

Synthesis and characterization of cation-exchanged laponite nanohybrids for use as drilling fluid viscosifier

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ABSTRACT

In this paper we report our new approach to synthesize cation-exchanged Laponite nanohybrids for use as gel-forming, viscosity and weighting material stabilizing additives for drilling fluid application. To synthesize the nanohybrids, we used a laser beam and ablated micron sized metal particles (Cu, Co, or Al) in an aqueous suspension containing 1 wt% laponite. As a result, the suspensions underwent a transition to a stable gel very quickly. Although the weight percent of the nanohybrids was negligibly small compared to that of Laponite, aqueous suspensions of these cation-exchanged Laponite crystals were highly viscous with excellent shear thinning and thixotropic behavior. The fluid gelled quickly when it was at rest nevertheless its structure was broken easily and it transformed into a low viscosity fluid quickly on shearing.

Keywords: Laser ablation, cation-exchanged laponite

1. INTRODUCTION

Following our previous report [1], in this paper we present our study on the use of the laser ablation in liquid technique to synthesize cation-exchanged laponite nanohybrids by ablating micron-sized metal powder dispersed in an aqueous solution containing deionized water and Laponite crystals. It has been known that cation-exchanged laponite nanohybrids are used widely in many different fields such as drilling fluids, catalysis, batteries, adsorption, cosmetics, etc. [2-9]. This is because they are characterized as fine particles with high degree of structural regularity, low level of impurities, high specific surface area with well adsorptive capacity of several chemical molecules and ions [2, 5]. Laponite is synthetic sodium magnesium silicate clay that has a layered structure. The Laponite crystals have a disk shape with a diameter of about 25 nm and a thickness of about 1 nm. When Laponite crystals are dispersed in water the sodium ions between the negatively charged silicate layers are released

and readily exchanged for other ions with high capacity (about 0.72 mM/100 g). Thus, when cation metal powders are ablated in it, it is possible for the ablated metal ions to intercalate into the interlayer region of the Laponite crystals. Chemical synthesis of cation-exchanged Laponite nanocomposites has been usually carried out by mixing Laponite in an aqueous salt solution containing large hydroxy metal cations. The charge exchange reaction between the clay sheets and the hydroxyl metal cations occurs. Upon heating to a high temperature, dehydration and dehydroxylation of the hydroxy occur and metal oxide clusters are formed between the interlayer region of the clay disks [2, 9]. Use of the laser ablation technique for this purpose, however, has not been previously demonstrated.

2. EXPERIMENTAL APPARATUS

Laser ablation of microsize metal powder (Co, Al, and Cu) dispersed in an aqueous solution containing deionized water Laponite crystals was carried out using a laser beam generated by a single-mode, Q-switched Nd-Yag laser operating at 532 nm with a pulse duration of 5.5 ns and 10 Hz repetition rate. To prepare the sample, we simply mixed Laponite powder and metal powder with deionized water (DW) and stirred the solution for 24 hours using a magnetic stirrer. We then filled the ablation cell with a suspension volume of about 60 mL and irradiated it with a laser beam. Laser fluence was 0.265 J/cm² for all tests. For all samples, the weight percent of laponite was 1% while the metal weight percents were 0.025% and 0.050%. All the solid masses were measured using a micro balance.

3. RESULTS AND DISCUSSIONS

Laponite is a synthetic sodium magnesium silicate clay. The Laponite crystals have a disk shape with a diameter of about 25 nm and a thickness of about 1 nm. When Laponite is dispersed in water the sodium ions are

released and the Laponite disks have a strongly negative face charge. The edge charge depends on the acid-base behavior of the Si-OH and Mg-OH amphoteric hydroxyl groups, which are the main species on the edge. Below pH 9, the magnesium ions dissolve in the solution and above pH 10, the dissolution of silica occurs [10]. In salt-free water, these disks are stabilized, separated by a few water layers by electrostatic repulsion between the negatively charged faces [10]. General observations of the prepared samples indicated that an aqueous solution of 1 weight percent Laponite remained free flowing even after several weeks of aging.

Photographs showing sol-gel transformation of aqueous solution containing 1 wt% laponite and 0.05 wt% metal powders before and after irradiation are shown in Fig. 1. When metal powders (Cu, Al, and Co) were mixed with the laponite suspensions, the resultant solutions had low viscosity and remained as a free flowing liquid. In fact the added powder particles had no effects on the suspension viscosity. The suspensions were not stable, metal particles were settled on the bottom of the vial quickly after less than 30 minutes. When these suspensions were irradiated with a laser beam of 532 nm, a sol-gel transition was induced which can be observed easily by looking at their colors that were changing during the irradiation. After about one hour of irradiation, the low viscosity free low liquid solution was transformed into a strong gel when the mixture was allowed to rest. As shown in Fig. 1(b) the gels were so strong that they can hold their own weights in the vials. The gels, however, could easily be reverted to a low viscosity liquid with simple shaking. The gel structure quickly reformed when the mixtures were again allowed to stand.

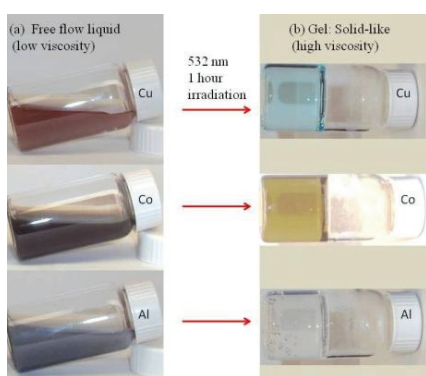


Figure 1. Photographs showing sol-gel transformation of aqueous solution containing 1 wt% laponite and 0.05 wt% metal powders after irradiation with a laser beam having fluence of 0.265 J/cm² and wavelength of 532 nm for one hour.

The UV-VIS absorption and transmission spectra of aqueous laponite suspensions, metal (Co, Cu, and Al) powder solutions and those prepared by irradiating the metal powder solutions with a 532 nm laser beam are shown in Fig. 2. The UV-VIS results for the aqueous laponite suspension showed that the suspension was transparent to the wavelength range from 300 to 900 nm. For shorter wavelengths, it became opaque and had a distinct absorption peak located at around 225 nm. For the metal powder solutions, there existed a distinctive feature in the UV-VIS results obtained for the solutions before and after being irradiated with a laser beam. Unlike the UV-VIS results obtained for metal powder solutions which showed that the solutions were opaque and significantly absorbed the light in the visible and near infrared region, the spectra obtained for the solutions after irradiation were similar to that of the aqueous laponite suspensions except that the absorption peaks were slightly red-shifted. For example, the solution containing aluminum and copper had the absorption peaks located at around 247 nm and 266 nm, respectively. The solution containing Co had the absorption peak at 264 nm with an absorption shoulder extended in the region from 380 to 390 nm. Thus, it can be concluded that the resulting materials have a physical structure that is similar to that of pure laponite disks.

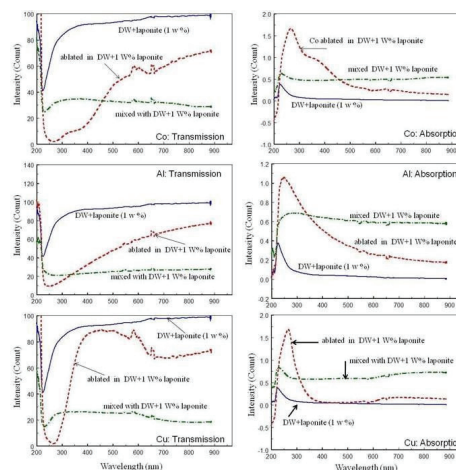


Figure 2. UV-VIS spectra of aqueous solution containing 1 wt% laponite and 0.05 wt% metal powders before and after irradiation with a laser beam having fluence of 0.265 J/cm² and wavelength of 532 nm for one hour.

Figure 3 shows the changing viscosities of the prepared cation-exchanged Laponite suspensions during the gel breakdown and buildup. Viscosity measurements were performed using a Brookfield DV-II Pro Viscometer with a small sample adapter (SSA18/13RPY). The adapter consisted of a cylindrical sample holder, a water jacket and

spindle. The viscometer drives the spindle immersed into the sample holder containing the test fluid sample. The viscometer can provide a rotational speed that can be controlled to vary from 10 to 200 rpm yielding a shear rate from 13.2 to 264 1/s. Viscosity is determined by measuring the viscous drag of the fluid against the spindle when it rotates. The sample holder can accommodate sample volumes up to 15 mL. The temperature of the sample is monitored by a temperature sensor embedded in the sample holder.

Several distinct features can be observed from Fig. 3: (i) The viscosities decreased rapidly with increasing shear rates indicating that the prepared suspensions are excellent shear thinning fluids. As indicated in the figures, the weight percents of metals were negligibly small compared to that of Laponite and yet the range of the viscosity reported here was several hundred times higher than those obtained for suspensions containing 1 weight percent Laponite. (ii) Suspension viscosity depends strongly on the amount of metal cation that was exchanged, and on the type of the metal used. (iii) During the gel breakdown, the thixotropic behavior of the suspension was negative that is, viscosity decreased with time. During gel buildup however, the measured viscosities exhibited a mixed thixotropic behavior for higher metal amount while a positive thixotropic behavior was observed for the suspension modified with lower amount of metals. In general, however, it is clear that for a given shear rate the suspensions reached a steady state condition quickly after shearing for about 5 to 10 minutes. Such fast breakup and buildup behavior are critical in many applications. One of such applications is for oil and gas drilling. During drilling, circulation might have to stop and start many times for various reasons. In a deep well, drill bits break more often, for example, and changing the bit often requires many hours. One of the most important requirements of any good drilling fluid is its ability to suspend cuttings and weight materials when circulation is stopped. If the solids are not kept in suspension during this time, their settling will result in deposition of solids on the bit which can become stuck. In order for the fluid to have an adequate suspending ability it must develop high gel strength quickly when the fluid is not in motion. Conventional drilling fluids with high gel strength usually require high energy to initiate circulation, generating pressure surges in the annulus while the flow is being reestablished. Although cation-exchanged Laponite suspensions have great gel strength at rest, the structure can be quickly broken. Therefore, they can be transformed into a low-viscosity fluid that does not induce significant friction losses during circulation and, yet, can quickly develop high gel strength after the pump is turned off, preventing solids from settling. It is noted that rheological properties of a thixotropic material depend not only on its initial strength but also on the shear rate and the shearing time, therefore, the measured values of these properties will

depend on how the sample is loaded into a viscometer and how long it is left at rest before shearing.

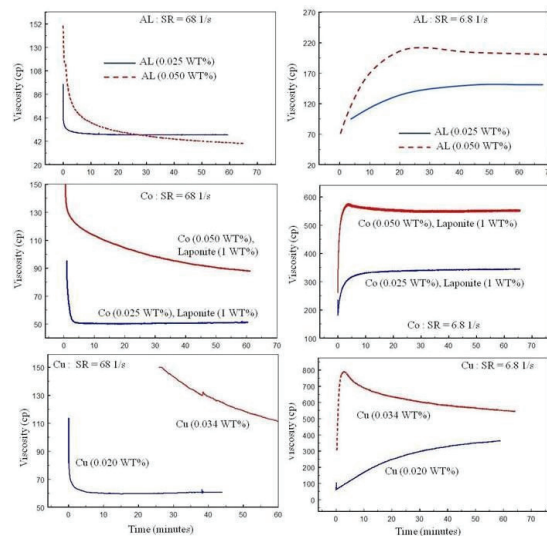


Figure 3. Changing viscosities of cation-exchanged Laponite suspensions during gel buildup and breakup; The suspensions were prepared by irradiating cation metal powder with DW and 1 weight percent laponite (measured at 25° C)

4. CONCLUSIONS

We have conducted a preliminary study on the use of laser-generated nanoparticles for maintaining rheological properties of Laponite suspensions at high temperature. To do so, we prepared cation-modified Laponite suspensions and examined the effects of Co, Al, and Cu, on the suspension structural, thixotropic, and rheological properties. To prepare the samples we used laser ablation of metal powder in liquid in the presence of Laponite and found that the technique can be used to successfully produce cation-modified Laponite crystals. Although the weight percent of the nanoparticles was negligibly small compared to that of Laponite, aqueous suspensions of these modified Laponite crystals were highly viscous with excellent shear thinning and thixotropic behavior. The fluid gelled quickly with significantly high gel strength when it was at rest nevertheless its structure was broken easily and it transformed into a low viscosity fluid quickly on shearing. Despite the fact that the laser-generated nanoparticle-Laponite mixtures were found to have promising shear thinning and thixotropic behaviors, the exact mechanism for the behavior was not identified by the characterization done so far. Nanoparticles and/or hydrated metal ions could be playing a role in the observed behaviors. In addition, the specific species comprising the

nanoparticles generated by the laser technique used in this study are not yet known. Answering these questions will be the goal of future investigations.

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