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Interfacial and foaming characterisation of mixed protein-starch particle systems for food-foam applications

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ABSTRACT

This work presents mixed protein-starch systems as effective foaming agents and stabilisers. The starch size and hydrophobicity play a dominant role in determining the levels of synergy observed. Egg White Protein (EWP) and Pea Protein Isolate (PPI) were selected at two concentrations (0.5, 1 wt. %) along with three starch species of concentrations between 0.5, 1, 3 & 5wt. %. Two commercial OSA-modified starches are compared to a native granule and its heat-treated counter part. The system's effectiveness to incorporate air (overrun) as well as its capacity to hold structure (half life) is evaluated. starch's physical properties (contact angle and size) and their effect on the nature of the Air/Water (A/W) interface (interfacial dilatation rheology, surface tension) are also explored. The effect of protein species as well as starch size and hydrophobicity on foam stability is determined and discussed. The study demonstrates that addition of OSA modified starch (0–5wt%) to (EWP) foams can enhance foam stability by up to 1200% without compromising the foaming capacity, mainly due to a hypothesised exclusion volume effect. Where as the larger heat-treated starch granule is found to increase stability of wet foams by 800%, through a combination of mechanisms.

1. Introduction

The essential building component of many aerated structures found in products such as cakes, breads and ice cream are protein foams (Davis, Foegeding, & Hansen, 2004). The inherent instability of these systems can make their use in industrial applications very difficult. In products where the final quality is largely dependent on the original foam, such as high-ratio cake formulations, Egg white proteins (EWP) remain the only alternative. Here the foam is required to withstand considerable stresses during processing and drying and remain aerated (Chesterton, Wilson, Sadd, & Moggridge, 2015). Thus no other protein species can compete with EWP's combination of foaming capacity and stability. However recent concerns over allergies, animal welfare and ecological problems has lead to a subsequent increase in prices and driving a concerted effort into finding alternative protein sources that can provide similar functionality in food systems (Damodaran, 1997).

Other species such as whey protein have been studied as potential replacers, however the lack of stability is a major problem (Foegeding, Davis, Doucet, & McGuffey, 2002). Pea protein isolate (PPI) has also been the subject of some recent studies. Its non-allergic nature and high nutritional value, make it a good candidate for food foaming applications (Gharsallaoui, Cases, Chambin, & Saurel, 2009).

Within many food systems proteins are present along with other surface active species. pH and presence of co-solutes has been shown to affect the nature of the protein at Air/Water (A/W) interface (Gharsallaoui et al., 2009). The presence of surface active particles such as cellulose and OSA modified starch have been shown to improve foam and emulsion stability (Murray, Durga, Yusoff, & Stoyanov, 2011). At pH close to the protein isoelectric point (PI), due to the low levels of electro-static and intra-molecular interactions, the rate of diffusion and adsorption are increased. However, these fast forming films were shown to have much lower interfacial elasticity than those formed in an acid or alkaline condition (Gharsallaoui et al., 2009).

Use of particles as stabilisers within foams can yield strong interfacial layers that can retard rates of coalescence and ripening. Inorganic particles such as silica (Binks & Horozov, 2005) and fat crystals (Murray et al., 2011) have been used for stabilisation of foams.

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The stabilisation of food foams by particles has been reviewed by (Murray & Ettelaie, 2004) and more recently by (Dickinson, 2010). The major parameters of the particles are the contact angle and their surface area, which determine the energy of desorption per particle (can be of order of several thousand kT (Hunter, Pugh, Franks, & Jameson, 2008)).

Starch in its native form is hydrophilic and thus will not adsorb at A/W interface. Hydrophobic modifications of starch is often induced through addition of Ocentyl succinic anhydride (OSA) which is approved for food applications at an added amount of up to 3%.

An alternative method for increasing the hydrophobicity of starch granules is through heat-treatment (physical modification) (Seguchi, 2001). Dry-heating of starch changes the surface character from hydrophilic to hydrophobic only by altering the nature of the surface proteins. Thus no specific labelling is required for use in food applications as the alteration is explicitly occurring on the granule surface (Seguchi, 2001).

Much of recent focus has been on the interactions of proteins and surface-active polysaccharides/particles within real food systems. The control and the manipulation of these interactions which can be associative or dissociative in nature are key in formulation of novel food products Damodaran, 1997. Functional properties of proteins such as surface activity, conformational stability, emulsifying and foaming capacity can all be manipulated with presence of polysaccharides, thus modifying the microstructure of the adsorbed layer (Damodaran, 1997; Schmidt, Novales, Boue, & Axelos, 2010). When the polysaccharide contains charged groups, these interactions are electrostatic in origin (Patino & Pilosof, 2011). However, shorter range interactions such as bridging by specific ions and hydrogen bonding can also be present in some cases (Dickinson, 2010).

Recent study into stabilisation of foams and emulsions by mixtures of proteins and particles observed that the addition of surface-active particles in the presence of protein facilitated the formation of a more rigid interfacial layer, due to enhanced packing at the interface. This augmentation of the interfacial layer in the presence of both particles and proteins was observed without any evidence of electrostatic interactions between the molecules (Murray et al., 2011). Even non-adsorbing particles can provide additional stability through “Stratification” of such particles in the intervening thin film. As long as the particles are well below the initial radius of the thinning film, they can get trapped and structure themselves into layers that are difficult to remove (Murray & Ettelaie, 2004).

The experiments presented within this article were undertaken based on two original hypotheses; 1.)The existence of proteins along with surface active particles at pH7 should enhance the stability of wet foams. 2.) The extent of any potential synergy between protein-starch particles systems should depend on protein type and starch physical and surface properties.

The focus of this study is to induce potential synergy at pH7 where electrostatic interactions between the molecules is minimised, with the aim of seeking out novel formulations for producing foams of high stability and comparable foaming capacity to EWP, that can serve as a potential (partial) replacers.

2. Materials and methods

2.1. Materials

Egg white protein from chickens (EWP) and rice starch (≤0.1wt.% Protein) were supplied by Sigma–Aldrich (UK). Pea protein isolate (PPI) was obtained from Kerry Ingredients (Listowel, Ireland). The compositions of the proteins used is shown in Table 1.

Table 1
Composition and pH (measured at concentration of 1wt.%) of EWP and PPI.

	EWP	PPI
Protein (wt.%)	85	86
Moisture (wt.%)	8.4	7.2
Fat (wt.%)	<0.1	0
Carbohydrate (−)	neg.	pos.
Ash (wt.%)	4.11	4.85
pH (−)	6.3	7.4

Table 2
The maximum air-phase fractions achieved for all foaming systems and their respective beating times.

ProteinConc(wt%)	*StarchConc(wt%)*	*EWP*		*PPI*	
		φ_{max}	T_{min}	φ_{max}	T_{min}
0.5[a]	0	0.82	3	0.84	3
	0.5	0.81	5	0.89	3
	1	0.79	5	0.86	5
	3	0.86	8	0.78	5
	5	0.85	8	0.77	5
1[a]	0	0.84	3	0.87	3
	0.5	0.80	3	0.86	3
	1	0.81	5	0.83	3
	3	0.88	8	0.76	3
	5	0.88	8	0.72	5
0.5[b]	0.5	0.81	3	0.88	3
	1	0.86	3	0.86	8
	3	0.93	5	0.86	8
	5	0.94	5	0.83	5
1[b]	0.5	0.80	3	0.84	5
	1	0.81	3	0.84	5
	3	0.88	3	0.75	8
	5	0.88	5	0.80	8
0.5[c]	1	0.85	5	–	–
	3	0.85	5	–	–
	5	0.84	5	–	–
1[c]	1	0.82	3	0.8	5
	3	0.81	5	0.79	5
	5	0.79	5	0.81	5

[a] OSA1.
[b] OSA2.
[c] H.T.

The two OSA-modified food grade starches (commercially available food-grade starches referred to as OSA1 & OSA2) were donated by an undisclosed source (for reasons of commercial confidentiality). Both starches were waxy maize derivatives with different levels of esterification (OSA substitution). The water used for all experiments was passed through a double distillation unit (A4000D, Aquatron, UK).

2.2. Starch treatment and characterisation

2.2.1. Heat-treatment

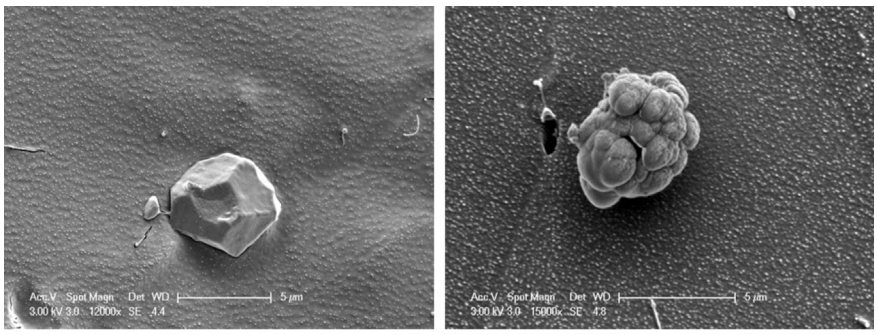
Rice starch was placed at a thickness of 1–2 mm in glass petri dishes and heated in an oven at 120 °C for 150 min in order to induce surface modification (Seguchi, 2001). Fig. 1.

2.2.2. Level of OSA substitution

The degree of OSA substitution was determined using titration method as described in (Rayner, Sjöö, Timgren, & Dejmek, 2012). According to the Eq. 1 shown below.

$$\%OSA = \frac{\left(V_{Sample} - V_{Control}\right)\cdot M \cdot 210}{W}\cdot 100\% \quad (1)$$

where V is the volume (ml) of NaOH required for the sample and



(a) Native (b) H.T

Fig. 1. Cryo-SEM micrographs showing rice starch a)untreated and b)post heat-treatment.

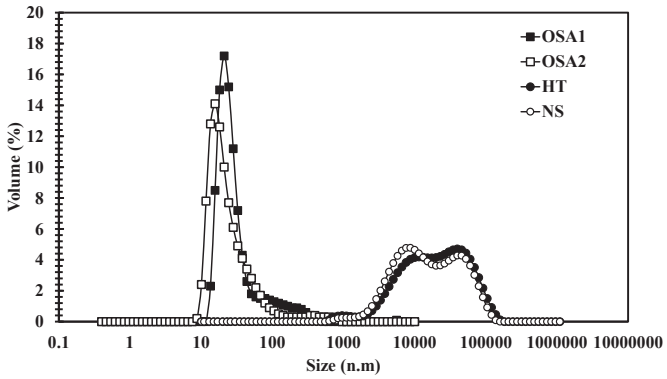


Fig. 2. Particle size distributions of starch particles. OSA1, OSA2, Heat-treated rice starch (HT) and native rice starch (NS).

the control titration, respectively, M is the molarity of NaOH (0.1 M), W is the dry weight of the starch (2.5)mg and 210 is molecular weight of the octenyl succinate group. The results of the titration are presented in Table 3.

2.2.3. Particle size measurements

The size OSA modified starches was measured by dynamic light scattering (DLS) using a Zetasizer Nano Series (Malvern Instruments, UK). The particle size distributions of the rice starch particles was determined by laser diffraction after dispersing the powders in water at a concentration of 1wt% and using a Malvern Mastersizer 2000 with a Hydro SM manual small volume dispersion unit attached (Malvern Instruments, UK). A refractive index (RI) of starch of 1.53 (Bromley & Hopkinson, 2002) was used for the measurement.

2.2.4. Microstructure visualization

Cryogenic scanning electron microscopy (Cryo-SEM; Philips XL30 FEG ESSEM) was used to visualise the microstructure of untreated and heat-treated rice starch in water. One drop of starch dispersion was frozen to approximately −180 °C in liquid nitrogen slush. Samples were then fractured and etched for 3 min at a temperature of −90 °C inside a preparation chamber. Afterwards, samples were sputter coated with gold and scanned, during which the temperature was kept below −160 °C by addition of liquid nitrogen to the system.

2.2.5. Contact angle (θ) measurements

Contact angle measurements for the particles were undertaken after pelletisation of the starch powders (force~1000N) so that a smooth surface was obtained for the depositing of a water drop. A Goniometer (Krüss instruments, Germany) was used to measure θ by a dynamic sessile drop method. Table 3 shows the comparison of the contact angles for the three starch species used in this study.

2.3. pH adjustment

A SevenEasy pH meter (Mettler Toledo, UK) was used to adjust the biopolymer dispersion's pH to 7.0 (using NaOH and HCL of 0.5 M fro Digma Aldrich, UK) before foaming at a temperature of 20 °C. The instrument was calibrated with standard buffer solutions of known pH. (Table 3).

2.4. Foam stability

The biopolymer solutions were whipped using a Hobart mixing unit (Ohio, USA) at the highest shear (i.e. shear rate of ~123 s^{-1}). The foam volume was then monitored over time using an automated web-cam (Logitech, Switzerland) taking pictures at predetermined 1 min intervals. The time taken for the foam to collapse to half of its original height was derived from the recorded images.

2.5. Foaming capacity

The capacity of the system to incorporate air was characterised by overrun measurements. The foam generated in the mixing unit was weighed in a standard weight boat (100 ml). The measurements of weight were used to calculate the overrun and air-phase fraction of the systems according to the following equations (Schmidt et al., 2010) (Phillips, Haque, & Kinsella, 1987);

$$\%Overrun = \frac{W_l - W_f}{W_f} \tag{2}$$

$$\varphi_A = \frac{Overrun}{(Overrun + 100)} \tag{3}$$

where;

W_l is the weight of liquid for a specific volume.
W_f is the weight of foam for a specific volume.

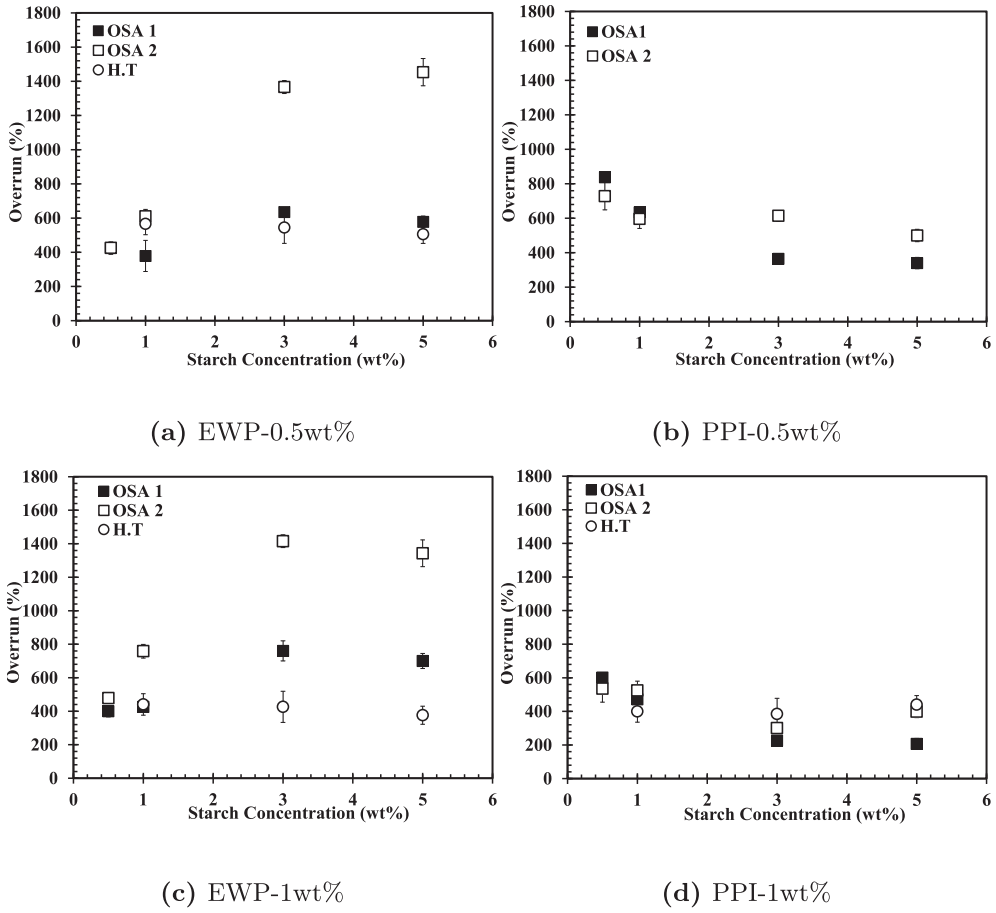


Fig. 3. The effect of starch concentration on the foaming capacity of protein solutions. a)EWP-0.5wt%, b)PPI-0.5wt%, c)EWP-1wt% & d)PPI-1wt%.

2.6. Foam physical characterisation

Whipping profiles were obtained for all the individual systems. This was done with the intention of maximising the air-phase fraction within each formulation and to ensure that all systems are within the wet foam boundary Fig 5. This ensured an unbias comparison of the foam systems. Foam structure is dependent on the liquid fraction (ϕ_l). Only at $\phi_l > 5\%$, the foam can be described as a wet foam. Above a critical liquid fraction of ϕ_l^* the bubbles no longer touch and it is no longer a foam but a suspension of bubbles. ϕ_l^* ~ 0.26 for ordered 3D and ~0.36 for disordered 3D foams (Cantat et al., 2013).

2.7. Surface tension

A Wilhelmy plate method was used to determine the static interfacial (surface) tensions. Measurements were on a K100 Tensiometer from Krüss GmbH, (Hamburg, Germany). All experiments were conducted so that equilibrium interfacial tensions were reached and recorded. All experiments were conducted at room temperature.

2.8. Interfacial dialational rheology

The dynamic air/water (A/W) surface dilational elasticity and viscosity were measured using a pendant-drop Sinterface PAT1 tensiometer (Sinterface, Berlin, Germany). A drop of the liquid sample with an area of 20 mm^2 was formed automatically at the tip of a syringe driven by a motor plunger within a thermostatically controlled glass cuvette set to 20 °C. The image of the drop was captured and digitised by a CCD camera. The interfacial tension (A/W) was calculated by analysing the profile of the drop and fitting it to the Laplace equation. After allowing 1000 s to reach equilibrium, sinusoidal oscillations of the interface occurred by injecting and extracting volume into and from the drop while the response in interfacial tension was recorded. The relative amplitude (DA/A) of the oscillations was set to 5% in order to stay within the linear viscoelastic region and the frequency ranged from 0.01 to 0.2 Hz while 0.01 Hz was the frequency chosen as the one relevant to foams (Schmitt, Bovay, & Rouvet, 2014). The dilatational parameters were calculated through a Fourier transformation algorithm implemented in the software package. The dilatational elasticity and viscosity were calculated from Eqs. 4 and 5.

$$|E| = A \cdot \frac{\Delta\sigma_{a/w}}{(\Delta A)} = E' + iE'' \tag{4}$$

$$\eta_d \cdot \frac{E''}{\omega} \tag{5}$$

where A is the area of the drop (mm^2), $\sigma_{a/w}$ the air/water interfacial tension ($mN\,m^{-1}$), E′ the dilatational elasticity ($mN\,m^{-1}$), E″ the loss dilatational modulus ($mN\ m^{-1}$), η_d the dilatational viscosity ($mN\,m^{-1}$) and ω the frequency (Hz).

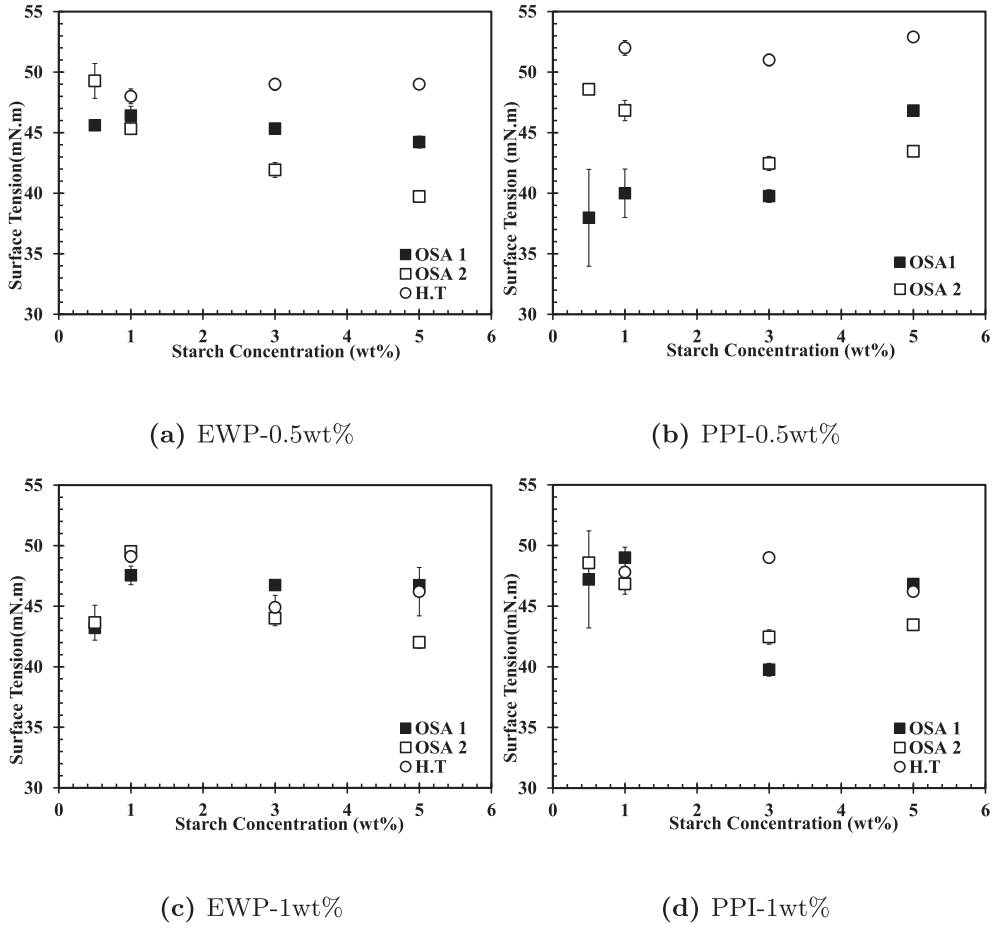


Fig. 4. The equilibrium surface tensions of the mixed protein-starch particle systems. a)EWP-0.5wt%, b)PPI-0.5wt%, c)EWP-1wt% & d)PPI-1wt%.

Table 3
Starch particle properties of OSA1, OSA2, Heat-treated rice starch (HT) and native rice starch (NS).

Starch	Size (μm)	Contact angle (θ)	ζ-potential (mV)	%OSA sub
OSA 1	0.15 ± 0.03	~90 ± 8	~−20	~2.49 ± 0.12
OSA 2	0.09 ± 0.01	~65 ± 6	~−30	~1.39 ± 0.30
HT	10.8 ± 0.8	~38 ± 7	–	–
N.S	9.6 ± 0.1	~25 ± 4	–	–

2.9. Statistical analysis

All measurements were performed on three samples and are reported as means and standard deviations, calculated using Excel (Microsoft, Redmond, WA, USA).

3. Results and discussion

3.1. Foaming capacity of mixed protein-starch systems

The PPI systems show little tolerance to the presence of starch and the overrun is compromised when compared to the original foam solutions (~650%). EWP foams on the other hand not only show greater tolerance, but even enhancements in overrun when combined with OSA2. The diversity of the proteins that form it, and the fact that they all serve different functions means EWP can entrap high volumes of air (overrun from ~550%). Since the quality of the foam is mainly dependent on the protein/emulsifier

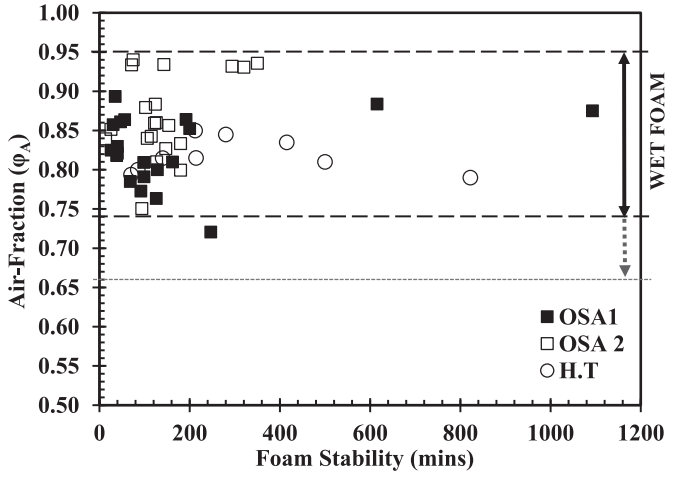


Fig. 5. The Air-phase fraction of all foaming systems shown to be within the wet foam boundary.

conformation at the interface. EWP is very effective in partial unfolding of its flexible macromolecule, thus enhancing its amphiphilic properties (Zmudzinski et al., 2014). This is the property that will facilitate the formation of the foam and moreover the property that makes EWP a good foaming agent (Yang & Foegeding, 2010) (Murray & Ettelaie, 2004).

This is not true of the pea globulins which are more sensitive to beating times, conditions and the presence of co-solutes. This is better highlighted when looking at the air-phase profiles in Table 2. At neutral pH, PPI has been shown to have higher molecular association (i.e. the molecular structure is not completely dissociated) thus significantly reducing its amphiphilic nature (Gharsallaoui et al., 2009). It is notable from Table 2 that addition of starch species increases the time taken to reach φ_{max} for both proteins. A possible explanation would be the reduction of the effective protein concentration present in the system with the addition of more starch.

It is readily stated that as the interfacial forces (resistive to bubble break-up) are lowered, the foaming capacity should increase accordingly. The changes in surface tension(σ), induced with the addition of starch are presented in Fig. 4.

The addition of starch is accompanied by changes in the surface tensions from the original protein solutions (~45 & ~42 mN/m for 0.5 & 1wt.% EWP respectively.~47 & ~46 mN/m for 0.5 & 1wt.% PPI respectively). There is a correlation between surface tension and overrun for the EWP systems. Fig. 4a and 4c demonstrate dependency of σ on the OSA2 concentration (i.e. increase in OSA2 concentration yields a reduction in the surface tensions observed at a given concentration of EWP). This is in accordance to the overrun data observed in Fig. 3a and 3c, where a reduction of ~8 mN/m is observed at 5wt% OSA2 and ~3 mN/m for 5wt% OSA1.

The presence of HT starch has little effect on the surface tension of the systems, but a slight increase is observed for 0.5wt% protein systems Fig. 4, which is reflected in an overrun compromise of ~20%. Furthermore it is reported that polydispersity (Fig. 2) of particles in wet foam systems can lead to dramatic reductions in foaming capacity (Dickinson, 2015). It was observed with Silica particles, that as the film thickness approaches the size of larger particles, they become pinned, constraining their diffusivity leading to a subsequent osmotic pressure gradient. This gradient will draw water from regions rich in larger particles thus thinning the film around the particle leading to rupture (Dickinson, 2015). Moreover the non-uniformity of particles surface, has been shown to cause piercing of the air-bubbles thus acting as an anti-foaming agent (Hunter et al., 2008) as indicated by the overrun reductions shown in Table 2. The H.T starch will form a different mixture with the protein. The larger area and the highly branched structure means that coacervation or phase segregation and even complexation can occur.

It is clear that the more hydrophobic OSA1 is not enhancing the overrun for either protein system. However OSA2 observes synergy with EWP and antagonistic effects when combined with PPI.

The better performance of OSA2 in terms of overrun within EWP systems can be attributed to its hydrophobicity, it is readily cited that $\theta_{optimum} = 60–70^{\circ}$ for foams and above these cited values the hydrophobicity of the particle can be detrimental to foam formation and stabilization (Hunter et al., 2008). Table 3 shows the contact angle of the three starches used within this study. The desirable contact angle of OSA2, means that it has the potential to compete with the proteins for the interface. Therefore OSA2 can preferentially adsorb at the interface. This is in contrast to OSA1, Fig. 3d where concentration has little effect on the foam overrun, suggesting that the EWP is dominating at the A/W interface.

For systems containing PPI, the reduction in overrun is linear when present along with H.T starch, whereas the OSA systems reduce the overrun dramatically (by 50%) when present at concentrations of ≥3wt%. The surface tensions corresponding to the PPI systems are more erratic (Fig. 4b and d), although OSA1 and OSA2 systems observe an overall increase in σ with increasing concentration, which is reflected in the lowering of PPI system's overrun Fig. 4b. The poor performance of these systems can be attributed to the fact that at higher pH above their iso-electric point, pea globulins are not completely dissociated (Gharsallaoui et al., 2009), so that less surface-active groups are less available for adsorption.

3.2. Foam stability of mixed protein-starch particle systems (OSA1 and OSA2 particles)

The stability of a given wet foam system is dependent on its air-phase fraction, with more dense foams staying stable for longer. However Fig. 5 shows that the foam systems used throughout this study were all within the wet-foam boundary and their stability remains largely independent of air-phase fraction. In Fig. 6, the stability of the systems are dependent on the protein type. At starch concentration of 0wt.%, EWP foams has half-life stability of ~108 min and ~106 min for 1wt.% and 0.5wt.% respectively, where as PPI foams were less stable (~75 min and ~48 min). As mentioned already, the hydrophobic groups of pea globulins at pH ≈ 7.0 (food products) are not sufficiently exposed thus surface-active groups are not available for adsorption. This could imply the exclusion of PPI from the interface, when combined with surface-active OSA starches.

EWP foam stability is dramatically increased (twelve fold increase at highest concentration of OSA1) at starch/protein ratios >3, despite little change in overruns. The major constituent ovalbumin is observed to readily coagulate at the interface forming a visco-elastic interfacial layer when present on its own (Zmudzinski et al., 2014). It can be observed that OSA2 starch only enhances the stability of EWP foams three fold (Fig. 6b); far less significant than the twelve fold increase observed for the more hydrophobic OSA1 (Fig. 6a). Since no associative interactions between the protein and the starch are expected Table 3, one of two mechanisms could be responsible for the enhanced stability observed for OSA1 systems.

Firstly as both molecules possess a negative charge, it could be that the net repulsion at a molecular level causes thermodynamic incompatibility (the system spontaneously separates into two distinct phases), which has been cited as causing synergistic effects (Patino & Pilosof, 2011). This effect will transition from low starch concentrations (i.e, where both are intimately mixed and form one-phase solution) to high starch concentrations, where phase separation occurs and a two-phase solution is formed. Similar effect can be observed in the half-life data, where at low starch/protein ratios (i.e. below 3 (w/w)) Fig 6a, the protein and starch co-exist in a single phase, where they mutually exclude one another. At concentrations below the critical starch/protein ratio, little or no enhancement compared to the original protein system is observed. Within these systems the critical concentration seems to be ~3 w/w, above which due to limited thermodynamic compatibility the starch concentrates the EWP protein at the interface.

A secondary mechanism explaining the enhanced stability of the systems containing OSA1 could be that augmentation of the already formed EWP interfacial layer can be induced due to the interactions and potential adsorption of the starch within the EWP interfacial layer. The OSA1 molecule could be inducing exclusion volume effects at neutral pH, this has been shown to modify the thermodynamic activity of the protein at the interface (Patino & Pilosof, 2011). Therefore, the protein at the interface would perform as a more concentrated film, leading to an increase in surface pressure. The strength of the interfacial film provides an energy barrier that prevents the diffusion of gas between different sized bubbles (disproportionation). During disproportionation the bubbles tend to shrink and in order for that to happen the bubbles have to work against the interfacial elasticity and viscosity which can suppress shrinkage (Murray et al., 2011). Therefore this hypothesis would mean that an enhancement in the interfacial

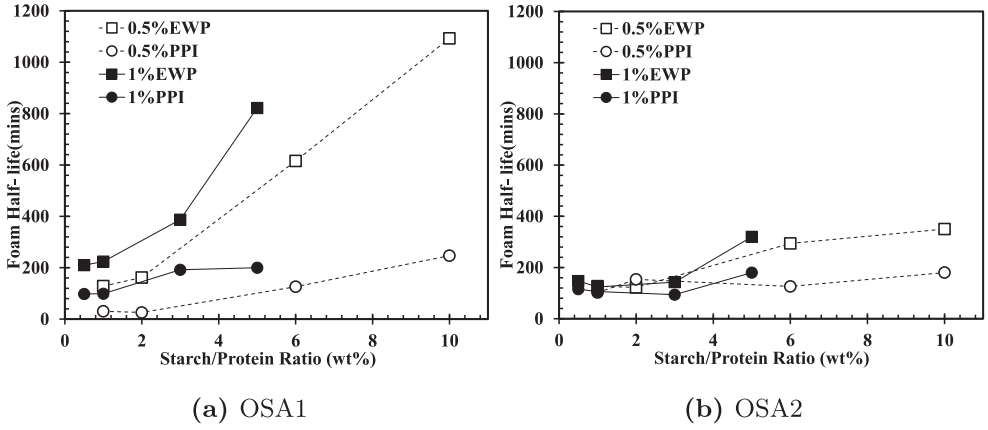


Fig. 6. The half-life stability of OSA-Protein stabilised foam systems. a) stability of OSA1-Protein stabilised foam systems &b) OSA2-Protein stabilised foam systems.

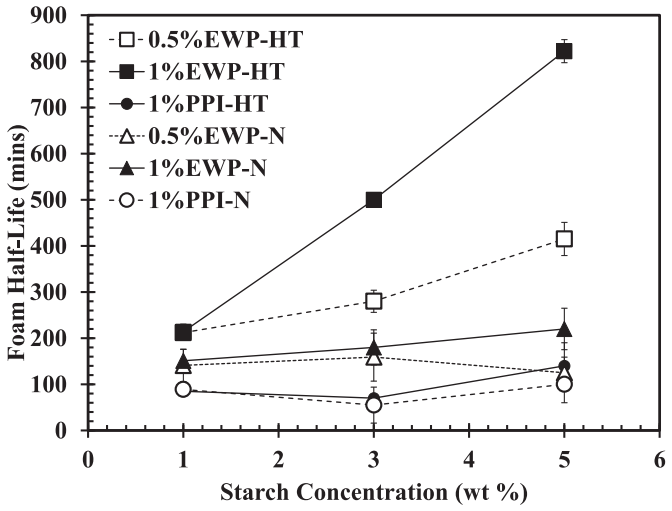


Fig. 7. Half-life stability of protein-HT starch systems shown as a function of starch concentration.

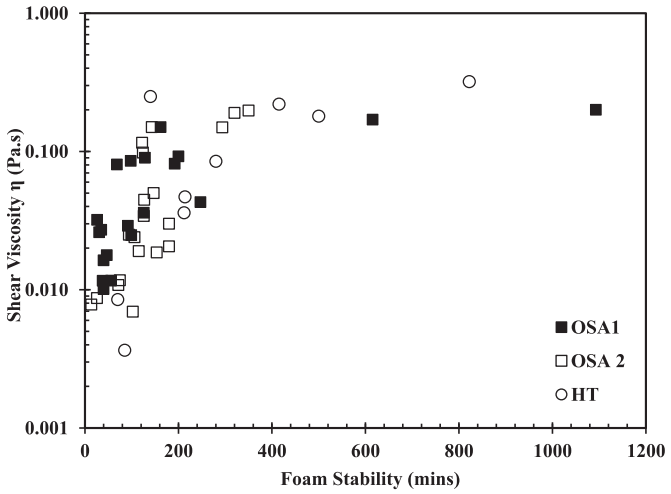


Fig. 9. Average shear viscosities (at 0.1 s^{-1}) of all foaming systems shown as a function of foam half-life stability.

properties of the formed interface should be observed. Dilatation moduli of EWP systems in Fig. 8, observes an enhancement in dilatation elasticity & viscosity of ~15 mN/m and ~10 mN/m respectively, which supports the second hypothesis where molecular crowding could be increasing the effective concentration of EWP at the interface thus strengthening the interfacial layer.

OSA2 systems observe lower levels of synergy. Due to its optimum contact angle, OSA2 could be competing with the proteins for interfacial space. The fact that little change in the foam half-life is observed above ratios of 3 w/w could be an indication that OSA2 could be initially dominating at the interface (due to smaller size and optimum contact angle) hence the facilitation of higher overruns, and it is the protein that is excluded. The protein then

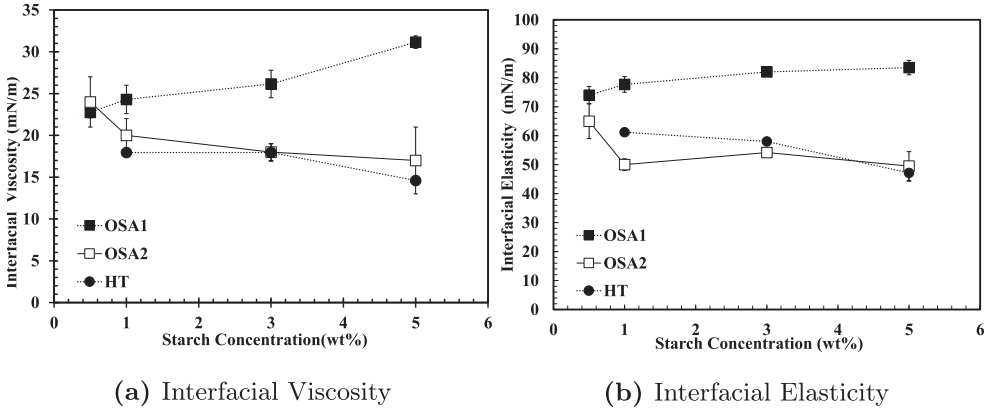


Fig. 8. The effect of starch addition on the interfacial dilatational properties; comparison between OSA 1 and H.T starch at frequency of 0.1 Hz @ 1% EWP (most stable formulations).

displaces the OSA2, at which point the excluded particles structure the lamella and contribute to drainage stability. The decrease in the dilational rheology Fig. 8 is indicative of competitive adsorption between the protein and the starch. However at high ratios, marginal increases (20%) in half-life are observed, compared to the lower ratios. At this point the non-adsorbing OSA2 particles could be structuring in the films (stratification), thus increasing systems stability only through retardation of rates of drainage, which is underlined when looking at Fig. 10b. The mechanism for enhanced stability cannot be ascribed to lower rates of dispropotionation as there is no enhancement observed in the dilational rheology of the interfacial films (Fig. 8). Therefore the increase in the stability is likely to be mainly due to stratification. Similar results have been observed for micellar surfactants (Nikolov & Wasan, 1997), solid silica particles and sodium caesinate systems (Dickinson, 2015).

3.3. *Stability of heat-treated systems*

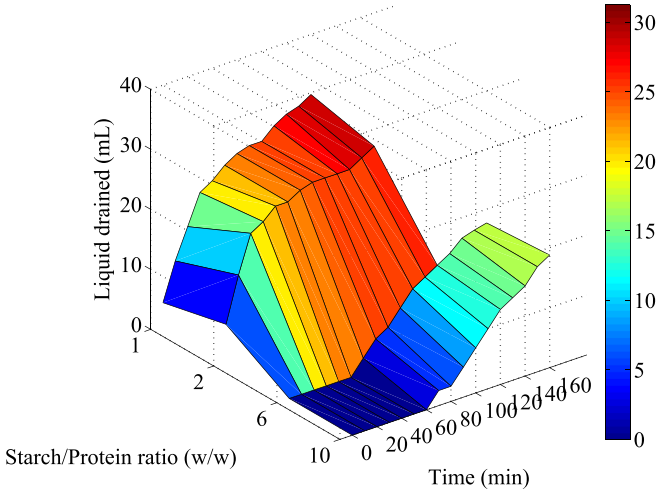
The half-life stability of HT starch systems showed better correlation to starch concentration than starch/protein ratio as shown in Fig. 7. The heat-treated starch, due to its much larger size and more hydrophilic nature, is less likely to adsorb at the A/W interface, even though heat is cited to denature the starch's surface proteins thus exposing the hydrophobic groups and increasing its adsorption capacity (Timgren, Rayner, Dejmek, Marku, & Sjöö, 2013).

As expected the nature of synergy observed with heat-treated starch is significantly different. It can be seen that H.T starch shows no enhancement in the interfacial dilational moduli. In fact the presence of starch can be detrimental to the dilational moduli, thus indicating that the enhancement in stability is not down to an interfacial augmentation as may be the case with OSA1. Although the size distribution of the H.T starch is polydispersed, and some of the smaller fractions may be able to co-adsorb at the interface, this however is not supported by interfacial dilational moduli (Fig. 8). Although interfacial shear rheology of the formed interfaces would have given a better indication of whether, any interfacial accumulation is occurring. The bulk phase viscosity affects the mobility of the continuous phase around the foam bubbles and therefore influences the rate of foam drainage (Yang & Foegeding, 2010). Fig. 9 demonstrates a weak correlation between half-life stability and shear viscosity exists for all foam systems studied, however the increase in viscosity is small (up to ~0.2 Pa s).This viscosity increase will not translate to significant reductions, thus decrease in the rate of drainage due to bulk phase viscosity effects are negligible.

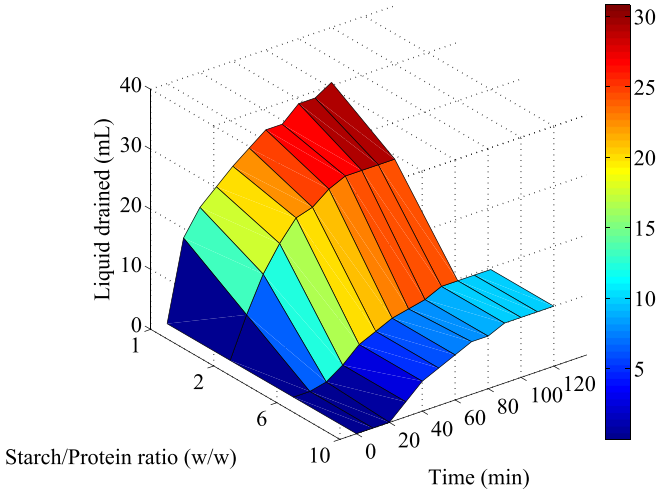
The H.T starch is likely to stabilise the foam system by a multitude of mechanisms. The drainage data (Fig. 10c), indicates that although initial rates of drainage are actually higher in comparison to the two OSA starches, the final volume of liquid drained is comparatively lower than the two OSA starches (by ~30%). The difference between the HT and NS is only in terms of surface properties. It has been well established that HT treated flours used in baking formulations allow for higher entrapment of air in the batter during the preparation stage (Chesterton et al., 2015). This has been put down to modified surface properties which allow participation at A/W interface, as well as an enhanced swelling capacity.

The volume of liquid drained, as the structure of the foam was collapsing until a maximum volume was reached (plateau) and is shown in Fig. 10. The drainage date allow for relative comparison of the rate at which volume of liquid drains from the foam. There are clear mechanistic differences between the stabilising particles and the rate at which their respective systems de-stabilise.

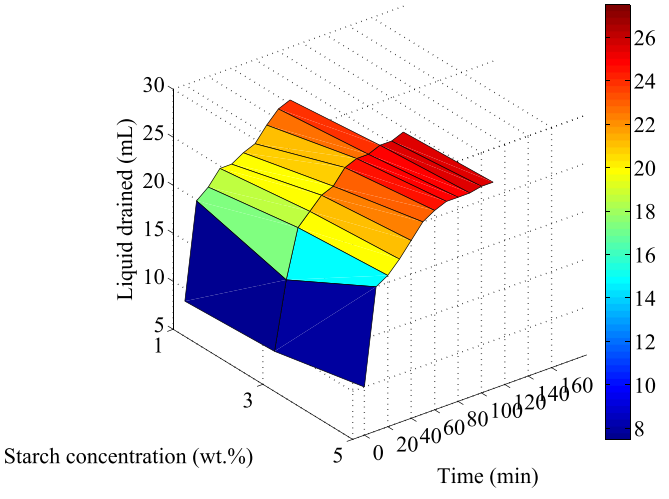
The drainage trend for the two OSA starches (Fig. 10a and b are very comparable. The initial rates and the final volume of liquid drained are significantly reduced as the starch/protein ratio is



(a) OSA1



(b) OSA2



(c) HT

Fig. 10. The effect of starch concentration on the rates of drainage of a)OSA1, b)OSA2 and c) HT systems.

increased. This is reflective of a step-wise thinning of the liquid films ascribed to the phenomenon of stratification. It has been observed that the total number of stepwise transitions increase with particle concentration and decrease with increasing particle size (Hunter et al., 2008) (Dickinson, 2010) (Binks & Horozov, 2005). This is highlighted when observing the rates of drainage for OSA2 (Fig. 10b) systems. At ratios >6, the volume of drained liquid is significantly reduced (i.e. by >60%). Although these systems show higher overruns (i.e. low liquid fraction, Table 2), the reduction is a good indication of the dominant stabilising mechanism. As the starch/protein ratio is increased to ratios of >6, the accumulation and structuring of the non-adsorbing starch is likely to be responsible for the enhanced half-life stability observed for EWP-OSA2 systems (Fig. 6).

OSA1 systems exhibit similar effects with a reduction of 50% in the volume of drained liquid as the starch/protein ratio >6. Structural stabilisation by non-adsorbing particles is most effective when the structured particles are close to being mono dispersed (Dickinson, 2015). Thus highlighting the mechanistic difference behind the drastically different drainage behaviours of OSA and H.T systems (Fig. 2). Furthermore the increase in the concentration of H.T has a slight compromising effect on the overrun of the systems, thus increasing the liquid fraction in the system. However the overall volume of liquid drained is lower than the OSA systems, even though the initial rate of drainage is greater, potentially indicating that HT starch is retarding rates of drainage by a "cork-like" mechanism where the hydrodynamic pressure is trapping the starch granule. Therefore no evidence of interfacial participation suggests the HT starch may only be contributing to the overall structural stability, where HT starch-protein networks are reducing the overall volumes of drained liquid and maintaining the foam structure for longer (Fig. 10).

4. Conclusions

It has been demonstrated that EWP-starch particle systems can act as effective stabilisers for wet foam systems. The level of starch size hydrophobicity play an important role on the level and the mechanism of synergy observed between the protein and the OSA starch. More hydrophobic OSA modified starch, showed significantly enhanced foam stability (up to 12 fold) when above the critical starch/protein ratios (i.e.>3). Interfacial enhancements were observed due to the interaction of the starch with protein interfacial layer. This is shown by the increase in dilational elasticity by ~15 mN/m and ~10 mN/m for dilational viscosity. Also a dramatic inhibition of initial rates of drainage can be observed, eluding to the fact that more than one mechanism could be responsible for the increased stability.

The less hydrophobic and smaller OSA2, did not exhibit the same levels of synergy with the EWP (enhancements of ~2 folds). It is hypothesised that protein eventually displaces OSA2 at the A/W interface, thus excluding it to the foam lamella, where at high ratios due to stratification lower levels of liquid drainage are observed.

Heat-treated rice starch particles which are much larger in size, also showed effective synergy with EWP. The nature of synergy seemed to differ from the OSA modified starches, as no interfacial enhancements were observed. However, despite the lower air-phase fractions considerably lower drained liquid volumes were observed, thus indicating that whilst the smaller fractions H.T starch have the potential to contribute at the interface, the dominant stabilising mechanism is likely to be due to bulk and film viscosity effects forming a barrier to drainage.

Acquisition of more information on drainage as well as detailed analysis of the thinning and rupture of the aqueous films would be useful for better understanding of the mechanistic factors determining the stability enhancements observed in the life times of EWP-starch particle wet foams.

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