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Rheological properties of aqueous silicon nitride suspensions

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The effect of surface modification of Si_3N_4 particle on the colloidal behavior and the rheological properties of aqueous Si_3N_4 suspensions under steady and oscillatory conditions are investigated in detail. Due to the decrease of the oxidizing level, the isoelectric point (IEP) of the modified particle shifts to basic region gently. Attempts have been made to apply rheological models to the suspensions with various solid volume fraction (ϕ). For the as-received suspensions, the Sisco model provides the best fit in the range of $\phi \leq 0.30$ while the Casson model in $0.35 \leq \phi \leq 0.45$. The shear behavior of modified suspensions fits to Sisco model in the range of $\phi \leq 0.40$ and Casson model in $0.45 \leq \phi \leq 0.54$. The rheological behavior of modified suspensions is improved efficiently. The critical strain decreases and the linear viscoelastic regime narrows continuously with increasing solid concentration. For the modified suspensions, the linear viscoelastic regime broadens and the corresponding elastic modulus decreases sharply. With increasing solid concentration, the characteristic frequency shifts toward lower frequencies and the suspension transforms from more viscous to more elastic. © *2001 Kluwer Academic Publishers*

1. Introduction

Colloidal processing technique such as slip casting or pressure slip casting has commonly been accepted as one of the most attractive routes in the fabrication of ceramic components with complex shapes. This is because that these techniques offer improved homogeneity and reliability, which can hardly be achieved through the conventional alternatives, e.g. dry pressing [1, 2]. In colloidal processing, water has always been used as a dispersing media because of low-cost and environmental protection. For this purpose, ceramic powder should be dispersed effectively in water medium to form a desirable suspension with the lowest viscosity and highest solid content which will produce a better green body as well as fine microstructure [1, 2]. This can usually be achieved with the help of appropriate dispersants that stabilize ceramic particles via an electrostatic repulsion or steric hindrance, or a combination of both.

The dispersion of colloidal particles in an aqueous media by electrostatic and/or steric effect has been investigated extensively [3]. The forms is managed by both attractive and repulsive forces between particles depending on surface charges. The net effect of these forces determines the state of dispersions. Ceramic particles are naturally positively or negatively charged depending on the pH conditions. The amount of charge can be easily measured via zeta potential. Zeta potential is the potential at the shear plane and is generally accepted as a reasonable measure of the amount of surface charge. The point at which the zeta potential is zero is termed the isoelectric point (IEP). At this pH value the electrostatic repulsive force is zero, so the particles aggregate together in a purely electrostatically stabilized system [4, 5]. However, for large zeta potential in magnitude electrostatic repulsive force is larger than van der Waals attractive force, which prevents particles from flocculating. Hence, during preparing a stable ceramic suspension it is necessary to have the knowledge of the IEP, so that a system has a pH far from that of IEP. In general, an electrostatic stabilization of suspension can be achieved by manipulating electrostatic charges on the particle surface by controlling pH and/or adding a dispersant into the suspension, which is adsorbed on the surface of particles thus increasing the repulsive force [6].

In all types of suspension shape-forming techniques ranging from slip casting to injection molding, the rheological properties of concentrated suspension play a key role in controlling the shape-forming behavior and optimizing the properties of the green body. For example, during slip casting of a suspension, the optimized rheological properties will minimize the density gradients, mass segregation of different components, and avoid strain recovery of the cast body after consolidation [7–10]. Fundamentally, the rheological properties of concentrated colloidal suspensions are determined by the interplay of thermodynamic and fluid mechanical interactions. With particles in colloidal size range (at least one dimension $<1\mu$m), the range and magnitude of the interparticle forces will have a profound influence on the suspension structure and, hence, the rheological behavior [10, 11].

The rheological behavior of concentrated suspension is affected by a number of factors including particle size distribution, particle shape and volume fraction of solid. The flow curve of suspension can provide information that relates to the interactions between the particles and the media. In particular, if an appropriate model can represent the data, the evaluation may become more convenient and effective [5]. Several models have been developed for non-Newtonian systems, including Bingham plastic model, Casson model, and Herschel-Buckley model [12]. These models have been widely and successfully used to explain, characterize, and predict the flow behavior for various systems. Nevertheless, not much has been reported in regard to the study of ceramic suspension systems by means of these models. In addition, colloidal suspensions usually exhibit viscoelastic properties that become more and more significant with increasing particle concentration. Thus, in order to achieve a through characterization of the rheological behavior of concentrated ceramic suspensions, the viscoelastic response should be taken into consideration, also because it can provide more detailed information about the structural conditions of the disperse phase in the equilibrium state.

The present work is intended to discuss how rheological measurements can elucidate important information concerning the properties of ceramic suspensions. We focused our attention mainly on the rheological characterization of aqueous Si_3N_4 suspensions. The influence of the surface modification of Si_3N_4 powders on the rheological properties of suspension is systematically investigated. Additionally, attempts have been made to apply rheological models to the suspensions.

2. Experimental procedure

2.1. Materials and surface modification

Commercially available Si_3N_4 powder (Starck LC-12, Germany) with an average particle size of 0.60 μm and a BET specific surface area of 21.0 $m^2 \cdot g^{-1}$ was used for the present study. In order to adjust the surface properties, the powders was leached with acidic aqueous solution ($pH = 2$) at first and then repeatedly rinsed with deionized water until that no change in conductivity was detected [13]. The dispersant used was an inorganic compound which was the best dispersing agent selected from a number of commercial dispersants through a series of sedimentation tests [14].

2.2. Preparation and characterization of suspensions

Suspensions of different solid volume fraction (ϕ) for rheological measure were prepared by the successive addition of various amounts of Si_3N_4 powders into deionized water containing 1.0 wt% dispersant, as calculated on the basis of dry Si_3N_4 powder. The solution pH was preadjusted to yield a value close to target pH ($pH = 11$), whereas subsequent adjustment of suspension pH was made using tetramethylammonium hydroxide (TMAH) or HCl. Wetting and dispersion were improved by both intermittent ultrasonic treatment and continuous stirring. This procedure was followed by ball milling in a ceramic jar with Si_3N_4 balls.

Zeta potential of Si_3N_4 particles was measured with dilute aqueous suspension in 10^{-3}M NaCl electrolyte on Zetasizer 4 (Malvern, UK). To determine the zeta potential as a function of pH, 10^{-2}N HCl and 10^{-2}N NaOH solutions were used to adjust pH to the desired values.

Rheological characterization was performed on Rheometeric Fluid Spectrometer II at 25 °C, with a couette (cup radius: 34.0 mm, bob radius: 32.0 mm, bob length: 33.3 mm) or a cone and plate measurement geometry (radius: 12.5 mm, angle: 0.1 rad). A small amount of silicone oil was floated on the sample to prevent evaporation. Steady shear measurements of the examined systems were performed by incrementing shear rate and measuring apparent viscosity. The viscoelastic properties of the suspensions were examined under oscillatory shear conditions. In order to determine the limits of linear viscoelastic regime, strain sweep experiments from 0.01 to 50 percent of strain were carried out at constant frequency. The mechanical spectra of the examined suspensions were evaluated by applying frequency sweep experiments in the linear viscoelastic region.

3. Results and discussion

3.1. Surface modification of Si_3N_4 powder

The effect of surface modification on zeta potential of Si_3N_4 particles is shown in Fig. 1. As can be seen, the IEP of modified Si_3N_4 particles shifts to alkaline region gently and the zeta potential of modified Si_3N_4 particle in alkaline region evidently increases in magnitude. According to Bergstrom [15], the shift of IEP is resulted from the decrease of the relative site density of acidic silanol group (−SiOH). The X-ray photoelectron spectroscopy (XPS) reveals a decreased O/Si ratio and an increased N/Si ratio (Table I), i.e., a decrease of the surface density of acidic silanol group after that the powder is leached. This may be resulted from the removal of an amorphous oxide phase by leaching solution, thus leaving a surface with relatively more basic

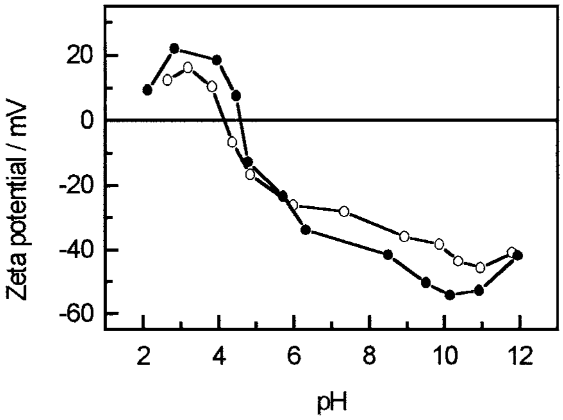

Figure 1 Effect of surface modification on zeta potential of Si_3N_4 powder (●) acid leaching, (○) as received.

TABLE I XPS results showing binding energy, bind width at half maximum (FWHM) and atomic ratios: N/Si and O/Si for two powders (three reference powders also included) [16]

Powder	Line spectrum	Binding energy/*eV*	FWHM	Atomic ratios N/Si	Atomic ratios O/Si
As received	Si 2*p*	102.1	2.3	0.95	0.16
	N 1*s*	397.3	2.0		
Acid leaching	Si 2*p*	101.8	2.1	0.99	0.13
	N 1*s*	397.6	2.0		
Si_3N_4	Si 2*p*	101.4 ~ 101.7			
	N 1*s*	397.3 ~ 397.7			
Si_2N_2O	Si 2*p*	101.7 ~ 102.2			
	N 1*s*	397.3 ~ 397.7			
SiO_2	Si 2*p*	103.6 ~ 103.7			

groups. Denny *et al.* showed that metal cation impurities such as Al^{3+} and Fe^{3+} in minute amounts would significantly depress the dissolution of silica probably because of the formation of a stable complex between silanol group and polyvalent metal cation [17]. This process can be described as following reaction:

$$(-\mathrm{SiOH})_m + \mathrm{Fe}^{3+} = (-\mathrm{SiOH})_{m-n}(-\mathrm{SiO})_n\mathrm{Fe}^{3-n} + n\,\mathrm{H}^+ (m \geq n, 3 \geq n \geq 1)$$

The results of inductively coupled plasma (ICP) analysis show that the amount of ferric oxide (Fe_2O_3) in leached powder decreased by 47% over the as-received powder. This indicates that acid leaching clears away metal impurities and thereby accelerates the dissolution of silica at the surface of Si_3N_4 powder.

3.2. Rheological behaviors of Si_3N_4 suspensions

The steady shear behavior of as-received Si_3N_4 suspensions at various solid volume fraction is shown in Fig. 2. All of the suspensions are characterized by a shear thinning which is associated with the disruption of suspension structure or shear induced alignment. At lower shear rates, the suspension structure is close to equilibrium because thermal motion dominates over the viscous force. At higher shear rates, the viscous force affects the suspension structure and shear induced alignment develops, and thus shear thinning occurs. On the other hand, for low solid loading suspension, the viscosity curve develops a constant viscosity at higher shear rate that commonly defined high-Newtonian region, which is the indicative of completely hydrodynamically controlled suspension structure. With increasing solid loading, high Newtonian region disappears gradually and shear thickening appears instead at high shear rate. The shear thickening maybe results from a flow instability which causes the particles to break out of their ordered layers at some critical level of shear stress (i.e. shear rate), thereby causing the rise in viscosity [18].

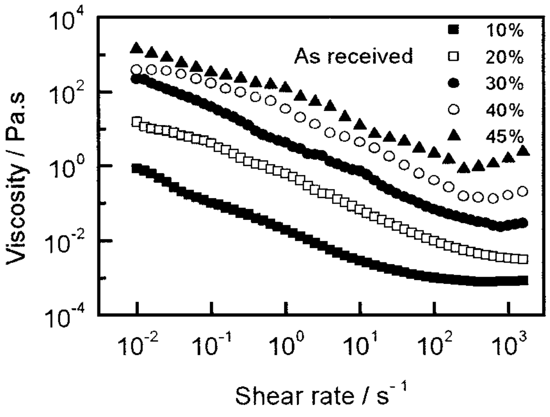

Figure 2 Viscosity curves of as-received Si_3N_4 suspensions at various solid loading.

Attempts have been made to apply rheological models to the suspensions. The experimental results indicate that any model shows a good fit to the rheological behavior of suspensions only within a specific shear rate range. Among the various rheological models existing in literature, including Bingham model, Herschel-Buckley model, Sisco model, and Casson model, the Sisco model provides the best fit in the range of $\phi \leq 0.30$ while the Casson model in the range of $0.35 \leq \phi \leq 0.45$ within a shear rate range of 0.001~800 s^{-1} and the fitting parameters of these two models are given in Tables II and III, respectively.

Sisco equation is $\eta = \eta_\infty + k \cdot \gamma^{\mathrm{n}-1}$. At $n = 0$, the equation transforms into $\eta = \eta_\infty + k \cdot \gamma^{-1}$, i.e., $\tau = k + \eta_\infty \cdot \gamma$, which is just Bingham model. It is evident that parameter k and η_∞ represent yield stress and limiting viscosity at high shear rates respectively. At $n = 1$, the equation transforms into $\eta = \eta_\infty + k$, which is Newtonian equation exactly. The increase of parameter k from 0.072 to 5.9 and the decrease of parameter n from 0.92 to 0.13 indicate that the yield stress increases gradually and the rheological behavior transforms from near Newtonian fluid into plastic fluid with increasing solid loading from 10 to 30 vol%.

Casson equation is $\tau^{1/2} = \tau_y^{1/2} + (\eta_c \cdot \gamma)^{1/2}$, where parameter τ_y and η_c represent yield stress and Casson viscosity respectively. The yield stress τ_y can be used as a parameter that quantifies the strength of suspension structure. As is expected, the yield stress τ_y and the Casson viscosity η_c increase simultaneously with increasing solid loading of suspensions.

TABLE II Fitting parameters to Sisco model for as-received Si_3N_4 suspensions at various solid loading

ϕ	$\eta_\infty / Pa \cdot s$	$k / Pa \cdot s^n$	n
0.10	0.0013	0.072	0.92
0.15	0.0019	0.53	0.83
0.20	0.0032	1.3	0.65
0.25	0.0073	2.9	0.27
0.30	0.017	5.9	0.13

TABLE III Fitting parameters to Casson model for as-received Si_3N_4 suspensions at various solid loading

ϕ	τ_y / Pa	$\eta_c / Pa \cdot s$
0.35	2.5	2.6
0.40	3.4	6.1
0.45	9.4	53

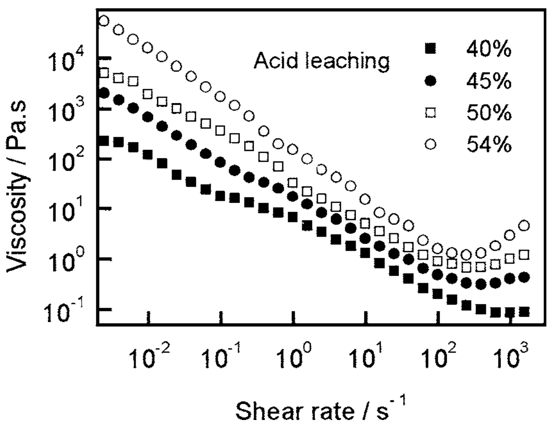

Figure 3 Viscosity curves of modified Si_3N_4 suspensions at various solid loading.

The steady shear behavior of modified suspensions is very similar to that of as-received suspensions, as is illustrated in Fig. 3. The shear behavior of modified suspensions fits to Sisco model in the range of $\phi \leq 0.40$ and Casson model in the range of $0.45 \leq \phi \leq 0.54$ perfectly. The fitting parameters of these two models are given in Tables IV and V, respectively. Comparison to that of as-received suspensions, the rheological behavior of modified suspensions is improved efficiently. For certain solid loading, the viscosity of modified suspension at any shear rate is lower than that of as-received suspension. Additionally, the 40 vol% as-received suspension exhibits shear thickening at high shear rate while the modified suspension develops still a high-Newtonian region even with a solid concentration of 45%. These effects of surface modification on the rheological behavior of Si_3N_4 suspension can be interpreted by taking the following three factors into account. Firstly, the zeta potential of Si_3N_4 particles in the alkaline region increases evidently in magnitude (Fig. 1), so the fluidity of suspension improves efficiently. Secondly, it is well known, there exist some silanol groups on the surface of Si_3N_4 particles that usually form an immobile water layer on the particle surface by hydrogen bond with water molecular [19]. As-received powder has more silanol group at the particle surface, which could result in multi-molecular adsorbed layer, increased efficient solid volume fraction and bad fluidity. On the other hand, modified powder has less silanol groups at the particle surface, which could result in mono-molecular adsorbed layer and improved fluidity. Additionally, the ICP results show that the amount of ferric oxide in modified powder decreased by 47% over the as-received powder. Thus, the decrease of the high valence counter-ion concentration (e.g., Fe^{3+}) is also responsible for improving the rheological behavior of suspension to a certain extent.

TABLE IV Fitting parameters to Sisco model for modified Si_3N_4 suspensions at various solid loading

ϕ	$\eta_\infty / Pa \cdot s$	$k / Pa \cdot s^n$	n
0.30	0.069	1.7	0.76
0.35	0.025	2.3	0.39
0.40	0.078	9.8	0.15

TABLE V Fitting parameters to Casson model for modified Si_3N_4 suspensions at various solid loading

ϕ	τ_y / Pa	$\eta_c / Pa \cdot s$
0.45	7.2	1.7
0.50	12.8	2.8
0.52	35.3	8.6
0.54	150	11.6

3.3. Viscoelastic properties of Si_3N_4 suspensions

Viscoelastic response often presents for concentrated suspensions because of the interaction between suspended particles [10]. Viscoelastic measurements can be performed to characterize the rheological behavior, in particular the effect of solid volume fraction. Oscillatory viscoelastic measurements are meaningful only under small amplitude of oscillation, so that the suspension structure is only slightly perturbed from rest. Fig. 4 illustrates the results of a typical strain sweep experiment of as-received Si_3N_4 suspension with a volume fraction of 40 vol%, showing that the behavior of the suspension changes from an elastic response (G' remains constant) to a flow response (G' decreases) with increasing strain amplitude. The elastic modulus G' is a measure of elastically stored energy through particle-particle interaction while viscous modulus G'' quantifies dissipated energy through particle-medium or medium-medium interactions. The viscous modulus G'' is attributed to bulk flow. Fig. 4 shows the linear viscoelastic regime below the critical strain, γ_c, where the elastic modulus G' starts to drop sharply. The effect of strain amplitude on the elastic modulus G' of the as-received Si_3N_4 suspensions and that of the modified Si_3N_4 suspensions at various solid volume fraction are given in Figs 5 and 6, respectively. As can be seen, the critical strain γ_c decreases continuously with the solid volume fraction. A similar behavior was found in a previous study on sterically stabilized suspensions of high concentration [20]. For certain solid volume fraction, the linear viscoelastic region of the

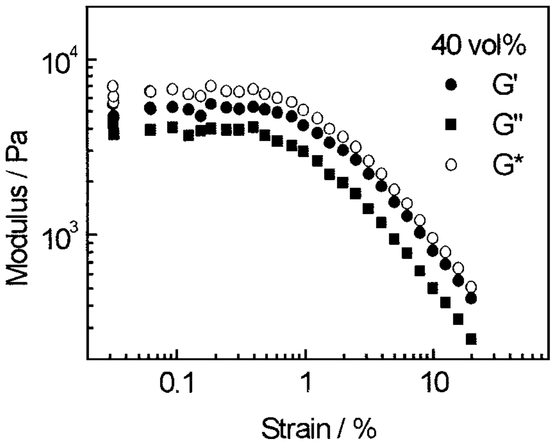

Figure 4 Storage G', loss G'' and complex G^* as a function of the strain amplitude for 40vol.% Si_3N_4 slurries in the dynamic tests.

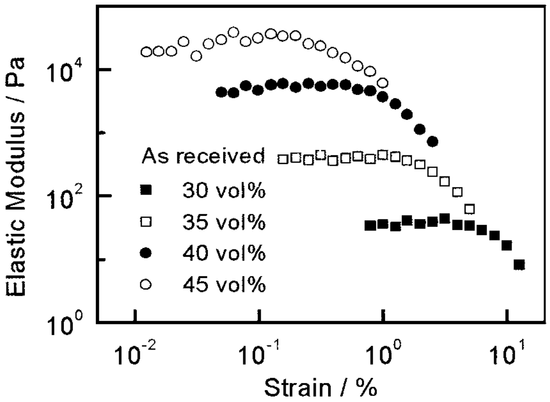

Figure 5 Storage G' as a function of the strain amplitude for as-received Si_3N_4 suspensions with various solid loading in the dynamic tests.

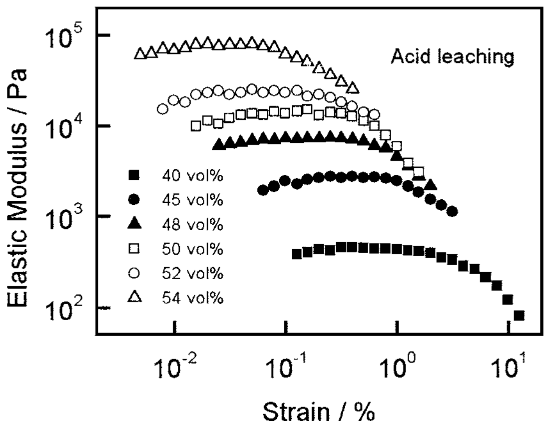

Figure 6 Storage G' as a function of the strain amplitude for modified Si_3N_4 suspensions with various solid loading in the dynamic tests.

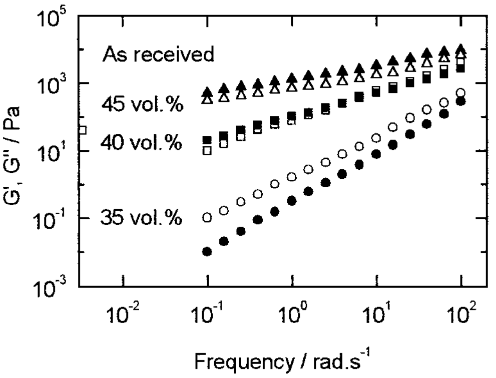

Figure 7 Storage G' and loss G'' (filled and unfilled symbols, respectively) as a function of the frequency for as-received Si_3N_4 suspensions ($\gamma\% = 0.001$).

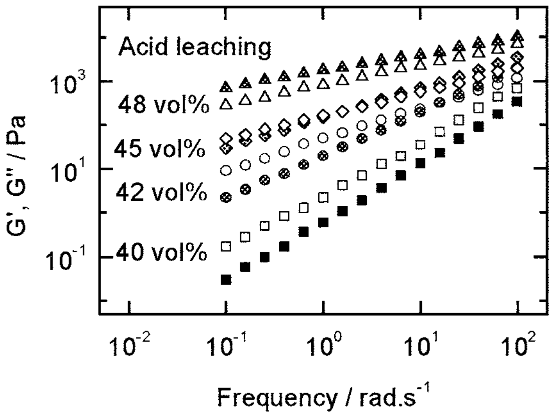

Figure 8 Storage G' and loss G'' (filled and unfilled symbols, respectively) as a function of the frequency for modified Si_3N_4 suspensions ($\gamma\% = 0.001$).

modified suspensions extends and the corresponding G' decreases sharply in comparison with that of the as-received suspensions. All the following frequency sweep measurements are performed at low strain amplitudes, $\gamma < \gamma_c$, where the viscoelastic response is linear.

Fig. 7 shows the effect of solid volume fraction of the as-received suspensions on the frequency dependence of the elastic modulus G' and the viscous modulus G''. In the frequency range examined, both moduli increase with frequency and the magnitude of the viscoelastic response increases with solid volume fraction. The viscoelastic response of the suspensions progressively changes from more viscous to more elastic. Similar behavior has been observed in previous studies [20–22]. For the lowest concentration, $\phi = 0.35$, the suspension is essentially viscous in nature ($G' < G''$) over the entire frequency examined. With increasing concentration to $\phi = 0.40$, the curve exhibits a characteristic frequency, ω_c, where $G' = G''$. With increasing concentration, the crossover shifts to lower frequencies. For the highest concentration, $\phi = 0.45$, the elastic modulus G' exceeds the viscous one G'' over the entire frequency range ($G' > G''$). The frequency sweep of the modified suspensions exhibits a very similar behavior to that of the as-received ones, as illustrated in Fig. 8. Comparison to that of the as-received suspensions, the modified suspensions transmit from viscous to elastic at higher concentration and the characteristic frequency ω_c shifts to higher frequency for certain solid concentration,.

On the other hand, the inverse of the characteristic frequency ($1/\omega_c$) provides a measure of the structural relaxation time of the suspension, t_r [22]. Since a simple mechanical model like the Maxwell model cannot depict the viscoelastic response of concentrated suspensions exactly, the viscoelastic measurements only yield an average t_r. It is well known that the structural relaxation time t_r increases with solid concentration of suspensions. At lower frequency, the characteristic experimental time (t_o) of the suspension longer than its t_r ($t_o > t_r$), thereby the perturbed structure formed during dynamic oscillatory measurement relaxes well. Thus, the suspension dissipates the most of energy and exhibits smaller elastic modulus. With increasing oscillatory frequency, the characteristic experimental time t_o shortens than its t_r ($t_o < t_r$), the perturbed structure cannot be relaxed perfectly. The energy is stored in the suspension so it exhibits more elastic.

4. Conclusions

The surface modification of Si_3N_4 particles by acid leaching and its effect on the colloidal behavior and the rheological properties of Si_3N_4 aqueous suspensions are investigated in detail. The IEP of the modified Si_3N_4 particle shifts to basic region due to the decreasing of the oxidizing degree on the surface of Si_3N_4 particle. Attempts have been made to apply rheological models to the suspensions. The Sisco model ($\eta = \eta_\infty + k \cdot \gamma^{n-1}$) provides the best fit in the range of $\phi \leq 0.30$ while the Casson model ($\tau^{1/2} = \tau_y^{1/2} + (\eta_c \cdot \gamma)^{1/2}$) in $0.35 \leq \phi \leq 0.45$ within a shear rate range of 0.001–800 s^{-1} for the as-received suspensions. The steady shear behavior of modified suspensions fit to Sisco model in the range of $\phi \leq 0.40$ and Casson model in $0.45 \leq \phi \leq 0.54$ perfectly. Comparing to that of as-received suspensions, the rheological behavior of modified suspensions is improved efficiently. The dynamic oscillatory experimental indicates that the critical strain decreases, the linear viscoelastic regime narrows and the corresponding elastic storage modulus G' increases continuously with increasing solid concentration. For the modified suspensions, the linear viscoelastic regime broadens and the corresponding G' decreases sharply. With increasing solid concentration, the magnitude of the viscoelastic response increases, the characteristic frequency ω_c shifts toward lower frequencies and the suspension transforms from more viscous into more elastic. The transformation takes place at higher solid concentrations for modified suspensions. Moreover, the frequency dependence of the viscoelastic properties of suspensions can be interpreted by the concept of the structural relaxation time.

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