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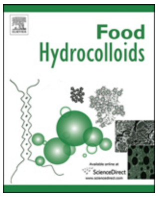

Comparison of polysaccharide degradations by dynamic high-pressure homogenization

A. Villay[a], F. Lakkis de Filippis[b], L. Picton[b], D. Le Cerf[b], C. Vial[a], P. Michaud[a,*]

[a] Clermont Université, Université Blaise Pascal, Laboratoire de Génie Chimique et Biochimique, Polytech' Clermont Ferrand, 24 avenue des Landais BP 206, 63174 Aubière cedex, France
[b] Université de Rouen, Laboratoire Polymères, Biopolymères, Surfaces, CNRS-UMR 6270 & FR3038, 76821 Mont Saint-Aignan, France

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ABSTRACT

The mechanical degradation of polysaccharides was investigated using dynamic high and ultra-high-pressure homogenization (HPH). The objectives were to reduce the molar mass of polymer chains, and simultaneously, the apparent and intrinsic viscosity of polysaccharides in solution. The influence of homogenization pressure (up to 200 MPa) and cycles was compared on polysaccharides with different physical and structure properties: namely, guar gum, hydroxyethylcellulose (HEC), sodium carboxymethylcellulose (Na-CMC), sodium alginate (Na-alginate) and gum arabic. HPH was applied on semi-dilute solutions. The apparent changes in molar mass, gyration radius and intrinsic viscosity were deduced from size exclusion chromatography coupled on-line with multi-angle laser light scattering, differential viscometer detector and differential refractive index detector (SEC/MALS/DV/DRI), while the evolution of the critical overlap concentration (C^*) was obtained by viscosimetry. A method based on a succession of homogenization cycles and polymer pre-concentration steps was developed to determine the minimum molar mass achieved at constant pressure. Molar mass, and intrinsic viscosity were shown to fall simultaneously while logically C^* increased during HPH for all polysaccharides, except gum arabic, probably because of its globular and branched structure. This highlights that the differences of polysaccharide structures and conformation (linear, branched…) exhibit a stronger impact on HPH treatments than polymer charge or molar mass. Finally, via an empirical approach linking the decrease of both molar masses and viscosities, we have evidenced a specific scaling exponent that should characterize the flexibility of the treated polymer (i.e. its ability to be degraded by HPH).

1. Introduction

Polysaccharides are defined as polymers of monosaccharides linked by glycosidic bonds and exhibiting a degree of polymerization higher than 10. These macromolecules, reaching sometimes several millions of Da, present a large structural variability and have been described as composed of neutral (pentoses and hexoses) and/or anionic monosaccharides (uronic acids) substituted or not by non-sugar compounds. For example, they may exhibit homopolymeric or heteropolymeric structures and linear or ramified conformations. These features lead to specific behaviours and different architectures in solution, resulting in spirals, sheets, and also single, double and triple helices (Rinaudo, 2004; Sutherland, 2007). The molar-mass distribution of polysaccharides is the primary parameter that influences directly their physicochemical properties in solution, such as apparent viscosity. This is the reason why many attempts to make the molar-mass distribution of polysaccharides more uniform and to control their average molar mass have been developed in the recent literature. These are based on the degradation of polysaccharides; the most popular of them are, namely, enzymatic, chemical and physical methods.

First, polysaccharide lyases and hydrolases (Cantarel et al., 2009) have been successfully used to depolymerize polysaccharides with a high level of specificity (Akpinar, Erdogan, & Bostanci, 2009; Kashyap, Vohra, Chopra, & Tewari, 2001; Vishu Kumar, Gowda, & Tharanathan, 2004). These techniques are simple but often limited by the commercial availability of enzymes, their cost and their sensitivity to denaturation. Chemical degradations after acidic and alkaline treatments or free radical mechanisms have also been frequently described for the preparation of oligosaccharides and low-molar-weight polysaccharides (Guilloux, Gaillard, Courtois, Courtois, & Petit, 2009; Jinglin, Shijun, Fengmin, Sun, & Yu, 2009; Rota et al., 2005). For example, acidic hydrolysis led to the effective degradation of polysaccharides, but generated a large amount

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* Corresponding author. Tel.: +33 (0)473407425.
E-mail address: philippe.michaud@univ-bpclermont.fr (P. Michaud).

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of monosaccharides and by-products (Akpinar et al., 2009; Garna, Mabon, Nott, Wathelet, & Paquot, 2006). Finally, the physical depolymerization of polysaccharides can be achieved by mechanical, thermal or thermomechanical treatments including thin-screw extrusion, jet-cooking, ultrasonication and microwave irradiation (Aida, Yamagata, Watanabe, & Smith, 2010; Cote & Willet, 1999; David & Boldo, 2008). The methods based on high-pressure processes, e.g. microfluidization and dynamic high-pressure homogenization (HPH), have also been tested on many polysaccharides, including chitosan, methylcellulose, inulin, xanthan, starch and β-glucan (Al-Assaf, Sakata, McKenna, Aoki, & Phillips, 2009; Floury, Desrumaux, Axelos, & Legrand, 2002; Kasaai, Charlet, Paquin, & Arul, 2003; Kivelä, Pitkänen, Laine, Aseyev, & Sontag-Strohm, 2010; Lagoueyte & Paquin, 1998; Nilsson, Leeman, Wahlund, & Bergenståhl, 2006; Ronkart et al., 2010).

Among all the above-mentioned methods, HPH seems to be a very versatile tool which presents the additional advantage to be commonly used in the industry. Dynamic high-pressure homogenizers are, indeed, usually operated to emulsify, disperse or mix products in the process industries. For food and chemical products, they are still used to stabilize and make emulsions more uniform (Innocente, Biasutti, Venir, Spaziani, & Marchesini, 2009), and for their viscosity control (e.g., for dressings, ketchup, dairy dessert, but also wax and silicones…). For chemicals and pharmaceuticals products, they have found applications for handling solid dispersions (Uchiyama, Tozuka, Asamoto, & Takeuchi, 2008). In biotechnologies, their main development consists of non-chemical cell disruption to extract the intra-cells substances (proteins, enzymes…) compounds (Middelberg, 1995). The inactivation of microorganisms by these homogenizers has also been investigated recently (Campos & Cristianini, 2007).

Dynamic pressure homogenization significantly differs from a simple batch pressure treatment. It consists in forcing continuously a liquid flow at low velocity using a volumetric pump through a restriction between a seat and a valve, the size of which can be imposed in order to control pressure drop. Between the valve and the seat, pressure also decreases because of the increase of velocity resulting from the mass balance under steady state conditions. Due to the small gap between valve and seat (a few hundreds micrometres), the residence time of the fluid is very short, about 10–100 μs. The specific power dissipation can be as high as 10^9–10^{11} W m^{-3}, but only in the localized region between valve and seat, i.e. in a small volume of fluid. The fluid dynamics in this region is of critical importance, but is also rather complex. Shear, elongation, turbulence, but also cavitation and the resulting shock waves when bubbles implode, have been suggested to explain how power dissipation proceeds (Floury et al., 2002; Innings & Trägårdh, 2007; Stang, Schuchmann, & Schubert, 2001). However, even for emulsification, a unified theory describing pressure homogenization has not yet achieved general acceptance. It is the same for the explanation of effects responsible for the change of structure of polysaccharides subjected to HPH. Except with inulin for which HPH treatments lead to the formation of a gel (Ronkart et al., 2010), depolymerization remains the rule for polysaccharide solutions. This is often coupled with changes in polydispersity and, probably, conformation of macromolecules (Al-Assaf et al., 2009; Floury et al., 2002; Kivelä et al., 2010; Nilsson et al., 2006). With HPH, the degree of mechanical degradation is known to be strongly dependent on the pressure and the number of homogenization cycles, but also on polymer concentration. In particular, HPH requires semi-dilute or concentrated solutions (Kivelä et al., 2010), that means above the critical overlap concentration (C^*).

From the literature, it appears that most investigations focused only on one polysaccharide, and that the evolution of C^* with HPH treatment was almost never accounted for when cycles were applied. As a result, the objective of the present work is to compare the effects of HPH on several polysaccharides with various physicochemical properties and structures. More this paper focuses on a better understanding of the relationship between the structure/conformation of polysaccharides and impact of HPH on semi-dilute solutions. To this end, a method aimed at maintaining polymer concentration above C^* during HPH has been developed, using pre-concentration steps between the homogenization cycles.

2. Materials and methods

2.1. Materials

The five polysaccharides used in the present work were guar gum (*Sigma Aldrich*, USA), sodium alginate (*Cargill France*), hydroxyethylcellulose (*Hercules-Aqualon*, France), sodium carboxymethylcellulose (*Hercules-Aqualon*, France) and gum arabic (*Colloïdes Naturels International*, France).

Each polymer was solubilized in a 0.1 mol L^{-1} NaCl solution stirring 24 h at room temperature before HPH treatments. The use of a ionic strength (NaCl) was motivated by the induced screening effect resulting on ionic polysaccharides (as Na-alginate and Na-CMC). This permits to avoid electro viscous or rigidifying effects due to electrostatic repulsions (Souguir, Roudesli, About-Jaudet, Le Cerf, & Picton, 2007). To homogenize solvent for polysaccharide solubilization, neutral polysaccharides (HEC and guar gum) were solubilized in the same NaCl solution. After each HPH treatment, the solutions of polysaccharides were freeze-dried under vacuum using a Heto Power Dry PL 6000-90 freeze dryer (*Thermo Scientific*, USA).

2.2. High-pressure homogenization

The APV 2000 apparatus (*Invensys APV*, France) is a conventional dynamic pressure homogenizer based on the valve and seat technology. It works at constant flow rate, about 11 L h^{-1} using a positive displacement pump, and is able to achieve up to 200 MPa. It consists of a two-stage valve, made of ceramics, as commonly found in the dairy and food industries for emulsion preparation. Despite a water circulation around the valve, temperature could not be maintained constant when ultra-high-pressure treatment was applied, as usual. Homogenization pressure was varied between 0 and 200 MPa at room temperature, using from one to six successive cycles. During processing, temperature rose by about +20 °C/100 MPa. The treated solution could, therefore, reach up to 60 °C and were left in an ice bath at the end of each cycle to achieve a final temperature close to room temperature before the following cycle. As temperature depended only on the applied pressure, this parameter did not impair the comparison between the different polysaccharides.

2.3. Determination of the critical overlap concentration

The critical overlap concentration represents the limit between two areas, dilute and semi-dilute regimes. Over C^*, i.e. in the semi-dilute regime, polysaccharide entanglements are more important and polymers are more sensitive to physical stress. C^* was deduced using viscosimetry. Apparent viscosity measurements were carried using a double concentric cylinder geometry with a stress-controlled rheometer AR-G2 (*TA Instruments*, France) equipped with a Peltier temperature control system. Temperature was set at 25 °C and viscosity was monitored in the following range of shear rate ($\dot{\gamma}$): 10^{-4}–10^3 s^{-1}. Data were collected and analyzed using the *Rheology Advance* software package and the Cross equation (Cross,