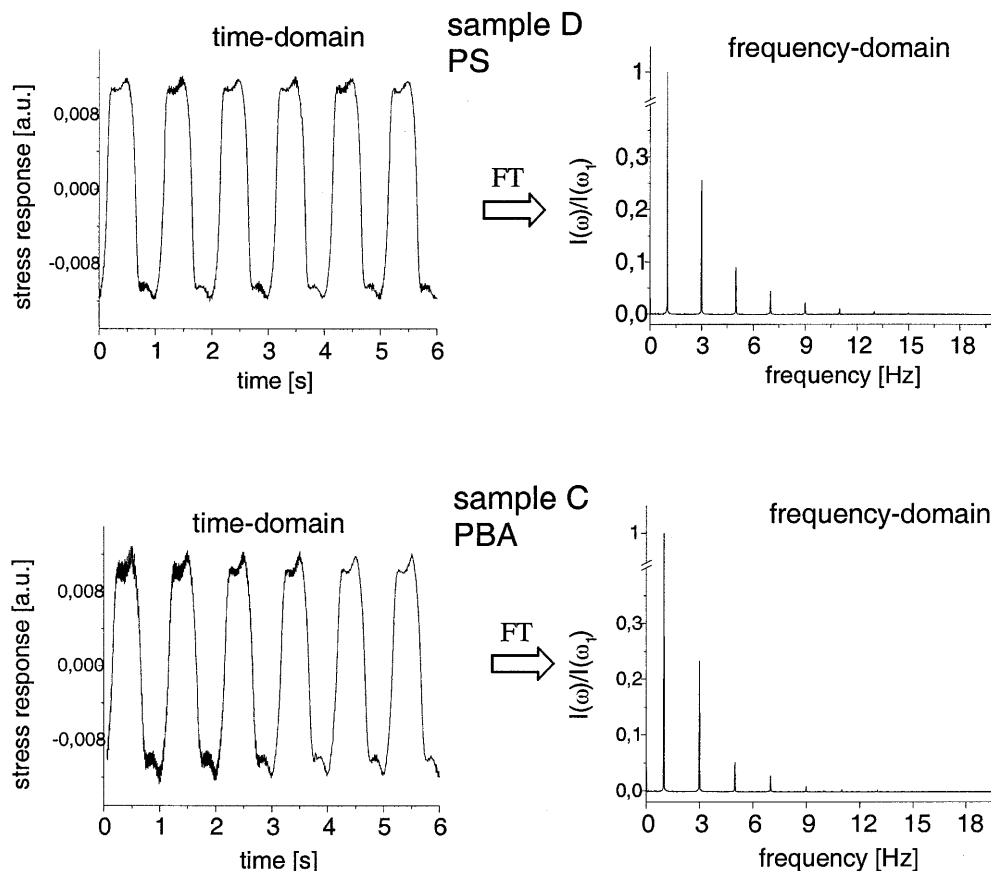
The analysis of the time-dependence force or torque in Eq. (3) results exclusively in odd harmonics of the fundamental excitation frequency (Gamota et al. 1993; Giacomini and Dealy 1993; Wilhelm et al. 1999). The spectral analysis of the time-dependent signal is obtained by Fourier transformation. A more fundamental mathematical description of Fourier transformation can be found in the literature (Bracewell 1986; Ramirez 1985). The experimental implementation in combination with a rheological experiments is described elsewhere (Wilhelm et al. 1999). Standard oscillatory shear experiments are performed in the linear response regime where higher harmonics are neglected and $|\eta^*|$ is defined only by the response at the fundamental frequency $\omega_1/2\pi$: $|\eta^*(\omega_1)| = (1/\omega)(G'^2(\omega_1) + G''^2(\omega_1))^{1/2}$.

Results

Effect of chemical composition of the latex particles

First, we discuss the non-linear response of two dispersions that are equal in particle size and volume

Fig. 2 Frequency- and time-domain data for: (a) sample D (polystyrene) and (b) sample C (polybutylacrylate), $\gamma_0 = 0.75$, $\omega_1/2\pi = 1$ Hz. Higher harmonics at odd multiples of the fundamental frequency are clearly visible, additionally the noise reduction of the Fourier transformation is visualized



fraction but differ in chemical composition. Sample C (see Table 1) consists of polybutylacrylate (PBA) particles ($T_g = 219$ K) and sample D of polystyrene (PS) particles ($T_g = 373$ K).

The corresponding flow curves obtained in steady shear experiments are shown in Fig. 3. The steady shear

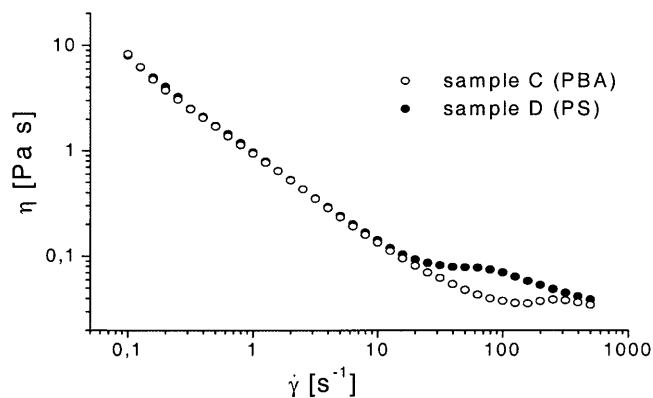


Fig. 3 Shear rate-dependent viscosity for two aqueous colloidal dispersions with different particle composition sample C consisting of polybutylacrylate and sample D of polystyrene particles. The two curves are basically identical for shear rates $< 20 s^{-1}$

viscosity of these samples do not show any significant differences at shear rates up to $20 s^{-1}$. In this shear rate range these two samples show highly non-linear behavior but cannot be distinguished in steady shear. Also the linear viscoelastic moduli G' and G'' (see Table 3) do not show significant differences between these two materials.

An example for the Fourier transform analysis at $\gamma_0 = 0.75$ shear amplitude and $\omega_1/2\pi = 1$ Hz oscillation frequency is given in Fig. 2 where time and frequency domain signals for the two different samples are shown. The spectra display only odd harmonics of the fundamental excitation frequency. Furthermore it is worth noting that the full information of the non-linear response is given in frequency space by the data points exclusively at $1\omega_1$, $3\omega_1$, $5\omega_1$, and so forth. Consequently, the random noise in the time domain data is efficiently suppressed by the FT-technique. Note that random noise is by definition not periodic.

For better comparison of the data obtained at different shear amplitudes the relative intensities $I(n\omega_1)/I(\omega_1)$ of the different overtones are plotted vs strain amplitude. The results obtained for samples C and D at a frequency of 1 Hz are summarized in Fig. 4. Again, the different behavior of the two samples is apparent at first sight. At the beginning of each run the

Table 3 Linear viscoelastic moduli G' and G'' obtained at $\gamma_0 = 0.01$ and $\omega_1/2\pi = 1$ Hz

Sample	G' [Pa]	G'' [Pa]
A	1.2	1.5
C	15.9	6.3
D	15.9	5.0
E.1	9.4	4.7
A.1	0.038	0.0015
E.2	0.033	0.0007

relative intensity of the third and higher harmonics evolved as a function of time. Typically 50–80 cycles were needed to establish steady state conditions. The standard deviation under these conditions was found to be $<0.5\%$ of the relative intensity $I(n\omega_1)/I(\omega_1)$.

Using $\omega_1/2\pi = 1$ Hz and a strain amplitude of $\gamma_0 = 1$ a maximum shear rate during a cycle $\dot{\gamma}_{\max} = \gamma_0 \cdot 2\pi\nu$, where ν is the applied shear frequency) can be calculated to be 6.28 s^{-1} . Up to this shear rate the steady shear viscosity of both samples is still the same (Fig. 3), but the relative intensities of the overtones extracted from the FT-experiment differ significantly for the polystyrene and the polybutylacrylate system. Due to the low viscosity the detected torque signal is very small. The noise level of the data consequently hindered the detection of the onset of the non-linearity. The critical strain amplitude for the cross-over from linear to non-linear response can only be estimated to be $\gamma_0 < 0.1$. Investigations on other samples showed that for $I(3\omega_1)/I(\omega_1) < 0.01$ the linear response data of G' and G'' was not affected. Further more it was possible to determine the onset of non-linear response at much lower strain amplitudes applying the FT-rheology approach (Wilhelm et al. 2000).

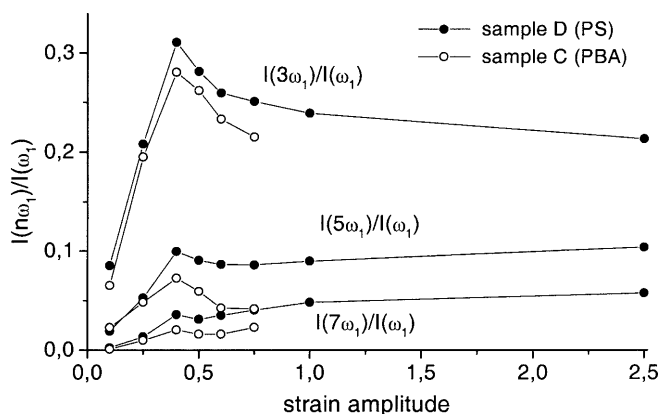


Fig. 4 Relative intensity of overtones corresponding to the harmonics at $3\omega_1$, $5\omega_1$, $7\omega_1$ as function of strain amplitude at 1 Hz oscillation frequency for sample C (polybutylacrylate) and D (polystyrene). The rigid PS displays more pronounced harmonics. The error is estimated as $\pm 0.5\%$

The normalized intensities of the overtones are always higher for the suspension of the hard PS particles than for the suspension of the soft PBA particles. However, there are also similarities in the non-linear behavior of the two systems. In both cases the intensities of the third and fifth overtones exhibit a sharp maximum at a strain amplitude $\gamma_0 \approx 0.4$ (corresponding to a maximum shear rate of 2.5 s^{-1}), while the seventh overtone increases monotonically.

Whether the differences observed in non-linear oscillatory shear are really due to the rigidity of the particles (or more precisely to their T_g) is not yet clear and requires thorough investigations on carefully characterized model dispersions, which are beyond the scope of this paper. Subtle differences with respect to colloidal interactions due to different particle surface properties or the hydrophobicity of the polymer could also be the source of the observed rheological phenomena. It is well known that PS and PBA differ significantly with respect to their hydrophobicity and also the distribution of the functional groups between the bulk particles and their surface. This depends additionally on the details of the polymerization conditions. However, the capillary forces controlling particle deformation during film formation aqueous polymer dispersions are on the order of 10^{-7} N (Vischers et al. 1997) and thus several orders of magnitude larger than the shear forces acting on a single particle in our experiments ($F = 6\pi r^2 \tau \approx 10^{-13}$ N, where r is the radius and τ the shear stress). Therefore, it seems rather unlikely that our non-linear oscillatory shear experiments pick-up effects are due to the deformability of the particles.

Effect of particle surface

The properties of colloidal dispersions as well as the film formation on drying actually depends on the surface of the particles (Klein and Daniels 1997). Therefore, the non-linear oscillatory shear response of dispersions containing particles similar in size and chemical composition but with different surface properties has been investigated by comparing the FT-spectra of samples A and E. While sample A contains only styrene and butylacrylate as monomers, sample E contains acrylamide and acrylic acid as additional hydrophilic co-monomers. This results in a swollen (“hairy”) surface layer. Due to this surface layer the hydrodynamic particle volume is increased and the steady shear viscosity of sample E is substantially higher than that of sample A if compared at constant solids content. In order to check the effect of the different particle surface properties on the non-linear rheology as revealed by the FT-technique, the solids content was adjusted such that both samples exhibit the same steady shear viscosity. The corresponding diluted sample E is labeled E.1.

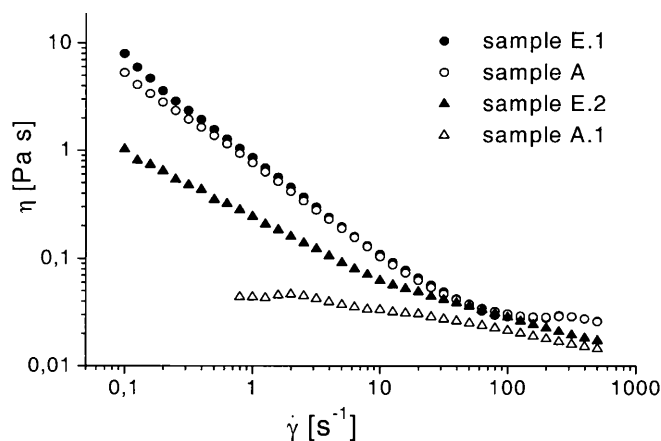


Fig. 5 Shear rate-dependent viscosity of samples A and A.1 as well as E.1 and E.2. For details of chemical composition and solids content see Tables 1 and 2. The strong reduction of the viscosity is clearly visible for decreasing solid content

The shear rate dependent viscosity of samples A and E.1 are shown in Fig. 5. The corresponding results from the FT-experiments are shown in Fig. 6. In contrast to the steady shear experiments Fourier transform rheology reveals very marked differences between those samples. For sample E.1 a pronounced maximum in the non-linearity is again observed at an amplitude of $\gamma_0 = 0.4$ even for the seventh harmonics. In case of sample A this maximum is observed only for the third harmonic, whereas the intensity of the higher harmonics increases monotonically and approaches a limiting value at strain amplitudes $\gamma_0 > 2$. Moreover, the intensities of the overtones are higher for sample E.1 than for sample A at all frequencies and amplitudes investigated. Also

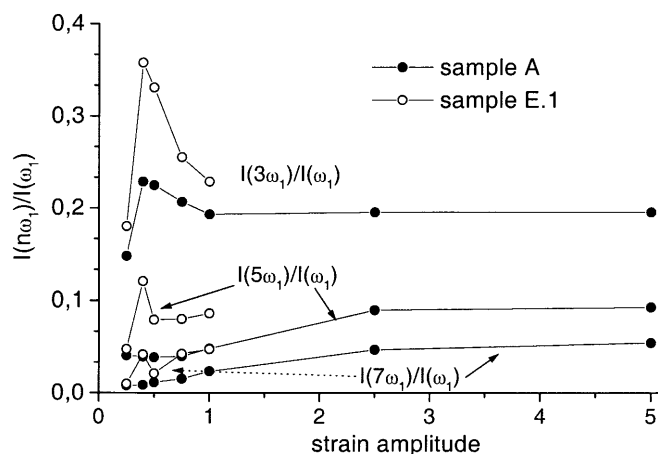


Fig. 6 The relative intensity of the higher harmonics vs strain amplitude as detected from the Fourier spectra of samples E.1 and A, of Tables 1 and 2, see also Fig. 5. Sample E.1 displays a more pronounced peak in the relative intensity of the higher harmonics. The error is estimated as $\pm 0.5\%$

the linear viscoelastic moduli reveal pronounced differences between sample A and sample E.1 (Table 3).

Effect of solids content and added salt

Generally, the non-linear rheological response of dispersions decreases drastically with decreasing solids content. This is demonstrated here for sample E. As shown in Fig. 7 the variation of the solids content (as volume fraction) from 0.49 to 0.36 results in a decrease of the relative intensity of the third overtone from almost $I(3\omega_1)/I(\omega_1) = 0.4$ to less than 0.05.

For samples A.1 and E.2 only the third overtone has been detected (see Fig. 7). This is due to the limited sensitivity of the torque transducers used here, but no principal limitation of the FT-technique. No significant difference is observed for the intensities of the third harmonics for these two samples. Also the linear viscoelastic moduli G' and G'' are virtually the same.

In contrast, the steady shear viscosity for sample A.1 is more than one order of magnitude below that of sample E.2 at shear rates $< 1 \text{ s}^{-1}$ (Fig. 6).

First experiments were performed in order to elucidate how a slight destabilization of the disperse systems by adding salt is reflected in the Fourier spectra. Results for system E obtained at $\omega_1/2\pi = 1 \text{ Hz}$ and $\gamma_0 = 1$ are shown in Fig. 8.

The signal intensity of $I(3\omega_1)/I(\omega_1)$ shows a decrease of non-linearity with increasing salt content as expected for a stable system where electrostatic interactions are

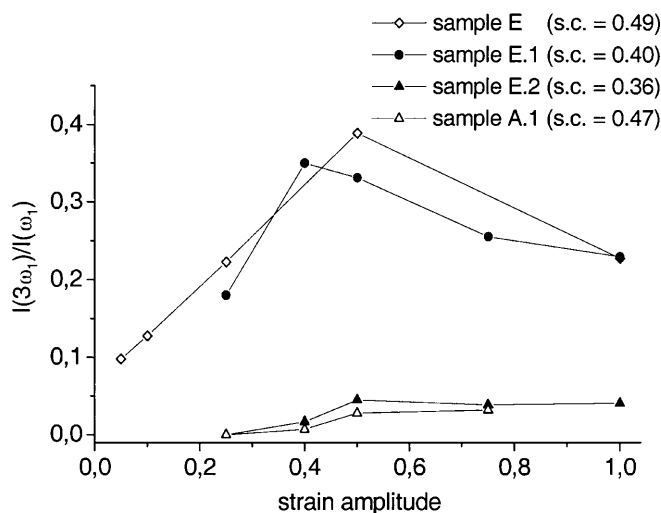


Fig. 7 Relative intensity of the third overtone at 1 Hz oscillation frequency for samples E, E.1, E.2, and A.1 (see Tables 1 and 2) as a function of strain amplitude. For lower solid content a strong reduction in the higher harmonics is visible. The error is estimated as $\pm 0.5\%$

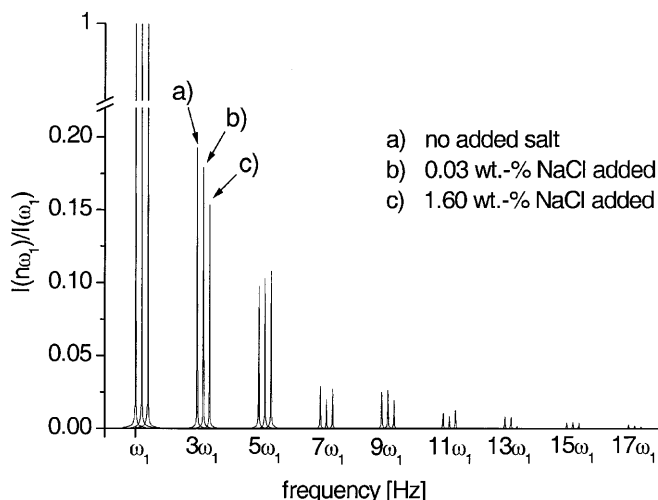


Fig. 8 Comparison of the FT spectra obtained for system E with and without added electrolyte: samples E, E.3 (1.5 wt% NaCl added), and E.4 (0.03 wt% NaCl added). Spectra are shifted horizontally for better comparison

more and more screened by the added electrolyte. This could be explained by the reduction of the Debye-length for increasing salt concentrations. Therefore we expect a more linear response as seen for $I(3\omega_1)/I(\omega_1)$. In contrast, the intensity of the fifth overtone slightly increases with increasing salt concentration. This could be an indication of the onset of aggregation or weak flocculation. This complex correlation between ionic strength and the intensities of the higher harmonics in non-linear oscillatory shear experiments seems to be worth further systematic experimental as well as theoretical investigations, which are beyond the scope of this paper.

Conclusion

An FT-rheological characterization of aqueous polymer dispersions with different surface properties is reported here for the first time. The results from Fourier transform rheology have been compared to steady and linear oscillatory shear experiments addressing the effects of solids and electrolyte content as well as

chemical composition and surface characteristics of the dispersed particles.

Stronger non-linear effects are observed for the dispersions of rigid PS particles than for the dispersions containing the soft PBA particles. This difference does not show up in the linear viscoelastic storage modulus G' and, moreover, no significant difference is observed in steady shear experiments in the corresponding shear rate range up to $\dot{\gamma} < 10^{-1} s^{-1}$.

The particle surface characteristics influences the non-linear response in oscillatory shear and the intensity of the mechanical overtones (harmonics) is found to be higher for the system with a more swollen surface layer as compared to the system with a smooth particle surface, although the solids content was adjusted to match the steady shear viscosity of the samples in a wide shear rate range. In this case differences are also found in the linear viscoelastic behavior, with a higher G' for the material showing stronger non-linearities.

Non-linear effects, as revealed by FT-rheology, strongly decrease upon dilution. The lowest solid content (volume fraction) at which reasonable data could be obtained (at least with the torque transducer used here) was around 0.36. In this range of low particle concentrations no differences were observed in the FT-experiments for the systems investigated here, whereas the differences in steady shear and linear oscillatory shear are very pronounced.

Finally, a significant influence of added salt onto the non-linear response could be detected for the system with the “hairy” particles. Surprisingly, the effect on the intensity of the third and fifth overtone are opposite and might be correlated to the stability of the system.

The observed phenomena cannot be explained in terms of constitutive equations or microstructural statistical mechanical models at present. Thus, FT-rheology applied to colloidal polymer dispersions yields information complementary to classical steady or linear oscillatory shear experiments and is hoped to stimulate theoretical work in this area.

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