

Yielding behaviour of organically treated anatase TiO₂ suspension

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Abstract

The rheological behaviour of anatase TiO₂ with organic coating has been investigated extensively in this study. The yield stress was measured over a wide range of solids concentration and pH using stress-controlled and speed-controlled rheometers. The organic treatment leads to a shift of the isoelectric point (IEP) from around pH 5.5 to pH 2.4. A maximum yield stress occurs in the vicinity of the isoelectric point determined by electrokinetic measurements. The transition of rheological behaviour between elastic solid and viscous liquid is represented by a stress plateau in a plot of stress against strain. It is hypothesised that the slope of the stress plateau reflects the uniformity of the structure, and hence the distribution of bond strength. Altering the concentration and the surface chemistry can vary the bond strength and its distribution, therefore, resulting in different types of failure: "ductile-type" or "brittle-type". pH and volume fraction dependence of yield stress could be described quantitatively using existing models with reasonable agreement.

Keywords : titanium dioxide, yield stress, suspension, pH

1. Introduction

Titanium dioxide pigment is an important material for many industrial applications, such as paper coating; printing textiles; paints; rubber latex and cosmetics. The rheological properties of TiO₂ suspensions play a significant role in the production of pigment and the applications. TiO₂ pigments are commercially produced in two different crystalline forms: anatase and rutile. To improve the dispersability in different media, many pigments are subjected to surface modification during production. Commonly, the TiO₂ particles are coated with other inorganic and/or organic materials. The presence of impurities complicates the surface chemistry of the particles, which in turn will profoundly influence the state of flocculation when a suspension is formulated and consequently, the rheological behaviour of the suspensions. A full understanding of the rheology of these suspensions is essential for optimising production and ultimate use.

Many studies have been carried out on the rheological properties of various TiO₂ suspensions (Liddell, 1996; Liddell *et al.*, 1996; Mikulasek *et al.*, 1997; Kosmulski *et al.*, 1999; Gustafsson *et al.*, 2001; Yang *et al.*, 2001). Liddell (1996) extensively investigated the rheology of rutile suspensions over a range of variables including pH, ionic

strength, solids concentration and particle size. Most recently, Gustafsson *et al.* (2001) studied the shear-induced aggregation of anatase dispersions. The pigment used contained phosphate impurities, which leads to a isoelectric point at very low pH value. The rheological properties of uncoated anatase dispersions have been studied over a wide range of solids concentration, pH and temperature by Yang *et al.* (2001). The flow curve was described by the Quemada or Casson model, and yield stress was correlated with the volume fraction of the suspensions by Zhou's model (Zhou *et al.*, 1995). Heijma and Stein (1993) and Strauss *et al.* (1993) reported that surface modification of TiO₂ pigment by adsorbing surface-active polyacrylic acid caused a dramatic change of dispersity and flow behaviour through electrostatic and steric forces.

The most important parameters used for describing the rheological properties of a suspension are its viscosity and yield stress. In many situations, particularly for highly concentrated suspensions, the yield stress turns out to be the most appropriate parameter for rheological characterization. Although the inadequacy of the rheological definition of this property has recently generated worldwide debate on the existence of yield stress (Barnes and Walters, 1985; Hartnett *et al.*, 1989; Barnes, 1999a; 1999b; Schurz, 1990; Evans, 1992; Spaans *et al.*, 1995), the concept remains as an important parameter in rheological fluid investigations and applications. This fact has been recognised for many years (Houwink and Decker, 1971). Yield

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stress is generally regarded as the transition stress between elastic solid-like behaviour and viscous liquid-like behaviour, and is related to particulate network structure. However, such transition can occur in a domain starting at a lower limit, corresponding to the elastic to plastic deformation, ending at a higher limit, corresponding to the transition of plastic deformation to viscous flow (Houwink, 1971; Kraynik, 1990; Uhlherr *et al.*, 2001). An understanding of this transition domain is rather lacking because few researches have focused on the structural interpretation of relevant rheological behaviour in this important domain.

This paper aims to investigate the shear-induced yielding behaviour of organically treated anatase suspensions. The effects of surface chemistry of particles and volume fraction on the transition of rheological behaviour from solid-like to liquid-like are of particular interest. The applicability of existing models relating yield stress to pH and volume fraction will be evaluated.

2. Experimental

A commercial TiO₂ pigment (A-HR) produced by Tioxide was used in this study. It is an anatase pigment with 98.7% purity and has an average crystal size of 0.15 µm. The material was treated with organics, but is free of inorganic impurities.

The particle size distribution of the pigment was measured using a Malvern MasterSizer/E. To break up loosely agglomerated particles, the sample was subjected to intensive stirring and an ultrasonic treatment for 5 minutes immediately before measurement. The volume average particle size is found to be 0.5 µm. This is significantly larger than the crystal size reported by the manufacturer. It indicates qualitatively the existence of aggregates.

Zeta potential of the pigment was measured as a function of pH using a Malvern Zetasizer 4. In the experiment, a very dilute dispersion was prepared and treated in an ultrasonic bath to break up aggregates. The pH value was adjusted by adding 0.1 M HNO₃ and measured by a microprocessor-based pH meter (HI9321, Hanna Instruments). The isoelectric point (IEP) was found at around pH 2.4. At natural pH, the pigment is well dispersed in water without significant flocculation, and no yield stress is detected for the suspension.

To prepare a stock suspension, the HNO₃ was added into deionised water to create a suspending medium with low pH and then TiO₂ pigment was dispersed in the acidic water. The pH of the suspension was further adjusted by adding more 2 M HNO₃. The suspension was then gently agitated for at least 24 hr to ensure an equilibrium state. The stock suspension has a concentration of 50 wt% and a pH value of 4.8. Suspensions with different pH values and concentrations were obtained by adding either HNO₃ or

water to the stock suspension. In some cases, a higher concentration was achieved by adding more TiO₂ pigment and reequilibrating. The solids concentration of the suspensions was measured by drying the sample in an oven at a temperature of about 110°C for at least 3 hours. The volume fraction for maximum packing was obtained by centrifuging the suspension at 3000 rpm for 10 minutes.

A stress-controlled rheometer (DSR, Rheometric Scientific Inc.) equipped with a vane with four blades was used to study the shear-induced solid-liquid transition behaviour of the suspensions. The surface of the vane was roughened to prevent possible slip, and the dimension of the vane is 25 mm in diameter and 25 mm in height. The yielding process was studied using a stress ramp technique. Creep tests were also conducted using the same system. For all measurements, the sample was placed in a container whose diameter and height were at least three times larger than those of the vane. To achieve a similar initial structure, the TiO₂ suspensions were always stirred for 5 minutes using a spatula prior to measurement. After inserting the vane, the samples were rested for one hour to minimise disturbances of the structure. A speed-controlled rheometer (Haake, RV20) was also used to determine the yield stress by the vane torsion method (Nguyen and Boger, 1985). With this measurement, each sample was tested with two vanes with different sizes at different rotational speeds, and a simple average value of the results was used.

3. Results and discussion

3.1. Characterization of surface chemistry properties

As a colloidal suspension, the rheological properties of TiO₂ suspension are directly associated with the surface chemistry condition of the particles. The TiO₂ pigment used in this study was organically treated. However, there is no detailed information on what organic species was added in the manufacturing stage. Thus, the surface chemistry condition of the pigment used is unclear. However, the zeta potential of the pigment can provide a qualitative measure of the magnitude and sign of the surface charge on the colloidal particles in suspension. The IEP of pH 2.4 determined by microelectrophoresis measurement is significantly different from the IEP of pH 5.5 for un-coated anatase TiO₂ particles (Yang *et al.*, 2001) (see Figure 1). This indicates that particles are highly negatively charged and have dense anionic ions on the surface. Thus, the interaction between particles should be governed by electrostatic forces. The total inter-particle potential energy between particles is expected to be the sum of van der Waals attraction and electrical double layer repulsion according to DLVO theory of colloid stability (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). Increasing the strength of H⁺ (decreasing the pH value of sus-

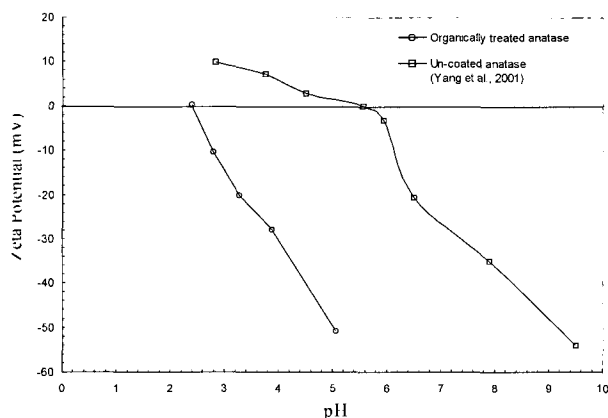


Fig. 1. pH dependence of zeta potential for different anatase pigments.

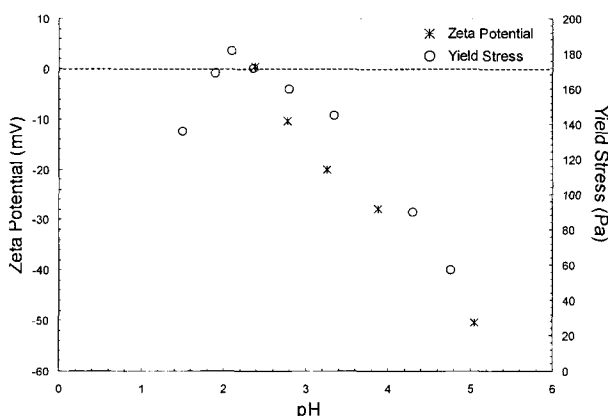


Fig. 2. A comparison of zeta potential and yield stress varying with pH.

pension) compresses the electrical double layer, thus reducing the repulsive forces and resulting in flocculation of the particles. At the isoelectric point, the repulsive forces disappear and the van der Waals attractive forces dominate the particle interaction, hence, the suspension is expected to be in a strongly flocculated state and has a maximum yield stress. Conversely, at the pH values where zeta potential is very large, the suspension is expected to be well dispersed, exhibiting negligible yield stress. The variations of zeta potential and yield stress of TiO₂ suspensions with decreasing pH are shown in Figure 2. The pH value where a maximum yield stress occurred is quite close to the isoelectric point determined by electrokinetic measurements. This confirms that pH corresponding to the maximum yield stress represents the condition of net zero surface charge on the TiO₂ particles, and hence only van der Waals attractive forces are present in the suspension. At pH values away from the isoelectric point, the yield stress decreases rapidly as the electrostatic forces become more important. The results of yield stress were obtained using the vane torsion technique with 50 wt% TiO₂ suspensions.

3.2. Shear-induced solid-liquid transition

Yield stress is generally regarded as the transition stress between elastic solid-like behaviour and viscous liquid-like behaviour. It was found that at small deformation up to a limit, there is a linear zone (a line of slope 1.0 on log-log coordinates) of stress versus strain and one “yield stress” - the transition point from linear to non-linear zones - can be determined at such limit (De Kee and Chhabra, 1994). Many researchers stated that transition begins at a lower limit, corresponding to the elastic to plastic deformation, and ends at a higher limit, corresponding to the transition of plastic deformation to viscous flow (Houwink and Decker, 1971; Kraynik, 1990; Uhlherr *et al.*, 2001). Thus, some researchers believe that there exist two types of yield stress, i.e. a “static” and a “dynamic” yield stress (Cheng, 1986; Toorman, 1997).

The shear-induced solid-liquid transition of TiO₂ suspensions has been studied by the stress ramp technique. During the tests, the stress increased at a constant rate, and the angular deflection was measured. The apparent shear strain was then obtained in terms of the geometry of the vane immersed in an infinite medium. Figure 3 shows a typical plot of shear stress against apparent strain and against strain rate for 50 wt% TiO₂ suspension with a pH value of 2.4 at different ramp rates. The curves of stain-stress show that, at lower stress values, the strain is a unique function of stress and independent of the ramp rate. This is conventional solid-like behavior. At larger stress values, the strain is not a unique function of stress, but depends on the ramp rate. This is consistent with the unbounded deformation of a viscous fluid under shear. A stress plateau separates the two regions. Also, it can be seen from the curve of strain rate-stress that, at large stress values, all results collapse onto a single curve, indicating that the shear stress is a unique function of strain rate. This is conventionally accepted as fluid behavior. For small values, the shear stress is a function of both strain rate and ramp rate. Again, there is a stress plateau between the two

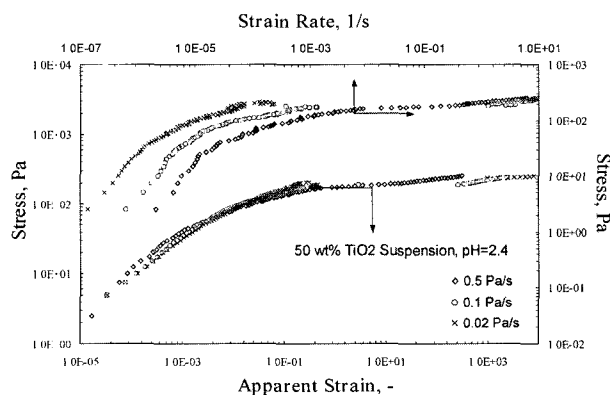


Fig. 3. Stress-strain and stress-strain rate behaviour for 50 wt% TiO₂ suspension.

regions. Clearly, the stress plateau represents the transition from elastic solid-like behavior to viscous liquid-like behavior, and is associated with the yielding process of viscoplastic materials. In terms of network bonds within the materials, the initial stage represents the elastic deformation of the network bonds. When the network bonds are stretched further, some weaker bonds start to break and local viscous flow occurs. When the stress increases to a certain level, the majority of the bonds break down rapidly over a narrow range of stress, and then the material begins to flow as a fully viscous liquid. The stress plateau reflects the breaking process of the majority of bonds and thus, the slope of the stress plateau actually represents the uniformity of bonding strength. A large slope implies that the breaking process occurs over a wide range of stress; hence, the structure of the material exhibits “ductile-type” failure. Conversely, a small slope reflects a narrow range of bond strength and hence, a more sudden failure. This could be visualized as more akin to “brittle” failure of the material structure. The structure of the material determines the type of yielding process, and ultimately the slope of the stress plateau in the strain-stress curve.

Studies have also been conducted on the creep behaviour of TiO₂ suspensions. In the creep tests, a constant stress was applied to the sample, increasing in successive small steps. The variation of the strain with time was recorded. The critical stress for yielding can be determined by a significant increase in the creep rate. The creep profiles of 47 wt% TiO₂ suspension at different shear stresses are shown in Figure 4. The deformation of a suspension during creep can generally be classified into three regions. First, there is an immediate strain response once a shear stress is applied. Then, the strain slowly increases with time at a constant rate. This is the expected creep characteristic of an elastic solid. But after a certain time, the creep rate of the suspension gradually increases, indicating that some viscous component is involved. After the transition region, the strain increases sharply with increasing time. A steady strain rate

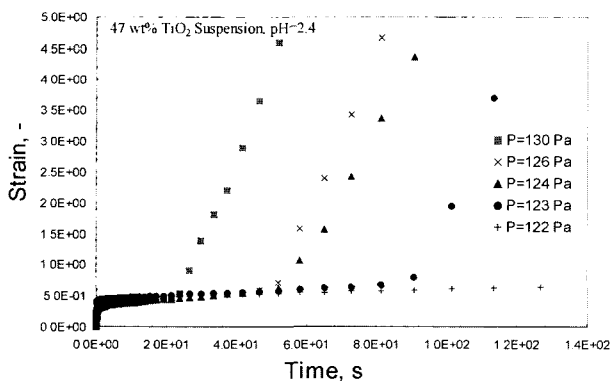


Fig. 4. Creep profile of 47 wt% TiO₂ suspension at different shear stresses.

is finally developed corresponding to a flow condition in the material. The region of solid-like creep is shortened with increasing applied stress. The results reveal the important fact that the yielding process of the material is time-dependent. A prolonged creep time could cause the failure of the material structure at a lower stress. The time-dependent behaviour of the yielding process is directly responsible for the diverse results in the determination of the yield stress using different techniques because of the different time frames involved. In this sense, a controversy on the existence of yield stress seems to be inevitable (Houwink and Decker, 1971).

3.3. Effects of surface chemistry conditions on yielding behaviour

Colloidal forces will play a significant role in the yielding behavior of TiO₂ suspensions. The two main colloidal forces acting on the particles are the van der Waals attractive force and the electrostatic repulsive force. For a given particle size and distribution, the van der Waals forces are essentially constant, whilst the electrostatic forces are highly sensitive to the pH of the medium. A variation in the electrostatic forces with changing pH can lead to a dramatic change in the interaction between particles, which in turn profoundly alters the yielding behavior of the suspension.

A dependence of the yield stress on the square of the zeta potential (ζ^2) was found in early studies (Kosmulski, Hunter *et al.*, 1968; Firth, 1976; Firth and Hunter, 1968; Firth, 1976). More recently, Kapur *et al.* (1997) proposed a new approach in attempting to describe the interdependence of the yield stress of a flocculated particulate suspension on the particle size, particle polydispersity and particle concentration on the basis of a three-dimensional, mechanically rigid particle network. Scales *et al.*, (1998) and Johnson *et al.*, (1998) extended the model by incorporating the effect of the interaction between particles caused by electrostatic repulsion forces. In their model, the van der Waals attractive forces and electrostatic repulsive forces were described by the DLVO theory. Hence, the relationship between the yield stress and Zeta potential was obtained. The model was simplified by normalizing the yield stress, τ_y , with respect to its maximum value at the iso-electric point, $\tau_{y,max}$, and was expressed as follows (Scales *et al.*, 1998, Johnson *et al.*, 1998):

$$\frac{\tau_y}{\tau_{y,max}} = 1 - \frac{24\pi\epsilon_r\epsilon_0\kappa_s^2 h_0^2}{A(1 + e^{-\kappa h_0})} \quad (1)$$

where A is the Hamaker constant of the colloidal material and h_0 is the minimum separation distance between particles in the flocculated state; ϵ_r is the dielectric constant, ϵ_0 is the permittivity of a vacuum and κ is the inverse Debye length. A feature of the above equation is to correlate the normalized shear yield stress with surface chemistry independently of the structural properties of particles. Thus, all

normalized data of yield stress for the suspensions with a variety of solids concentrations should collapse onto a single master curve in a plot against the square of zeta potential or pH.

The results of electrokinetic measurements and yield stress measurements for a 50 wt% anatase suspension with varying pH value have been shown in Fig. 1. It is seen that the iso-electric point electrokinetically determined is at pH 2.4 while the pH corresponding to the maximum yield stress is 2.1. The difference may be due to the use of different pH electrodes in the two measurements. Also, the pH was measured in very dilute suspensions in the electrokinetic measurement, while pH was directly measured in concentrated suspensions in the case of yield stress measurement. The latter could be slightly different from the true value of the supernatant. A similar problem existed in other reported studies (Scales *et al.*, 1998), and no conclusive explanation was given. To fit the data into the model, an adjustment of the pH value has been made for the results from yield stress measurements. All pH values obtained in concentrated suspensions were shifted by an amount of 0.3 so that the pH corresponding to the maximum yield stress agrees with the iso-electric point deter-

mined by the electrokinetic measurements.

Figures 5 and 6 show the variations of normalized yield stress with pH and ξ^2 , respectively, for suspensions with 50 wt% solids concentration. The normalized yield stress varies with pH following a parabolic profile and peaks at pH corresponding to the iso-electric point. Plotting the normalized yield stress against ξ^2 shows a linear relationship. Eq. 1 is fitted to the experimental data, and the value of approach distance h_0 is found to be 15.2 Å. Theoretically, the closest distance of approach between two particles can be assumed to be 5.5 Å corresponding to one water molecule with 2.75 Å in diameter adsorbed to each particle (Kapur *et al.*, 1997). A larger value of h_0 calculated from the model fitting of experimental yield stress suggests that the coating of organic molecules on the particle surface not only shifts the iso-electric point but also pushes out the distance of approach. Surface roughness certainly also contribute to the larger value of h_0 . The Hamaker constant used in the model for TiO₂ in water is 6.5×10^{-20} J taken from the early studies (Kapur *et al.*, 1997).

In a more detailed study, the effect of surface chemistry on the shear-induced yielding behavior of TiO₂ suspensions has been analyzed over a wide range of pH. Figure 7 shows the strain-stress curves of 50 wt% TiO₂ suspensions with different pH values at a ramp rate of 0.1 Pa/s, while Figure 8 extracts only the stress plateau of the curves in Fig. 7. Clearly, the slope of the stress plateau decreases as pH decreases towards the isoelectric point. This means that the stress range of the yielding process becomes narrower. A narrow stress range for the yielding process implies more uniform bonding strength within the network, hence, resulting in a sudden “brittle-type” structure failure. Conversely, a wide stress range for the yielding process implies a gradual and partial breakdown of particle bonds, which is caused by a wide distribution of bonding strength.

Variations of the slope of the stress plateau and yield stress with varying pH are plotted in Figure 9. The results indicate that reducing pH of the suspension towards the

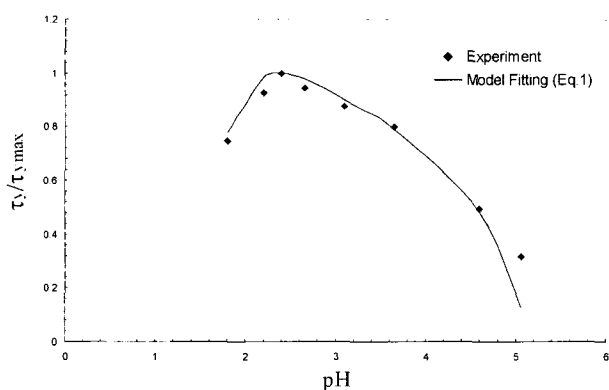


Fig. 5. Variation of normalized yield stress with pH for 50 wt% TiO₂ suspension.

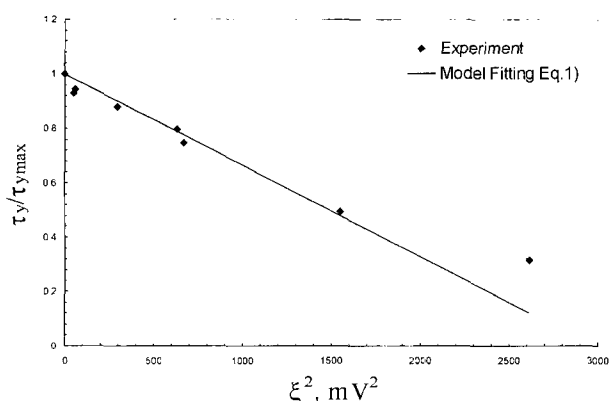


Fig. 6. Normalized yield stress as a function of ξ^2 for 50 wt% TiO₂ suspension.

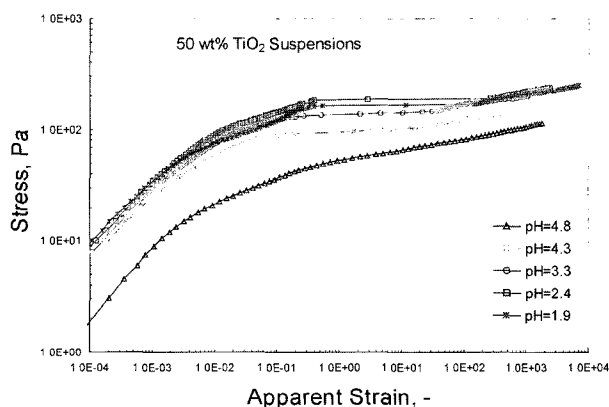


Fig. 7. Effect of pH on transition behaviours of 50 wt% TiO₂ suspensions.

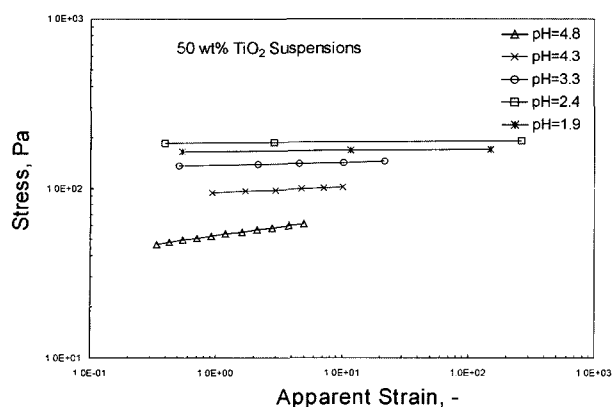


Fig. 8. Variation of stress plateau of 50 wt% TiO₂ suspensions with different pH values.

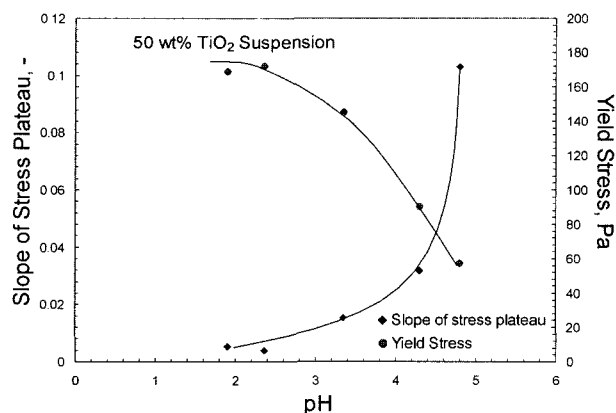


Fig. 9. Variations of slope of stress plateau and yield stress with pH for 50 wt% TiO₂ suspensions.

iso-electric point can increase not only the bond strength (position of the stress plateau), but also the uniformity of bond strength (slope of the stress plateau). This is because the distribution of surface charge on particles may be non-uniform. To improve the dispersability in various media, the TiO₂ pigment is commonly treated with different organics in the micronization stage of production. Cheever (1964) studied the adsorption of some organic surfactants on rutile TiO₂ surfaces using the electron microscopy and found that the organics adsorb in patches or on preferred sites on the particle surface rather than as uniform monolayers. Hence, the electrostatic repulsive forces acting on particles could also be not uniform, resulting in non-uniform bond distribution. With increasing concentration of H⁺, the anionic charges on particles due to the presence of organics gradually decrease towards zero when the iso-electric point is reached. Hence, the electrostatic repulsive forces gradually disappear and the van der Waals attractive forces eventually dominate the interaction between particles, resulting in more uniform bond strength. As a result, the structure of TiO₂ suspension fails more suddenly, in a “brittle” manner.

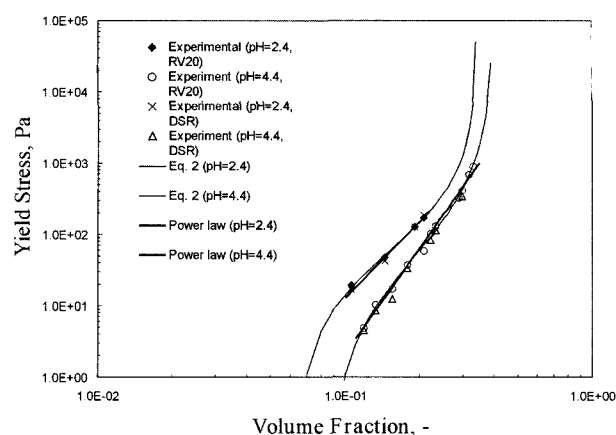


Fig. 10. Variation of yield stress with increasing solid volume fraction.

3.4. Effects of solid volume fraction

At a well-defined condition of surface chemistry and given particle size and distribution, the volume fraction of solids determines the concentration of particle-particle bonds and the density of network junctions, and thus, the strength of the network. Therefore, the yield stress of suspensions increases sharply with an increase in the particulate volume fraction. In this study, effects of solids concentration have been investigated over a wide range of volume fraction at pH values of 2.4 and 4.4, corresponding to the conditions of the isoelectric point and a weakly flocculated network. These constant surface chemistry conditions enable the study to focus on the purely structural effects on the network strength and bonding uniformity of flocculated suspensions. Figure 10 shows the variation of yield stress with increasing volume fraction at pH values of 2.4 and 4.4. The data include the results measured by stress-controlled rheometer (DSR) and rate-controlled rheometer (RV20). Clearly, the alteration of the surface chemistry of the particles towards the iso-electric point effectively increased the flocculation of particles, which leads to a lower packing density and a higher yield stress.

The dependence of yield stress on volume fraction for a flocculated suspension is commonly described using a power law expression (Thomas, 1961; Wildemuth and Williams, 1985; Leong *et al.*, 1995; Zhou *et al.*, 1999). For a suspension with a certain particle size, the relationship between yield stress τ_y and solids volume fraction ϕ can be expressed as follows:

$$\tau_y = A \times \phi^B \quad (2)$$

The yield stress is associated with a continuous, mechanically rigid particulate network. On the basis of the Quemada equation (Quemada, 1984), the yield stress can be simply related to a shear-dependent structural parameter, maximum packing fraction ϕ_m (Barnes, 1999, Zhou *et al.*, 1995). Zhou *et al.* (1995) proposed a model to correlate the

yield stress with the volume fraction in the following form:

$$\tau_y = \tau_c \left(\frac{\frac{1}{\phi} - \frac{1}{\phi_{m0}}}{\frac{1}{\phi} - \frac{1}{\phi_{m\infty}}} \right)^p \quad (3)$$

where ϕ_{m0} and $\phi_{m\infty}$ are the maximum packing fraction at zero shear and infinite shear stress respectively; p and τ_c are model parameters. The equation indicates that the yield stress increases from 0 to ∞ when actual volume fraction increases from ϕ_{m0} and $\phi_{m\infty}$. This model was used to fit data for suspensions of uncoated anatase TiO₂ with reasonable agreement (Yang *et al.*, 2001).

The yield stress values obtained from experiments are fitted by Eqs. 2 and 3, and the model parameters obtained are shown in Table 1. The value of $\phi_{m\infty}$ is experimentally determined by means of a centrifuge, and other parameters in Eq. 3 are determined by non-linear regression. The results from the model fitting using Eqs. 2 and 3 are shown in Fig. 10 for comparison with experiments. Although Eq. 3 is based on a simplified theory, the agreement between model fitting and experimental results is remarkably good. The power law expression (Eq. 2) is only able to describe the relationship between yield stress and volume fraction for suspensions with moderate yield stresses over a relatively small volume fraction range.

Varying the volume fraction of suspension can change not only the bonding strength of the network, but also the uniformity of bonding strength. Figure 11 shows the variation of the slope of the stress plateau and vane yield stress with increasing volume fraction at different surface chemistry conditions. It can be seen that yield stress increases

Table 1. Model parameters of Eqs.1and 2 for organically treated anatase suspensions

pH	ϕ_{m0}	$\phi_{m\infty}$	p	τ_c	A	B
2.4	0.065	0.343	0.805	20.08	$4.68 \cdot 10^3$	3.56
4.4	0.088	0.399	0.657	14.41	$1.74 \cdot 10^5$	4.91

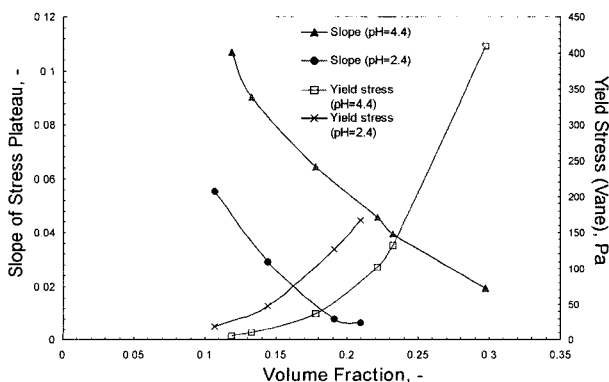


Fig. 11. Effect of volume fraction on slope of stress plateau.

with increasing volume fraction of suspension, but the slope of the stress plateau varies in the opposite direction. It can be assumed that the bonds between particles in suspensions are heterogenous in a less concentrated suspension. Some particles may have more neighbours and more bonds, thus, stronger local bonding strength. On the other hand, other particles may have weaker bonding strength because of fewer bonds with neighbours. When the network of a suspension is subjected to a shearing force, the parts with weaker bonding strength will be broken down first, hence exhibiting a gradual yielding process. However, with increasing particulate volume fraction, particles are more crowded together and the number of neighbours that bond with any given particle in the network is effectively increased. Thus, the local bonding strength is increased and the interaction between particles becomes more homogenous. An electron photograph of anatase TiO₂ pigment shown in another study (Yang *et al.*, 2001) has suggested that the particles are dispersed in water as small flocs. The results from the analysis of the particle size distribution also indicate that aggregation was present in our TiO₂ pigment. If this is the case, the system can be viewed as a series of weakly interconnected aggregate structures comprising strongly interacting primary particles (Zhou *et al.*, 1999). The forces holding these aggregates together are variable. The weak linkages between flocs can be broken down under a lower stress than those bonds within the aggregate. However, with increasing solids concentration, particles are becoming more crowded together and the number of such weak links diminishes gradually.

Figure 12 plots the slope of the stress plateau against yield stress for different pH conditions. It is clearly indicated that the surface chemistry determines the magnitude of the slopes. Decreasing pH towards the isoelectric point leads to a significant change in the “brittleness” of the structure. With the same values of yield stress, the strongly flocculated structures, corresponding to the isoelectric point, behave more “brittle” than those weakly flocculated.

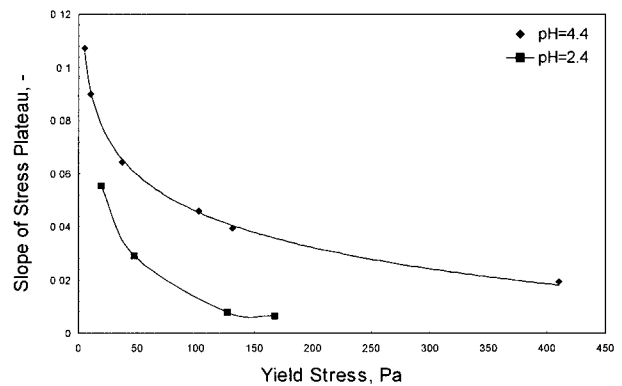


Fig. 12. Comparison of uniformity of bonding strength at different surface chemistry conditions.

4. Conclusions

The presence of organics on the titanium dioxide pigment greatly changes the surface chemistry and consequently, alters the rheological behaviour of TiO₂ suspensions. Adjusting the pH level of the suspension can effectively control the flocculation state of particles. It results in different bonding strength in the structure, hence, different yield stress. A maximum yield stress measured by vane torsion is in the vicinity of the isoelectric point determined by electrokinetic measurements.

There exists a clear stress plateau between elastic region and viscous flow for TiO₂ suspensions, which represents the transition of rheological behaviour from solid-like to liquid-like. The slope of the stress plateau reflects the uniformity of the structure, and hence the distribution of bonding strength. Depending on the inter-particle forces, the yielding process could occur over a wide or a narrow range of stress, which implies a “ductile-type” or “brittle-type” failure. The uniformity of bonding strength could be varied through concentration, or through extent of flocculation. Either adjusting pH towards the isoelectric point or increasing solids concentration can enhance the bonding strength and make it more uniform, hence, resulting in a more “brittle” structure that fails more abruptly.

The effect of surface chemistry on the yield stress can be described by the Scales model. The variation of normalised yield stress with pH for different volume fraction collapses onto a single master curve. The relationship of yield stress and volume fraction can be fitted over a wide range of volume fraction using the Zhou model.

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