

RHEOLOGICAL PROPERTIES OF ACID-ACTIVATED BENTONITE DISPERSIONS

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Abstract—Acid-activated bentonites are utilized in many applications, including those that depend on their rheological properties and behavior, but little information is available regarding the rheological characteristics of this important industrial material. The purpose of this study was to investigate the effects of solids concentration, salt concentration, and pH value on the shear rate, shear stress, and other flow parameters of acid-activated bentonite suspensions. Activated Na-bentonite was prepared using sulfuric acid. Flow curves of the suspensions were modeled using the Herschel-Bulkley equation, which performed well for this system. The Herschel-Bulkley yield stress increased with the solids concentration and showed a maximum and minimum at the NaCl concentrations of 0.001 M and 0.01 M, respectively, and increased again slightly with further increases in NaCl concentration. The yield stress was at a maximum and a minimum at pH values of ~5 and ~7, respectively, followed by a slight increase with pH under alkaline conditions. The variations in dispersion rheological properties can be attributed to the change in the particle-association modes under different conditions.

Key Words—Acid-activated Bentonite, Herschel-Bulkley Model, NaCl Concentration, pH, Solids Concentration.

INTRODUCTION

Bentonite is used extensively in a wide range of applications *e.g.* in the oil industry and for environmental protection. Natural bentonites usually do not exhibit sufficient adsorption and catalytic properties for some of these purposes, so they are treated in order to enhance these properties (Saoussen *et al.*, 2006; Zorica *et al.*, 2006). Treatments include reaction with inorganic acids such as HCl, HNO₃, and H₂SO₄ to remove some impurities and thereby to significantly increase specific surface area and pore structure (Mills *et al.*, 1950; Heyding *et al.*, 1960; Komadel *et al.*, 1996; Jovanovic *et al.*, 1996; Van Rompaey *et al.*, 2002; Komadel, 2003; Brezovska *et al.*, 2005; Grzegorz and Dorota, 2006; Noyan *et al.*, 2007). The surface area, porosity, and pore-size distribution of acid-activated bentonite depend on the mineralogical and chemical composition of the activated bentonite, type and concentration of the inorganic acid used in the process, and on the temperature and time of activation (Noyan *et al.*, 2007). Acid-activated bentonites have been used in various applications such as adsorbents, catalysts, bleaching earths, carbonless copy paper, electrodes, organoclays, nanocomposites (Eisenhour and Reisch, 2006; Önal and Sarıkaya, 2007), and more recently as pigment in ink-jet-paper coating (Londo *et al.*, 2001). Understanding the rheological properties of bentonite

dispersions is essential to determine the optimal production conditions for these applications (Besq *et al.*, 2003). In addition, a systematic study of the variations in rheological properties with particle size, the types of clay-particle association, suspension pH, and the charge distribution on the clay surface can lead to a better understanding of the interactions between clay particles, because the rheological properties of bentonite dispersions can be greatly affected by the interactions between charged clay particles as well as the interactions between clay and water molecules (Günister *et al.*, 2006). Permien and Lagaly (1994a) studied the flow behaviors of Na-bentonite and Na-montmorillonite dispersions in the presence of acids and found that the shear stress increased steeply when pH decreased from 5 to 3. The dispersion rheological properties, however, were independent of the kinds of acid as long as the specific adsorption of the acid or its anion was excluded (Janek and Lagaly, 2001). The rheological properties of acid-adjusted dispersions can be affected by the release of structural cations such as Al³⁺ or Mg²⁺, related to the proton attack of smectite particles (Banin and Ravikovitch, 1966; Davey and Low, 1971; Chen *et al.*, 1990; Permien and Lagaly, 1994b).

Although many have studied the properties of bentonite, the rheological properties of dispersions of bentonite and, in particular, acid-activated bentonite, are not fully understood (Janek and Lagaly, 2001). A rheological study of acid-activated bentonite dispersions was, therefore, undertaken and the results are reported here. The objective was to examine the effects of solids concentration, NaCl concentration, and pH value on the rheological properties.

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MATERIALS AND METHODS

Materials

Na-bentonite, or activated Na-bentonite, was obtained from Fenghong Clay Chemicals Co., Ltd. (Zhejiang, China) and had the following major-element chemistry: 57.74% SiO₂, 16.65% Al₂O₃, 1.47% Fe₂O₃, 2.36% CaO, 3.63% MgO, 4.14% Na₂O, 0.67% K₂O, 0.097% TiO₂, and 0.028% MnO₂, and 13.08% loss on ignition (LOI). The specific surface area of the sample was 6.2 m²/g.

H₂SO₄ (98%) and all other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the reagents were analytical grade.

Preparation of acid-activated bentonite

Na-bentonite was treated with sulfuric acid using a wet-chemistry method in which the mass ratio of liquid to solid was 4:1. Specifically, the mixture of sulfuric acid and Na-bentonite was kept at 90°C for 2 h in a water bath. The solid product was collected and washed with distilled water until free of SO₄²⁻ (tested using a 2% BaCl₂ solution). The products were then dried at 105°C for 6 h, broken down to 5–10 mm, and then ground to <74 μm using an A11 basic analytical mill (IKA, Germany). The product pH value and specific surface area were 2.75 (10%) and 26.1 m²/g, respectively. The major-element chemistry of the acid-activated bentonite was: 70.12% SiO₂, 14.46% Al₂O₃, 1.24% Fe₂O₃, 0.58% CaO, 2.71% MgO, <0.10% Na₂O, 0.73% K₂O, 0.12% TiO₂, and 0.021% MnO₂, and 9.89% LOI.

Suspension preparation

The dispersions of acid-activated bentonite were prepared at concentrations of 5 wt.%, 10 wt.%, 15 wt.%, and 20 wt.% by mixing dried, acid-activated bentonite with deionized water at an agitation rate of 450 rpm for 30 min. Previous dispersing tests showed that for acid-activated bentonite, the concentration of 10 wt.% corresponded to the best dispersing properties, so the effects of the salt concentration as well as the pH value on the rheological properties were examined at this suspension concentration in which the NaCl concentrations were 10⁻³ M, 10⁻² M, 10⁻¹ M, and 1 M, respectively. The sample pH was adjusted using 1 M NaOH solution. The pH values were measured using a PHS-2C pH meter (Shweiyee, China).

Rheological measurements

The rheological properties were measured using a rheometer AR 550 (TA Instruments, USA) equipped with parallel plate geometry 40 mm in diameter. All rheological measurements were conducted at 25°C. The flow curves were analyzed using the Herschel-Bulkley equation (Herschel and Bulkley, 1926):

$$\tau = \tau_y + K(\dot{\gamma})^n \quad (1)$$

where τ and τ_y are the shear stress and the yield stress, respectively; $\dot{\gamma}$ is the shear rate; K is the flow consistency index (units of mPa·s^{*n*}), while n is defined as flow behavior index and is a dimensionless quantity.

XRD analysis

The structural changes in the Na-bentonite after the acid treatment were examined using a Bruker D8X X-ray powder diffractometer (XRD) with 0.15418 nm CuK α radiation, operating at 40 mA and 40 kV. The scanning rate was 2°2 θ min⁻¹. The specific surface area of the sample was measured by N₂ adsorption (ST2000 Specific surface area analyzer, Beijing Analytical Instrument Technology Co., Ltd., China).

Scanning electron microscopy

The particle association at different pH values was examined using a Quanta200 scanning electron microscope (SEM) (FEI Company, Holland).

RESULTS

Effects of dispersion concentration

Rheological properties are usually sensitive to solids concentration (Günister *et al.*, 2006). The rheological behaviors of acid-activated bentonite dispersions were measured at several concentrations. The effect of acid-activated bentonite solids concentration on flow curves of shear stress-shear rate (Figure 1) showed that they were well described by the Herschel-Bulkley model, and the characteristic rheological parameters were extracted by fitting the experimental data to this model. Variation in the Herschel-Bulkley yield stress as a function of solids concentration (Figure 2), the flow behavior index (Figure 3), and the flow consistency index (Figure 4) revealed that the shear stress, the yield stress, and the flow

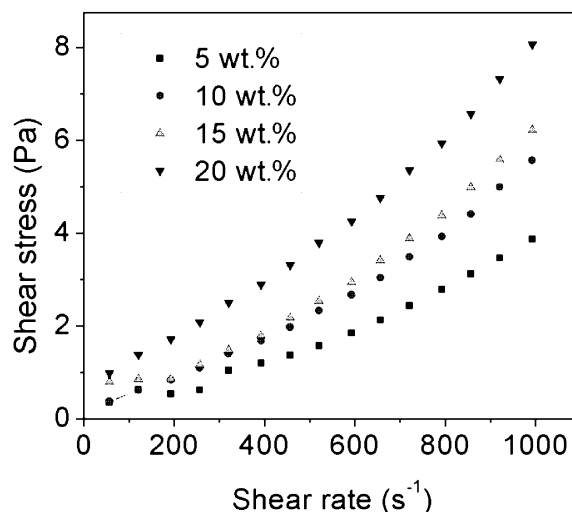


Figure 1. The effect of solids concentration on flow curves of shear stress-shear rate.

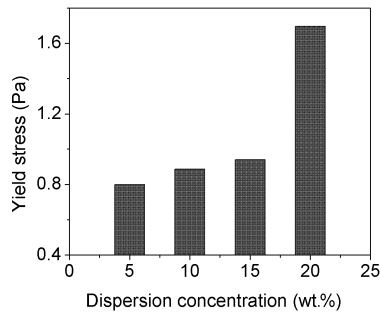


Figure 2. Variation of yield stress with solids concentration.

consistency index increased with solids concentration and, in particular, both the shear stress and yield stress increased sharply as the solids concentration increased from 15% to 20%. On the other hand, the flow behavior index decreased with the solids concentration.

Effects of NaCl concentration

The rheological properties of acid-activated bentonite dispersions at different NaCl concentrations (Figure 5), the yield stress (Figure 6), the flow behavior index (Figure 7), and the flow consistency index (Figure 8) as a function of NaCl concentration revealed that a maximum yield stress was obtained at the NaCl concentration of 0.001 M while a minimum occurred at 0.01 M. Both the shear stress and yield stress increased with further increases in NaCl concentration. In addition, the flow consistency index decreased with NaCl concentration but then leveled off at 0.1 M NaCl concentration. The flow behavior index increased with increasing NaCl concentrations up to 0.1 M, but decreased slightly when the concentration exceeded 1 M.

Effects of pH

The rheograms of 10% acid-activated bentonite dispersion at different pH values (Figure 9) and the variation of the yield stress as a function of pH (Figure 10) showed that a maximum and minimum yield stress were observed at pH values of ~5 and 7,

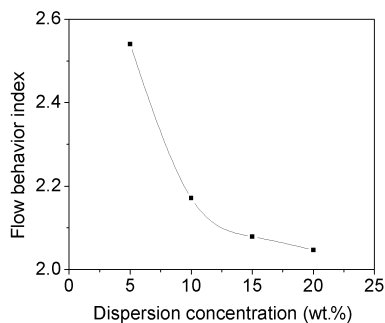


Figure 3. Variation of the flow behavior index with solids concentration.

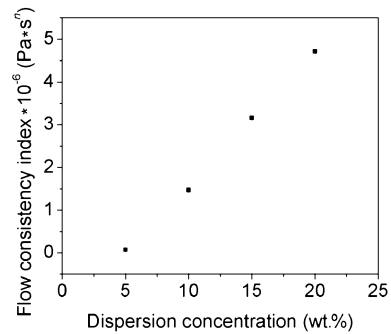


Figure 4. Variation of the flow consistency index with solids concentration.

respectively. Both pH values were much greater than the pH of the original acid-activated bentonite dispersions (pH = 2.75). In addition, the yield stress increased only slightly as the pH increased to alkaline conditions.

The variation of the flow behavior index (Figure 11) and the flow consistency index (Figure 12) as a function of pH revealed that the flow behavior index decreased with pH under acidic conditions, reached the minimum at ~pH 7, and increased slightly with further pH increases. On the other hand, the flow consistency index changed slightly in a pH range from 2.75 (the original pH value of acid-activated bentonite dispersions) to 7, and reached the minimum at pH ~5. In contrast, the flow consistency index increased significantly with alkaline pH.

DISCUSSION

The layer spacing of bentonite was checked with XRD before and after acid treatment. The patterns (Figure 13) showed that acid treatment shifted the d_{001}

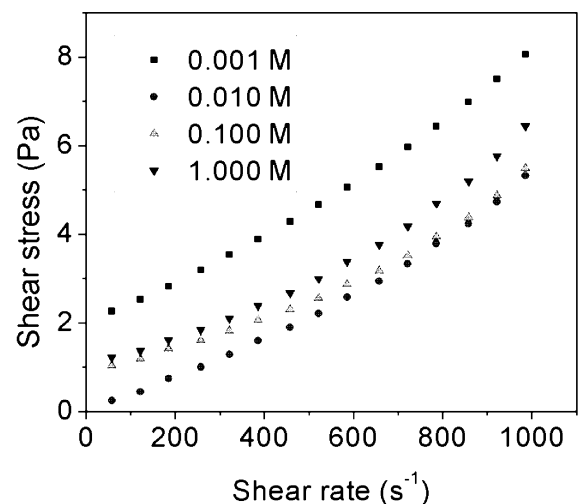


Figure 5. The effect of NaCl concentration on the flow curves of the shear stress-shear rate.

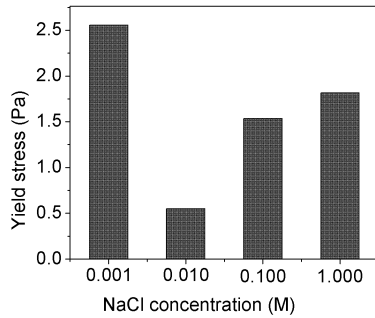


Figure 6. Variation of yield stress with NaCl concentration.

peak of the original sample from 1.26 nm to 1.49 nm, indicating that the impurities in the interlayer may have been dissolved, and the exchangeable cations may have been replaced by H^+ ions of small radius. Meanwhile, the cations such as Al^{3+} and Mg^{2+} were leached from the octahedral and tetrahedral sheets (Zorica *et al.*, 2006), which was verified by comparing the chemical analyses of the sample with that of the product. All of these could contribute to the increase in both the basal spacing and the specific surface area.

Characteristic of bentonite particles is a negatively charged basal surface (F) and a pH-dependent charge at the edges (E). Consequently, three modes of clay particle association are possible in suspension, *i.e.* EF, EE, and FF. Specifically, in a situation where the pH is less than the isoelectric point, whereby the edge has a positive net charge, the EF association would occur. On the contrary, when the pH is greater than the isoelectric point, the edge is negatively charged and, consequently, all EF, EE, and FF associations can be formed (Van Olphen, 1977; Benna *et al.*, 1999; Lagaly and Ziesmer, 2003). In the present study, because the pH of the acid-activated bentonite dispersions was 2.75, which was much less than the isoelectric point of 7, the EF association with a 'house-of-cards' structure was formed in the dispersions. In addition, other than the experiments in which the effects of pH were examined, all other experiments were conducted under acidic conditions.

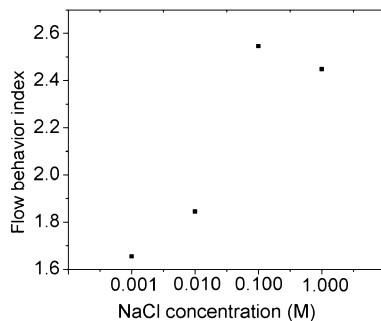


Figure 7. Variation of the flow behavior index with NaCl concentration.

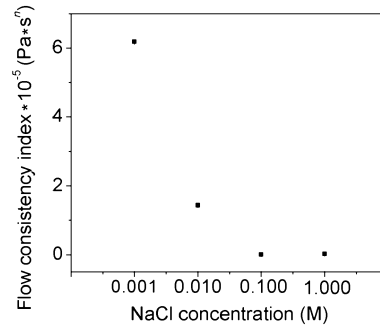


Figure 8. Variation of the flow consistency index with NaCl concentration.

In the present study, the Herschel-Bulkley model was found to fit the rheogram data well under all conditions. The flow curves were, therefore, evaluated and analyzed based on the Herschel-Bulkley rheological parameters, in particular the yield stress.

At pH 2.75, the Herschel-Bulkley yield stress increased with the dispersion concentration due to the increase of clay particle number in the dispersions (Günster *et al.*, 2006). The more clay particles, the more inter-particle EF combinations were possible, which led to a significant increase in the network structure strength.

Inorganic salts could destabilize aqueous dispersions of bentonite. The electrical double layer surrounding the clay mineral particles, which stabilized the dispersions, was compressed by the salt cations (Van Olphen, 1977; Luckham and Rossi, 1999), which could have changed the mode of particle association thus affecting the inter-particle network. This network, in turn, would strongly affect the mechanical and flow properties of the clay suspensions. Specifically, under acidic conditions, both

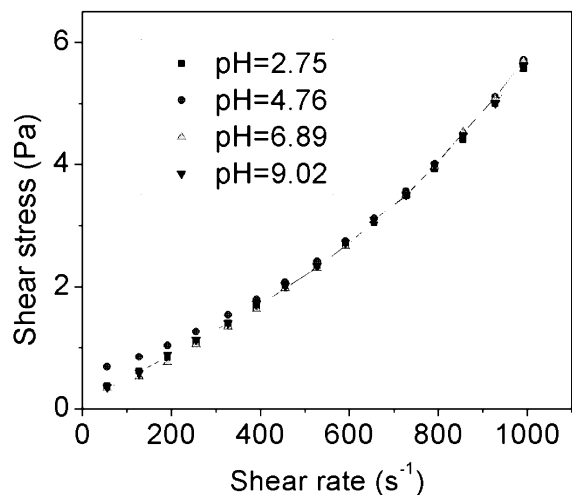


Figure 9. The effect of pH on the flow curves of the shear stress-shear rate.

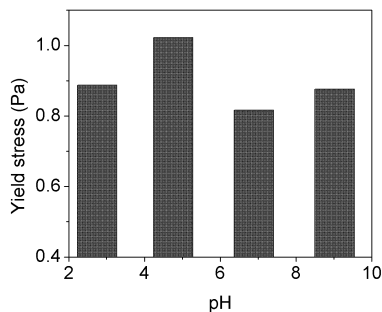


Figure 10. Variation of yield stress with pH.

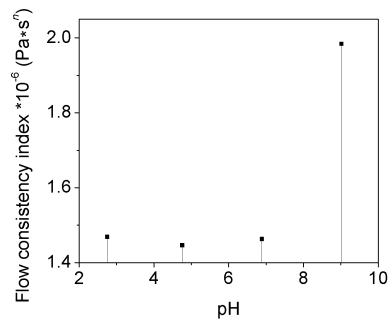


Figure 12. Variation of the flow consistency index with pH.

negatively and positively charged sites coexisted on the surface of the clay mineral particles. At low electrolyte concentrations, the positive charge at the edge of clay layers could have been screened by the negative electrostatic field from the face of the basal plane and, therefore, could not be 'felt' by approaching particles (Tombácz and Szekeres, 2004). Above a threshold electrolyte concentration, the positively charged edge could not be screened completely. The inter-particle attraction between the oppositely charged parts may have led to the edge-to-face (EF) association.

In the absence of electrolyte, the EF association cannot be formed because of the screening of the positive double layer around the plate edge, which may be responsible for the observed small shear stress and yield stress. At a small NaCl concentration, 0.001 M, which was probably larger than the threshold electrolyte concentration, the inter-particle attraction coming from the electrostatic attraction between the oppositely charged parts may result in a strong EF association. As a result, the yield stress increased. At the still greater NaCl concentrations, the electric double layers around the clay plate face and edge were further compressed. Consequently, the interactions between clay plate faces and between the face and edge of clay plates were attractive because of the domination of van der Waals attraction over the electrostatic repulsion (Permien and Lagaly, 1994b). As a result, the major association structure was FF, because the area of the clay plate

face was much larger than its edge (Benna *et al.*, 1999; Lagaly and Ziesmer, 2003). The yield stress, therefore, decreased explaining why the minimum yield stress was observed at the NaCl concentration of 0.01 M. The result was similar to that reported by Yildiz *et al.* (1999), in which it was attributed to the electroviscous effect. At NaCl concentrations >0.01 M, however, the yield stress increased again, which can be attributed to the attractive forces between the particles, according to Yildiz *et al.* (1999).

Under acidic conditions, a large amount of positive charge was on the edge of the bentonite lamellae. Consequently, the attractive interaction between the positively charged edge and the negatively charged plate face, and, therefore, the yield stress, increased with the decrease in pH (Tombácz and Szekeres, 2004). However, the maximum yield stress (Figure 10) was not at the smallest pH value studied here (2.75); due to the shielding of the positive double layer around the plate edge in the absence of electrolytes, the strong EF association cannot be formed at the natural pH of 2.75. In addition, the pH regulator, NaOH, is itself an electrolyte which may lead to the appearance of the maximum yield stress around pH 5 due to the compression of electric double layers around the clay plate face and edge, forming a strong EF structure. Furthermore, at

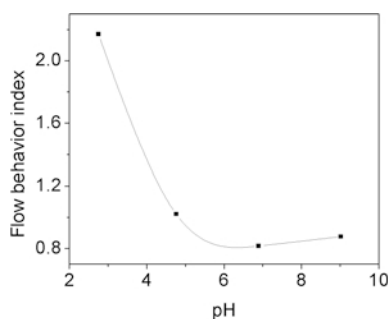


Figure 11. Variation of the flow behavior index with pH.

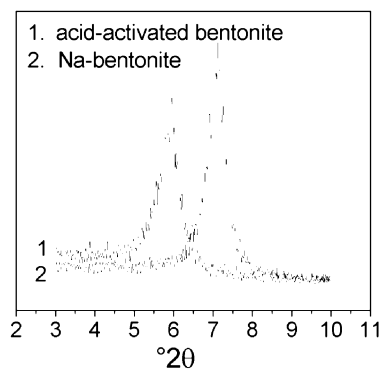


Figure 13. XRD patterns of the Na-bentonite and acid-activated bentonite.

pH values close to 7, where the edge charge was zero, the yield stress decreased, which may be due to the formation of the FF association. Finally, under alkaline conditions where the pH is above the isoelectric point, both the edge and face of the clay plates were negatively charged, the diffuse double layer was compressed by the electrolyte, and the van der Waals attractive force was dominant, leading to EF, EE, and FF associations (Benna *et al.*, 1999; Lagaly and Ziesmer, 2003). The slight increase in yield stress here may be attributed to the larger number of EE associations than at the lesser NaCl concentrations.

The particle association was examined by scanning electron microscopy (SEM) at different pH values (Figures 14 and 15). The images were produced *in situ* in an environmental SEM (FEI Quanta 200, Holland). The results showed that under acidic conditions, the clay platelets seemed to associate in EF mode (Figure 14). Under alkaline conditions, the association mode was both FF and EE (Figure 15). The modes can be attributed to variation in the relative orientation between two platelets: the faces of two platelets are somehow perpendicular to each other when the edges are positively charged, and parallel to each other when the edges are negatively charged (Luckham and Rossi, 1999).

CONCLUSIONS

The effects of solids concentration, salt concentration, and pH on the rheological properties of acid-activated bentonite dispersions were studied. The results showed that the rheograms were well fitted by the Herschel-Bulkley model. Rheological data from the suspension varied due to the different type of particle association. With increasing solids concentration, both

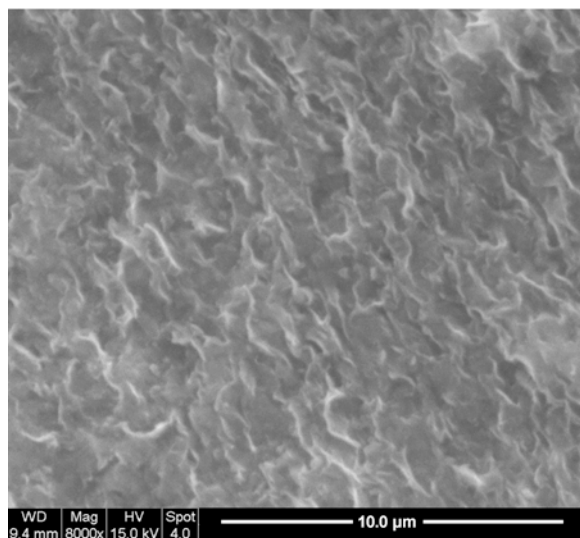


Figure 14. SEM image of 10% acid-activated bentonite at pH = 5.

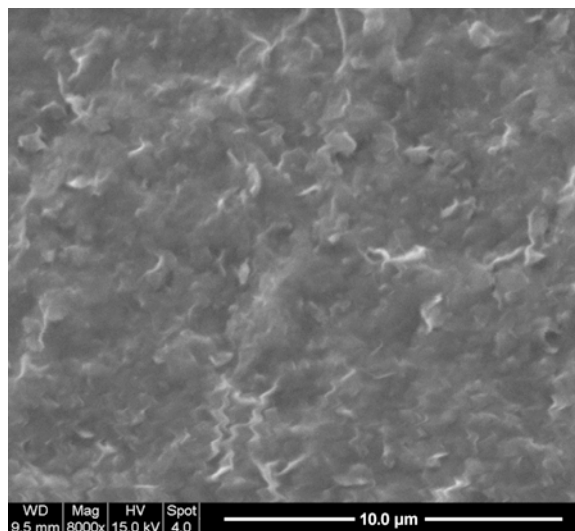


Figure 15. SEM image of 10% acid-activated bentonite at pH = 9.

the yield stress and the flow consistency index increased, but the flow behavior index decreased. For salt addition to the dispersions, the maximum yield stress was observed at 0.001 M and a minimum at 0.01 M, respectively. The maximum is due to the strong EF association and the minimum to the weak FF association. The flow behavior index increased up to the NaCl concentration of 0.1 M whereas it decreased slightly at 1 M. For the range of pH values studied, the yield stress showed a maximum and minimum around pH values of ~5 and ~7, respectively. The flow behavior index decreased with pH value until a pH of 7 was reached and then increased slightly in alkaline conditions (pH >7). The change may have been due to the change in edge charge with pH value, leading to the EF association under acidic conditions with EE, EF, and FF associations persisting under alkaline conditions.

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