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Stretching properties of xanthan and hydroxypropyl guar in aqueous solutions and in cosmetic emulsions

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ABSTRACT

Filament stretchability of xanthan gum (XG) and hydroxypropyl guar (HPG) was investigated in aqueous solutions (0.125, 0.25, 0.5, 1, 1.2 and 1.5% w/w) and in O/W emulsions using a texture analyzer. Additionally, rheological characterizations were carried out on the systems and shear and oscillation parameters were used to interpret stretching properties. XG solutions exhibited a solid-like behavior with rheological parameters much higher than for HPG one whatever the concentration. Filament stretching values of XG solutions were superior to HPG for concentration below 1% w/w and then became comparable for higher concentrations. No meaningful relationship was found between rheological and stretching values. Synergy was observed for all XG/HPG mixtures at 0.125, 0.25 and 0.5% influencing both the rheological and the filament stretching values. The 25/75 XG/HPG ratio showed the maximum synergistic effect at all concentrations while the filament stretchability was enhanced in a wider range of ratios. XG and HPG did not present the same behavior in emulsions. No clear synergistic effect was observed and XG markedly influenced the emulsion filament stretching.

1. Introduction

Among the various texture properties characterizing emulsion type products, stretching property is one of the most recently investigated (Gilbert, Loisel, Savary, Grisel, & Picard, 2013a; Gilbert, Savary, Grisel, & Picard, 2013b; Niedzwiedz, Buggisch, & Willenbacher, 2010; Chan et al., 2007; Chan et al., 2009). Extensional deformation, filament stretching, stringiness and cohesiveness are the different terms expressed for this property. Two distinct apparatuses are mostly applied to measure filament stretching including capillary break-up elongation rheometer (CaBER) and texture analyzer. The rheological analysis with a CaBER is based on the formation of an unstable fluid filament by imposing a rapid axial step-strain of prescribed magnitude. The filament is then allowed to relax until breakup under the action of its own dynamics. The relaxation and decay of the necked sample is governed by different forces, e.g. viscous, elastic, gravitational and capillary forces (Sujatha, Matallah, Banaai, & Webster, 2008). Main advantages of this technique are that it can create a pure extensional flow and is applicable to viscous fluids over a wide viscosity range (Chan et al., 2007; Niedzwiedz et al., 2010). In the second method using a texture analyzer, fluids are compressed and stretched at a controlled speed to allow filament formation (Chan et al., 2009; Gilbert et al., 2013a). The maximum breaking length, corresponding to the maximum length (L_{max}) measured just before the filament broke, is recorded using a high speed video camera. Recent works highlight a possible prediction of the stringiness of cosmetic emulsions using this technique (Gilbert et al., 2013a, 2013b). In addition, compared to the CaBER, the texture analyzer has the benefit to be a widespread, easy to use and comprehensive technique in the cosmetic field.

Emulsions' filament stretching property is not widely studied applying texture analyzer. In a previous study the effect of eight natural and synthetic polymers at a concentration of 1% w/w was investigated on filament stretching properties of oil-in-water (O/W) emulsions (Gilbert et al., 2013a). Among the polymers investigated, xanthan gum (XG) and hydroxypropyl guar (HPG) showed the highest values of stretchable length.

XG is an ionic heteropolysaccharide produced by the bacterium *Xanthomonas campestris* and its molecules consist of a main chain of (1,4)-β-D-glucose residues with a trisaccharide side chain attached to every other glucose. The side chains are linked through the 3

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positions and consist of β-D-mannose, (1,4)-β-D-glucuronic acid, and (1,2)-α-D-mannose. The inner mannose may be acetylated and the terminal mannose may be pyruvated (Fitzpatrick, Meadows, Ratcliffe, & Williams, 2013). This natural gum exhibits many advantages as a thickener, stabilizer, gelling agent and suspending agent and is nowadays widely used in a broad range of products, including foods, pharmaceuticals, cosmetics, personal care, drilling muds, etc. because of its unique rheological properties (Faria et al., 2011).

Guar gum is a naturally occurring polymer extracted from the seeds of *Cyamopsis tetragonalobus* plant. It consists of a linear backbone of β-1,4-linked D-mannose units and is randomly substituted by α-1,6-linked galactose side chains. The mannose to galactose ratio (M/G) ranges from 1.5/1 to 2/1 mainly due to climate variations. Guar gum is widely used in a variety of industrial applications because of its low cost and its ability to produce highly viscous solutions even at low concentrations (Gong et al., 2012). HPG is prepared from native guar gum via an irreversible nucleophilic substitution, using propylene oxide in the presence of an alkaline catalyst (Lapasin, De Lorenzi, Pricl, & Torriano, 1995). Compared with native guar gum, HPG shows better solubility and thermal stability in aqueous solution. HPG is widely used in many industrial sectors such as oil recovery, paints, mineral industry, and personal care (Wu et al., 2010).

A synergistic interaction occurs between XG and galactomannans such as guar gum and locust bean gum as well as with glucomannans such as konjac mannan. This interaction results in enhanced viscosity or gelation and is dependent on the gum ratio in the mixture, pH and ionic environment (Sworn, 2009). Various XG/guar ratios have been reported for the maximum synergy which could be related to the microbial strains, the production conditions, the chemical structures of used gums and the environmental conditions. Tako and Nakamura (1985) reported the maximum dynamic modulus with a ratio of 66/33 for XG/guar while a 40/60 ratio was found by Schorsch, Garnier, and Doublier (1997), 60/40 by Secouard, Grisel, and Malhiac (2007) and 20/80 by Sworn (2009).

The XG/guar synergy is notably temperature dependent since higher temperatures substantially enhance the molecular associations between XG and guar (Khouryieh, Herald, Aramouni, & Alavi, 2006).

To date, most of the studies focused on a rheological characterization of the XG/galactomannans systems and on the synergistic effect between XG and HPG do not include the evaluation of their stretching properties neither in solutions nor in O/W emulsions. The aim of the present study was first to characterize the effect of XG and HPG on the stretching properties of aqueous solutions. To that purpose, rheological measurements including oscillatory and flow tests were carried out in a rheometer, and stretchability was investigated using a texture analyzer. Then mixtures of XG and HPG in aqueous solutions were prepared and characterized in the same manner to highlight synergistic effects between both biopolymers, to determine the specific ratios of interaction and to characterize the effect of such synergy on stretching properties. Then the XG/HPG ratio having the maximum synergistic influence on stretching properties was used in a cosmetic grade O/W emulsion and analyses were performed to compare the polymers behaviors in the two different systems.

2. Materials and methods

2.1. Materials

Cosmetic grade xanthan gum (Rhodicare T) and hydroxypropyl guar gum (Jaguar HP105) were kindly given by Rhodia, France. Other ingredients required for emulsion formulation were butylene glycol (Acros Organics, France), dimethicone (Dow Corning, Belgium), isohexadecane (IMCD, France), paraffin (Baeriocher, France), and steareth 2, steareth 21 and stearic acid (Croda, France). The preservative (Dekaben MEP®) is a mixture of phenoxyethanol, methylparaben, ethylparaben and propylparaben (Jan Dekker International, France).

2.2. Methods

2.2.1. Polymers in aqueous solutions

In a first step, a range of different concentrations (0.125, 0.25, 0.5, 1, 1.2, and 1.5% (w/w)) of each polymer in water was prepared. Each polymeric agent was slowly dispersed in water to obtain the final concentration. The dispersions were stirred at room temperature using a mechanical stirrer at 400 rpm for 4 h to ensure the complete polymer solubilization in water. The preservative was then added at 0.5% w/w at room temperature. Each polymer solution was finally degassed using a vacuum pump and then stored at 4 °C.

In order to investigate the synergistic effects of XG and HPG on stretching properties, a series of gums mixture at different XG/HPG proportions (15/85, 20/80, 25/75, 30/70, 35/65, 40/60, 50/50, 60/40, 75/25, 80/20 and 85/15) at three different concentrations (0.125, 0.25 and 0.5% (w/w)) were prepared. For each mix solution (20 mL), the required quantity of each polymer solution previously prepared was put into a 60 mL glass flask and then stirred at 1800 rpm for 2 min using a laboratory mixer (MS2 Minishaker, IKA Works Inc., Wilmington, NC, USA). To provide a better mixing between both polymer solutions, the flasks were stored in incubator at 40 °C for 12 h and then directly analyzed after cooling to ambient temperature.

2.2.2. Polymers in emulsions

In the second step, the effect of polymers in emulsion was investigated. For this purpose nine O/W emulsions, as typical cosmetic creams type, varying by the texturing agent or association of texturing agents and their concentrations were prepared. An additional O/W emulsion without any texturing agent was prepared and used as a reference in order to assess the contribution of polymers on the final stretching properties of the emulsions, and so-named the Control emulsion in the rest of the study. The emulsion composition and preparation method were the same used as in a previous study (Gilbert et al., 2013a) and are not detailed here. XG and HPG were incorporated in the emulsion at a concentration of 0.25, 0.5 and 1% (w/w), alone or in a 40/60 (XG/HPG) proportion. As described for the incorporation of one polymer, the 40/60 (XG/HPG) mixtures (0.25, 0.5 and 1% (w/w)) were first predispersed in butylene glycol at room temperature under manual stirring using a spatula, in order to allow the polymer grains disaggregation from each other thus ensuring its complete hydration when added to the emulsion. The emulsions were then stored at ambient temperature for 24 h to ensure polymer complete hydration and finally preserved at 4 °C before further analysis.

2.2.3. Solutions and emulsions rheology

All rheological tests were performed with a controlled stress rheometer (HR 1, TA Instruments, New Castle, Delaware, USA) at 25 °C. Measurements were made in triplicate and a fresh sample was loaded for each run. A solvent trap was used to prevent solvent evaporation during measurements. Once loaded, samples were allowed to relax and equilibrate at least for 2 min prior to any measurement. Duration of equilibration step was determined with preliminary time sweep experiments: evolution of G' and G'' was monitored during 30 min at a 0.5% strain and 1 rad s^{-1} frequency;

equilibration time of 2 min corresponds to the time necessary to reach constant viscoelastic parameters.

2.2.3.1. Shear tests. Flow tests were carried out using a cone-plate PMMA device (0°59′ cone angle, 40 mm diameter, 27 μm gap). The flow properties were obtained by recording shear stress and viscosity values when shearing the samples at increasing shear rates ranging from 0.001 to 1000 s^{-1} (logarithmic mode) for 180 s. Such total experimental time did not made possible to reach the steady-state viscosity from flow curves. Indeed the Newtonian viscosity was obtained from the response at low shear for each flow curve in order to compare the different systems.

2.2.3.2. Oscillation tests. Oscillation strain sweep tests were carried out at a frequency of 1 rad s^{-1} with strain increasing from 0.01 to 100% (logarithmic mode), using a 4° cone-plate PMMA device (40 mm diameter, 130 μm gap).

2.2.4. Stretching properties of the solutions and the emulsions

The same instrumental settings developed in a previous study (Gilbert et al., 2013a) were applied to measure the filament stretching properties of the solutions and the emulsions. Samples were examined at room temperature using a Texture Analyzer TA.XT Plus (Stable Micro Systems, Godalming, Surrey, UK) equipped with a 5 kg load cell. This device allows up and down vertical displacement at a maximum rate of 40 mm s^{-1}.

A specific compression/stretching test was developed using the cylindrical probe P/0.5R (1/2 in. diameter, Radius Edge BS: 757 and ISO: 9665 Gelatine Bloom Cylinder probe, Delrin). 100 μL of product were delivered on the horizontal base using a Microman® M250 GILSON. The probe compressed the product at a fixed gap between the bottom plate and the probe (0.8 mm), and then stretched it at a constant speed (40 mm s^{-1}). The filament stretching was monitored using a Bosch Dinion CCD camera to determine the exact breaking point of the filament thus allowing measuring its breaking length (expressed in mm). The stretching behavior images were recorded at 30 frames s^{-1} using the Ulead Media Studio 8.0 (Ulead Systems) software and processed with the Image J software. The maximum stretchable length, noted L_{max}, was used to quantify the product's stretchability. All measurements were performed six times to calculate a representative average value.

2.2.5. Statistical analyses

The statistical analysis of collected data was performed using XLSTAT software from Addinsoft (version 2012.1.01). A one-way analysis of variance (ANOVA) was applied to compare the differences between the samples at a 5% level of significance.

3. Results and discussion

3.1. Rheological and stretching properties of pure solutions

Rheological characterizations were carried out for pure polymer solutions. Both gums presented a shear thinning behavior related to the orientation of macromolecules along the stream line of the flow, more pronounced for XG solutions as a consequence of its molecular semi-flexible structure. At low shear rates, the polysaccharide molecules intertwined to form entanglements or aggregates, and the high viscosity is due to the large fluids flow resistance (Risica, Barbetta, Vischetti, Cametti, & Dentini, 2010; Xu, Xu, Liu, Chen, & Gong, 2013). The rheological values including the Newtonian viscosity, storage modulus (G'), loss modulus (G'') and tangent delta (ratio of G'' to G') of pure solutions of XG and HPG at different concentrations are summarized in Table 1. The Newtonian viscosity was calculated by averaging the viscosity values in the first plateau of apparent viscosity as a function of shear rate (s^{-1}); G', G'' and tangent delta values were collected on the linear region of the viscoelasticity curves as a function of oscillation strain.

As classically observed, the Newtonian viscosity increased with concentration for both polymers. Due to its molecular semi-flexible structure, XG solutions exhibited the highest viscosities. As expected, it was also observed the most pronounced shear-thinning behavior for XG compared to HPG solutions at the same concentration (Sworn, 2009).

Considering the viscoelastic properties, whatever the concentration between 0.125 and 1.5%, HPG solutions exhibit a predominant liquid-like behavior with G'' higher than G'. As the concentration of HPG increased, G', G'' increased, tangent delta decreased as the result of elasticity enhancement; this is the consequence of both chains entanglement and increased interactions between macromolecules.

Furthermore, except at 0.125% where a predominant liquid-like behavior is obtained ($G'' > G'$), all XG solutions above 0.25%, exhibited a predominant elastic behavior ($G' > G''$). As concentration increased, G', G'' increased and tangent delta decreased to reach a plateau from 1% XG in solution. It is remarkable that, from a concentration of 1%, XG exhibit a weak strain overshoot on the G'' (results not shown); when strain is increased after the linear region, G' begins to drop while G'' first increases to reach a maximum and then decreases. This phenomenon, characteristic of concentrated XG solutions, is known as the weak strain overshoot phenomenon, due to the formation of a weakly structured material (Hyun, Kim, Ahn, & Lee, 2002). Also referred as a weak gel-like behavior, it illustrates the ability for the system to resist against deformation up to a given strain. Then, after a critical strain and unlike strong gel, G'' decreases and this complex structure is destroyed and begins to flow. This may be due to the stiffness and the highly extended

Table 1
Rheological values of xanthan gum (XG) and hydroxypropyl guar (HPG) solutions.

XG (% w/w)	Newtonian viscosity (Pa s)	G' (Pa)	G'' (Pa)	Tangent delta
0.125	0.17 ± 0.01	0.06 ± 0.00	0.13 ± 0.00	2.19 ± 0.04
0.25	1.38 ± 0.01	0.97 ± 0.03	0.67 ± 0.02	0.70 ± 0.01
0.5	22.50 ± 1.40	6.25 ± 0.07	2.20 ± 0.02	0.36 ± 0.01
1	84.80 ± 7.30	26.61 ± 0.39	7.18 ± 0.21	0.27 ± 0.01
1.2	127.10 ± 7.50	37.29 ± 0.63	9.54 ± 0.16	0.26 ± 0.01
1.5	174.10 ± 9.20	50.78 ± 0.59	12.63 ± 0.11	0.25 ± 0.01
HPG (% w/w)				
0.125	0.06 ± 0.02	0.01 ± 0.00	0.02 ± 0.00	3.53 ± 0.17
0.25	0.16 ± 0.01	0.01 ± 0.00	0.06 ± 0.00	7.12 ± 0.58
0.5	0.63 ± 0.03	0.16 ± 0.00	0.55 ± 0.00	3.55 ± 0.10
1	8.80 ± 0.40	3.25 ± 0.08	5.52 ± 0.05	1.71 ± 0.02
1.2	16.80 ± 0.43	6.71 ± 0.12	9.68 ± 0.11	1.44 ± 0.01
1.5	33.00 ± 1.09	15.07 ± 0.21	18.59 ± 0.24	1.23 ± 0.01

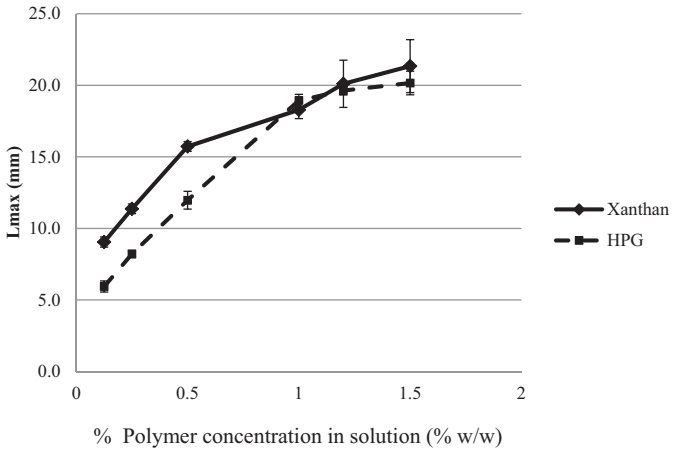

Fig. 1. Filament stretching (L_{max}) of xanthan and hydroxypropyl guar (HPG) solutions.

structure of the macromolecules of XG, as well as its tendency to form weak interactions between polymer chains.

For both gums, G' and G'' showed an exponential increment with concentration. Noteworthy is the more pronounced rise in G' for XG than for HPG with increasing concentration. This result reflects the higher magnitude of elasticity and the structuration effect of the XG solution when compared to HPG.

The stretching properties of both gums solutions are presented in Fig. 1, with L_{max} as a function of polymer concentration. In both cases, L_{max} increased with the polymer concentration, starting from low extensional properties (values between 5 and 10 mm) to reach higher values, around 20 mm, for the solutions containing 1.5% (w/w) of polysaccharides. Between 0.125% and 0.5%, XG and HPG solutions show a linear L_{max} increase with highest values for XG solutions compared to HPG ones. Then, unlike what was observed with shear and oscillation rheology, slope changes are observed for XG solutions with a slope reduction while a linear increase in L_{max} for HPG was noticed until 1% concentration followed by a logarithmic increase tending to an asymptotic value. As a consequence, same values of L_{max} for XG and HPG were reported at two different concentrations, 1% and 1.2%, respectively. At 1.5%, the difference between both gums again became significant at a 5% level ($P = 0.017$) and XG exhibited stretching property fairly higher than HPG. The lack of correlation between rheological and stretching properties is interpreted as the difference between extensional flow and shear flow. In a shear flow, molecules most likely rotate in the presence of a differential velocity profile across the flow field. In contrast, during an extensional flow, the favored molecular orientation tends to be the direction of the flow field, possibly leading to a maximum stretching of the molecules and a large tension to the polymer chain. Therefore, polymer molecules have a tendency to produce a significantly larger resistance to deformation in an extensional flow when compared to that in a shear flow (Barnes, Hutton, & Walters, 1989; Chan et al., 2009). Molecule resistance to stretching appears to be dependent on polymer concentration in solution for XG and HPG, and also related to their special configuration during stretching.

The other phenomena influencing the XG flow properties is called jamming transition; XG molecules, as relatively stiff polyelectrolytes, undergo a jamming transition which is induced by random blocking of the dynamics of the rigid molecules. The jamming transition of XG solutions can be modified by the ionic strength (Maurer, Junghans, & Vilgis, 2012). Jamming transition may induce a partially spring-like behavior in XG molecules thus affecting their extensional properties which is not visible in shearing flow. Few data are available in the literature concerning extensional properties of polysaccharides solutions, however, it is known that XG has complex rheological properties in extensional flow.

Extensional properties of dilute XG solutions in the absence or in the presence of electrolytes have been investigated by Carrington, Odell, Fisher, Mitchell, and Hartley (1996) in order to understand the conformation of XG macromolecules in the presence of salts and at different concentrations. They suggested an ordering state at higher concentrations due to intermolecular effects.

In aqueous solution, XG undergoes a well-known order (helix) to disorder (coil) transition depending on temperature, ionic strength and pH (Milas, Reed, & Printz, 1996; Capron, Brigand, & Muller, 1997). At room temperature, in the presence of external ionic strength, XG is known to be in an ordered conformation as a double-stranded wormlike chain conformation (Paradossi, Chiessi, Barbiroli, & Fessas, 2002). The coaxial double helix for the ordered XG conformation suggested by many researchers may be responsible for larger stretched filament if compared to the HPG not having this conformation.

Few studies focused on the conformation of HPG in aqueous solutions in diluted, semi-diluted and concentrated regimes (Risica et al., 2010; Duxenneuner, Fischer, Windhab, & Cooper-White, 2008). Extensional properties of hydroxyethyl ether guar gum has been studied using CABER rheometer by Duxenneuner et al. (2008). They studied shear, apparent extensional viscosities and viscoelastic properties of a series of dilute and semi-dilute gums solutions (0.01, 0.1, 0.5 w/w). They assumed that at a concentration below 0.2% w/w, extensional response is due mostly to alignment and extension of individual chains and above 0.2% w/w extensional response is mostly governed by significant interchain interactions and not entanglements as would be expected in rigid-rod systems. This behavior is due to the intrinsic semi-flexible nature of these modified guars along with reduced levels of hydrogen bonding in solution (as a result of the hydrophobic substitution).

3.2. Rheological and stretching properties of mixed solutions

Combinations of XG and guar gums are known to show a synergistic viscosity increase, i.e. the observed viscosity is higher than the sum of viscosities of each gum alone. To our knowledge, combination of XG and HPG were not studied while the substitution could have an impact on synergy. Thus, it was important to evidence the occurrence of a synergistic effect between our samples. This was reached by studying both the Newtonian viscosity at low shear rate and the viscoelastic properties of mixtures as a function of XG proportion and at different total polymer concentrations. The Newtonian viscosity at low shear rate of various mixtures of XG and HPG gum at three total concentrations is presented in Fig. 2. One can observe that the Newtonian viscosity of the mixture was mainly higher than the viscosity of the pure gum solutions (corresponding to the values at 0 and 100% in the x-axis for HPG and XG pure solutions, respectively). As a result a synergistic effect was demonstrated between XG and HPG for concentrations ranging from 0.125% to 0.5%. Moreover a maximum value of viscosity was evidenced for the ratio of 25/75 (XG/HPG).

For gums concentrations above 0.5%, it was not possible to obtain homogeneous mixtures using the same protocol of preparation. For this study, we chose a preparation procedure for solutions at room temperature in order to match the procedure used for emulsions and to avoid the order–disorder transition in XG molecules. At 0.5% concentration, gelation occurred for some ratios in XG and led to difficulties to obtain uniform mixture solutions.

To better characterize the rheological properties of mixtures, their viscoelastic properties were measured following the same procedure as for pure polymer solutions. G' and tangent delta of mixed solutions are presented in Fig. 3. Solutions exhibited a

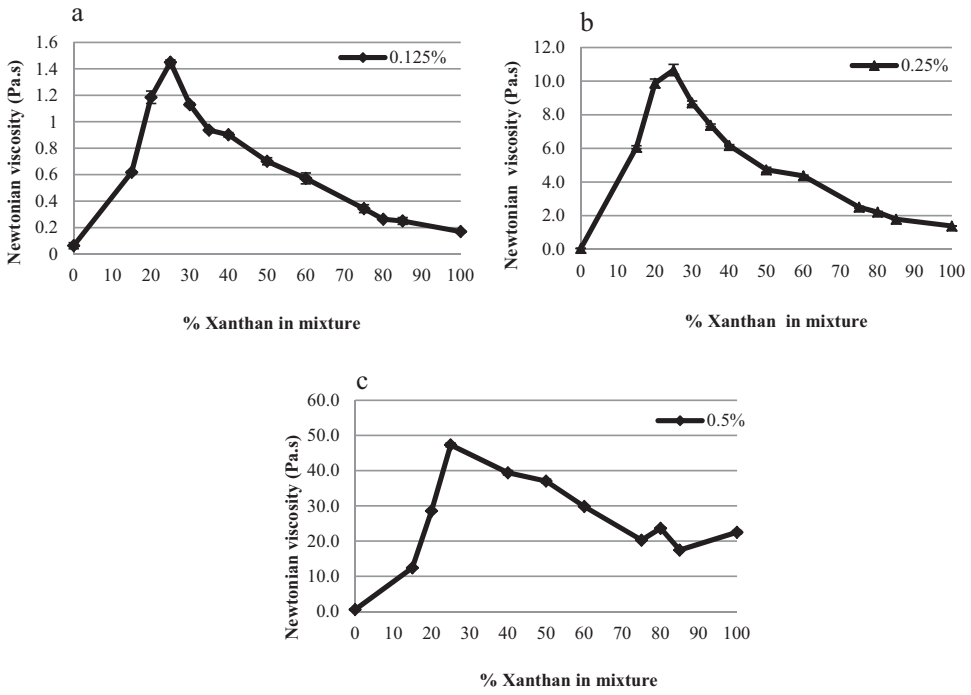

Fig. 2. Viscosity graphs of mixed solutions as a function of xanthan percentage in ratio at three concentrations (a = 0.125%, b = 0.25% and c = 0.5%).

solid-like behavior having the tangent delta value lower than 1 except for the pure HPG solutions and at 0.125% concentration for ratios above 60/40 XG/HPG. However, the G' values remained fairly low (<8 Pa) and the lowest value reached by tangent delta was 0.22, thus reflecting structures of weak gels. As for the viscosity (Fig. 2), the G' graphs show quite similar shape for the three polymer concentrations. The curves describe a maximum around 25/75 ratio but with a wide maximum range. The G' appears stable from 25 to 60% XG in mixture at 0.5% concentration (maximum G' value about 7 Pa), from 20 to 35% for 0.25% (maximum G' value about 1.7 Pa) and from 20 to 30% for 0.125% (maximum G' value about 0.24 Pa). Moreover, only at 0.5% concentration, viscoelastic spectra of mixtures from 50% to 100% XG exhibited a weak strain overshoot on G'' in relationship with the typical viscoelastic behavior reported previously for XG. Therefore, this means that at higher polymer concentrations G' tends to reached a plateau in a wider range of ratios; this may be related to both the well-known synergy between XG and guar, currently observed even at low XG content, and of the weak gel behavior induced by XG; therefore, of maximum of elastic behavior is observed in a fairly large XG/HPG ratio range as the consequence of these contributions. Nevertheless, at high XG content (i.e. above gums 70/30 ratio), the synergy is weakened and the mixture's behavior becomes mainly governed by XG thus explaining the G' increasing. In their study, Pinheiro et al. (2011) studied the evolution of G' for mixtures of XG and guar gum at a total polymer concentration of 1% and obtained a maximum only for 20/80 (XG/G) ratio, unlike what we observed. These differences could be related to a different preparation of polymer solutions or the hydroxypropyl substitution on the guar gum. Otherwise, tangent delta parameter shows minimum values for the 25/75 ratio whatever the concentration; this ratio corresponds to the maximum synergy for the gums in these conditions.

Several models have been proposed explaining the intermolecular binding mechanism causing the synergy between XG and guar gums. These models do not provide a unique explanation for XG–guar interactions and are not discussed herein (Cairns, Miles, Morris, & Brownsey, 1987; Chandrasekaran & Radha, 1997; Cheetham & Punruckvong, 1989; Tako & Nakamura, 1985). The aim of the present study was rather to understand how the synergistic effect between the two gums may affect the stretching properties of the solution, so the stretching properties of XG–HPG mixture solutions were studied as formerly mentioned. The L_{max} of mixture solutions as a function of polymers concentration is reported in Fig. 4. Results indicate that L_{max} significantly changes with both the concentration and the ratio of XG. The solution stretching ability increases with the increase of total polymer concentration. This illustrates thus that the synergistic effect also expressed itself in filament stretching. Interactions between macromolecules enhanced

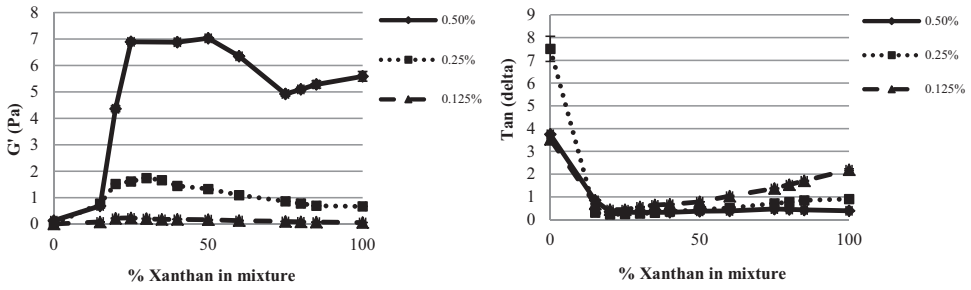

Fig. 3. G' and tangent delta graphs of mixed solutions as a function of xanthan percentage in ratio at three concentrations.

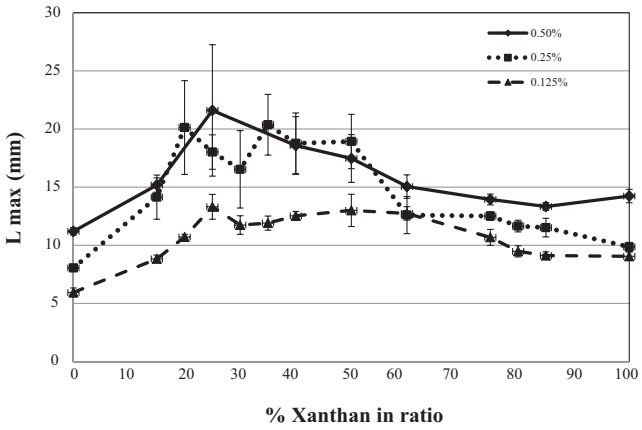

Fig. 4. Filament stretching (L_{max}) of xanthan–hydroxypropyl guar mixture solutions.

the stretching properties of the solutions as a result of an increase in the resistance to the deformation. At the three concentrations, the maximum synergies were observed for XG/HPG ratios between 25/75 and 50/50. The highest filament lengths were obtained for the ratios of 25/75 at 0.125% (13.3 mm), 35/65 at 0.25% (20.4 mm) and 25/75 at 0.5% (21.6 mm).

The synergy induces an increase in the L_{max} but also an increase in the standard deviation of the measurements. As seen, the L_{max} has a considerable standard deviation in ratios from 20 to 40% XG at 0.25 and 0.5% concentrations because of gelation effect; the filament stretched well in some repeats and rapidly broke for some others.

More uniform the solution, more filament stretching is repeatable. This non-uniformity of these solutions is demonstrated in Fig. 5 for 25/75 at 0.25% as the images of filaments just one frame before filament breaking. For this example, measurements varied from 15.77 to 19.87 mm. It is thus remarkable to obtain filament stretching that reflects the interactions between XG and HPG.

Consequently, the synergy between XG and HPG enhances the rheological properties of the systems, on the one hand, and boosts the stretching capacities on the other hand. Moreover results revealed that there was a relationship between the extensional behavior and the rheological parameters considering either the Newtonian viscosity or G'. The more viscous and elastic are the solutions the higher stretching properties are observed. Nevertheless, this relationship is not strong enough to envisage a prediction of the stretching properties using rheology. This conclusion considering only systems with XG and HPG complements a previous study from Gilbert et al. (2013a), focused on different hydrophilic polymers either natural, naturally-derived and, synthetics. In this work, authors showed that solutions containing synthetic polymers formed firm gels that appeared the less stretchable. Oppositely, the present study establishes that it is possible to obtain in certain conditions, weak gels owning important stretchability. With these two different gel behaviors, it is important to note that the stretching properties are not lonely governed by the rheological properties.

3.3. Rheological and stretching properties of emulsions

In the second part, the synergistic effect of XG and HPG on stretching properties of an O/W emulsion (cosmetic cream) was investigated, at 3 distinct polymer concentrations: 0.25, 0.5 and 1%, respectively. The concentration at 0.125% was not selected since filament stretching observed in aqueous solutions was weak. Besides, the concentrations higher than 1% were not considered because they are not consistent with cosmetic applications. Regarding the ratios in XG/HPG, we investigated three different fractions: 0/100, 40/60 and 100/0. All rheological and textural analyses were realized in the same conditions as the ones performed for the solutions.

Emulsions are mainly thermodynamically non-equilibrated systems due to an excess of the mixture surface free energy. Obviously emulsions containing several ingredients and more potential interactions with polymers have more complex rheological characteristic if compared with the pure polymer solutions. For instance there is undoubtedly an interrelation between the rheology of interfacial surfactant layers and the stability of emulsions because the latter is determined mainly by the elasticity (thermodynamic factor) and viscosity (kinetic factor) in droplet interactions (Derkach, 2009).

Results indicate that all prepared emulsions demonstrated a Newtonian plateau at low shear followed with a shear-thinning behavior; the Newtonian viscosity of emulsions containing the gums at three concentrations is presented in Fig. 6. It is worth mentioning that the Newtonian viscosity as observed as a plateau in flow graphs of solutions was not directly accessible for emulsions at 0.25 and 0.5% polymer content while it was surprisingly accessible at 1%. Consequently, the Newtonian viscosity value was obtained by computing the data using the Cross model which mathematically calculated the viscosity limit at low shear. Other rheological models were also tested but did not fit well.

The calculated viscosity of Control emulsion without any polymer was 209.4 Pa.s which is higher than those of emulsions at 0.25% and for two ratios at 0.5% meaning that at these concentrations, XG and HPG surprisingly did not act as viscosity enhancer.

Another point is that the gum mixtures synergy did not govern the emulsions rheological behavior at 0.5 and 1% polymer content as the emulsions with only XG showed a higher viscosity when compared to those prepared with the 40/60 XG/HPG ratio. As a result, the XG/HPG gum mixtures synergistic effect observed in solution was not observed in emulsions according to the rheological measurements. This may be related to some physicochemical factors including the polymer interaction with other ingredients or the presence of oil phase as micro globules. Many other

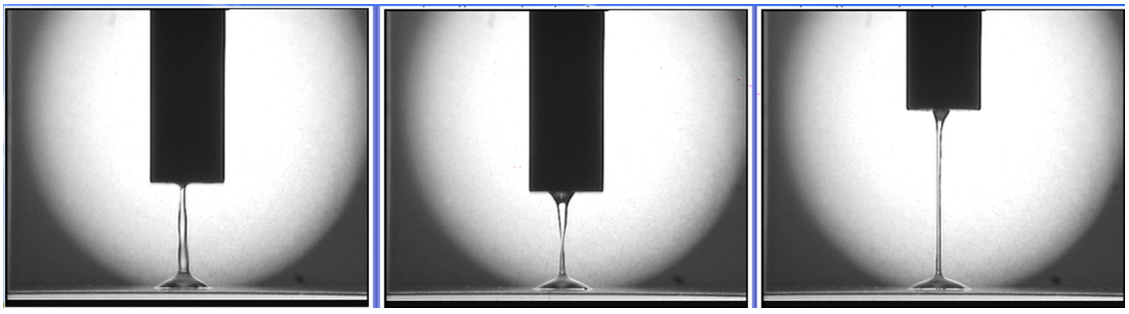

Fig. 5. Stretching filament of three xanthan/hydroxypropyl guar solutions (25/75) at 0.25%. The photos were taken one frame before filament breaking.

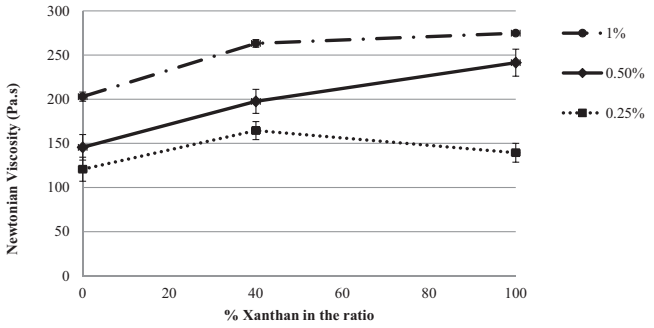

Fig. 6. The Newtonian viscosity of emulsions containing xanthan, hydroxypropyl guar and 40/60 mixture at 0.25%, 0.5% and 1%, respectively.

factors including the rheological behavior of the continuous phase, deformation and break-up of droplets in emulsions during flow, the nature of the particles, their concentration, their size distribution, microscopic droplet structure and finally the droplet–droplet interfacial interactions are also important (Lorenzo, Zaritzky, & Califano, 2008).

The filament stretching results of emulsions is presented in Table 2. The Control emulsion without polymer had the L_{max} equal to 11.5 mm; as seen, in contrast to polymer viscosimetric behavior, both polymers positively influenced the filament stretching at all concentrations. At 0.25%, the filament stretching was fairly stable for the different ratios, while at 0.5 and 1%, a progressive effect of polymers on filament stretching occurred. Similarly to emulsions viscosity, the synergistic effect was not observed for filament stretching. Emulsions containing pure XG had the maximum L_{max} at all concentrations and stretchability was improved with an increasing proportion of XG. Gilbert et al. (2013a) showed that among eight natural and synthetic polymers used in the same emulsion formulation, XG had the maximum stretchability at 1% concentration confirming a strong interaction between this gum and other ingredients in emulsion.

XG is usually added to the aqueous phase of O/W emulsions to form complex aggregates through hydrogen bonds and polymer entanglement in order to retard the creaming caused by flocculation of dispersed droplets. The increased viscosity results in a reduced Brownian movement of droplets and imparts the additional elastic properties to the whole system so that emulsion creaming is strongly inhibited (Hemar, Tamehana, Munro, & Singh, 2001; Lorenzo et al., 2008). On the one hand, in addition to its anti-creaming role, XG in collaboration with other ingredients in aqueous phase acts as a plasticizing agent leading the filament more stretchable. On the other hand, it seems that jamming transition of XG molecules in emulsions due to their interactions with other ingredients is less evident permitting the emulsions to stretch more than the solutions. This aspect of XG functionality affected by other ingredients needs more investigations to precisely determine the types and degree of these interactions. Indeed, Różańska et al. (2013) have studied extensional properties of oil-in-water emulsions stabilized by polysaccharides, and in particular XG and guar gum. They compared aqueous solutions and emulsions containing those polysaccharides at different concentrations and oil volume fractions. They showed that extensional properties depend on the nature of polysaccharides incorporated, and so, on the rheology of the continuous phase but also on the volume fraction of oil phase and more particularly on the flocculation state of the droplets.

Table 2
Filament stretching (in mm) of emulsions containing xanthan gum (XG) and hydroxypropyl guar (HPG).

XG/HPG ratio (%)	Total polymer concentration in emulsion (% w/w)		
	0.25%	0.5%	1%
0/100	15.46 ± 0.42	23.06 ± 0.57	26.3 ± 1.11
40/60	17.15 ± 0.56	27.54 ± 1.54	29.4 ± 1.64
100/0	17.57 ± 0.66	29.83 ± 0.53	39.5 ± 2.01

4. Conclusion

The potential relationship between rheological values and filament stretching property of xanthan gum (XG) and hydroxypropyl guar (HPG) was investigated in pure and mixed aqueous solutions and also in cosmetic emulsions. In pure solution, distinct rheological behaviors were observed between XG and HPG. At the various concentrations, XG solutions were more viscous with a solid-like behavior. Concerning their stretchability, XG showed higher values than HPG for concentration below 1% w/w and then filament stretching properties were close for both polymers at higher concentrations. These results could be related to specific conformations of each macromolecule. Accordingly results reveal a link between filament stretching and rheological properties, but not strong enough to envisage prediction. In mixed solutions, a pronounced synergistic effect was observed for XG/HPG solution at a 25/75 ratio at the different concentrations (0.125%, 0.25% and 0.5% w/w). Noteworthy is the influence of the synergy on the stretching property since the interaction between XG and HPG results in an enhancement of the maximum filament length. Considering emulsions, stretching properties of the ones containing HPG or XG were higher than the stretching properties of the aqueous solutions containing the same concentration of pure polymer. No synergy was evidenced between the two gums: stretching properties of the emulsions containing mixture of XG and HPG increase with the total concentration of polymers and, at a fixed total concentration, with the amount of XG in mixture. However, XG demonstrated the major role in viscosity and filament stretching increment. This could be related to interactions between XG and other ingredients present in the emulsion. So, more rheological and textural parameters should be investigated in order to understand how XG governs the behaviors of the system and why no interaction was observed with HPG.

References

Barnes, H. A., Hutton, J. F., & Walters, K. (1989). Extensional viscosity. In *An introduction to rheology*. Amsterdam: Elsevier Science Publishers.
Cairns, P., Miles, M. J., Morris, V. J., & Brownsey, G. J. (1987). X-Ray fibre-diffraction studies of synergistic, binary polysaccharide gels. *Carbohydrate Research*, *160*(0), 411–423.
Capron, I., Brigand, G., & Muller, G. (1997). About the native and renatured conformation of xanthan exopolysaccharide. *Polymer*, *38*(21), 5289–5295.
Carrington, S., Odell, J., Fisher, L., Mitchell, J., & Hartley, L. (1996). Polyelectrolyte behaviour of dilute xanthan solutions: Salt effects on extensional rheology. *Polymer*, *37*(13), 2871–2875.
Chan, P. S.-K., Chen, J., Ettelaie, R., Alevisopoulos, S., Day, E., & Smith, S. (2009). Filament stretchability of biopolymer fluids and controlling factors. *Food Hydrocolloids*, *23*(6), 1602–1609.
Chan, P. S.-K., Chen, J., Ettelaie, R., Law, Z., Alevisopoulos, S., Day, E., & Smith, S. (2007). Study of the shear and extensional rheology of casein, waxy maize starch and their mixtures. *Food Hydrocolloids*, *21*(5–6), 716–725.
Chandrasekaran, R., & Radha, A. (1997). Molecular modeling of xanthan:galactomannan interactions. *Carbohydrate Polymers*, *32*(3–4), 201–208.
Cheetham, N. W. H., & Punruckvong, A. (1989). Gel-permeation and optical rotation studies on xanthan–galactomannan interactions. *Carbohydrate Polymers*, *10*(2), 129–141.
Derkach, S. R. (2009). Rheology of emulsions. *Advances in Colloid and Interface Science*, *151*(1–2), 1–23.
Duxenneuner, M. R., Fischer, P., Windhab, E. J., & Cooper-White, J. J. (2008). Extensional properties of hydroxypropyl ether guar gum solutions. *Biomacromolecules*, *9*(11), 2989–2996.
Faria, S., de Oliveira Petkowicz, C. L., de Morais, S. A. L., Terrones, M. G. H., de Resende, M. M., de França, F. P., & Cardoso, V. L. (2011). Characterization of xanthan gum produced from sugar cane broth. *Carbohydrate Polymers*, *86*(2), 469–476.
Fitzpatrick, P., Meadows, J., Ratcliffe, I., & Williams, P. A. (2013). Control of the properties of xanthan/glucomannan mixed gels by varying xanthan fine structure. *Carbohydrate Polymers*, *92*(2), 1018–1025.

Gilbert, L., Loisel, V., Savary, G., Grisel, M., & Picard, C. (2013). Stretching properties of xanthan, carob, modified guar and celluloses in cosmetic emulsions. *Carbohydrate Polymers*, *93*(2), 644–650.

Gilbert, L., Savary, G., Grisel, M., & Picard, C. (2013). Predicting sensory texture properties of cosmetic emulsions by physical measurements. *Chemometrics and Intelligent Laboratory Systems*, *124*(0), 21–31.

Gong, H., Liu, M., Chen, J., Han, F., Gao, C., & Zhang, B. (2012). Synthesis and characterization of carboxymethyl guar gum and rheological properties of its solutions. *Carbohydrate Polymers*, *88*(3), 1015–1022.

Hemar, Y., Tamehana, M., Munro, P. A., & Singh, H. (2001). Influence of xanthan gum on the formation and stability of sodium caseinate oil-in-water emulsions. *Food Hydrocolloids*, *15*(4–6), 513–519.

Hyun, K., Kim, S. H., Ahn, K. H., & Lee, S. J. (2002). Large amplitude oscillatory shear as a way to classify the complex fluids. *Journal of Non-Newtonian Fluid Mechanics*, *107*, 51–65.

Khouryieh, H. A., Herald, T. J., Aramouni, F., & Alavi, S. (2006). Influence of mixing temperature on xanthan conformation and interaction of xanthan–guar gum in dilute aqueous solutions. *Food Research International*, *39*(9), 964–973.

Lapasin, R., De Lorenzi, L., Pricl, S., & Torriano, G. (1995). Flow properties of hydroxypropyl guar gum and its long-chain hydrophobic derivatives. *Carbohydrate Polymers*, *28*(3), 195–202.

Lorenzo, G., Zaritzky, N., & Califano, A. (2008). Modeling rheological properties of low-in-fat o/w emulsions stabilized with xanthan/guar mixtures. *Food Research International*, *41*(5), 487–494.

Maurer, S., Junghans, A., & Vilgis, T. A. (2012). Impact of xanthan gum, sucrose and fructose on the viscoelastic properties of agarose hydrogels. *Food Hydrocolloids*, *29*(2), 298–307.

Milas, M., Reed, W. F., & Printz, S. (1996). Conformation and flexibility of native and re-natured xanthan in aqueous solutions. *International Journal of Biological Macromolecules*, *18*, 211–221.

Niedzwiedz, K., Buggisch, H., & Willenbacher, N. (2010). Extensional rheology of concentrated emulsions as probed by capillary breakup elongational rheometry (CaBER). *Rheologica Acta*, *49*(11–12), 1103–1116.

Paradossi, G., Chiessi, E., Barbiroli, A., & Fessas, D. (2002). Xanthan and glucomannan mixtures: Synergistic interactions and gelation. *Biomacromolecules*, *3*(3), 498–504.

Pinheiro, A. C., Bourbon, A. I., Rocha, C., Ribeiro, C., Maia, J. M., Gonçalves, M. P., Teixeira, J. A., & Vicente, A. A. (2011). Rheological characterization of kappa-carrageenan/galactomannan and xanthan/galactomannan gels: Comparison of galactomannans from non-traditional sources with conventional galactomannans. *Carbohydrate Polymers*, *83*, 392–399.

Różańska, S., Broniarz-Press, L., Różański, J., Mitkowski, P. T., Ochowiak, M., & Woziwodzki, S. (2013). Extensional viscosity of o/w emulsion stabilized by polysaccharides measured on the opposed-nozzle device. *Food Hydrocolloids*, *31*(1), 130–142.

Risica, D., Barbetta, A., Vischetti, L., Cametti, C., & Dentini, M. (2010). Rheological properties of guar and its methyl, hydroxypropyl and hydroxypropyl-methyl derivatives in semidilute and concentrated aqueous solutions. *Polymer*, *51*(9), 1972–1982.

Schorsch, C., Garnier, C., & Doublier, J.-L. (1997). Viscoelastic properties of xanthan galactomannan mixtures: Comparison of guar gum with locust bean gum. *Carbohydrate Polymers*, *34*(3), 165–175.

Secouard, S., Grisel, M., & Malhiac, C. (2007). Flavour release study as a way to explain xanthan–galactomannan interactions. *Food Hydrocolloids*, *21*(8), 1237–1244.

Sujatha, K. S., Matallah, H., Banaai, M. J., & Webster, M. F. (2008). Modeling step-strain filament-stretching (CaBER-type) using ALE techniques. *Journal of Non-Newtonian Fluid Mechanics*, *148*(1–3), 109–121.

Sworn, G. (2009). Xanthan gum. In G. O. Phillips, & P. A. Williams (Eds.), *Handbook of hydrocolloids* (p. 186). Cambridge, UK: CRC Press, Woodhead Publishing Ltd.

Tako, M., & Nakamura, S. (1985). Synergistic interaction between xanthan and guar gum. *Carbohydrate Research*, *138*(2), 207–213.

Wu, X., Ye, Y., Chen, Y., Ding, B., Cui, J., & Jiang, B. (2010). Selective oxidation and determination of the substitution pattern of hydroxypropyl guar gum. *Carbohydrate Polymers*, *80*(4), 1178–1182.

Xu, L., Xu, G., Liu, T., Chen, Y., & Gong, H. (2013). The comparison of rheological properties of aqueous welan gum and xanthan gum solutions. *Carbohydrate Polymers*, *92*(1), 516–522.