



## **Mechanistic analysis of aggregation of colloidal particles: Effect of surface-sorbed polymer**

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The aggregation of colloidal particles in aqueous media was investigated in the presence of a polymer (humic acid in the present study) as function of time. The carbon black nanoparticles (CB-NPs) were selected as representative colloidal particles. The aggregation characteristics were assessed with the information of hydrodynamic size, particle sedimentation rate, and visual images of suspensions. The concentration of humic acid was varied from 0 to 10 mg/L. In addition, zeta potential, water contact angle, and polymer sorption to CB-NPs was examined to complement stability analyses. CB-NPs suspension always exhibited the negative values of zeta potential, and when the polymer was added zeta potentials became relatively more negative due to the polymer adsorption to CB-NPs. The CB-NPs were found to be hydrophobic, whereas they became hydrophilic in the presence of polymer. Aggregation tests showed that the hydrodynamic size of CB-NPs increased fast and sedimentation rate was high in the absence of polymer. However, the polymer-adsorbed CB-NPs were substantially stable. In order to analyze the results of aggregation test, Derjaguin–Landau–Verwey–Overbeek (DLVO) theory was employed. The classical DLVO theory could not support the experimental observations in the presence and absence of polymer. However, extended and modified DLVO theories, that also accounted for hydrophobic-attractive forces due to the inherent nature of CB-NPs and steric repulsive forces associated with the brush-like conformation of polymer adsorbed to CB-NPs, better described CB-NPs' stability in the absence and presence of polymer, respectively. More interestingly, in some cases where the polymer was present in CB-NPs suspension, sedimentation results were not consistent with the modified DLVO interaction energy profiles because the predicted energy barrier was insurmountable for CB-NPs to overcome by diffusion. A possible explanation Nanoscale surface roughness that has recently been reported to play great role in changing the magnitude of energy barrier, was introduced as a possible explanation, and relevant results will be discussed.

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