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On the Modeling of the Rheological Behavior of Bentonite Dispersions in Polymer Solutions

Dominique Dupuis[1]*, Karim Bekkour[2], K. Ben Azouz[1,2]

[1] Laboratoire de Physique et Mécanique Textiles, 11 rue A. Werner, 68093 Mulhouse cedex, France
[2] Laboratoire ICube, Université de Strasbourg – CNRS 2, rue Boussingault, 67000 Strasbourg, France

*Corresponding author: dominique.dupuis@uha.fr
Fax: x33.3.89596339

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Abstract:
Bentonite dispersions in polymer solutions may behave as gel like materials. Under stress, the structure formed at rest is progressively destroyed and a solid-liquid transition occurs. The rheological characterization of such kind of systems is often done by applying stress ramps of the sample. A simple Herschel-Bulkley equation is not convenient to fit the answer of the material to the ramp since it does not take in account the effect of time. The models for yield stress fluids involving two viscosity levels are not convenient too since they don't take in account the elastic behavior at low stresses. We propose in this paper two equations in order to determine some parameters characterizing the rheological behavior of such systems. The results obtained both in oscillatory and permanent shear are compared according to Winter's representation and a rescaling of the complex modulus is proposed to superimposed the data in the solid/liquid transition region.

Key words:
bentonite, carboxymethylcellulose solution, yield stress, Cox-Merz rule

1 INTRODUCTION

Many applications bring in dispersions of clay particles in various kinds of suspending media: cosmetics formulation, fiber technology or drilling fluids for oil recovery. For instance, the presence of clay as a filler in a polymeric matrix improve fire resistance of fibers [1, 2]. In water-based drilling fluids, bentonite dispersions in carboxymethylcellulose (CMC) aqueous solutions are widely used [3]. The specific multiscale organization of the clay particles and the balance between the particle/particle and particle/suspending medium interactions lead to the formation of various types of particle associations [4]. Then, complex rheological behavior may be observed: thixotropy, existence of a yield stress, gel-like behavior. Complex flow curves are obtained [5]. When the suspending liquid is a salt aqueous solution, sol-gel transitions depend on the particle concentration and on the ionic strength [6]. In a polymer solution or in a polymeric matrix, intercalation of the polymeric chains between clay platelets may occur [7, 8]. Usually, the rheological properties of clay dispersions are very sensitive to the mechanical history (especially the stirring time) of the samples and are time-dependent [9–11]. To model thixotropic phenomena, a structural kinetic approach is sometimes used [12, 13]. Long-term ageing (up to 1000 days) effects have also been investigated in case of laponite/PEO-water solution [14].

The concept of yield stress and its experimental determination have already been widely discussed in the literature. The basic simple idea is that, for a yield stress fluid, the material flows if the applied stress σ is larger than a critical one σ_y. Below this value, there is no flow. This behavior can be modelled by the well known Bingham or Herschel-Bulkley equations. But, in fact, the transition between "no flow" and "flow" is not so easy to determine. In other words, what physically happens below the yield stress? The review paper by Barnes [15] presents experimental results on different materials such as penicillin broth, carbopol dispersions or blood. The results, plotted as viscosity versus the shear stress, display a high Newtonian plateau value followed by a sharp decrease of the viscosity at the yield stress. Such two viscosity level curves can be modelled using an Ellis model or a composite Ellis model [16]. But, in other systems, a transition between a solid-like and a liquid-like behavior is observed. In case of physical gels, carbopol gels for instance, the transition is not abrupt but occurs over a

0.5HVB5. For B5, there is a smoother increase of the strain at low stress in the range which had been explored. So, the second equation is introduced to take in account this effect. Five parameters are defined: the classical parameters of the H-B model, a critical strain related to the transition between the "yielding" and the flow regimes and an exponent a related to the stress-strain dependence at low shear stresses.

The behavior of the two systems characterized by the same bentonite concentration seems quite similar; nevertheless, the origin of these gel-like behaviors is not the same. Previous studies had shown that ageing has different effects on these two systems [27]: one observes an increase of the yield stress for B5 which becomes more and more elastic (below the yield stress). This is the contrary for 0.5HVB5, which flows easier according to the ageing. Bentonite is a montmorillonite, characterized by a multi-scale organization [41]: platelets are regrouped and form primary particles, which are themselves associated to form aggregates. In water at pH10 according to [4, 28, 29] bentonite particles form quite open 3D structures and ageing favors swelling of particles and the increase of inter-particules connections. The value of the parameter *a*, smaller than 1, is probably related to a progressive breakdown of the microstructure of the gel. In the CMC/water solution, X-ray diffraction spectra show that there is no exfoliation of the clay platelets and no intercalation of the polymeric chains. The polymer prevents the exfoliation. So, the network results from connections between clay particles or aggregates through the chains and the crosslinks should be quite labile. The yield stress determined for B5 is larger than for 0.5HVB5, probably due to stronger interaction energy between the particles. The modulus *G* is larger for 0.5HVB5 than for B5 what incites to assume a greater density of the crosslinks in the first case. Oscillatory measurements give a lot of information on the material in the linear regime. Cox-Merz rule does not apply in our cases since the systems are complex and modification of their microstructure occurs under stress. We use the representation proposed by Winter and compare the shear viscosity versus stress to the complex viscosity versus the complex modulus. This representation emphasizes the "solid-liquid" transition. A rescaling of the magnitude of the complex modulus, based on the parameters determined by the models leads to a quite good superposition of transition zones obtained in permanent and oscillatory shear flows. Finally, it is important to observe that the systems are time dependent and the models represent the answer of the systems to a given solicitation and do not provide "intrinsic" properties of the material. Nevertheless, it allows comparison between different materials submitted to the same solicitation.

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