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Rheology of Laponite-scleroglucan hydrogels

R. Lapasin [a,*], M. Abrami [b], M. Grassi [a], U. Šebenik [c]

[a] University of Trieste, Engineering and Architecture Department, Piazzale Europa, I-34127, Trieste, Italy
[b] University of Trieste, Life Sciences Department, Cattinara Hospital, Strada di Fiume 447, Trieste I-34149, Italy
[c] University of Ljubljana, Faculty of Chemistry and Chemical Technology, Večna pot 113, 1000 Ljubljana, Slovenia

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ABSTRACT

Both Laponite and scleroglucan can find several applications in various fields (from industrial to biomedical one) in virtue of their peculiar features and rheological properties displayed in aqueous phases. Structural states of Laponite dispersions strongly depend on concentration and ionic strength. When attractive and repulsive interparticle interactions are so effective that they lead to arrested states (attractive gel or repulsive glass), the rheological behavior of the dispersion undergoes a sharp transition, from quasi-Newtonian to markedly shear thinning and viscoelastic. Conversely, scleroglucan solutions gradually change to weak gels with increasing polymer concentration. The present work is concerned with aqueous Laponite-scleroglucan mixed systems, obtained according to different preparation modes, and is aimed at examining how much the content and proportion of both components affect the viscoelastic and flow properties of the mixed system.

1. Introduction

Both scleroglucan, a neutral biopolymer, and Laponite, a synthetic clay, have separately found numerous applications in various industrial fields as well as in pharmaceutical and biomedical areas, by virtue of the structural features and rheological properties which are displayed, when they are dissolved or dispersed in water at sufficiently high concentration.

Scleroglucan is a nonionic polysaccharide secreted exocellularly by filamentous fungi of the genus *Sclerotium*. Its primary structure consists of a linear backbone of (1,3)-β-linked D-glucopyranosyl residues bearing a single (1,6)-β-linked D-glucopyranosyl unit every three sugar residues of the main chain (Rinaudo & Vincendon, 1982). Both in aqueous solution and in the solid state, scleroglucan adopts a highly ordered, rigid, triple helical tertiary structure (triplex), which consists of three individual strands composed of six residues in the backbone per turn. The three strands of the triplex are held together by interstrand hydrogen bonds at the center of the triplex. The (1 → 6)-linked β-D-glucopyranosyl side groups protrude from the outside of the triplex, so preventing intermolecular aggregation and polymer precipitation (Bluhm, Deslandes, Marchessault, Pérez, & Rinaudo, 1982; Fariña, Siñeriz, Molina & Perotti, 2001; Palleschi, Bocchinfuso, Coviello, & Alhaique, 2005; Yanaki & Norisuye, 1983). The triplex conformation is destabilized only in dimethyl sulfoxide or strong alkaline conditions and is characterized by a high rigidity which is responsible of the peculiar properties exhibited by aqueous scleroglucan solutions in a wide pH range and even at relatively high temperatures. A soft transition from sol to weak gel properties with increasing polymer concentration can be detected in both continuous and oscillatory shear tests (Grassi, Lapasin, & Pricl, 1996; Lapasin, Pricl, & Esposito, 1990). As triplex clustering increases leading to the formation of a three-dimensional hydrogel network, shear thinning behavior becomes more marked and ultimately an apparent yield stress can be individuated from flow curves, thixotropic responses becomes more and more evident, and a progressive transition is observed in the mechanical spectra with prevailing elasticity over the whole frequency window.

Due to the marked shear thinning behavior of its hydrogels, scleroglucan is used as thickener and suspending agent to impart adequate rheological properties and improve stability of disperse systems in several industrial sectors (Lapasin & Pricl, 1995). Nonionic polymers usually show only slight interactions with nonionic and cationic surfactants and can be conveniently employed for the preparation of stable cosmetic O/W emulsions since both polymer and surfactant mixtures can contribute independently and positively to the stabilization of the dispersed phase (Bais, Trevisan, Lapasin, Partal, & Gallegos, 2005). Scleroglucan is not toxic and does

* Corresponding author.
E-mail addresses: rlapasin@alice.it, romano.lapasin@dia.units.it (R. Lapasin), MICHELA.ABRAMI@phd.units.it (M. Abrami), mario.grassi@dia.units.it (M. Grassi), Urska.Sebenik@fkkt.uni-lj.si (U. Šebenik).

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not alter blood or living tissues; when applied to skin or eyes it does not cause sensitization. In addition, it belongs to the group of biological response modifiers, which have been attributed with antitumor effects in many cases (Bohn & BeMiller, 1995). All these characteristics are very important, especially when preparing both pharmaceutical and cosmetic emulsions.

Among biopolymers, scleroglucan and its derivatives appear to be particularly well suited for the formulation of hydrogel matrices for sustained drug release of bioactive molecules, because of their peculiar features such as high biocompatibility, biodegradability, bioadhesivity, chemical and thermal resistance and good mechanical properties (Coviello, Grassi, Lapasin, Marino, & Alhaique, 2003; Coviello et al., 2005; Grassi, Lapasin, Pricl, & Colombo, 1996; Grassi et al., 2009; Matricardi, Onorati, Coviello, & Alhaique, 2006; Viñarta, François, Daraio, Figueroa, & Fariña, 2007). In the field of enhanced oil recovery (EOR) scleroglucan is assessed as environmentally friendly viscosifying agent in virtue of its no toxicity and biodegradability. Indeed, it is quite suitable for formulating water based drilling muds to be employed in harsh environments owing to its good stability towards high salinities, temperatures and alkaline conditions, moderate interactions with surfactants and its robust shear tolerance (Baba Hamed & Belhadri, 2009; Gallino, Guarneri, Poli, & Xiao, 1996; Kulawardana et al., 2012; Sveistrup, van Mastrigt, Norrman, Picchioni, & Paso, 2016).

On the other hand, Laponite is currently used as a rheology modifier in various technological applications, such as surface coatings, ceramic glazes, paints, home care and personal care products, as well as film forming agent and in pharmaceutical and nanocomposite formulations.

Laponite is a synthetic hectorite manufactured by processing combined salts of sodium, magnesium and lithium along with sodium silicate with an empirical chemical formula $Na^{+0.7}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]^{-0.7}$. Laponite nanoparticles are rigid disc-shaped crystals with a thickness of 1 nm, an average diameter of 30 nm, a bulk density of $2.65{\cdot}10^3$ kg/m^3. Each platelet is composed of an octahedral magnesia sheet that is sandwiched between two tetrahedral sheets of silica. The isomorphic substitution of divalent magnesium by monovalent lithium causes a deficiency of positive charge, which is balanced by sodium atoms residing in the interlayer space. When dispersed in aqueous media the sodium ions are released, leading to a permanent negative charge distribution on both opposite faces of Laponite disks. Positive charges on the rim are due to the protonation process of the local hydroxide groups.

Because of all these peculiar platelet features, aqueous Laponite dispersions can display a variety of structural conditions and, consequently, of rheological properties for different particle concentrations and ionic strength values. Marked shear thinning or plastic behavior and highly elastic responses are exhibited when interparticle (attractive or repulsive) interactions are so effective to generate arrested states of various nature (attractive gel, Wigner or repulsive glasses). Numerous investigations have been addressed to define the state diagram of aqueous Laponite dispersions in the ionic strength vs clay concentration plane, i.e. to individuate the different regions of isotropic liquids, disordered (gels and glasses), ordered (nematic phases), flocculated states (Cummins, 2007; Gabriel, Sanchez, & Davidson, 1996; Jabbari-Farouji, Tanaka, Wegdam, & Bonn, 2008; Levitz, Lécolier, Mourchid, Delville, & Lyonnard, 2000; Mourchid, Lécolier, Van Damme, & Levitz, 1998; Mourchid, Delville, Lambard, Lécolier, & Levitz, 1995; Mongondry, Tassin, & Nicolai, 2005; Ruzicka & Zaccarelli, 2011; Ruzicka, Zulian, & Ruocco, 2004; Ruzicka, Zulian, & Ruocco, 2006; Tanaka, Meunier, & Bonn, 2004; Tanaka, Jabbari-Farouji, Meunier, & Bonn, 2005). The various contradictions emerging from the comparison of the proposed Laponite dispersion state diagrams are partly apparent and can be mainly ascribed to different aging times and, secondarily, to different protocols of samples preparation or Laponite type (Ruzicka & Zaccarelli, 2011). Indeed, time elapsed after dispersion preparation plays a paramount role since even very low Laponite concentration dispersions can undergo aging up to a final arrested state. Regarding the different time evolution of the sol/arrested state transition in salt-free aqueous systems (ionic strength $\approx 2 \times 10^{-4}$ M), two distinct non-ergodic states (gel and repulsive glass) have been individuated at lower and higher concentrations, respectively (Ruzicka et al., 2004). In these two regions, the attractive (rim–face) and repulsive (face–face, rim–rim) electrostatic interactions between platelets are, respectively, dominant in the formation and stability of the arrested structure. At very low concentration (below 1.0 wt%) the slow gelation process, originating from the attractive interparticle interactions and the relevant clustering, is followed by an extremely slow phase separation between clay-poor and clay-rich phases on the year timescale (Ruzicka et al., 2011). At even higher concentration (above 3 wt%) the formation of nematic microdomains was postulated on the basis of birefringence measurements between crossed polarizers (Mourchid et al., 1998). Upon increasing ionic strength above 10^{-4} M, the role of electrostatic repulsions decreases in favor of attractive interactions between the oppositely charged edges and faces of the clay platelets. Accordingly, the amplitude of the gel region increases and the gelation time strongly decreases. At high salt concentrations, the energy barrier to particle aggregation is strongly reduced and phase separation in the form of large aggregates occurs.

Several studies have been carried out on aqueous Laponite-polymer systems, obtained by dispersing nanoparticles in polymeric matrices or adding polymer to Laponite dispersions. The scenarios drawn by the structural conditions of these mixed systems may be even more complex than those exhibited by the corresponding simple systems (water-Laponite and water-polymer) owing to various possible interaction modes between platelets and polymer chains. The balance of different competitive mechanisms related to polymer adsorption (steric hindrance, change in superficial charge, depletion, bridging, increase in the solution viscosity) can assist or hinder the aging dynamics and the formation of a final arrested state (glass or gel), strongly depending on the polymer concentration and molecular weight. If superficially adsorbed, short flexible polymer chains can provide steric stabilization owing to excluded volume effects between polymer segments, thus inhibiting or slowing down the aggregation process when edge-to-face attractive interactions are potentially dominant. At higher molecular weights, adsorbed polymer chains may be long enough to bridge between particles, so promoting particle clustering or the formation of an associative network. Beyond particle surface saturation, depletion forces can promote particle aggregation in the presence of free nonadsorbed chains in solution. As polymer concentration increases, interactions between adsorbed layers and free chains can result in re-stabilization of clusters and, above the overlap concentration, cluster–cluster attractions increase so becoming long ranged. All these structural effects have been postulated for Laponite dispersions containing poly(ethylene oxide) (PEO) which can be considered a paradigmatic example of platelet dispersions in neutral polymer solutions, from dilute to concentrated regime (Baghdadi, Sardinha, & Bhatia, 2005; Baghdadi, Jensen, Easwar, & Bhatia, 2008; Kishore, Chen, Ravindra, & Bhatia, 2015; Mongondry, Nicolai, & Tassin, 2004; Zulian, Ruzicka, & Ruocco, 2008; Zulian, Augusto De Melo Marques, Emilitri, Ruocco, & Ruzicka, 2014).

As several other complex systems, Laponite–PEO systems exhibit intriguing macroscopic behavior by varying the applied shear conditions, since various structural changes can be produced on different length scales for a range of clay and PEO concentrations (Daga & Wagner, 2006; de Bruyn, Pignon, Tsabet, & Magnin,