

Influence of Sodium Polystyrene Sulfonate to Aging of Laponite Aqueous Suspensions

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Abstract – Laponite aqueous suspensions are widely used in science and industry. Recently polymer-Laponite composites attracted great attention due to their remarkable physical properties. In present paper study of aging process of aqueous suspension of Laponite and sodium polystyrene sulfonate is described. For investigation two methods were used: small-angle X-ray scattering (SAXS) and small-amplitude oscillatory shear (SAOS) rheology. Concentration of Laponite were fixed at 2.5%wt and concentration of PSS-Na was varied in range 0-0.5 %wt.

Key words – Laponite, PSS, aging, aqueous suspension, SAXS, rheology.

I. Introduction

Laponite is synthetic clay, which belong to smectite group [1]. Its empirical formula $\text{Na}_{0.7}[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4]_{0.7}$ [2]. Laponite consist of discotic particles with thickness of $h \approx 1$ nm and diameter of $d = 25-30$ nm[3]. In water media these disks bare strong negative charge on the basal surface (700e per particle) Moreover Laponite particles could bare positive charge on the rim depending on the pH[4].

Phase diagram of Laponite aqueous suspension contains sol, gel, glass and nematic states[5][6] depending on its concentration and ionic strength. Furthermore these systems are complicated by aging process, which is transition from sol state to non-ergodic one[7].

Kinetics of aging process of Laponite suspensions could be tuned by using different additives. We have chosen polystyrene sulfonate since it could interact with Laponite particle due to negative charge its chains bare. Laponite – sodium polystyrene sulfonate composites were studied before, but only in films [8][9]. In contrast to those papers we have investigated polymer/clay system in aqueous media.

II. Experimental

In this study we used Laponite RD (Rockwood Additives Ltd., UK) without additional treatment. Polystyrene sulfonate was obtained by multiple sulfonation of polystyrene by sulfuric acid. Its average molar mass was $M = 145000$ g/mole.

Rheology tests were performed at small-amplitude oscillatory rheometer HAAke MARS III (Haake, Karlsruhe, Germany). Small-angle X-ray scattering measurements were carried using digital detector Elexience.

All samples were prepared in same way: by mixing stock solutions of PSS and stock suspension of Laponite which were prepared by using ultrasonication.

III. Results and discussions

As one can see from Fig. 1 adding of sodium polystyrene sulfonate caused acceleration of aging process of Laponite suspension. Estimated ergodicity-breaking time t_g^* was obtained as time point at which slope of power law dependence of complex viscosity on aging time changed. Adding of 0.01%wt and 0.1%wt PSS-Na decrease t_g^* by the factor of 2 and 10 respectively.

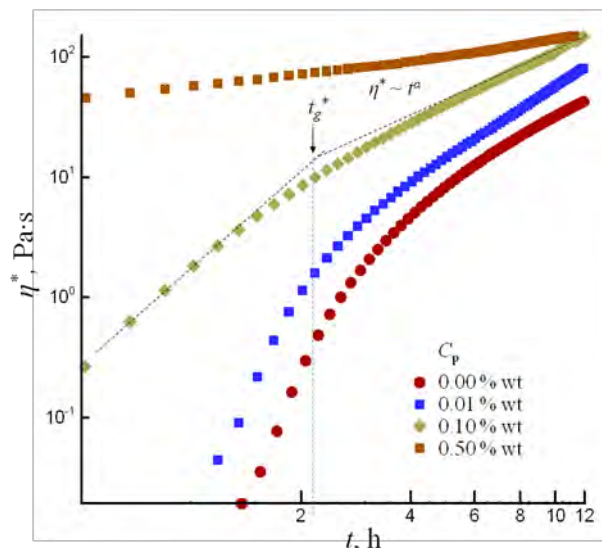


Fig. 1. Complex viscosity η^* versus aging time at different PSS-Na concentrations

SAXS data reflected input of Laponite particles thus as SLD contrast between solvent and PSS was negligible.

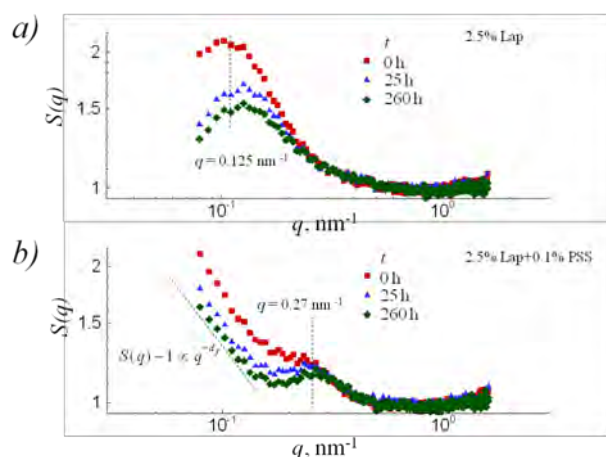


Fig. 2. Structure structure factor $S(q)$ calculated from SAXS data for pure 2.5%-Laponite suspension (a) and one with adding of 0.1%wt PSS-Na (b)

To extract important information about structure of Laponite – PSS-Na composites we derived static structure factor $S(q)$ as scattering intensity $I(q)$ divided by Laponite particles form-factor $P(q)$, which was calculated in accordance to Guinier formula for disks[10]. Structure

factor of pure Laponite suspension has clear peak at $q=0.125$ nm, which obviously corresponds to interparticle distance (~ 50 nm). At low q range $S(q)$ decreases. All this indicate glass state. But for clay suspension with 0.1%wt PSS the peak shifts to $q=27$ nm and its significant growing at low reveals large-scale inhomogeneties, all these signs indicate gel state. So adding of PSS-Na caused transition of Laponite suspension form glass to gel state.

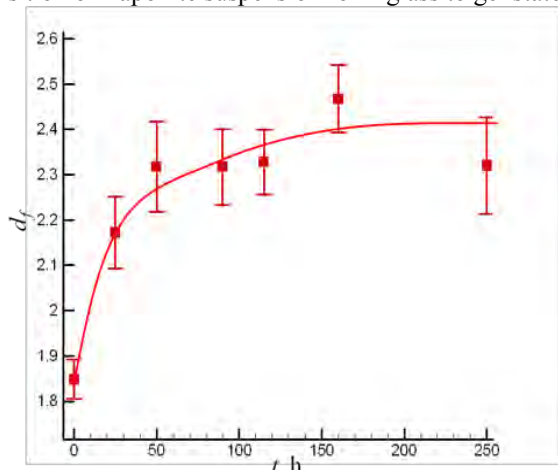


Fig. 3. Fractal dimension d_f versus aging time for 2.5%-Laponite suspension with 0.1%wt of PSS-Na

In addition we obtained fractal dimension of gel network by interpolating structure factor by power-law $S(q) \sim q^{-d_f}$. Figure 3 represent dependence of fractal dimension on aging time for Laponite suspension with 0.1%wt of PSS-Na. Its growing with time points out that network become more homogeneous.

Conclusion

In this paper results of study of aging in Laponite – PSS-Na aqueous suspensions is presented. Investigated samples had fixed value of Laponite concentration 2.5%wt and concentration of PSS-Na within 0-0.5%wt. All of them were sedimently stable and transparent (visually observed flocculation didn't occur). The results of rheology tests have shown that adding of polyelectrolyte to Laponite aqueous suspension caused decreasing of ergodicity-breaking time by the factor of 2 for at PSS-Na concentration 0.01%wt and by the factor of 10 for 0.1%wt of PSS-Na. In contrast to salt-contained Laponite suspensions, for which opaque flocs appear at ionic strength $I_S > 20$ mM, polyelectrolyte-clay system in aqueous media didn't undergo flocculation process even at ionic strength $I_S = 24.2$ mM. Thus we assumed that

influence of polyelectrolyte to clay suspension was due to decreasing of Debye screening length and crosslinking of Laponite particle by polyelectrolyte as well.

Small-angles X-ray scattering spectrum indicated that adding of PSS-Na to clay suspension caused its transition from initial glass state to gel one, which is typical for lower Laponite concentrations ($C_L < 2\%$ wt). Moreover, fractal dimension of gel network increased during aging process, thus structure was becoming more homogeneous.

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