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SHORT COMMUNICATION

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

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Abstract The molecular weight (*Mw*) effect of polystyrene sulphonate (PSS) on the yield stress of ZrO_2 dispersion was evaluated. Three "monodispersed" samples with *Mw* of 1430, 9960 and 130,000, and two broad distribution samples of *Mw* 70,000 and 1.0 million were investigated. Adsorbed PSS gave rise to charged patch attraction that enhanced the maximum yield stress, $\tau_{y_{\max}}$, of dispersions at charge neutral condition [3]. As a PSS patch consists of only one molecule, the patch size should increase with increasing *Mw*. For PSS of *Mw* 1430 with just only seven repeating units the patch formed would be rectangular (linear) and small with a high charge density. For *Mw of 9960* and higher, the patch would be irregular in shape with a smaller charge density. At a moderate surface coverage of ~20%, the $\tau_{y_{\max}}$ increases quite sharply from *Mw* 9960 to 130,000 and very gradually from 130,000 to 1.0 million. From *Mw* 9960 to 130,000, the strength of the patch attraction increases quite strongly with increasing patch size. From *Mw* 130,000 to 1million, the small increase in $\tau_{y_{\max}}$ reflected a limiting patch size effect. At the limiting size, the attraction is at maximum strength. At the same coverage, PSS of *Mw* 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 $\tau_{y_{\max}}$. 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 (*Mw*) 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, $\tau_{y_{\max}}$, 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 *Mw* distribution that meant a range of patch size was present. A uniform patch size can only be achieved by using PSS with a narrow *Mw* distribution. The effect of patch size on charged patch attraction can be studied by using "monodispersed" PSS of different *Mw*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 *Mw* 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 homogeneous.

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.

Table 1 The molecular weight data from sodium salts of polystyrene sulphonate

Polymer (sodium salt)	*Mn*	*Mw*	*Mw*/*Mn*
PSS-1K	1,200	1,430	1.19
PSS-9K	8,600	9,960	1.16
PSS-130K	124,000	130,000	1.05

The zeta potential was measured with a Matec 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, $pH_{\varsigma=0}$, 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 $pH_{\varsigma=0}$ was 4.0 and at 0.35 dwb% PSS it was only 2.0.

In an earlier study [3], we reported a higher $pH_{\varsigma=0}$ 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 thereby indicating a systematic difference in $pH_{\varsigma=0}$ 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 $pH_{\varsigma=0}$ of 6.0 was reported.

At $pH_{\varsigma=0}$ 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, σ_o, at $pH=pH_{\varsigma=0}$ can

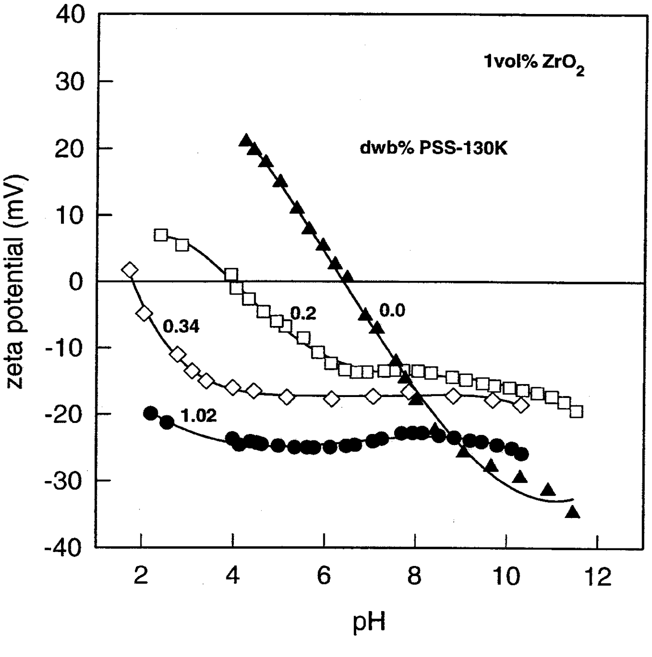

Fig. 1 The effect of poly[sodium 4-styrene sulphonate] of *Mw* 130000 on the zeta potential-pH behaviour of a ZrO_2 dispersion

be calculated. This task is made easier by two factors; first the adsorption of PSS, like polyacrylic acid [5], is 100% and second the polymer is completely dissociated or fully charged at pH above 2.0 [3, 6].

Hence the equation for σ_o, at $pH = pH_{\varsigma=0}$ is

$$\sigma_o = -\sigma_{PSS} = -\frac{m \cdot N_{av} \cdot e}{A_s}$$

where σ_{PSS} is the charge density due to adsorbed PSS, m the total moles of repeating unit, N_{av} the Avogadro number, e the electronic charge and A_s the total surface area of ZrO_2. At $pH_{\varsigma=0}$ the σ_o was 2.9 $\mu C/cm^2$ and 8.8 $\mu C/cm^2$ for 0.1 dwb% and 0.34 dwb% PSS [3]. The absorption density for 0.1 dwb% and 0.34 dwb% PSS was 0.06 mg/m^2 and 0.21 mg/m^2.

The effects of PSS concentration on the yield stress-pH behaviour of 56 wt% ZrO_2 dispersions are shown in Fig. 2a–c for PSS-1K, PSS-9K and PSS-130K. In the absence of PSS, the yield stress curve was typically bell shape with a maximum yield value of 750 Pa. For PSS-1K and at 0.1 dwb% polymer concentration the maximum yield stress, $\tau_{y_{\max}}$, was the same as that without additives but for PSS-9K and PSS-130K it was slightly lower. Also, the yield stress curve was very flat at $\tau_{y_{\max}}$. The plateau spanned over 4 pH units for 0.1 dwb% PSS-1K. In contrast, the curve was bell shaped for 0.1 dwb% PSS-9K. The bell shape became less pronounced as the *Mw* of PSS increases.

At the higher PSS concentration of 0.34 dwb% the $\tau_{y_{\max}}$ increased quite considerably for both PSS-1K and –130K, almost double that without the additives. However, for PSS-9K the $\tau_{y_{\max}}$ was slightly smaller than that with no additives. Charged patch attraction was also present for PSS-9K otherwise the $\tau_{y_{\max}}$ would be much smaller because of steric effects [5]. The yield stress curve for PSS-1K and PSS-9K displayed two plateau regions. The $\tau_{y_{\max}}$ was at pH 3.0 located in the second region. The *Mw* of PSS had no effect on the pH of $\tau_{y_{\max}}$. The zero zeta potential condition was also located in the second plateau region.

The ionic strength was maintained approximately constant in this study. From the quantity of nitric acid used to get to the maximum yield value, the ionic strength was on the order of 0.05 mol/l (1:1 electrolyte) for all dispersions.

The effect of PSS *Mw* on the reduced maximum yield stress for 0.1 dwb% and 0.34 dwb% PSS is shown in Fig. 3. The reduced parameter is defined as the ratio of maximum yield stress in the presence of PSS to that without, $\tau_{y_{\max_{PSS}}}/\tau_{y_{\max_o}}$. At polymer concentration of 0.1 dwb%, the reduced maximum yield stress did not show a significant *Mw* effect. However, at 0.34 dwb% PSS a significant effect was observed. The ratio was 1.6 at *Mw* 1430, which decreased to a minimum of about 0.8 at *Mw* 9960 and then increased again at higher *Mw*. Included in the plot were data for broad *Mw* distribution PSS of *Mw* 70,000 and 1,000,000 taken from Fig. 2d, e. The data fitted the trend, displayed by the 'monodispersed' PSS, very well. A limiting ratio of 2.0 was achieved at *Mw* of 1 million.

The surface coverage was 475 $Å^2$ and 151 $Å^2$/repeating unit for 0.11 dwb% and 0.34 dwb% PSS. This represented 6.3% and ~20% of complete coverage using the monolayer coverage value for sodium dodecyl sulphonate of 30 $Å^2$/molecule [7]. The actual surface coverage will be slightly higher because of the repeating unit being larger than the sulphonate head group. The surface coverage will be much larger if it were calculated based upon patch area occupied by PSS molecule [3].

The concentration of the ZrO_2 dispersions used in this study was 56 wt% solids. The volume fraction of solids is relatively low, only 0.15. When flocculated a very open network structure is formed. The 3D-network structure occupied the whole volume of the dispersion. At the junction points within the network the coordination number is 3. In the linear chain between junction points it is 2. The strength of this network structure is dependent upon the nature and strength of the surface forces. The yield stress is an excellent parameter for characterising the strength of this structure. Within the network there may be localised areas of weak structures. It is these weak structures that yield first during the yield stress measurement. Then the stronger structures will follow. In the opposite situation where the network contains localized areas of strong structures then the yield stress characterises the strength of the weak structures, as the strong ones remain intact during yielding. When the continuous 3-D structure is strong (by analogy the foundation and load bearing structure of a house) with the weak structures being discontinuous and randomly distributed (the walls of a house) then the yield stress is contributed by both the weak and strong structures as both will yield.

At low polymer concentrations of 0.1 dwb% PSS, the network may consist of a mixture of charged patch attraction and interactions between bare surfaces, especially when the amount adsorbed was not sufficient for all interactions to be charged patch in nature. At $pH_{\varsigma=0}$ of 6.0 the positive charge density of the bare surface was quite small, only 2.9 $\mu C/cm^2$. The interactions between bare surfaces will be attractive but will be weaker than the attraction at the isoelectric point of pH 7.0. The small reduction in $\tau_{y_{\max}}$ for PSS-9K and PSS-130K at 0.1 dwb% is a reflection of a slightly weaker structure. A mixture of relatively strong charged patch attraction and weak bare surface interactions formed this structure. At the same polymer concentration, there was an absence of $\tau_{y_{\max}}$ reduction for PSS-1K. This was due to the presence of more charged patch interactions to compensate for the weaker bare surface interactions. There were about seven times more molecules (or patches) for PSS-1K than PSS-9K at the same polymer concentration.

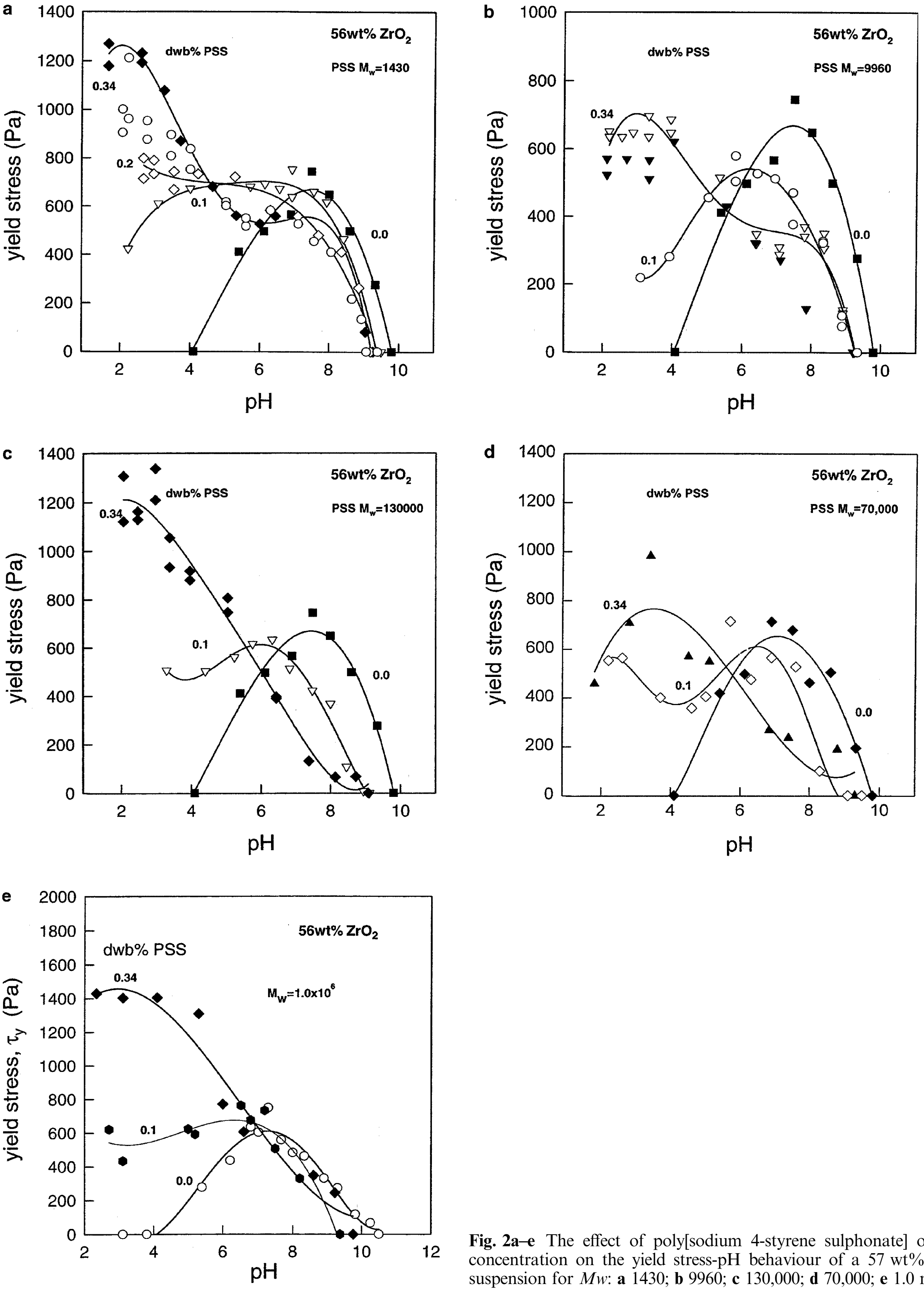

Fig. 2a–e The effect of poly[sodium 4-styrene sulphonate] or PSS concentration on the yield stress-pH behaviour of a 57 wt% ZrO_2 suspension for *Mw*: **a** 1430; **b** 9960; **c** 130,000; **d** 70,000; **e** 1.0 million

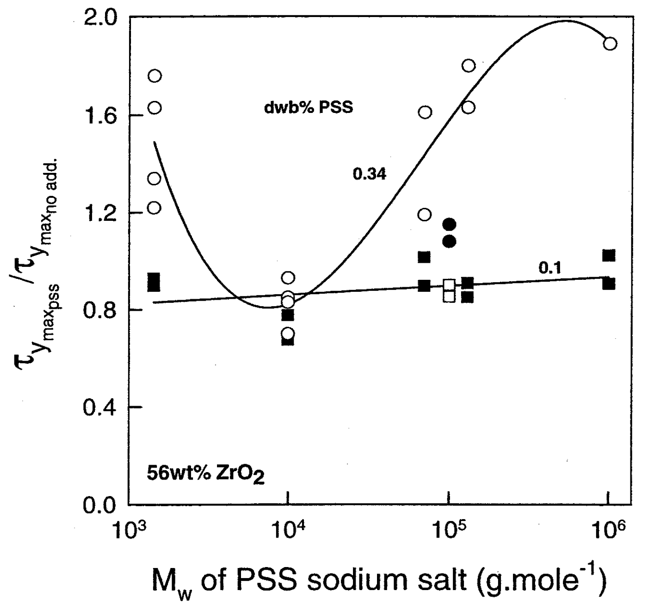

Fig. 3 The effect of PSS *Mw* on the reduced maximum yield stress of ZrO$_2$ dispersions. The *open square* □ and *solid circle* ● were data for 0.1 dwb% and 0.34 dwb% PSS taken from [3]

At ~20% coverage or 0.34 dwb% PSS, the $\tau_{y_{\max}}$ for PSS-1K and PSS-130K was about twice as large as that without additives. For PSS-9K the $\tau_{y_{\max}}$ showed a slight decrease. As long as the decrease was small, this meant that charge patch attraction was in operation though it may be weak in the case of *Mw* 9960.

When the *Mw* of the PSS was very low, the patch formed is (linear) rectangular in shape with a small area. For PSS of *Mw* 1430, the number of repeating unit is only 7. The patch area should be approximately equal to 7 times the area of the sulphonate group. Since the area per sulphonate is ca 30 Å^2 [7], the resultant area of a patch would be about 210 Å^2. This gave a net charge density of −44.8 μC/cm^2, after subtracting 8.8 μC/cm^2 for the underlying surface charge density, for each patch.

When the *Mw* was relatively large, the PSS patch formed would most likely be irregular in shape. As the segments of the PSS molecule are unlikely to be tightly packed and aligned on the particle surface, the patch area formed will therefore be relatively high [3]. The charge density will hence be relatively low. PSS with a *Mw* of 9960 and 130,000 has an average repeating unit of 49 and 647. Such large molecules will form a reasonable size patch.

The combination of small rectangular patch and high patch number density were responsible for the high maximum yield stress of 1100 Pa at surface coverage ~20% for *Mw* 1430. The attraction between the high negative density of the PSS rectangular patch and the relatively small positive charge density of the bare surface was quite strong. In that small surface area at the closest point of interactions between two particles where the interactions are most intense, they could be a number rectangular-bare patch interactions giving rise to a relatively large yield stress.

For the irregular shaped patches, the increase in $\tau_{y_{\max}}$ from *Mw* of 9960 to 130,000 was a patch size effect. This reflects a stronger attraction associated with a larger patch size. The small increase in $\tau_{y_{\max}}$ as *Mw* increased from 130,000 to 1.0 million was an indication of a limiting patch size effect. Beyond the limiting size the attraction will not increase in strength, i.e. the patch attraction is at maximum strength.

At present there is no theoretical or quantitative relationship between the radius of gyration (or *Mw*) of a molecule in solution and the patch area. It is therefore appropriate to assume that the irregular shape patch area, A_{P}, is proportional to the area occupied by a PSS molecule and hence

$$A_{\mathrm{P}} = K(nA_{\mathrm{sulphonate}})$$

where n and $A_{\mathrm{sulphonate}}$ are the number and area of one repeating unit and K the proportionality factor. $A_{\mathrm{sulphonate}}$ is about 30 Å^2. When the PSS molecule is stretch out on the particle surface, K takes the value of 1.0. The analysis of a previous study [3] found that an appropriate value for K was about 2.0 for irregular shape patch. Based on this patch area, the charge density is −18 C/cm^2 at $\tau_{y_{\max}}$ for 0.34 dwb% PSS with *Mw* ranging from 9960 to 1.0 million.

The forces contributing to $\tau_{y_{\max}}$ were steric, van der Waals and charged patch attraction. The steric and van der Waals contributions were taken as equal to the $\tau_{y_{\max}}$ obtained for polyacrylic acid at the same surface coverage of PSS. Adsorbed polyacrylic acid at the same surface coverage of 0.34 dwb% PSS reduced $\tau_{y_{\max}}$ for the same ZrO$_2$ dispersion by 55%. Figure 4 showed the relationship between the yield stress fraction due to charged patch attraction and patch area. The yield stress fraction was expressed as a ratio of yield stress due to charged patch attraction, $\tau_{y_{cp}}$, to the maximum yield stress without adsorbed PSS, $\tau_{y_{\max},o}$. The patch area was calculated for PSS of *Mw* ranging from 9960 to 1.0 million. The charged patch contribution increased from 0.4 to 1.6 times $\tau_{y_{\max},o}$ as the patch area increased from 30 nm^2 to 3000 nm^2. The value of 1.6 appeared to be the limit of the charged patch contribution.

Data for PSS of *Mw* 1430 were included in Fig. 4. The charged patch attraction contribution was about 1.04 times $\tau_{y_{\max},o}$. Note that the PSS patch is rectangular with a higher charge density than that of the irregular shape patch formed by the higher *Mw* species.

To explain the *Mw* effect on the $\tau_{y_{\max}}$, consider the charged patch interaction between two spherical particles each with a patch of opposite charge occupying half the sphere, i.e. the surface coverage of the patch is 50%. At charge neutral condition, the attraction between the

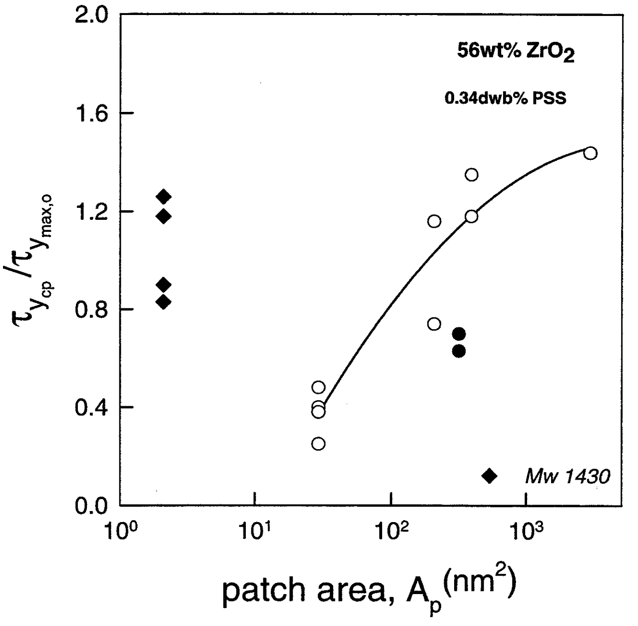

Fig. 4 The effect of patch area on the ratio of yield stress due to charged patch attraction to the maximum yield stress without PSS. The *solid circle* ● was for data taken from [3]

oppositely charged patches should be strongest. Now the patch is broken into smaller pieces. These are distributed evenly on the surface of the two particles. The charged patch attraction between these two particles would be weaker. At 0.34 dwb% PSS, the surface coverage based on PSS patch area for *Mw* 9960 to 1 million was about 36%.

Conclusion

At ~20% surface coverage and within the *Mw* range of PSS of between 9960 to 130,000, the increase in the strength of charge patch attraction with increasing patch size is quite sharp. There is a limiting (maximum) patch size where the charge patch attraction is at maximum strength.

Low *Mw* PSS of 1430 formed small rectangular (or line) patches of high charge density. At ~20% surface coverage, the interaction between these PSS patches and bare surfaces has the same strength as that of the van der Waals attraction without adsorbed additives.

At low surface coverage of 6%, the maximum yield stress was not affected significantly by PSS *Mw*. The flocculated network structure consisted of a mixture of charged patch attraction and bare surface-surface (weaker) interactions.

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