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Effect of ammonium polyacrylate on rheology of anatase TiO_2 nanoparticles dispersed in silicon alkoxide sols

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Abstract

Ammonium polyacrylate (NH_4PA) was introduced into powdered mixtures consisting of anatase-structured TiO_2 nanoparticles and silicon alkoxide precursors at the sol level, and the rheological behavior of the mixtures was examined under various solid loadings ($\phi = 0.05$–0.13 in volumetric ratios), shear rates ($\dot{\gamma} = 1$–$1000\,s^{-1}$) and NH_4PA concentrations. The alkoxide precursors were mixtures of tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$), ethyl alcohol (C_2H_5OH), H_2O and HCl in a constant $[H_2O]/[TEOS]$ ratio of 11. The nanoparticle–sol mixtures generally exhibited a pseudoplastic flow behavior over the shear-rate regime examined. The NH_4PA appeared to serve as an effective surfactant which facilitates the suspension flow by reducing the flow resistance at low NH_4PA concentrations. At $\phi = 0.10$, a viscosity reduction ca. 85% was found at $\dot{\gamma} = 10\,s^{-1}$ when the NH_4PA concentration was held at 2.5 wt.% of the solids. As the NH_4PA exceeded a critical level, e.g., $[NH_4PA] \geq 3.0$ wt.%, the NH_4PA acted as a catalyst which quickly turned the TiO_2–silica sol mixtures ($\phi = 0.10$) into a gelled structure, resulted in a pronounced increase of mixture viscosity. The maximum solids concentration (ϕ_m) of the mixtures was experimentally determined from a derivative of relative viscosity, i.e., $(1-\eta_r^{-1/2})$–ϕ dependence. The estimated ϕ_m increased from 0.127 to 0.165 when NH_4PA of 0.5 wt.% was introduced into the TiO_2–silica sol mixtures.

Keywords: D. TiO_2; Sol–gel; Surfactant; Rheology; Aggregation

1. Introduction

TiO_2–SiO_2 composites in thin film or colloidal form are materials of great technological interests. The interests mainly stem from the generation of highly potent oxidants (i.e., holes) at the semiconductor surface when the wide-bandgap semiconducting material (i.e., TiO_2) is illuminated by light. The oxidant generation allows for the use of the composite materials in photocatalytic detoxification process of aquatic environments. An enhanced photocatalytic performance of particulate TiO_2–SiO_2 mixtures has been reported [1–4], which surpassed the photodecomposition efficacy of pure, anatase TiO_2 phase. The existence of SiO_2 is thought to change the surface acidity of the composites [2], producing effective adsorption sites of significantly larger population than that of the pure TiO_2. These sites are desirable at locations near the photocatalytic TiO_2 phase in order to facilitate a rapid scavenging of holes generated from the oxidants (e.g., hydroxyl radicals). Recombination of the photogenerated electron (e^-) and hole (h^+) is then suppressed, leading to an increased quantum yield.

Various methods have been used to fabricate the TiO_2–SiO_2 composites. These include sol–gel solution technique, impregnation, homogeneous precipitation, flame pyrolysis and ion-beam implantation [5,6]. With the sol–gel technique, in particular, the chemical composition can be well controlled in molecular-level mixing, and a composite structure with a high specific surface area together with a well-defined pore-size distribution ranging in mesoporous region is attainable. In addition, the isolated Ti–O–Si centers are resistant to leaching so that this type of catalyst can be used as a highly active and selective catalyst for partial oxidation of liquid-phase hydrocarbons under very mild operating conditions [6]. When TiO_2 and SiO_2 powders were used as the starting material for the composite mixtures, Richmond et al. [7] pointed out that the TiO_2 particles adsorb preferentially on the SiO_2 particle surfaces, forming SiO_2 aggregates with the TiO_2 particles coated on the surface. This changed the

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surface characteristics of the particles, as well as the structure of the composite mixtures and the mixture rheology. In this regard, we present here a method to fabricate uniform TiO_2–SiO_2 composites through mixing of anatase-structured TiO_2 nanoparticles with silicon alkoxide precursors to form "flowable" powdered dispersions. A uniform dispersion of TiO_2 nanoparticles in the silica sol with a high Ti/Si ratio is aimed so that the powdered dispersion may later be "consolidated" into a gelled structure with desirable function and hierarchy via typical wet-processing routes. A surfactant of ammonium polyacrylate (NH_4PA) is introduced into the nanoparticle mixtures, and the effect of the NH_4PA to the dispersion quality of the mixtures is examined via rheological characterizations.

2. Experimental procedure

TiO_2 nanoparticles (P25, Degussa Ltd., Germany) with an average particle size about 21 nm and a specific surface area $50 \pm 15\,m^2/g$ (vendor specification) were used as the starting material. The powder is about rectangle in shape and is apparently agglomerated (Fig. 1) from the scanning electron microscopy (SEM, JSM6700F, JEOL, Japan). Reagent-grade tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$), ethyl alcohol (C_2H_5OH), H_2O and HCl (all from Aldrich Chemicals) in a constant $[H_2O]/[TEOS]$ ratio of 11 were used as the precursor sol and were mixed with the nanoparticles in various volumetric solids concentrations ($\phi = 0.05$–0.13). The polyelectrolyte surfactant used was a commercially available ammonium polyacrylate (NH_4PA, A-6114, Toagosei Chemical, Japan) and the surfactant concentration was up to 3 wt.% of the solids. The NH_4PA typically presents a linear backbone consisting of carbon–carbon bonds, with a $COONH_4$ side group attached to the carbon atom [8].

The powdered mixtures were ball-mixed in polyethylene bottles using high-purity alumina balls as the mixing media for 24 h. Their viscosity (η_s) was determined by a strain-controlled concentric viscometer (VT550, Gebruder HAAKE GmbH, Germany) equipped with a sensor system (MV-DIN 53019, HAAKE, Germany) of a cone-cup geometry operated at a constant temperature (25 °C). The measurement was performed with a steady increment of shear rate ($\dot{\gamma}$); to which, the rate was increased in every $1\,s^{-1}$ over the shear-rate range of 1–10 s^{-1}, every $10\,s^{-1}$ over 10–100 s^{-1} and every $100\,s^{-1}$ over 100–1000 s^{-1}. The rheological properties were all measured after 20 s of duration when shear rate reached each pre-determined rate level over the entire shear-rate range investigated.

3. Results and discussion

The TiO_2 nanoparticle–silica sol mixtures generally exhibited a shear-thinning flow behavior over the shear-rate

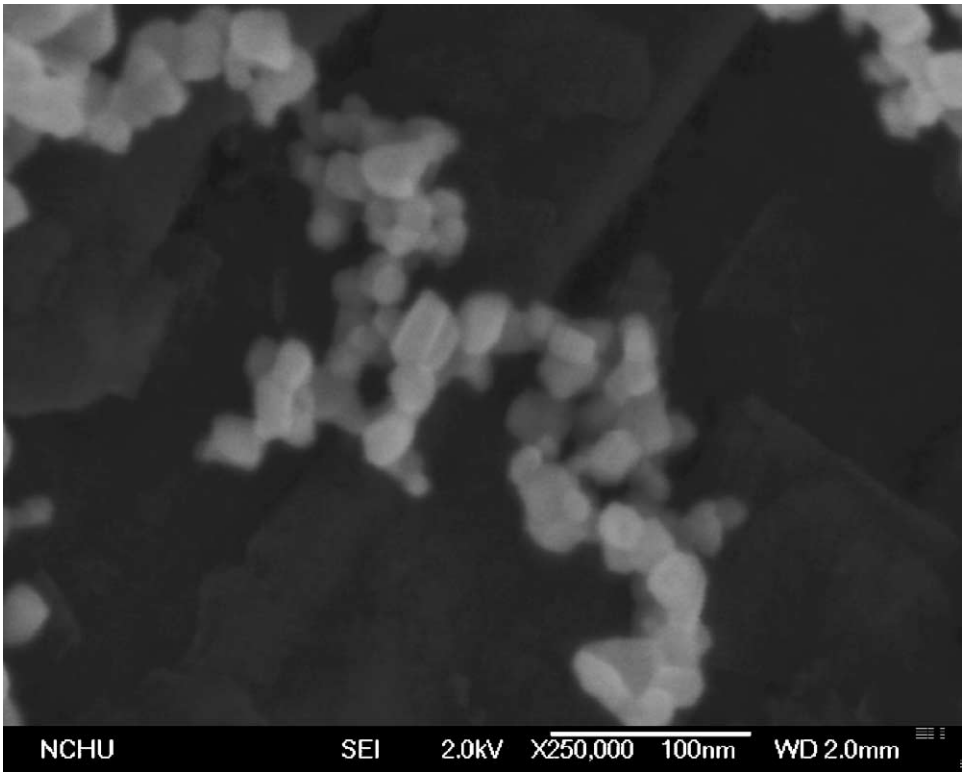
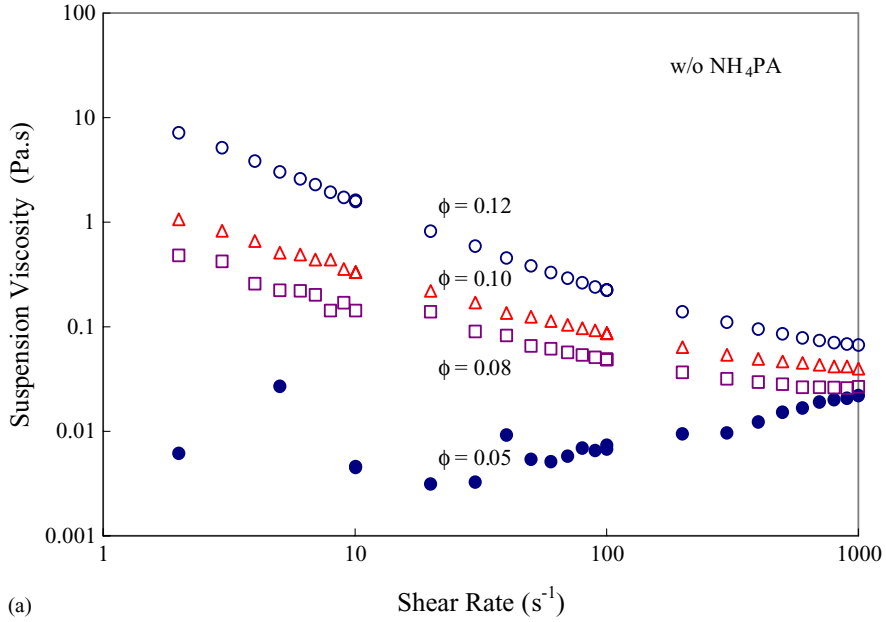
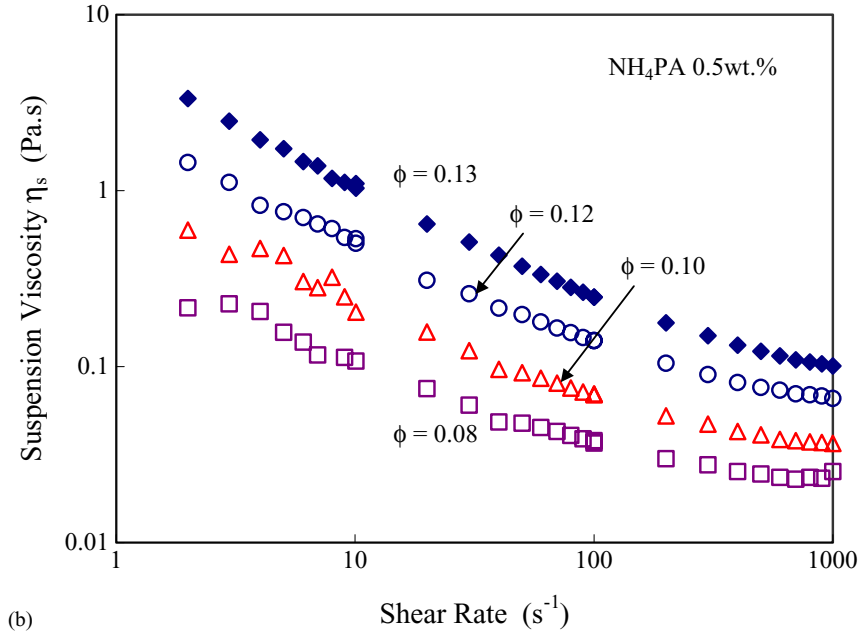


Fig. 1. Particle morphology of the TiO_2 nanoparticles used in the study.



(a)



(b)

Fig. 2. The η_s–$\dot{\gamma}$ dependence for the particulate sol mixtures of various solids concentrations. (a) Without the NH_4PA; (b) with 0.5 wt.% NH_4PA.

range examined (Fig. 2). This indicates that the powder agglomerates existing in the sol liquid were broken up into smaller flow units by the increased shear force, hence resulted in the reduction of suspension viscosity (η_s) as shear rate increased. In Fig. 2, the addition of NH_4PA appeared not to alter the shear-thinning flow character of the suspensions; nonetheless, η_s apparently reduced upon the NH_4PA addition when comparing the viscosity of the suspensions at identical solids loadings. In addition, the introduction of anatase TiO_2 nanoparticles to the silica sols appeared not to catalyze the sols transforming into a gelled network structure. This was most apparent when the suspensions were highly concentrated. Taking the NH_4PA-doped suspensions with $\phi = 0.13$ as an example (Fig. 2b), the suspensions initially showed a solid-like characteristic when the nanoparticles were first introduced into the sol–NH_4PA liquid mixtures. The nanoparticle suspensions then became apparently "flowable", i.e., resembled the flow of a concentrated paste, when subjected to the ball-mixing process. The lack of catalyzing effect further reveals that the dominant factor determining the suspension rheology was most likely the interparticle attractions involved in the powdered mixtures. This is considered valid when a low level of NH_4PA doping ($\leq$0.5 wt.%) existed in the nanoparticle-sol suspensions.

It may be interesting to note that the suspensions appeared to change toward a Bingham-plastic (or even a shear thickening) flow from the shear-thinning flow behavior as shear rate further increased toward the higher end. This suggests that the particle-packing configuration in the sol liquid tended to become more uniform in the packing efficiency as shear rate increased. As the particulate structure becomes more uniform, the suspension flow would become less sensitive to the applied shear rate, hence approaching toward a Bingham-like flow. Additionally, the shear thickening flow was likely due to a perturbation occurring in the uniformly packed suspension structure as shear rate exceeded a critical level [9]. A more voluminous flow was resulted, leading to an increase in the flow resistance and accordingly a viscosity increase. Noted that the viscosity scattering found at the low shear rates for the less concentrated $\phi = 0.05$ suspension (Fig. 2a) was mainly because of the viscosity measured fell in a range of the lower bound of the detecting sensor employed, and was considered only good for reference purposes.

The nanoparticle suspensions began to flow as the applied stress exceeded a certain critical level, i.e., the yield stress (τ_y) of the suspensions. Various empirical models were used to estimate τ_y [10]:

Bingham plastic model:

$$\tau = \tau_{y,b} + \eta_s \dot{\gamma} \quad (1)$$

Casson model:

$$\tau^{1/2} = \tau_{y,c}^{1/2} + (\eta_s \dot{\gamma})^{1/2} \quad (2)$$

Herschel-Bulkley model:

$$\tau = \tau_{y,h} + K\dot{\gamma}^n \quad (3)$$

where $\tau_{y,b}$, $\tau_{y,c}$ and $\tau_{y,h}$ are yield stress parameters determined from Bingham, Casson and Herschel-Bulkley models, respectively; K and n are structure-dependent parameters that can be determined experimentally. As shown in Table 1, τ_y increases with ϕ, regardless of the models used. This increase becomes much pronounced as ϕ increased above 0.10, indicating that the suspension τ_y is critically dependent on ϕ. The NH_4PA addition appears to result in a τ_y reduction.

Table 1
The yield stress of the nanoparticle–sol mixtures determined from various models

Solids concentration (ϕ)	Suspension yield stress τ_y (Pa)		
	Bingham model	Casson model	Herschel-Bulkley model
0.05	0 (N.A.)	0.01 (N.A.)	0 (N.A.)
0.08	1.7 (1.0)	0.7 (0.3)	1.6 (1.0)
0.10	3.6 (2.4)	1.8 (1.1)	3.1 (2.1)
0.12	15.9 (5.4)	12.1 (2.5)	15.4 (4.6)
0.13	N.A. (11.4)	N.A. (6.1)	N.A. (9.9)

The numbers in parentheses are yield stresses of mixtures with 0.5 wt.% NH_4PA. N.A.: not applicable.

Since τ_y is considered the stress required for the nanoparticles to break up the interparticle bonds in order for the particles to roll over the neighboring ones in given carrier liquid under shear forces, a decreased τ_y value is thus an indication of a more relaxed particulate structure in the flocculated suspensions. Noted that the Bingham plastic model appears to present the highest yield stress among all the above models examined (Table 1), presumably due to the assumed linear τ–ϕ dependence in the equation used as $\tau > \tau_y$.

Relative viscosity of the suspensions (η_r) can be defined as the suspension viscosity (η_s) divided by the viscosity of the suspending liquid (η_o). As shown in Fig. 3, η_r of the nanoparticle–sol mixtures exhibited a non-linear dependence with ϕ, and (again) the non-linearity appeared to become more pronounced as $\phi >\sim 0.1$. A model proposed recently by Liu [11] was used in the study to predict the theoretical, maximum solids fraction (ϕ_m) allowable for the powdered suspensions. The equation has a general form:

$$\eta_r = [a(\phi_m - \phi)]^{-m} \quad (4)$$

where a is a constant, and m is a flow-dependent parameter. The term ($\phi_m - \phi$) is physically reasoned as the effective space allowable for the particles to move freely in given carrier medium for the flow to occur. When ϕ approaches ϕ_m, η_r approaches infinity. The suspension hence ceases to flow and behaves solid-like. ϕ_m can be determined from a $(1 - \eta_r^{-1/m})$–ϕ relationship, which often follows a linear relationship over a broad range of particle fractions [12,13]. Fig. 4 shows the experimentally determined $(1 - \eta_r^{-1/m})$–ϕ dependence by assuming the flow index (m) equals to 2. The flow index generally falls in a range of $m = 2$–3 [11–13]. By extrapolating the $1 - \eta_r^{-1/2}$ to unity, ϕ_m is determined as $\phi_m = 0.127$–0.162 at $\dot{\gamma}$ of 100 s^{-1}. The ϕ_m determined is critically dependent on the NH_4PA concentration, and the incorporation of NH_4PA in the sol liquid appears to result in an increase of ϕ_m.

η_s of the nanoparticle–sol mixtures alters upon a further increase of NH_4PA concentration above 0.5 wt.% (Fig. 5). A pronounced viscosity decrease occurred when the NH_4PA concentration exceeded 1.0 wt.% and reached a minimum (∼85% viscosity reduction at $\dot{\gamma}$ of 10 s^{-1}) as the concentration was of 2.5 wt.%. Noted that the viscosity reduction was still a "respectable" 62% when the shear rate was increased to 100 s^{-1}, even though the viscosity change in absolute values appeared less pronounced than that of the $\dot{\gamma} =$ 10 s^{-1} case. The suspension viscosity yet rapidly increased to about the same level as that of the suspensions without the NH_4PA doping as the NH_4PA concentration approached 3 wt.%. Further increase of the NH_4PA concentration to the nanoparticle–sol mixtures only resulted in an immediate formation of a solid-like "bulk", which virtually showed no evidence of fluid-like deformation upon an excessive shearing. Exact mechanisms about the sol-to-gel transition are not clear at present; nonetheless, two types of gelation schemes are generally considered responsible for the sol–gel derived

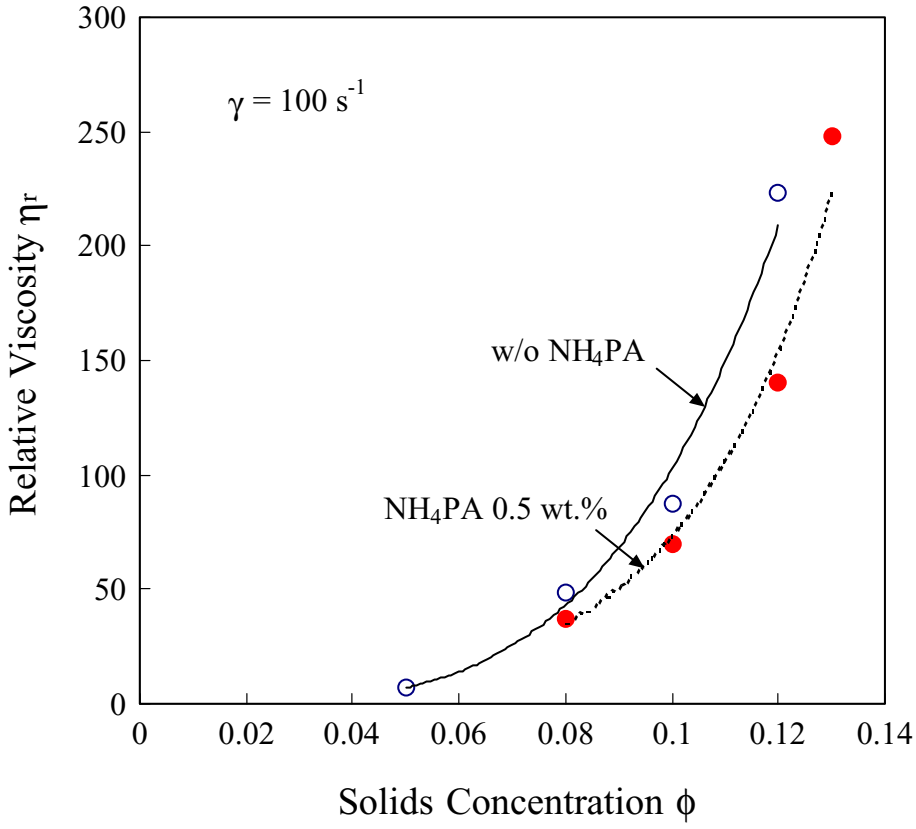


Fig. 3. The η_r–ϕ dependence of the particulate sol mixtures at $\dot{\gamma}$ of $10\,s^{-1}$.

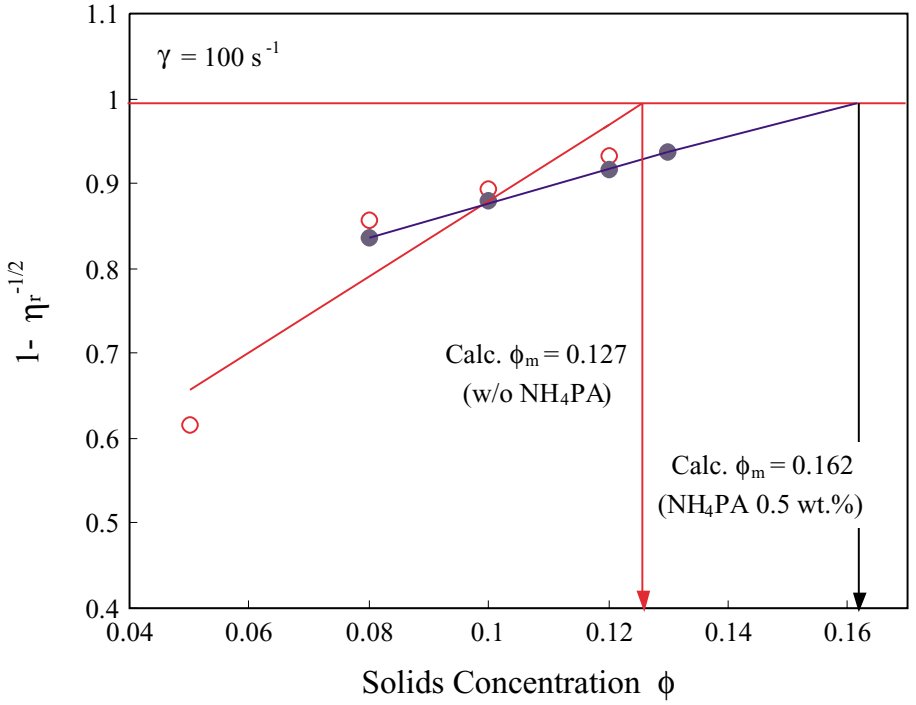


Fig. 4. The $(1-\eta_r^{-1/2})$–ϕ dependence for the determination of the maximum solids concentration (ϕ_m).

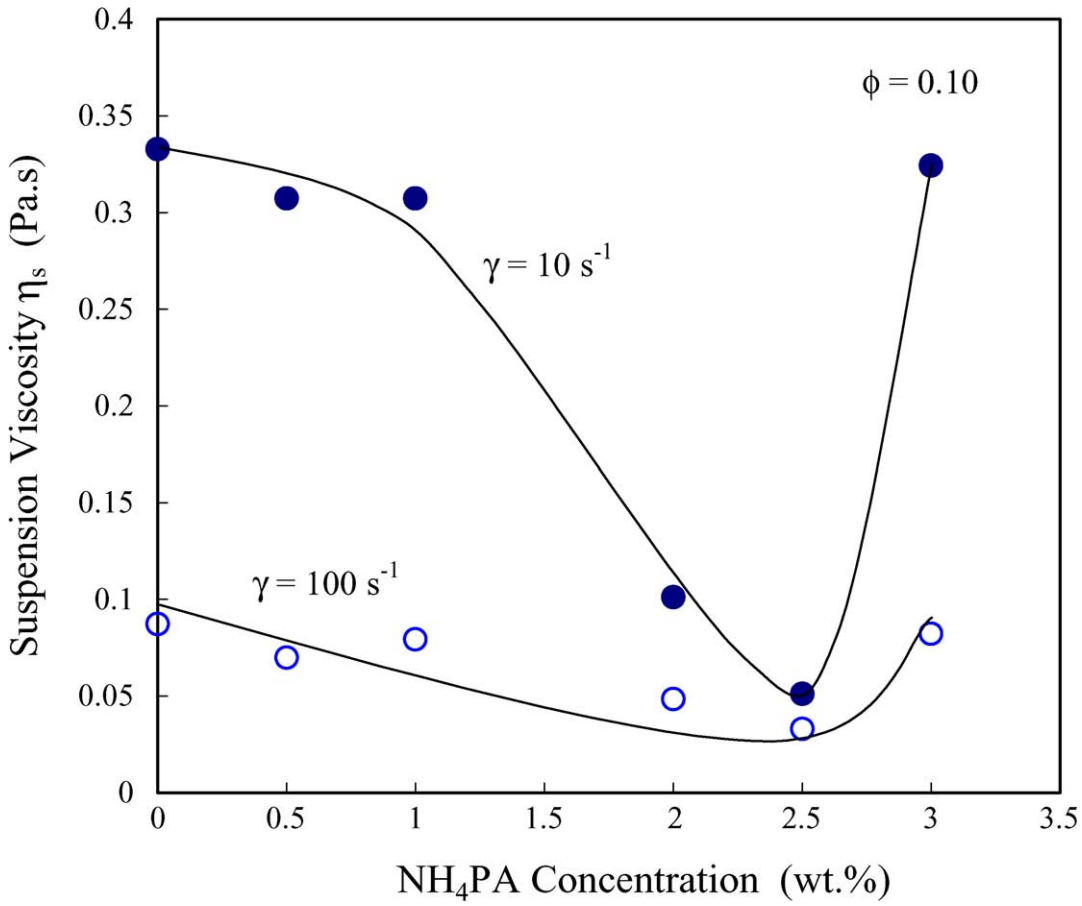


Fig. 5. The η_s of the particulate sols varies with the NH_4PA concentration at shear rates of 10 and 100 s^{-1}.

glasses [14]: (1) hydrolysis and polymerization of silicon alkoxides to form a covalent-bonded crosslinked gel; (2) aggregation of particulate sols existing in an aqueous medium to form a porous aggregate structure composed of an interconnected three-dimensional network of hydrogen-bonded crosslinks. A separate experiment by mixing the sol liquid solely with the NH_4PA revealed that the sol quickly changed to gel as the NH_4PA concentration >3.0 wt.%. This finding reveals that the NH_4PA served as an effective surfactant to the TiO_2 nanoparticle–silica sol mixtures only when the concentration was held below a certain extent (i.e., ≤2.5 wt.% in our model mixtures). Further increase of the NH_4PA above the critical level facilitated catalysis of the sol liquids by possibly the hydrolysis and polymerization of the silicon sols into a gelled crosslink structure, so the nanoparticle–sol mixtures turned into a solid-like bulk character.

4. Conclusions

The rheological behavior of anatase-structured TiO_2 nanoparticle–silicon sol mixtures was examined when ammonium polyacrylate (NH_4PA) of various concentrations was introduced into the particulate sols. The NH_4PA appeared to facilitate the suspension flow by reducing the TiO_2 agglomerates into smaller floc units, so that the flow resistance was reduced. A theoretical maximum solids concentration was accordingly resulted (ϕ_m increased from 0.127 to 0.162) when NH_4PA of 0.5 wt.% was added into the particulate sol mixtures. The viscosity reduction was most pronounced when the NH_4PA concentration was held under 2.5 wt.% of the solids at $\phi = 0.1$. A rapid sol–gel transition was found when the NH_4PA concentration exceeded the critical level (≥3.0 wt.%), and the transition was most likely due to the hydrolysis and polymerization of the silicon sols.

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