Chemical and microstructural controls on viscoplasticity in Carbopol hydrogel

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ABSTRACT

Many engineering and natural materials, as well as earth systems, exhibit a combination of elastic-plastic and viscous behaviors, but precisely evaluating their rheology, and the micromechanics and chemical-mechanical feedbacks governing such rheology, can be a challenge. The cross-linked polymer Carbopol has long been used to explore fundamental rheological behaviors, most recently including fracturing during viscous creep in nature. Here, through rheometer experiments we establish that Carbopol 940 is, to a first order, a Herschel-Bulkley material. However, we further establish that the yield stress and viscosity are affected by chemically-sensitive micromechanical controls, namely pH and concentration of the polymer mixture. We explore these effects via the novel use of cryogenic scanning electron microscopy (SEM). Through the SEM imaging we show that there is a semi-quantitative relationship between pH, porosity at the >10-µm scale, and yield stress, a result of the ionic repulsion between polymer links at the molecular scale. We appeal to a model wherein the yield stress is a direct function of jamming expressed at the SEM scale, similar to those described in granular systems. As the pH of polymer dispersion increases, and the porosity decreases, the yield strength increases as a result of the increasingly jammed system. The initial viscosity is thus controlled by the yield stress, but after failure evolves with increasing shear rate due to characteristic unjammed flow of the material. The different controls on the yield stress versus viscous flow rates has implications for borehole engineering efforts (carbon capture and storage) employing Carbopol, and could prove instructive for modeling of natural viscoplastic deformation.

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1. Introduction

Polymers that behave as shear-thinning fluids under some conditions, and brittle solids under others, find widespread use in a variety of industries. Notably hydrocarbon production efforts and planned carbon capture and storage (CCS) efforts, employ pH-triggered polymer gels, such as the polyacrylic acid, to seal leakage pathways within wellbores [1,2]. These materials, by virtue of their rate-dependent properties, have also found use in physical models of tectonic processes including fracture propagation and shear localization [3], phase mixing [4–8], and heat transfer [9–13]. The relationship between shear localization and fracturing in

Carbopol is particularly intriguing because: (a) such failure can be tuned by the pH of the mixing reagent, a very direct chemo-mechanical coupling, and (b) its shear-thinning properties have historically been used to explore rheological transition [14]. The different time scales of fracture and creep in Carbopol suggest that there is a yield-stress arising from the polymer micromechanics, which also affects the manner in which brittle and ductile deformation interact. It therefore may be possible to continue to use Carbopol, and/or similar polymers, to explore viscoplastic deformation that is widely recognized as a key part of lithospheric geodynamical behavior, though challenging to model [15].

Here we present rheometer experiments and SEM imaging of Carbopol 940 (C940), which is stronger and more viscous than C934 [2]. The polymeric gel behaves like a non-Newtonian fluid [16], but as long as the shear stress is below certain values, the gel will not flow and reversible, elastic deformation will occur. Above these
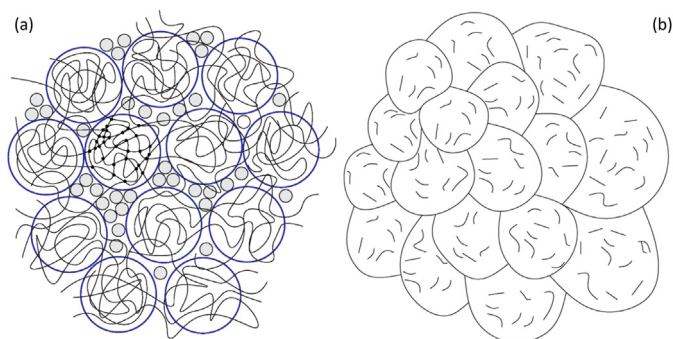
Fig. 1. A schematic representation of the structure of Carbopol gel, dilute (After [16]) (a) and close packed (Motivated by [26]) (b).

values, the polymer flows and irreversible, plastic deformation occurs.

The properties of C940 are well-suited for experimentation and imaging in pursuit of establishing rheological properties and their interdependence on pH. We know of few previous examples where such investigations were undertaken minus the standard characterization of the industrial material. Through our analyses, we identify the micromechanical SEM-scale (>10-μm) length scales that correlate with Carbopol mechanics, via the application of both environmental SEM (ESEM) and a new methodology that involves a Cryogenic SEM. Then, we use the yield stress and viscosity characterizations provided by the storage (elastic) and loss (viscous) moduli along with the microstructural length scales to propose a conceptual model for micromechanical jamming. Lastly, we propose a simple scaling that can relate Carbopol rheology to larger, more under-constrained earth systems, such as used for CCS.

2. Carbopol

Most Carbopol polymers are high molecular weight carboxyvinyl, homo- and co-polymers of acrylic acid that are cross-linked by polyethers like allyl sucrose [17]. The pendant groups which are mainly methyl and methylene groups are arranged syndiotactically in which repeating units have alternating configuration [18,19]. The dry white powder polymer has particles with an average diameter of few microns, which swell to 10 times their initial diameter (1000 times their initial volume) with neutralization. These particles thus define the highly cross-linked structure of polymer chains, which are surrounded by solvent, in this case water (Fig. 1a) [20]. The cross-linked chains achieve a close packing and make small spherical globules, which are less than a micron in diameter (Fig. 1b). Thus, the polymer has a hierarchical structure in which smaller agglomerated particles make much bigger spherical entities. The thickening mechanism of polymer is depicted

schematically in Fig. 2. The polymer is highly coiled in a powder state but the cross-linked structure starts to uncoil when dispersed in water. The extended structure of the polymer network is obtained in the presence of a base, where the reaction between polymer and base leads to ionization along the polymer backbone. The resulting negative charges lead to the electrostatic repulsion and hence expansion of polymer chains to the extended structure [20–23].

In our previous work [2], the yield stress value of 1 wt% Carbopol 934 was increased from 7 Pa to 84.1 Pa as the pH was increased from 3.3 to 4.1, which could be attributed to the gel formation. The polymer gel has a yield stress, below which the material behaves like an elastic solid and above it a liquid [14]. We use a constant stress rheometer and improved technique [2,14] to accurately measure the yield stress particularly in the low shear rate range and correlate it to the microstructure of the gel.

3. Methodology

3.1. Materials

C940 was obtained from the Lubrizol Company in powder form. Investigations show that C940 forms clear gel which is more homogeneous over the range of pH compared to Carbopol 934 [24]. The polymer is described as high molecular weight polyacrylic acid with methyl and methylene substituent groups arranged syndiotactically along the polymer chain [24]. Sodium hydroxide was purchased from Fisher Scientific Inc. in liquid form.

3.2. Sample preparation

Deionized water with pH close to 7.0 was weighed in a beaker. Carbopol powder was weighed in an antistatic polymeric dish using analytical balance with ± 0.001 g accuracy. In our case we prepared 3.0 wt % polymer solution by adding 30.9 g of polymer to 1000 g of deionized water. A three-blade mechanical stirrer was used to disperse polymer into the water. The agitator was set at 150 rpm. Higher speeds causes the polymer molecules to break down resulting in permanent strength loss while lower mixing speed leads to the formation of lumps. Sieved powder was added progressively over 45 min during mixing. The dispersion was covered and stirred for one day to ensure the polymer was fully hydrated and dispersed. A solution of 1.0 M NaOH was added to the dispersion to adjust the pH to the desired values. Samples with pH ranging from 2.3 to 12.0 were prepared (Table 1). A waiting period of 24 h was necessary to make sure the sample is evenly neutralized and the gel at equilibrium. The pH of samples was measured one year later and a very good agreement between measurements was observed. To eliminate trapped air bubbles, samples were centrifuged at 2000 rpm for 10 min. The samples were stored in a covered
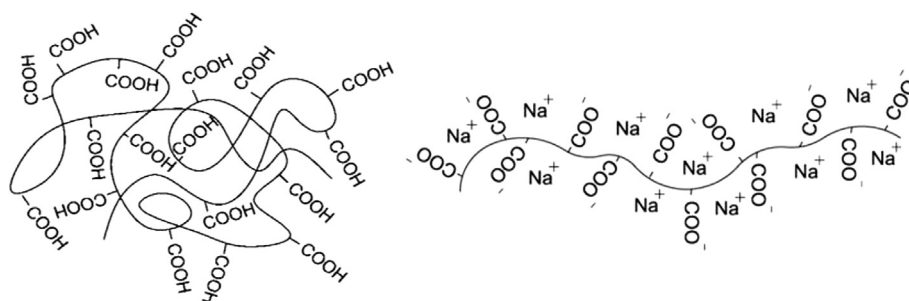
Fig. 2. The thickening steps of Carbopol gel, entangled polymer (left) and deionized microgel (right) (After Lubrizol Advanced Materials, 2001).