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Thixotropic properties of aqueous suspensions containing cationic starch and aluminum magnesium hydrotalcite-like compound

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Abstract

The rheological properties of aqueous suspensions consisting of cationic starch (CS) and positively charged aluminum magnesium hydrotalcite-like compound (HTlc) were investigated. Special emphasis was placed on the thixotropic phenomena. With the increase of mass ratio (R) of HTlc to CS, the equilibrium viscosity (η_{eq}) and the consistency coefficient (m) values of the suspensions increase in the range of neutral and alkaline pH (higher than 6.5) while decrease in the range of acid pH (lower than 6.5). With the increase of pH value, the η_{eq} and m values of the suspensions in the R range of 0–0.08 studied increase initially and then decrease, appearing a maximum value at about pH 7.41 ± 0.25. The CS/HTlc suspensions display viscid character and the yield point of the suspensions was not observed except the suspension with $R = 0.08$ in the pH range of 7.66–9.70, which showed a yield point and viscoelasticity. The CS/HTlc suspensions may display different thixotropic types: negative, complex or positive thixotropy, depending on pH and R value. The thixotropic type of the CS/HTlc suspension may be transformed from negative (pure CS solution), through complex ($R = 0.02$), into positive thixotropy ($R = 0.05$ and 0.08) with the increase of R in the studied R range of 0–0.08, and the thixotropic strength of the suspensions increases initially and then decreases with pH value in the pH range studied. The mechanism of the thixotropic phenomenon is discussed.

Keywords: Rheology; Thixotropy; Suspension; Cationic starch; Hydrotalcite-like compounds

1. Introduction

The term 'thixotropy' was introduced to describe the reversible isothermal gel/sol/gel transformation induced by shearing and subsequent rest. Actually, it is a shear-thinning phenomenon with time factor, now called positive thixotropy. There are many systems such as drilling mud, paint and coating and so on displaying positive thixotropy. On the contrary, negative thixotropy, also called antithixotropy, is a rheological phenomenon characterized by a flow-induced increase of the viscosity in time. The phenomenon of negative thixotropy was first described over 50 years ago and was observed for a wide range of polymer solutions [1–3] and some solid–water dispersions [4,5]. In 1989, Hou et al. [6] found another thixotropic phenomenon, named complex thixotropy, in the suspension of aluminum magnesium hydrotalcite-like compounds (HTlc)/Na-montmorillonite, where positive thixotropic character and negative thixotropic character, early and late, appeared for a given suspension. From then on, a lot of researches [7–10] concerned with the thixotropy of HTlc/clay suspensions have been done and it was found that under different conditions, the suspensions can display different thixotropic properties, i.e. the type of thixotropy of the suspensions may be influenced by measuring condition, pH and electrolyte etc. Up to now, all the complex thixotropic phenomena were observed in the suspensions consisted of HTlc having permanent positive charges and clay, montmorillonite or kaolinite, having permanent negative charges. An interesting and important question needed to be made clear is whether the complex thixotropy is a universal natural phenomenon existing in suspensions. So, to find new suspensions displaying complex thixotropy and to investigate the methods controlling the thixotropic types of suspensions have become an important research focus. This paper will present

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the experimental results about the thixotropy of cationic starch (CS)/Al–Mg-HTlc suspensions.

Cationic starch (CS) is a positively charged polymer, and a large-scale commercial product that has widespread uses in many fields [11–17] such as papermaking chemical, topical drug delivery systems and oilfield applications. HTlc is a positively permanently charged inorganic materials, having the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}]^{x-}\cdot mH_2O$ [18], where M^{II} and M^{III} are divalent and trivalent metal cations, respectively; A^{n-} is the charge compensating anions, or gallery anion; m is the number of moles of co-intercalated water per formula weight of the compound; x is the number of moles of M^{III} per formula weight of the compound. The HTlc is structurally characterized as containing brucite (magnesium hydroxide)-like layers where some divalent metal cations have been substituted by trivalent metal cations to form positively charged sheets. The metal cations occupy the centers of octahedra whose vertexes contain hydroxide ions. These octahedra are connected to each other by shared edges to form an infinite sheet. The cationic charges in the layers have been termed permanent positive charges, and they are compensated by the hydrated anions between the stacked sheets. In recent years, interest has grown in the preparation, the characterization and the properties of HTlc because HTlc may be widely utilized in many fields such as catalysts and catalyst precursors, antacids, the preparation of pigments, the treatment of waste water, sunscreen agents, anionic exchangers, sorbents and rheology modifiers for both aqueous and nonaqueous system [7,19–22].

Although the extensive studies on CS [11–17,23,24] and HTlc [6–10,18–22], respectively, have been reported, the rheological behavior of CS/HTlc suspensions has not received attention. The aim of this study was to examine the rheological, especially thixotropic, properties of CS/HTlc suspensions. Special emphasis was placed on the influences of pH and mass ratio (R) of HTlc to CS on the thixotropy of the suspensions. The results can lead us to understand the microstructure change within CS/HTlc suspensions under shear and at rest, and it is helpful to apprehend the thixotropic phenomenon more deeply.

2. Experimental

2.1. Materials

2.1.1. Cationic starch

The corn starch used in the experiments was supplied by Xingmao Corn Developing Ltd. (Zhucheng, China) and of 99.6% purity. The cationic substituent is quaternary ammonium, with chloride as counter-ion. The CS sample consists of 72% of branchend amylopectin, and 28% of linear amylose. Elemental analysis of the CS sample was performed with an elemental analyzer (VarioEL III, Elementar Analysensysteme GMbH) to show that the percent contents of carbon, hydrogen and nitrogen are 40.70, 7.18 and 1.55, respectively. The degree of substituent (DS) is 0.2. Average molecular weight was analyzed using gel penetration chromatography (Agilent1100, America) to be 5.01×10^5 g/mol.

2.1.2. Cationic starch stock solution

The dry CS sample was dissolved in water to a concentration of 20 g/l and stirred with a magnetic stirrer for 4 h, after which it was heated at 90 °C for 30 min in order to dissolve sufficiently. The stock solution was stored in a refrigeratory at 4 °C and used within 14 days in order to avoid substantial level of degradation.

2.1.3. Aluminum magnesium hydrotalcite-like compound

Mg–Al HTlc sol was synthesized by a co-precipitation method [7]. The molar ratio of Mg/Al, pH and solid content of the obtained HTlc sol are about 2:1, 9.50 and 12.86 wt%, respectively. The average diameter and isoelectric point (IEP) of the HTlc were determined by using zetasizer 3000 automatic particle diameter and zeta potential determination apparatus (Malvern Instruments Ltd.) to be 105 nm and pH 11.2, respectively.

2.1.4. CS/HTlc suspensions

Appropriate amount of HTlc sol and deionized water were added in 20 g/l CS stock solution, stirring vigorously to obtain the CS/HTlc suspensions with different mass ratio (R) of HTlc to CS. The concentration of CS in all suspensions was fixed at 15 g/l, and the HTlc content changed from 0 to 0.12 wt% for suspension with R from 0 to 0.08. For simplicity, suspensions with $R = 0$ (pure CS solution), 0.02, 0.05 and 0.08 were signed as S0, S2, S5 and S8, respectively. The pristine pH of the 15 g/l CS solution is 8.60, and that of CS/HTlc suspensions is about 8.80. The expected pH values of the suspensions were adjusted by 1 M HCl and NaOH solutions. After aged for about 24 h, the pH of suspensions, which was employed in the experiments, was determined again before the experiments.

All other chemicals were analytical grade.

2.2. Methods

2.2.1. Rheological curve and viscosity

The rheological curves were measured by a controlled stress rheometer (RS75, Haake Inc., Germany) equipped with the Z41 concentric cylinder system at 25 ± 0.1 °C. After equilibration, test samples were sheared at a programmed rate increasing from 0 to 1000 s^{-1} in 8 min to obtain flow curves. The flow curves were evaluated by using the following rheological models:

1. Power law model:

$$\tau = m\dot{\gamma}^n, \quad (1)$$

where τ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), m is the consistency coefficient (Pa s^n), and n is the fluidity index (dimensionless).

2. Herschel–Bulkley model:

$$\tau = \tau_0 + m\dot{\gamma}^n, \quad (2)$$

where τ_0 is yield stress.

The viscosity (η) can be caculated from:

$$\eta = \tau/\dot{\gamma}. \quad (3)$$