Temporal Decoupling of Viscosity Growth and Particle Aggregation in Shear-Induced Gelation

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Aqueous suspensions composed of silica nanoparticles and poly(ethylene oxide) (PEO) exhibit a reversible gelation phenomenon known as "shake-gels." These suspensions remain in a flowable, sol-like state at rest but temporarily transition to a gel-like state when agitated by hand or subjected to shear flow. Under steady shear at a constant shear rate, the viscosity increases abruptly after an induction period, resulting in gelation. Despite extensive research, the dynamics of gelation, particularly the relationship between the rheological response and internal structural evolution, remain poorly understood.
To elucidate the gelation dynamics, time-resolved rheo-USAXS (ultra-small-angle X-ray scattering) measurements were performed on aqueous mixed suspensions composed of silica nanoparticles and PEO under a constant shear rate. This technique enabled the simultaneous acquisition of temporal evolution of viscosity and scattering profiles reflecting particle-scale structures (**Fig. 1(a)**). When steady shear was applied, a sharp increase in viscosity was observed accompanied by gelation. Simultaneously obtained scattering profiles revealed that the dispersed particles became aggregated cluster structures. Notably, the increase in viscosity occurred prior to discernible changes in scattering intensity (**Fig. 1(b)**). This temporal dissociation suggests that a polymer-mediated network structure, which cannot be observed by USAXS, increased the viscosity of suspensions. This study is the first to demonstrate that viscosity growth occurs before particle aggregation during shake-gel gelation. This finding provides new insight into the stepwise development of gel network structures.

Keywords:
Rheo-USAXS, Shake-gel , Shear thickening, Silica nanoparticles, Poly(ethylene oxide)

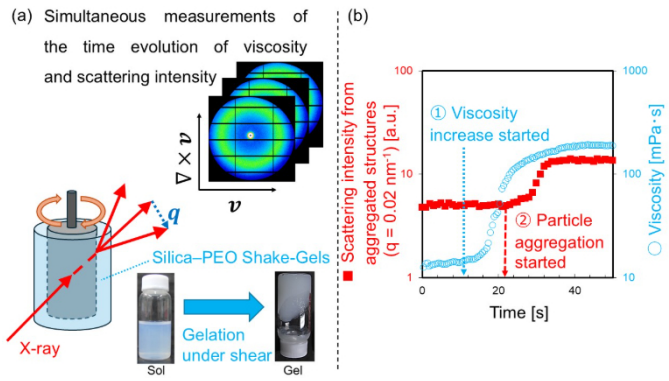

Fig.1 (a) The outline of the time-resolved Rheo-USAXS. (b) Viscosity increases preceded particle aggregations.

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