

Effect of the formulation on the continuous manufacturing of foamed products

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Abstract

The aim of this work is to understand the effects of the rheological and interfacial properties of a model food on continuous foaming operation in laminar flow conditions. The rheological properties of food model (glucose syrup) were adjusted using three polysaccharides: xanthan, LM pectin and guar. Interfacial properties were varied using two kinds of proteins: Na-caseinates and whey proteins (WPI). Foaming was studied in a narrow annular gap column at constant gas-to-liquid flow rate ratio as a function of rotation speed N . Overrun, bubble size distribution, average bubble diameter d_{32} and stability over time were used to characterize foams. Results showed that blow-by occurred during the foaming of formulations including either 0.1% xanthan or guar without proteins, while 0.1% pectin allowed the total incorporation of the gas phase for all N values with d_{32} about 50 μm . This was related to the tendency of this formulation to solidify under shear flow. In the absence of polysaccharides, only syrups containing WPI were able to form foams with the desired overrun with d_{32} around 20 μm . Indeed, blow-by was favoured for high N values with Na-caseinates. This confirmed the key role of interfacial elasticity and viscosity on the continuous foaming operation. For protein-polysaccharide mixtures, guar did not interact with proteins. As a result, the WPI-guar formulation exhibited nearly the same rheological properties and foaming ability as glucose syrup with WPI. Conversely, overrun was reduced in WPI-xanthan mixtures and high N values favoured blow-by, although d_{32} decreased to 15 μm due to the higher viscosity of these formulations. This confirmed that a matrix exhibiting viscoelastic behaviour under shear flow played a negative role on gas dispersion during foaming. On the contrary, WPI-pectin mixtures provided abundant foams with d_{32} about 15 μm and an improved stability due to the enhanced ability of WPI-pectin mixtures to solidify after foaming. While WPI reinforced the time-dependent behaviour of pectin in glucose syrup, Na-caseinates inhibited this effect and blow-by was reported when pectin and Na-caseinates mixtures were subjected to foaming. This highlighted the strong influence of protein-polysaccharide interactions on overrun. Conversely, bubble diameters in foams were less dependent on polysaccharides and could be adequately described using an approach involving a laminar Weber number based on the apparent viscosity of the foam during foaming.

Keywords: food foam, foaming process, foam formulation, polysaccharides, proteins

1. Introduction

Whipping or foaming process denotes a unit operation of food engineering that consists in dispersing and stabilizing a gas phase in the form of tiny bubbles into a continuous solid or semi-solid matrix in order to confer an aerated structure to a food material. Although foams can be found in textile, building trade, oil industry, personal care..., they play a key role in the food industry. Baked products, extruded and expanded cereal products, meringue, confectionaries, whipped cream, ice cream, fruit fools and mousses based on meat, fish or vegetable constitute a few examples of aerated food products (Campbell & Mougeot, 1999; Balerin et al., 2007). Foaming operation is usually devoted to make lighter products, but also to modify the appearance and the texture of food products by conferring cohesion and flexibility with a homogeneous aspect and a more uniform distribution of the flavour. Foaming operation has therefore been applied for developing new products adapted to consumer choice and needs, using air as a zero-cost ingredient. As mentioned by Campbell & Mougeot (1999), it became a key processing operation in the food industry in the nineties, but it is still not fully understood because it results from the complex interplay between formulation and process conditions. The end-use properties of foams depend not only on their gas content (namely, overrun) and their bubble size distribution, but also on their microstructure, and particularly on the distribution of the ingredients between the bulk and the gas-liquid interface (Stanley et al., 1996). This should especially ensure that the presence of a porous structure does not impact negatively the shelf-life.

Until the nineties, research on foaming focussed on the ingredients and mainly on proteins that can play the role of foaming agent in food. However, foaming agents must simultaneously give abundant but also stable foams. Among food proteins, white egg and whey proteins have been identified as ingredients of high nutritional and functional interests that exhibit high foaming and stabilizing properties. For example, β -lactoglobulin which is the main protein of whey, is able to undergo denaturation and form surface gels at the air-water interface (Dickinson, 1992), but also to stabilize food by heat-induced gelation (Gosal & Ross-Murphy, 2000). However, proteins alone cannot generally provide stable foams without the addition of other stabilizing agents; the most common are gelatine and polysaccharides. Polysaccharides are typically used in food industry for their texturing properties as thickening and gelling agents (Dickinson & McClements, 1995). As proteins, their properties have been mainly studied without taking into account the interactions with other ingredients. However, polysaccharides interact often with proteins and mixtures of polysaccharides usually present synergistic properties. For instance, mixtures of guar and xanthan exhibit high gelling properties, while guar and xanthan used separately as thickening agents do not present gelling properties (Pal, 1996). The theoretical understanding of the stability of protein-polysaccharide mixtures in water has gained a considerable interest in the food industry in the last decade when a few ternary diagrams have been established and when the interactions between polysaccharides and proteins have been clearly described (Syrbe et al., 1998). These can be summarized as follows:

- *miscibility and compatibility*; this situation is a general rule in food.
- *thermodynamic incompatibility* leading to phase separation when proteins and polysaccharides repel each other; the segregation of the biopolymers takes place and two distinct immiscible phases can be formed, each of them being enriched with only one biopolymer species.

- *complex coacervation* when the biopolymers attract each other; phase separation may occur: in this case, one phase contains coacervates, whereas the other one is depleted of polymers.

For concentrated media, phase separation does not usually occur because the system is “gelled” by the high viscosity of the matrix, which leads to locally-segregated microstructures (Syrbe et al., 1998; Sanchez et al., 2000). Consequently, the control of the kinetic of stabilization and phase separation allows to obtain a variety of microstructures and therefore interesting properties. This can be achieved by several formulation factors, such as pH, ionic strength and concentration (Zhang & Foegeding, 2003; Zhang et al., 2004). It should be mentioned that the microstructure of products containing proteins and polysaccharides is also affected by mechanical and heat treatments (Walkenström et al., 1999), although these have been often disregarded in the literature on ternary food systems. Indeed, mechanical treatments are of utmost importance in foaming operation in which bubbles are formed through destabilization of the primary microstructure of the raw material, but need the formation of a new stable network in order to ensure the shelf-life of the porous structure. This is the reason why the influence of formulation should not be studied separately from the operating conditions of foaming operation.

Specific research on continuous foaming operation started in the nineties (Djelveh & Gros, 1995; Hanselman & Windhab, 1999). One can distinguish the experimental contributions that dealt with model media (Hanselman & Windhab, 1999; Müller-Fischer et al., 2006; Balerin et al., 2007; Narchi et al., 2007) from those that involved real food and models close to real food products (Thakur et al., 2003, 2005; Vial et al., 2006a, 2006b). Foaming was shown to constitute an illustration of product-oriented engineering, as described by Charpentier (2000, 2002). These authors attempted to quantify the influence of formulation on bubble size distribution through physicochemical parameters, such as viscosity and surface tension, using a dimensionless Weber number that derives from the capillary number applied to describe the break-up of a single bubble/drop in the laminar regime (Grace, 1982; Walstra, 2003). Such an approach was often successful for a defined recipe, but could not be generalized because it did not account for dynamic surface properties, such as interfacial viscosity and elasticity, as well as matrix elasticity (Narchi et al., 2007). Several works have also demonstrated the role of the geometry of the foaming device and of operating conditions, such as rotation speed and residence time (Thakur et al., 2003, 2005; Labbafi et al., 2005). However, the attempts to study ternary model food with proteins and polysaccharides in continuous foaming are scarce in the literature: Hanselmann & Windhab (1999) used guar, but only as a viscosity modifier agent, while Bouaouina et al. (2005) studied the substitution of gelatine by a polysaccharide mixture in the typical formulation of a dairy topping.

In this work, the objective is to better understand the effect of the rheological and interfacial properties of a model food on continuous foaming operation in laminar flow conditions using a Newtonian model matrix in which proteins will be added to modify the interfacial properties, while polysaccharides will be included to adjust the rheological properties. Three polysaccharides, namely guar, low-methoxy (LM) pectin and xanthan, as well as two families of milk proteins (whey proteins and Nacaseinates) will be used. Then, continuous foaming experiments will be carried out in order to examine the relationship between the physicochemical properties of the raw materials, the process conditions and the end-use properties of the foams.

2. Materials and methods

2.1. Products

For all model media, the matrix was a Newtonian glucose syrup solution (Glucidex IT21, *Roquette Frères*, France) in which syrup concentration allowed to vary the viscosity η . A relationship between η , syrup concentration and temperature was established in a previous work (Narchi et al., 2007). The objective was to maintain the laminar regime during foaming, regardless of operating conditions, which was always achieved when $\eta \geq 1$ Pa.s at 20°C. The interfacial properties of the solutions were studied by the addition of 2% (w/w) commercial milk proteins: either Na-caseinates (α 116, *Soussana*, France; including 88% w/w proteins) or WPI (Prolacta90, *Lactalis*, France; including more than 90% w/w proteins in which about 53% w/w corresponded to β -lactoglobulin). These proteins were selected because they exhibit far different interfacial behaviours at the air-water interface. Na-caseinate solutions in water present a lower surface tension than WPI solutions of similar concentration, which shows that interfaces stabilized by Na-caseinates should be more stable from a thermodynamical point of view (Rouimi et al., 2005). Similarly, dynamic surface tension measurements from the literature showed that Na-caseinates migrate faster than whey proteins to the interfaces, which is in agreement with their differences in molecular weight and their respective macromolecular structures (Dickinson, 1992). However, WPI was reported to exhibit a far higher interfacial viscosity and elasticity than Na-caseinates (Rouimi et al., 2005). This may partly explain why Na-caseinates are recognized for their high emulsifying properties, but display lower foaming properties than WPI (Dalgleish et al., 2002; Damodaran, 2004).

In order to study the effect of polysaccharides on their foaming properties, three polysaccharides were added to the glucose syrup solutions at a concentration of 0.1% (w/w): xanthan (Grinsted® Xanthan 80, *Danisco*, Denmark), guar (Meypro® Guar Csa M-100) and pectin (Unipectine-LM OF 300C, *Cargill Inc.*, USA). These polysaccharides were selected because they cover different types of properties:

- Guar is a neutral polysaccharide, the most important in the family of galactomannans. It presents a high molecular weight (about 10^3 kDa) and provides high shear-thinning behavior due to topological entanglements (Bourriot et al., 1999). Conversely, it exhibits no gelling properties.
- Xanthan is a natural exopolysaccharide with a higher molecular weight than guar (between 10^3 - 10^4 kDa). Its non-gelling and strongly shear-thinning behavior has been extensively studied (Capron et al., 1997; Rodd et al., 2000). This is mainly explained by the rigidity of xanthan chains and by the weakness of the network between macromolecules that involves hydrogen bonds. Contrary to guar, xanthan is a carboxylated biopolymer that is negatively charged in the usual range of pH of food and can therefore present electrostatic interactions with proteins. However, thermodynamic incompatibility remains the rule (Syrbe et al., 1998).
- Pectin is, as xanthan, an anionic carboxylated polysaccharide, but of molecular mass far lower than guar and xanthan (about 10^2 kDa). It is normally classified according to its degree of methoxylation DE that defines the conditions in which pectin is able to form gels (Thakur et al., 1997). Contrary to xanthan-milk protein mixtures, miscibility, complex coacervation and phase separation are possible as a function of the respective pectin, protein and calcium contents as well as pH conditions (Beaulieu et al., 2001; Girard et al., 2007). However, the non-amidated LM-pectin (DE \approx 38%) used in this work has no gelling properties without calcium

addition, despite the high glucose syrup content. Similarly, pectin should only weakly interact with milk proteins at pH 7 because of their isoelectric points between 4.6 and 5.2. Conversely, pectin could interact with glucose syrup because sugar and similar solutes generally tend to dehydrate the pectin macromolecules in solution.

All the formulations used in this work were prepared using a high-speed mixer (UMC-5, *Sympak Group*, Germany) at ambient temperature under vacuum. They were kept overnight at ambient temperature to ensure the full hydration of proteins and polysaccharides, as well as the development of interactions between proteins, polysaccharides and molecules of glucose syrup. In all model media, no apparent phase separation was observed. The pH was always around 7, regardless of the addition of proteins and polysaccharides.

2.2. Foaming operation

Gas dispersion was carried out in the narrow annular gap unit described by Djelveh and Gros (1995) and used in previous works (Thakur et al., 2003, 2004, 2005). It consists of a jacketed stainless steel cylindrical column (410 mm length and 35 mm diameter) equipped with three four-flat-right-angled-blade impellers. Experiments were carried out under atmospheric pressure. The jacket allowed to maintain the temperature at $22\pm 1^\circ\text{C}$ for all experiments using a WKL-600 thermocryostat (*Lauda France*, France). Rotation speed N was varied continuously from 400 to 1600 rpm using a speed-controlled IK LaborTechnik RE-16 engine, while the torque between the shaft and the impeller was measured during foaming using an IK MR-D1 device (*Ika-Werke GmbH*, Germany). On the basis of the results of Thakur et al. (2004), the average shear rate applied to the fluids in the foaming device can be estimated using the following expression:

$$\dot{\gamma} = K_S N \quad (1)$$

in which K_S is the dimensionless shear constant that was found to be about 51 ± 1 . Gas and liquid phases were introduced separately from the bottom of the column using a mass flowmeter (*Emerson Brooks Inst.*, USA) and a peristaltic pump (*Cole-Parmer Instr. Co.*, USA) respectively. Gas flow rate (G) was 10 mL/min, while liquid flow rate (L) was fixed at 30 mL/min for all experiments. Steady-state conditions were assumed when both torque and the density of the foamed product at the column exit were constant over time.

2.3. Measuring techniques

Model media were characterized in terms of density, rheological and interfacial properties. Their viscosity η and first normal stress difference N_1 were measured under flow conditions in the range of shear rate in the range of interest of foaming operation, i.e. $10\text{-}1000\text{ s}^{-1}$ at operation temperature of foaming. A stress-controlled rheometer (SR-5 from *Rheometric Scientific*, USA) equipped with a 40 mm plate-plate geometry was used with 0.5 mm gap, together with a Peltier circulator for temperature control. The elastic (G') and viscous (G'') moduli as well as the complex viscosity η^* were obtained in the oscillatory mode under similar conditions using either strain sweep test at 1 Hz in the 1-100% strain range, or frequency sweep test at 2% strain in the 0.1-10 Hz domain. Surface tension σ was measured using a K12 tensiometer (*Krüss GmbH*, Germany) and Wilhelmy's plate method at 20°C for 1 hour without dilution. Rheological and surface tension measurements were done in triplicate.

Model media were characterized in terms of overrun, bubble size distribution and rheological properties. Overrun ϕ is defined as the volume expansion ratio due to the gas phase in the matrix. It can be estimated using densimetry on the basis of Eq. (2):

$$\phi = \frac{\rho_L - \rho_F}{\rho_F} \quad (2)$$

in which ρ_L and ρ_F are the respective densities of the matrix and the foam. These were measured as the mass-to-volume ratio of these materials using a beaker of known volume. For statistical purpose, these measurements were repeated at least three times. Overrun could be compared to the maximum overrun ϕ_{\max} value resulting from a mass balance on the gas phase under steady state conditions:

$$\phi_{\max} = \frac{G}{L} \quad (3)$$

A total incorporation of the gas phase was achieved only when $\phi = \phi_{\max}$. For measuring bubble size and distribution in foams, a fraction of the foamed product from the exit of the column was introduced in an on-line image analysis system based on optical microscopy, using a camera mounted on an inverted microscope Axiovert-25 (*Carl Zeiss Jena GmbH*, Germany). The commercial software package Image Pro+ 4.01 (*MediaCybernetics*, MD, USA) was used to measure the diameter of individual bubble d_i and to build an estimation of the bubble size distribution. The mean bubble size was expressed in terms of Sauter mean diameter (d_{32}), which corresponded to the surface-average diameter of at least 500 bubbles from three different samples:

$$d_{32} = \frac{\sum d_i^3}{\sum d_i^2} \quad (4)$$

As the main destabilization mechanism was bubble creaming, foam stability over time was quantified by measuring once per day during seven days after foaming the evolution of the height of the interface that separates a free-of-bubble matrix from a gas-enriched foam in a closed container filled with foams.

3. Results and discussion

3.1. Influence of polysaccharide addition on matrix properties

3.1.1. Matrix without proteins

The viscosity of the matrix in which polysaccharides were used as additives was a Newtonian glucose syrup with $\eta = 1.0 \pm 0.05$ Pa.s at 25°C between 10 and 10³ s⁻¹ and of surface tension σ about 64 mN/m, close to that of tap water. As expected, the surface tension of the syrup was not significantly affected by the addition of any of the three polysaccharides. Conversely, these provided three far different effects on the rheological properties of the matrix. First, the addition of 0.1% (w/w) guar in the syrup did not change significantly the value of the matrix viscosity: η was about 1.1 Pa.s and the fluid remained Newtonian (Figure 1a). Roughly, the viscosity was similar to the value obtained by an increase of 0.1% dehydrated glucose syrup in the solution. This corresponds to a situation in which guar macromolecules do not interact between themselves, first because of their low concentration, but also because they present a good affinity with glucose, maltose and other oligosides of the glucose syrup.

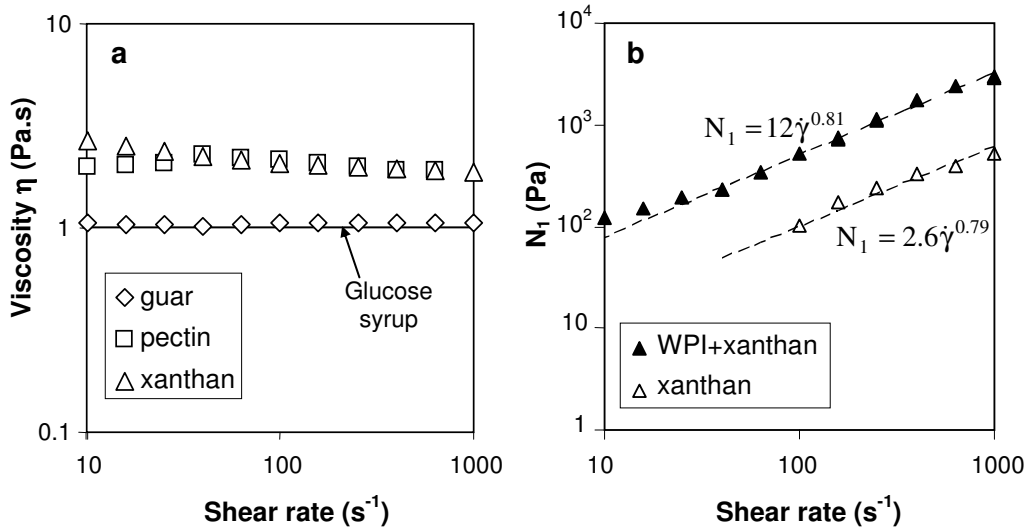


Figure 1: Effect of the addition of 0.1 (w/w) polysaccharides: (a) on flow curves in a 1 Pa.s glucose syrup; (b) on N_1 of 0.1% xanthan and xanthan+2% (w/w) WPI recipes.

Conversely, the addition of 0.1% (w/w) xanthan doubled approximately the viscosity of the matrix; the flow curve looked like a Newtonian plateau at high shear rate, following a typical non-Newtonian shear-thinning behaviour at lower shear rate. The presence of measurable first normal stress difference N_1 between 10^2 - 10^3 s^{-1} confirmed this assumption; in this region, N_1 could be roughly fitted using a power-law model as a function of shear rate $\dot{\gamma}$: $N_1 = 2.6\dot{\gamma}^{0.79}$ (Figure 1b).

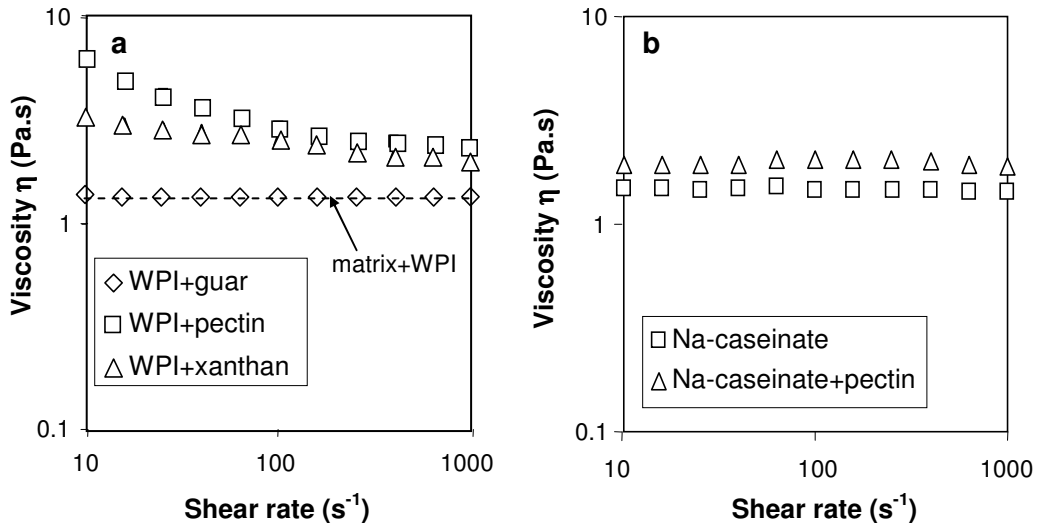


Figure 2: Effect of the addition of 0.1 (w/w) polysaccharides on flow curves: (a) in a 1 Pa.s glucose syrup+2% (w/w) WPI; (b) in a 1 Pa.s glucose syrup+2% (w/w) Na-caseinates with and without 0.1% pectin.

Using this model, the dimensionless Weissenberg number Wi defined as

$$Wi = \frac{N_1}{2\eta\dot{\gamma}} \quad (5)$$

was nearly constant, about 0.2, which showed that viscous behaviour prevailed under shear flow. This corroborates that xanthan play a role as a thickener.

The rigidity of xanthan chains, as well as their negative charge probably maintain the ability of xanthan to form a network through hydrogen bonds.

Despite the addition of 0.1% (w/w) LM pectin in the 1Pa.s glucose syrup, the flow curve was still nearly Newtonian and approximately confounded with that of xanthan between 10^2 - 10^3 s^{-1} (Figure 1a), but without any measurable N_1 values. As pectin is poorly thickening, this high viscosity level confirmed the presence of interactions between pectin and glucose syrup. However, no gel structure could be observed, which was expected: the non-amidated LM pectin should not be able to form gels without the addition of calcium cation. This was also validated by oscillatory measurements using the G''/G' ratio, denoted loss tangent or $\tan\delta$, which measure the viscoelasticity at low deformation. When $\tan\delta$ tends to infinity, the fluid is very viscous and it tends to 0 for an elastic solid. In this work, $\tan\delta$ was higher than 20 with guar, around 10 with pectin and between 3 and 6 for xanthan, both in strain sweep tests and in frequency sweep tests. Nevertheless, pectin mixtures exhibited surprising trends: flow curves could be replicated, but not repeated because an increase of viscosity was observed after each run, which seemed characteristic of a time-dependent behaviour. This increase corresponded to regions in which the mixture tended to crystallize on the plate of the rheometer. Oscillatory experiments versus time at high strain $\gamma=10^4\%$ and 1 Hz were carried out to validate these results that were not observed previously on other formulations. Figure 3 illustrates the experimental data and shows the continuous increase of complex viscosity η^* as a function of time, but also the key influence of shear that could be reduced when a rest period was applied. This time-dependent behaviour was probably related to sugar and similar solutes generally that tend to dehydrate the pectin molecules in solution. At high solids, when there was less water available to act as a solvent for pectin macromolecules, the tendency of the pectin-glucose syrup system to solidify was consequently enhanced.

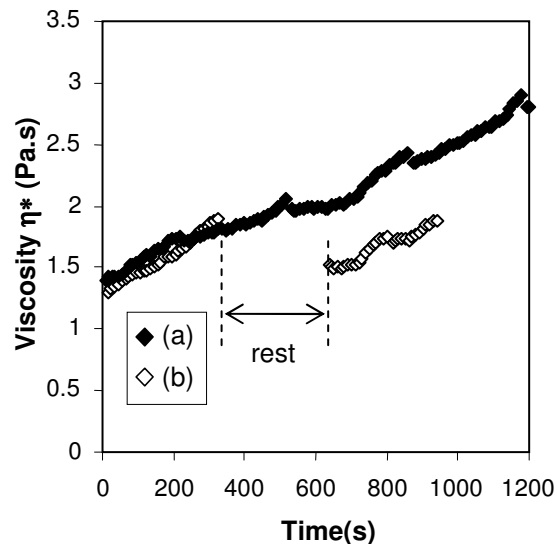


Figure 3: Oscillatory tests versus time at constant strain and frequency ($10^4\%$; 1 Hz) for the 0.1% pectin recipe: (a) one stage of 1200 s; (b) two stages of 300 s separated by a rest period of 300 s.

3.1.2. Matrix with proteins

The influence of the addition of 2% (w/w) WPI in a 1 Pa.s glucose syrup was reported in a previous work (Narchi et al., 2007). Roughly, the model food remained

Newtonian, but viscosity increased about $\eta=1.35$ Pa.s, while surface tension was decreased by the addition of whey proteins around $\sigma\approx 50$ mN/m. As above, the addition of polysaccharides did not change significantly the surface tension of the matrix that was governed by WPI. On viscosity, the influence of the addition of 0.1% (w/w) guar (Figure 2a) was similar to that illustrated by Figure 1a without WPI: guar increased only slightly the viscosity up to 1.4 Pa.s, but formulation remained Newtonian. Again, interactions between guar and glucose syrup prevailed over guar-guar and WPI-guar interactions. Conversely, the addition of xanthan and pectin lead to a shear-thinning behaviour with a plateau region at high shear rate (Figure 2a). This was more pronounced with pectin than xanthan, contrary to Figure 1a. This shear-thinning behaviour was however reduced for both polysaccharides in the range of shear rate 10^2 - 10^3 s⁻¹ in which a Newtonian approximation could still be applied. Surprisingly, at high shear rate, a comparison between Figure 1a and Figure 2a showed that flow curves tended to behave as if there was no WPI in the recipe at high shear rate. However, WPI increased the matrix elasticity under shear flow in the presence of xanthan by a factor 5. Indeed, the first normal stress difference followed could also be fitted by a power-law model $N_1 = 12\dot{\gamma}^{0.81}$ with nearly the same exponent as without WPI (Figure 1b). As a result, Wi was again nearly constant, but was around 1, which is characteristic of a pronounced viscoelastic behaviour. For pectin, the behaviour observed previously without proteins was reinforced by WPI. Apparent viscosity at 10 s⁻¹ was about twice as high as that of xanthan, which confirmed additional interactions between pectin, WPI and glucose syrup. Similarly, the time-dependent behaviour leading to solidification under shear appeared as before, although the first normal stress differences were still not measurable. Oscillatory measurements confirmed these conclusions. With WPI+pectin, glucose syrups exhibited $\tan\delta$ values between 3-5, while $\tan\delta$ fell to the range 1-3 with WPI+xanthan, which highlights the elastic behaviour of WPI-xanthan mixtures in glucose syrup.

Table 1. Summary of the rheological behaviour of the binary and ternary formations studied in this work.

	Under flow	At low deformation
Glucose syrup		Newtonian
Glucose syrup+2% proteins		Newtonian
0.1% guar		as 1 Pa.s glucose syrup
0.1% guar + 2% WPI		as 1 Pa.s glucose syrup+2%WPI
0.1% xanthan	nearly Newtonian, slightly viscoelastic	slightly viscoelastic
0.1% xanthan + 2% WPI	shear-thinning and viscoelastic	viscoelastic
0.1% pectin	time-dependent effects	slightly viscoelastic time-dependent effects
0.1% pectin + 2% WPI	shear-thinning time-dependent effects	viscoelastic time-dependent effects
0.1% pectin + 2% Na-caseinates		Newtonian

When WPI was replaced by 2% (w/w) Na-caseinates in a 1 Pa.s glucose syrup, the formulation remained Newtonian, but viscosity increased up to 1.5 Pa.s (Figure 2b), which was only slightly higher than one with WPI. Conversely, surface tension decreased at about 44 mN/m, which is in agreement with data when this protein is present in water (Rouimi et al., 2005). When 0.1% pectin was added to Na-caseinates, surface tension was not modified; viscosity increased, but flow curves still exhibited Newtonian trends without measurable N_1 values (Figure 2b) and the time-dependent

behaviours was reduced. As a result, Na-caseinates appeared to decrease the interactions between pectin and glucose syrup, contrary to WPI.

3.1.3. Summary

As a conclusion, the formulations defined above cover a large range of interfacial and rheological properties. For surface tension, the values depend only on the presence of proteins. For rheology, a wide variety of behaviours was reported, including Newtonian and viscoelastic fluids, but also a time-evolving fluid that tends to solidify under shear. These are summarized in Table 1.

3.2. Analysis of foaming experiments

3.2.1. Foaming of glucose syrup solutions with polysaccharides

Foaming was conducted under steady state flow conditions for glucose syrup formulations including 0.1% of the three polysaccharides respectively. These can be compared to the gas dispersion experiments of Narchi et al. (2007) in glucose syrups of various viscosities between 1 and 2 Pa.s. First, formulations including guar and xanthan were unable to incorporate all the gas phase, regardless of rotation speed, exactly as glucose syrups without additives. For xanthan, blow-by was observed, which corresponded to an intermittent slug flow (Taitel & Dukler, 1976; Narchi et al., 2007). These results could be expected, due to the absence of surface-active agent able to stabilize the gas-liquid interfaces in these media. Additionally, elasticity under flow induced by xanthan was too small to avoid coalescence of large bubbles, contrary to polyacrylamide formulations of Narchi et al. (2007). Guar seemed to make gas dispersion even more difficult because a stratified flow was observed in the horizontal pipe at the outlet of the foaming device (Taitel & Dukler, 1976). Conversely, a total incorporation of the gas phase was observed with pectin, whatever the rotation speed between 400 and 1600 rpm. As a result, the maximum overrun of 33% was always achieved. As an illustration, images of bubbles are reported in Figure 4. Bubble size distribution were always monomodal and the average bubble diameter decreased significantly when N was increased from 400 to 1200 rpm, while it remained constant for a further increase in rotation speed (Table 2). A comparison with bubble size distributions measured without additives demonstrated however that both were roughly similar. This showed that the time-dependent behaviour of pectin plays a role mainly on bubble stabilization over time. Bubble stability was however limited to a few hours at rest, which is in agreement with the results of section 3.1.

Table 2. Comparison of Sauter diameter d_{32} and standard deviation σ_d of bubble size distributions for a glucose syrup ($\eta=1.5$ Pa.s) and a glucose syrup+pectin formulation ($\eta\approx 1.8$ Pa.s).

N (rpm)	Glucose syrup		Glucose syrup+pectin	
	d_{32} (μm)	σ_d (μm)	d_{32} (μm)	σ_d (μm)
400	59	23	66	22
800	46	17	55	17
1200	49	14	40	12
1600	46	14	41	10

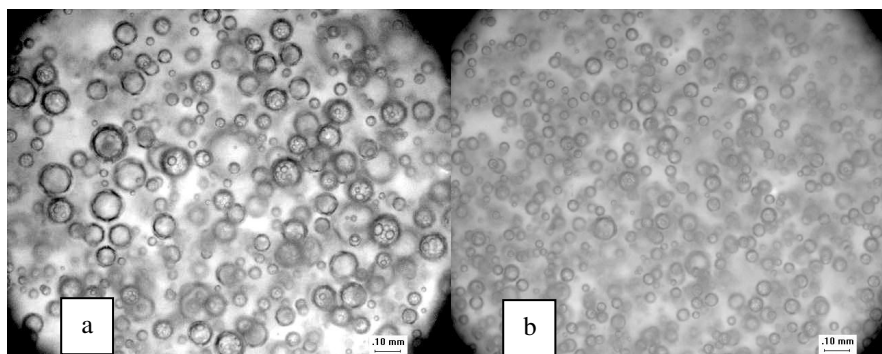


Figure 4: Images of bubble distribution in pectin+glucose syrup for G/L=10/30: (a) $N=400$ rpm, (b) $N=1600$ rpm.

3.2.2. Foaming of polysaccharide-WPI mixtures in glucose syrup solutions

Narchi et al. (2007) showed that foaming was significantly improved by the addition of 2% whey proteins in a 1 Pa.s glucose syrup whatever the gas-to-liquid flow ratio between G/L=10/30 and G/L=30/30 ($\text{mL}\cdot\text{min}^{-1}$ gas)/($\text{mL}\cdot\text{min}^{-1}$ liquid). The maximum overrun was always achieved at low G/L and low rotation speed, but ϕ was reported to decrease when G/L and N were simultaneously increased. These results will be used as a reference in Figure 5. Additionally, foam stability was limited to a few hours. For the formulations including polysaccharides, the addition of guar did not change significantly the results. Overrun (Figure 5), bubble diameters (Table 3) and foam stability were similar to those observed without guar. This is in agreement with the rheological analysis in section 3.2.1 which showed that guar did not modify significantly the properties of syrup+WPI mixtures. For xanthan, far different results were observed. A total incorporation of the gas phase could never be achieved and overrun was limited to 22%. Additionally, overrun decreased when rotation speed was increased and blow-by appeared when N was higher than 800 rpm (Figure 5). d_{32} values were reported to be constant, about 14 μm (Table 3). The influence on bubble size could be attributed to the higher viscosity: a comparison with a formulation based on WPI in glucose syrup with $\eta=1.8$ Pa.s exhibited similar bubble size (Table 3). Conversely, the $\eta=1.8$ Pa.s syrup+WPI recipe provided a total incorporation of the gas phase, which was not the case with xanthan. As a result, the poor values obtained in this case can be attributed to the high viscoelastic behaviour of the matrix ($Wi\approx 1$) which is known to make gas dispersion more difficult (Mighri et al., 1998).

On the other hand, WPI+pectin formulations always lead to total gas dispersion (Figure 6), as pectin without WPI (section 3.2.1), but also as WPI without pectin (Narchi et al., 2007). However, a comparison between Table 2 and Table 3 shows that bubble sizes were far lower than with pectin alone. Similarly, WPI+pectin reduced slightly d_{32} in comparison to WPI foams based on a 1 Pa.s glucose syrup, but d_{32} values were similar to those of foams based on a 1.8 Pa.s glucose syrup (Table 3). This indicates that bubble size seems mainly controlled by matrix viscosity, although quantitative analysis of data is required to validate this experimental conclusion. It should be mentioned that, large differences arose on foam stability. WPI or WPI-guar foams were stable about 1 day, while the stability of WPI-pectin foams achieved a stability of 7 days. As a conclusion, WPI-pectin mixtures combined the advantages of WPI and pectin on foaming: whey proteins were able to stabilize bubbles during foaming and pectin to provide the long-term stability by the slow development of a solid structure. Conversely, viscoelasticity under shear, i.e. high Weissenberg

number, should be avoided because they oppose to gas dispersion: they give small bubbles, but with low overrun.

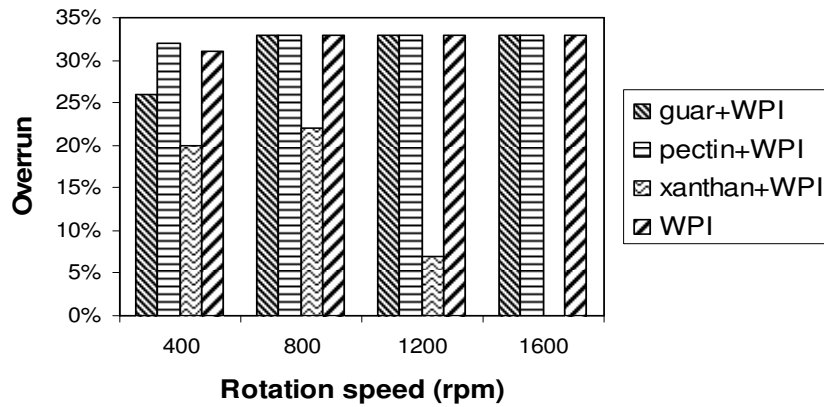


Figure 5: Overrun values in formulations including WPI as a function of rotation speed for G/L = 10/30.

Table 3. Comparison of Sauter diameters of foams for WPI formulations based on a 1 Pa.s glucose syrup with and without polysaccharides.

N (rpm)	d_{32} (μm)				
	WPI	WPI+guar	WPI+xanthan	WPI+pectin	WPI ($\eta=1.8$ Pa.s)
400	19	20	14	15	13
800	19	17	14	15	15
1200	17	14	12	15	15
1600	16	16	13	15	15

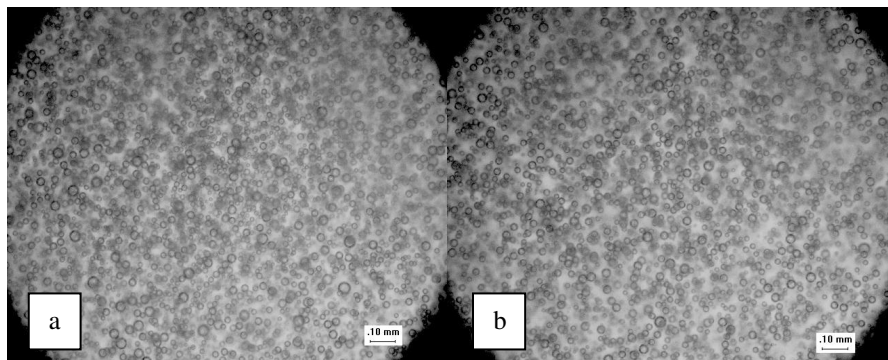


Figure 6: Images of bubble distribution in WPI+pectin recipe for G/L=10/30 and (a) N=800 rpm, (b) N=1200 rpm.

3.3. Foaming of polysaccharide-Na-caseinates mixtures in glucose syrup solutions

In order to confirm the respective role of interfacial and rheological properties, foaming experiments were carried out with Na-caseinates and Na-caseinates-pectin mixtures. Na-caseinates are known to be less efficient foaming agents in comparison

to whey proteins, especially because they did not protect efficiently bubbles against coalescence. This was attributed to the low interfacial viscosity and elasticity that they developed at the air-water interface (Rouimi et al., 2005). For continuous foaming, this was illustrated by Table 4: total gas dispersion could not be achieved and high rotation speed favoured blow-by. The addition of pectin did not change these trends, mainly because the time-dependent solidification effect was reduced. Although surface tension was lower than with WPI, foams presented both a short-time and a long-time stability defect. This confirmed also the experimental results of Narchi et al. (2007) with Tween 80 as a foaming agent that exhibited exactly the same trends.

Table 4: Overrun and d_{32} values for foams using a 1 Pa.s glucose syrup with Na-caseinates and Na-caseinates-pectin.

N (rpm)	Overrun (%)		d_{32} (μm)	
	Na-caseinates	Na-caseinates +pectin	Na-caseinates	Na-caseinates +pectin
400	23	7	26	67
800	20	16	18	18
1200	10	14	16	22
1600	<5%	8	-	18

3.4. Discussion

Experimental data has given evidence that the following conditions were required to achieve the desired overrun:

- The presence of tensioactive agents to stabilize bubbles during and just after foaming, but with a high interfacial viscosity and elasticity inhibiting coalescence, rather than a low surface tension;
- A weak matrix elasticity due to its negative role on gas dispersion, which is in agreement with the literature (Flumerfelt, 1972; Mighri et al., 1998);
- A matrix able to provide long-term stability by a time-evolving behaviour. In this work, the solidification of pectin and WPI-pectin in glucose syrup was used, but similar mechanisms could also be found in the literature: for example, tempering to control fat crystallisation in whipped cream (Gravier et al., 2006), ice recrystallisation in ice cream (Regand & Goff, 2003) or the strengthening of gelatine gels during storage (Anton et al., 2005) have been described.

Two of these three conditions were governed by polysaccharides in this work. Conversely, the mean bubble size seemed less dependent of polysaccharides and more closely linked to matrix viscosity. For foams, d_{32} may be related to the geometry of the foaming device and to process conditions if one considers that a single bubble is subjected to a dynamic equilibrium between coalescence and break-up in a pseudo-homogeneous fluid presenting the viscosity of the foam μ . Using this assumption, the dimensionless laminar Weber number We defined as

$$We = \frac{\mu \cdot (K_S N) \cdot d_{32}}{\sigma} \quad (6)$$

was often shown to be equal to a critical Weber value We_C that was a constant for WPI-stabilized foams. For foams, We_C was usually between 0.3 and 0.8 in the literature as a function of recipe, pH and mixer geometry (Djelveh & Gros, 1995;

Thakur et al., 2003; Balerin et al., 2007). These values were also in good agreement with the results of Williams et al. (1997) for a single drop stabilized by WPI. Equation (6) was also successfully applied by Jansen et al. (2001) for concentrated emulsions and by Hanselman & Windhab (1999) for foams using offline measurements of the foam viscosity, but also by Narchi et al. (2007) on the basis of an estimation of the process viscosity μ using an in-line measurement of torque on the shaft of the impeller of the foaming device when no blow-by occurred. Indeed, when overrun is high, μ may widely differ from the viscosity of the ungasged matrix η . In this work, μ was measured in-line, as in Narchi et al. (2007), using the method described by Thakur et al. (2004).

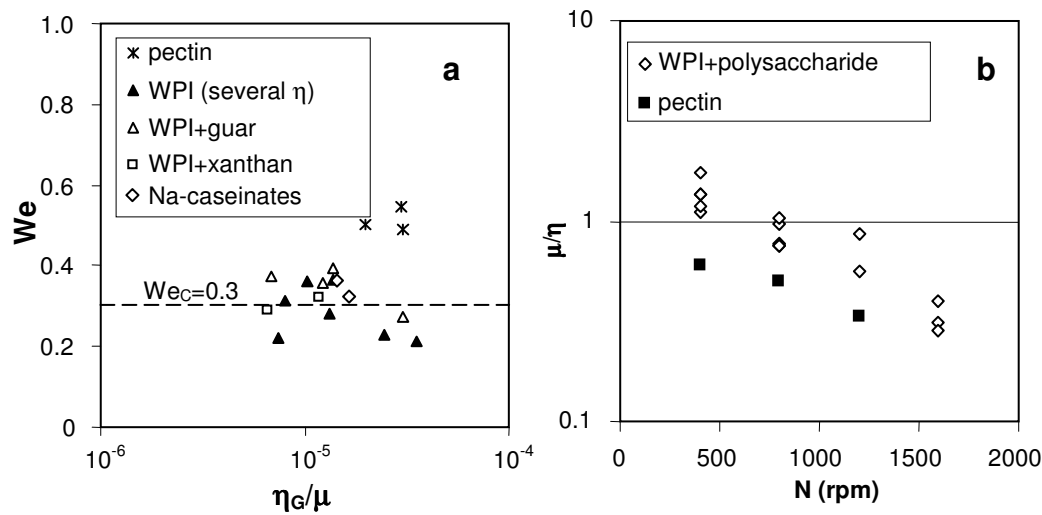


Figure 7: Evolution of the laminar Weber number as a function of the η_G/μ viscosity ratio (a) and of the μ/η viscosity ratio as a function of rotation speed N (b).

In Figure 7a, We is plotted as a function of the ratio η_G/μ in which η_G is the viscosity of the gas phase. The results show that the assumption $We = We_c$ is valid with $We_c = 0.3 \pm 0.1$ for recipes including WPI, regardless of polysaccharide and η . This confirms quantitatively the determining role of process viscosity μ during foaming on d_{32} . We_c values were also in agreement with previous results (Narchi et al., 2007). With Na-caseinates (with and without pectin), data without blow-by gave We_c values similar to WPI foams (Figure 7a). This is contrary to the results of Williams et al. (1997) on a single drop in water that found lower We_c values with WPI than caseins because of their different behaviour at the air-water interface. This is however not surprising because interfacial viscosity and elasticity modified strongly the viscosity of water at the interface in Williams et al. (1997), while this effect was probably dampened by the high viscosity of glucose syrup in this work. Even with a viscoelastic fluid (WPI+xanthan), We_c was about 0.3, which illustrates that elasticity influenced more overrun than bubble size (Figure 7a). Without proteins, only the recipe including pectin could be analyzed. We_c values were higher, as expected, which denoted a dynamic equilibrium displaced towards coalescence. However, We_c had a different meaning in this case, as it should measure rather the kinetics of the time-dependent solidification of the matrix that inhibits coalescence than the interfacial equilibrium. As the deviation from We_c with protein foams remained small (We_c is between 0.5-0.6 in Figure 7a for pectin), this means that the solidification mechanism is rapid which limits coalescence. Conversely, bubble size reduction during foaming appears to be limited by the shear-thinning behaviour of foams. Indeed, process viscosity μ exhibited a shear-thinning behaviour (Figure 7b), which is

not surprising if foams are compared to emulsions or suspensions. However, μ appeared to depend also on bubble-bubble interactions, i.e. on bubble size, because the probability of two bubbles to collide increases when d_{32} decreases: the lowest μ values were reported in pectin formulation without WPI (Figure 7b) when bubbles presented the highest d_{32} (Tables 2 to 4).

As a conclusion, the formation of stable foams in continuous foaming operation requires to control the competition between gas dispersion (that constitutes a destabilization of gas-liquid interfaces) and stabilization mechanisms that can be divided into interfacial and bulk mechanisms. When interfacial stabilization was weak, i.e. without proteins, a rapid bulk stabilization mechanism was shown to be able to stabilize foams with a bubble size relatively close to that imposed by viscosity when coalescence was inhibited by proteins. Conversely, when stabilization was too rapid, for example for a viscoelastic matrix, gas dispersion was harder. This may also explain qualitatively why the equilibrium size of a single drop under shear flow was reported to increase in the presence of surfactants like Tween 80 or proteins like caseins, whereas it decreased with globular proteins such as whey proteins (Williams et al., 1997). Indeed, surfactants and caseins diffuse towards and stabilise quickly the interfaces, while globular proteins modify gradually the interfacial properties due to a slower succession of mechanisms after adsorption, such as unfolding and surface gelation. Consequently, further attempts to correlate formulation, physicochemical properties of raw materials, process conditions of continuous foaming operation and end-use properties of foams should be aimed at investigating the kinetics of interfacial stabilization mechanisms and particularly the impact of protein-polysaccharide interactions. While the effect on the average bubble size is limited, they clearly influence overrun, probably because they govern the effectiveness of bubble coalescence in collision.

4. Conclusions

In this work, model media have been used to better understand the effects of the rheological and interfacial properties of a model food on continuous foaming operation in laminar flow conditions. Without proteins, only a glucose syrup including pectin was able to incorporate all the gas phase and provide foams owing to a time-dependent solidification behaviour under shear flow that was attributed to pectin dehydration by glucose syrup. By adding proteins without polysaccharides, only WPI solutions were able to form foams with the desired overrun and with far smaller bubbles than without protein addition. The poor foaming ability of Na-caseinates was attributed to their low interfacial elasticity and viscosity that did not protect efficiently bubbles against coalescence. For protein-polysaccharide mixtures, guar did not interact with proteins and the WPI-guar formulation exhibited nearly the same rheological properties and foaming ability as glucose syrup with WPI. Conversely, overrun was reduced in WPI-xanthan mixtures by the viscoelastic behaviour of this recipe, although bubble size remained small. Conversely, WPI-pectin mixtures provided abundant foams with an improved stability due to the enhanced ability of WPI-pectin mixtures to solidify after foaming, whereas Na-caseinates inhibited this effect, which lead to blow-by. This highlighted the strong influence of protein-polysaccharide interactions during foaming, especially on overrun. On the other hand, bubble diameters depended less on polysaccharides and could be adequately described using an approach involving a laminar Weber number based on the apparent viscosity of the foam during foaming. Consequently, further attempts to correlate formulation, physicochemical properties of raw materials, process conditions of continuous foaming operation and end-use properties of foams

should be aimed at including the effect of protein-polysaccharide interactions on the kinetics of interfacial stabilization, especially in relation to bubble coalescence.

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