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# Shear interfacial viscoelasticity of native and hydrophobically modified xanthan at oil/water interface

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## ABSTRACT

In this study, we investigate the shear viscoelasticity of xanthan and hydrophobically modified xanthans at silicone oil/water interface. Xanthan is well known to adopt two distinct conformations in water solution, a rigid conformation at low temperature and a flexible one at high temperature. Hence, we first studied the un-modified xanthan as a function of temperature and showed that its interfacial viscoelasticity depends on the xanthan conformation as in bulk but evolves the opposite way after heating: *i.e.*, the bulk viscoelasticity is weakened after thermal treatment while interfacial viscoelasticity is reinforced. Ergo, we proved that for xanthan, bulk and interfacial viscoelastic properties act independently. Then, we investigated the effect of hydrophobic modification of xanthan on its interfacial properties. We demonstrated that, before any thermal treatment, the more grafted the polymer, the higher the interfacial properties of modified xanthans are also improved after thermal treatment but the improvement is much less pronounced for grafting densities above 8% which is explained by different chains organization at the interface.

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## 1. Introduction

Since the pioneering work of Landoll (Landoll, 1982) regarding the solution and interfacial properties of hydrophobically modified cellulose, polymeric surfactants based on polysaccharides are of growing interest because of their water solubility, biocompatibility and biodegradability. These surfactants can be obtained by grafting hydrophobic moieties onto the polysaccharide backbone, such as dextran (Chebil, Desbrieres et al. 2013; Covis, Ladaviere et al. 2013; Rotureau, Leonard et al. 2004), cellulose (Akiyama, Kashimoto et al. 2005; Camino, Sanchez et al. 2011; Landoll, 1982; Mezdour, Lepine et al. 2008), pullulan (Duval-Terrie, Huguet et al. 2003; Henni, Deyme et al. 2005) or chitosan (Babak, Lukina et al. 1999; Desbrières & Babak, 2006). Due to their amphiphilic structure, they can be adsorbed at oil/water (Camino et al., 2011; Mezdour et al., 2008; Rotureau et al., 2004) or air/water (Chebil et al., 2013; Henni et al., 2005; Landoll, 1982; Rotureau et al., 2004)

\* Corresponding author. Normandie Univ, France. *E-mail address:* frederic.renou@univ-lehavre.fr (F. Renou). interface, thus forming an interfacial film. This film can decrease the interfacial tension, but it can also own specific rheological properties. Indeed, some interfacial layers are elastic (Babak, Desbrieres et al. 2005; Camino et al., 2011; Mezdour, Cuvelier et al. 2007) whereas other can be considered as viscous (Desbrières & Babak, 2006; Erni, Windhab et al. 2007). Their behavior strongly depends on the organization of the amphiphilic chains within the layer. While it is well-known that the hydrophobic moieties (Desbrières & Babak, 2006; Henni et al., 2005) and polymer concentration (Babak et al., 2005; Covis et al., 2013; Mezdour et al., 2007) greatly affect this organization, the impact of the rigidity of the hydrophilic backbone, however, is less investigated (Desbrières & Babak, 2006). In a previous work (Boy Comesse et al. 2014) we studied the

In a previous work (Roy, Comesse et al. 2014), we studied the bulk rheological properties in solution of an amphiphilic xanthan obtained by chemical grafting of octyl moieties onto its carboxylate functions. Xanthan is an anionic polysaccharide which can adopt two different conformations in aqueous solution: an ordered, rigid double-helix strand structure at low temperature and high ionic strength and a disordered, flexible coil state at high temperature and low ionic strength (Milas & Rinaudo, 1979; Morris, Rees et al.







1977). This reversible order-to-disorder transition is characterized by a specific temperature named conformational temperature (Tm) which leads to a strong decrease in xanthan rheological properties (Capron, Brigand et al. 1998; Choppe, Puaud et al. 2010; Lecourtier, Chauveteau et al. 1986). In Addition, ionic strength influences Tm, the higher the ionic strength, the higher Tm (Milas & Rinaudo, 1986). In our experimental conditions, xanthan was modified under its rigid helical conformation (Roy et al., 2014). We proved that the presence of these hydrophobic moieties had little or even no impact on the conformation, and thus, on the organization of the helical chains in solution. Above c\*\*, amphiphilic xanthan chains form a viscoelastic network of rigid helices, similar to the one observed for unmodified xanthan (Choppe et al., 2010; Cuvelier & Launay, 1986; Rochefort & Middleman, 1987; Ross-Murphy, Morris et al. 1983) but with locally intermolecular hydrophobic interactions, which strongly slow down the dynamics.

The aim of this paper is to study the interfacial rheological properties of unmodified and hydrophobically modified xanthan at the oil/water interface. For this purpose, oscillatory measurements were realized with a double wall ring geometry. Amphiphilic xanthans with grafting densities comprised between 0 and 39% were characterized, in order to determine the influence of the proportion of hydrophobic moieties on the interfacial properties. To the best of our knowledge, this is the first time that the interfacial rheological properties of xanthan and its derivatives are described. Moreover, during the analyzes, samples were submitted to a heating and cooling ramp. This allowed us to study the impact of chains conformation and the thermal history on the interfacial behavior of xanthan and hydrophobized xanthans.

## 2. Materials and methods

#### 2.1. Materials

Xanthan was kindly provided by Danisco (France). The substitution degrees of acetate and pyruvate determined by <sup>1</sup>H NMR were 0.87 and 0.49 respectively. Its moisture and protein contents were respectively 10.8% (determination by thermogravimetric analysis) and less than 1% (determination by the Bradford procedure). 2,2,3,3-d (4)-3-(trimethylsilyl)propionic acid sodium salt (TSP), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDAC), N-hydroxysuccinimide (NHS) and octylamine were purchased respectively from Alfa Aesar, Acros Organics, Merck and Sigma Aldrich. All reagents were used without further purification. Silicone oil was purchase from PSL and is a viscosity oil standard (ASTM:N10) with a low viscosity (h = 18.32 mPa s at T = 20 °C).

## 2.2. Synthesis of hydrophobically modified xanthan

Hydrophobically modified xanthans were obtained via a carbodiimide-mediated peptide coupling reaction based on a procedure described elsewhere (Roy et al., 2014). Briefly, the reaction took place in water in two steps. During the first step, EDAC, a water-soluble carbodiimide, and NHS, a co-reagent, were added to an aqueous solution of acidified xanthan (0.1% w/v, 300 mL). The pH was then adjusted to 4.5 with 1 M HCl and the solution was left under stirring at low temperature (T < 5 °C) for two hours. During the second step, octylamine was added to the medium, and the pH was adjusted to 10 with 1 M NaOH. Afterward the solution was left under stirring at room temperature for 16 h. All the reagents (EDAC, NHS and octylamine) were added in the same stoechiometry with respect to the carboxylic functions, and was adjusted depending on the targeted grafting density (Roy et al., 2014) Purification of the grafted xanthans was conducted by successive dialysis steps against HCl (pH = 3 for 24 h), NaCl 0.1 M (24 h), distilled and ultrapure water during 8 days. Finally, the polymer was freezedried and recovered as a white solid. Several syntheses with the same stoechiometry gave the same grating densities within 3% thus proving the high reproducibility of the protocol.

Precursor refers to a xanthan that underwent all of the above synthesis and purification procedures, but without addition of the coupling agents during the first step of the modification process in order not to graft octylamine. Therefore, precursor is our reference as an unmodified xanthan. The nomenclature used for the modified polysaccharides, also called derivatives, is  $X^{A}C_{8}$ , where A is the grafting density (*i. e.*, the number of octylamine group per xanthan repeating unit) and  $C_{8}$  stands for the number of carbon atoms in the alkyl chain.

### 2.3. Characterization methods

#### 2.3.1. <sup>1</sup>H NMR analysis

300 MHz <sup>1</sup>H NMR spectra were recorded at 80 °C, using a BrukerAvance300 spectrometer. The determination of the grafting density of our samples were done using a procedure described elsewhere (Roy et al., 2014).

### 2.3.2. Polarimetry

The Tm of xanthan was determined using polarimetry. Polymers solutions at 1 g/L were prepared by dissolving the required amount of powder in ultrapure water under stirring at room temperature overnight. Then the pH and the conductivity were respectively adjusted to 4.3 with HCl 0.1 M and/or NaOH 0.1 M and to 1 mS/cm with NaCl(s). Afterward, the solutions were gently centrifuged for 3 min in order to get rid of air bubbles. Optical rotation measurements were performed at 436 nm on a Perkin-Elmer 241 polarimeter using a 1 dm pathlength cell (1 mL). Data were measured every 5 °C from 25 °C to 80 °C (after 30 min of thermal equilibrium at each temperature). A sigmoid shape of the optical rotation versus temperature curve was obtained and Tm was, when possible, determined by mean of the tangent method.

#### 2.3.3. Circular dichroism

Circular dichroism (CD) spectra were recorded with a CD spectropolarimeter (Jobin-Yvon, France) in the UV range of 200–270 nm with a quartz cell with an optical path of 0.5 cm at room temperature. Spectra were averaged over 5 scans with a bandwidth of 2 nm then smoothed. Xanthan solutions at 1 g/L were prepared by dissolving the required amount of powder in NaCl 0,01 M under stirring at room temperature overnight. Afterward, the solutions were gently centrifuged for 3 min in order to get rid of air bubbles. The CD spectra of the solvent has been measured within the same conditions then subtracted as a baseline.

#### 2.3.4. Interfacial rheological measurements

#### > Geometry setup

Interfacial rheological measurements were carried out with a stress controlled rheometer DHR2 (TA Instruments) with a Peltier temperature control device using a double wall-ring geometry (DWR). The geometry consists of a mobile Pt/Ir ring with a square-shaped cross section, positioned at the oil/water interface, and a fixed cup made of teflon, placed directly onto the Peltier heated bottom plate. This setup was designed in order to make the contribution of bulk rheology negligible compared to interfacial one, thus with a high Boussinesq number (Bo $\gg$ 1).

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