

Role of the Surface Treatment in the Deflocculation of Kaolinite

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Suspensions of untreated and properly treated Na-exchanged kaolinite have been subjected to rheological investigations using sodium hexametaphosphate (NaHMP) or sodium disilicate (DIS) as deflocculants. The treatment of the clay consisted of a 24 h contact with solutions of NaHMP or DIS and separation of the resulting solid phase. This was then used to form the suspensions subjected to the rheological measurements. The results indicate that the dispersion ability of each deflocculant is remarkably influenced by the type of treatment. In particular, with respect to the untreated kaolinite, the efficiency of DIS is dramatically increased when the clay has been previously treated with a NaHMP solution. On the other hand, a decrease in the dispersant ability of NaHMP is observed from the untreated kaolinite to the one previously treated with DIS.

I. Introduction

DEFLOCCULANTS are inorganic or organic chemicals able to produce a strong decrease in the viscosity of a suspension. They are used in all the stages of the ceramic processing in which the raw materials (such as the clays), handled as suspensions, need to maintain a viscosity value under control, independent of the particular flow or rest conditions that they are subjected to (storage in tanks, transportation through pipes and tubes, wet milling, casting procedure, etc.).^{1–4} Sodium silicates and polyphosphates are among the most used inorganic deflocculants in clay suspensions. Their performances, however, are very different and each of them acts properly in a peculiar range of operative conditions. The origin of these different dispersion abilities has to be sought in the different mechanisms of action, and the differences in the macroscopic properties of the suspensions, like apparent viscosity, are strictly related to the specific microscopic interactions between the deflocculant and the clay surface. In some cases, moreover, the combined use of silicates and polyphosphates imparts a kind of synergic effect in the deflocculation of clays.⁵

In a previous paper,⁵ the rheological behavior of mixtures of deflocculants was studied and compared with that of each single dispersing agent. The most relevant result was that, in the cases considered, the apparent viscosity response and the time-dependent behavior observed using the most efficient single deflocculant may also be yielded using a proper mixture. This fact could be a real economic advantage but, until now, no action model concerning deflocculant mixtures has been proposed. Moreover, several dispersing agents, such as silicates and hexametaphosphates, are able to induce chemical modifications in

the clay surface,^{6–9} even though this fact has not yet been clearly correlated to the deflocculation mechanism.

To make a contribution toward the understanding of the deflocculation mechanism of mixtures of dispersants, rheological investigations have been performed on suspensions of untreated and properly treated Na-exchanged kaolinite using sodium hexametaphosphate (NaHMP) or sodium disilicate (DIS) as deflocculant agents. The preliminary treatment of the clay consisted of a 24 h contact with solutions of NaHMP or DIS and separation of the resulting solid phase (the “treated” kaolinite). The aim of this paper is to establish how the efficiency of a deflocculant is changed when it acts on a kaolinite whose surface has been modified by temporary contact with another deflocculant.

II. Experimental Procedure

Well-ordered kaolinite KGa-1b was purchased by the Clay Minerals Society (Source Clay Repository, University of Missouri, Columbia, MO). Its characteristics are reported in Andreola et al.⁷ Sodium chloride, NaHMP, and DIS were Carlo Erba products. As both the investigated deflocculants (NaHMP and DIS) can strongly interact with ions¹⁰ such as Mg^{2+} and Ca^{2+} , and this can affect their dispersion activity, the kaolinite was completely sodium exchanged through several washings with 0.5M NaCl. The excess of chloride was then eliminated with distilled water. The kaolinite thus obtained (Na-kaolinite), dried at 50°C, was the starting material.

Na-kaolinite was subjected to a treatment consisting of a 24 h contact with a 15 mM solution of one of the deflocculants (NaHMP or DIS) followed by separation of the resulting solid phase (the treated kaolinite). In this way, two different solid samples were obtained: the one related to NaHMP treatment (hereafter HMP-kaolinite) and the other to DIS treatment (hereafter DIS-kaolinite). The specific procedure used was as follows: 12 g of Na-kaolinite was mixed in 50 mL of a 15 mM solution of deflocculant; the suspension obtained was shaken for 24 h in an orbital incubator (Stuart Scientific Orbital Incubator SI50, Redhill, U.K.) at room temperature and 200 rpm speed. The solid phase was then separated by centrifugation at 3500 rpm twice for 10 min (ALC Centrifuge PK110, Milan, Italy), washed with distilled water, and again centrifuged. The treated kaolinite thus obtained (HMP-kaolinite and DIS-kaolinite) was dried at 50°C. To ensure that the procedure itself did not introduce differences in the investigated materials, the Na-kaolinite used in the rheological measurements was also subjected to the same procedure substituting the deflocculant solution with simple distilled water. Pycnometric measurements did not show any difference in the density of untreated and treated kaolinites ($d = 2.65$ g/mL). Rheological measurements were performed under isothermal conditions at 30°C using a Couette System Control Rate Haake Viscosimeter RV20 (Haake Technik GmbH, Vreden, Germany), equipped with a coaxial cylinder-measuring sensor ZA1, just after the milling dispersion (10 min). The suspensions subjected

G. Franks—contributing editor

Manuscript No. 20953. Received September 4, 2005; approved October 5, 2005.

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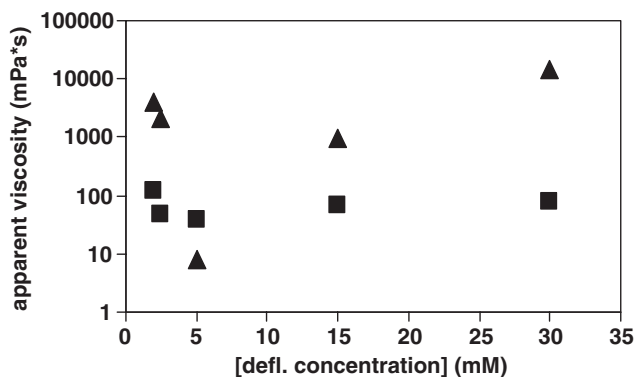


Fig. 1. Apparent viscosity values of Na-kaolinite suspensions at 30% v/v dispersed with DIS (▲) and at 45% v/v dispersed with NaHMP (■) plotted on a logarithmic axis as a function of deflocculant concentration, recorded at a shear rate of 50 s^{-1} .

to rheological measurements were prepared by adding a 5 mM deflocculant solution (NaHMP or DIS) to solid samples of Na-kaolinite (hereafter Na-kaolinite+HMP or Na-kaolinite+DIS), of HMP-kaolinite (hereafter HMP-kaolinite+HMP or HMP-kaolinite+DIS) and of DIS-kaolinite (hereafter DIS-kaolinite+HMP or DIS-kaolinite+DIS) at different volumetric fractions of the solid phase. The concentration of the deflocculant (5 mM) was chosen at around its higher dispersion efficiency in the range of the investigated volumetric fractions of the solid phase: it was almost the same for NaHMP and DIS (Fig. 1).

The rheological measurements were performed using a step procedure consisting of eight steps at different constant shear rates, each lasting 1 min. Preliminary measurements showed that a time duration of 1 min is enough for the shear stress to reach a steady-state condition. To cancel the previous rheological history of the samples, a “preshear” at a shear rate of 300 s^{-1} followed by a period of rest was applied. In the next six measuring steps, the shear rates were: 50, 100, 150, 200, 250, and 300 s^{-1} . The apparent viscosity values reported are the mean value of at least five measurements and were found to be reproducible within $\pm 6\%$.

III. Results and Discussion

Rheological measurements were performed on Na-kaolinite+DIS and on HMP-kaolinite+DIS at different solid phase volume fractions. Surprisingly, dramatic differences in the viscosity values of the two systems were observed (Fig. 2): in fact, at the same solid phase volume fraction, HMP-kaolinite+DIS invariably shows much lower viscosity values: at 40% of solid phase volume fraction (v/v) and shear rates of 100 and 300 s^{-1} the apparent viscosities found for Na-kaolinite+DIS were 1028

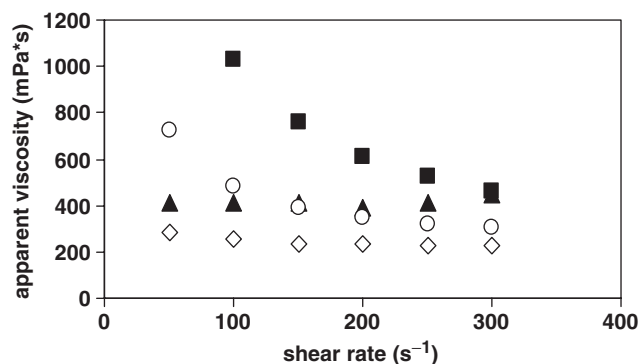


Fig. 3. Apparent viscosity values as a function of the shear rate for Na-kaolinite+DIS at 40% v/v (■), HMP-kaolinite+DIS at 56% v/v (▲), Na-kaolinite+HMP at 55% v/v (◇), and DIS-kaolinite+HMP at 55% v/v (○).

and $461 \text{ mPa} \cdot \text{s}$, respectively; however, in the case of HMP-kaolinite+DIS, at the same shear rates, the measured values were only 25 and $23 \text{ mPa} \cdot \text{s}$, respectively. The observed decrease in viscosity of the suspensions obtained by replacing Na-kaolinite with HMP-kaolinite is, therefore, quite relevant, over one order of magnitude.

Moreover, in our experimental configuration, the limit value of measurability of the viscosity (hereafter, the limit value of measurability) was observed to be slightly over 40% v/v in the case of Na-kaolinite+DIS and quite over 57% v/v in the case of HMP-kaolinite+DIS. It is worth noting that the apparent viscosity of HMP-kaolinite+DIS at 57% v/v is even lower than that of Na-kaolinite+DIS at 40% v/v. Differences can also be observed in the shear rate dependence of the apparent viscosity. In fact, even if a direct comparison between them is not possible because of the very relevant differences in viscosity measured at the same solid-phase fraction, as a matter of fact, HMP-kaolinite+DIS at high solid-phase volume fractions (55%–57% v/v) shows a rather limited or negligible dependence of the apparent viscosity on the shear rate (Fig. 3), while the viscosity of Na-kaolinite+DIS at the limit value of 40% v/v strongly decreases with increasing shear rate (Fig. 3). Thus, the treatment of kaolinite with NaHMP confers a certain degree of stability to the suspensions toward the changes in shear rate. This property, together with the very relevant decrease in viscosity, is very important from a technological point of view and makes the HMP-kaolinite+DIS system suitable for all the steps of the industrial processes. In all the ranges of investigated solid-phase volume fractions, no meaningful difference in the rheological responses of Na-kaolinite+DIS and DIS-kaolinite+DIS was observed (Fig. 2).

A somewhat opposite rheological behavior as a function of the solid-phase volume fraction, however, has been shown by the Na-kaolinite+HMP and DIS-kaolinite+HMP systems. In fact, in this case, Na-kaolinite+HMP is characterized by apparent viscosity values and by a limit value of measurability, respectively, lower and higher than those of DIS-kaolinite+HMP (Fig. 4). Moreover, at high solid-phase volume fractions, Na-kaolinite+HMP exhibits a more limited dependence of the apparent viscosity on the shear rate than DIS-kaolinite+HMP (Fig. 3): the untreated kaolinite, therefore, shows a “better” rheological behavior than the treated one. Na-kaolinite+HMP and HMP-kaolinite+HMP show a quite similar rheological behavior (Fig. 4).

HMP is known to adsorb on aluminol edge sites^{6,11} forming an inner-sphere surface complex and, as a consequence of the treatment of Na-kaolinite with a NaHMP solution, the HMP-kaolinite obtained retains a certain amount of HMP bound onto the surface. The presence of this charged species could be the reason for the increase in dispersion efficiency of DIS solution. DIS, in fact, may interact with the kaolinite surface through a condensation reaction between silanol groups of the defloccul-

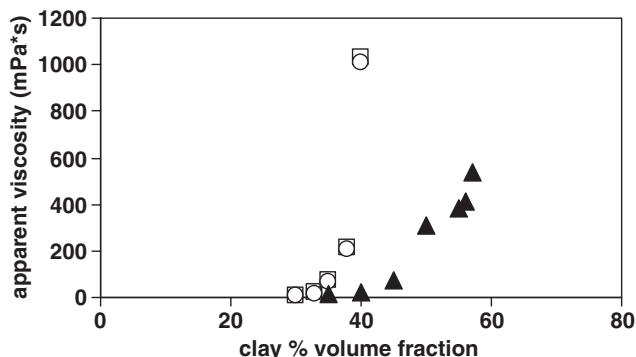


Fig. 2. Apparent viscosity values, recorded at a shear rate of 100 s^{-1} , as a function of the solid % volume fraction for Na-kaolinite+DIS (□), DIS-kaolinite+DIS (○), and HMP-kaolinite+DIS (▲).

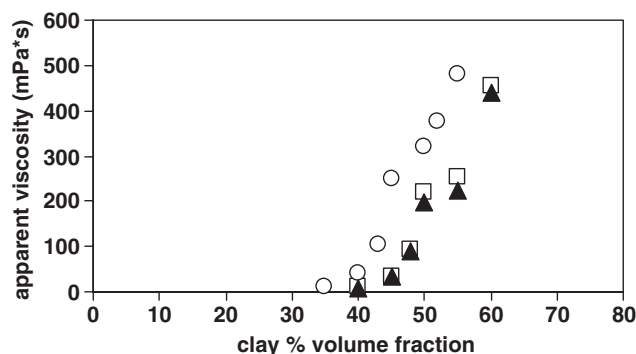


Fig. 4. Apparent viscosity values, recorded at a shear rate of 100 s^{-1} , as a function of the solid % volume fraction for Na-kaolinite+HMP (□), DIS-kaolinite+HMP (○), and HMP-kaolinite+HMP (▲).

ant and surface hydroxyls of the clay but also through hydrogen and van der Waals bonds.^{6,12} Therefore, the presence of already adsorbed HMP (on edge sites only) does not affect the overall interaction ability of DIS in a relevant manner. On the contrary, the treatment with DIS could cause extensive condensation between DIS and the aluminol sites^{6,12} of the kaolinite (edge) surface, and this could (partially) prevent the adsorption of HMP, thus reducing the efficiency of its deflocculant activity.

IV. Conclusions

The obtained results indicate that Na-kaolinite+HMP shows the lowest viscosity, confirming that NaHMP is the most effi-

cient dispersing agent. However, HMP-kaolinite+DIS also reveals a remarkably lower viscosity than Na-kaolinite+DIS, suggesting that a simple proper treatment of kaolinite can dramatically increase the efficiency of a middling but cheap deflocculant such as DIS.

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