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Charged patch attraction in dispersion: effect of polystyrene sulphonate molecular weight or patch size

Abstract The molecular weight ($M_w$) effect of polystyrene sulphonate (PSS) on the yield stress of ZrO$_2$ dispersion was evaluated. Three “monodispersed” samples with $M_w$ of 1430, 9960 and 130,000, and two broad distribution samples of $M_w$ 70,000 and 1.0 million were investigated. Adsorbed PSS gave rise to charged patch attraction that enhanced the maximum yield stress, $\tau_{\text{ymax}}$, of dispersions at charge neutral condition [3]. As a PSS patch consists of only one molecule, the patch size should increase with increasing $M_w$. For PSS of $M_w$ 1430 with just only seven repeating units the patch formed would be rectangular (linear) and small with a high charge density. For $M_w$ of 9960 and higher, the patch would be irregular in shape with a smaller charge density. At a moderate surface coverage of $\sim 20\%$, the $\tau_{\text{ymax}}$ increases quite sharply from $M_w$ 9960 to 130,000 and very gradually from 130,000 to 1.0 million. From $M_w$ 9960 to 130,000, the strength of the patch attraction increases quite strongly with increasing patch size. From $M_w$ 130,000 to 1 million, the small increase in $\tau_{\text{ymax}}$ reflected a limiting patch size effect. At the limiting size, the attraction is at maximum strength. At the same coverage, PSS of $M_w$ 1430 also displayed a strong charge patch attraction. This was attributed to a higher number of charged patch interactions at the closest point of separation and also to the high charge density of the PSS patch. The low surface coverage of 6% revealed no significant molecular weight effect on $\tau_{\text{ymax}}$. The network structure consisted of a mixture of charge patch and bare surface interactions.

Key words Molecular weight · Charged patch attraction · Yield stress · Zeta potential · Dispersions · Polystyrene sulphonate

Introduction

Charged patch attraction was first proposed qualitatively by Gregory [1, 2] to explain the flocculation of his colloidal dispersions by a high molecular weight ($M_w$) cationic polyelectrolyte. A positive patch is formed when the charge of the adsorbed polyelectrolyte molecule exceeds the underlying negative surface charge, in the area occupied by the molecule. The attraction is between the positive patch and a bare negative surface of a second particle. At rest the interacting particles must be at the state of minimum free or maximum attractive energy, i.e. the negative and positive patches must be in perfect alignment.

We reported charged patch attraction arising from adsorbed polystyrene sulphonate (PSS) in ZrO$_2$ dispersions from yield stress measurements [3]. Each patch consists of only a single PSS molecule. Aggregation of the PSS molecules on the particle surface was unlikely. PSS is a highly charged molecule and does not associate in solution and there is no reason that it should associate on the particle surface. Charged patch attraction was
not very strong and has the same magnitude as the van der Waals [4]. This attraction doubled the maximum yield stress, \( \tau_{\text{max}} \), of a ZrO\(_2\) dispersion at 30% surface coverage and at charge neutral condition. High ionic strengths diminished the attraction, an indication of the electrostatic nature of the interaction. Charged patch attraction was unfavourable at high surface coverage due to the lack of bare patches.

A number of patch parameters affect the attraction and these are patch size, potential or charge density and alignments [4]. In this study the effect of patch size on the maximum yield stress was evaluated. In the previous study [3] only one PSS molecular weight was evaluated. This PSS had a broad \( M_w \) distribution that meant a range of patch size was present. A uniform patch size can only be achieved by using PSS with a narrow \( M_w \) distribution. The effect of patch size on charged patch attraction can be studied by using “monodispersed” PSS of different \( M_w \)s. The surface coverage and the charge density of the patch, whenever possible, should be kept constant. The surface coverage was kept constant by fixing the PSS concentration used as the adsorption is 100%. The charge density of the patch at the pH of maximum yield stress is assumed constant at fixed PSS concentration. This assumption may not be valid for very low \( M_w \) PSS. Analysis of charged patch attraction is focused at the pH of zero zeta potential so as to avoid complication arising of other electrostatic forces.

Materials and methods

The ZrO\(_2\) powder has a BET surface area of 16.8 m\(^2\)/g measured with a Tristar 3000 and was earlier degassed at 300 °C for 2 h. The oxide has a median size of 0.2 µm which was determined using a Coulter LS230. Three “monodispersed” samples of fractionated sodium poly[4-styrene sulphonate] (PSS), denoted as PSS-1K, PSS-9K and PSS-130K, were obtained from Polyscience Inc. Their GPC molecular weight data were tabulated in Table 1.

In the preparation of a typical dispersion, PSS was first dissolved in a known amount of distilled water made alkaline by the addition of 1 or 2 drops of 8 mol/l NaOH solution. The ZrO\(_2\) powder was then added. The mixture was sonicated for about 1 min with a Misonix XL2020 ultrasonic processor. The resultant dispersion was generally dispersed and homogenous.

In order to minimise dilution effects, concentrated nitric acid (1 mol/l to 15.8 mol/l) was used to change the pH of the dispersion. Sonication was employed to disperse the added acid droplets in the dispersion. After each pH change the dispersion was allowed to stand for about 2 h. The dispersion was stirred vigorously with a spatula immediately before the yield stress measurement. The yield stress was measured with a Bohlin VOR viscometer adapted to do vane measurement.

The zeta potential was measured with a Mutek ESA 9800 apparatus. A 1.0 vol.% dispersion was used for the measurement.

Results and discussion

The effect of PSS-130K concentration on the zeta potential-pH behaviour of 1 vol.% ZrO\(_2\) dispersion is shown in Fig. 1. In the absence of PSS, the ZrO\(_2\) displayed an isoelectric point (pI) at pH 7.0 ± 0.3. The shift of the pH of zero zeta potential, \( pH_{\zeta=0} \), to a lower pH by PSS was a typical behaviour of adsorbed anions. The degree of shift was much greater compared with the weaker polyacrylic acid at the same concentration of repeating unit of polymer [3]. At 0.2 dwb% PSS (dwb% is g/polyelectrolyte/100 g ZrO\(_2\)) the \( pH_{\zeta=0} \) was 4.0 and at 0.35 dwb% PSS it was only 2.0.

In an earlier study [3], we reported a higher \( pH_{\zeta=0} \) of 2.9 for 0.34 dwb% PSS. Also the pI of the ZrO\(_2\) was higher than that in this study by about the same amount whereby indicating a systematic difference in \( pH_{\zeta=0} \) between the two studies. This clearly must be a calibration error of the pH probe in the zeta potential apparatus. For 0.1 dwb% PSS a \( pH_{\zeta=0} \) of 6.0 was reported.

At \( pH_{\zeta=0} \) the amount of negative charge from adsorbed PSS must equal the positive surface charge. Thus, from the amount of PSS adsorbed the positive surface charge density of ZrO\(_2\), \( \sigma_{\text{sp}} \), at \( pH = pH_{\zeta=0} \) can

<p>| Table 1 The molecular weight data from sodium salts of poly-styrene sulphonate |
|-----------------|------------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Polymer (sodium salt)</th>
<th>( M_n )</th>
<th>( M_w )</th>
<th>( M_w/M_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSS-1K</td>
<td>1,200</td>
<td>1,430</td>
<td>1.19</td>
</tr>
<tr>
<td>PSS-9K</td>
<td>8,600</td>
<td>9,960</td>
<td>1.16</td>
</tr>
<tr>
<td>PSS-130K</td>
<td>124,000</td>
<td>130,000</td>
<td>1.05</td>
</tr>
</tbody>
</table>

Fig. 1 The effect of poly[sodium 4-styrene sulphonate] of \( M_w \) 130000 on the zeta potential-pH behaviour of a ZrO\(_2\) dispersion.