**Master's Thesis of Science
in Agricultural Biotechnology**

Gastrointestinal and rheological properties of emulsion-filled starch gels

전분 에멀션 젤의 장내 소화 및 물성학적 특징

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Advisor: Choi, Young Jin

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February, 2021

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ABSTRACT

Emulsion-filled gel is a system that collects emulsion in hydrogel, and has both high stability, which is an advantage of hydrogel, and fat-soluble material transportability, which is an advantage of emulsion. In this study, the emulsion-filled gel was stabilized by using modified corn starch, which can act as emulsifier and gelide at the same time, and the physical and storage stability and intestinal digestion characteristics of this emulsion gel were analyzed. The modified corn starch was manufactured through the reflux process of octhenyl succinic acid for the emulsification of corn starch and the sedimentation and freezing drying process, and the heat treatment process was used to act as a gelling agent. When the modified starch was used less 3 wt%, the water's interfacial surface was stabilized by starch, and if more than 4 wt% were used, emulsion gel, in which oil drops were collected in gel, was manufactured. The higher the concentration of replaced starch and oil, the higher the storage modulus and loss modulus, and the storage modulus of emulsion gel reached about 10,000 Pa when the maximum of 8 wt% starch was used. Experiments in quantifying free fatty acids released by emulsion gel in the *in vitro* small intestinal environment confirmed that the higher the concentration of starch created a more rigid network structure, the lower the initial digestion rate of the oil inside the emulsion gel and the 150-minute

digestion rate (78% with 3 wt% starch; 70% with 8 wt% starch). In addition, after stored at room temperature for 60 days, it was observed that oil particles were dispersed without causing layer separation, and confirmed that they formed a stable emulsion. In summary, these results suggest that emulsion-filled gel developed in this study can be used as a carrier with both the properties of emulsion and hydrogel, so this study could serve as a basis for the study of developing gel-type carriers using health functional substances.

Keyword : Emulsion-filled gels, OSA-starch, hydrogel, emulsion rheology, *in vitro* gastrointestinal digestion

I. INTRODUCTION

Oil-in-water emulsions have been widely utilized in various domains such as food, cosmetics, and pharmaceutical industries as a proper carrier system to transport hydrophobic components (McClements, 2007, 2015). However, conventional emulsion systems are thermodynamically unstable so water and oil phases are easily separated through various physicochemical mechanisms; including flocculation, creaming, Ostwald ripening and coalescence (McClements, 2014). The stability of emulsions can be enhanced by confining oil droplets in a gelled continuous phase which has three-dimensional network. Formation of hydrogel network interrupts the movement of oil droplets, thus preventing creaming, coalescnece and flocculation of emulsions. Such emulsion systems, fabricated with the advantage of hydrogels, are named ʽemulsion gelʼ or ʽemulsion-filled-gelsʼ (Torres, Murray & Sarkar, 2016; Mun et al., 2015). In food industry, emulsion-filled gel is a desirable feature in manufacturing food products because it can stabilize food texture and can be used as a carrier of lipophilic nutraceuticals (Komaiko & McClements, 2015). Hence, it is important to design such

emulsion-filled gels using biopolymers, such as starch, which is the second most abundant biopolymer in nature.

In food industry, gum, starch and protein can be used to form emulsion-filled gels to make continuous phase to gel. Especially, whey protein isolate has been researched for producing emulsion gel systems due to their characteristics both as an emulsifier and a gelling agent (Khalesi et al., 2019; Dickinson, 2012; Sala et al., 2007; Chen & Dickinson, 1999; Boutin et al., 2007). Native starch is also widely used in commercial applications and its versatility as a gelling agent is well recognized (Teyssandier, Cassahnau, Gerard, & Mignard, 2011; Zhang et al., 2013). On the other hand, the use of starch in emulsion-filled gel has relatively little study because of the properties of starch. Starch is water soluble, but the amount of starch that can be dispersed in the water is limited depending on the water amount. Moreover, starch cannot work as emulsifier because it doesn't have the characteristics of hydrophobicity. However, as the drastic changes in the microstructure and viscoelastic properties of starch gels can be generated by shearing during gelatinization, emulsion-filled gels with starch are needed to be researched more.

Starch, one of the most important ingredients in foods, can be used as an emulsion stabilizer when it is modified with octenyl succinic anhydride (OSA),

so, fabrication of emulsion-filled gel system applying starch as emulsifier and gelling agent can be considered. In oil-in-water emulsion system, emulsion stabilizer is required both hydrophobicity and hydrophilicity to stabilize oil and water interface (Fonseca, 2018). Starches have hydrophilic characteristics because these are composed of α-(1→4) linear and β-(1→6) branched glycosidic bonds. Therefore, to use starches are emulsifier, starches can be modified with octenyl succinic anhydride (OSA) by esterification under alkaline condition to provide some degree of hydrophobicity. OSA-modification is widely applied to use starch as an emulsifier (Baydoun, Furrer, Gurny, & Muller-Goymann, 2004; Viswanthan, 1999; Prochaska et al., 2007)

Emulsion filled gel can be produced by two steps; embedding an emulsion into a gelled continuous phase or a pre-gel solution, followed by gelation (Farjami et al., 2019). Emulsions with Sunflower oil stabilized by OSA starch were incorporated into native starch gels (Torres et al., 2017). In contrast, emulsions stabilized by other emulsifiers were added into whey protein isolate, gum or gelatin solutions and gelation was induced (Rosa et al., 2016). In order to increase the utilization and efficiency of the conventional process, including the two steps, a new method fabrication is required.

The rheological properties of emulsion are decided by the concentration of gelling agent and the property of oil droplets (Chen & Dickinson, 1998;

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Dickinson, 2012; Richardson, Robinson, Ross-Murphy, & Todd, 1981; van Vliet, 1988). Polysaccharide, which stabilizes and gelled emulsions, increases the viscosity of aqueous and give different rheological properties. So polysaccharides have been used to control the rheology of emulsions according to the purpose of emulsion. Soft solid systems containing dispersed oil particles (fillers) have different gel strength with the contribution of the filler particles. According to their contribution to continuous gel network rheology, fillers can be classified as either ʽactiveʼ or ʽinactiveʼ filler (Ring & Stainsby, 1982; Rosa, Sala, van Vliet, & van de Velde, 2006). When the particles have a strong interaction with the gel network, they increased gel strength of emulsion-filled gel and these fillers are called ʽactive fillerʼ. In contrast, an inactive filler does not contribute to the strength of gel network because it has little chemical affinity for the polymer of the continuous phase.

In general, oil-in-water emulsion can improve the absorption of poorly water soluble netraceuticals in dispersed form (Porter, Trevaskis, & Charman, 2007). However, too rapid digestion of the emulsions by enzymes in the intestines decreases netraceutical-solubilizing ability, resulting in a reduction of bioavailability (Porter, Kaukonen Boyd, Edwards, & Charman, 2004). Therefore, control of the lipid digestion rate in the human tract is important and recently, the digestion of oil droplets imbedded in a solid-like or solid

matrix has received attention. The impact of the different biopolymer networks on lipid digestion was investigated in the system of emulsion-filled gels by incorporating caseinate/monoglyceride stabilized emulsion into a gelatin network, casein network and starch dispersion (Wooster et al., 2014; Golding et al., 2011). Since lipolysis occurs at the surface of lipid droplets, the accessibility of the oil-water interface can be reduced in the emulsion-filled gels because the oil droplets are embedded in a three-dimensional network (Corstens, 2017). Therefore, tuning the structural and rheological properties of emulsion matrices provides a potential way to control the release of oil and lipid digestion (Qing Guo et al., 2016).

The conventional processes of preparing emulsion-filled gels require an emulsification step and a second step of making aqueous phase into gels, and emulsifiers and gelling agents are required at each step. In this study, I fabricated emulsion-filled gels stabilized by maize starch modified with octenyl succinic anhydride (MS) in the absence of additional emulsifiers or gelling agents to simplify this complex process. I observed rheological and texture properties of emulsion-filled gels depending on the concentration of MS. The effects of the matrix structure on the lipolysis and digestion of lipid was investigated to see the probability of application as controlled lipolysis system in the GI trac

II. MATERIAL AND METHODS

2.1. Materials

Maize starch was provided by Roquette S. A. (Lesterm, France). Nile red, OSA, dimethylsulfoxide, α-amylase, pancreatin, pepsin, invertase from bakers' yeast, bile extract and amyloglucosidase were purchased from Sigma Aldrich Co. (St. Louis, MO, USA). All other chemicals were of analytical reagent grade.

2.2. Maize starch modified with octenyl succinic anhydride (MS) preparation

Maize starch (48g) was dispersed in 1600 mL of double-distilled water (DDW). After the pH of the paste was adjusted to 7.5−8.5 with 0.5 M NaOH, 7.2 mL of OSA solution (0.2 g mL^{-1} in ethanol) were added slowly for 3 h. The reaction between maize starch and OSA was facilitated by stirring for 3 h at pH 8.0-9.0, which was achieved by adding 0.5 M NaOH. Next, the pH of the suspension was adjusted to 6.5 using 0.5 M sulfuric acid. The mixture was centrifuged (Supra22K, Hanil Science Industrial Co., Ltd., Incheon, Korea) at 4500 relative centrifugal force (RCF) for 40 min, and the precipitate was

washed twice with DDW and lyophilized using as FD5508 freeze-dryer (IlShinBioBase Co. Ltd., Yangju, Korea). After being dried and powdered, the precipitate was used as MS.

2.3. Determination of degree of substitution (DS)

The DS of MS was determined using the pre-reported method (Ren et al., 2016), with slight modification. 0.2 g of dried MS was dispersed in 10 mL of dimethylsulfoxide by heating (50°C, 20 min). After cooling to 25°C, 4−6 drops of phenolphthalein indicator were added to the solution, which was titrated with 0.05 M NaOH until a permanent pale pink color was observed. The DS was calculated by the following equation (Ren et al., 2016):

$$DS = \frac{162 \times V \times M}{1000\ W - 266 \times V \times M}$$

where, V is the volume of 0.05 M NaOH used for titration, M is the molarity of NaOH solution (0.05 M), and W is the weight of MS (0.2 g).

2.4. Fourier transform infrared spectroscopy measurement

Maize starch, OSA modified maize starch (MS), emulsion emulsified with maize starch and emulsion emulsified with MS were investigated using

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a Fourier transform-infrared spectrophotometer (Nicolet 6700, Thermo Fisher Scientific, Waltham, MA, USA) at 25°C to verify esterification between the starch hydroxyl groups and OSA molecules. For each sample, at least 32 scans were performed from 650 to 4,000 cm^{-1} at 8 cm^{-1} resolution.

2.5. Preparation of oil-in-water emulsion-filled gels stabilized by MS

Oil-in-water emulsion gels were prepared at 25°C by mixing 20 wt% canola oil with an aqueous phase containing 3−8 wt% MS and 0.02% w/v sodium azide, using a high-shear blender (Ultra-Turrax T25D; Ika Werke GmbH & Co., Staufen, Germany) at 10,000 rpm for 2 min at ambient temperature. Then the droplet size was further reduced and matrix was gelled by a probe-type sonicator (VCX 750, Sonics & Materials Inc., Newtown, CT, USA) for 10 min at amplitude of 60%, duty cycle of 1s. To gelatinize the MS, the sonication treatment was conducted in a jacketed beaker at 68°C.

2.6. Rheological characterization

The rheological properties of the emulsions were measure at 20°C using a rotational rheometer (Rheostress RS 1; HAAKE Instruments, Karlsruhe,

Germany) equipped with a probe of plate-and-plate geometry (diameter, 20 mm; gap, 7 mm). The size of the emulsion-filled gel was 2.0 cm × 7.0 mm (diameter × height). Prior to measurement, the sample was left at ambient temperature for 1 h to equilibrate to the test temperature. For dynamic shear measurement, oscillation frequency sweep tests were conducted at frequencies (ω) ranging from 0.1 to 10.0 rad s^{-1}; and a constant value of τ (1.0 Pa) was applied to maintain the linear viscoelasticity of the emulsions during the test. The storage modulus (G'), loss modulus (G''), and tan δ (G''/G') were obtained as a function of ω.

2.7. Instrumental texture profile analysis (two-cycle compression test)

The size of the emulsion-filled gel was 2.5 cm × 7.0 mm (diameter × height). TPA was carried out using a CT3 10K texture analyzer (Brookfield, USA), attached with a 10-kg load cell. A 50.8 mm diameter cylinder probe was used to compress the sample, which were compressed twice to 50% deformation at a compression rate of 2.0 mm s^{-1} at ambient temperature. Hardness, cohesiveness, adhesiveness, springiness, resilience, gumminess and chewiness were calculated in the report of each sample by the software provided along with the instrument.

2.8. Determination of the in vitro digestion patterns of the emulsions

The simulated in vitro digestion test model was slightly modified from a previously described (Ban, Park, Lim, Choi, & Choi, 2015), as follows:

I. Sample preparation: emulsion-filled gels with 3 and 8 wt% MS were prepared. The emulsion-filled gel with 8 wt% MS was cut into 0.4 mm to simulate oral bite and to make similar size of human gel boluses (Guo et al., 2013).

II. Mouth (pH 7; 5 min): 5 g of the emulsion-filled gel was blended with 6 mL of simulated salivary medium.

III. Stomach (pH 2; 2 h): 12 mL of simulated gastric juice was added to the digesta.

2.9. Monitoring lipolysis of the emulsions in vitro in simulated small intestinal fluid

In vitro small intestinal lipolysis of the emulsion-filled gel was monitored using titration method with slight modification. *In vitro* digestion test was carried from the stomach steps. After the stomach digestion, 23 mL of the chyme was adjusted to 50 mL with 10mM sodium phosphate buffer (pH 7 at

37°C) and the solution was neutralized to pH 7 with 2.5 M NaOH. Finally, the hydrolysis of the emulsion-filled gel digesta (25 mL) was monitored by measuring the amount of 0.05 M NaOH used to neutralize the solution after the addition of simulated small intestinal fluid (8 mL) using automatic titration unit (842 Titrando; Metrohm AG, Herisau, Switzerland) based on the lipase-induced hydrolysis of one triacylglycerol into one monoacylglycerol and two free fatty acid (FFAs). The simulated fluid was prepared by dissolving NaCl, $CaCl_2$, bile extract, invertase, α-amylase, amyloglucosidase and pancreatic lipase in 10 mM sodium phosphate buffer (pH 7 at 37°C) at concentrations of 43.75, 11.25, 100, 1.875, 5, 1.25, and 12.5 mg mL^{-1}, and was adjusted to pH 7 at 37°C using 2.5 M NaOH solution. The amount of FFAs released was calculated in to %FFA value using the following equation:

$$\%FFA = 100 \times \frac{\left(V_{NaOH} \times m_{NaOH} \times M_{Canola\,oil} \right)}{\left(W_{Canola\,Oil} \times 2 \right)}$$

where V_{NaOH} is the volume (L) of the NaOH solution used to neutralize the FFAs, m_{NaOH} is the molarity (0.05 mol L^{-1}) of the NaOH solution, $M_{canola\,oil}$ is the molecular weight (876.6 g mol^{-1}) of canola oil, and $W_{canola\,oil}$ is the total weight (0.5 g) of canola oil the was present in the initial reaction vessel. Blank experiments were also conducted with the starch gels formed with 3 and 8 wt%

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MS to revise the effect of starch digestion to the pH change. To compare the extent of lipolysis, the areas under the %FFA curves (AUG_{150min}) in the emulsion-filled gel system were calculated using the following equation:

$$k = 13012 \times \%FFA_{k-1} + \%FFA_k \times \Delta t$$

where k is the unit for the module divided after every 5 min of the total reaction time (150 min) and Δt is the time gal between modules (5 min).

2.10. Microscopic observation

The microstructures of emulsion-filled gels stored for 1 or 30 day at 20°C were observed using a confocal laser scanning microscope (CLSM) (TCS SP8 X; Leica, Mannheim, Germany). Canola oils was dyed with Nile red. A 633 nm laser was used to excite Nile red. A drop of the emulsion-filled gels was placed on a slide glass, covered with a coverslip.

2.11. Determination of the storage stability

To evaluate the stability of the emulsion-filled gels at ambient temperature, vials containing the emulsion-filled gels were stored in a chamber at 20°C for 60 days.

2.12. Statistical analysis

Rheological properties and gastrointestinal digestion patterns of emulsion-filled gels were analyzed by Sigmaplot 10.0 (Systat Software, San Jose, CA, USA). These experiments were conducted triplicate.

III. RESULTS AND DISCUSSION

3.1. Infrared spectra of MS

The infrared spectra of MS and maize starch without OSA-modification showed that the esterification between maize starch and OSA was successfully carried out (Fig. 1 and 2). Furthermore, the infrared spectra of emulsion with MS and maize starch without OSA-modification implied that the esterification was maintained during emulsion-filled gel preparation. In the MS and the emulsion with MS spectrum, bands at $1570\ cm^{-1}$ was additionally revealed that was not existed in the non OSA-modification spectrum. The band at $1570\ cm^{-1}$ indicated the existence of carboxylate RCOO- and it means that OSA was added onto hydroxyl group of starch (Fonseca-Florido, 2018). OSA-modification gave hydrophobic characteristics on the maize starch and MS could have amphiphilic characteristics to stabilize oil and water interfaces as emulsifiers.
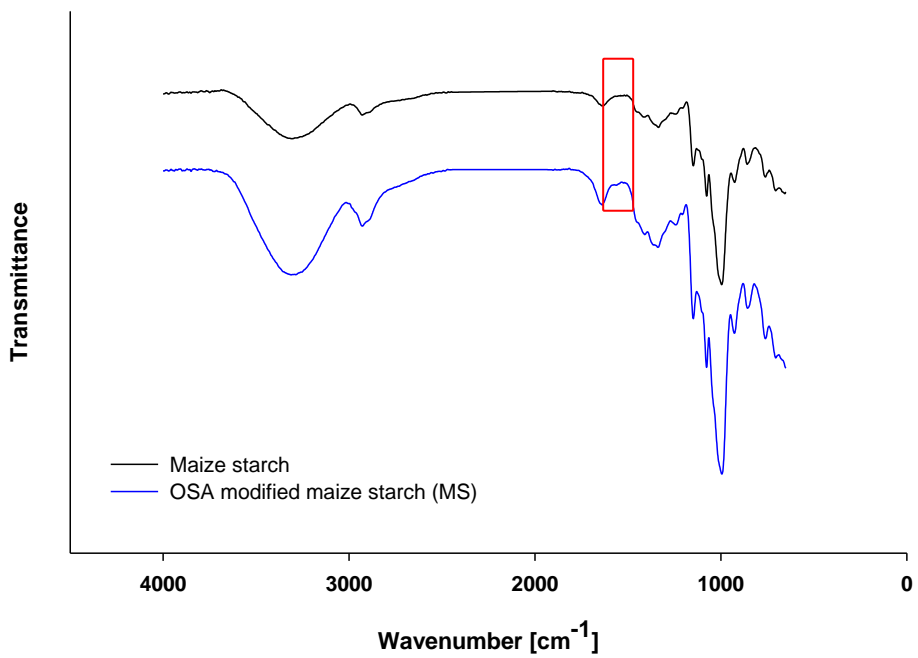
Figure 1. Infrared spectra of natural maize starch and OSA modified maize starch (MS).
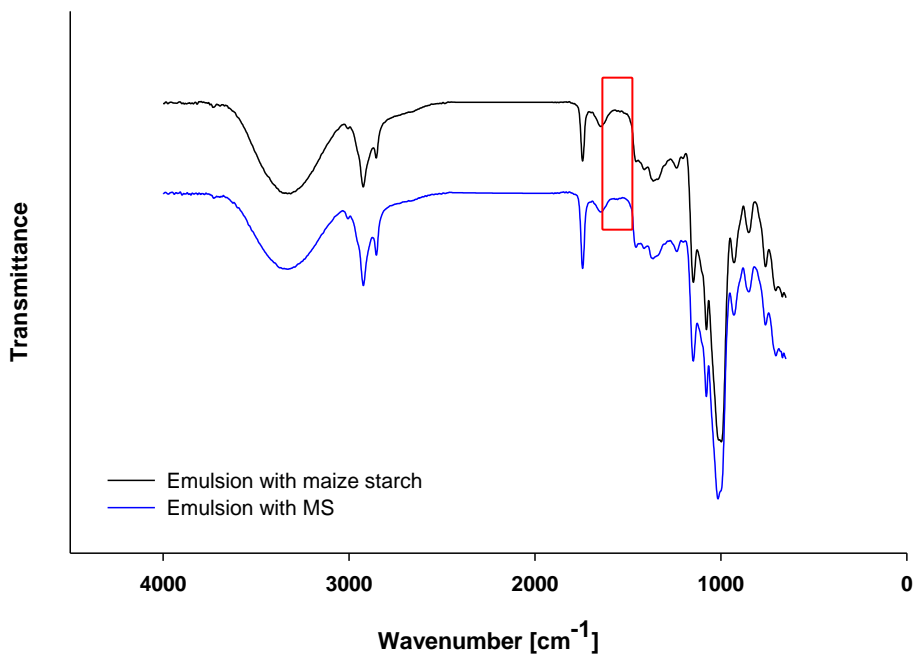
Figure 2. Infrared spectra of emulsion with maize starch and OSA modified maize starch (MS).

3.2. Formation of the emulsion-filled gel

Appearance of emulsions with natural maize starch and MS were observed to see the amphipathic of MS by OSA modification. Maize starch without OSA-modification could not stabilized oil-water interfaces. However, as the starch had hydrophobicity by OSA-modification, MS could stabilize oil-water interfaces and produce emulsion-filled gels (Fig. 3a). By the fabricated methods, emulsions were formed with 20 wt% oil in the range of 3−8 wt% of MS concentration (Fig. 3b). Dyed oil droplets of the emulsion-filled gels were observed with confocal laser to see the size and distribution of oil droplets in the starch gel matrix. Oil droplets of the emulsion-filled gels with 3 and 8 wt% MS, were stuck into the starch matrix (Fig. 4). The size of oil droplets significantly decreased as the concentration of MS increased, indicating that the more MS acted as emulsifier to stabilize the interface of water and oil droplets. As the decrease of the oil droplets size and the gelation of matrix happened simultaneously during the process of sonication with heat, oil droplets existed in contact with the oil particles next to it. The oil droplets were located close each other when the concentration of MS was 3 and 8 wt%. I could say that the aggregation was happened between the oil droplets. In the conventional emulsion system, emulsion stability is relatively low when the aggregation happened, because aggregation caused the coalescence and

separation of oil layer and water. On the other hand, in this emulsion-filled gel system, although there was aggregation, any separation of oil and water was found and there was no coalescence. It meant that the emulsion-filled gels in this system had high stability because the small oil droplets were stuck in the three dimensional network of continuous phase.

(a)

Emulsion with maize starch   Emulsion with MS

(b)

3 wt%   4 wt%   5 wt%   6 wt%   7 wt%   8 wt%
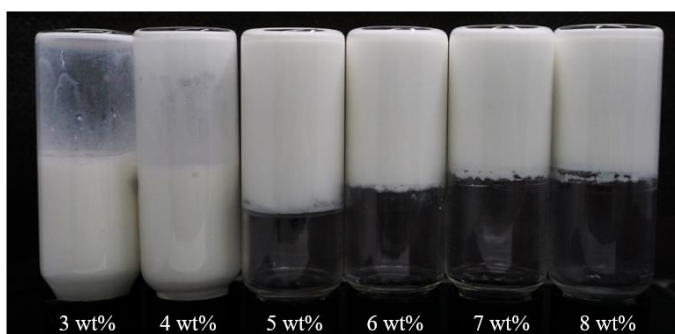
Figure 3. (a) Emulsion-filled gels with maize starch and MS. Letters in photo demonstrate the concentration of MS (b) appearance of emulsion-filled gels with different concentration of MS and 20 wt% of oil concentration.
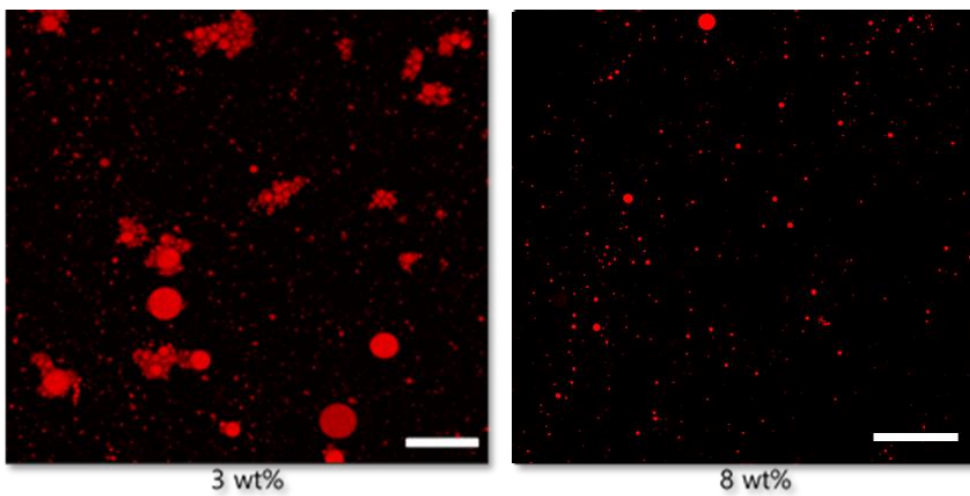
Figure 4. Confocal laser scanning micrographs of the emulsion-filled gels stabilized with 3 and 8 wt% MS dyed with Nile red (bars, 40 μm).

3.3. Viscoelasticity of the emulsion-filled gels

Viscoelastic behavior of emulsion-filled gels was characterized by oscillatory frequency sweep test. Dynamic mechanical spectra (G' and G" moduli) of emulsion-filled gels were demonstrated in Fig. 5 and 6. The G' modulus, storage modulus, shows the magnitude of the energy that is stored in the material whereas, the G" modulus, loss modulus, is the energy that is lost as viscous dissipation per cycle of deformation (Saha & Bhattacharya, 2010; Sharoba, 2005). In the lowest concentration of MS, emulsion-filled gel showed the behavior of typical viscoelastic fluid that the G' modulus and the G" modulus increased and crossed as oscillation frequency was increasing. The 3 wt% of MS did not contribute to significant strengthening of gel matrix, probably the MS molecules were mainly absorbed at the surface of the oil droplets (Dickinson & Chen, 1999). However, in the emulsions-filled gels with ≥ 4 wt% MS, the G' modulus is higher that the G" modulus through the whole measured frequency range, so the emulsion-filled gel had gel-like properties. As the continuous phase was gelled, the emulsion-filled gels showed frequency independent rheological properties. The G' and G" moduli were steady as the increase of the frequency, until the structure was destroyed by the high frequency.

Moreover, progressing MS concentration brought the increase of the G' and G" moduli. The addition of MS has more significant impact on the elastic modulus of the emulsion-filled gels than the viscous modulus and the G' modulus of the emulsion-filled gels with 8 wt% was over 10,000 Pa. Similar behavior of the modulus with raising starch concentration was also observed in starch-based dairy desserts (Tarrega and Costell (2006). The explanation about the relationship of starch concentration and viscoelasticity of emulsion-filled gel may be related to the development of as entanglement network between adsorbed and non-adsorbed molecules of biopolymers, forming a three-dimensional network (Dickinson, 2003; Gamonpilas et al., 2011). Dynamic moduli of Orange juice, honey and yogurt were measured to compare the rheological properties of foods and emulsion-filled gels. The orange juice showed the rheological characteristics of solution, and honey has the properties concentrated solution. Yogurt showed frequency independent rheological properties, indicating the yogurt acted as gel. When compared to the rheology of food, emulsion-filled gels with over 5 wt% MS had rigid matrix than yogurt, and emulsion-filled gel with 3 wt% MS has similar rheological properties of orange juice. Especially, the G' modulus of emulsion-filled gel with 8 wt% MS was similar to the G' modulus of oleogels (Martins et al., 2017).

In the previous study, the G' modulus of emulsion gel emulsified with 2 wt% OSA modified starch and gelled with 20 wt% native starch was about 2,000 Pa (Torres, 2017). Compared to the previous study, the emulsion-filled gel in this system showed higher G' modulus when the MS was used as emulsifier and gelling agent than when the MS was used as emulsifier and native maize starch was used as gelling agent (Fig. 9). It indicated that the only use of MS contributed to the formation of gel matrix and strengthen the interaction between the starch in the continuous phase and in the surface of oil droplets. It could be explained by two phenomena, i.e. the formation of amylose-OSA and amylopectin-OSA inclusion complexes, and the formation of hydrophobic associations between OSA chains (Fernando et al., 2005). The formation of amylose-OSA and amylopectin-OSA could join neighbor chains and network could be formed. Hydrophobic interactions between OSA chains located in neighbor may also lead the formation of network. This affinity gave wider range of rheological properties and compact matrix with relatively low concentration of starch to the emulsion-filled gels, indicating broad application of food from solution to rigid solid.

The G' and G'' moduli increased rapidly when the oil was added to the MS and water phase (Fig. 10). The G' and G'' moduli were not significantly different in the starch gel with 3, 5 and 8 wt% of MS, but the elasticity and

viscosity of the emulsion-filled gels increased significantly as the concentration of MS increased. When the oil was added to the water and starch phase, the emulsion-filled gels were formed and these showed much stronger matrix than the starch gels with the same concentration of MS. The G' and G" moduli also increased significantly when the oil fraction went up from 5 to 20 wt% (Fig. 11). As more amount of oil was added, the emulsion-filled gels showed gel and rigid solid properties. These results indicated that the oil droplets acted as gelling agent in this system. According to their contribution to continuous gel network rheology, fillers, which are the dispersed droplets, can be classified as either 'active' or 'inactive' filler. When the particles have a strong interaction with the gel network, they increased gel strength of emulsion-filled gel and these fillers are called 'active filler'. In contrast, an inactive filler does not contribute to the strength of gel network because it has little chemical affinity for the polymer of the continuous phase. In this system, oil droplets were acted as an active filler and they had chemical affinity for the starch of the water phase. This property of the oil droplets contributed to the strength of gel network, and the viscosity and the elasticity of the emulsion-filled gels increased rapidly with the increase of oil fraction and add of oil to the starch paste.

Figure 5. Change of storage modulus (G') of emulsion-filled gels with different

MS concentration and 20 wt% of oil concentration during a frequency sweep

at 20°C measured by oscillatory viscoelastic analysis.
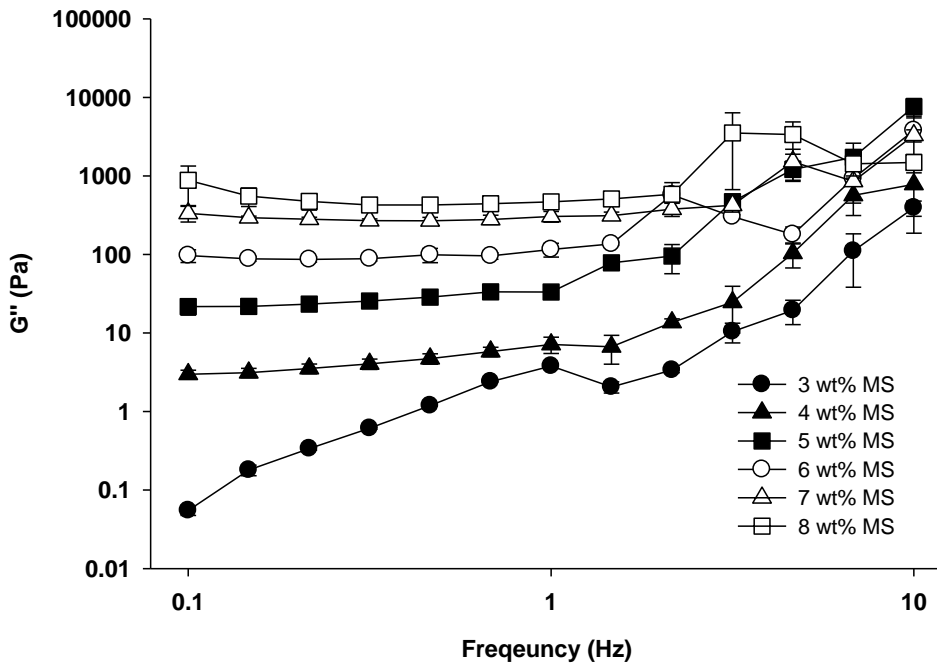
Figure 6. Change of loss modulus (G") of emulsion-filled gels with different MS concentration and 20 wt% of oil concentration during a frequency sweep at 20°C measured by oscillatory viscoelastic analysis.
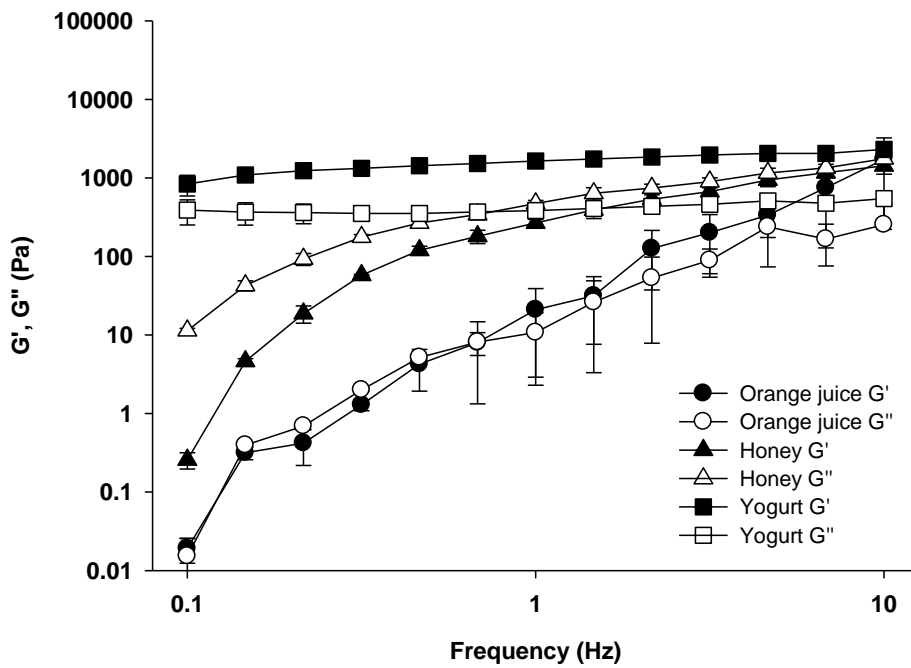
Figure 7. Change of moduli (G' and G") of orange juice, honey and yogurt during a frequency sweep at 20°C measured by oscillatory viscoelastic analysis.
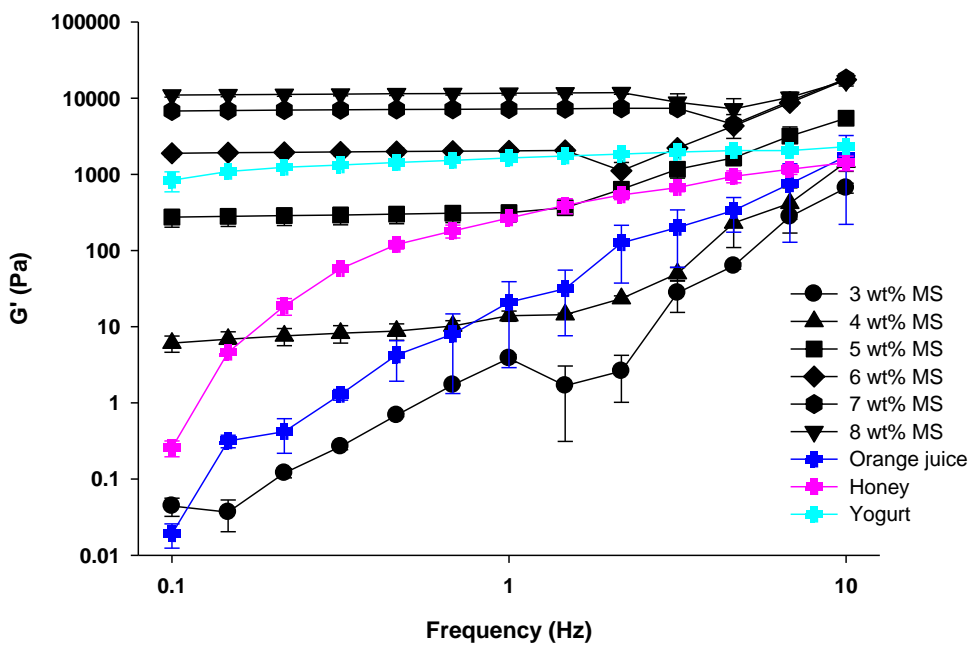
Figure 8. Change of storage modulus (G') of foods (orange juice, honey and yogurt) and emulsion-filled gels with different MS concentration and 20 wt% of oil concentration during a frequency sweep at 20°C measured by oscillatory viscoelastic analysis.
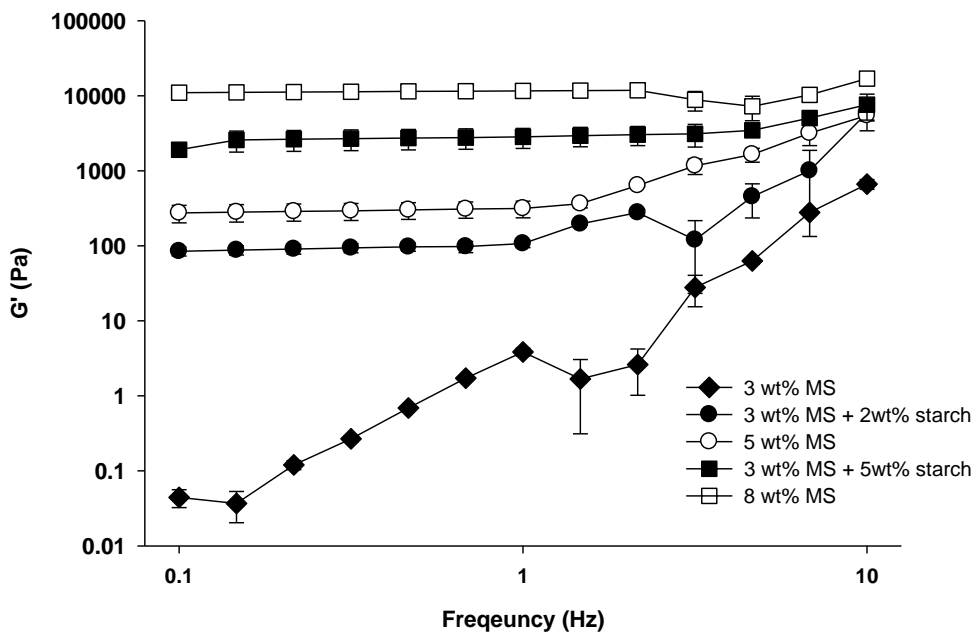
Figure 9. Change of storage modulus (G') of emulsion-filled gels with different

MS and maize starch concentration and 20 wt% of oil concentration during a

frequency sweep at 20°C measured by oscillatory viscoelastic analysis.
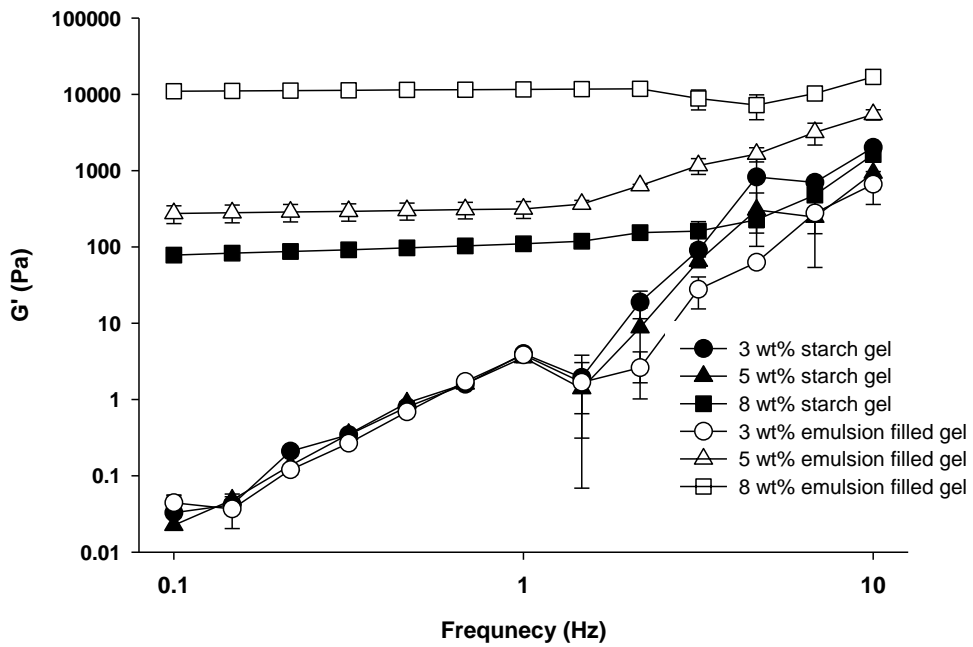
Figure 10. Change of storage modulus(G') of emulsion-filled gels with different MS concentration and 20 wt% of oil concentration and starch gels during a frequency sweep at 20°C measured by oscillatory viscoelastic analysis.
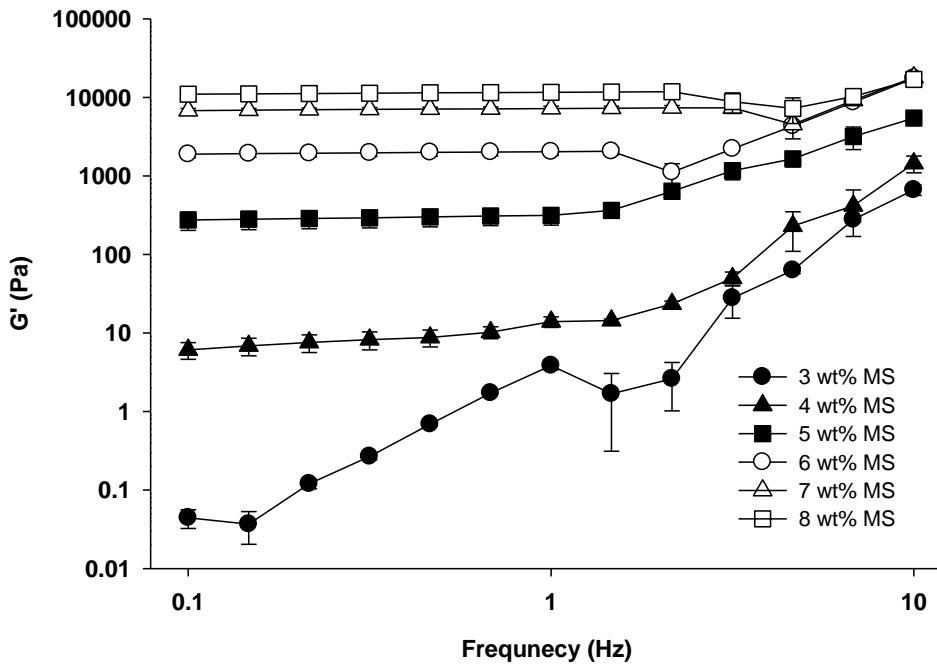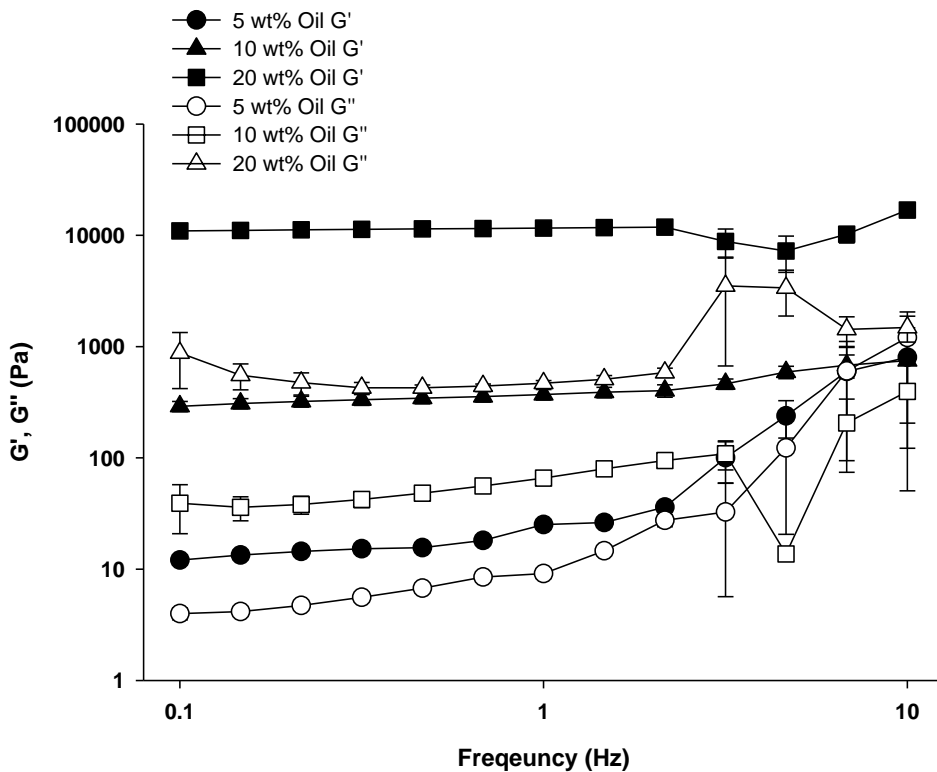
Figure 11. Change of moduli (G' and G") of emulsion-filled gels with different oil concentration and 8 wt% of MS concentration during a frequency sweep at 20°C measured by oscillatory viscoelastic analysis.

3.4. Texture profile analysis of the emulsion-filled gels

The texture profile analysis (TPA) was performed with cylinder probe with 50 % deformation to see the property of emulsion-filled gels in the mouth. TPA is an important imitative test for textural properties, performed as a two-bite compression test, and provides a link between mechanical characteristics and textural attributes during oral processing (Chen, 2009). Texture profile analysis has been used for analysis of o/w emulsions, such as mayonnaise and salad dressings (McMulle, Gorcea, & Chen, 2016). The textural properties of emulsion-filled gels stabilized and gelled with different concentration of MS are presented in Table 1. The emulsion-filled gels with 3 and 4 wt% of MS had solution or weak gel property, so they could not maintain specific form to perform the texture profile analysis. When the concentration of MS was over 5 wt%, the emulsion-filled gel could last the specific form because it acted like solid or rigid gel. Hardness is used to estimate the maximum force required to compress the sample during the first and second bite and is related to the strength of the gel network (Swain, Rao & Nayak, 2005). The highest values of hardness were presented in the samples with the highest content of MS (8 wt%) and then, in samples containing 7 wt% and 6 wt% of MS. The hardness of the emulsion-filled gel with 5 wt% of MS was 132.11 g and the hardness increased rapidly to 918 g when the concentration of MS was 8 wt%. The

hardness of the second bite also increased rapidly when the MS was added to the emulsion-filled gels system. The results indicated that the ratio of MS influenced the textural properties of emulsion-filled gels. As the enough polymer acted as gelling agent in the continuous phase, the three-dimensional network got harder and compact structure. Gumminess is an indicator of the amount of work needed to make a food sample ready to swallow (Sharma et al., 2017). Gumminess value increased significantly ($p < 0.05$) when the concentration of MS increased from 5, 6 wt % to 7 wt% and 8 wt%. The highest value was 171.17 g for the emulsion-filled gels stabilized and gelled with 8 wt% of MS. It meant that more work was required to make the emulsion-filled gel with 8 wt% of MS ready to swallow compared to the emulsion-filled gels with 5, 6 and 7 wt% of MS. In other words, as the starch contributed to form firmer network, stronger continuous gel network was formed and it was needed to bite with more energy to make it ready to swallow. Chewiness is associated with the ease/difficulty in chewing food and forming a bolus before swallowing (Goswami, 2015). As the value of chewiness gets higher, it means that the sample needs mor energy to form a bolus for swallowing, with harder network. The chewiness value of the emulsion-filled gels increased significantly ($p < 0.05$) as the concentration of MS increased and the value was the highest when the 8 wt% of MS was used to form

emulsion-filled gels. This results also suggested that the gel network of emulsion-filled gels became harder with the addition of starch and required more energy to form bolus which is appropriate for swallowing. These results were derived from the original characteristics of starch and the dimensional structure of the matrix formed by the starch. As the matrix was structured closely with the polymer, the oil droplets acted as active filler, and droplets also contributed the polymer to get closer. The natural properties of starch and the interactions between three components, oil droplets, water and starch, emulsion-filled gels had rigid structure depended on the concentration of MS.

Table 1. Texture profile analysis of emulsion-filled gels with different MS concentration and 20 wt% of oil concentration

Concentration of MS (wt%)	Texture parameters			
	Hardness1 (g_f)	Hardness2 (g_f)	Gumminess (g_f)	Chewiness (mJ)
5	132.11 ± 19.79[a]	94.11 ± 14.06[a]	52.11 ± 14.06[a]	1.06 ± 0.34[a]
6	409.89 ± 1.84[b]	254.44 ± 13.34[b]	72.78 ± 7.83[ab]	1.64 ± 0.31[ab]
7	662.78 ±15.85[c]	348.11 ± 42.67[c]	95.44 ± 9.43[b]	2.12 ± 0.51[b]
8	918.00 ± 0.47[d]	459.67 ± 14.61[d]	171.17 ± 15.3[c]	3.57 ± 0.00[c]

Note: All values are the means ±SD of 9 determinations. Different letters (a-d) are significantly different in the Tukey's test ($p < 0.05$).

3.5. Starch digestion patterns of emulsion-filled gels

Starch digestion patterns are monitored by appearance of emulsion-filled gels in simulated salivary medium and gastric, duodenal, and bile juices as Table 2. Emulsion-filled gel with 3 wt% MS was prepared as liquid and emulsion-filled gels with 5 and 8 wt% MS was prepared in 4 mm × 4 mm × 4 mm boluses with similar size distributions to human gel boluses (~ 4.0 and 0.9 mm for the soft and hard gels respectively) (Guo et al., 2013). After 5 min of *in-vitro* oral digestion and 2 h of gastric digestion, emulsion-filled gels and fluid mixture were digested by invertase, α-amylase, amyloglucosidase and pancreatic lipase. During the *in-vitro* small intestinal digestion, the pH of digesta solution was maintained 7.0 by 0.05 M NaOH solution. The appearance of emulsion-filled gels was captured at 0, 15, 30, 60, 90, 120 and 150 min of small intestinal digestion (Fig. 12). In emulsion-filled gel with 3 wt% of MS, the mixture of emulsion-filled gel and small intestinal fluid was opaque at 0 min, and it became transparent yellow after 15 min of small intestinal digestion. It meant that the digestion of starch was mainly done within the first 15 min under the small intestinal condition when the concentration of MS was 3 wt%. In emulsion-filled gel with 5 wt% of MS, the boluses of emulsion-filled gels were splited partially when they went through the mouth and stomach because the matrix were weak solid status when it

compared to the matrix of starch gel with 8 wt% MS. Under the condition of small intestinal, the size of emulsion-filled gels became smaller with the enzymatic digestion of starch. Small size boluses which were separated from the original boluses became smaller size faster than the bigger boluses. After about 60 min of digestion, only small size boluses of emulsion-filled gels were left, which represented that most of starch were digest within 60 min under the small intestinal digestion condition. When the concentration of MS was 8 wt%, there were no separated small boluses of emulsion-filled gels after oral and gastric digestion, because the continuous matrix had compact three dimensional network with enough amount of starch as gelling agent. During the small intestinal digestion, the edge of boluses of emulsion-filled gels became rounded with the digestion of starch and the size of boluses became smaller constantly as the time passed. As the average size of boluses were bigger than when the concentration of MS was 5 wt%, it took more time to digest the starch of emulsion-filled gels. With the change of appearance of emulsion-filled gels, I observed that the more time was required to digest starch with the increase of concentration of MS. This results are based on the amount of starch and the degree of rigidity of the matrix accordingly. As the concentration of starch increased, the continuous phase had strong network, and the size of boluses was maintained during the oral and gastric digestion,

which caused the relatively slow digestion of starch in the small intestinal condition. I also predicted that this pattern of starch digestion would give effect to the lipid lipolysis.

Table 2. Formulations and concentrations of the various media and juices for the simulated in vitro digestion test of

the emulsion-filled gels

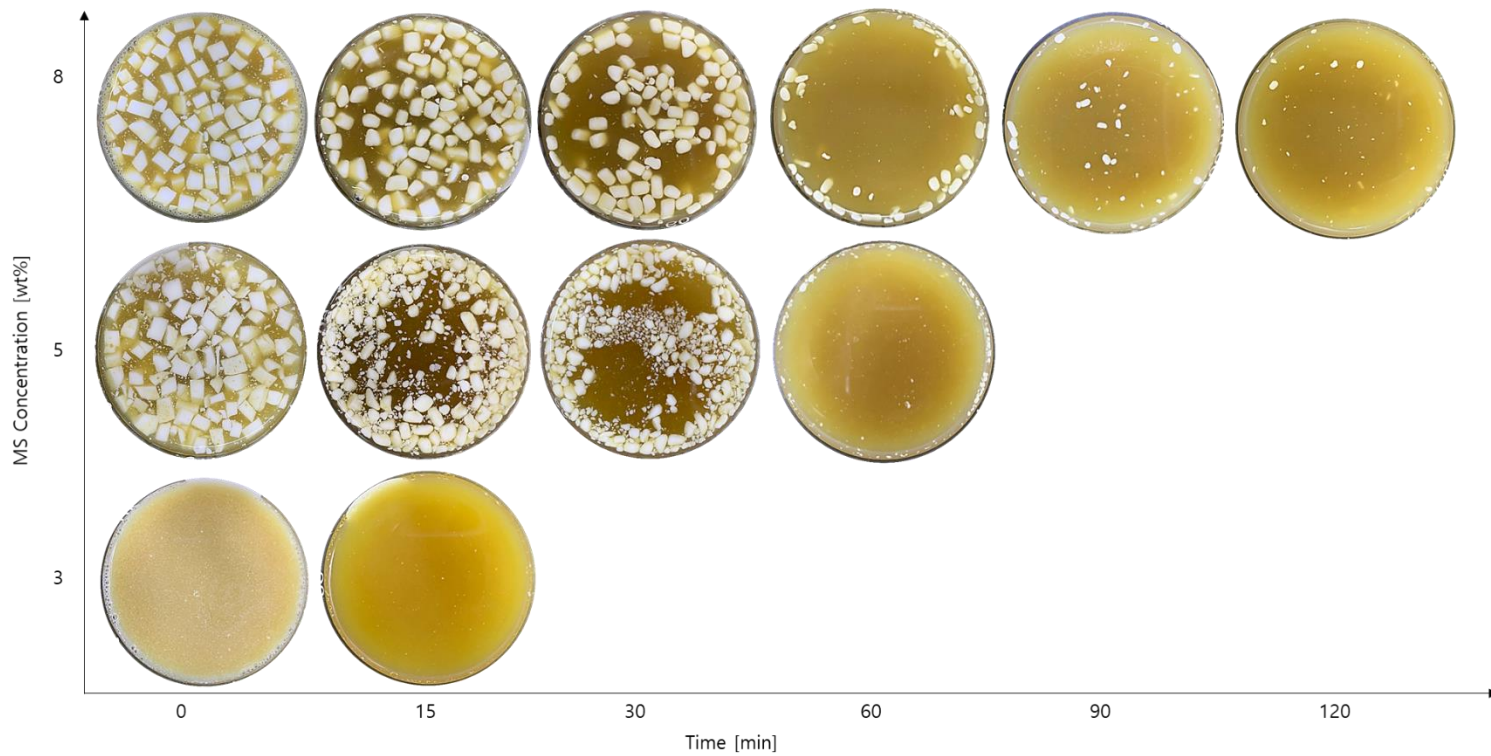|	Saliva medium	Gastric juice	Small intestinal juice
Inorganic solution	2.1 mL NaHCO$_3$ g L^{-1} 1.1 mL KCl 89.6 g L^{-1} 1.1 mL NaH$_2$PO$_4$ 88.8 g L^{-1} 0.2 mL NaCl 75.3 g L^{-1} 1.1 mL Na$_2$SO$_4$ 57 g L^{-1} 1.1 mL KSCN 20 g L^{-1}	1.7 mL NaCl 175.3 g L^{-1} 1.0 mL KCl 89.6 g L^{-1} 2.0 mL CaCl2·H2O 22.2 g L^{-1} 0.3 mL NaH$_2$PO$_4$ 88.8 g L^{-1} 1.1 mL NH$_4$Cl 30.6 g L^{-1}	10 mM sodium phosphate buffer (pH= 7)
Organic solution	0.9 mL urea 25 g L^{-1}	3.8 mL urea 25 g L^{-1} 1.1 mL glucose 65 g L^{-1} 1.1 mL glucosamine hydrochloride 33 g L^{-1} 1.1 mL glucuronic acid 2 g L^{-1}	
Add to mixture inorganic + organic solution	1.7 mg uric acid 2.7 mg mucin 33.3 mg α-amylase	0.33 g BSA 0.3 g mucin 0.28 g pepsin	0.35 g NaCl 90 mg CaCl$_2$·2H$_2$O 0.8 g Bile extract 40 mg α-amylase 15 mg invertase 6.7 mg amyloglucosidase 0.1 g lipase
pH	6.8	1.3	7.0

Figure 12. Appearance of emulsion-filled gels with different MS concentration with the hydrolysis of starch during the intestinal digestion.

3.6. Lipolysis of the emulsion-filled gels

The emulsion-filled gels with 3 wt% of MS were prepared in liquid and the emulsion-filled gels with 8 wt% of MS were prepared in boluses with 4 mm × 4 mm × 4 mm boluses with similar size distributions to human gel boluses (~ 4.0 and 0.9 mm for the soft and hard gels respectively) (Guo et al., 2013). Lipolysis of ingested emulsion droplets occurs mainly in the small intestine with the action of pancreatic lipases (70-90%) (Armand, 2007). The released amounts of FFAs were calculated by the amount of added 0.05 M NaOH (Fig. 13). As the lipolysis was occurred, free fatty acids were produced, which caused the decrease of pH of solution. With the amount of NaOH used to neutralize the released free fatty acids, I calculated the FFA%.

The released amounts of FFAs were 78.5 and 70.0 % for the 3 and 8 wt% MS concentrated emulsion-filled gels, respectively (Fig. 14). The total amount of FFAs released by the lipolysis was not significantly different ($p < 0.05$). The FFA release profiles of emulsion-filled gels showed an induction period (time after that digestion starts) when the concentration of MS was 8 wt%. Compared to the emulsion-filled gel with 3 wt% MS, the digestion of the emulsion-filled gels with 8 wt% MS started after about 5 min of intestinal digestion began. I can call this time induction period. Such an induction period has also been reported by others for indigestible gel matrices (Sarkar et al.,

2015). FFA (%) data indicated that most of the changes occurring in the small intestine took place within 30 min in the emulsion-filled gels with 3 wt% MS. On the other hand, it took about 40 min to lipolysis most of the oil droplets in the emulsion-filled gels with 8wt% MS. This result had coincidence with the digestion of starch mentioned before. The digestion of starch in the emulsion-filled gels with 8 wt% of MS took more time than in the emulsion-filled gels with 3 wt% of MS. As the starch was digested rapidly, the lipolysis took shorter time in the liquid emulsion. Lipolysis was significantly faster ($p < 0.05$) in the emulsion-filled gel with 3 wt% during 100 min of small intestine condition.

The areas under the %FFA curves were calculated to compare the extent of lipolysis depending on the concentration of starch. The areas under the %FFA curves (AUC_{150min}) data showed that the extent of lipolysis was significantly lower in the emulsion-filled gels with 8 wt% MS than the emulsion-filled gels with 3 wt% MS. These results indicated that lipid digestion was slowed down by the gelation of matrix. Generally, the rate of substrate and digestive enzyme reaction is proportional to the surface area of substrate (Armand et al., 1992; Borel et al., 1994), so that the pattern and the rate of lipolysis can be effected by the size and state of emulsion-filled gels. Our interpretation is that when the concentration of MS increased, gelatinized starch formed dimensional

structure, which formed firm matrix. Oil droplets in the emulsion-filled gels embedded in the gel matrix, and the network structure of starch gel particles hindered contact of enzyme and oil droplets. So the oil droplets started to contact to the enzyme after the starch gel was digested and the gel structure was destroyed when the emulsion-filled gel is solid. As a result, oil droplets were exposed to lipase and bile gradually, which explained a lower extent of lipolysis and the induction period. In the emulsion filled gel with 8 wt% MS, the breakup of oil droplets hardly occurred because of the low oil droplet release from the gel network; the gel network hindered the collision of oil droplets; the limited access of lipase to oil droplet surfaces. These results indicated that the lipolysis of emulsion-filled gels in the small intestine can be controlled by the concentration of MS and the lipid digestion can be modulated by designing the gel structure of the matrix. Other studies have reported that the impact of colloidal structure of gastric digesta of whey protein emulsion gels (Qing Guo et al., 2016), emulsion-alginate beads designed to control intestinal lipolysis (Corstens et al., 2017) and influence of chitosan-coating on the digestion of emulsions (Jo et al., 2019).
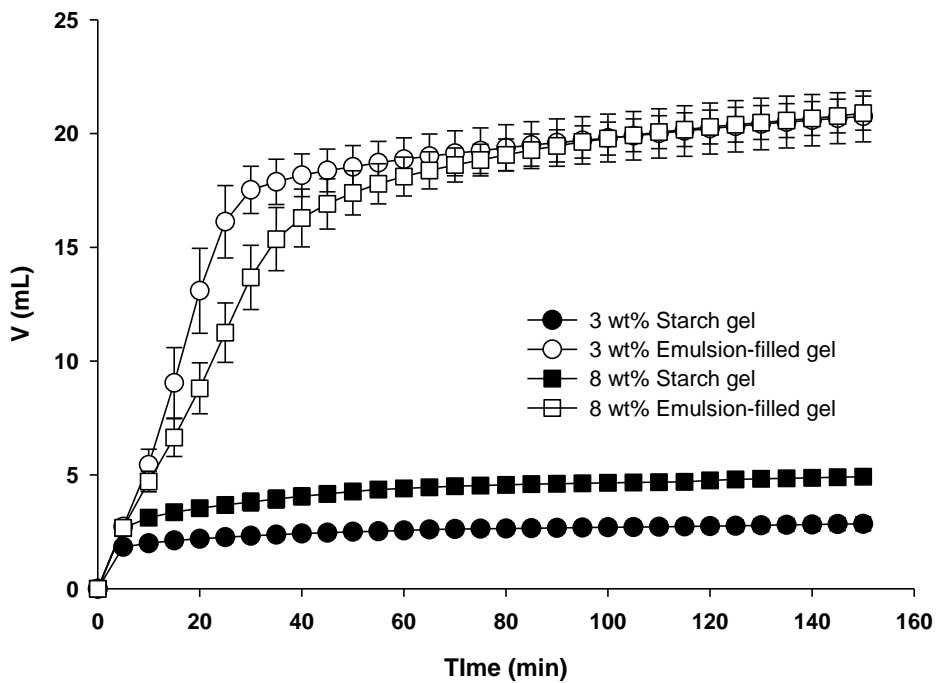
Figure 13. Curves for the amount of NaOH to neutralize the starch gels and emulsion-filled gels with 3 and 8 wt% MS during the intestinal digestion.
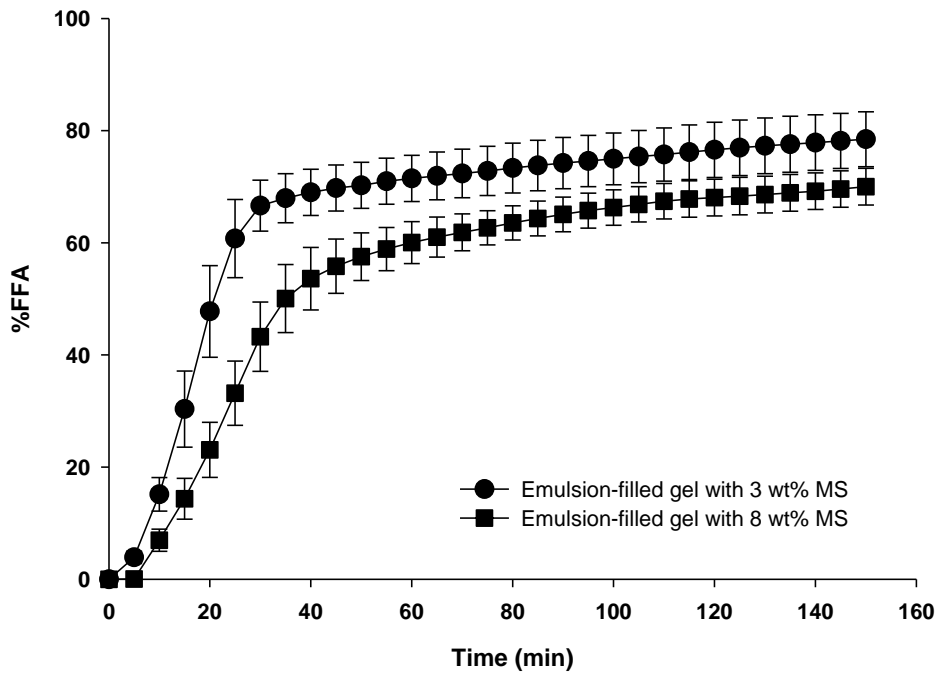
Figure 14. Curves for the percentages of free fatty acids (%FFA) released from the emulsion-filled gels with 3 and 8 wt% of MS during the intestinal digestion.
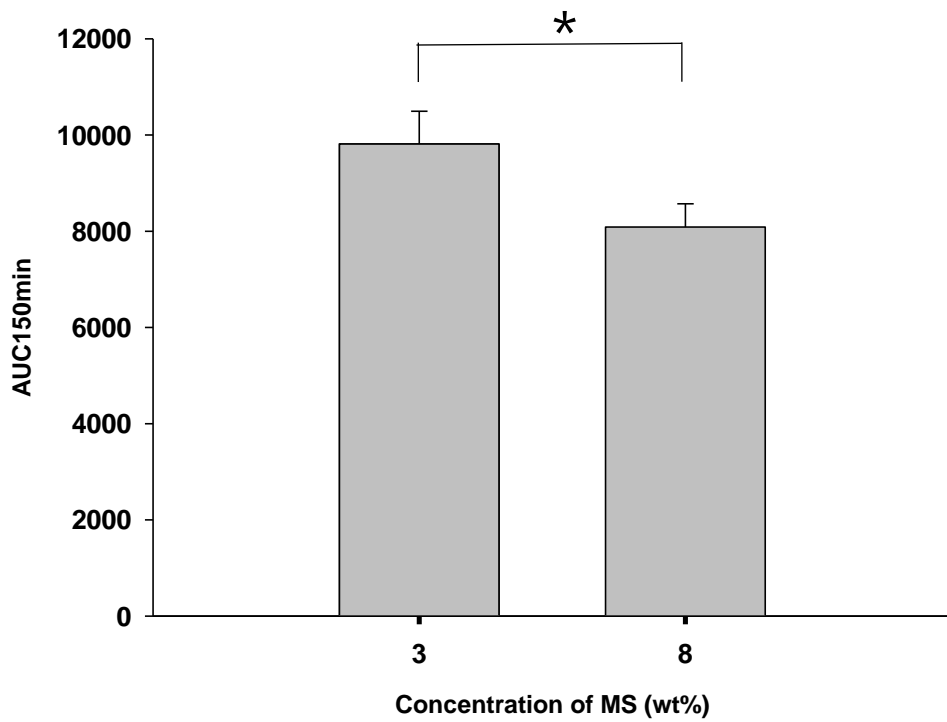
Figure 15. Area under the %FFA curves (AUC_{150min}) (*, $p<0.05$).

3.7. Storage stability of emulsions-filled gels

Storage stability of emulsion is one of the major part of emulsion research because of application in industrial fields. In particular, emulsion-filled gels are expected to be more stable than conventional emulsions because the oil droplets are trapped in the three dimensional gel matrix and hardly move. Storage stability of emulsion-filled gels was observed by appearance of emulsions in vials and distribution of oil droplets.

Storage stability of emulsion-filled gels with 3−8 wt% of MS in vials was shown in Figure 16. Emulsion-filled gels were stored in 20°C for 8 weeks. Emulsion-filled gels with 3 wt% of MS was liquid and emulsion-filled gels with 4 wt% of MS was weak gel. When the concentration of MS was over 5 wt%, emulsion-filled gels became solid, and they maintained as solid for 8 weeks. There were no coalescence, flocculation, and creaming during the storage in the all range of starch concentration. The changes of confocal laser scanning micrographs of the emulsion-filled gels stabilized with 3 and 8 wt% MS also showed that there were no coalescence, flocculation when the concentration of MS was 8 wt%. It meant that the enough amount of starch as emulsifier and gelling agent stabilized the oil droplets and entrapped the oil droplets in the gel matrix for at least 60 days.

(a) 1 day

3 wt% 4 wt% 5 wt% 6 wt% 7 wt% 8 wt%

(b) 60 day

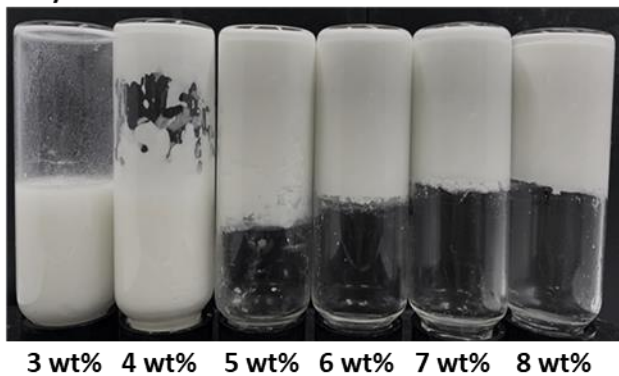3 wt% 4 wt% 5 wt% 6 wt% 7 wt% 8 wt%
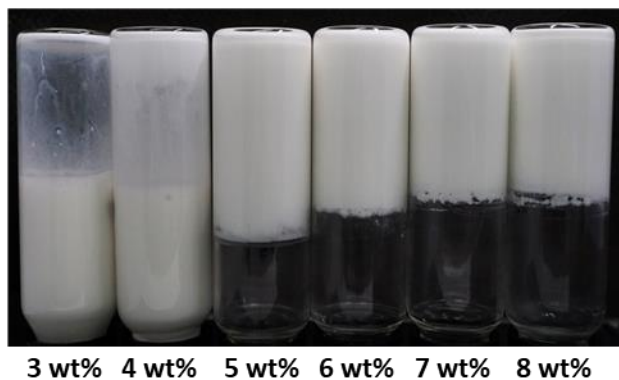
Figure 16. Changes in appearance of emulsion-filled gels stabilized by different concentration of MS during storage for 60 days in ambient temperature.
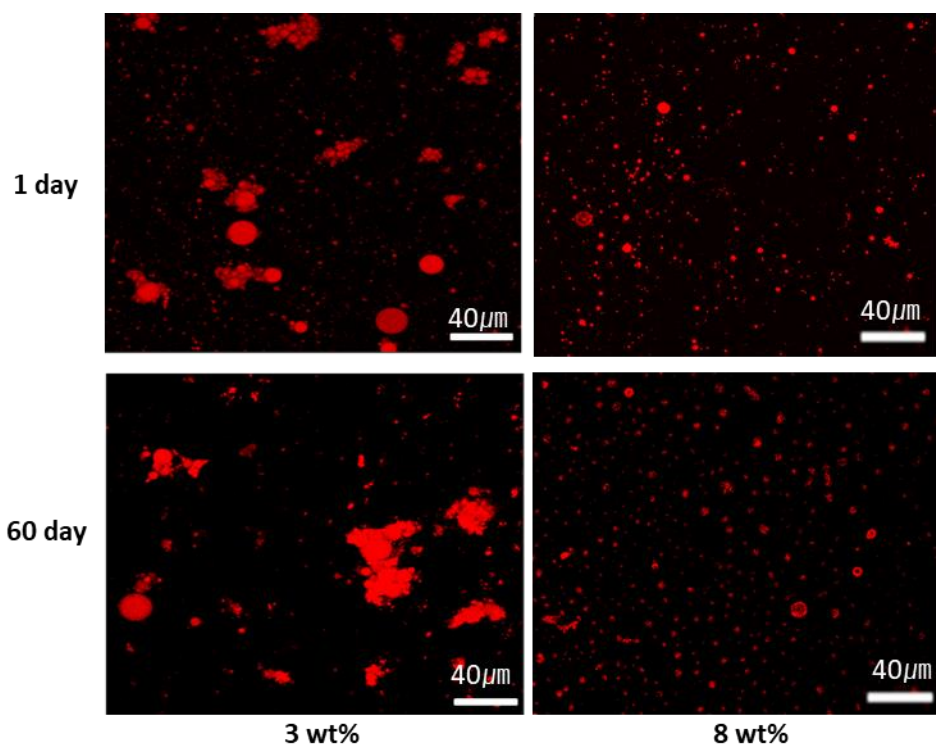
Figure 17. Changes of confocal laser scanning micrographs of the emulsion-filled gels stabilized with 3 and 8 wt% MS dyed with Nile red (bars, 40 μm).

IV. CONCLUSION

In this study, OSA modification of starch paste was carried out successfully and it maintained during the freeze drying and emulsion preparation steps. OSA-modification increased hydrophobicity of starch and it could stabilize oil-water interfaces and forms emulsion-filled gels that contain and stabilized oil droplets in the continuous gel matrix. The fabricated emulsion-filled gels method was simplified with the modification of two steps: gelling phase and emulsification into one step. MS was acted as emulsifier and gelling agent in the one step of sonication and heating. The emulsion-filled gels had different rheological properties depending on the concentration of MS. Storage and loss moduli of the emulsion-filled gels increased with increase of MS and oil concentration. When MS and oil concentration was high enough, storage modulus was higher than loss modulus in frequency range, then it had gel or hard solid properties. When oil was added, the storage modulus increased significantly, which meant the oil droplets were acted as gelling agent, because they were active fillers. There were reduction time in the lipolysis of in-vitro small intestinal digestion, when the concentration of MS increased and the emulsion-filled gels became solid. As the compact starch gel matrix hindered the contact of lipase and oil droplets, the digestion of lipid happened after the digestion of starch that formed three dimensional

network. Oil droplets showed constant sizes and there were no creaming and separation of oil and water for 8 weeks which meant that   Emulsion-filled gels have good stability in the ambient temperature. Emulsion-filled gels stabilized and gelled by OSA modified starch did not need any more additional substances or processes and had wide range of rheological characteristics with relatively small amount of starch. It also showed the possibility of control the digestion rate of nutraceuticals with the concentration of starch , so it can be expected to be applied in various fields in foods, including health functional food, substitute of solid fat and low fat foods.

V. REFERENCES

Armand, M. (2007). Lipases and lipolysis in the human digestive tract: Where do we stand? *Current Opinion in Clinical Nutrition and Metabolic Care, 10*(2), 156−164.

Armand, M., Borel, P., Ythier, P., Dutot, G., Melin, C., Senft, M., et al. (1992). Effects of droplet size, triacylglycerol composition, and calcium on the hydrolysis of complex emulsions by pancreatic lipase: An in vitro study. *Journal of Nutritional Biochemistry, 3,* 333−341.

A. Viswananthan. (1999). Effect of degree of substitution of octenyl succinate starch on enzymatic degradation. *Journal of Environmental Polymer Degradation, 7,* 185-190.

Borel, P., Armand, M., Ythier, P., Dutot, G., Melin, C., Senft, M., et al. (1994). Hydrolysis of emulsions with different triglycerides and droplet sizes by gastric lipase in vitro. Effect on pancreatic lipase activity. *Journal of Nutritional Biochemistry, 5*, 124−133.

Chen, J. (2009). Food oral processing-a review. *Food Hydrocolloids, 23*(1), 1-25.

C. Boutin, H.J. Giroux, P. Paquin, M. Britten. (2007). Characterization and acid-induced gelation of butter oil emulsions produced from heated

whey protein dispersions, *International Dairy Journal. 17*(6), 696-703.

D. Goswami, R. K. Gupta, D. Mridula, M. Sharma, S. K. Tyagi. (2015). Barnyard millet based muffins: physical, textural and sensory properties. *LWT Food Science and Technology, 64*(1), 374-380.

Dickinson, E., & Chen, J. S. (1999). Heat-set whey protein emulsion gels: Role of active and inactive filler particles. *Journal of Dispersion Science and Technology, 20*(1−2), 197−213.

E. Dickinson. (2012). Emulsion gels: The structuring of soft solids with protein protein-stabilized oil droplets. *Food Hydrocolloids, 28*(1), 224-241.

F. E. Ortega-Odega, H. Larsson, A.-C. Eliasson. (2005). Gel formation in mixtures of hydrophobically modified potato and high amylopectin potato starch. *Carbohydrate Polymers, 59*, 313-327.

G. Sala, G.A. van Aken, M.A.C. Stuart, F. van de Velde. (2007). Effect of droplet-matrix interactions on large deformation properties of emulsion-filled gels. *Journal of Texture Studies, 38*(4), 511-535.

H. Khalesi, B. Emadzadeh, R. Kadkhodaee, Y. Fang. (2019). Effect of Persian gum on whey protein concentrate cold-set emulsion gel: Structure

and rheology study. *International Journal of Biological Macromolecules, 125*, 17-26.

J. Chen, E. Dickinson. (1998). Viscoelastic properties of heat-set whey protein emulsion gels. *Journal of Texture Studies, 29*(3), 285-304

J. Chen, E. Eickinson. (1999). Effect of surface character of filler particles on rheology of heat set whey protein emulsion gels. *Colloids and Surfaces B: Biointerfaces, 12*(3), 373-381.

K. Prochaska, P. Kedziroa, L.J.Thanh, G. Lewandowicz. (2007). Surface activity of commercial food grade modified starhes. *Colloids and Surfaces B: Biointerfaces, 60*, 187-194.

L. Baydoun, P. Furrer, R. Gurny, C.C.Muller-Goymann. (2004). New surface-active polymers for ophthalmic formulations: evaluation of ocular tolerance. *European Journal of Pharmaceutics and Biopharmaceutics, 58*, 169-175.

Marins, A. J., Viecente, A. A.,Cunha, R. L., & Cerqueira, M. A. (2018). Edible oleogels: an opportunity for fat replacement in foods. *Food & Function, 9*(2), 758-773.

Mcclements, D. J. (2007). Critical review of techniques and methodologies for characterization of emulsion stability. *Critical Reviews in Food Science and Nutrition, 47*(7), 611-649.

Mccelments, D. J. (2015). Encapsulation, protection, and release of hydrophilic active components: Potential and limitations of colloidal delivery systems. *Advances in Colloid and Interface Science, 219*, 27-53.

McMullen, R. l., Gorecea, M., & Chen, S. (2016). Emulsions and their characterization by texture profile analysis. *In Handbook of formulating dermal applications: A definitive practical guide,* 129-153

M. Golding, T. J. Wooster, L. Day, M. Xu, L. Lundin, J. Keogh, P. Clifton. (2011). Impact of gastric structuring on the lipolysis of emulsified lipids. *Soft Matter, 7*(7), 3513-3523.

M. Jo, C. Ban, K.K.T. Goh, Y.J. Choi. (2019). Influence of chitosan-coating on the stability and digestion of emulsions stabilized by waxy maize starch crystals. *Food Hydrocolloid, 94*, 603−612.

Mun, S., Kim, Y. −R., Shin, M., & McClements, D. J. (2015). Control of lipid digestion and nutraceutical bioaccessibility using starch-based filled hydrogels: Influence of starch and surfactant type. *Food Hydrocolloids, 44*, 380-389.

Ortiz, K. Hol, F.J. Troost, A.A.M. Masclee, K. Schroën. (2017). Emulsion-alginate beads designed to control in vitro intestinal lipolysis: towards appetite control. *Journal of Functional Foods, 34*, 319−328.

P. Rosa, G. Sala, T. van Vliet, F. van de Velde. (2006). Cold gelation of whey protein emulsions. *Journal of Texture Studies, 37*(5), 516-537.

Q. Guo, A. Ye, M. Lad, D. Dalgleish, H. Singh. (2016). Impact of colloidal structure of gastric digesta on in-vitro intestinal digestion of whey protein emulsion gels. *Food Hydrocolloids, 54*, 255−265.

R.K. Richardson, G. Robinson, S. B. Ross-Murphy, S. Todd. (1981). Mechanical spectroscopy of filled gelatin gels. *Polymer Bulletin, 4*(9), 541-546.

Saha, D., & Bhatacharya, S. (2010). Hydrocolloids as thickening and gelling agents in food: a critical review. *Journal of Food Science and Technology, 47,* 587−597.

Sarkar, A., Juan, J.-M., Kolodziejczyk, E., Acquistapace, S., Donato-Capel, L., & Wooster, T. J. (2015). Impact of protein gel porosity on the digestion of lipid emulsions. *Journal of Agricultural and Food Chemistry, 63*(40), 8829−8837.

Sharoba, A. M., Senge, B,. El-Mansy, H. A., Bahlol, H. E., & Blochwitz, R. (2005). Chemical, sensory and rheological properties of some

commercial German and Egyptian tomato ketchups. *European Food Research and Technology, 220*, 142−151.

Sharma, M., Kristo, E., Corredig, M., & Duizer, L. (2017). Effect of hydrocolloid type on texture of pureed carrots: Rheological and sensory measures. *Food Hydrocolloids, 63,* 478-487.

S. Ring, G. Stainsby. (1982). Filler reinforcement of gels. *Progress in Food and Nutrition Science, 6*, 323-329.

Swain, S., Rao, K. K., & Nayak, P. L. (2005). Biodegradable polymers: IV. Spectral, thermal, and mechanical properties of cross-linked soy protein concentrate. *Polymer International, 54*(5), 739-743.

Tárrega, E. Costell. (2006). Effect of inulin addition on rheological and sensory properties of fat-free starch-based dairy desserts. *International Dairy Journal, 16*(9), 1104−1112.

T. Farjami, A. Madadlou. (2019). An overview on preparation of emulsion-filled gels and emulsion particulate gels. *Trends in Food Science & Technology, 86*, 85-94.

Teyssandier, F., Cassagnau, P., Gerard, J. F., & Mignard, N. (2011). Sol-gel transition and gelatinization kinetics of wheat starch. *Carbohydrate Polymers, 83*(2), 400-406.

T. J. Wooster, L. Day, M. Xu, M. Golding, S. Oiseth, J. Keogh, P. Clifton. (2014). Impact of different biopolymer networks on the digestion of gastric structured emulsions. *Food Hydrocolloids, 36*, 102-114.

Torres, O., Tena, N. M., Murray, B., & Sarkar, A. (2017). Novel starch based emulsion gels and emulsion microgel particles: Design, structure and rheology. *Carbohydrate Polymers, 178*, 86−94.

T. van Vliet. (1988). Rheological properties of filled gels. Influence of filler matrix interaction. *Colloid & Polymer Science, 266*(6), 518-514.

Zhang, N., Liu, H., Yu, L., Liu, X., Zhang, L., Chen, L., et al. (2013). Developing gelatin-starch blends for use as capsule materials. *Carbohydrate Polymers, 92*(1), 455-461.

국문초록

에멀션 젤은 하이드로젤 내에 에멀션이 포집된 것으로, 하이드로젤의 장점인 뛰어난 안정성과 에멀션의 장점인 지용성 물질 운반성을 모두 지니는 시스템이다. 본 연구에서는 유화제 역할과 젤화제 역할을 동시에 할 수 있는 변성 옥수수전분을 사용하여 에멀션 젤을 안정화하였고, 이 에멀션 젤의 물성학적 특성과 저장 안정성, 그리고 장내 소화 특성을 분석하였다. 변성 옥수수전분은 옥수수전분이 유화능을 지니도록 하기 위하여 옥테닐호박산 치환 과정과 침전 및 동결 건조과정을 거쳐 제조하였고, 열처리 과정을 통해 젤화제로 작용하도록 하였다. 변성 옥수수전분을 3 wt% 이하로 사용해 에멀션 제조 시 기름(20 wt%)과 물의 계면이 전분에 의해 안정화 되었고, 4 wt% 이상 사용할 경우에는 연속상이 젤화되면서 기름 방울이 젤에 포집된 형태인 에멀션 젤이 제조되었다. 에멀션 젤은 치환된 전분과 기름의 농도가 높을수록 높은 저장탄성률과 손실탄성률을 나타냈으며, 최대치인 8wt%의 전분을 사용할 경우 에멀션 젤의 저장탄성률은 약 10,000 Pa 에 달했다. *In-vitro* 소장 환경에서

에멀션 젤이 방출하는 자유지방산을 정량하는 실험을 통해 전분의 농도가 높아 더 견고한 3 차원 네트워크 구조를 형성할수록 에멀션 젤 내부 기름의 장내 초기 소화 속도와 150 분 동안의 소화율(3 wt% 전분 사용 시 78%; 8 wt% 전분 사용 시 70%)이 유의미하게 감소함을 확인하였다. 또한 60 일간 상온에서 저장한 경우, 층 분리를 일으키지 않고 오일 입자가 분산되어 있음을 관찰하여 에멀션의 안정성이 유지됨을 알 수 있었다. 요컨대, 이 결과들은 본 연구에서 개발된 에멀션 젤이 에멀션의 특성과 하이드로젤의 특성을 모두 갖춘 운반체로서 활용될 수 있다는 것을 시사하여, 본 연구는 건강기능성물질을 이용하여 식품용 젤 형태의 운반체를 개발하려는 연구에 기초 자료를 제공할 수 있을 것이다.

주요어 : 에멀션 필드 젤, 옥테닐호박산 전분, 하이드로젤, 에멀션 유변학, 생체외 위장내 소화

학번 : 2019-24395