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Stretching properties of xanthan, carob, modified guar and celluloses in cosmetic emulsions

Laura Gilbert, Vincent Loisel, Géraldine Savary, Michel Grisel, Céline Picard*

Université du Havre, URCOM, EA 3221, FR CNRS 3038, 25, rue Philippe Lebon B.P. 540, 76058 Le Havre Cedex, France

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ABSTRACT

The filament stretching properties of various polysaccharides (including xanthan, carob, hydroxypropyl guar, hydroxypropylmethyl and hydroxyethyl celluloses) were investigated and compared to synthetic polymers generally used as texturing agents in cosmetic emulsions. The stretchability was examined by sensory evaluation as “the amount of sample that strings rather than breaks when fingers are separated”. Different behaviors were evidenced: the xanthan emulsion showed the highest stretchability, followed by the hydroxypropyl guar and hydroxyethyl cellulose emulsions while the synthetic polymers presented stretching properties to a much lesser extent. The instrumental characterization of the stretchability was conducted at a controlled speed and recorded with a camera using a texture analyzer. The maximum stretchable length at 40 mm/s was highly significantly correlated to the sensory *Stringiness*, thus allowing a good predictability of this attribute. Finally, this method was applied to aqueous solutions to better understand the role of the polymers in emulsion and to validate the measurement on a wider range of products.

1. Introduction

Emulsions have found extensive applications in many areas, e.g. food industry, cosmetics, paints, pharmaceuticals and many household products. Their texture properties are known to be of great importance, more particularly in food and in cosmetics fields where the consumers’ preference is closely connected to the texture of the product. As a consequence, sensory analysis has been widely used and developed over the last few decades to characterize human’s perception (Meilgaard, Civille, & Carr, 2006) of various types of emulsions. However, using sensory analysis implies some inconveniences when considering its important cost of time and money on the one hand, and volunteers’ subjective evaluation on the other hand. Besides, rheological measurements are also very useful to characterize the flow properties of emulsions and to provide important information about their physical stability as well as to allow predicting their behavior during manufacturing and application (Barnes, 1994; Tadros, 1994, 2004). In addition, texture analysis is commonly used in the food industry to characterize the mechanical properties in various systems such as emulsions. It may be also helpful for analyzing the properties related to the texture of cosmetic products, although surprisingly very few studies have focused on this type of products (Lemaitre-Aghazarian et al., 2004; Smewing & Jachowicz, 2007).

Among the various texturing properties characterizing cosmetic products, this work focused on one particular sensory attribute related to stretching phenomena. This attribute expressed as *Cohesiveness* or *Stringiness* (Civille & Dus, 1991, 2005; Lee et al., 2005) is evaluated during the pick-up, which corresponds to the properties perceived in the hand when the product is taken from its container. Civille and Dus (1991) defined the *Stringiness* as “amount sample deforms or strings rather than breaks when fingers are separated”. This definition, a bit confused, means that the stringier a product, the more it makes long filaments. The sensory evaluation of this attribute is therefore related to samples’ extensional properties. These features can be also instrumentally quantified by various means, including Capillary Break-up Elongation Rheometer (CaBER). In CaBER experiments, a pure extensional flow is created by suddenly stretching the fluid to produce a filament between two parallel plates. The resulting liquid bridge deforms gradually under the action of viscoelastic and capillary forces, contracts, and finally breaks. The transient neck diameter, time evolution of the neck curvature, the region of deformation and the filament lifetime are extracted in order to characterize non-uniform filament thinning (Bourbon et al., 2010; Chan et al., 2007, 2009; Niedzwiedz, Buggisch, & Willenbacher, 2010). Nevertheless, elongational flow behavior remains complex to set up on the one hand, and CaBER’s measurements are rather different from the sensory assessment of the *Stringiness* on the other hand, the sensory

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* Corresponding author. Tel.: +33 232 744 394; fax: +33 232 744 391.
E-mail address: celine.picard@univ-lehavre.fr (C. Picard).

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evaluation consisting on measuring a maximum filament breaking length.

The objectives of this work were firstly to set up a simple instrumental characterization of the sensory attribute *Stringiness*, and secondly to explore the effects of different hydrophilic polymers, more particularly polysaccharide-based ones, on stretching properties of oil-in-water (O/W) cosmetic emulsions. The choice of hydrophilic polymers is justified as they are widely used in O/W emulsions as thickeners and rheology modifiers, but also as emulsion stabilizers, emulsifiers, or moisturizers. We therefore selected two natural polysaccharides, namely xanthan gum (Xanthan) and locust bean gum (Carob). Xanthan is a high molecular-weight extracellular polysaccharide composed of a cellulosic backbone substituted at every second glucose residue with a charged trisaccharide side chain; this side residue owns both acetate and pyruvic acid groups, each with a substitution degree less than 1, the value depending on the sample's fermentation and post-fermentation treatment (Hassler & Doherty, 1990). Xanthan is a polyelectrolyte with a helical secondary structure thus inducing high stabilization ability of dispersions as a result of its high viscosity at rest. Locust bean gum, from *Ceratonia Siliqua* is a galactomannan, a non-ionic polysaccharide with a backbone composed of mannose residues (M), substituted by galactose (G), with a M/G ratio of 3.5. Both are used as thickeners and suspending agents and exhibit specific rheological properties. Then we selected three non-ionic polysaccharides naturally-derived of guar or cellulose, namely hydroxypropyl guar gum (HP guar), hydroxyproprylmethyl cellulose (HPM cellulose) and hydroxyethyl cellulose (HE cellulose). HP guar has the same backbone as carob but with a higher galactose content (M/G = 1.8) and is modified with propylene oxide. HPM and HE cellulose are modified with propylene oxide and chloroacetic acid, and ethylene oxide, respectively. For these semi-synthetic polymers, the chemical modification makes it easier the powder hydration and solubilization in water, and also allows a better control of the final viscosity enhancement; these polysaccharide-derivatives are currently used as thickeners and suspending agents for many applications. Finally, three synthetic polymers were chosen for the present study, namely ammonium acryloyldimethyltaurate/VP copolymer (AADMT-co-VP), carbomer (PAA) and laureth-7, C13-14 isoparaffin, polyacrylamide (PA). AADMT-co-VP is a synthetic co-polymer of acrylamidomethylpropane sulfonic acid and vinylpyrrolidone; PAA is a crosslinked poly(acrylic acid) and PA is an inverse emulsion of polyacrylamide in paraffin. These synthetic polymers are used as gelling agents and stabilizers for cosmetic formulations.

Each polymer was incorporated in an O/W emulsion at a concentration of 1% (w/w). In addition, a formulation without any polymer was also prepared to be used as a control. The nine emulsions were sensory assessed for the attribute *Stringiness*. Classic rheological measurements, including oscillatory and flow tests were carried out and an imitative test of the sensory protocol was set up using a texture analyzer; fluids were compressed and stretched at a controlled speed to allow forming a filament. The maximum breaking length, corresponding to the maximum length measured just before the filament broke, was recorded using a camera. The influence of different testing conditions, respectively: the compression distance, the number of cycles of compression/stretching and the stretching speed, was investigated. A series of aqueous solutions containing each of the cited polymers at a concentration of 1% (w/w) was also assessed using the same analytical protocols in order to characterize the stretching properties of the polymers alone, without interaction with any ingredients such as when incorporated in the emulsion.

Table 1
List of ingredients used for the oil-in-water emulsions formulations.

	Ingredients (INCI name)	Suppliers	Content (%, w/w)
	Distilled water		79.5
Aqueous phase	Butylene glycol	Acros Organics	4
	Polymer	See Section 2.1.1	1
Oil phase	Dimethicone	Dow Corning	1
	Steareth 2	Croda	3
	Steareth 21	Croda	2
	Isohexadecane	IMCD	7
	Paraffin	Baeriocher France	1.5
	Stearic acid	Croda	0.5
Preservative	Phenoxyethanol, Methylparaben, Ethylparaben, Propylparaben	Jan Dekker International	0.5

2. Materials and methods

2.1. Materials

2.1.1. Polymers used

Five hydrophilic carbohydrate polymers, namely xanthan gum, galactomannans and cellulose derivatives, and three synthetic polymers were selected for their frequent use in the cosmetic field. These eight polymers are identified for the rest of the study by a code given in brackets hereafter. These are a ceratonia siliqua gum (Carob) obtained from Degussa (trade name: Viscogum BJ); a xanthan gum (Xanthan) and a hydroxypropyl guar gum (HP guar) purchased from Rhodia (trade names: Rhodicare T and HP 105, respectively); a hydroxyethyl cellulose (HE cellulose) provided by Hercules (trade name: Natrosol 250 HHBR); and a hydroxypropylmethyl cellulose (HPM cellulose) obtained from Dow Chemical (trade name: Methocel E4QG). The three synthetic hydrophilic polymers used were an ammonium acryloyldimethyltaurate/VP copolymer (AADMT-co-VP) from Clariant (trade name: Aristoflex AVC); a carbomer (PAA) from Lubrizol (trade name: Carbopol Ultrez 10) and a laureth-7, C13-14 isoparaffin, polyacrylamide (PA) from Seppic (trade name: Sepigel 305). All these polymers were of cosmetic grade.

2.1.2. Polymers in emulsions

Eight O/W emulsions, as typical cosmetic creams, only varying by the texturing agent added, were prepared (ingredients list given in Table 1). Each hydrophilic polymer was incorporated at a concentration of 1% (w/w) in the emulsion. An additional O/W emulsion without any texturing agent was prepared and used as a reference in order to assess the contribution of each polymer on the final stretching properties of the emulsions, and so-named the Control emulsion in the rest of the study. The emulsions were prepared by using the following process: first the ingredients of the oil phase were mixed at 75 °C under mechanical stirring. In the same time, except for the Carob and the PAA, each polymer was 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 Carob gum required to be primarily hydrated in water at 80 °C during 2 h, while the PAA was directly added to the water phase prior to emulsification and before swelling by pH adjustment. The oil phase was then added to the distilled water at 75 °C under mechanical stirring (Turbotest VMI®, 400 rpm) for 1 min. The emulsion was then homogenized at 11,000 rpm during one additional minute using a T25 digital

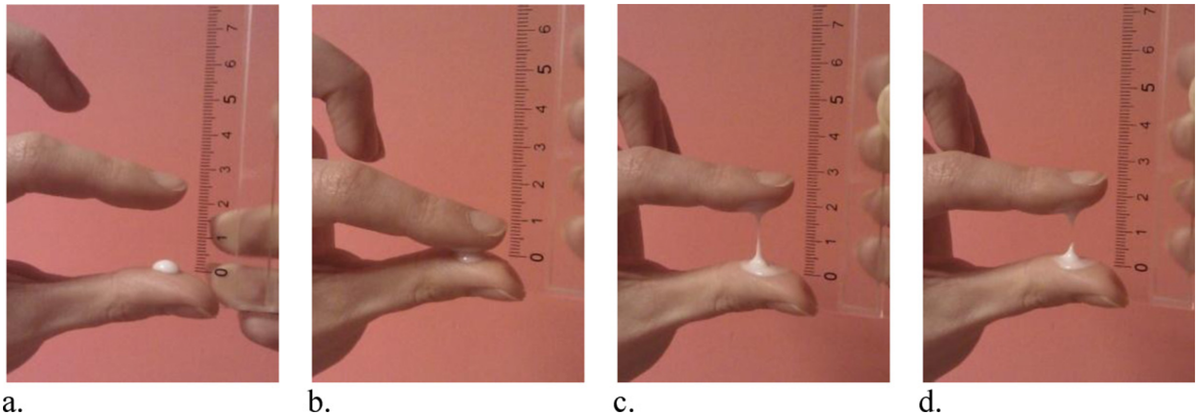

Fig. 1. Different steps of the *Stringiness* sensory evaluation protocol (detailed in Section 2.2.1) for the HPM cellulose emulsion.

ultra-turrax IKA® equipped with the dispersing element S25N-25F (rotor-stator turbine). Finally, each emulsion was continuously stirred using a Turbotest apparatus, until it cooled down to 30 °C. The polymer, when it was predispersed in butylene glycol, was incorporated during the emulsion's stirring, whereas the base triethanolamine (TEA) was added to the emulsion containing the PAA to reach a final TEA/PAA ratio of 1:1 in the preparation. Indeed, PAA polymer as supplied is dry, tightly coiled acidic molecules. Once dispersed in water, the molecules begin to hydrate and partially uncoil. The most common way to achieve maximum thickening from PAA polymer is by converting the acidic polymer to a salt. This was easily achieved by neutralizing the PAA with the base TEA. Finally, preservative and water loss compensation were added and the emulsions were kept under stirring during 15 additional minutes at room temperature. The emulsions were then stored at 4 °C to ensure preservation before further analysis.

2.1.3. Polymers in solutions

Each polymeric agent was dispersed in water to obtain a final concentration of 1% (w/w). The dispersions were stirred at room temperature for the two celluloses, the PA and the PAA. The base triethanolamine (TEA) was added to the solution containing the PAA to reach a final TEA/PAA ratio of 1:1 in the preparation, in order to achieve maximum thickening from PAA as for the emulsion. A temperature of 85 °C was necessary to ensure the Carob hydration and thus a total dispersion. The AADMT-co-VP was also added in water at 85 °C and the HP guar and the Xanthan at 50 °C to make the solubilization easier. The preservative Dekaben MEP® from Jan Dekker (Phenoxyethanol, Methylparaben, Ethylparaben, Propylparaben) was finally added in each solution at 0.5% (w/w) at room temperature. All the solutions were then stored at 4 °C.

2.2. Methods

2.2.1. Sensory evaluation of the stretching properties of the emulsions

Based on the literature (Civille & Dus, 1991, 2005; Lee et al., 2005), we developed a precise protocol for the evaluation of the attribute *Stringiness* in four steps: (a) using Microman® M250 GILSON, panelists were asked to deliver 100 μL of product on tip of thumb and to place thumb horizontally at eye level, with a ruler placed vertically behind the thumb, the graduation 0 at cream level, then (b) compress and (c) spread fingers 10 times at a rate of two compressions per second (a metronome set was used to mark time). The maximum length of filament obtained in millimeters was measured, as the *Stringiness* evaluation (d). Fig. 1 presents the corresponding four steps of the evaluation protocol.

Sixteen female panelists (ages 25–50), from Caucasian origin, were selected among volunteers from Le Havre University's employees, for their motivation, and their ability to describe and rate selected skinfeel properties. The evaluation was performed in a sensory laboratory composed of sixteen individual booths. Each sample was assigned a random three-digit code and presented in a 5 mL jar at room temperature. The order of presentation of the samples was changed every session to avoid a bias in rating scores. The *Stringiness*' evaluation was preceded by two training sessions. The 9 O/W emulsions were evaluated by the 16 panelists with 2 replicates.

2.2.2. Rheology of the emulsions and the solutions

All rheological tests were performed with a controlled stress rheometer (AR 2000, TA Instruments) 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 acclimatize at least for 2 min prior to any measurement.

2.2.2.1. 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 0.01 to 1000 s^{-1} (logarithmic mode) for 150 s.

2.2.2.2. Oscillations tests. Oscillations 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).

2.2.3. Instrumental evaluation of the stretching properties of the emulsions and the solutions

The filament stretching properties of the emulsions and the solutions were examined at room temperature using a texture analyzer TA.XT Plus (Stable Micro Systems) equipped with a 5 kg load cell. This device allows up and down vertical displacement at a maximum rate of 40 mm/s.

A specific compression/stretching test was developed using the cylindrical probe P/0.5R (½ 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 to a fixed gap between the bottom plate and the probe, and then stretched it at a constant speed. The filament stretching was monitored by 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 using

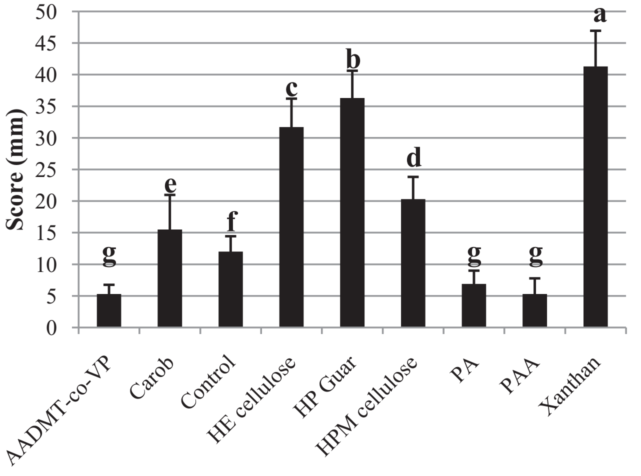

Fig. 2. Sensory scores obtained by the panel for the evaluation of the *Stringiness* on the 9 O/W emulsions (codes detailed in Section 2.1.1). The scores are averaged over the panelists and the repetitions, and given with their standard deviation and Tukey's group ($P < 0.05$).

the software Ulead Media Studio 8.0 (Ulead Systems) and processed with the software Image J. The maximum stretchable length, noted $L_{\max}$, was used to quantify the product's stretchability. The influence of different test parameters, namely the compression distance, the number of cycles of compression/stretching and the stretching speed, was investigated.

2.2.4. Statistical analyses

The statistical analysis of collected data was performed using XLSTAT software from Addinsoft (version 2012.1.01). A two-way analysis of variance (ANOVA) with interaction was applied to the sensory data in order to investigate the panel performance. The two cross factors were products and assessors. When significant differences were revealed between products ($P < 0.05$), mean intensities (over assessors and repetitions) were compared using the Tukey multiple comparison test to form different groups of products. Pearson's correlation coefficients (r_p) were calculated between sensory and instrumental data, to highlight whether significant correlations ($P < 0.05$) between both types of data exist or not.

3. Results and discussion

3.1. Stretching sensory properties of the emulsions

The sensory characterization of the emulsions stretching properties was carried out with the evaluation of the attribute *Stringiness* by a panel of sixteen assessors. First, a product × assessor ANOVA with interaction was conducted to assess the performance of the panel for the evaluation of the *Stringiness*. The analysis showed that the effect of the repetition and the interaction product × assessor was not significant ($P = 0.17$), thus proving that a consensus among panelists was reached; panelists were reproducible in their judgment and the panel was repeatable. In addition, the products were highly significantly discriminated ($P < 0.0001$). Fig. 2 summarizes the mean intensity scores (averaged over the assessors and the repetitions), associated with their standard deviations (SD) and Tukey's groups for the nine O/W emulsions. Seven distinct groups could be distinguished based on the Tukey's test, thus showing a great products diversity for the *Stringiness* with lengths of filament ranging from 5.3 mm for the PAA and AADMT-co-VP based emulsions to 41.3 mm for the Xanthan one. The three synthetic polymers clearly brought no *Stringiness* to the emulsions, as their scores were very low, even when compared to the Control emulsion (12.0 mm). For these products, when fingers were separated, samples directly broke without forming a filament but only a peak was created due to their high consistency. The measure of 5–7 mm corresponded to the height of this peak. On the contrary, the five carbohydrate polymers brought different degrees of *Stringiness* to the emulsions, ranging from intermediate values for the Carob and the HPM cellulose ones (15.5 and 20.3, respectively), to quite high intensities for the HE cellulose and the HP guar ones (31.3 and 36.3, respectively), and to very high value for the Xanthan one.

In order to study the relationships between the stretching properties and rheological behaviors of the emulsions, rheological measurements were then performed.

3.2. Rheological properties of the emulsions

3.2.1. Shear rheology

First, we analyzed the flow behavior of the 9 O/W emulsions. All the emulsions exhibited a shear-thinning behavior. The three creams containing a synthetic polymer owned a yield stress and higher values of viscosities and shear stresses than all the other emulsions. Similar flow behavior was observed for the emulsions containing a polysaccharide but differences between the curves were nevertheless noticeable. The values of viscosity and shear stress at 0.1, 1, 10, 100 and 1000 s^{-1} were collected for each product, as partly resumed in Table 2. The flow curves allowed evidencing the extreme shear-thinning behavior of the Xanthan emulsion with high values of viscosities at low shear rates as the consequence of its molecular semi-flexible structure (Quintana, Califano, Zaritzky, Partal, & Franco, 2002; Rodd, Dunstan, & Boger, 2000). As visible in Table 2, the classification of the emulsions viscosities markedly varies with the range of the shear rate. Pearson's correlation coefficients were calculated between each shear flow parameter and the *Stringiness* for the 9 O/W emulsions. However, no significant correlation could be highlighted whatever the shear rate.

3.2.2. Oscillation rheology

Strain sweep experiments ranging from 0.01 to 100% were carried out at 25 °C and at a frequency of 1 rad s^{-1}. Fig. 3 shows the mechanical spectra of the 9 O/W emulsions. All the emulsions exhibited a predominant elastic solid behavior ($G' > G''$) on the linear viscoelastic region (LVR), which had an upper limit around the percent of strain. The emulsions containing a synthetic polymer (Fig. 3b) showed much higher values of G' and G'' than the polysaccharides or the control ones (Fig. 3a). Besides, the viscous modulus of the synthetic emulsions showed a maximum around 10% of strain, featuring a gel structure (Bais, Trevisan, Lapasin, Partal, & Gallegos, 2005), maybe less cohesive than the carbohydrate based emulsions. The values of G', G'' and $\tan\delta$ on the LVR, the crossover point of G' and G'', and the corresponding strain ($\gamma_{G'=G''}$) and stress ($\sigma_{G'=G''}$) were collected for the 9 O/W emulsions. Pearson's correlation coefficients were calculated between each rheological parameter and the *Stringiness* for the 9 O/W emulsions. It appeared that the *Stringiness* was significantly ($P = 0.05$) positively correlated to the crossover strain $\gamma_{G'=G''}$ ($r_p = 0.686$) and negatively correlated to the moduli G' and G'' on the LVR and to the crossing over point $G' = G''$ (−0.675, −0.714 and −0.677, respectively). However, these coefficients were not high enough to envisage a good prediction of the emulsions' stretching properties.

Finally, as the classic rheology did not suitably allow characterizing the emulsion's stretching properties, we therefore decided to attempt to set up an instrumental test to mimic the sensory protocol, thus enabling a characterization of the stretching properties of the emulsions and, more especially, of the carbohydrate polymers.

Table 2
Values of viscosity (Pa s) at 0.1, 10 and 1000 s^{-1} (means ± SD) for the 9 O/W emulsions obtained with the shear flow test. The data are given in descending order.

Emulsions	η (0.1 s^{-1})	Emulsions	η (10 s^{-1})	Emulsions	η (1000 s^{-1})
PAA	748.2 ± 35.2	PAA	43.8 ± 1.3	PAA	1.6 ± 0.00
AADMT-co-VP	380.4 ± 13.1	AADMT-co-VP	25.3 ± 0.1	AADMT-co-VP	1.0 ± 0.0
PA	136.5 ± 5.7	PA	9.3 ± 0.1	PA	0.50 ± 0.00
Xanthan	128.4 ± 9.3	HE cellulose	4.8 ± 0.0	HE cellulose	0.26 ± 0.00
HP guar	108.2 ± 0.4	Carob	4.4 ± 0.1	Carob	0.25 ± 0.00
HE cellulose	101.1 ± 2.5	HP guar	3.6 ± 0.0	HPM cellulose	0.24 ± 0.00
Carob	85.9 ± 4.0	Xanthan	3.2 ± 0.1	HP guar	0.18 ± 0.00
HPM cellulose	53.6 ± 2.3	HPM cellulose	2.6 ± 0.0	Xanthan	0.10 ± 0.00
Control	42.4 ± 2.3	Control	1.5 ± 0.0	Control	0.07 ± 0.00

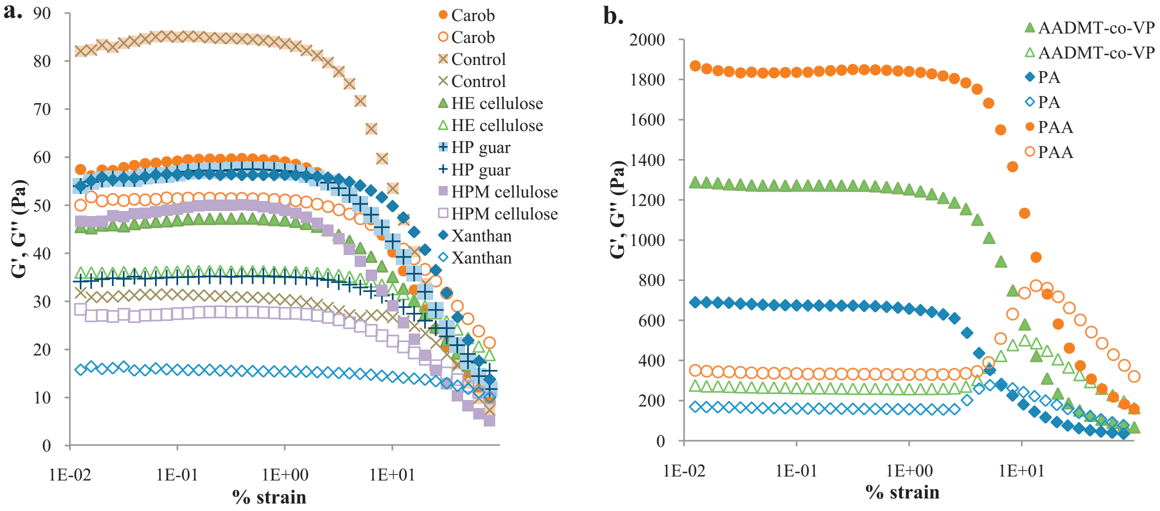

Fig. 3. Viscoelastic characterization of the 9 O/W emulsions (codes detailed in Section 2.1.1) at 1 rad s^{-1}. Each curve presents the mean values over three tests. The standard deviations remain lower than 5%, and are not shown for a better readability. Solid symbols: storage modulus, G'; hollow symbols: loss modulus G''. Part (a) corresponds to the emulsions containing a carbohydrate polymer and the control one; part (b) corresponds to the emulsions containing a synthetic polymer.

3.3. Stretching instrumental properties of the emulsions

3.3.1. Set-up and optimization of the protocol

The emulsions filament stretchability was investigated using a texture analyzer TA.XT Plus. The compression/stretching protocol was performed with the cylindrical probe P/0.5R, having a diameter similar to a forefinger. The same amount of product than for the sensory evaluation (100 μL) was delivered on the lower plate of the texture analyzer using a Microman® M250 GILSON. The sensory evaluation procedure consisted to put the forefinger and the thumb in touch in order to compress the product, and then separate them to stretch the product ten times. In order to set up an instrumental imitative test, close to the sensory one, the influence of two factors was studied: (i) the number of cycles of compression/stretching to make before filament breaking length measurement, and (ii) the minimum gap to let between the probe and the base during the test. We thus measured the breaking length of the emulsions after 1, 5 and 10 cycles at 40 mm/s with using the texture analyzer, in order to compare instrumental to sensory results obtained with 10 cycles. The means ± SD for 1 and 5 cycles are shown in Fig. 4 for a gap of 0 mm. It appeared that the maximum stretchable length was greater and closer to sensory evaluations by making only one cycle whatever the emulsion, which was predictable. Indeed, by making 5 or 10 cycles of compression/stretching, the product was much more extensively strained when compared to the sensory protocol, as the consequence of the hardness of the probe and base surfaces if compared to the fingers' skin elasticity. Besides, one side effect of repeated compression/stretching cycles was the involvement of micro air bubbles, which led for some products to not a lonely but several filaments after 5 and 10 cycles. It was therefore difficult to properly measure the stretching properties of each emulsion. On the basis of these observations, it was decided to keep a protocol with only one compression/stretching cycle. Concerning the gap to let between the probe and the base when the probe compresses the product, we performed two different tests: on the one hand, each

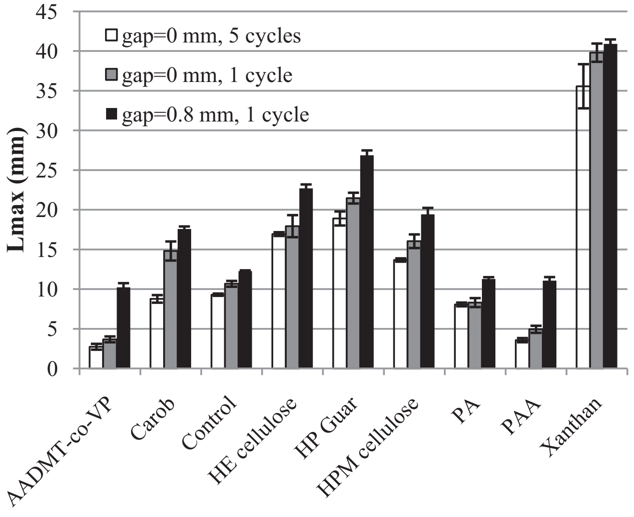

Fig. 4. Instrumental measurements of the stretching properties (L_{max}) of the 9 O/W emulsions (codes detailed in Section 2.1.1) at 40 mm/s, with different operative conditions.

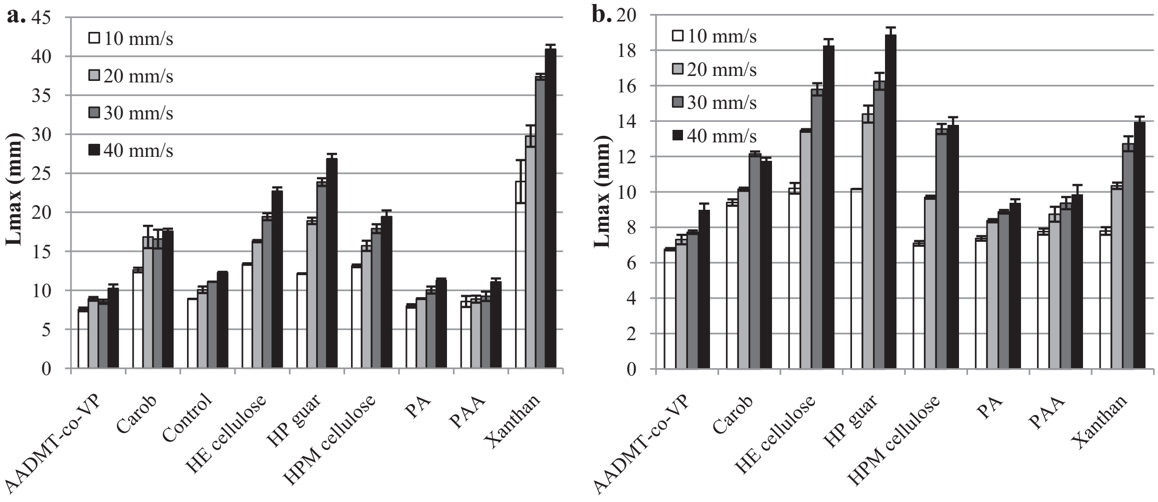

Fig. 5. Influence of the test rate on the stretching properties (L_{max}) of the emulsions (a) and the polymer solutions (b).

emulsion was subjected to one cycle of compression/stretching at 40 mm/s, by fully compressing the product between the probe and the base; the gap was thus equal to 0 mm, as for the sensory protocol. On the other hand, the emulsions were subjected to one compression/stretching cycle at 40 mm/s, but leaving a 0.8 mm gap between the probe and the base. This value of 0.8 mm corresponded to the required height to get the fluid shape of a short cylinder owing same diameter as the probe. Corresponding results are also presented in Fig. 4. One can observe that the maximum filament lengths were higher when compressing the product with a gap of 0.8 mm. In fact, when the product is compressed to a gap of 0, the material is totally squeezed out the gap and then sucked in when the probe goes up to stretch it. The obtained product deformation is thus higher than for the sensory protocol. Indeed, although the fingers were in touch for the product compression, the surface of the fingers being rounded and highly elastic, the product was not completely ejected to the sides before stretching it. That is why values obtained with a gap of 0.8 mm were better correlated with the sensory evaluation of the *Stringiness*. Indeed, the Pearson's correlation coefficient between the *Stringiness* and the stretching length with a gap of 0.8 mm was equal to 0.941, whereas without any gap, it was equal to 0.911.

As a conclusion, we decided to choose the protocol consisting of one compression/tension cycle with a gap of 0.8 mm between the probe on the down position and the base of the texture analyzer. The experimental conditions were softer and the solicitation closer to the sensory one.

3.3.2. Influence of the stretching speed

The influence of the stretching speed on the emulsions filament stretchability was investigated on the basis of the protocol described above. To that purpose, the stretchability test was carried out at various speeds: 10, 20, 30 and 40 mm/s with the texture analyzer, the results (means ± SD) being presented in Fig. 5a. At 10 mm/s, the differences between the emulsions were minimized, since the maximum lengths varied in a limited range between 7.6 (AADMT-co-VP) and 13.4 mm (HE cellulose) for all the emulsions except for the Xanthan one which was much above(23.9 mm). This may be due to the gravity, which has a higher contribution than the stretching properties of the polymers when the test is performed at low speed. Moreover, the maximum stretching length increases with the stretching rate for all emulsions, this being consistent with a previous work by Chan et al. (2009) performed on casein and starch aqueous solutions. However, as visible in Fig. 5a, the stretching speed very lowly impacted the maximum stretching lengths of the synthetic emulsions; indeed, the synthetic polymers did not significantly impact the emulsions stretching properties, since even the Control emulsion showed higher stretching properties. Furthermore, on the contrary, the Xanthan and HP guar emulsions were the much impacted by the stretching speed, since the corresponding maximum stretching lengths were roughly doubled when the displacement rate changed from 10 to 40 mm/s. In addition, the Pearson's correlation coefficients were calculated between the sensory evaluation of the *Stringiness* and the instrumental maximum stretching lengths measured at 10, 20, 30 and 40 mm/s. They showed a significant positive correlation, increasing with the instrumental stretching speed, as they were equal to 0.828, 0.900, 0.929 and 0.941, respectively.

As a consequence, the compression/stretching protocol performed at 40 mm/s therefore enables a quite good instrumental characterization of the stretching properties. As an illustration, Fig. 6 presents three images of the maximum breaking length obtained for the Control (a), HPM cellulose (medium degrees of stretchability) (b) and HP guar (high degrees of stretchability) (c) emulsions at 40 mm/s.

3.4. Stretching instrumental properties of the polymers aqueous solutions

The eight aqueous solutions of polymer at a concentration of 1% (w/w) were also instrumentally assessed with the optimized developed protocol (0.8 mm gap, 1 compression/stretching cycle) in order to characterize the stretching properties of each polymer when considered alone, with no interaction with any ingredient such as when incorporated in the emulsion; results are presented in Fig. 5b. In all cases, exactly as for the emulsions, the maximum stretching length of each polymer increases with the stretching speed. The aqueous solutions containing a synthetic polymer were the least stretchable, with similar values than the corresponding emulsions. However, the polysaccharides solutions showed lower maximum stretchable lengths than those for the corresponding emulsions, even if the ranking of the carbohydrate polymers remained approximately the same. At 40 mm/s, the Carob and HPM cellulose exhibited medium stretching properties (11.8 and 13.8 mm), the HE cellulose and HP guar high stretchability (18.3 and 18.9 mm), but the Xanthan was surprisingly not the highest stretchable system (13.9 mm). Therefore, the stretching behavior of the Xanthan solution really significantly differed from the corresponding emulsion. These differences for the carbohydrates stretching properties between emulsions and solutions may result

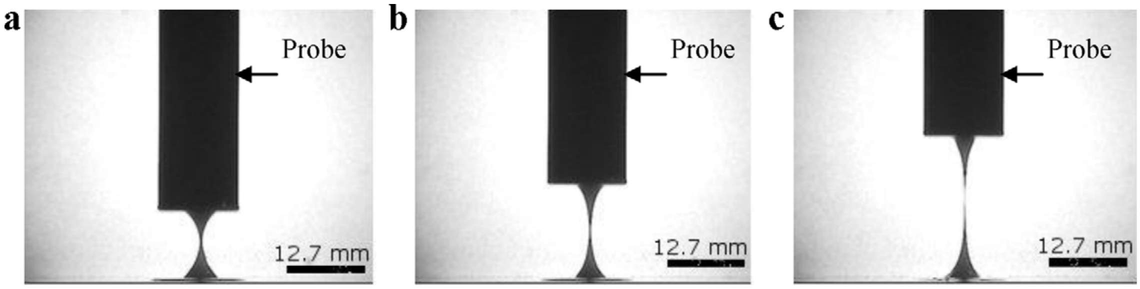

Fig. 6. Images of the stretching properties (L_{max}) of the Control (a), HPM cellulose (b) and HP guar (c) emulsions. Experiments were performed at 40 mm/s, with the P/0.5R probe and a gap of 0.8 mm over 1 cycle.

from the occurrence of specific interactions between the polymer chains and the other ingredients present in the emulsions. On the opposite, the high elastic character brought by the synthetic polymers may induce a constant stretching property whatever the system, in the presence or not of other ingredients.

4. Conclusion

The filament stretching properties of cosmetic O/W emulsions only differing by the polymer used as hydrophilic texturing agent were investigated. The stretching behavior was first sensory assessed by the attribute *Stringiness*. The evaluation of this attribute highlighted significant differences in the behavior of the different emulsions, thus evidencing the significant influence of the polymer structure. A simple-and-imitative instrumental test was then set up using a texture analyzer. The maximum breaking length of single filaments was analyzed as a function of stretching rate; the higher the stretching speed, the longer the filament length. In addition, the maximum breaking length measured at 40 mm/s was highly significantly correlated to the sensory *Stringiness* ($r_p = 0.948$), thus allowing a good predictability of this attribute. The Xanthan-based emulsion showed the highest stretchability, followed by the HP guar and HE cellulose emulsions; the Carob and the HPM cellulose emulsions presented stretching properties to a lesser extent. Nevertheless, the aqueous solutions of polymers obtained lower maximum breaking lengths, especially the Xanthan, which suggests that the different ingredients present in the emulsions could interact together to enhance or attenuate the polysaccharide's intrinsic stretchability. Further work is in progress to better understand these different contributions.

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