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ORIGINAL CONTRIBUTION

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Reological behaviour of concentrated monodisperse suspensions as a function of preshear conditions and temperature: an experimental study

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Abstract The influence of preshearing on the rheological behaviour of model suspensions was investigated with a stress-controlled cone-and-plate rheometer. The used matrix fluids showed Newtonian behaviour over the whole range of applied shear stresses. Highly monodisperse spherical glass spheres with various particle diameters were used as fillers. By applying steady preshearing at a low preshear stress, where a diffusion of particles can be expected, it was found for all model suspensions investigated at volume fractions ranging from 0.20 to 0.35 that the time-temperature superposition in the steady shear and in the dynamic mode holds within the chosen temperature range. Furthermore, all presheared model suspensions displayed a high and a low frequency range which are either separated by a shoulder or by a plateau value of G′ at intermediate frequencies. It could clearly be demonstrated that the low frequency range strongly depends on the preshear conditions. Hence, the features observed in the low frequency range can be attributed to a structure formation of a particulate network. In the high frequency range a frequency-dependent behaviour was observed which obeys the classical behaviour of Newtonian fluids ($G' \propto \omega^2$, $G'' \propto \omega$). The resulting temperature shift factors from the dynamic and the steady shear mode are identical and independent of the volume fraction and the particle size of the filler.

Key words Monodisperse suspensions · Dynamic-mechanical properties · Time-temperature-superposition · Preshearing

Introduction

Suspensions containing high volume fractions of solid particles are frequently encountered in transport and in manufacturing processes. Printing inks, food stuff or dyes are only some examples for industrial applications of filler-modified fluids. From the processing side, however, it is important to predict the rheological properties as a function of various parameters, including volume fraction Φ_t, particle shape and size distribution, specific surface area of the particles and fluid properties, as well.

Progress both in theoretical description and experimental measurements has been made in recent years for concentrated suspensions containing monodisperse and polydisperse particles. A significant body of work has focused on the effect of particle properties (Dabak and Yucel 1986; van der Werff and de Kruif 1989; Tsai et al. 1992) and on the effect of the matrix properties on the shear viscosity function of concentrated suspensions (Tsai and Viers 1987; Chang et al. 1993).

In comparison to the extensive information available on the viscosity function in steady shear there are only few studies which investigated the development of the viscoelastic material functions of concentrated suspensions. Some work on the dynamic mechanical properties of colloidal and non colloidal concentrated suspensions has been reported by Matsumoto et al. (1975), Gadala-Maria and Acrivos (1980), Shikata and Pearson (1994), Aral and Kalyon (1997) and Watanabe et al. (1996). Some of the named authors (Matsumoto et al. 1975; Shikata and Pearson 1994) detected secondary plateau in the frequency-dependent dynamic functions of concentrated suspensions similar to the rubber plateau of polymeric systems. The existence of a secondary plateau suggests the existence of long-time relaxation processes in a network structure associated with interactions between solid particles (Matsumoto et al. 1975). The assumption of a particle network development as a result of aggregation in suspensions implies interactions between the components of a filled system but the origin for this phenomenon is still not well understood. Computer simulations of the mean interparticle distances (IPD) as a function of the volume fraction Φ_t using a unit cell model give rise to the assumption of a structure formation of particles in the suspensions because the calculated IPD values are orders of magnitude larger than the distances which have to be considered when dealing with interactions of the particles themselves (Kaschta et al. 1998) or with interactions via matrix molecules adhered to the surface of the particles (Castellani and Lomellini 1993). In the literature it is found that concentrated suspensions exhibit structures which may be shear induced (Gadala-Maria and Acrivos 1980). The diffusion of particles can lead to a collective migration of particles if gradients are present either in the particle volume fraction or in the shear rate distribution (Gondret and Petit 1997; Breedveld et al. 1998). Leighton and Acrivos (1987) demonstrated that even non-colloidal particles show a diffusion-like behaviour in low Reynolds number flow, where inertial effects are negligible. For example, it was found by performing transient experiments at constant torque in a Couette-system that particle migrations lead to two phenomena: (a) a short-term viscosity increase due to an inhomogeneous concentration profile which leads to a particle migration across the streamlines; (b) a long-term viscosity decrease due to particle migration from the sheared gap into the unsheared reservoir (Leighton and Acrivos 1987). Similar transient phenomena were also detected by other authors performing rheological experiments in a cone-and-plate geometry (Kaschta et al. 1998).

Only a small amount of literature can be found on investigations of the validity of the time-temperature superposition for concentrated suspensions (Shikata and Pearson 1994; Watanabe et al. 1996). Some authors found that the time-temperature superposition holds within a certain temperature range for colloidal suspensions (Shikata and Pearson 1994). The time-temperature superposition fails in most cases for gelling suspensions (Choi and Krieger 1986) and a superposition of the dynamic material functions could not be obtained (Rueb and Zukoski 1998). Results on the validity of the time-temperature superposition for suspensions of non-colloidal particles are rare as well (Friedrich et al. 1995). A systematic investigation of the rheological properties of concentrated suspensions depending on the preshear conditions cannot be found in the literature.

The intention of this study is to characterise well defined model suspensions of colloidal and non-colloidal particles in the steady shear and in the dynamic mode and to find out whether for this model suspensions the time-temperature superposition is valid by conducting the following simple rheological experiments. Increasing the *preshear time* at low *preshear stresses* where a diffusion-like behaviour of particles is expected (Leighton and Acrivos 1987) significant changes of the subsequently measured dynamic properties can be observed which are very similar to the changes of the dynamic properties which can be detected during the network building process of crosslinking polymers (Winter and Chambon 1986). It will be shown that a systematic preshearing leads to a defined structure of particles which is essential for the application of the time temperature superposition at low stresses and frequencies. However, our experiments in the dynamic mode are limited to conditions where the response is linear.

Experimental

Materials

Three non-polar low molecular weight polyisobutylenes (PIB 1, PIB 2, PIB 3) with a density of $\rho_{\mathrm{Matrix}}(30\ ^\circ\mathrm{C})\rho_{\mathrm{Matrix}} \approx 0.90$ g/cm^3 were chosen as the matrix fluids (see Table 1). From GPC-experiments the weight average molecular weight M_w and the molecular weight distribution M_w/M_n given in Table 1 were obtained by applying the universal calibration principle to the calibration curve of polystyrene.

Two samples of highly monodisperse glass spheres [Mono(-sphere) 250 and Mono(-sphere) 1200 from Merck] were chosen as the fillers. The particle diameters were calculated from REM photographs (see Fig. 1). At least 200 individual particle diameters were analysed and the average diameters x_n and x_v were calculated. x_n represents the number-average diameter, x_v is the volume average diameter and n_i the number of counted particles with a diameter d_i:

$$x_n = \frac{\sum_i n_i \cdot d_i}{\sum_i n_i} \qquad (1)$$

Table 1 Characteristics of the used matrix fluids

Newtonian fluids	Density ρ_{Matrix} at T = 30 °C [g/cm^3]	Molecular weight M_w [g/mole]	M_w/M_n	η_{Matrix} at T = 31.3 °C [Pas]
PIB-1	0.89	1.87×10^3	1.50	10.4
PIB-2	0.89	3.39×10^3	1.68	26.8
PIB-3	0.90	6.03×10^3	1.89	112.7

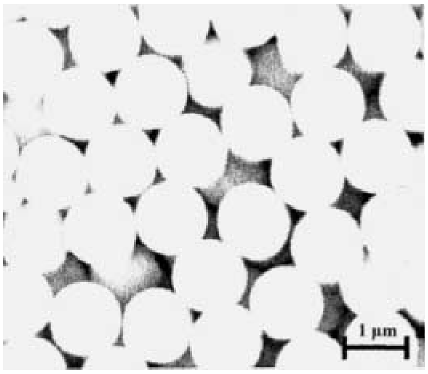

Fig. 1 REM-photograph of monodisperse glass spheres (Mono 1200)

$$x_v = \frac{\sum_i n_i \cdot (d_i)^4}{\sum_i n_i \cdot (d_i)^3} \tag{2}$$

The polydispersity index (PDI) was obtained as follows:

$$\mathrm{PDI} = \frac{x_v}{x_n} \tag{3}$$

The characteristic features (density, x_n, PDI) of the used fillers are given in Table 2. It is worth mentioning that the polydispersity index of the used fillers results in PDI = 1.03 for Mono 1200 and PDI = 1.05 for Mono 250. Similar polydispersity indices were found by Kim and Suh (1999) for highly monodisperse PMMA-particles.

Sample preparation

In order to reduce effects of adsorbed water on the hydrophilic surface of the particles the chosen fillers were dried at 200 °C for 24 h before mixing. In TGA-experiments a weight loss of 2% could be observed during the desiccation of the particles. The model suspensions of dried particles with filler contents up to 35 vol.% ($\Phi_t = 0.35$) were mixed with a stirrer for several hours. Since entrapped air would lead to falsified rheological results the obtained suspensions were carefully degassed in vacuum before starting the rheological experiments.

Rheological measurements

The rheological features of the model suspensions were examined by a stress controlled rheometer (Bohlin CSM). The steady-shear viscosity functions and the dynamic oscillatory data were measured with a truncated cone-and-plate geometry (gap height 150 μm). For the investigations of the influence of the preshear conditions on the validity of the time-temperature superposition for concentrated suspensions the temperature range was varied between 26 °C≤T≤55 °C. Before starting the rheological measurement either in the steady shear or in the dynamic shear mode the suspensions were presheared at a low fixed preshear stress $\tau_{PS} = 0.19$ Pa for different preshear times Δt_{PS} at each temperature T. It has to be mentioned that a fresh sample was used for each run. For the dynamic mode it is essential to note that the critical strain for the linear-viscoelastic response is strongly dependent upon the frequency ω used. Hence, the critical strain for leaving the region of linear-viscoelastic response in the dynamic oscillatory mode was determined over the whole frequency range for each temperature. In the following only strain-independent values of the shear moduli are reported. A survey of the sensitivity of the linear-viscoelastic response of suspensions to strain and frequency can be found in the appendix.

Table 2 Density ρ_{particle}, particle diameter and polydispersity index of the fillers used

Monodisperse, non porous particles	Samples	Density ρ_{particle} [g/cm^3] (25 °C)	Number average diameter x_n [μm]	PDI
Glass-spheres (SiO_2)	Mono 250	1.95	0.27	1.05
Glass-spheres (SiO_2)	Mono 1200	2.05	1.18	1.03

Results and discussion

Rheological characterisation of the continuous media used

In steady-shear experiments the chosen matrix fluids displayed Newtonian behaviour in the range of shear stresses investigated (0.19 Pa≤τ≤256 Pa). Newtonian viscosities ranging from $\eta_{\text{Matrix}} = 10.4$ Pas to $\eta_{\text{Matrix}} = 112.7$ Pas were found at a reference temperature of T = 31.3 °C (see Table 1).

The dynamic-mechanical material functions of the used Newtonian matrices (PIB 1, PIB 2, PIB 3) are shown in Fig. 2 for a temperature of T = 31.3 °C. It is obvious that the polyisobutylenes PIB 1, PIB 2 and PIB 3 only display a weak elasticity identified by the very low values of G' at small frequencies ω. For the chosen polyisobutylenes a frequency-dependent behaviour can be observed over the investigated frequency range which corresponds to the well known behaviour of Newtonian fluids ($G' \propto \omega^2; G'' \propto \omega$) in good approximation. Due to the viscosities of the used matrix fluids sedimentation effects can be excluded for the suspensions during the time of measurement.

Influence of the preshearing on the steady-shear viscosity functions of concentrated suspensions at a fixed temperature

In order to investigate the effect of preshearing on the steady shear viscosity functions of concentrated monodisperse suspensions at a fixed reference temperature (i.e. at T = 31.3 °C) the Newtonian fluid PIB 1 and the non-colloidal fraction Mono 1200 were used. The volume fraction was set to $\Phi_t = 0.35$. All suspensions were presheared at a fixed preshear stress of $\tau_{PS} = 0.19$ Pa for various preshear times Δt_{PS}. On the one hand a diffusion like behaviour of particles can be expected for the very low preshear stress applied ($\tau_{PS} = 0.19$ Pa) (Leighton and Acrivos 1987), on the

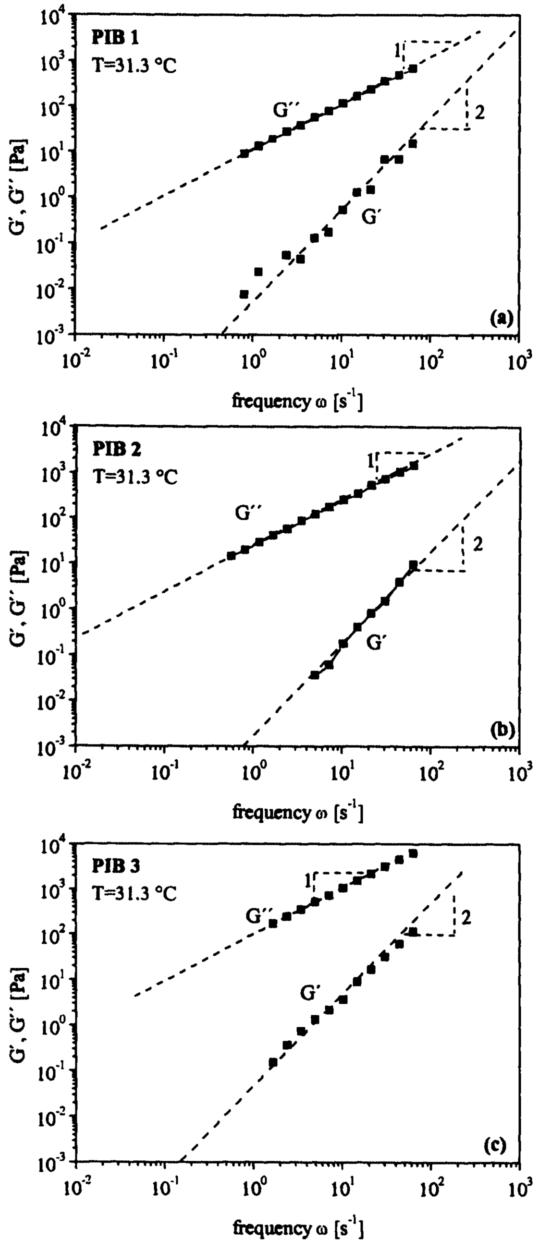

Fig. 2a–c Dynamic-mechanical material functions of the used polyisobutylenes at T = 31.3 °C: **a** PIB 1; **b** PIB 2; **c** PIB 3

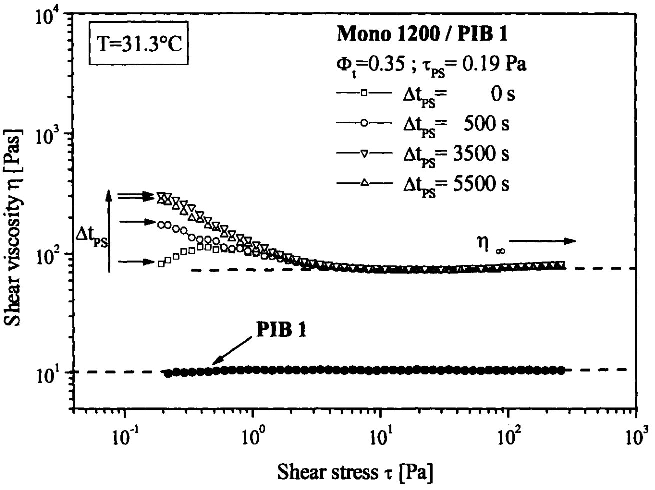

Fig. 3 Steady shear viscosity functions at T = 31.3 °C of a suspension ($\Phi_t = 0.35$) of the system Mono 1200/PIB 1 for different preshear times Δt_{PS} at a fixed preshear stress $\tau_{PS} = 0.19$ Pa and corresponding viscosity function of the unfilled matrix PIB 1

other measuring artefacts can be excluded since the applied preshear stress ($\tau_{PS} = 0.19$ Pa) is far away from the lower bound of measurable stresses ($\tau_{min} = 0.059$ Pa) for the chosen cone and plate geometry (cone angle 4°, radius 20 mm). The influence of the preshear condition on the viscosity function of a concentrated suspension is shown in Fig. 3. By a systematic increase of the preshear time Δt_{PS} at a fixed preshear stress of $\tau_{PS} = 0.19$ Pa a distinct increase of the shear viscosity η is found at small shear stresses τ (see Fig. 3). It is worth mentioning that the effect of wall-slip which was additionally checked by varying the gap height in a parallel plate geometry can be excluded for the suspensions investigated. The increase of the shear viscosity η at small stresses τ in Fig. 3 can be attributed to a formation of a particle network due to particle diffusion during preshearing. Applying the preshear stress τ_{PS} for preshear times of $\Delta t_{PS} \geq 3500$ s results in a plateau value (see Fig. 3). Hence, it can be concluded that for the given preshear stress of $\tau_{PS} = 0.19$ Pa and a preshear time of $\Delta t_{PS} = 3500$ s the network formation process is completed. The different preshear histories do not affect the resulting shear viscosities η_∞ in the high-shear stress state where a Newtonian behaviour can be observed (see Fig. 3). The influence of the preshear time Δt_{PS} (at a constant preshear stress τ_{PS}) on the stress dependence of the shear viscosity is less pronounced for lower volume fractions Φ_t and nearly vanishes for concentrations below $\Phi_t < 0.20$ (Schmidt 2000). Similar results were obtained by Kaschta et al. (1998) for suspensions of PMMA spheres in Newtonian silicon oils as a matrix.

The transient viscosity of $\eta^+(t)$ at a shear stress of $\tau = 0.19$ Pa which is identical to the applied preshear stress of $\tau_{PS} = 0.19$ Pa is shown in Fig. 4 for the suspension (Mono 1200/PIB1) and for the unfilled matrix PIB 1.

As expected for a low molecular weight fluid a time dependence of the viscosity of the matrix PIB 1 could not be observed. In contrast to the matrix the concentrated suspension ($\Phi_t = 0.35$) displays a characteristic short term increase of the shear viscosity $\eta^+(t)$ (see Fig. 4) which was also observed by Leighton and Acrivos (1987). Furthermore, Fig. 4 indicates that after approximately 3500 s the shear viscosity $\eta^+(t)$ reaches a plateau value which can be related to the completed

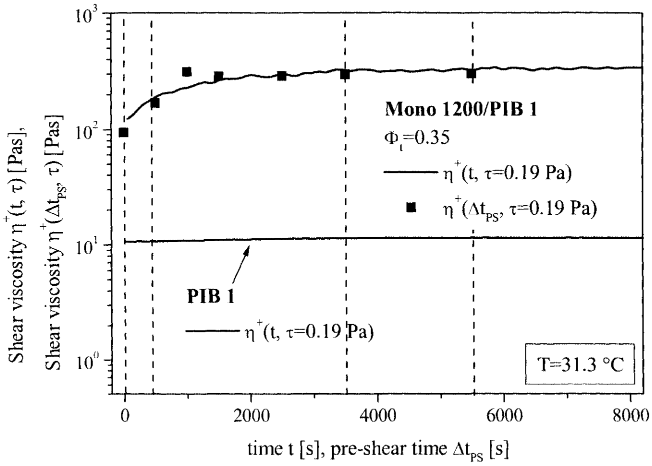

Fig. 4 Transient shear viscosity η^+(t) of a suspension ($\Phi_t = 0.35$) of the system Mono 1200/PIB 1 and of the unfilled matrix PIB 1 at a shear stress of $\tau = 0.19$ Pa, T = 31.3 °C

structure formation. Additionally, the startup values of the viscosity function at $\tau = 0.19$ Pa for various applied preshear times Δt_{PS} which are marked by arrows in Fig. 3 are represented in Fig. 4 by the solid symbols. Due to the consistency of both results it can be concluded that during the preshearing of concentrated monodisperse suspensions at a low constant preshear stress τ_{PS} a short-term increase of the shear viscosity η^+(t) is observed which corresponds to the transient behaviour for the chosen shear stress τ. The samples representing the different stages of the postulated particle network forming process which are indicated in Fig. 4 by vertical lines were subjected to oscillatory shear. From the dynamic-mechanical data, conclusions can be drawn with respect to a structure build-up by comparing the received dependencies to the characteristics which are observed during the formation of a chemical network (Winter and Chambon 1986).

Influence of preshearing on the dynamic mode of concentrated suspensions at a fixed temperature

Winter and Chambon (1986, 1987) characterised the rheological behaviour during the crosslinking reaction of well-defined polyurethanes (PU). A time sweep experiment was interrupted at chosen stages of the cross-linking process in order to measure the frequency dependence of G′ and G″. Performing frequency sweeps shortly before the onset of gelation, i.e. the material is still a liquid, it was found that both moduli distinctly decrease at low frequencies which corresponds to the typical linear behaviour of a viscoelastic liquid. Shortly after the onset of gelation the storage modulus G′ tended towards a limiting value at low frequencies, demonstrating the existence of a frequency-independent elasticity which is a characteristic of a solid material. These network building polymers are changing from a viscoelastic liquid to a viscoelastic solid by chemical crosslinking, thereby creating a three-dimensional network. Furthermore, Winter and Chambon (1986, 1987) showed that at the gel-point the storage and loss modulus have the same power law functions.

The model suspensions investigated were subjected to the dynamic mode at the different stages of the preshearing process marked by the vertical lines in Fig. 4. Figure 5 displays the frequency dependence of the system Mono 1200/PIB 1 with a volume fraction of $\Phi_t = 0.35$ at a fixed temperature of T = 31.3 °C for these preshear histories. At different preshear times Δt_{PS}, i.e. at different stages of the physical particle network formation, the model suspension displays obvious differences in the dependency of G″ and G′ on the frequency ω. Without preshearing ($\Delta t_{PS} = 0$ s) the suspension was found to be still a viscoelastic liquid indicated by the decrease of G″ with ω and G′ with ω^2 at low frequencies. With growing preshear times Δt_{PS} the frequency dependence of G′ at lower frequencies becomes weaker, indicating an increase of elasticity in comparison to the non-presheared state. Both moduli of the suspension approach a scaling with ω in the low frequency range. This result is in accordance with the assumption that at progressing stages of the structure forming process, the suspension is transferred from a viscoelastic liquid to a state between a viscoelastic liquid and a viscoelastic solid. Even at a stage where the network forming process is completed the G″ values of the suspension investigated exceed the G′ values over the entire frequency range covered, indicating that the

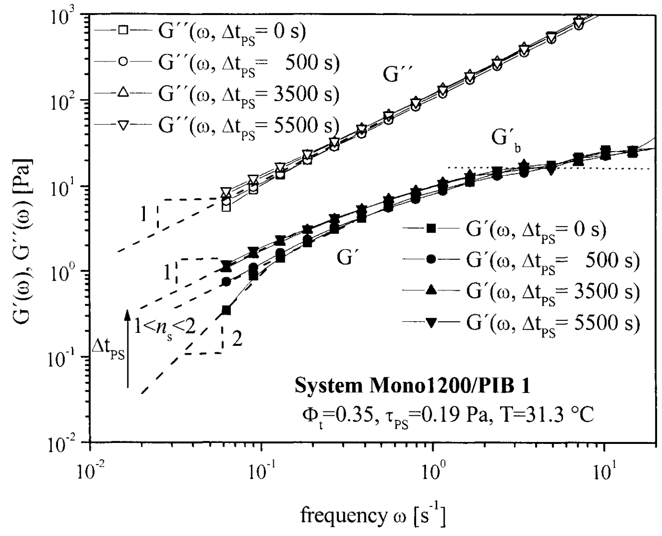

Fig. 5 Dynamic moduli G′ and G″ as a function of frequency at different stages of the network forming process. ($\Phi_t = 0.35$, System Mono 1200/PIB 1, T = 31.3 °C)

viscous component is dominant over its elastic part. However, an equilibrium modulus of G′ at low frequencies ω which can be regarded to be a characteristic feature of a solid material cannot be found.

The frequency dependency observed for the model suspension is very similar to results of Shikata and Pearson (1994). They also found a bending shape of G′ and an approximately linear dependency of G″ on the frequency ω for concentrated colloidal suspensions. However, the particles used in this study (Mono 1200) can be regarded to be non-colloidal ($x_n > 1$ μm) and hence effects due to Brownian motion should play a minor role. Furthermore, Shikata and Pearson (1994) postulated the existence of a plateau modulus (G'_b) of G′ in the high-frequency range as they observed a slight increase of G′ at lower temperatures and high frequencies. From Fig. 5 such a slight increase of G′ at high frequencies can be supposed, too. In order to prove whether this feature of G′ indicates the beginning of a particular high-frequency range, measurements at other temperatures were performed in order to expand the frequency range making use of the time-temperature superposition principle. Previous to showing the results from the time-temperature superposition principle in the dynamic mode the temperature dependency of the suspensions investigated in the steady-shear mode is characterised in the following chapter.

Time-temperature superposition of concentrated suspensions in the steady-shear mode

The temperature dependency of the shear viscosity η_{Matrix} (T) of the used matrix PIB 1 can be seen from the Arrhenius-expression expressed by Eq. (4). Hence, the ratio of η_{Matrix} (T) and η_{Matrix} (T_0) defines the temperature shift factor a_T

$$\log a_T(T, T_0) = \log\frac{\eta_{\mathrm{Matrix}}(\tau, T)}{\eta_{\mathrm{Matrix}}(\tau, T_0)} = \frac{E_A}{2.3\cdot R}\cdot\left[\frac{1}{T} - \frac{1}{T_0}\right] \quad (4)$$

whereas E_A is the flow activation energy and R = 8.3 J/K × mole the gas constant. T_0 which is a reference temperature was chosen as $T_0 = 40$ °C. The activation energy of the matrix PIB 1 follows as $E_A = 51.2$ kJ/mole.

For the investigation of the validity of the time-temperature superposition of suspensions in the steady shear mode a concentrated suspension ($\Phi_t = 0.30$) containing particles of Mono 1200 in the polyisobutylene PIB 1 as the matrix fluid was prepared. Before starting the measurement it was assured that for each temperature investigated the maximum increase in shear viscosity was reached by applying the fixed preshear stress of $\tau_{PS} = 0.19$ Pa for a preshear time of $\Delta t_{PS} = 5500$ s. The resulting steady-shear viscosity functions at temperatures ranging from 31.3 to 55 °C are shown in Fig. 6. The temperature dependency of the steady-shear viscosity functions η_{Susp} of the investigated suspensions (Mono 1200/PIB 1) from Fig. 6 and the shift factor a_T can be described similar to Eq. (4) as Fig. 7 demonstrates. Data taken at $T_0 = 40$ °C were chosen as a reference. Figure 7 also contains the data of the temperature shift factors a_T of the unfilled matrix PIB 1 (open symbols). They lie on one straight line. The consistence of the flow activation energies of a matrix fluid and the suspension was also found by other authors (Shikata and Pearson 1994; Watanabe et al. 1996). Remarkably the temperature dependency of the presheared suspension in the region of small shear stresses ($\tau = 0.19$ Pa) and in the region of dominating hydrodynamic forces ($\tau = 256$ Pa) is identical within the accuracy of the measurement.

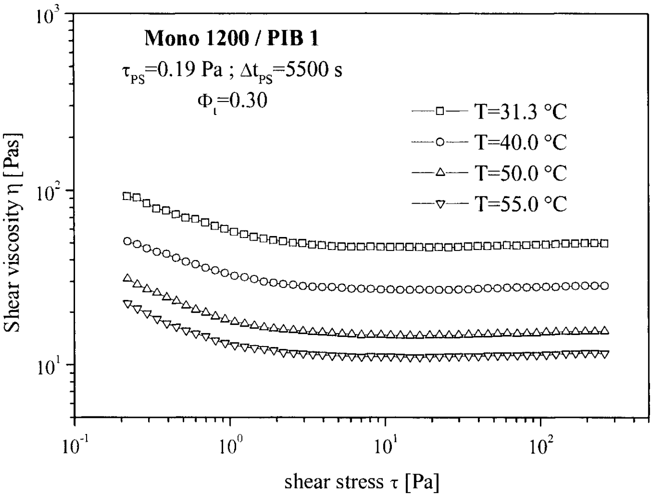

Fig. 6 Viscosity functions $\eta(\tau)$ for the suspension of the system Mono 1200 /PIB 1 ($\Phi_t = 0.30$) in the temperature range 31.3 °C≤T≤55 °C

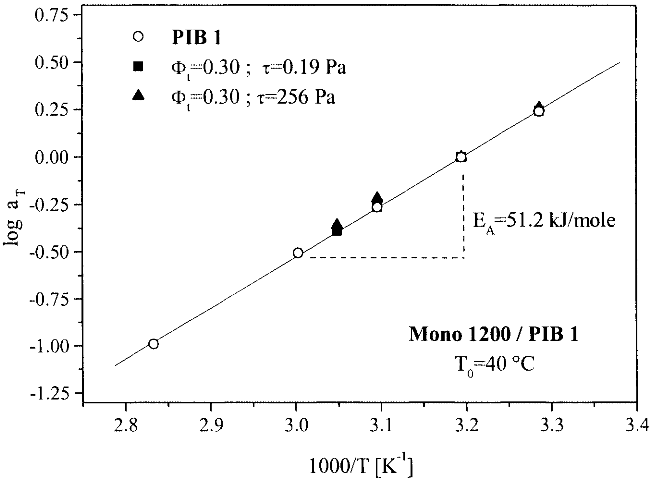

Fig. 7 Temperature dependent shift factors a_T of the unfilled fluid (PIB 1) and the model suspension ($\Phi_t = 0.30$, Mono 1200/PIB 1)

As the shift factors of the suspensions and the unfilled matrix coincide well, it can be concluded that the observed temperature dependency of the viscosities of the investigated suspensions is strictly controlled by that of the matrix.

Higher temperatures than 55 °C could not be measured because a larger change of the fluid density ρ_{Matrix} as a function of temperature leads to a reduced filler content Φ_t. A reduced filler content Φ_t at elevated temperatures T implements lower viscosities η_∞ in the high-shear-stress state. From the literature it is well known that, especially at high volume fractions ($\Phi_t > 0.50$), differences in the filler content below 1 vol.% can lead to significant changes of the high-shear-stress viscosity η_∞ of more than a decade (Barnes et al. 1987).

For a better understanding of the temperature dependency of the suspensions obtained in the steady shear mode, Krieger's considerations (Krieger 1972) on monodisperse suspensions are discussed. Krieger demonstrated that the relative shear viscosity $\eta_{\mathrm{rel}} = \eta_{\mathrm{suspension}}/\eta_{\mathrm{Matrix}}$ of a concentrated suspension of monosized spherical particles is a universal function of two dimensionless quantities: the volume fraction Φ_t and a reduced stress τ_{red}. The reduced shear stress τ_{red} is defined as

$$\tau_{\mathrm{red}} = \frac{\tau \cdot \mathrm{x}_{\mathrm{n}}^3}{8 \cdot \mathrm{kT}} \tag{5}$$

where τ is the shear stress, k the Boltzmann constant and $\mathrm{x_n}$ the number average particle diameter. For a variation of the viscosity of the matrix fluid η_{Matrix} at a *fixed* temperature and for different particle diameters $\mathrm{x_n}$, mastercurves of the relative η_{rel} viscosity as a function of τ_{red} were obtained by several authors (Krieger 1972; Choi and Krieger 1986; Willey and Macosko 1978).

A variation of the temperature T simultaneously induces a change of the viscosity of the matrix η_{Matrix}. As chemical reactions between the particles and the matrix can be excluded at elevated temperatures a mastercurve of $\eta_{\mathrm{rel}}(\tau_{\mathrm{red}})$ should be obtained for a variation of the viscosity $\eta_{\mathrm{Matrix}}(\mathrm{T})$ by introducing a reduced stress according to Eq. (5) as well. Considering the temperature dependency of the unfilled matrix PIB 1 a mastercurve can be obtained for the presheared suspension (Mono 1200/PIB 1, $\Phi_t = 0.30$) for the temperatures ranging from 31 to 55 °C as Fig. 8 demonstrates.

For the presheared suspension of monodisperse particles investigated it follows from Fig. 8 that the relative viscosity η_{rel} is neither a function of temperature T nor a function of the viscosity η_{Matrix} if plotted as a function of τ_{red}. Interestingly these facts are not restricted to the state where the suspension behaves like a Newtonian liquid but holds for the region of low stresses τ_{red} as well. The shear viscosity function $\eta_{\mathrm{rel}}(\tau_{\mathrm{red}})$ in Fig. 8 can be described by

$$\eta_{\mathrm{rel}}(\tau_{\mathrm{red}}) = \eta_{\mathrm{rel},\infty} + \left(\frac{\eta_{\mathrm{rel},0} - \eta_{\mathrm{rel},\infty}}{1 + b\tau_{\mathrm{red}}}\right) \tag{6}$$

where $\eta_{\mathrm{rel},0}$ is the relative viscosity in the region of low stresses τ_{red} and $\eta_{\mathrm{rel},\infty}$ the relative viscosity in the "high-shear-stress state" (Larson 1999). The fitting parameter b results as $b = 0.15$. In accordance with results from other authors (Rueb and Zukoski 1998) a secondary Newtonian plateau $\eta_{\mathrm{rel},0}$ in the region of very low stresses τ_{red}, which is predicted by applying Eq. (6), could not be detected within our experimental window.

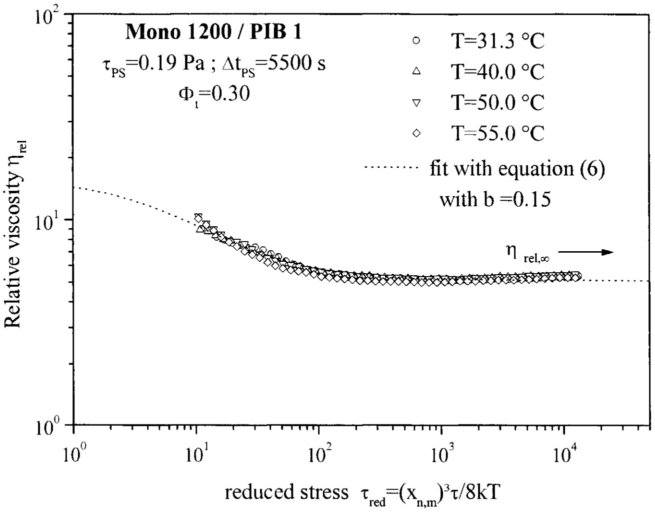

Fig. 8 Relative viscosity function $\eta_{\mathrm{rel}}(\tau_{\mathrm{red}})$ for the suspension of the system Mono 1200/PIB 1 ($\Phi_t = 0.30$) at different temperatures

Time-temperature superposition in the dynamic mode

The suspension presented in Figs. 4 and 5 was used for the determination of the temperature dependence in the dynamic mode. By applying the shear stress of $\tau_{\mathrm{PS}} = 0.19$ Pa for at least 3500 s it was assured that a defined structure was reached before starting the dynamic-mechanical experiments (see also Fig. 5). Figure 9 shows a double-logarithmic plot of the obtained master curves of G′ and G″ as a function of ωa_{T}, where a_{T} is the shift factor. The measurements were performed at several temperatures ranging from 26 to 55 °C. The reference temperature was set to $\mathrm{T_0} = 40$ °C. G′ and G″ can be superimposed by a horizontal shift along the log ω axis. A common shift factor a_{T} is obtained for both moduli G′ and G″. As can be seen from Fig. 9 the time-temperature superposition in the dynamic mode can successfully be applied to extend the accessible frequency range. In comparison to Fig. 5 the postulated increase of G′ in the high-frequency range can clearly be identified from Fig. 9. In part a time-temperature superposition in the dynamic mode could

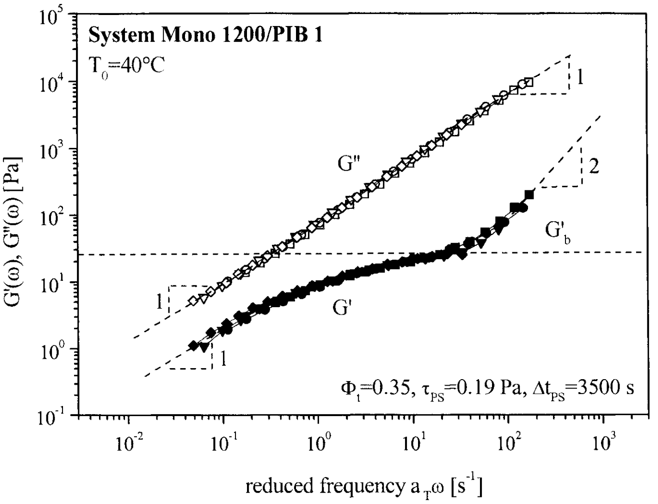

Fig. 9 Time-temperature superposition of G′ and G″ for the model suspension (Mono 1200/PIB 1), $T_0 = 40$ °C

successfully be applied to suspensions by Shikata and Pearson (1994) and Aral and Kalyon (1997), too. The applicability of the time-temperature superposition principle is also well known for polymeric liquids, e.g. Ferry (1980). The bending shape of G′ in Fig. 9 seems to be a characteristic feature of a heterogeneous two-phase system (Shikata and Pearson 1994; Watanabe et al. 1996; Kitade et al. 1997; Bousmina 1999). Shikata and Pearson (1994) and Watanabe et al. (1996) also report the bending of G′ and the linear dependency of G″ on ω for suspensions with a Newtonian matrix and a high volume concentration of colloidal spherical silica particles. For immiscible polymer blends with a high viscosity ratio of the two phases Kitade et al. (1997) published the bending of G′(ω) and the linear G″(ω) curves as well. For polymer blends Bousmina (1999) analysed the bending shape of G′ from a theoretical point of view by using the Palierne model (Palierne 1990) with changing interfacial tension.

At intermediate frequencies a plateau value G'_b is found in Fig. 9. A similar plateau value G'_b at intermediate frequencies was recently predicted by Fahrländer and Friedrich (1999) using a modified model of Palierne (1990) to describe the dynamic properties of PS/PMMA-blends with a sphere in sphere morphology. At frequencies ω above the plateau value G'_b the models developed by Fahrländer and Friedrich (1999) and Bousmina (1999) display the characteristics of the matrix polymer. As can be seen from Fig. 9 the investigated model suspension approximately shows the behaviour of a Newtonian fluid ($G' \propto \omega^2$;$G'' \propto \omega$) at frequencies higher than that of the plateau value G'_b. Hence, the observed dependency of G′ and G″ on the frequency ω in the high frequency range obeys the usual behaviour of Newtonian fluids (see also Fig. 2).

The temperature shift factors a_T from Fig. 9 are plotted in Fig. 10 as a function of the reciprocal temperature T^{-1} (filled circles). They are compared to the shift factors a_T for the matrix (PIB 1, open circles) which were determined in steady-shear experiments according to Eq. (4) and to the temperature shift factors a_T which were obtained for a suspension of a lower volume fraction ($\Phi_t = 0.30$) containing identical particles (Mono 1200) in the same matrix PIB 1 (see Fig. 7). As can be seen from Fig. 10 all data sets coincide very well. It can be concluded that the temperature dependency of the relaxation processes for the model suspension investigated is independent of the volume fraction Φ_t of the filler and strictly controlled by the viscosity of the matrix fluid η_{matrix}.

Influence of the matrix fluid and filler content on G″(ω) and G′(ω)

In order to investigate the influence of the fluid properties on the dynamic-mechanical properties of concentrated monodisperse suspensions, the Newtonian materials PIB 2 and PIB 3 of a higher viscosity were used as the matrix fluids (see Table 1). In comparison to the investigated suspension shown in Fig. 9, a lower fixed volume fraction ($\Phi_t = 0.20$) of the glass spheres Mono 1200 was chosen. Before starting the dynamic experiments the suspensions were presheared at the fixed preshear stress of $\tau_{PS} = 0.19$ Pa until the maximum structure in steady shear was reached. As Fig. 11 indicates, the time-temperature superposition holds within the range of the temperatures investigated from 26 to 50 °C for both systems (Mono 1200/PIB 2 and Mono 1200/PIB 3). The reference temperature was set to $T_0 = 40$ °C.

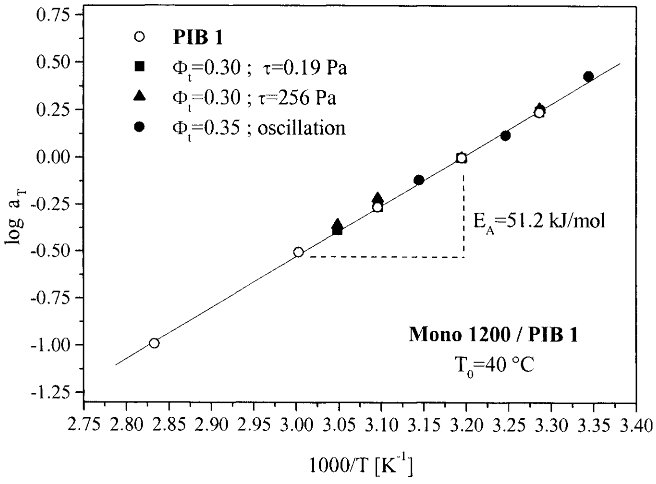

Fig. 10 Temperature shift factor a_T as a function of T^{-1} for model suspensions and the unfilled matrix

Furthermore, it can clearly be seen from Fig. 11 that the height of the shoulder of G′ is nearly independent of the used matrix fluid. With increasing matrix viscosity η_{Matrix} (PIB 3) the end of the shoulder of G′ is shifted towards lower frequencies (see Fig. 11). The frequency dependence of G″ is found to be independent of the used viscosities η_{Matrix} of the matrix fluids ($G'' \propto \omega$) but G″ is higher for the matrix PIB 3 than for PIB 2. In the high frequency range a frequency dependence of G′ is observed for both systems (Mono 1200/PIB 2 and Mono 1200/PIB 3) which obeys the behaviour of a Newtonian fluid ($G' \propto \omega^2$). For G″ the relation $G'' \propto \omega$ is valid over the whole frequency range. By comparing the dynamic behaviour of the suspensions shown in Fig. 11 with the results from Fig. 9 it becomes obvious that the height of the shoulder of G′ strongly increases with the volume fraction Φ_t of the suspension.

Influence of particle size on G″(ω) and G′(ω)

In order to investigate the influence of a particle size variation on the dynamic-mechanical properties of concentrated monodisperse suspensions, the particles Mono 1200 ($x_n = 1.18$ μm) and Mono 250 ($x_n = 0.27$ m) were chosen as fillers (see also Table 2). For both fillers the Newtonian PIB 1 was used as the matrix component. A fixed volume fraction of the filler of $\Phi_t = 0.20$ was selected for both systems. Recently Bousmina (1999) demonstrated that the parameter $2\gamma_{LS}/x_n$ has an effect on the bending shape of G′(ω) of immiscible polymer blends. γ_{LS} represents the interfacial tension and x_n the number average particle diameter of the disperse phase. For a larger value of the parameter $2\gamma_{LS}/x_n$ Bousmina (1999) observed a larger shoulder formation of G′ with increased plateau values. Assuming that the interfacial tension γ_{LS} of the two suspensions (Mono 1200/PIB 1 and Mono 250/PIB 1) is the same, they only differ with respect to the particle size x_n. Before starting the dynamic-mechanical experiments the suspensions were presheared at the fixed preshear stress of $\tau_{PS} = 0.19$ Pa until a defined maximum structure in steady shear was reached. From Fig. 12 it is obvious that the time-temperature superposition holds for the temperatures ranging from 26 to 55 °C. This has to be expected as the temperature dependence of the suspensions is governed by that of the matrix as shown in Fig. 10. As Fig. 12 indicates the height of the shoulder of G′ increases slightly with decreasing particle size x_n. The frequency dependence of G″ is independent of the used particle sizes x_n within the accuracy of the measurement. Also for emulsions it was found that the G′(ω) data were significantly affected by the preshear rates and the droplet sizes (i.e. particle sizes) as well, but the G″(ω) data were not (Graebling et al. 1993; Kitade et al. 1997). For both types of glass spheres the frequency dependency of G′ and G″ in the high frequency range corresponds to that of a Newtonian fluid and no significant differences in the dynamic moduli can be detected for both systems. Hence, it can be concluded that the particle size x_n in the range given by the two types of glass spheres does not affect the complex viscosity $|\eta^*|$ (or the complex relative viscosity $|\eta^*|_{\mathrm{rel}} = |\eta^*|_{\mathrm{Susp}}/|\eta^*|_{\mathrm{matrix}}$ since the matrix PIB 3 was kept constant) of concentrated monodisperse suspensions. This result is well known from investigations of

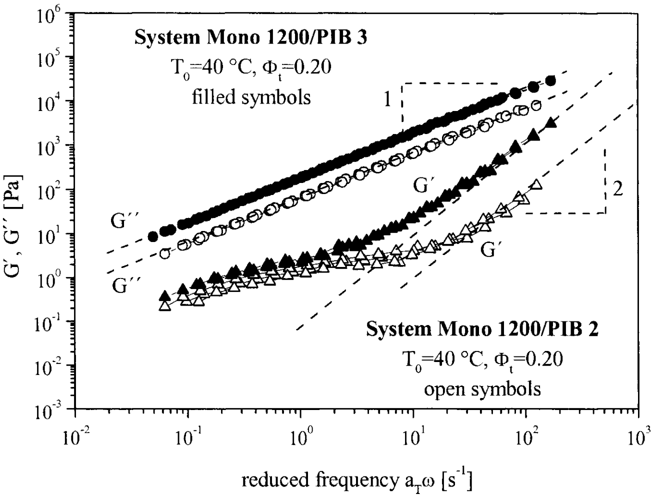

Fig. 11 Time-temperature superposition of G′ and G″ for the model suspensions (Mono 1200/PIB 2 and Mono 1200/PIB 3) which vary with respect to their matrix fluid. The filler (Mono 1200) and the volume fraction ($\Phi_t = 0.20$) is kept constant, $T_0 = 40$ °C

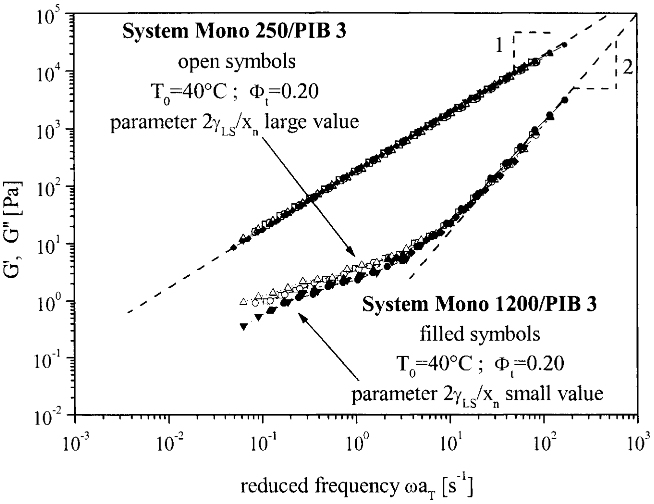

Fig. 12 Time-temperature superposition for two model suspensions (systems Mono 1200/PIB 3 and Mono 250/PIB 3) which vary with respect to their particle diameter x_n. The matrix fluid (PIB 3) and the volume fraction ($\Phi_t = 0.20$) is kept constant, $T_0 = 40$ °C

monodisperse suspensions in steady shear experiments (Krieger 1972). Also Choi and Krieger (1986) found that the relative viscosity η_{rel} of Newtonian monodisperse suspensions is independent of the particle sizes used.

Conclusion and outlook

From the experimental results on the suspensions investigated it can be postulated that a network structure is formed by applying preshearing at low Reynolds-numbers. As a consequence of the applied preshearing the suspensions displayed non-Newtonian behaviour at low shear stresses and Newtonian behaviour at high stresses. The assumption of a shear induced network build-up of particles in a model suspension can be justified by comparing the obtained rheological features to the rheological properties that are obtained during the crosslinking reaction of polymeric systems (Winter and Chambon 1986, 1987). By varying the *preshear time* at low *preshear stresses* a behaviour similar to the frequency sweeps of crosslinking polymeric systems was observed, indicating the progressing structure build-up of the filled systems. Hence, the *preshear time* can be regarded as being correspondent to the *reaction time* in crosslinking systems. The driving force for a structure build-up of particles can be attributed to the *shear diffusion* by applying low *preshear stresses*.

Within a certain temperature range where the fluid density ρ_{Matrix}, and hence the adjusted volume fraction Φ_t, can be regarded to be constant a validity of the temperature superposition was observed for steady shear and dynamic-mechanical material functions after preshearing. In steady shear experiments it could be demonstrated for presheared suspensions that a superposition of the relative viscosities η_{rel} could be achieved over the investigated temperatures ranging from 26 to 55 °C by introducing a reduced shear stress τ_{red} according to Krieger (1972). Hence, it was concluded that the relative viscosity η_{rel} is neither a function of the viscosity of the matrix fluids η_{Matrix} nor a function of the temperature T. By successfully applying the time-temperature superposition to the presheared suspensions the accessible frequency range was extended in the dynamic mode. For the suspensions investigated two frequency dependent regimes of G′ were detected which are either separated by a shoulder formation or a plateau value of G′. The experimental results obtained suggest that it can be regarded as an universal, characteristic feature of heterogeneous two-phase systems (Shikata and Pearson 1994; Watanabe et al. 1996; Kitade et al. 1997; Bousmina 1999). The low frequency range was found to be dependent on the preshear conditions. In the high frequency region a behaviour was observed which corresponds to that of the unfilled Newtonian matrices. Furthermore, it could be demonstrated that a higher total volume fraction Φ_t and a lower particle size x_n increase the height and the shape of the shoulder of G′. A higher molecular weight of the matrix fluid was found to shift the plateau value of G′ to lower frequencies. The observed temperature dependency of the suspensions investigated, which can be described by an Arrhenius-expression, was found to be identical to the temperature dependency of the matrix fluids.

The theoretical description of the phenomena observed will be the objective of future research work. Further

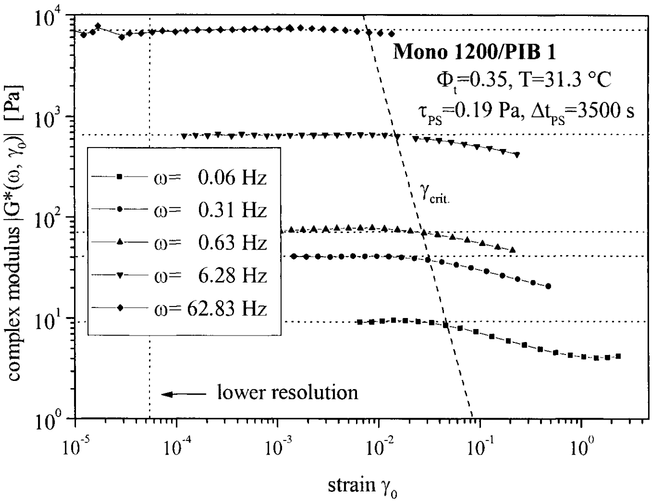

Fig. 13 Complex modulus $|G^*|$ as a function of the strain amplitude γ_0 for a pre-sheared suspension of the system (Mono 1200/PIB 1) at different frequencies ω (T = 31.3 °C). The volume fraction amounts to $\Phi_t = 0.35$

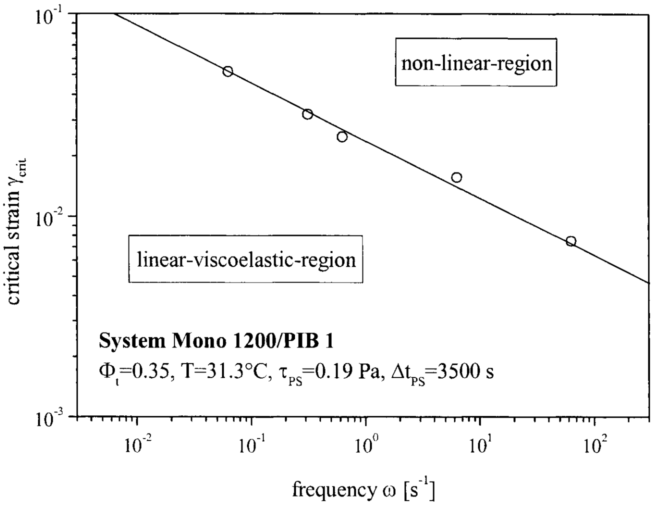

Fig. 14 Critical deformation amplitude γ_{crit} as a function of the applied frequency ω for a pre-sheared suspension of the system (Mono 1200/PIB 1) at T = 31.3 °C. The volume fraction amounts to $\Phi_t = 0.35$

experimental investigations will focus on the rheological properties of concentrated *polydisperse* suspensions which depend on the preshear conditions, as well.

Appendix

The aim of the appendix is to show the dependency of the linear-viscoelastic response of suspensions on the applied strain amplitude γ_0 and frequency ω. It is worth mentioning that an FT-analysis of the incoming signals did not reveal any non-harmonic components for all the dynamic experiments performed. The range of the linear-viscoelastic response was defined as follows.

Per definition the complex modulus $|G^*|$ is the ratio of the stress amplitude τ_0 and strain amplitude γ_0. The linear viscoelastic region can be defined by plotting the complex modulus $|G^*|$ vs. γ_0. Reaching a deviation of $|G^*|$ from its constant value of 5% with increasing strain amplitude γ_0 a critical deformation amplitude $\gamma_{\text{crit.}}$ is defined which determines the boundary of the linear-viscoelastic region.

These dependencies are demonstrated for a concentrated monodisperse suspension of the system PIB 1/Mono 1200 at a fixed reference temperature (i.e. at $T = 31.3$ °C). The volume fraction was set to $\Phi_t = 0.35$. All suspensions were presheared at a fixed preshear stress of $\tau_{PS} = 0.19$ Pa for a preshear time of $\Delta t_{PS} = 3500$ s. Figure 13 shows the dependency of $|G^*|$ on the strain amplitude γ_0 at different frequencies ω. It can clearly be seen from Fig. 13 that the applied strain γ_0 and frequency ω have a strong influence on the range of the linear-viscoelastic response for suspensions. By determining the critical deformation amplitude $\gamma_{\text{crit.}}$ according to the described procedure and by plotting $\gamma_{\text{crit.}}$ vs. the applied frequency ω in Fig. 14, the strong dependency of the linear-viscoelastic response of suspensions on the frequency ω becomes obvious.

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