

RHEOLOGICAL CHARACTERIZATIONS OF DISPERSIONS OF CLAY PARTICLES IN VISCOELASTIC POLYMER SOLUTIONS

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ABSTRACT:

In this work, we consider model fluids which are dispersions of clay particles in aqueous solutions of carboxymethyl cellulose. Their rheological properties are measured in both steady and oscillatory shear flows. We present the experimental results obtained for different polymer concentrations and for three different molecular weights of the polymer. The clay is a bentonite sample and the particle concentration is fixed to a value of 5 %. The mechanical properties of these materials is the result of a competition between different mechanisms: association-dissociation of aggregates of particles, adsorption of polymer on the particles and desorption of solvent molecules from the particles, bridging of the particles by long polymer chains.

ZUSAMMENFASSUNG:

In dieser Arbeit werden Modelldispersionen aus Tonpartikeln in einer wässrigen Carboxymethylzellulose-Lösung betrachtet. Ihre rheologischen Eigenschaften werden sowohl in stationären als auch in oszillatorischen Scherströmungen untersucht. Wir präsentieren die experimentellen Resultate, die für verschiedene Polymerkonzentrationen und für drei unterschiedliche Molekulargewichte des Polymers erhalten wurden. Das Tonmineral ist ein Bentonit, und die Partikelkonzentration beträgt 5 %. Die mechanischen Eigenschaften dieser Materialien resultieren aus einem Wechselspiel verschiedener Mechanismen: Assoziation und Dissoziation der Partikelaggregate, Adsorption des Polymers auf den Partikeln und Desorption der Lösungsmittelmoleküle von den Partikeln sowie Brückenbildung zwischen den Partikeln durch lange Polymerketten.

RÉSUMÉ:

Nous considérons dans ce travail des dispersions de particules dans des solutions aqueuses de carboxymethyl cellulose. Les propriétés rhéologiques de ces fluides sont mesurées à la fois en écoulement de cisaillement permanent et oscillatoire. Nous présentons des résultats expérimentaux obtenus pour différentes concentrations en polymère et pour trois masses molaires différentes. L'argile considérée est une bentonite et sa concentration est fixée à 5 %. Les propriétés mécaniques de ces matériaux sont le résultat d'une compétition entre différents mécanismes : association et dissociation des agrégats de particules, adsorption du polymère sur les particules, désorption des molécules de solvant, pontage entre les particules par les longues chaînes de polymère.

KEY WORDS: carboxymethyl cellulose, bentonite, particle suspension, rheology, dispersions, viscoelasticity, aging

1 INTRODUCTION

The study of the rheological properties of suspensions of solid particles in complex fluid, is of great importance since these kinds of compounds are developed in a lot of applications in areas as different as the development of drilling fluid for oil recovery [1] or fiber science and technology [2]. For instance, dispersions of titanium

dioxide in foam may be used for coating of fabrics [3]. Another example is the introduction of clay particles in a polymer melt in order to improve the fire resistance of the fibers [2–4]. Many results offer a new promising way for flame retarding textiles with a permanent effect at relatively low cost and keeping the basic properties of the textiles [2]. Polymer-clay is very attractive due to the fact that small amount of

In water, there is probably a dissociation of the aggregates and perhaps a partial exfoliation of the clay particles leading to the formation of an open tri-dimensional structure with an elastic behaviour as it can be seen from oscillatory measurements. In the polymer solution, at the beginning of the aging process, a yield stress can be determined especially in the case of high polymer concentration and/or molecular weight. Along aging, this yield stress tends to disappear and the system becomes more fluid. Initially, large aggregates are present in the dispersion. The stirring of the sample every day would lead to the rupture of the aggregates in smaller ones while the penetration of the macromolecules within these aggregates becomes easier together with their adsorption on the clay particles. For a young system, the shape of the curve of Figure 3 means that different mechanisms successively occur to explain the sharp decrease of the viscosity [30, 34]. There is probably formation of a thin depletion layer in the vicinity of the solid surfaces of the rheometer geometry which acts as a lubrication layer. As the shear stress increases, the rupture of the large aggregates induces a further fall of the viscosity. Then, the orientation of the particles and the conformation change of the macromolecules in the flow takes place leading to a shearthinning behaviour.

Rossi et al. [12] explain that, a consequence of the adsorption of polymer on the particles is the desorption of solvent molecules from the surface of particles and water molecules may be transferred from the surface to the bulk. In the equilibrium state, the system does not consist of large bentonite aggregates dispersed in a polymer solution but of small aggregates coated by polymer in a less concentrated polymer solution. This argument combined with the existence of the depletion layer could explain the Figure 15 where the viscosity of CMC1HVB5 is smaller than CMC1HV.

The oscillatory measurement in the linear domain (i.e. in the limit of low shear stresses) characterizes the structure not perturbed by the flow. The addition of particles in a low polymer concentrated solution leads to a rise of the moduli (Figure 12) by two order of magnitude for $c_p = 0.1\%$. While for $c_p = 2.5\%$, the order of magnitude of the moduli is the same than for the polymer solution but the shape of the mechanical spectra is different. In the first case $c_p = 0.1\%$, corresponding to a dilute/semi-dilute regime, the polymer chains connect the particles and aggregates and an elas-

tic network is formed. For low molecular weight chains (LV on Figure 13) G' is much larger than for HV. The exfoliation is not cancelled by the presence of polymer and there is probably a combination of the effect observed for B5 and the crosslinks formation due to the presence of the polymer. When c_p increases, in the semi dilute/concentrated regime, the mechanical properties of the network is mainly controlled by the macromolecular chains and the elastic modulus increases with the molecular weight (Figure 14).

In some systems in polymer melts, the absence of terminal zone is related to incomplete relaxation due to physical jamming with a solid-like behaviour, because of the mesoscopic structure of highly anisotropic clay tactoids [10, 35]. From our mechanical spectra, the behaviour appears to be that of physical viscoelastic gels, with a terminal zone shifted towards lower frequencies as polymer concentration increases, corresponding to longer lifetimes of network junctions. The mechanical behaviour of the systems bentonite/aqueous polymer solutions considered here is the result of a competition between different mechanisms:

- Association-dissociation of aggregates of particles
- Adsorption of polymer on the particles and desorption of solvent molecules from the particles
- Bridging of the particles by long polymer chains

Then, different kinds of elastic networks may be formed which are destroyed when the shear stress exceeds some critical value, leading to the flow of the systems.

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