Viscosity and Acid Stability in Low-fat Mayonnaise with Varying Proportions of Xanthan Gum and Guar Gum
Abstract

Mayonnaise is a mixture of egg yolk, vinegar, water, spices and 70-80% oil forming a semi-solid oil-in-water emulsion. When preparing a low-fat mayonnaise with an increased water content, thickening agents are required for increased viscosity and emulsion stability. The hydrocolloids xanthan gum and guar gum are sometimes used for this purpose and they act synergistically creating a viscosity increase. However, guar gum has poor acid stability, and because mayonnaise is an acidic product guar gum will eventually start to degrade causing a viscosity decrease and subsequent emulsion separation. Despite this fact, guar gum and xanthan gum are extensively used in mayonnaises today.

The aim of this degree project was to explore how the synergy between guar gum and xanthan gum influences the viscosity of a low fat mayonnaise and whether high acidity will have an impact on the viscosity over a 4-week period. This was to examine if and so, how a mayonnaise recipe can be modified to maintain a cost efficient product with the desired rheological properties in times of hydrocolloid price fluctuations. The study was conducted by preparing 15 mayonnaises with 50% fat, either at pH 3.5; 4 or 5 and a total of 0.6 % hydrocolloids with varying proportions of guar gum and xanthan gum. The mayonnaise samples were studied by measurements of viscosity, color changes and a visual comparison of their mayonnaise-like flow-properties compared to Hellmann’s Real Mayonnaise used as reference.

The viscosity of the mayonnaises increased with increasing ratio of guar gum. On the other side, there were greater viscosity losses in mayonnaises with increasing ratio of guar gum 4 weeks after preparation compared to 4 days, with no apparent signs of correlation between higher acidity and hydrocolloid degradation. Mayonnaises with 20% xanthan gum and 80% guar gum had the texture most similar to the reference. In these low-fat mayonnaises, the use of more xanthan gum led to an undesired “slimy” texture and a lower viscosity – an important aspect if adjusting a low-fat mayonnaise recipe by increasing the ratio of xanthan gum. Because a commercial mayonnaise sometimes is consumed several months after manufacturing, that time frame is most likely required in order to fully measure how much the high acidity in mayonnaise will affect its viscosity. This project has shown a pattern where viscosity in the assessed mayonnaises starts to decrease a few weeks after preparation. However to find out exactly to what extent and how this would affect the overall product, and ultimately: if guar gum/xanthan gum combinations are suitable for long-term mayonnaise applications, further studies are required.

Keywords

Mayonnaise, hydrocolloids, viscosity, stability, xanthan gum, guar gum, pH
Thanks

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1 Svensk sammanfattning

“Viskositet och syrastabilitet i majonnäs med låg fetthalt och olika proportioner av xantan och guarkärnmjöl.”


Syftet med examensarbetet var att undersöka hur synergin mellan guarkärnmjöl och xantangummi påverkar viskositeten i en lågfettsmajonnäs och huruvida en hög syrahalt kommer att påverka viskositeten under en 4-veckorsperiod. Detta för att se om och i så fall hur ett majonnäsrecept kan modifieras för att erhålla en kostnadsseffektiv produkt om priset på hydrokolloider växlar. För arbetet bereddes 15 majonnäser med 50% fetthalt, antingen med pH 3,5; 4 eller 5 och totalt 0,6% hydrokolloider med olika proportioner av guarkärnmjöl och xantangummi. Majonnäserna undersöktes genom mätning av viskositet, färgförändringar och en visuell jämförelse av deras majonnäsliknande flytegenskaper i förhållande till Hellmann’s Real Mayonnaise som användes som referens.

Viskositeten i majonnäserna ökade med ökande halt guarkärnmjöl. Å andra sidan minskade viskositeten i högre grad med ökande halt guarkärnmjöl 4 veckor efter tillverkning jämfört med 4 dagar, men inga tydliga samband mellan högre syrahalt och nedbrytning av hydrokolloider syntes. Majonnäser med en blandning av 20% xantangummi och 80% guarkärnmjöl hade den konsistens som var mest lik referensen. I dessa försök med lågfettsmajonnäser ledde användandet av högre halt xantangummi till en oönskad ”slimig” textur och en lägre viskositet – en viktig aspekt om ett recept på lågfettsmajonnäs ska modifieras genom att öka halten xantangummi. Eftersom en kommersiell majonnäs ibland konsumeras flera månader efter tillverkning så är det troligtvis den tidsramen som krävs för att helt kunna mäta hur mycket den höga syrhalten i majonnäs kommer att påverka dess viskositet. Detta projekt har påvisat ett mönster där viskositeten i de analyserade majonnäserna börjar minska några veckor efter tillverkningen. Men för att få reda på exakt i vilken utsträckning och hur detta skulle påverka produkten i sin helhet, och i slutändan: om kombinationen med guarkärnmjöl och xantangummi är lämplig för majonnäser med lång hållbarhet krävs ytterligare studier.
2 Introduction

Mayonnaise is said to be one of the oldest and most commonly used condiments in the world today (1). It is a semi-solid oil-in-water emulsion and traditionally made of a mixture of egg yolk, vinegar, water, spices and 70-80% oil that is slowly added and whisked into the mixture forming an emulsion of closely packed oil droplets. Influenced by health concerns there has been an increasing demand for low-fat foods. However, as fat influences rheological properties, flavour, mouthfeel and texture these sensory properties are often difficult to reproduce in low-fat foods (1). Creating a sufficient consistency in a low-fat mayonnaise requires the addition of thickening agents, i.e. hydrocolloids or food gums. Hydrocolloids are regularly used in mayonnaise and other condiments; they are usually added to increase viscosity, which is a physical property that can be related to suspension of solid particles, emulsion stability and pourability (2).

Mayonnaise is an acidic product with a pH around 4 depending on the amount of vinegar added and commercial mayonnaises must maintain its viscosity throughout a long shelf life. For long-term stability, the incorporated hydrocolloids need to have sufficient acid stability because a low pH can cause hydrocolloids to degrade leading to a viscosity decrease (3). In food applications, two or more hydrocolloids are often added. A common combination is the microbial product xanthan gum and the seed gum guar gum, these two act synergistically creating a viscosity increase. However, because of the poor acid stability of guar gum, if the pH is below 5 the viscosity will gradually decrease and cause subsequent emulsion separation after a few weeks. Therefore, manufacturers are advised to be cautious when using guar gum in low pH applications (3). Despite this fact, guar gum and xanthan gum are extensively used in mayonnaises today. There are also studies on low-fat mayonnaises where guar gum is included in the optimal blend of hydrocolloids (4).

Because seed gums are derived from plants, their prices are more sensitive to climatic variations than the price of xanthan gum that is produced in fermentation tanks (2). For this reason, knowledge on how hydrocolloids interact in products like mayonnaise and how they are affected by factors such as pH and storage time could possibly contribute to a more cost efficient product if the recipe can be adjusted when hydrocolloid prices fluctuate.

This degree project is conducted on behalf of Caldic Sweden AB.

2.1 Aim and objectives

The aim of this degree project is to explore how the synergy between guar gum and xanthan gum will influence the viscosity of a low fat mayonnaise and whether high acidity will have an impact on the viscosity over a 4-week period. This is to examine if and how a mayonnaise recipe can be modified to maintain a cost efficient product with the desired rheological properties if hydrocolloid prices fluctuate.

The study is conducted by preparing 15 mayonnaises with either pH 3.5; 4 or 5 and with different proportions of added guar gum and xanthan gum. The mayonnaise samples were studied by using measurements of viscosity, color changes and a visual comparison of their mayonnaise-like flow-properties. The measurements were conducted at 4 days and 4 weeks after preparation with additional measurements 6 weeks after preparation.
3 Background
The first part of the following background will address rheological properties and food emulsions in general. The second part will cover mayonnaise as a specific form of emulsion as well as guar- and xanthan gum and their synergistic effect on the rheological properties of mayonnaise that will be examined in this project.

3.1 Rheology, flow properties
Rheology is the science devoted to deformation and flow properties of fluids and solid materials (5) and how materials respond to applied forces and deformations, usually as a function of time (6). Rheological properties of foods could be seen as a subcategory of food texture. Selected key concepts in rheological studies will we explained in the following sections.

Viscosity (η for apparent viscosity or μ for Newtonian viscosity) is defined as “the internal resistance to flow” (6), simply put it describes how thick the consistency of a material is.

Stress (σ) is a measurement of force generally expressed with the unit Pascal, Pa. Depending on the direction of the force relative to the surface of the area impacted, either a normal stress or a shear stress will be experienced. Normal stress is the result of a force directly perpendicular to the surface, usually from tension or compression such as chewing a piece of gum or kneading of dough. Shear stress is the result of a force acting in parallel to the sample surface, for example spreading butter on toast or stirring a spoon in a bowl of yoghurt (6).

Strain is a dimensionless quantity defining the relative deformation of a material and the direction of the applied stress. Just as with the previously mentioned term “stress”, there is normal strain (ε) when normal stress is applied perpendicularly, as well as shear strain (γ) when a material encounters shear stress (6) (Figure 1).

\[
\text{Figure 1. Shear strain (γ) in a cube, adapted from (6).}
\]

Shear strain rate, or simply shear rate (\dot{\gamma}) is the degree of deformation, or change in strain with respect to time (dγ/dt) commonly used to quantify strain during fluid flow with the unit s⁻¹. When liquids such as water are exposed to shear they display irrecoverable deformation. The deck of cards analogy is common when explaining the shear rate concept. Each card in the deck represents an infinitely thin layer of fluid, (Figure 2) the upper card is set in motion with a constant horizontal velocity (U) and a known distance (h) to the next parallel layer of fluid giving the approximate quotient \dot{\gamma} = U/h. This type of strain is called simple shear and could be defined as “a laminar deformation along a plane parallel to the applied force” (6) (Figure 2).
Newtonian fluids
For the simplest kind of fluids, so called Newtonian fluids, at the given temperature the viscosity is constant and independent of shear rate and time (Figure 3, 1st graph). Pure liquids as well as diluted solutions and dispersions – such as water, milk, and vegetable oil – usually behave as Newtonian fluids. For these fluids the viscosity as a function of shear rate and shear stress is constant according to equation 1 and called Newtonian viscosity ($\mu$). Typically for liquids, including Newtonian fluids, the viscosity will decrease when temperature increases (6).

\[ \mu = \frac{\sigma}{\gamma} \quad [\text{Eq 1}] \quad (6) \]

Non-Newtonian fluids
Apparent viscosity ($\eta$), is a function defined as the shear-dependent viscosity. The apparent viscosity function is the result of the shear stress divided by shear rate measured in Pa·s, according to equation 2 (6).

\[ \eta = f(\gamma) = \frac{\sigma}{\gamma} \quad [\text{Eq 2}] \quad (6) \]

This relationship applies for non-Newtonian fluids, usually more concentrated solutions and dispersions. In food applications, most fluids do not exhibit Newtonian flow behavior. In these fluids, the flow will change with shear rate such as pumping or mixing speed. If viscosity decreases with increasing shear rate, the material is shear thinning or pseudoplastic or plastic (Figure 3, 2nd graph). In contrast, if the material thickens as the shear increases it is called shear thickening or dilatant, this can apply for corn starch slurries (6).

Pseudoplasticity/plasticity and dilatancy are properties that are independent of time but there are materials where viscosity will change with time at constant shear rate. Fluids that thin with time are referred to as thixotropic – in other words time dependent shear thinning. When monitoring the viscosity at constant shear rate with respect to time, thixotropic fluids will generate a hysteresis curve, (Figure 3, 3rd graph). An example is when pumpkin pie filling is mixed at constant speed for a longer time, it will become less viscous because of its thixotropic properties caused by destruction of weak bonds that links the molecules (6). Thickening agents, as will be discussed later, simultaneously show some properties of an ideal solid and some flow properties of an ideal liquid. In other words, they are viscoelastic (7). Elastic behavior means that a material instantaneously deforms under an applied stress to a constant strain, although it will return immediately to its original shape as the stress is released (8).
Figure 3. Theoretical flow curves of fluids with different flow behaviors, with viscosity (apparent viscosity) (η) as a function of shear rate (\(\dot{\gamma}\)) from left to right: Newtonian, pseudoplastic and thixotropic behavior. Adapted from (9).

Pseudoplasticity and plasticity are somewhat similar although in plastic fluids there is a yield stress present (6). Plastic fluids, sometimes referred to as Bingham plastic, will not flow until shear stress (\(\sigma\)) exceeds the yield value (\(\sigma_0\)) (Figure 4)(10). The curve marked “generalized plastic” in figure 4 is more representative of the actual behavior of a plastic liquid. Examples of fluids with plastic behavior include suspensions such as mayonnaise, ketchup and toothpaste (10).

Figure 4. Basic shear diagram illustrating typical behavior of real fluids, adapted from (10).

Throughout this project work, the term “viscosity” will be used when “apparent viscosity” is implied.

3.2 Consistency coefficient, comparing viscosity

(Apparent) viscosity (\(\eta\)) can be determined as a function of shear rate and a consistency coefficient (K) which reflects the average viscosity of the fluid, can be calculated according to the following Power Law model, equation 3 (4):

\[
\eta = K \cdot \dot{\gamma}^{n-1} \quad \text{[Eq 3] (4)}
\]

\(\eta\) is the apparent viscosity in Pa·s, K is the consistency coefficient (Pa·s\(^n\)), \(\dot{\gamma}\) is shear rate (\(s^{-1}\)) and \(n\) is a dimensionless flow behavior index determining whether the fluid is Newtonian, pseudoplastic/plastic (\(n<1\)) or dilatant (\(n>1\)) (4). The logarithmic form of equation 3 is as follows:

\[
\ln(\eta) = \ln K + (n - 1) \cdot \ln \dot{\gamma} \quad \text{[Eq 4] (4)}
\]

\(y\) intercept \(x\) slope
Equation 4 can be constructed as a regression equation for a straight line where ln η is plotted as a function of ln ‘γ. In this regression equation the intercept represents ln K and consequently the consistency coefficient K can be calculated by using the empirically collected data η and ‘γ from viscosity measurements (Figure 5).

In this work, the consistency coefficients for different mayonnaise formulations will be calculated and the coefficients will then be used to compare the non-Newtonian viscosity of different mayonnaises.

3.3 Colloids
A colloid is generally defined as “a system containing particles that are clearly larger than small molecules (say, solvent molecules), yet too small to be visible” (8), more specifically a colloidal system contains particles in the size range of about 1 nm to 0.1 mm (8). The colloidal systems are divided into lyophilic or lyophobic colloids. Lyophilic or “solvent loving” colloids are formed simply by dissolving a material in an appropriate solvent and the system, i.e. the solution, will be thermodynamically stable. Lyophobic colloids require energy to form when one phase is dispersed into a continuous phase. Once formed, the system, i.e. the dispersion, will not be thermodynamically stable. An interface between two phases, like water and oil, contains excess free energy, proportional to the interfacial area, and to minimize the interfacial free energy the interface will become as small as possible. Consequently, an external force needs to be applied in order to enlarge the interfacial area (8). An example demonstrating this phenomenon is when we pour oil in a glass of water: a visible layer will separate these two phases, and if the system is stirred oil droplets will temporarily form, thus enlarging the interface area. If no stabilizing agents are added, the oil and water will separate and return to the state when the two phases are separated.

3.4 Dispersions
A few foods are homogenous solutions; this is the case for cooking oil and some drinks, but most foods are dispersed systems. Where there is a dispersed state, different components are in different compartments meaning it is not a thermodynamically stable system (8). Dispersion is defined as “a system of discrete particles in a continuous phase” (8). Depending on what phase is dispersed, it is either a foam if these particles are gaseous, an emulsion if liquid and a suspension if solid (8) (Table 1).
Table 1. Complete range of the different types of colloidal dispersions, adapted from (11).

<table>
<thead>
<tr>
<th>Continuous Phase</th>
<th>Dispersed Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>None</td>
</tr>
<tr>
<td>Liquid</td>
<td>Foam</td>
</tr>
<tr>
<td>Solid</td>
<td>Solid foam</td>
</tr>
</tbody>
</table>

An emulsion consists of two immiscible liquids with one dispersed in the other in the form of small spherical droplets possibly stabilized by an emulsifying agent (Figure 6 (12). Emulsions can be either water-in-oil (w/o) such as butter and margarine or oil-in-water (o/w) like milk, cream and mayonnaise (13).

Figure 6. Schematic diagram of an oil-in-water emulsion, adapted from (12), with emulsifier-coated droplets that are dispersed in the continuous water phase.

3.5 Surfactant

Amphiphilic molecules have both hydrophilic and hydrophobic properties and when they are in a solution and in contact with a phase surface they can strongly adsorb and accumulate in the interface. This adsorption will lower the surface free energy, and therefore the surface tension (8). The amphiphilic substances are also called surfactants. When surfactants are added in an o/w emulsion they can adsorb in the water/oil interface and lower the interfacial tension. They can also adsorb on the oil droplets and delay the droplet coalescence where they fuse with one and other. Figure 7 illustrates two oil droplets that approach each other during emulsification. In this context the surfactants are called emulsifiers and stabilizers (8). What is more, small amphiphilic molecules can also form micelles that can carry hydrophobic molecules like oil droplets in their interior. In food applications, proteins are often the surfactants of choice, mainly in o/w emulsions (8).

Figure 7. Two oil droplets in a water phase approaching each other during emulsification and surfactants on the oil droplet surface creating a monolayer of closely packed molecules, adapted from (8).
3.6 Dispersion properties
There are some important factors that determine emulsion properties. Droplet size distribution is one of them; where smaller drops generally make more stable emulsions. However, the smaller droplet size, the more energy is required in the dispersion process and more emulsifier must be added (8). Also the composition and thickness of the surface layer surrounding the droplets and composition of the continuous phase affect physical stability (8). The concentration of fat droplets has a major role in determining physiochemical, sensory and physiological properties in an o/w emulsion. Examples of sensory attributes often desired are creaminess, thickness or richness, and they usually increase with increasing fat droplet concentration (12).

3.7 Creating an oil-in-water emulsion
A typical emulsion contains oil, water and emulsifier, which are mixed by using energy (usually mechanical). The energy needed to deform and break up droplets is generally produced by the rapid and intense pressure fluctuations arising in turbulent flow, ideally by a high-pressure homogenizer. High-speed stirrers, faster and longer stirring result in smaller droplets. Emulsifiers are needed both for the formation of the emulsion and also to provide stability once the emulsion is made providing long-term stability against coalescence, when two smaller oil droplets merge to form a larger one (8) (Figure 8). When an emulsion degrades the oil droplets become larger through coalescence, and that usually means that the color becomes darker (3).

![Figure 8. Coalescence induced by rupture of the thin film between close oil droplets, adapted from (8).](image)

3.8 Mayonnaise
Mayonnaise is a semi-solid oil-in-water emulsion (1). When preparing a mayonnaise, the oil has to be gradually added and whisked into the aqueous phase to form closely packed oil droplets. It is important to point out that if the oil and aqueous phase are mixed at once, this will result in a water-in-oil emulsion with a consistency much like the oil itself (14). Real mayonnaise is a standardized product that according to FDA, (US Food and Drug Administration) requires at least 65% oil (15) and may not contain any hydrocolloid stabilizers (3). Some typical mayonnaise recipes are as follows (Table 2):

| Table 2. Typical mayonnaise recipes, with, and without added hydrocolloids, expressed in weight percent, adapted from (16). |
|-----------------|-----------------|
| **80% Oil Formula** | **%** | **Low Fat Formula** | **%** |
| Vegetable oil | 80 | Vegetable oil | 50 |
| Egg yolk | 6 | Other thickeners | 4 |
| Sugar | 1 | Egg yolk | 4 |
| Salt | 1 | Sugar | 1,5 |
| Spices (e.g. mustard) | 0,5 | Salt | 0,7 |
| Water | 7,5 | Spices | 1,5 |
| Vinegar | 4 | Water | 35,3 |
| | | Vinegar | 3 |
3.9 Egg yolk as emulsifier

Egg yolk is the most commonly used emulsifier in mayonnaise (17) although synthetic chemical emulsifiers may be used (3). Liquid egg-yolk itself is an emulsion containing hydrophobic granules suspended in an aqueous phase that holds most of the protein (17). Egg yolk contains a complex mixture of components like the phospholipid lecithin (14) and a number of proteins including the predominant lipoprotein found in the egg yolk – lipovitellin (18). Proteins improve the interface properties of an emulsion by forming a protective steric barrier around the oil droplets (19). Proteins work well as stabilizers in o/w emulsions because they are surface active, water-soluble and very resistant to coalescence (8). However, processes such as freezing or freeze drying (but not pasteurization) severely disrupt the structure of egg yolk and this will affect its emulsifying properties resulting in larger oil droplets more prone to coalesce (14).

3.10 Thickening agents

Influenced by health concerns, there has been a demand for foods with reduced sugar and fat content; therefore low-calorie and low-fat recipes are frequently made as alternatives to traditional foods (1). However, as fat influences rheological properties, flavor, mouthfeel and texture these sensory properties may be difficult to reproduce in low-fat foods. To produce a low-fat mayonnaise, the dispersed oil phase has to be decreased and the water content increased. Increasing the viscosity of the water phase requires thickening agents. The lower the fat content in an o/w emulsion, the more important is the role of thickeners and emulsifiers (20). Thickeners help increase the stability of the interfacial film that separates the droplets and prevent coalescence (19).

Hydrocolloids are a group of polymers with long chains of polysaccharides or proteins with the ability to form viscous dispersions when dispersed in water; they act as thickening agents. Hydrocolloids are hydrophilic compounds with a large number of hydroxyl groups and high affinity for water molecules (7). Hydrocolloids are common additives in condiments where they are added in order to increase viscosity, to facilitate suspension of solid particles, to increase emulsion stability and to enhance pourability (2). They are used to improve quality traits and shelf life and the two main applications are as thickening agents and gelling agents. Some food applications for thickeners are dressings, dairy products, cake batter and toppings; in these applications starches, cellulose derivatives, xanthan gum, microcrystalline cellulose, locust bean gum and guar gum can be used (3,7). Gelling agents are used in puddings, jellies and marmalade, some important gelling agents for these purposes are modified starch, carrageenan and gellan gum (7).

3.10.1 Use of thickeners

What thickener to use for a certain food application depends on a number of factors; desired viscosity and rheology, the pH of the system, interactions with other ingredients and the cost and amount needed to achieve the desired characteristics. Also the gum’s ability to work as a binder, foam stabilizer, fat mimetic, suspension stabilizer, whipping agent and syneresis inhibitor (preventing the appearance of fluid droplets on the gel surface) needs to be taken into consideration (8). Furthermore, the manufacturing process has to be taken into account as well and affects the choice of thickening agents in the highest degree (J.Ekvall, personal communication, May, 2016). Adding thickening agents to an emulsion increases the stability and viscosity of the aqueous phase by slowing down oil droplets movement (4).
Textural properties could be, for example, elastic or brittle, long or spreadable, chewy or creamy depending on which hydrocolloid is used and that choice will also affect sensory properties like opacity, mouthfeel and taste (7).

### 3.10.2 Polysaccharide stability

A concentrated polysaccharide dispersion will gain higher viscosity from physical entanglement of disordered “random coils” when the hydrocolloids make contact which will limit the movement of these molecules resulting in an entangled network, i.e. the process of thickening (7). A gel is a three-dimensional network of connected molecules or particles like emulsion droplets or molecular aggregates, that like a sponge surrounds a volume of a continuous liquid phase. These networks are usually polysaccharide or protein molecules. Proteins are more stable to hydrolytic cleavage than polysaccharides that might undergo depolymerization during food processing or storage. On the other hand unlike proteins, polysaccharides do not undergo denaturation. To what extent a polysaccharide gel undergoes depolymerization and consequently loses viscosity depends on acidity (pH), temperature, enzymes, time and structure of the polysaccharide. To compensate for this breakdown, which also is a determinant of shelf life, more gum in the formulation or a more acid-stable gum can be used (8). Different hydrocolloids show different stability at a low pH. High acidity can cause hydrocolloids to degrade leading to a viscosity decrease and loss in emulsion stability. Commercial dressings and condiments usually have a long shelf life and must maintain their viscosity during that time. Since dressings often have a low pH, the incorporated hydrocolloids must have sufficient acid stability to preserve the viscosity and stability of the emulsion (3).

### 3.11 Guar gum, E 412

One way for plants to store energy is to convert excess sugars and polymerize them into insoluble reserve polysaccharides that can later be enzymatically degraded to their constituent soluble sugars. The most common reserve is a polymer of D-glucose i.e. starch, although other sugars can be incorporated into polymers. Galactomannan is a group of polysaccharides with other incorporated sugars that have special functions (2). Today, galactomannan is retrieved from three plant species and used as commercial food gums; guar gum, locust bean gum and tara gum. Guar gum, obtained from the seeds of *Cyamopsis tetragonolobus*, is cultivated in India and Pakistan, and yields the highest viscosity of all natural, commercial gums. For seed gums, as with all harvest, availability is dependent on the infrastructure of collection and factors like periods of drought or rain, therefore the price can vary. For instance, in 1995 locust bean gum prices had an almost sevenfold increase compared to previous year (2).

#### 3.11.1 Chemical structure

Galactomannans are a group of linear polysaccharides that consist of a backbone, or main chain, of 1,4-linked β-D-mannose residues (β-D-mannopyranosyl) with single-unit branches α-D-galactose residues (α-D-galactopyranosyl) attached with a glycosidic bond to C-6 of the mannose (Figure 9) (2). Different gums have different degrees of galactose substitution. In guar gum about half of the main chain units contain a galactose unit (8), ratio 1:2, whereas in locust bean gum, the ratio is 1:4 (2).
3.11.2 Properties and applications
Guar gum is the lowest cost hydrocolloid on a usage level basis (3) used typically at 0.05-0.25 weight percent (8). It is widely used in food formulations owing to its low cost and consumer acceptance since it may be labeled as a natural substance that does not undergo chemical change or modification (2). Galactomannans show pseudoplastic flow behavior and thixotropy (21). Guar gum is rarely used alone in dressings, instead it is often combined with xanthan gum to lower the total cost. However, although guar gum produces decent viscosity initially (2), it has poor long-term acid stability and after a few weeks in a pH below 5 it will start being hydrolyzed by the acid, losing its viscosity and causing emulsion separation. Manufacturers are advised to be cautious about using guar gum in salad dressings (3), yet guar gum is extensively used in mayonnaise applications today, despite its claimed poor acid-stability.

3.12 Xanthan gum, E 415
When production of xanthan gum started in the 1960s, it was the first of a new generation of polysaccharides manufactured through biotechnology and able to compete with natural food gums. Xanthan gum is a commonly used food gum produced in fermentation tanks using the bacterium Xanthomonas campestris. This bacterium is naturally found on leaves of plants of the cabbage family and it produces the polysaccharide xanthan (8). Because xanthan is made by fermentation, production and availability are not depending on external factors like climate and weather and will not affect the price or quality of the product (2).

3.12.1 Chemical structure
The primary structure of a xanthan gum molecule consists of a cellulose-like backbone of 1,4-linked β-D-glucose, D-glucose is sometimes referred to as dextrose (23), with side chains that represent about 60% of the molecule containing two mannose and one glucuronic acid (Figure 10). According to Jansson et al. (1975), there is a pyruvic acid residue carried by half of the mannose units (8).
3.12.2 Properties and applications
Xanthan is soluble both in hot and cold water and stable in acidic systems making it suitable for mayonnaise applications as it also produces high viscosity at low concentrations (8). Aqueous solutions of xanthan are very shear thinning and unlike guar gum, xanthan gum shows no evidence of thixotropy (24). Its shear-thinning character is more prominent than that of other gums, this behavior makes xanthan gum solutions easy to pour, mix or pump (2). Xanthan has a resistance to hydrocolloid degradation owing to its secondary structure with side chains “wrapped around” the cellulose backbone. Xanthan gum in solution is stable between pH 2.5-11, resistant to enzyme degradation and will keep all its viscosity after defrosting in a microwave oven (2).

It is possible to prepare emulsions with xanthan that are stable against separation for up to three years. Xanthan is typically used at a level of 0.05-0.5 weight percent and interacts synergistically with guar gum to increase the viscosity of a solution. It also facilitates the suspension of oil droplets (25). Because xanthan will hydrate rapidly it is recommended to disperse xanthan in oil or a powder like salt or sugar before addition to the aqueous phase in order to avoid formation of lumps (2)(25). Xanthan gum is popular especially for pourable salad dressings, however it could produce dressings perceived as elastic or “gloppy” (2) and “chunky” which might be a problem in low-calorie dressing where the concentration exceeds 0.5 % (3).

3.13 Guar-gum/Xanthan gum synergy
There is a synergetic interaction between guar gum and xanthan gum leading to a viscosity increase that is broadly used in the food industry (2). The synergistic effect is explained by the interaction between the unsubstituted “smooth” regions of the guar gum molecule and the xanthan gum molecule (Figure 11) (2).
Figure 11. The hypothesized interaction of xanthan gum and galactomannans, forming a viscous gel.
1: Double helical molecules of xanthan gum, 2: “smooth” regions of galactomannan, 3: “hairy” regions with a high density of branched mannose units. Adapted from (8) and (2).

The optimal blend of guar gum and xanthan gum may vary depending on application and additional ingredients. Xanthan-guar blends are generally less efficient in stabilizing emulsions. In a study where the composition to achieve desired stability, textural and rheological properties were examined, the best formulation was 6,7 % MDG (egg yolk substitute) with 36,7 % guar gum and 56 % xanthan gum in a mayonnaise with 60 wt% oil and 0,36 wt% stabilizers and emulsifier (4). In distilled water and a 1 % total gum concentration, the ideal ratio resulting in the highest viscosity is 80% guar gum and 20% xanthan gum (2) (7) (Figure 12).

Figure 12. Viscosity of guar-xanthan blends at 1% total gum concentration and shear rate 21s⁻¹ (200 rpm). Adapted from (2).

3.14 Technical background

Characterizations of thickeners may involve rheology, structure, microscopic and molecular characterization using instruments such as viscometers, rheometers, texture measuring systems, scanning electron microscope and NIR (7). In this project a rotational viscometer was used for viscosity measurements. A color measurement instrument will be used as a way of measuring determining stability based on the assumption that when an emulsion degrades the oil droplets become larger through coalescence, and that usually means color becomes darker.
4 Materials and methods

4.1 Raw materials characterization
Ingredients for the mayonnaises were provided by Caldic Sweden AB. The added oil was rapeseed oil (Aarhuskarlshamn AB, Sweden). Hydrocolloids used were KELTROL®F Xanthan Gum (CPKelco) and CERAMEHL Guar Gum Type 166 (Roeper, Germany). Pasteurized and sprayed dried egg yolk powder (Källbergs, Sweden) was used as emulsifier and Absolut ren ättika 24% (Perstorp Ättika, Sweden) was used as vinegar. To prevent microbial growth 0.05% granular potassium sorbate (C₆H₇KO₂) was added (Natong Acetic Acid Chemical CO Ltd, China). The reference Hellmann’s Real Mayonnaise (Unilever) was purchased at a local grocery store.

4.2 Reference
Hellmann’s Real Mayonnaise consumer pack 400g was used as a reference. It was chosen for its high fat content much like that of traditional mayonnaise and because it does not include added hydrocolloids. The ingredients were, in the order written on the label: 78% rapeseed oil, water, 7.9% whole eggs and egg yolks, vinegar, salt, sugar, lemon juice concentrate, Calcium Disodium EDTA, natural flavors and coloring. The measurements were made 8 months prior to the reference sample’s expiration date and 4 days after opening with pH 3.7.

4.3 Recipe
Caldic provided an already existing hydrocolloid-containing recipe for mayonnaise. This recipe was chosen for its 50% fat content to ensure sufficient viscosity yet allow added hydrocolloids to exert a measurable effect. The supervisor at Caldic selected proportions of xanthan gum and guar gum to be analyzed and appropriate pH-values for measurements. The combinations are shown in Table 3.

Table 3. The types of mayonnaises prepared and analyzed with percentages of xanthan gum (X) and guar gum (G) and their respective pH.

<table>
<thead>
<tr>
<th>pH 3,5</th>
<th>20 X / 80 G</th>
<th>35 X / 65 G</th>
<th>50 X / 50 G</th>
<th>65 X / 35 G</th>
<th>80 X / 20 G</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 4</td>
<td>20 X / 80 G</td>
<td>35 X / 65 G</td>
<td>50 X / 50 G</td>
<td>65 X / 35 G</td>
<td>80 X / 20 G</td>
</tr>
<tr>
<td>pH 5</td>
<td>20 X / 80 G</td>
<td>35 X / 65 G</td>
<td>50 X / 50 G</td>
<td>65 X / 35 G</td>
<td>80 X / 20 G</td>
</tr>
</tbody>
</table>

An initial trial mayonnaise was made with 0.3 weight percent (wt%) hydrocolloids (100% xanthan). This did not result in a mayonnaise, thus the amount of hydrocolloids was doubled to 0.6% which was used in the subsequent experiments. The required amount of vinegar to obtain pH 3.5; 4 and 5 respectively was still to be determined and the water content was adjusted after the amount of vinegar required to reach the desired pH. Two batches of mayonnaises were made; the first one was used for the long-term measurements and the second batch to be able to get a better determination of viscosity at 4 days after preparation. One mayonnaise with pH 3.5 and 100% xanthan gum and one mayonnaise with pH 4 and 100% guar gum were made as well. The final recipe and amounts for batch 2 are shown in Table 4.
Table 4. Final recipe for the mayonnaises with ingredients in wt% and grams of each ingredient for each pH in batch 2.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>unit (wt%)</th>
<th>150 g pH 3.5</th>
<th>150 g pH 4</th>
<th>150 g pH 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>50</td>
<td>75</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>Hydrocolloid</td>
<td>0.6</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Egg yolk powder</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Sugar</td>
<td>3.5</td>
<td>5.25</td>
<td>5.25</td>
<td>5.25</td>
</tr>
<tr>
<td>Salt</td>
<td>1.3</td>
<td>1.95</td>
<td>1.95</td>
<td>1.95</td>
</tr>
<tr>
<td>Potassium sorbate</td>
<td>0.05</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
</tr>
<tr>
<td>Water</td>
<td>42.55</td>
<td>59.3</td>
<td>62.1</td>
<td>63.4</td>
</tr>
<tr>
<td>Vinegar 24%</td>
<td>4.5</td>
<td>1.7</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td><strong>TOTAL:</strong></td>
<td><strong>100</strong></td>
<td><strong>150</strong></td>
<td><strong>150</strong></td>
<td><strong>150</strong></td>
</tr>
</tbody>
</table>

4.4 Emulsion preparation
The method of preparation was based on instructions from the provided recipe and was modified to suit the equipment available. Either 200 g or 150 g (for batch 1 and batch 2, respectively) of each mayonnaise sample were prepared. The mayonnaise samples were prepared using a hand held mixer (Braun 600 W turbo) with a wire whisk attachment used at speed adjustment 9/12. Each mayonnaise was made in a three-step procedure. In the first step the water phase (water, egg yolk powder, salt, sugar and potassium sorbate) was added to a 600 mL plastic beaker and mixed together for 30 seconds. Parallel to this, the oil phase, with hydrocolloids and oil were mixed for 30 seconds in a 250 mL glass beaker to suspend the hydrocolloids. In the second step, the oil phase was gradually added to the water phase during 2 minutes and followed by 30 seconds of additional mixing. In the third step vinegar was added and mixed for 30 seconds and the pH was measured (Hanna Instruments pH meter pH 209). In the first mayonnaise made at either pH 3.5; 4 or 5, pH was measured after the addition of vinegar and water was adjusted accordingly to achieve the right proportions. When finding the right amount of vinegar to reach the desired pH, the following mayonnaises with the same pH were not measured. Instead, the vinegar was added according to the previous determination of the vinegar needed. The mayonnaise samples were transferred to bottles with a cap and stored in a refrigerator until analysis. Mayonnaises in the first batch were kept in glass bottles and the second batch kept in plastic bottles due to availability. Both batches were kept in a refrigerator.

4.5 Standardizing addition of hydrocolloids
When the mixture of oil and hydrocolloids was added to the water phase the glass beaker could not be completely emptied; almost 1 gram of the oil phase remained in the beaker. To ensure that the same amount of hydrocolloids would be added every time, 2% extra oil and 2% extra hydrocolloids were added to the oil phase. When the mixture was poured in to the water phase, the beaker weight was continuously measured so that only the exact amount of the oil phase stated in the recipe was used. This procedure was based on the assumption that the hydrocolloids were evenly suspended in the oil after having been whisked for 30 seconds.

4.6 Viscosity analysis
In Food Analysis (Nielsen, 2010), the rotational viscometer is described as the primary instrument for rheological measurement owing to its delivery of rapid and fundamental information. Rotational viscometry engages a test fixture (sometimes called spindle or bob) with a known geometrical shape that rotates in a sample. Through this rotation, the
sample is sheared by the spindle that is suspended from a torque measuring device. In this study, the rheological properties were measured with a rotational viscometer (Brookfield DV-II+ Pro Viscometer). A spindle (#64) with the shape of a concentric cylinder was used, 3,1 cm high and a diameter of 3 mm (6). The Brookfield viscometer (Figure 13) displays viscosity as 1 cP (centipoise) which equals 1 mPa·s, $10^{-3}$ Pascal seconds (26).

Due to limited access during classes at Linnæus University, mayonnaises from batch 1 were measured at separate occasions; mayonnaises with pH 5 were measured 3 days after preparation, while those with pH 4 and 3.5 at 4 days after preparation. Mayonnaises were kept at constant temperature (19 °C ± 0.6) at the time of measurement. Mayonnaises from batch 1 had to be transferred to 100 mL glass beakers when measured (5 cm diameter) because the storage bottles were too narrow to fit the measuring device. Batch 2 was measured in their storage cups (4.9 cm diameter). Viscosity in the unit cP was recorded after 15-20 seconds at each shear rate when the numbers were stabilized. For certain shear rates the viscosity value would not stabilize at any point, therefore an approximate viscosity value was recorded, roughly in the middle of the highest and lowest values that were displayed. Viscosity was measured at shear rates 0.5; 1, 2, (as well as 2.5 rpm for batch 2) 4, 5, 10, 20, 50 rpm.

4.7 Color measurement

CIE 1976 L*ab* (CIELAB) is a color scale that is designed to match human color perception and it is based on the theory that assumes that the receptors in the human eye perceive hue (object’s color) as the following pairs of opposites: a-scale: red (values>0) versus green (values<0) and b-scale: yellow (values>0) versus blue (values<0).

What is more, the CIELAB model also incorporates a L-scale that measures the lightness (luminous intensity of a color): L-scale: light (values 51-100) versus dark (values 0-50).

When the color of two objects x and y is compared, this can be expressed as:

\[
\begin{align*}
\Delta L^* &= L_x^* - L_y^* \\
\Delta a^* &= a_x^* - a_y^* \\
\Delta b^* &= b_x^* - b_y^*
\end{align*}
\]

The total difference (distance) between the object colors can be calculated as $\Delta E$ according to equation 5:

\[
\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad [Eq 5] (27)
\]
MiniScan® XE Plus HunterLab Portable Color Measurement (Figure 14) was used as the spectrally based color measurement instrument.

From each batch, a spoonful of mayonnaise, (10 g ± 0.5) was transferred to a petri dish and was measured with its lid on with MiniScan® with the petri dish placed on a black matte background. The MiniScan® was calibrated with a black metal surface and a white porcelain plate. The first measurement was made when samples had been kept refrigerated for 2 weeks. The second measurement was made when they had been kept refrigerated for 3 weeks, followed by 5 days at room temperature.

5 Results

5.1 Visual textural analysis and spoonability

All prepared mayonnaises were slightly fluffy or bubbly like an uneven mousse after a few days in its container; this was not the case for the reference, Hellmann’s Real Mayonnaise (Figure 15). However when stirred slightly with a spoon, all mayonnaises would form a smoother mayonnaise without its mousse-like consistency.

The reference mayonnaise was smooth, thick and creamy, with no signs of air bubbles. It had a short consistency, and made more of a click when dropped. The two opposites, 20X/80G and 80X/20G; with the lowest and highest amounts of xanthan gum were compared with the reference mayonnaise. The mayonnaise with a greater ratio of xanthan gum had a consistency that was slightly lumpy, not as creamy and smooth as the reference. This formulation was thinner, had a longer, runny texture, slightly slimy and oily. The reference mayonnaise would stick to the spoon leaving some mayonnaise on the spoon surface (Figure 16, 1st image) whereas the higher xanthan mayonnaise left clear oily-looking spots on the spoon while sliding off (Figure 16, 3rd image).
Out of the two, the 20X/80G was most similar to the reference mayonnaise and creamier than 80X/20G. The 20X/80G also had a longer texture though not as long as 80X/20G (Figure 16, 2nd image). There was no noticeable texture difference between pH 3.5, 4 and 5, the differences were mostly seen between different hydrocolloid blends.

Figure 16. Turning a spoonful of mayonnaise samples to the side, slightly shaking it to make it come off the spoon. From left to right: reference mayonnaise, 20% xanthan gum 80% guar gum, and 80% xanthan gum 20% guar gum.

5.2 Rheological flow behavior

All mayonnaises showed shear thinning flow behavior. The flow curves displayed in figure 17 at interval 0.5-5 rpm (left) and 0.5-50 rpm (right) show that the different mayonnaises clearly have different viscosities at lower shear rates and similar viscosity at the higher shear rate 50 rpm.

Figure 17. Flow curves for mayonnaises with pH 3.5 at lower shear rates to the left, and all shear rates including 50 rpm to the right.

The reference Hellmann’s Real mayonnaise showed very prominent thixotropy (Figure 18). Practically half the viscosity was lost at 0.5 rpm after having stirred at 50 rpm and gradually lowered the shear rate back to 0.5 rpm again. There was no significant thixotropy in any of the prepared mayonnaises.
5.3 Viscosity at lower shear rates

All mayonnaises were measured to compare viscosity at lower shear rates, including the reference mayonnaise and the two mayonnaises with 100% guar gum and 100% xanthan gum. Because the viscosity at lower shear rates is of relevance for the consumer experience (J.Ekvall, personal communication, May, 2016), a model for comparing viscosities in this range was created. The three values of viscosity $\eta$ (converted to unit Pa·s) at the lowest shear rates 0.5; 1 and 2 rpm were summed up creating a reference number to compare the viscosities. The higher the number, the greater is the viscosity at lower shear rates. Each reference number received a color in a Table 5, the highest number was colored black, the lowest number white, and different shades of gray in between. The higher the reference number, the darker color. The lower table “Average” shows that the viscosity generally increases with the increasing ratio of guar gum, the only discrepancy appears between 35X/65G and 50X/50G in pH 5. The most prominent synergy, i.e. the highest initial viscosity, can be seen at 80% guar gum and 20% xanthan gum.

Table 5. Result from batch 1, 2 and their combined averages (Pa·s) as the sum of the viscosity at the shear rate 0.5; 1 and 2 rpm. Darker color represents higher initial viscosity.

<table>
<thead>
<tr>
<th>Batch 1</th>
<th>20 X/ 80 G</th>
<th>35 X/ 65 G</th>
<th>50 X/ 50 G</th>
<th>65 X/35 G</th>
<th>80 X/20 G</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 3.5</td>
<td>759</td>
<td>871</td>
<td>701</td>
<td>623</td>
<td>511</td>
</tr>
<tr>
<td>pH 4</td>
<td>790</td>
<td>785</td>
<td>666</td>
<td>744</td>
<td>640</td>
</tr>
<tr>
<td>pH 5</td>
<td>655</td>
<td>657</td>
<td>641</td>
<td>636</td>
<td>567</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Batch 2</th>
<th>20 X/ 80 G</th>
<th>35 X/ 65 G</th>
<th>50 X/ 50 G</th>
<th>65 X/35 G</th>
<th>80 X/20 G</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 3.5</td>
<td>949</td>
<td>614</td>
<td>737</td>
<td>626</td>
<td>659</td>
</tr>
<tr>
<td>pH 4</td>
<td>930</td>
<td>848</td>
<td>733</td>
<td>639</td>
<td>645</td>
</tr>
<tr>
<td>pH 5</td>
<td>879</td>
<td>750</td>
<td>808</td>
<td>742</td>
<td>595</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Average</th>
<th>20 X/ 80 G</th>
<th>35 X/ 65 G</th>
<th>50 X/ 50 G</th>
<th>65 X/35 G</th>
<th>80 X/20 G</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 3.5</td>
<td>854</td>
<td>742,5</td>
<td>719</td>
<td>624,5</td>
<td>585</td>
</tr>
<tr>
<td>pH 4</td>
<td>860</td>
<td>817</td>
<td>699,5</td>
<td>691,5</td>
<td>642,5</td>
</tr>
<tr>
<td>pH 5</td>
<td>767</td>
<td>703,5</td>
<td>724,5</td>
<td>689</td>
<td>581</td>
</tr>
</tbody>
</table>

The reference Hellmann’s Real mayonnaise with 78% fat produced a higher viscosity than all other mayonnaises. Looking at the viscosity of 100% xanthan gum and 100% guar gum respectively in Table 6 compared to mixtures in Table 5, the synergy between the two leading to a viscosity increase is observable in almost every mayonnaise. Although the total amount of hydrocolloid added is the same, the two combined will produce a greater viscosity than each hydrocolloid added alone. Though guar gum alone
produces the lowest viscosity out of all mayonnaises measured, a higher proportion guar gum in combination with xanthan gum, led to higher viscosity.

Table 6. The viscosity, expressed as the sum of the viscosity at shear rate 0.5; 1 and 2 rpm in reference mayonnaise, 100% xanthan gum and 100% guar gum with pH 4.

<table>
<thead>
<tr>
<th></th>
<th>Real Mayo</th>
<th>100% X</th>
<th>100% G</th>
</tr>
</thead>
<tbody>
<tr>
<td>viscosity</td>
<td>1110</td>
<td>581</td>
<td>368</td>
</tr>
</tbody>
</table>

5.4 Viscosity change at different stages

As an additional analysis, the viscosity of four mayonnaises was also measured 2 weeks and 6 weeks after initial preparation. These mayonnaises were 50X/50G at all three pH’s and 20X/80G at pH 4. Longitudinal viscosity measurements of 100% xanthan gum and 100% guar gum were also conducted. When comparing these mayonnaises, both the viscosity coefficient K and the sum of the viscosities at shear rate 0.5; 1 and 2 rpm were used as the measure of viscosity (Figure 19). In every mayonnaise measured 2 weeks after preparation the viscosity increased compared to the viscosity 4 days after preparation, and the viscosity decreased another 2 weeks later. After 6 weeks, also depending of the method of comparison, viscosity would either increase or decrease slightly. When comparing η, all samples showed a viscosity decrease from week 4 to week 6. The mayonnaise with 100% xanthan gum and pH 3.5 lost some viscosity after 6 weeks, while 100% guar gum and pH 4 increased its viscosity after 4 weeks. The 20X/80G showed only a small change throughout the period. There does not seem to be any correlation between a higher acidity and greater loss of viscosity within the 50/50 series.

5.5 Final viscosity change after 4 weeks

The viscosity of the mayonnaises measured at 3 days (for pH 5) and 4 days (for pH 3.5 and 4) after preparation and finally 4 weeks after preparation were converted into the viscosity coefficient (K) using the Power law and the viscosity comparison values (η) with the sum of the three lowest shear rates (0.5; 1 and 2 rpm). The changes in viscosity expressed in percent (viscosity after 4 weeks divided by the first measurement) for both comparison methods (K and η respectively) and for each mayonnaise are listed in table 7. The average % change within each pH and within each blend of xanthan and guar gum are also included and numbers are colored the same way as Table 5. Here, the
greatest viscosity loss was colored black, the lowest number white, and different shades of gray in between. A darker color represents a greater viscosity loss in percent, only shown in the average value columns. A vague pattern can be seen: there seem to be a greater viscosity loss with increasing ratio of guar gum and also with increasing pH.

Table 7. Viscosity change expressed in percent in each mayonnaise between 4 days and 4 weeks after preparation. The average percent change in expressed in K and η within each pH and within each blend of xanthan and guar gum. The greater the average viscosity loss, the darker the color.

<table>
<thead>
<tr>
<th>pH</th>
<th>20X/80G</th>
<th>35X/65G</th>
<th>50X/50G</th>
<th>65X/35G</th>
<th>80X/20G</th>
<th>Average percent change within each pH (K)</th>
<th>Average percent change within each pH (η)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 3.5</td>
<td>K</td>
<td>-7</td>
<td>-11</td>
<td>5</td>
<td>13</td>
<td>5,6</td>
<td>-0,4</td>
</tr>
<tr>
<td></td>
<td>η (0.5×1+2)</td>
<td>-2</td>
<td>-2</td>
<td>3</td>
<td>5</td>
<td>3,8</td>
<td>1,8</td>
</tr>
<tr>
<td>pH 4</td>
<td>K</td>
<td>-2</td>
<td>3</td>
<td>8</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>η (0.5×1+2)</td>
<td>-2</td>
<td>3</td>
<td>8</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 5</td>
<td>K</td>
<td>-10</td>
<td>-4</td>
<td>-2</td>
<td>-6</td>
<td>-9,2</td>
<td>-10</td>
</tr>
<tr>
<td></td>
<td>η (0.5×1+2)</td>
<td>-10</td>
<td>-4</td>
<td>-2</td>
<td>-6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Using the CIELAB model, the total differences between the mayonnaise colors are shown in Figure 21. Comparing pH 4 and 5, changes are slightly smaller with higher ratios of xanthan gum.

5.6 Color change
After 3 weeks in refrigerator and 5 days at room temperature in a petri dish, mayonnaises were measured with the MiniScan®, four of them were photographed (Figure 20). Mayonnaises with pH below 4 visibly turned more yellow with a translucent gel like texture filled with observable air bubbles.

Figure 20. Appearance of mayonnaises after 3 weeks refrigerated storage followed by 5 days in room temperature. Upper row from left to right: reference mayonnaise pH 3.7 and 80X/20G in pH 3.5. Lower row: 80X/20G at pH 4 and 5. Mayonnaises with pH below 4 turned yellow with a translucent gel like texture filled with visible air bubbles.
6 Discussion

6.1 Visual textural analysis and spoonability
None of the mayonnaises had a texture that was identical to the reference mayonnaise although the 20X/80G was the most similar and the least “slimy”. At time of writing, xanthan gum prices are roughly twice as high as that of guar gum (J.Ekvall, personal communication, May, 2016). As previously mentioned, seed gum prices are more sensitive to climatic variations, and if guar gum prices were to increase beyond xanthan gum prices, the question is whether a mayonnaise recipe could be modified to provide a less expensive product. With increasing ratio of xanthan gum the texture moves further away from the reference. Using more xanthan gum would both lower the viscosity (thus requiring more hydrocolloids to compensate for the loss) and add undesirable rheological properties to the product, which would become lumpier, slimy and less creamy. However, 0.6 wt% hydrocolloids is a large amount and significantly higher than what is usually added in mayonnaises. By using less hydrocolloids and more oil, the undesired properties caused by the hydrocolloids would be less prominent, if even noticed at all. It is important to point out that the aim of this project was not to create an ideal mayonnaise, but to explore the effects of hydrocolloids in a mayonnaise and how high acidity would affect them. These effects are usually more noticeable in a lower-fat application. Possible recipe modifications are probably best investigated in the actual type of mayonnaise to be modified.

6.2 Rheological flow behavior
As suspected, all mayonnaises showed a shear thinning flow, though the thixotropy was not very prominent. The reference mayonnaise on the other hand showed strong thixotropy. This feature is probably something a consumer would not notice; these results mainly show that this is one of the rheological differences between mayonnaise with and without hydrocolloids.

6.3 Viscosity at lower shear rates
In accordance with literature (2), the viscosity will increase with increasing ratio guar gum in a guar-xanthan blend. With 0.6% hydrocolloids in a 50% fat mayonnaise with 20% xanthan gum and 80% guar gum, viscosity will be reasonably close to a 78% fat reference mayonnaise. Increasing the amount of hydrocolloids could likely produce equally high viscosity, however that would most likely also increase the flow properties.
characteristic to these hydrocolloids which are not always desirable since they differ from traditional mayonnaise.

6.4 Viscosity change at different stages

Interestingly, the formulation with 100% guar gum highlights one important difference between the two methods that were used to characterize the viscosity: the viscosity coefficient (K) and the viscosity comparison values (η). When expressing viscosity in “K”, guar gum seems to have a higher viscosity than most samples at 4 weeks. Just by looking at the actual mayonnaise sample it is obvious this is not the case, because the 100% guar gum sample had the consistency of a pourable dressing, which is not the case for all other samples that were thicker. Because the coefficient K represents the viscosity of the sample, it takes into account the viscosity at the highest shear rates as well, and since guar gum is not as shear thinning as xanthan gum, it gets a higher overall viscosity (K). When comparing η at the lowest shear rates on the other hand, it is obvious the 100% guar gum is less viscous, however the variations from measurement at 6 weeks and one day later are greater using this method. Here, only three values are taken into account whereas when comparing “K” at least eight values are used. The method to compare the sum of the η-values at lower shear rates is not an established method and considered to be a complement to the more established measurement of coefficient K.

The findings from measurements at different stages were not completely in accordance with theory. Xanthan gum is supposed to be stable in acidic environments as low as pH 2.5. Still, its viscosity had decreased in pH 3.5 while guar gum is said to be very sensitive to high acidity yet its viscosity increased after 4 weeks in pH 4. Overall there seems to be slight viscosity losses in most samples, roughly linear decreases. The unpredicted variations of 50X/50G at pH 3.5 could possibly be due to its low pH. Mayonnaise samples in the petri dishes revealed that mayonnaises with a pH below 4 underwent a major emulsion break, turning into a yellow gel. Because mayonnaise is an emulsion that is not a thermodynamically stable system, the viscosity is not only dependent on the hydrocolloids ability to stabilize the water phase, but also the stability of the emulsion itself. Hydrocolloids can help to stabilize an emulsion but emulsion breaking may affect the viscosity more than the degradation of the hydrocolloids.

Though it was only 6 weeks between preparation and the last measurements, there is a noticeable trend in mayonnaises with a combination of guar gum and xanthan gum; viscosity start decreasing after around 2 weeks, regardless of pH, but to what extent this decline will continue after long term storage cannot be answered based on these results. As the average mayonnaise could be consumed several months after manufacturing, an experiment like this should preferably be conducted during at least that time frame to fully see to what extent the high acidity in a low-fat mayonnaise affects the viscosity.

6.5 Final viscosity change after 4 weeks

There was no clear pattern in the change in viscosity between different levels of acidity although there was a vague pattern where viscosity seemed to decrease more at higher pH. The obtained results are not coherent with theory, as lower pH would be expected to have a greater effect on hydrocolloid breakdown and mayonnaise viscosity, this can not be seen with these measurements. It seems like the low pH strongly affected the emulsion causing both color and consistency to change. However, these results are not entirely relevant. “Viscosity at different stages” shows that viscosity will keep increasing from 4 days to 2 weeks after preparation and these results solely compare the
viscosity after 4 days and 4 weeks. This means the viscosity might have increased during this period reaching peak viscosity, which would be a better initial value for measuring viscosity decrease. It is possible that the hydrocolloids require around two weeks to build up the maximal viscosity in the mayonnaise, this could be a reason why some hydrocolloids seem to retain their viscosity even after 4 weeks in an acidic environment. This is possibly due to a great viscosity increase during the first couple of weeks and a decrease that just about reached the initial viscosity 4 weeks after preparation. This phenomenon was not known when choosing measurement occasions. Consequently, these results cannot fully explain how much of the maximal viscosity was lost due to high acidity. There is one tendency to be seen however: the higher ratio of guar gum, the greater viscosity decrease. This is in accordance with the theory; guar gum is more sensitive to high acidity than xanthan gum, therefore it would be expected that the viscosity decreases more rapidly in a mayonnaise that contains more guar gum.

6.6 Color change
The color change measurements aimed to compare emulsion stability of the mayonnaises. In an unstable emulsion, the color is suspected to change. The mayonnaises with pH 3,5 and even the reference mayonnaise with pH 3,7 turned into a translucent yellow gel. This is not ideal for the color measurement because the black background will affect the measurements; which is one reasons the pH 3,5 seems to have changed dramatically, and it is obvious, just by looking at Figure 20, that these emulsions have changed. The high acidity might not only have affected the hydrocolloids but also denatured the egg yolk. It is difficult to compare the ability of the hydrocolloids to stabilize the emulsion when the emulsions broke at that low pH.

6.7 Mayonnaise preparation
The tool for preparing the mayonnaises was not ideal for this purpose. With the hand held mixer used, the time for mixing was not exactly the same for each mayonnaise. Furthermore different angles and hand movements during mixing could affect the formation of oil droplets and the droplet size, which consequently will affect mayonnaise properties. Utilizing adequate equipment equivalent to the actual equipment used when producing mayonnaise would ensure more reliable results. A high speed shear mixer is normally used, and is even a requirement for some hydrocolloids and applications.

6.8 Measurement uncertainties
Whether the mayonnaises have the exact right pH (3,5; 4 or 5) is not certain because of difficulties measuring pH in an emulsion. What is certain though is that 0,4, 1,7 and 4,5 g of vinegar was added respectively according to the intended pH. It is easier to measure pH in a clear homogenous solution than in an emulsion since the latter is an unstable two phase system.

The original plan was to make two viscosity measurements at each shear rate in each mayonnaise formulation and use the average values of the viscosity measurements to construct the flow curves. However, as the measurements took a long time to perform and the mayonnaise samples would gain viscosity each day of storage, this was not a feasible procedure. Consequently, only one viscosity measurement of each shear rate was performed in each mayonnaise formulation. As the flow curves were based on these data, the results are less reliable than if the viscosity values were calculated as an average of two or more measurements.
Another uncertainty is the weighing of xanthan gum and guar gum powder. The smallest amount weighed was for the 20/80 blends, which was as low as 0.184 g and 0.734 g each for a 150 g mayonnaise. Therefore, a small error in weighing could alter the proportions considerably and thus have a great impact on the viscosity. Making a larger batch would reduce the error margins but on the down side this would also produce large amounts of excess mayonnaise. In one study of mayonnaise they made each mayonnaise 800 gram, as an example (4).

The values obtained from the Brookfield DV-II+ Pro viscometer may have some uncertainties. The viscometer relied on manual reading and in some mayonnaises the viscosity value on the instrument display would vary or “jump”, not stabilizing at any point, making it difficult to decipher the correct value. Including higher shear rates as well, like 100 rpm, could have improved the obtained data.

7 Conclusions

Mayonnaises with a mixture of 20% xanthan gum and 80% guar gum had the highest viscosity at low shear rates regardless of pH at 4 days after preparation. Measurements on selected mayonnaises 2 weeks after preparation revealed that viscosity continues to increase, generally followed by a decrease 4 and 6 weeks after preparation.

Out of all the formulated mayonnaises with a fat content of 50%, there is no proportion of the 0,6% added hydrocolloids that will create a mayonnaise with a visual texture exactly like the reference mayonnaise with 78% fat although 20X/80G was the mayonnaise most similar to the reference.

One aim of this project was to determine whether a mayonnaise recipe could be modified depending on guar gum and xanthan gum prices to achieve a viscous yet cost efficient product. Because there is an evident relationship between viscosity and increasing amounts of guar gum combined with xanthan gum, this is possible in theory. However, changing the proportions could significantly alter the texture in undesired ways, especially in low-fat applications with larger amounts of added hydrocolloids such as the mayonnaises prepared in this project. This does not necessarily apply for mayonnaises with a higher fat content and lower hydrocolloid content where hydrocolloids will be less prominent.

Four weeks was not enough time to be able to confidently conclude how low-fat mayonnaises with varying hydrocolloid composition would be affected by acidity levels, although there seem to be a somewhat greater viscosity loss in mayonnaises with increasing ratio of guar gum – as suspected. Because a commercial mayonnaise sometimes is consumed several months after manufacturing, an experiment like this would preferably be conducted during at least that time frame to fully see how much the high acidity in mayonnaise will affect its viscosity. Preparing larger mayonnaise samples and using a high-speed mixer followed by more frequent measurements throughout a longer period are factors that could provide more valid results. This project has shown a pattern where viscosity in the assessed mayonnaises starts to decrease a few weeks after preparation. However to find out exactly to what extent and how this would affect the overall product, and ultimately: if guar gum/xanthan gum combinations are suitable for long-term mayonnaise applications further studies are required.
8 References


