Colloid Polym Sci 276:274–277 (1998)

SHORT COMMUNICATION

H. Wan-Guo
S. De-Jun
H. Shu-Hua
Z. Chun-Guang
W. Guo-Ting

Study on the thixotropy of aluminum magnesium hydroxide–Na-montmorillonite suspension

Received: 4 February 1997
Accepted: 15 October 1997

H. Wan-Guo (✉) · S. De-Jun · H. Shu-Hua
Z. Chun-Guang · W. Guo-Ting
Institute of Colloid and Interface Chemistry
Shandong University
Jinan, Shandong 250100
P.R. China

Abstract In this paper, the thixotropy of the aqueous suspension consisting of aluminum magnesium hydroxide (AMH) possessing permanent positive charges and Na-montmorillonite possessing permanent negative charges was studied. Besides positive thixotropy and negative thixotropy, a novel thixotropic phenomenon was found, i.e., a given system studied may display, early and late, positive thixotropic character and negative thixotropic character, we describe it as "complex thixotropy". The content of the suspension and electrolyte may influence the forms of thixotropy of the suspension studied.

Key words Dispersion – thixotropy – aluminum magnesium hydroxide – montmorillonite – rheology

Introduction

The term "thixotropy" was originally proposed by Peterfi to describe a rheological phenomenon defined as a reversible decrease in viscosity with shearing time when a fluid flows at constant shear rate [1]. 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 etc. displaying positive thixotropy. Shear-thickening phenomenon with shearing time factor, i.e., a reversible increase in viscosity with time at constant shear rate, was found later, which was called "negative thixotropy" [1–3]. But it was found that most of the systems displaying negative thixotropy were polymer solutions and a few solid–water dispersions showed negative thixotropy. In 1978 Heckroodt [4] found that the suspensions of clays from South Africa displayed negative thixotropy. Recently, Chen Zhong-Qi et al. [5, 6] have found that the suspensions of hydrolyzed polyacrylaminde (HPAM)–Na-montmorillonite and HPAM–silica may display negative thixotropy under certain conditions when investigating its rheological characteristics and have proposed the "shield effect" theory to explain the cause of negative thixotropy in polymer–solid suspension. However, during our recent studies on thixotropy of solid aqueous dispersion, the negative thixotropy has also been found in the suspension of aluminum magnesium hydroxide (AMH)–Na-montmorillonite (Mt). Moreover, we have also found a novel thixotropic phenomenon: a given system may display, early and late, positive thixotropic character and negative thixotropic character, which has not been reported in literature; we described it as "complex thixotropy" in the paper. AMH particles are positively charged and Mt particles are negatively charged under the condition studied, so the AMH–Mt suspension studied is a special system consisting of charged particles of opposite signs on which not much work has been reported also. The novel rheological phenomenon should be related to the particularity of the system and indicates a special mechanism of structure destruction and formation processes in the system which cannot be explained with the previous theories [1, 3]. A preliminary investigation on the novel rheological phenomenon is described in this paper.

N 930

Experimental

AMH sol and Mt suspension used in the study are the same as that used in Ref. [7], their pH values were previously adjusted to 9.5 with NaOH and HCl solutions before use. The mean particle size and anion exchange capacity of AMH are 0.11 μm and 2.8 mmol/g, respectively. The mean particle size and cation exchange capacity of Mt are 3.57 μm and 1.0 mmol/g, respectively.

The following method was used to study the thixotropy in the work with reference to experiments described by Heckroodt [4] and Chen Zhong-qi [5, 6, 8]. AMH sol and Mt suspension were mixed with a certain ratio (R) of AMH to Mt by stirring for 20 min using a high-speed mixer (Model GJ-1, Jiangyin Second Electrical Machinery Plant), then the viscosity (η_t) of the system at different "settling time" (t) was measured at a constant very low shear rate of $10\,s^{-1}$ with rotational viscosimeter (Model ZNN-D6, Qingdao Camera Factory). The time interval from stopping vigorous stirring to starting measurement was strictly controlled to be 10 s. θ is used to describe the type and strength of thixotropy:

$$\theta = G(\eta_t - \eta_0) ,$$

where, η_0 is the viscosity at $t = 0$, G is a proportionality coefficient and define $G = 1$ for simplicity [6]. Increase of θ with t, i.e., recovery of interparticle structure during the gentle stirring, means positive thixotropy while the decrease of θ with increasing of t, i.e., destroying the interparticle structure formed through the mechanical coagulation during the gentle stirring, means negative thixotropy.

The concentration (%) used in the paper is weight percent (w/w) if without special indication.

Results and discussion

Thixotropy of AMH–Mt suspension

Figures 1 and 2 show the thixotropic curves at various R values of AMH to MT with the Mt contents of 4.00% and 2.00%, respectively. It may be observed that pure Mt suspensions ($R = 0$) of 4.00% and 2.00% display positive thixotropy and its thixotropy may be apparently affected by AMH and may show different types and strength at different R. For the systems of high Mt content of 4.00% (see Fig. 1), at $R = 0.10$ the θ value increases initially and then gradually reaches a constant value with t, showing positive thixotropy, and at $R = 0.20$ and 0.30 the θ values initially increase also, but then decrease showing a maximum value in the thixotropic curves. The initial increase of θ value with t is a positive thixotropic characteristic while the succeeding decrease with t is a negative thixotropic characteristic, which indicates that the system studied may display different thixotropic characteristics during different setting time intervals. This novel thixotropic phenomenon has not been reported before, we call it "complex thixotropy". The suspensions at $R = 0.40$ and 0.50 do not display apparent complex thixotropy;

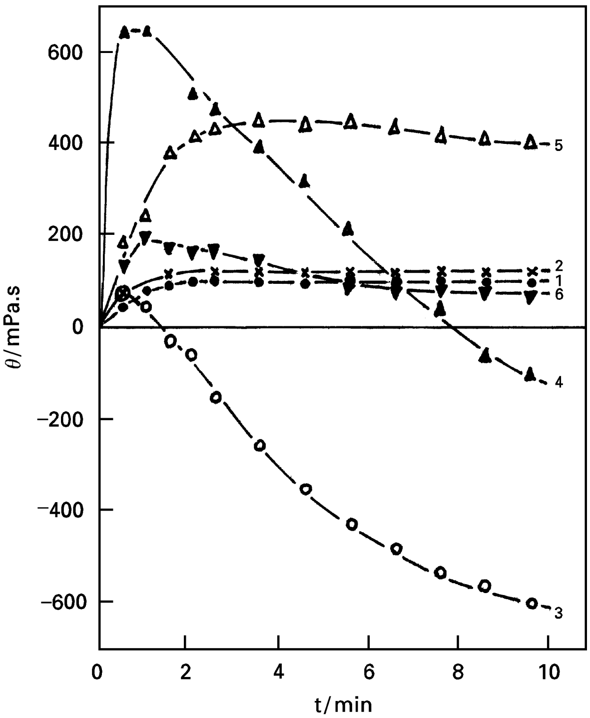

Fig. 1 Effect of AMH/Mt ratio on thixotropy of 4.00% MT system: R: (1) 0; (2) 0.10; (3) 0.20; (4) 0.30; (5) 0.40; (6) 0.50

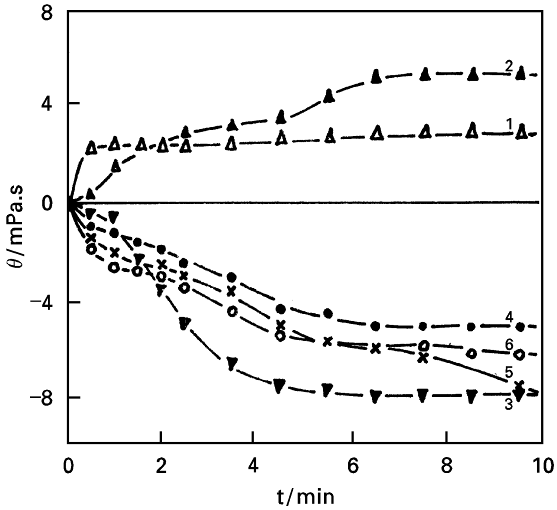

Fig. 2 Effect of AMH/Mt ratio on thixotropy of 2.00% MT system: R: (1) 0; (2) 0.10; (3) 0.20; (4) 0.30; (5) 0.40; (6) 0.50

however, they show positive thixotropy as a whole. For the systems of lower Mt content of 2.00% (see Fig. 2), the thixotropy is positive at $R = 0.10$, which is in agreement with that of the systems of 4.00% Mt, and in the R range from 0.2 to 0.5 the thixotropy of the systems is negative, which is not in agreement with that of the systems of 4.00% Mt. The above results show that AMH–Mt suspensions may display positive, negative and complex thixotropy, respectively, depending on the solid contents and relative ratios of AMH to Mt.

Effect of electrolyte

Figure 3 shows the effect of NaCl on the thixotropy of AMH–Mt system with 4.00% Mt at $R = 0.30$. It can be seen that the θ values decrease with increase of NaCl concentration. The θ value is usually used to express the relative strength of thixotropy [5, 6, 8], the higher the θ value, the stronger the positive thixotropy and the weaker the negative thixotropy. On the contrary, the lower the θ value, the weaker the positive thixotropy and the stronger the negative thixotropy. So, the results in Fig. 3 show that NaCl enhanced the negative thixotropy of the system and weakened the positive thixotropy of the system.

Figure 4 shows the thixotropic curves of the 4.00% Mt system with 0.10 mol/l NaCl at various R values. Comparing Fig. 4 with Fig. 1 it can be seen that the presence of NaCl transferred the thixotropic type from positive to negative for the systems with $R = 0$ and 0.10, and from complex to negative for the system with $R = 0.2$. However, it did not change the thixotropic type of the system at $R = 0.3$ but apparently enhanced its negative thixotropy, and it weakened apparently the positive thixotropy of the systems with $R = 0.40$ and 0.50. These results support the suggestion that NaCl may enhance the negative thixotropy and weaken the positive thixotropy of the AMH–Mt suspension indeed.

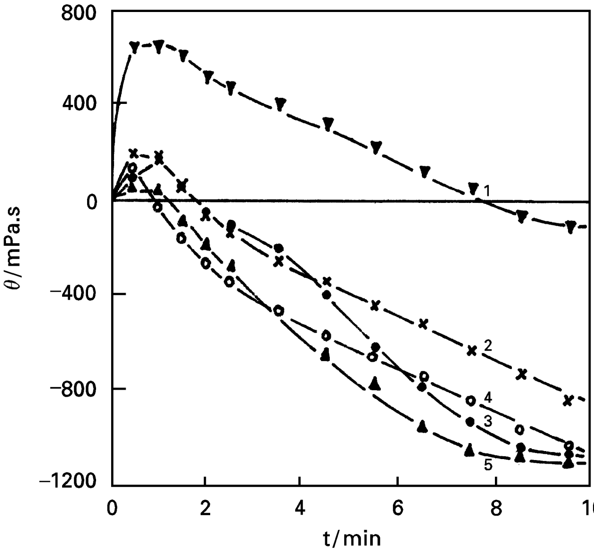

Fig. 3 Effect of NaCl on the thixotropy of system with 4.00% MT and $R = 0.30$. Contents of NaCl (mol/l): (1) 0; (2) 0.02; (3) 0.04; (4) 0.06; (5) 0.10

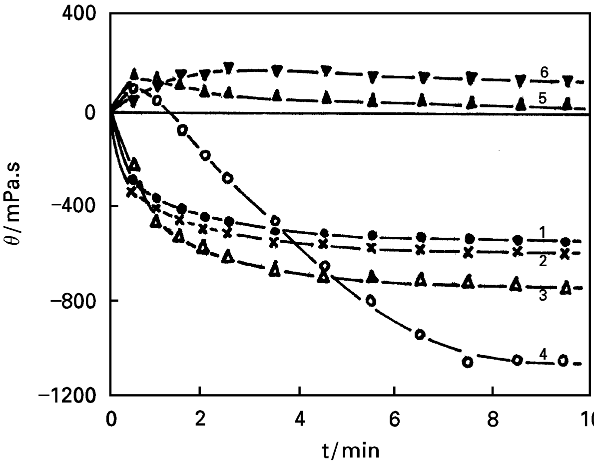

Fig. 4 Thixotropy of system with various AMH/Mt ratio in the presence of NaCl. (NaCl Content: 0.10mol/l, Mt content: 4.00%) R: (1) 0; (2) 0.10; (3) 0.20; (4) 0.30; (5) 0.40; (6) 0.50

Mechanism of thixotropy

Up to now, the mechanism of the thixotropic phenomenon has not been thoroughly understood. Formerly, much work has been done on the positive thixotropy: the widely known mechanism is that structures existing among the particles may be gradually destroyed by shearing thereby to decrease the viscosity of the system, which shows shear-thinning behavior, and after stopping shearing the structures may be formed again, but the structure formation process has a relaxation time, so the viscosity of the system increases gradually with setting time. This consideration may explain the positive thixotropic results observed in clay suspension of the Mt content of 4.00% and 2.00%. Most studies on the negative thixotropy are concerned with polymer solutions and many theories such as "aggregation theory", "crystallization theory" and "network theory" have been proposed [3, 9] but they cannot be used to explain the negative thixotropy of a suspension [8]. The "shield effect" theory proposed by Chen Zhong-qi et al. [5] may explain the negative thixotropic results of the polymer–solid suspensions, but cannot explain the results of AMH–Mt suspensions. The special thixotropic behaviors in the AMH–Mt suspensions indicate the existence of special interactions between the particles in the system. Therefore we should investigate the mechanism of the special thixotropy according to the speciality of the system studied with reference to the previous theories.

In AMH–Mt suspension of pH 9.5, AMH particles possess positive charges while Mt particles possess negative charges [10]. So, some structures may exit because of electrostatic attraction between the two kinds of particles [7]. The high-speed stirring may destroy part of the structures among particles and thereby enhance dispersity of the system obviously. During settling, the destroyed structures may recover through the following three forms. First form: the two kinds of particles approach each other to form the steric continuous net-work structures over the whole system, viscosity of the system will increase gradually and θ value will increase with t, i.e., positive thixotropy. Second form: the two kinds of particles may directly form discrete densed floc units, which decreases the viscosity of the system, showing that θ decreases with increasing t, i.e., negative thixotropy. For this system, the vigorous stirring may enhance the form of the steric continuous net-work structures over the whole system by increasing dispersity of the system and thereby may increase the structure strength. Third form: the structure formation process in the system may be divided into two stages: first stage, forming steric continuous structures the same as the first form above which shows positive thixotropic character; second stage, forming dense floc units the same as the second form above which shows negative thixotropic character. On the whole, the system possessing the two stages will show complex thixotropy.

The structure formation process in dispersion is dependent on the concentration and relative ratio of two kinds of particles. It may be seen from Figs. 1 and 2 that the systems of lower Mt content (2.00%) are more likely to display negative thixotropy, which is because, the floc units are formed easily under this condition, and that the systems at higher Mt content (4.00%) are more likely to display complex and positive thixotropy, which is because steric continuous structures are more likely to form. When the authors studied heterocoagulation of AMH–Mt suspension [7], we found that the floc units were formed easily in a certain range of R value, and beyond which the coagulation became weaker. In the R range of stronger coagulation, the negative thixotropy are more likely to occur and beyond the R range the coagulation is weaker and positive thixotropy are more likely to occur. When the tendency to form floc units is similar to that to form steric continuous structures, the system may show complex thixotropy. It can be seen from Fig. 1 that in the R range lower than 0.10 and higher than 0.40 the systems of 4.00% Mt display positive thixotropy, which shows weaker coagulation, however, in R range of 0.20–0.30 the systems display complex thixotropy, which shows the tendency to form floc units is similar to that to form steric continuous structures under this condition. It can be seen from Fig. 2 that systems of 2.00% Mt with R lower than 0.10 display positive thixotropy which shows weaker coagulation, and the systems in the R range of 0.20–0.50 display negative thixotropy which shows stronger coagulation.

Electrolyte may enhance the coagulation of the system, so the addition of NaCl decreases the θ value and increases negative thixotropy. By comparing Fig. 4 with Fig. 1 it can be seen that the 0.10 mol/l NaCl transforms the systems with $R = 0$ and 0.10 from positive thixotropy to negative thixotropy and the system with $R = 0.20$ from complex thixotropy to negative thixotropy, and weakens the positive thixotropy of systems at $R = 0.40$ and 0.50.

In addition, we have studied the changes of θ with t at shear rates of 170 and 340 s^{-1}, and found the results were similar to that at a shear rate of 10 s^{-1}. The "hysteresis circles" of various systems studied have been measured, also, and did not find any valuable law. It is a problem to be investigated that if the "hysteresis circles" of suspension can accurately reflect the complex thixotropy.

Conclusions

The aqueous suspension consisting of aluminum magnesium hydroxide and Na-montmorillonite may display positive and negative thixotropy in different conditions. In addition, it may show a novel thixotropic phenomenon called "complex thixotropy". The content of the suspension and the addition of electrolyte may influence the forms of thixotropy of the suspension studied.

Acknowledgement We are grateful to Prof. Chen Zhong-Qi (Qingdao Institute of Chemical Technology, P.R. China) for his checking and approving our paper and making valuable suggestions.

References

1. Chen Zong-Qi et al (1991) Chem Bull 2:31–34
2. Crane J, Schiller D (1956) J Polymer Sci 23:93–97
3. Quadrat O (1985) Adv Colloid Interface Sci 24:45–75
4. Heckroodr RO, Ryan W (1978) Trans J Brit Ceram Sci 77:180–183
5. Chen Zhong-Qi et al (1989) Acta Chim Sinica 47:152–157
6. Chen Zhong-Qi et al (1990) Acta Chim Sinica 48:666–672
7. Hou Wan-Guo et al (1995) Chem Res Chinese Universities 11(4):316–322
8. Chen Zhong-Qi et al (1991) Acta Chim Sinica 49:462–467
9. Bradna P, Quadrat O, Dupuis D (1995) Colloid Polym Sci 273:642–647
10. Hou Wan-Guo et al (1995) Chem J Chinese Universities 16(8):1292–1294