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SHORT COMMUNICATION

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Flow behaviour of titanium dioxide dispersions in the presence of 2-hydroxyethyl cellulose

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Abstract The effects of 2-hydroxyethyl cellulose (HEC) of weight-average molecular weight 15,000, 90,000 and 7,20,000 on the rheological properties of TiO_2 dispersions were evaluated. For all three HECs, the maximum yield stress, $\tau_{y_{max}}$, (occurred at zero zeta potential), decreased with increasing HEC concentration. Interestingly, the largest reduction in $\tau_{y_{max}}$ was observed with the HEC with the highest molecular weight. This reduction was attributed to steric interaction arising from adsorbed HEC. Adsorbed high-molecular-weight HEC formed an effectively thicker steric barrier because of its larger size and higher adsorption capacity. Bridging interactions that were expected to be important for the high-molecular-weight HEC were found to be unimportant here. In the flocculated regime, HEC enhanced the shear-thinning characteristics of the TiO_2 dispersions.

Key words 2-hydroxyethyl cellulose · Titanium dioxide · Molecular weight · Steric yield stress · Viscosity

Introduction

TiO_2 is an extremely important industrial material with wide ranging applications. Its most important application is probably as a pigment for the paint and paper industries. Nanosized TiO_2 is an excellent UV absorber and, hence, is widely used in UV protection creams. The processing of TiO_2 dispersions, especially in paints and creams, involves the addition of a range of additives. The functions of these additives are to confer either the desired dispersion rheological behaviour or the desired finished product properties.

A range of additives is used in ceramic slip processing [1, 2]. These additives function as dispersants, binders, thickeners, plasticisers, etc. They are mainly ionic or polar nonionic organic compounds. Those additives that adsorb on oxide particles will certainly affect the nature of the particle–particle interactions and, hence, the rheological behaviour of the dispersions. Adsorbed additives in TiO_2 and ZrO_2 dispersions have been reported to give rise to a range of surface forces. These forces were steric [3–5], bridging [6], hydrophobic [7, 8] and charged-patch [9, 10] and the additives used were mainly anionic.

Nonionic polymeric additives such as poly(vinyl alcohol) and polyacrylamide, especially the high-molecular-weight species, were reported to play the role of a bridging agent [11–14]; however these studies were not conducted at the zero zeta potential condition, where the action of the electrostatic forces may be eliminated. The data obtained were, therefore, the result of the interplay of several surface forces. In this study the effects of a nonionic polar polymer on the interparticle force of TiO_2 dispersions evaluated in terms of a yield stress are reported. The analysis of the forces was performed at the zero zeta potential condition, where the yield stress is a maximum [3, 4].

Materials and methods

The TiO_2 powder (Aldrich; anatase; 99 + % purity) used in most of this work was cleaned prior to use as this commercial sample had an isoelectric point (pI) at about pH 2.4 which was much lower than the reported values of 6.0–6.5 [15]. The lower pI was believed to be caused by some anionic contaminants, such as phosphate ions [16]. For the series of yield-stress measurements on TiO_2 suspensions with 2-hydroxyethyl cellulose (HEC) (weight-average M_w 15,000), the pure grade TiO_2 from Hopkin & Williams, which has a pI at 6.0, was used directly.

Cleaning the TiO_2 powder

The method used for cleaning the TiO_2 powder was a modified method given in the literature [16]. The TiO_2 powder was suspended in 3M warm NaOH solution (50–60 °C) for 2–3 h with occasional stirring with a glass rod. After the suspension had cooled to room temperature and had separated into two layers, the upper layer (3 M NaOH solution) was carefully drained off. To reduce the concentration of NaOH trapped in the lower layer, it was washed twice with 1 M NaOH solution. Each time after washing, the suspension was again left to separate into two layers before draining off the upper layer. The washing process was performed several times with distilled water until the formation of the two layers was difficult to achieve. At this stage, the powder in the suspension was collected on a double-layered, 100%-cotton cloth and was washed many times with distilled water until the pH of the filtrate was about 7. The wet powder was dried overnight in an oven at 110 °C.

Using this treatment, the TiO_2 powder has a Brunauer–Emmett–Teller (BET) surface area of 9.5 $m^2 g^{-1}$, which was determined using an accelerated surface area and porosimetry system (Micromeretic ASAP 2000). (The BET surface area of the untreated TiO_2 was 9.8 $m^2 g^{-1}$.) The pI of the treated TiO_2 was at pH 6. The maximum yield stress, $\tau_{y_{max}}$, at the pI was used as a check for the reproduciblity of the experiment. $\tau_{y_{max}}$ was very reproducible for a given batch of TiO_2. It varied within an acceptable limit of about 10%. To minimise irreproduciblity of the $\tau_{y_{max}}$ values, the same batch of purified TiO_2 was used throughout a whole series of measurements on an additive, including the blank.

The additives used were 2-hydroxyethyl cellulose (HEC) of weight-average molecular weights 15,000, 90,000 and 720,000. The HEC-15000 was supplied by Union Carbide, whereas the HEC-90000 and HEC-720000 were supplied by Aldrich, USA. The following procedure was applied for the preparation of a typical TiO_2 dispersion containing an additive. For example, for the preparation of 0.05 dwb% [dwb%, dry weight basis = g(100 g $TiO_2)^{-1}$] HEC-90000 in 40 wt% TiO_2, 25.0 g TiO_2 powder was weighed into a plastic vial. In a separate beaker, 0.0125 g HEC-90000 was added to 37.515 g distilled water. This mixture was sonicated in a bath until the additive dissolved completely. (In cases where the HEC is at a high concentration and is not soluble in distilled water under normal conditions, dilute NaOH solution was added dropwise to aid in the dissolution of the HEC). The HEC solution was added to the TiO_2 powder in the plastic vial to give a suspension of 40 wt% of TiO_2 with 0.05 dwb% HEC-90000. The dispersion was then sonicated for about 1 min with the sonic probe of a Misonix ultrasonic liquid processor (model 2020). The sonifier was operated at 30–40% of the maximum power output of 550 W. Sonication break downs the dried agglomerate powder into primary particles. The prepared suspension was kept for at least 1 day prior to the measurements. Concentrated nitric acid solutions (1–5 M) were used to change the dispersion pH so as to minimise the extent of dilution. After each pH change, the dispersion was stirred vigorously with a spatula and left to stand for a while before the pH and yield stress or viscosity measurements were conducted. The pH was measured with a pH and conductivity meter (model alpha 200). (After each yield stress or viscosity measurement, the pH was measured again to confirm the pH of the suspension.) The yield stress was measured directly with a Bohlin VOR modified vane rheometer (vane-in-cup) at ambient temperature (25–28 °C). A vane attached to a torsion head was immersed in a flocculated dispersion contained in the cup. The cup was rotated very slowly and the maximum torque exerted on the vane by the dispersion was recorded. From the maximum torque and the dimensions of the vane, the yield stress was calculated. The viscosity was measured with the Bohlin VOR cone-and-plate rheometer.

Results and discussion

The effects of HEC of weight-average molecular weight 15,000, 90,000 and 720,000 on the yield stress–pH behaviour of TiO_2 suspensions are shown in Figs. 1–3. Note that different TiO_2 batches (all with similar pI) were used, but for each HEC molecular weight the same TiO_2 batch was used. In all cases the maximum yield stress, $\tau_{y_{max}}$, at high additive concentrations was much lower than that without additives. This reduction was clearly a steric effect. HEC must have adsorbed on TiO_2 to form a steric layer. The extent of the $\tau_{y_{max}}$ reduction was a function of HEC molecular weight and concentration. The pH of $\tau_{y_{max}}$ was unaffected by HEC, a clear indication of the nonionic nature of the polymer.

The strength of the adsorption bond formed between the nonionic polymer and the particle surface is generally quite weak. This physical bond is either a hydrogen bond or is van der Waals in nature. It has an energy of only about 0.5 *kT* [17]. For a polymer

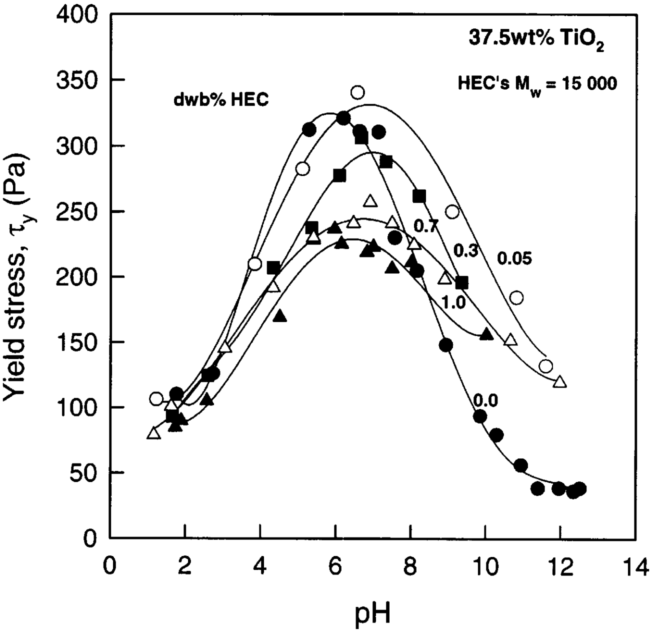

Fig. 1 Effects of 2-hydroxyethyl cellulose (HEC) of molecular weight (M_w) 15,000 on the yield stress–pH behaviour of TiO_2 dispersions

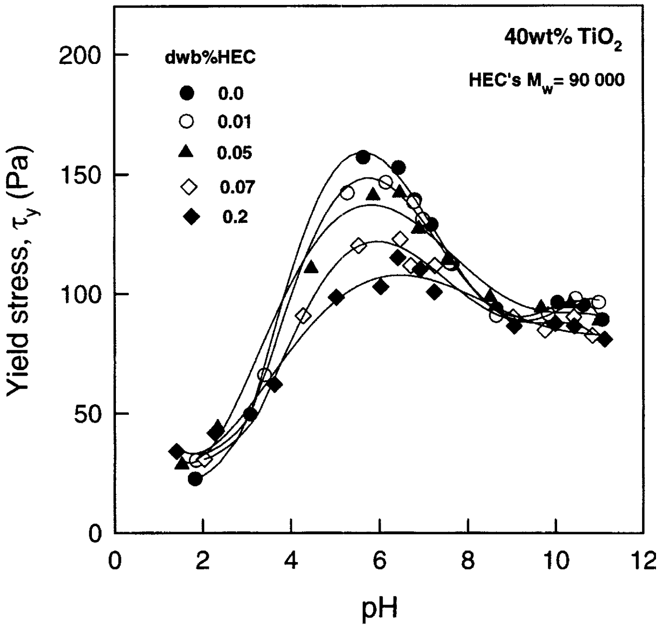

Fig. 2 Effects HEC of M_w = 90,000 on the yield stress–pH behaviour of TiO$_2$ dispersions

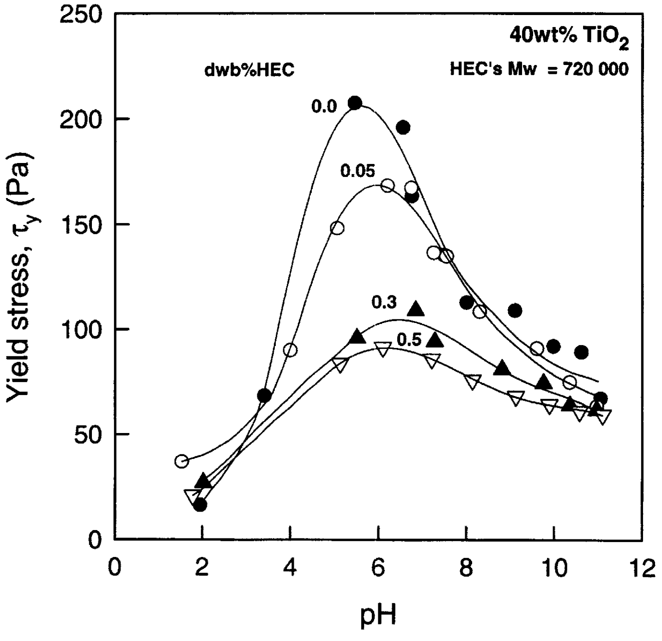

Fig. 3 Effects of HEC of M_w = 720,000 on the yield stress–pH behaviour of TiO$_2$ dispersions

molecule to stay permanently adsorbed many segments have to be adsorbed on the particle surface at the same time, so the net bonding strength of the molecule must be able to withstand the thermal Brownian motion and the usual external agitation. High-molecular-weight HEC will, therefore, adsorb readily and display a high adsorption capacity. The opposite is true for the low-molecular-weight species.

A plot of the ratio of the maximum yield stress with additives to that without, $\tau_{y_{\max(\mathrm{add})}}/\tau_{y_{\max(\text{no add})}}$, is shown in Fig. 4 as a function of HEC concentration for the three molecular weights. It shows clearly the molecular-weight dependence of the maximum yield stress reduction. A larger reduction was observed with increasing HEC molecular weight. For the molecular weight of 720,000, the ratio was 0.45 at 0.5 dwb% HEC, a 55% reduction in the maximum yield stress. Even at a very low additive concentration, where bridging tends to be important, the ratio was less than 1.0 for the high-molecular-weight HEC. For the low-molecular-weight HEC of 15,000, the ratio was 0.7 at 1.0 dwb% HEC, i.e. a 30% reduction.

The effective thickness of the steric layer formed by the adsorbed additives determined the extent of $\tau_{y_{\max}}$ reduction [3]. This effective thickness parameter was defined for a surface coverage that is not at the monolayer layer coverage to account for the $\tau_{y_{\max}}$ reduction observed at low additive concentrations [3, 4]. This parameter is a function of the degree of adsorption and the size (or molecular weight) of the adsorbed molecule. Unlike polyelectrolytes, where adsorption is commonly close to 100% [4], a nonionic polymer such as HEC does not adsorb as readily for obvious reasons.

The degree of surface coverage or adsorption usually increased with increasing HEC concentration for all molecular weights. This gave rise to an effectively thicker

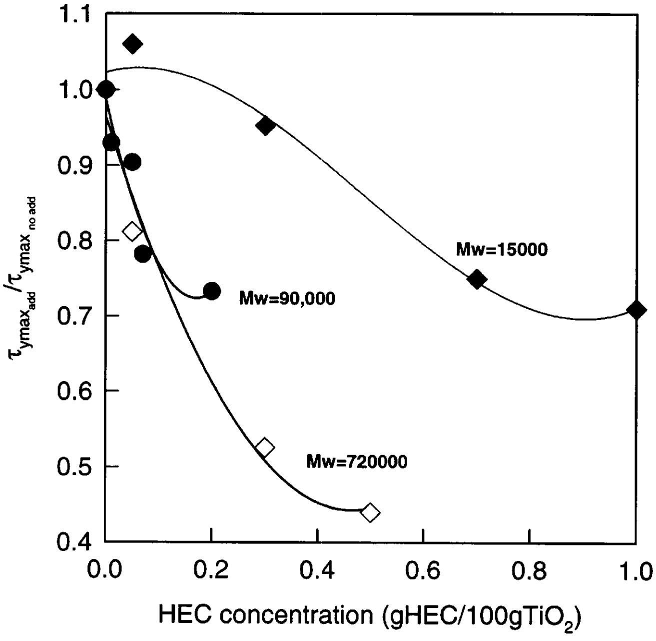

Fig. 4 Plot of the ratio of the maximum yield stress with additives to that without as a function of HEC concentration for M_w = 15,000, 90,000 and 720,000

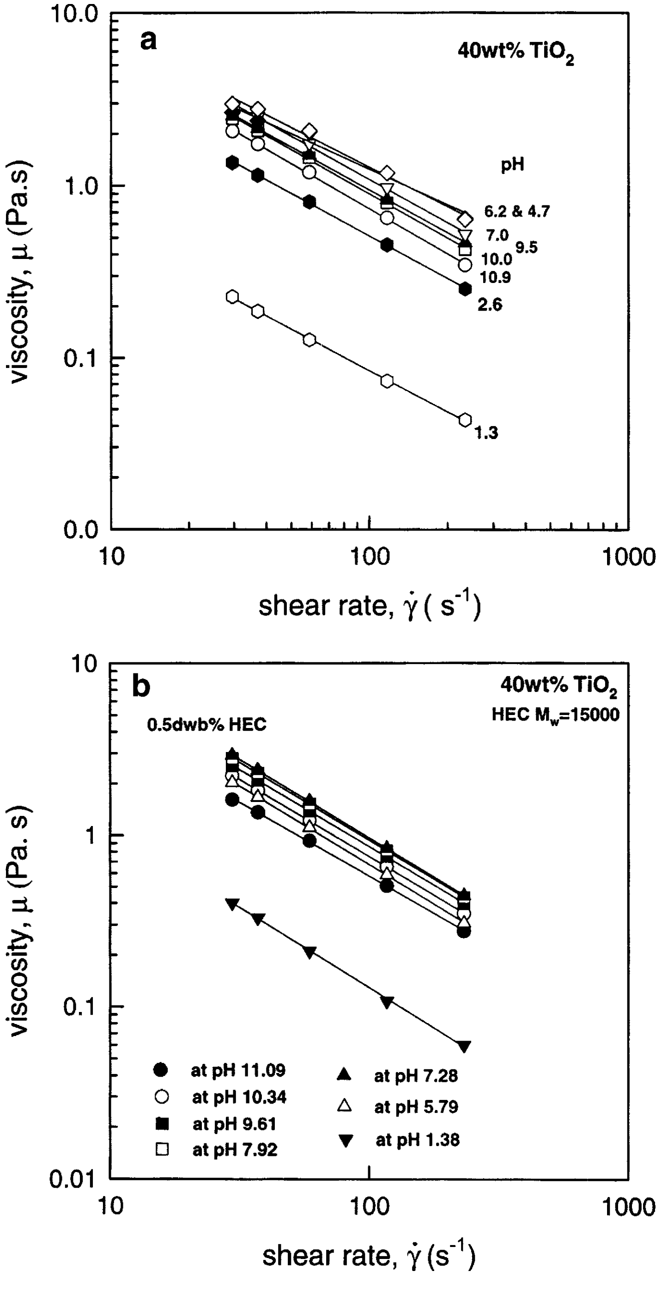

Fig. 5 Effects of pH on the viscosity–shear rate behaviour of TiO$_2$ dispersions for **a** no HEC and **b** 0.5 dwb% HEC of M_w = 15,000

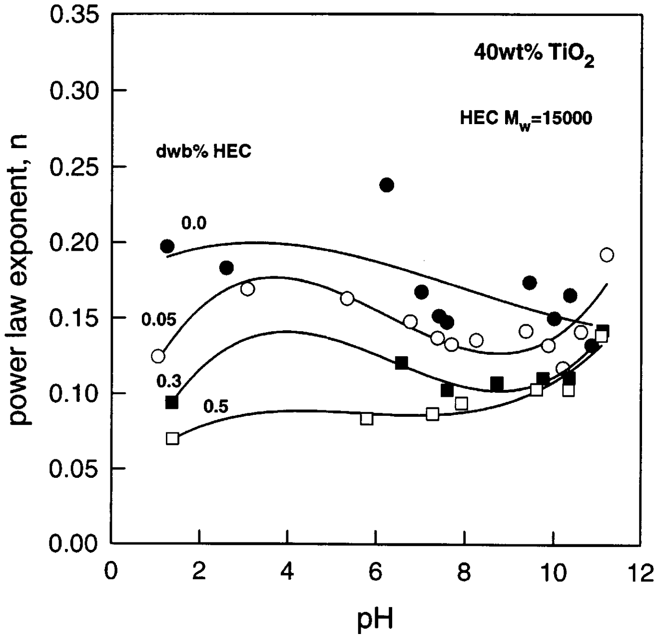

Fig. 6 Dependence of the power-law index, n, on pH for TiO$_2$ dispersions containing HEC of M_w = 15,000 in the concentration range 0.0 to 0.5 dwb% HEC

steric layer that explained the smaller $\tau_{y_{max}}$ values at high additive concentrations for any given HEC molecular weight.

At a given additive concentration, the surface coverage should also increase with increasing HEC molecular weight. This is because a high-molecular-weight molecule tends to stay more "permanently" adsorbed, leading to a greater adsorption capacity. This higher surface coverage partly explained the greater reduction in $\tau_{y_{max}}$ observed with the high-molecular-weight HEC at a given additive concentration. Another contributing factor to the $\tau_{y_{max}}$ reduction is the size of the adsorbed molecule [2]. Unlike polyelectrolytes [4], which adsorb lying flat on the particle surface, nonionic polar polymers do not assume such a conformation upon adsorption. The polymer adsorbs with loops sticking out into the solution. Such conformations project an effectively thicker steric layer.

Bridging interactions are thought to be common and important for high-molecular-weight hydrophilic polymers in aqueous dispersions. The smaller $\tau_{y_{max}}$ compared with that without additive for high-molecular-weight HEC suggests that bridging is not important, even at a very low concentration of 0.01 dwb% HEC for a molecular weight of 90,000. Bridging, even if present, must be very weak.

Figure 5a shows a plot of the viscosity versus the shear rate for a 40 wt% TiO$_2$ suspension, illustrating the pH effect, while Fig. 5b is a similar plot for the dispersion containing 0.5 %dwb HEC of M_w = 15,000. Similar plots for other concentrations of HEC can also be prepared but they are not shown here for brevity. It is observed that the relationship between the logarithm of the viscosity and the logarithm of the shear rate is clearly linear. A power-law model,

$$\mu = K\dot{\gamma}^{n-1} ,$$

therefore describes the flow behaviour, where μ is the viscosity, K the consistency index and n the shear rate ($\dot{\gamma}$)

exponent. When *n* is very much smaller than 1.0 the fluid is said to be highly shear-thinning.

The dependence of *n* on pH for TiO_2 suspensions with 0.0, 0.05, 0.3 and 0.5 dwb% HEC of $M_w = 15000$ is shown in Fig. 6. For all dispersions the pH has only a slight effect on *n* in the flocculated pH regime. All dispersions were highly shear-thinning as reflected by the small values of *n*. Almost all *n* were less than 0.2. For the blank, *n* has a value ranging from 0.15 to 0.2. In the presence of HEC, it was even smaller and it decreased with increasing HEC concentration. In summary, HEC has the effect of enhancing the shear-thinning characteristics of the TiO_2 dispersions.

Conclusions

1. Adsorbed high-molecular-weight HECs displayed predominantly steric interactions. Bridging interactions were found to be not important.
2. HEC enhanced the shear-thinning characteristics of TiO_2 dispersions.

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