EFFECTS OF POLYSTYRENE ADSORPTION ON STRUCTURE AND RHEOLOGY OF SILICA SUSPENSIONS

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In this study, we have investigated effects of polymer adsorption on the structures and the rheological behavior of the silica suspensions as functions of concentrations of polymer and silica using the small angle neutron scattering (SANS) technique and rheometer .

Four monodisperse polystyrene (PS) samples with the molecular weights of 9.68×10^3 (PS-1), 96.4×10^3 (PS-10), 355×10^3 (PS-35) and 706×10^3 (PS-70) were used and Aerosil silica was employed. Spectrograde trans-decalin was used as the solvent. The silica contents were 5.7, 8.6, and 11.5 wt% and the PS concentrations examined were 0.57, 1.72, and 2.87 wt%.

To determine the amount of PS adsorbed on the silica surfaces, the PS concentrations of PS in the supernatants were measured using UV spectro photometer.

SANS measurements were performed a using the University of Tokyo SANS-U instrument. The wavelength of neutron was selected to be 0.70 nm. The samples were transferred to a quartz cell of path length of 2 mm. The sample to detector distances of 4 and 12 m correspond to the wave vector (q) range from 0.005 to 0.677 nm^{-1}.

Dynamic viscoelastic measurements were performed using an MR-300 with a cone and plate geometry (plate diameter: 32 mm; cone angle: 5°). The measurements were carried out at a strain of 1.0 % in the linear range of responses. The frequency range was changed from 0.025 to 5.03 rad s^{-1}. The measuring temperature was fixed at 27 ± 0.5 °C.

The plateau adsorbed amount of PS increased with an increase in the molecular weight and it attained a constant above the molecular weight of 355×10^3. The corresponding adsorbed amounts of PS-1, PS-10, PS-35, and PS-70 were 0.808, 2.10, 2.45, and 2.45 mg/m^2, respectively.

In double logarithmic plots of scattering intensity (I(q)) against q for the 8.61 wt% silica suspension in various PS solutions, log(I(q)) scales linearly with log(q) with a slope of ca. -2.0 below q = 0.145 nm^{-1} and above which a plot of log(I(q)) against log(q) yields a straight line with a slope of ca. -3.2. The former slope can be related to the mass fractal dimension (Dm) for the aggregated objects, while the latter slope gives the surface fractal dimension (Ds) according to the relationship, $I(q) \sim q^{-(6-Ds)}$.[1,2] At higher q regimes the Polod's law (Ds = 2) was not held, indicating that the surfaces of the primary particles are not smooth.

According to the scaling concepts for the colloidal aggregation, two distinct, limiting regimes of irreversible colloid aggregation have been proposed: diffusion-limited cluster-cluster aggregation (DCCA)[3] and reaction-limited cluster-cluster aggregation (RCCA)[4] correspond to the limiting cases of rapid and slow aggregation of colloidal

particles, respectively. For the DCCA model the fractal dimension becomes 1.78 ± 0.05 and for the RCCA model the fractal dimension becomes 1.98 ± 0.04. The resulting mass fractal dimension in this study is consistent with the RCCA model prediction.

Furthermore, the silica suspensions in PS solutions showed the stronger scattering intensity than that in the solvent at the lower q regimes with an increase in PS molecular weight. This means that adsorption interaction between PS and silanol groups on the silica surface causes partial flocculation of the silica particles and then results in formation of some flocs, and that the larger PS chains more effectively flocculate the silica particles.

The values of G' for the silica suspension in the solvent showed no frequency dependence, indicating the formation of silica aggregates like as gels by hydrogen bonding between silanol groups. Similar frequency dependency for G' was observed for the silica suspensions in the PS-1 and PS-10 solutions. The G' values for the silica suspensions in the PS solutions are nearly equal to that of the silica suspension in the solvent for the respective silica contents, except for the 11.5 wt% silica suspension in 1.72 wt% PS-1 solution. This suggests that PS adsorption occurs no breaking the silica aggregates. The 11.5 wt% silica suspension in 1.72 wt% PS-1 solution resulted in the larger G' value than that without PS. This indicates that due to the higher silica contents, free PS chains remained in the dispersion medium can easily make chain entanglements between the adsorbed chains.

On the other hand, above the molecular weight of 355×10^3 the G' values showed a slightly frequency dependence. This is attributed to partial breaking the aggregated structures in the silica suspensions by adsorption of PS. The G' values for the silica suspensions in PS-35 solutions were larger than those in PS-70 solutions at the entire frequency ranges. The difference should be related with the probability of PS adsorption, namely a longer polymer chain easily adsorbs between different particles. The G' values for the silica suspensions in the presence of PS-35 and PS-70 increase with PS concentration. This should be attributed to chain entanglements between PS chains adsorbed on separate aggregates as well as those involving nonadsorbed PS chains.

It is important to discuss the dependence of the G' on the volume fraction (ϕ) of the silica particles to understand what mechanism control in the formation of the gel network structure. We found the silica suspensions in the solvent and in PS-1 and PS-10 solutions to show a power law behavior, i.e. $G' \sim \phi^n$. The value of n was obtained to be 4.3, irrespective of the silica suspension and the resulting exponent agrees with the prediction of Ball and Brown[5] based on a RCCA model. This result is consistent with that of SANS.

References
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