Master's Thesis of Science in Agriculture

Surface Energy and Microstructure of Fresh and Processed Foods and Their Relation to Foreign Matters Adhesion

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Surface Energy and Microstructure of Fresh and Processed Foods and Their Relation to Foreign Matters Adhesion

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Abstract

Food surface properties, such as wettability and microstructure, are primarily responsible for the adhesion of foreign matters (particulate matters, pesticides, microorganisms, etc.) to foods. Among the foreign matters, air pollution caused by particulate matters (PM) has become a global issue. PM is known to threaten human health by causing respiratory and cardiovascular disease. PM can be introduced to human gastrointestinal tract through food intake, causing inflammation and changes in gut microbiota. Even at low PM concentrations, prolonged exposure to PM can cause significant accumulation of PM in food surfaces is expected to be strongly influenced by properties of food surfaces, but few studies have been reported. Fresh foods are perishable, therefore, postharvest technology is required to reduce quality loss during storage and retail process. Commonly used food packaging material is chemical synthesized and their non-degradable characteristics cause environmental issues. Edible coating is an alternative material, a thin material attached to the surface forming a barrier and functioning as a physical protectant.

This paper examines surface properties that may affect the interaction between foreign matters, PM and edible coating solution, and food surfaces, including surface wettability and surface microstructure. Understanding the adhesion of PM onto food surfaces can provide useful guidance for classifying foreign matter-interactive foods and controlling food chains to ensure food safety against PM or an efficient use of resources to prevent any waste or product loss.

Six popular food products (perilla, scallion, bell pepper, red lettuce, sundae, and laver) were analyzed. To determine the SFE, static contact angles of six liquids (water, diiodomethane, 2-propanol, ethylene glycol, formamide, and glycerol) were measured and analyzed with OWRK (Owens, Wendt, Rabel and

Kaelble) and Zisman methods. To quantify the microstructure, amplitude and distance roughness parameters, such as arithmetical mean height (*Ra* and *Sa*), root mean square height (*Rq* and *Sq*), maximum height (*Rz* and *Sz*), and mean width of profile elements (*RSm*), were measured by confocal laser scanning microscopy. Laver and sundae showed highSFE (45.5 ~ 58.7 mN/m), while scallion tail had the lowest value (17.6 mN/m), indicating that sundae had the strongest tendency to interact with foreign matters among the tested foods and scallion tail had the lowest tendency. The red lettuce (adaxial) showed relatively high amplitude roughness, whereas the laver, perilla (adaxial), and bell pepper were low. Distance parameters were high at scallion tail and low at perilla adaxial.

The adhesion of PM and chitosan solution to the real food surfaces were determined by the amount of adsorbed PM on the surface and the wettability of coating solution, respectively, followed by statistical analysis to correlate the adhesion and the food surface properties. The result shows that the PM adhesion on the food surface was mainly affected by the surface microstructre, more specifically, mean width between the surface elements.

The results obtained in this study provide a useful information to understand the surface characteristics and their effects on the foreign matter adhesion which can be a guideline to ensure food safety related to contamination of PM, a potential risk to human health, and efficient use of resources to prevent any waste or product loss.

Key words: Food surface, Adhesion, Surface wettability, Microstructure, Particulate matter, Edible coating

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Chapter 1.

Research background

1. Food Surface

Food surface is the outmost layer of food acting as a barrier exposed to atmosphere and plays an important role in the interactions with foreign matters, for example, rain drops retention on the agricultural products, attachment of microbial contaminants, chemical contaminants including pesticide residues or detergent used in kitchen, air pollutants such as particulate matter and cooking ingredients. (Ashokkumar et al., 2012; Fernandes et al., 2014; Gao et al., 2020; Noh et al., 2019; Przybysz et al., 2020). Food surface properties are related to the physical, sensory, and textural properties of final products, such as product appearance, texture, shelf-life, taste perception, and rheology of the products (Rosell et al., 2018).

1.1. Surface properties

Adhesion of foreign matters such as microbial, chemical contaminants and particulate matters occur at food surface and affected by various food surface properties. These properties include surface microstructure, surface wettability, surface charge, surface area, chemical composition, temperature and, etc.

1.1.1 Surface wettability

Wettability is one of basic properties of a solid surface playing important role in many biological, chemical, and physical processes in agriculture, food, and pharmaceutical industries and also in daily life (Huhtamäki et al, 2018; Rossi et al., 2018).

1.1.1.1 Definition

Food surface wettability, the phenomenon of wetting or non-wetting of a solid material by a liquid, can be quantified with contact angle measurement (Karbowiak et al., 2006). A good wettability is that strong affinity appears between liquid and solid and tends to adhere to each other (Michalski et al., 1997).

(1) Surface tension

Surface tension (γ) is free energy of the surface at any gas/liquid interface defined as force per unit length or energy per unit area. In thermodynamics, the term energy per unit area is called surface free energy for solid and liquid surfaces (Jouyban and Fathi-Azarbayjani, 2012). The surface tension of liquid can be directly measured, but for the solid surface, surface free energy can be measured indirectly using contact angles. (Gao et al., 2018; van Oss et al., 1986 and 1988; Zisman, 1964)

(2) Contact angle (contact angle, *θ*)

Contact angle of a liquid drop represents the surface tension measured at the liquid/gas/solid surface three-phase boundary, which is at equilibrium when the droplet is sitting (static) on a solid surface (Nairn et al., 2011). Fig.1.1.

The Young's equation explains the relationship between solid surface tensions γ_{SG} (N/m), liquid surface tension γ_{LG} (N/m) and the interfacial tension between solid and liquid γ_{SL} (N/m) with liquid contact angle θ. (Eq. 1)

$$\gamma_{\mathrm{SG}} = \gamma_{\mathrm{SL}} + \gamma_{\mathrm{LG}} \cos\theta \qquad (1)$$

The measured contact angle value is between 0° to 180°. Contact angle 0° means complete spreading on solid done by a deposited liquid and 180° is no wetting (Karbowiak et al., 2006). Normally contact angle between 0-90° is considered as good wetting and bigger than 90° indicates un-favorable wetting (Yuan and Lee, 2013)

Water contact angle measurement is the most widely used method to quantify the wettability of a solid surface evaluating the contact angle under 65° as hydrophilic and over 65° as hydrophobic surface (Vogler 1998). When a liquid droplet is deposited on a solid food surface, there are 2 further situations are expected. One is that the solid surface is well wetted by the liquid showing the low contact angle. And the other is that not wetted showing high contact angle. (Fig. 1.2.)

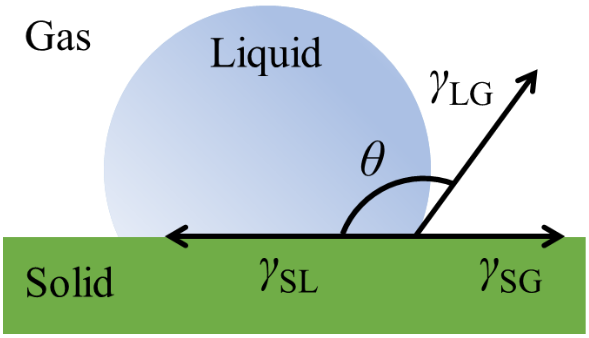


Fig. 1.1. Contact angle (*θ*) between liquid droplet and solid surface

* This figure was published "Current research status and analysis methods on the effects of food surface properties on particulate matter adsorption (2021)" in Food Science and Industry (Lim et al., 2021).

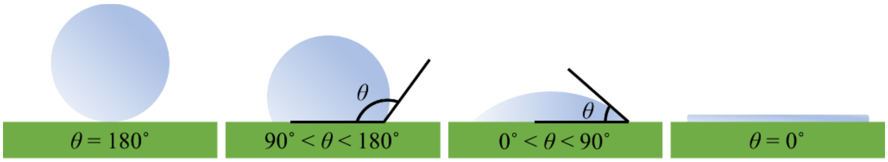


Fig. 1.2. Contact angle (θ) of a droplet on a solid surface (Lim et al., 2021)

* This figure was published "Current research status and analysis methods on the effects of food surface properties on particulate matter adsorption (2021)" in Food Science and Industry (Lim et al., 2021).

1.1.1.2. Main technologies for surface tension measurement

To measure the surface tension, contact angle measurements can be performed using various methods including Wilhelmy plate method, capillary rise method, goniometer and sessile drop methods as described in Fig. 1.3. (Dingle and Harris, 2005; Jouyban and Fathi-Azarbayjani, 2012).

(1) Wilhelmy plate method

Metal plate is attached vertically to the balance via thin metal wire and can be used to measure equilibrium interfacial tension at an air-liquid or liquid-liquid interface. Plate is immersed into and pulled out of the test liquid. During the experiment, the force are recorded and two contact angles (advancing and receding contact angle) with surface tension is calculated. The static surface tension (γ, N/m) can be calculated using the Wilhelmy equation (Eq. 1) (Michalski et al., 1997)

$$\gamma = \frac{F}{l \cos \theta} \qquad (2)$$

where F is the wetting force difference between immersion and withdrawl (N/m), l is the wetted perimeter of the plate, and θ is the contact angle (advancing or receding).

(2) du Noüy ring method

Du Noüy ring method is used traditionally in static surface or interfacial tension measurement. Similar to the Wilhelmy plate method in using the balance. A ring is required to be wetted by dipping in the liquid then being pulled to measure the force exerted on the ring (Fig. 1.3.). Maximum pulling force on a ring by the surface is measured and it is possible to measure the interfacial tension at bot liquid-air and liquid-liquid interface based on the (eq. 2) (Bodour and Miller-Maier, 1998)

$$\gamma = \frac{F}{p \cos \theta} f \quad (3)$$

where p is the three-phase contact line perimeter, and f is the correction factor. The θ is the contact angle and F is the acting force on the thre-phase contact line (Tyowua et al., 2018).

(3) Maximum bubble pressure

This is one of dynamic surface tension measurement methods involving flow of a gas bubble blown at a constant rate through a capillary in a liquid. The dynamic surface tension can be calculated by Young-Laplace equation (Eq. 4)

$$\gamma = \frac{\Delta P_{\max} R}{2} \quad (4)$$

where $\Delta P_{\max}$ is the maximum pressure diffefrence, and R is the capillary radius. A single interfacial tension value is coming from each bubble (Garret and Ward, 1989).

(4) Drop volume (weight) method

Among other surface tension measurement, drop shape techniques are considered as reliable and easy method (Jouyban and Fathi-Azarbayjani, 2012). Weighing the mass of the liquid drop or volume which falls off from capillary tip with known diameter. As falling off drop weight is related to the interfacial tension, the known gravitational force is use for calculation.

$$W = V\Delta\rho g = 2\pi r f \quad (5)$$

where $\Delta\rho$ is the density difference between heavy and light phase, g is the gravitational constant, *r* is capillary radius tip and f is empirical drop correction factor (Jouyban and Fathi-Azarbayjani, 2012).

(5) Pendant drop method

Whilhelmy plate technique requires zero contact angle when liquid contacts the plate therefore the potein solutions and high viscous solutions are difficult to use. For viscous solutions, static methods (sessil drop, spinning drop and pendant drop method) are generally used (Arashiro and Demarquette, 1999). Pendant drop can produce accurate static and dynamic interfacial tensions and contact angle measurement for viscous solutions. The equation used to pendant drop method is Bashforth and Adams which is based on Laplace's equation. (Eq. 6)

$$\gamma = \frac{\Delta\rho g D_e^2}{H} \quad (6)$$

where *g* is gravitational constant, $\Delta\rho$ is the density difference, *D* is the equatiorial diameter of drop at the apex and *H* is the shape factor.

(6) Sessile drop method

Analysis of profile of the drop deposited on a solid surface. When the contact angle is small, it is difficult to observe the contact angle. Using sessile drop technique, contact angle between solid, liquid and gas phases is determined. By solving Young's equation (Eq. 1), properties of solid surface can be characterized (Dingle and Harris, 2005).

(7) Spinning drop method

This method is a profile analysis of less dense phase liquid drop rotating in a heavy phase contained in a tube. The tube with longtitudinal axis case the lower density fluid to centrifuge to center and form an elongated drop. Interfacial tension can be calcualated from Vonnegut's Equation (Eq. 7)

$$\gamma = \frac{1}{4} r^3 \Delta\rho\omega^2 \tag{7}$$

where r is the radius of cylindrical drop, $\Delta\rho$ is the density difference between the drop and fluid and ω is the rotational velocity. This technique is adequate for measuring very low interfacial tension (Jouyban and Fathi-Azarbayjani, 2012).

(8) Capillary rise method

Applied widely in pharmacy being considered as a standard method for surface tension and wettability of a liquid determination. This method is based on measuring the penetration time needed for a liquid to reach a certain height. According to the rising speed, the contact angle can be calculated (Ramírez-Flores et al., 2010; Xue et al., 2006). Capillary penetration of liquid using the pressure difference across the invading liquid meniscus is considered to calculate the surface tension described by Washburn equation (Eq. 8).

$$h^2 = \frac{tR\gamma_{\mathrm{LG}} \cos\theta}{2\eta} \tag{8}$$

where h is the moved distance by liquid, t is time for solvent to rise, R is the pore radius, γ_{LG} is the surface tension of liquid, θ is the contact angle and η is the viscosity of liquid (Karbowiak et al., 2006).

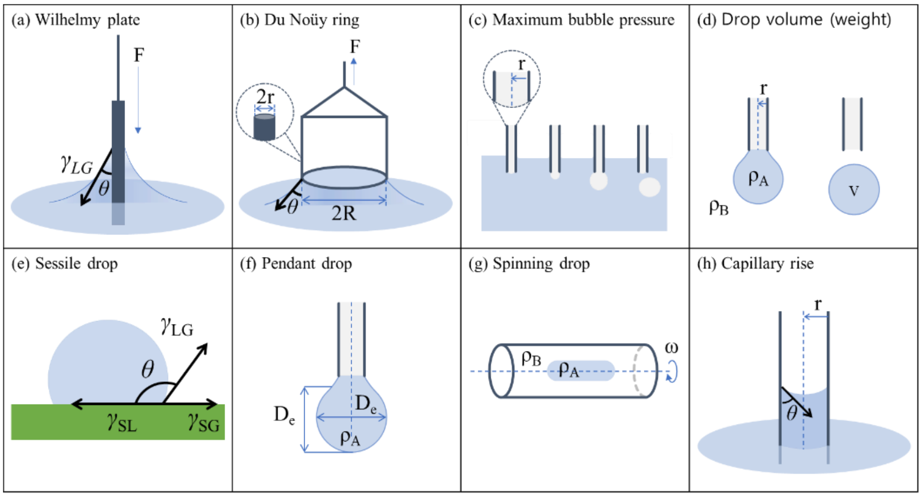


Fig. 1.3. Schematics of surface tension measurement methods (Jouyban and Fathi-Azarbayjani, 2012; Lim et al., 2021; Tyowua et al., 2018)

1.1.2. Surface microstructure

Food microstructure is defined as the spatial arrangement of its structural components and their interactions, also have significant impact on the physical, sensory, and textural properties (Rosell et al., 2018).

1.1.2.1. Definition

Many food materials are semi-solids with fragile microstructure (Chen, 2007). Food microstructure can be defined as the spatial arrangement of the cell and the intercellular space in food material (Aguilera, 2005). Food composition and organization have a great impact on stability, structure, and nutritional value of food product. As structural changes during food processing can degrade food quality, a major concern is to preserve the original microstructure of the food materials (Rosell et al., 2018). Microstructure properties such as grooveness, pores are the features found on the food surface including morpholometrical variables in plant surface, epidermal cells, epicuticular wax crystals and thickness and trichomes (Castanheiro et al., 2021; Gorb and Gorb, 2008; Nairn et al., 2011). These features characterize the surface texture repetitive or random deviation from the nominal surface that forms the three dimensional topography of the surface. Surface texture includes (1) roughness (nano- and microroughness), (2) waviness (macroroughness), (3) lay, and (4) flaws (Bushan, 2001). Their has been many studies on the effect of plant leaf surface or food contact surface microstructures on foreign matter adsorption such as microbial adhesion, particulate matter and uneven surfaces, crevices, or pores may hide the microorganisms (Chen et al., 2017; De-la-Pinta et al., 2019;

Wang et al., 2009). In study of the settlement of M. galloprovincialis, surface texture was the key factor having more effect than wettability in settlements. Settlement rate and attachment strength was high at 400 µm grooves which was bigger than the larvae.

1.1.2.2. Main technologies for microstructure measurements

Chen (2007) classified surface characters which affect to the surface texture perception as glossiness, roughness/smoothness, moistness, freshness, grittiness, coarseness, stickiness, lubricity, flakiness, fibrousness, juiciness. And among these mentioned characters, only a few of surface-related characters (roughness, glossiness, grittiness, moistness) can be quantified by physical techniques (Chen, 2007). Surface roughness can be defined as a collective measure of the magnitude and density of surface asperities (Chen, 2007). Topographical features are most influential and most widely used parameters in surface characterization studies (Chen, 2007). Surface microstructure measurement techniques can be categorized into contact-based and non-contact-based instruments. (Table. 1.1.)

Scardino et al. (2006) studied diatom attachment on microtextured surface and they reported that the number of the attachment points on a surface is related. Surface can be visualized with feature shapes such as peaks and valleys on the horizontal plane. Two dimensions by a cross-sectional line profile and three dimensions by the surface topography are available.

Table. 1.1. Main technologies for surface microstructure measurements (Chen, 2007; Rosell and Garzon et al., 2018; Verboven et al., 2018)

Types		Methods	
Surface contacting	Surface profile tracking	Contact profilometry	Stylus profiler
			Atomic force microscopy (AFM)
Non surface-contacting	Two-dimensional (2D) imaging techniques	Optical microscopy	Bright filed microscopy
			Dark filed microscopy
			Phase contrast microscopy
			Fluorescence microscopy
			Surface Glistening Points (SGP) method
		Electron microscopy	Scanning electron microscopy (SEM)
			Environmental SEM (ESEM)
			Cryo-SEM
	Three-dimensional (3D) imaging techniques	Confocal laser scanning microscopy (CLSM)	
		Optical coherence tomography (OCT)	
		Whiter light scanning interferometry (WLSI)	

2. Foreign matters

In this sturdy, any substances that are capable of being adhered onto the food surface will be defined as a foreign matter.

2.1. Types of foreign matters

On the surface of food, many foreign matters can be attached and found such as chemical materials and miroorganisms. Considering the circular food system, foods go through production, processing, retail and consumer stages to be finally consumed (Thakali and MacRae, 2021). In each stage, some substances (foreign matters) can be attached to the food surface either intentionally or non-intentionally. Intentionally used materials are irrigation water, pesticides, fertilizers at production stage, detergents, coating solution and diatomaceous earth particles at processing stage, and sauces, cooking oils, detergent at consumer stage. However, if the food is exposed to external environment, non-intentional attachment of rain drop, insects, pollen and contaminants such as contaminated soil, heavy metals, particulate matters, foodborne pathogens can happen during all stages (Thakali and MacRae, 2021).

2.2. Particulate matters

2.2.1. Definition

The particulate matter (PM) is a term referring to mixed substances of solid and liquid. The composition, size and emission source vary between locations and time. The size of particulate matter is ranging from 0.01 to 100 μm aerodynamic diameter (AQEG, 2005), and generally classified as coarse particle for diameter from 2.5 to 10 µm, fine particle from 0.1 to 2.5 µm and ultrafine particle smaller than 0.1 µm in diameter (Beckett et al., 1998; Oberdörster and Utell, 2002).

In Korea, air quality issue including particulate matter is defined and managed via Clean air conservation act of 2020 and the Special act on the reduction and management of fine dust of 2020. According to these acts, particulate matter is notated with the term "fine dust" which is defined as inhalable dust among the particulates floating in the air or falling down in the air. The dust with a diameter under 10 µm is defined as PM10 and the dust with a diameter under 2.5 µm is PM2.5. In addition, Nitrogen oxides, sulphur oxides, volatile organic compounds and other substances prescribed by Ordinance of the Ministry of Environment are defined as substances which can be converted into Particulate matter in the air (Clean air conservation act, 2020; Special act on the reduction and management of fine dust, 2020).

2.2.2. Characteristics and emission source

Particulate matters (PM) can be emitted from both natural and anthropogenic sources. PM originated from nature include dust, soil, sea salt, forest fire or volcanic ash, pollens, some microorganism, and the oxidation of biogenic reactive gases. PM originated from anthropogenic source are fossil fuel combusition, industrial activities, cigarette smoking, home cooking and etc. (Anderson et al., 2012; Hu et al, 2015; Joo and Ji, 2020; Kelly and Fussell, 2012) PM in urban areas, vehicles and fossil fuel power plants are main source of emission (Kelly and Fussell, 2012).

Particulate matters are also classified by its creation stages, primary particulate matters (PPM), and secondary particulate matters (SPM). PPM are emitted directly from the emission source such as vehicle combustion, industrial process, soil dusts and marine aerosol. When PPM is generated from the source, atmospheric pollutants, gaseous precursors, such as sulfur dioxide, nitrogen oxides, ammonia, and volatile organic compounds are generated together with PPM. SPM is a result coming from chemical reaction of PM producible substances emitted from direct source and then neutralized by atmospheric ammonia derived from agricultural sources in the atmosphere (Kelly and Fussell, 2012; Kim et al., 2015).

Particulate matter composition differs depending on the collect location, emission source and season, also it has different pattern in a day (Ham et al., 2016; Hu et al., 2015; Lee et al.,2015). Also, it is affected by meteorological condition and particulate matter generated in a region can move to another region (Hu et al., 2015).

2.2.3. Impact on human health

In 2013, International Agency for Research on Cancer (IARC), the specialized cancer agency of the World Health Organization, classified the particulate matter as carcinogenic to humans (Group 1) (IARC, 2013). The Ministry of Environment of the Republic of Korea retains the national air quality standard for Particulate matter concentration to protect public health based on the Enforcement decree of the framework act on environmental policy. The standards limits the annual average of PM10 to 50 μg/m3 and PM2.5 to 15 μg/m3 and the 24-hour average of PM10 to 100 μg/m3 and PM2.5 to 35 μg/m3.

Wide range of diseases can be occurred due to particulate matter exposure. It is well known that PM penetrate into the human body through respiratory tract and the particles having less than 10 μm in diameter can have impact on human health. PM10 are usually trapped in the upper airways, while PM2.5 can penetrate deeper to the alveolar portions of the lung (Table. 1.2.). The smaller a particle is, the deeper penetration to the lung (Kim et al., 2015). PM related health problem is increasing hospital admissions, emergency room visits, respiratory symptoms and cardiovascular diseases, decreased lung function, and premature mortality (Guaita et al., 2011; Halonen et al., 2009; Perez et al., 2012; Samoli et al., 2008). Oxidative stress is suspected as one of the major mechanisms of these genotoxic effects (Kim et al., 2015). There are studies that exposure to PM is related with low birth weight in infants, pre-term deliveries, and possibly fetal and infant deaths (Son et al., 2012; Woodruff et al., 2006). Exposure to PM produces a uniform degree of mortality in exposed populations, in spite of its diverse sources (Veronesi et al, 2002).

Table. 1.2. Potential deposition locations of particulate matters according to the size in respiratory system (Kim et al., 2015)

Respiratory system	PM size (μm)
Nasal passages	7 – 11
Pharynx	4.7 – 7
Trachea	3.3 – 4.7
Primary bronchi	3.3 – 4.7
Bronchi branches	1.1 – 2.1
Bronchioli	0.65 – 1.1
Alveoli	0.43 – 0.65

2.3. Edible coating

2.3.1. Definition

Edible coating is thin material based on biopolymers forming a layer on the food product surface to protect the fresh products from the mechanical, physical, chemical and microbiological damage during storage and distribution process. There are edible film which has similar use of purpose and material (Falguera et al., 2011; Sobral et al., 2008), but the main difference between the edible film and coating is separability. Film is a separable material from the food but coating is applied directly on the food surface by dipping, spraying, or brushing or replacing natural protective waxy coatings (González-Aguilar et al., 2008).

2.3.2. Applications

Fresh foods such as fruits, vegetables, meats and seafoods are perishable after harvested, butchered or caught. Therefore, postharvest technology are required to reduce quality loss during storage and retail process. As mentioned in advance, edible coating is a thin material attached to the surface forming a barrier and functioning as a physical protectant. Commonly used food packaging material is chemical synthesized therefore non-degradable characteristics causes enviromnetal issues. As a alternative material edible coating is getting attention and studied.

Edible coating can be used widely in food industry for preventing or reduction of moisture transfer, gas exchange, antimicrobial infection of fresh foods such as fruits and vegetables to improve or maintain the physicochemical, chemical and sensory quality and shelf life (Martín et al., 2019; Riva et al., 2020). Common materials used in edible coatings are polysaccharide, protein, lipid, or multicomponent mixtures.

The envelope types (packaging, wrapping or coating) are important for conservation, distribution and marketing of food products. Their functions are to protect the product from mechanical, physical, chemical damage and microbiological activities. These characteristics are influenced by parameters such as the kind of material implemented as structural matrix (composition, molecular weight distribution), the conditions under which films are preformed (type of solvent, pH, components concentration and temperature) and the type and concentration of additives (plasticizers, cross-linking agents, antimicrobials, antioxidants or emulsifiers) (Guilbert et al., 1996; Rojas-Grau et al., 2009).

2.3.3. Materials for edible coating

There are many materials that can be used for edible coating. Major materials for producing an edible coating are polysaccharides, proteins, and lipids with other agents for fresh produces such as fruit, vegetables and marine products. Expecting effects of edible coating are water loss reduction, internal CO2 reduction, less color change, acidity maintenance, shelf life increase, quality loss prevention, less ethylene production, chlrorophil loss delay, after-ripening delay, weight loss reduction and firmness (Dhall, 2013).

(1) Polysaccharides

Abundant and various natural source, excellent gas barrier property can be formed. Cellulose, starch, gums and chitosan are commonly used and their linear structure is able to make the film tough, flexible, transparent and resistant to fats and oils (Dhall, 2013).

Cellulose derivatives such as carboxymethyl cellulose (CMC), methyl cellulose (MC), hydroxypropyl methyl cellulose (HPMC), and hydroxypropyl cellulose (HPC) have ability to generate good film with characteristics of odorless and tasteless, flexible, resistant to oil and fats, water solubility, permeability of transmitting moisture and oxygen. Higher molecular weight can form better mechanical properties, but these materials are expensive to be used industry (Dhall, 2013).

Starch is the storage polysaccharide of plants and it is renewable and suitable raw material for industrial uses. It is well known that the most starches are composed of two types of glucose polymers which are amylase and amylopectin (Rodríguez et al., 2006). Having characteristics of inexpensiveness, renewability and good mechanical properties allows the starch based film to replace the plastic polymer. High amylose starch based film can form a good barrier to oxygen but amylopectin is not a good choice as it generates weaker tensile strength and elongation. Starch requires plasticizer to form a film such as glycerol, polyether and urea that are able to limit microbial growth by decreasing water activity.

(2) Chitin and Chitosan

Chitin is the second abundant biopolymer from nature, found in exoskeleton of crustaceans, fungal cell walls. Chitosan is a derivatives of chitin and is structurally similar to cellulose. Chitosan coating can delay ripening and decreasing transpiration rates of fruit and vegetables by forming semipermeable, clear tough, flexible and good oxygen barriers (Dhall, 2013).

2.3.4. Chitosan edible coating

Chitosan is a material of polysaccharide derived from partially deacetylated derivative of chitin. Its chemical structure is a linear unbranched polymer of β-(1-4)-linked d-glucosamine and N-acetyl-d-glucosamine (Malerba et al., 2018).

Chitin is the second most abundant polysaccharide source in nature after cellulose (Shahidi et al., 1999), being found in several organisms such as fungi, algae, marine invertebrate and arthropods (Kurita, 2006). Although the chitin is available from various sources, the main source of chitosan is marine crustacean's shell waste of crab, shrimp, lobster, etc.

Chitosan is widely used in food, agriculture, fishery, and pharmaceutical industries, having numerous advantages in safety, cost, and biodegradability. Its low toxicity, high lethal dose of 1.6g/kg of body weight in rats, is well known characteristic and enabled chitosan to be accepted as a dietary supplement and a food additive in many countries (Casariego et al., 2008).

In agriculture, chitosan is effective in plant productivity, protection against the pathogens and extending shelf life of fruit and vegetables (Casariego et al., 2008). The mechanism of antifungal and antibacterial properties of chitosan comes from its cationic characteristic interacting with bacterial cell wall, cell membrane and cytoplasm through electrostatic interactions (Duan et al., 2019).

Chitosan has been applied as biomaterials due to its biocompatible and non-toxic characteristics after the biodegradation. Moon and Lim (2020) reported the possibilities of chitin and chitosan as dental products such as toothpastes and mouthwashes to prevent dental caries based on their antibacterial properties.

When chitosan is used as edible coating material for fruits and vegetables, it can form semi-permeable coating for perishable products (Shahidi et al., 1999) and carry food ingredients such as antimicrobials, texture enhancers and nutraceuticals to obtain better quality and functionality (Duan et al., 2019).

3. Adhesion of foreign matters to food surfaces

Adhesion can be defined as molecular interactions at the interface between different materials (Marshall, 2010). Food surface as an adherend and the foreign matter as an adhesive make the interface. Adhesion in food industry, mechanical interlocking and wettability are mainly used (Michalski, 1997).

On the food surfaces, whether it is intended or not, many foreign matters can be attached such as particulate matter, chemical products (pesticides, fungicide, detergent, coating solution, etc.) and microorganisms and the retention or detachment of foreign matter may have a broad range of affects to related activities including processing, storage and consumption.

During cultivation plants surface can be contaminated by particulate matter adhesion, then enter to gastrointestinal system in human body. Some studies were conducted to investigate the particulate matter adhesion on some fruits and leafy vegetables (Jia et al., 2018; Noh et al., 2019; Przybysz et al., 2020; Rai, 2016)

Plant cultivation requires the use of agrochemical aiming at crop yield increase and protection from pests. To obtain the efficacy in application, adjustment of formula has to be considered depending on the wettability of targeted plant, because the adherence, rebound and retention of sprayed droplet is affected by the leaf surface wettability (Gao et al., 2020; Nairn et al., 2011; Puente and Baur., 2011; Wu et al., 2020)

3.1. Thermodynamic influence

Adhesion is attributable to electrodynamic intermolecular forces existing at the interfaces (liquid-liquid, liquid-solid and solid-solid) and the interfacial attraction between the adhesive and adherend can be expressed in terms of reversible work of adhesion which is equivalent to material surface tension. Zisman introduced the concept of critical surface tension of solid surface (Gindl et al., 2001) and there are concepts based on surface free energy components, Owen, Wendt, Rabel, and Kaelble method describes that the surface energy is sum of polar and dispersive component (Gao et al., 2018) and van Oss et al. (1988) used Lifshitz-van der Waals, Lewis acid and Lewis base components in adhesion process.

4. Research significance

Food surface is the most outer part of a food where many interactions occurs and its properties such as wettability and the roughness play an important role on the interactions of food surface and foreign matters.

Whether it is intended or not, many foreign matters can be attached on the food surfaces such as particulate matter, chemical products (pesticides, fungicide, detergent, coating solution, etc.) and microorganisms and the retention or detachment of foreign matter may have a broad range of affects to related activities including processing, storage, and consumption.

A research showed that the roughness parameters of tiles for agri-food buildings and cleanability of wheat flour residue are not related directly but have linear combination with the selected roughness parameters (Rz, Rt and Mr_2), so the residues size is necessary to be considered.

Residue removal on the surface is related to physico-chemical properties (Barreca et al., 2017).

Researches on particulate matter impacts on human health are mostly focused on cardiovascular and respiratory systems, and there are a few studies on the particulate matter impact on gastrointestinal tract. To the best of our knowledge, no studies are done to figure out what effects can have food surface properties on the particulate matter.

Though there are some reported evidences suggesting that particulate matter can be entered to the gastrointestinal tract by intaking contaminated food, and those PM can have adverse effects such as altering gut microbiota and immune function and development of gastrointestinal inflammatory diseases (Salim et al., 2014), study on the potential interaction particulate matters with food surface are still in its early stage.

Chitosan is one of edible coating material, an example of intended application of foreign matters, as a protective package material for fresh food having multiple advantages such as nontoxic, biocompatible, biodegradable and fungicidal properties and ability to elicit plant defense responses (Ali et al. 2011 and 2012; Lin and Zhao 2007; Maqbool et al. 2010).

The significance of the work presented could lead to identifying the food surface properties and how these properties are related to the foreign matter adhesion. Understanding the effects of food surface properties could provide better guidelines to ensure food safety related to contamination of particulate matter, a potential risk to human health, and efficient use of resources to prevent any waste or product loss.

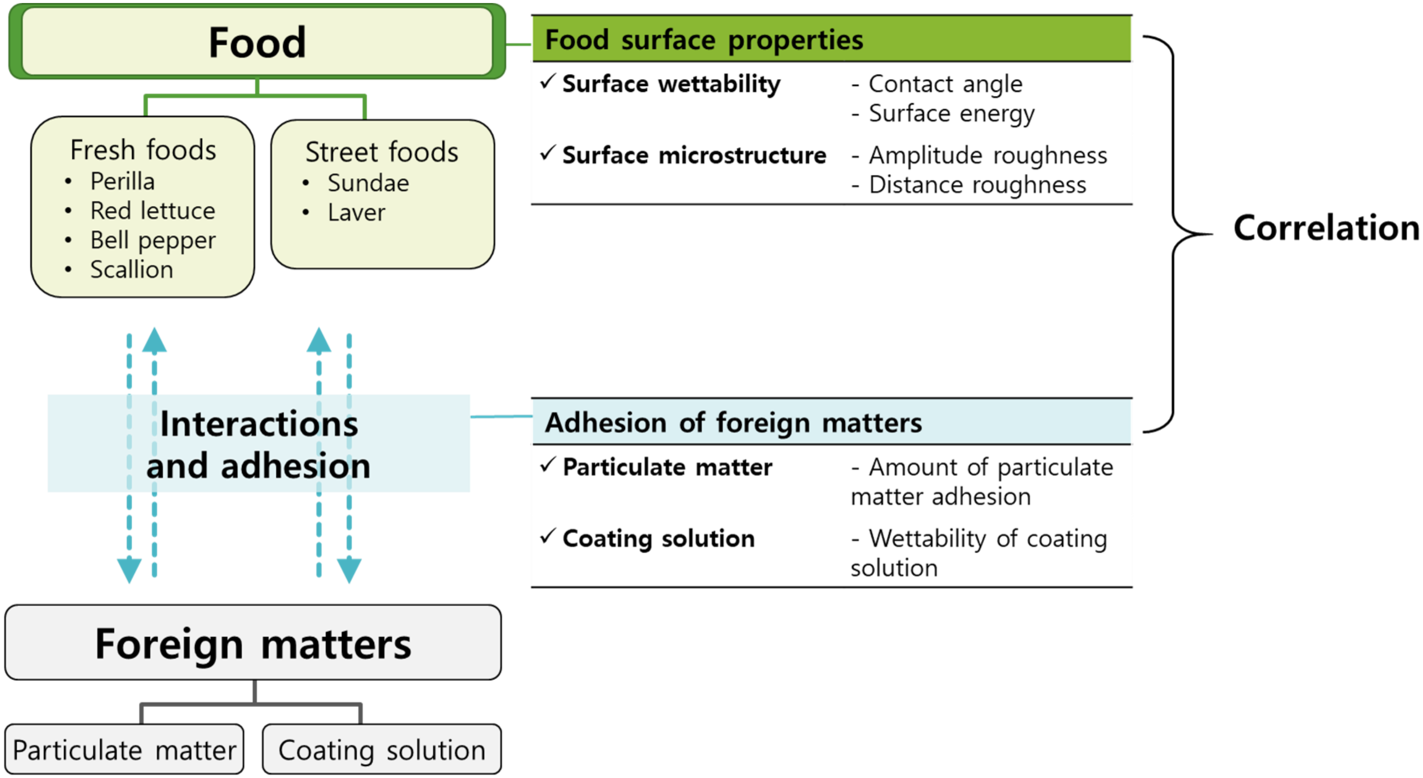


Fig. 1.3. Research strategy

5. Overall objectives

The study aimed to investigate the surface properties of six populmar food products, including perilla, scallion, bell pepper, red lettuce, sundae and laver and examine the effects of the surface properties on the adhesion of foreign matters, including PM and chitosan solutions.

In the first part in Chapter 2, food surfaces properties were characterized by analyzing their surface free energy (SFE) and roughness. For SFE, OWRK (Owens, Wendt, Rabel, and Kaelble) and Zisman methods were used by measuring static contact angles of six liquids (water, diiodomethane, 2-propanol, ethylene glycol, formamide and glycerol) on the food surfaces. For the surface roughness, profile and areal roughness parameters were measured using confocal laser scanning microscopy (CLSM).

In the second part in Chapter 3, the effects of the surface properties of the foods on the adhesion of PM and chitosan solution were analyzed. The chitosan solution was selected as an edible coating model. The adhesion of PM and chitosan solution to the food surfaces were determined by the amount of adsorbed PM on the food surface and the wettability of coating solution, respectively, followed by statistical analysis to correlate the adhesion and the food surface properties. The Fig. 1.3. shows the research strategy.

Chapter 2

Determination of food surface properties

1. Introduction

Food surface is the outmost layer of food exposed to atmosphere and plays an important role when interact with foreign matters such as rain drops, microbial contaminants, chemical contaminants, air pollutants and etc (Ashokkumar et al., 2012; Fernandes et al., 2014; Gao et al., 2020; Noh et al., 2019; Przybysz et al., 2020). And the adhesion of these foreign matters are affected by various food surface properties and no matter what it was intended or not, these foreign matters can adhere to the food surfaces and may have affects to related activities including processing, storage, and consumption (Duan et al., 2019; Jia et al., 2018; Nairn et al., 2011; Noh et al., 2019; Przybysz et al., 2020; Puente and Baur, 2011; Rai, 2016). Food surface wettability and microstructure can be the main factors to affect the adhesion phenomena (Huhtamäki et al, 2018; Plumier et al., 2019; Wang et al., 2009). A good wettability is that strong affinity appears between liquid and solid and tends to adhere to each other (Michalski et al., 1997). There has been many studies on the effect of plant leaf surface or food contact surface microstructures on foreign matter adsorption such as microbial adhesion, particulate matter and uneven surfaces, crevices, or pores may hide the microorganisms (Chen et al., 2017; De-la-Pinta et al., 2019; Wang et al., 2009). It is necessary to understand the food surface properties, to ensure the food safety related to contamination or an efficient use of resources.

In this chapter, it was aimed to investigate the surface wettability and microstructure of six popular food products (perilla, scallion, bell pepper, red lettuce, sundae and laver) by analyzing their surface free energy (SFE) and roughness.

2. Materials and methods

2.1 Materials

2.1.1 Fresh produce

Four fresh produce items, perilla (*Perilla frutescens* Britton), Scallion (*Allium fistulosum* L.), red lettuce (*Lactuca sativa* L.), bell pepper (*Capsicum annum* L.), are obtained from local stores. Fresh produces are stored in refrigerator (4°C) until the experiment. Before experiments, they were rinsed with running tap water then distilled water to remove soil. Measurements were done for the clean surfaces without any visible damage. Remaining water on the surface are removed by using kimwipes gently tapping the surface not to be damaged (Fogg, 1947).

2.1.2 Processed foods

Two processed foods, sundae (traditional Korean blood sausage) is purchased from Jinsung Food (Eumseong, Korea), dried laver (*Porphyra* sp.) from Sung Gyung Food Co., Ltd. (Daejeon, Korea) is purchased from local store and gimbap was purchased from local restaurants. Sundae is a ready-to-eat food and generally prepared by steaming porcine intestines stuffed with varius ingredients including minced pork, starch noodles, pork blood, and vegetables (Kim et al., 2021). Bulk packaged sundae was cut and divided into vinyl bags (18×28 cm) and vacuum sealed to be stored in refrigerator until the experiment. Before the experiment, sundae was cooked by boiling in vacuum sealed bags for at least 15 min then bags were opened and cooled with single-use plastic bag (high density polyethylene bag) covered for at least 1 h in contact angle measurement room. The measurements were done for the outer part of casing which is porcine small intestines. Gimbap is a popular food in korea, usually contains cooked white rice and other ingredients and rolled up with dried laver sheets and it is seasoned (brushed) with sesame oils (Kim et al., 2015; Mouritsen et al., 2018). Dried laver was stored in room temperature with silica gel and gimbap was used on the same day of purchase.

2.1.3 Liquids for wettability measurement

Six liquids with known surface tension components (polar and dispersive components) are used for contact angle measurement and the surface energy of solid calculation: deionized water, diiodomethane (99%, Alfa Aesar, Ward Hill, MA, USA), ethylene glycol (99.5% Junsei Chemical Co., Ltd, Tokyo, Japan), formamide (99%, Daejung chemicals & metals Co., Ltd, Siheung, Korea), glycerol (99.5%, FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) and 2-propanol (99.9%, FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan). Their surface tension information (Correia et al., 1997; Janczuk and Białlopiotrowicz, 1989; Janczuk et al., 1993) and the volume quantity used for the contact angle measurements using a microliter pipette are described in Table 2.1.

Table. 2.1. Surface tension parameters (mN/m) of six liquids used for experiments (Correia et al., 1997; Janczuk and Białlopiotrowicz, 1989; Janczuk et al., 1993)

	Surface tension γ_l (mN/m)	**Dispersive component γ_l^d (mN/m)**	**Polar component γ_l^p (mN/m)**	**Volume for 6 mg (µl)**
Water (W)	72.8	21.8	51.0	6.00
2-propanol (2P)	23.0	19.5	3.5	7.64
Diiodomethane (DM)	50.8	50.42	0.38	1.80
Ethylene glycol (EG)	48.2	31.52	16.68	5.38
Formamide (F)	57.3	28	29.3	5.29
Glycerol (G)	63.3	33.6	29.7	4.76

2.2 Contact angle measurement

Static contact angle measurement was performed according to Mostafavi (2019), Gao et al. (2018) and Zhao & Jiang (2018) with some modifications. Contact angle data was obtained by contact angle goniometer (Phoenix-MT(M), Surface Electro Optics, Suwon, Korea), and captured image was analyzed by software (Surfaceware, Surface Electro Optics, Suwon, Korea). Static contact angle (θ) of the manually deposited droplet on the food surface using a microliter pipette, 6 mg of liquid drops (5 to 45 droplets) were deposited on the different food surfaces. Measurements were performed at 20°C and relative humidity 40% in a temperature- and humidity-controlled room. To control the room temperature and humidity condition, room ventilation system, humidifier (DP 9000 UH, Zhongshan Xinhao Electric Co. Ltd, Guangdong, China), and dehumidifier (DNDE100-13021, Winix, Siheung, Korea) were set and refrigerating bath (RW-2025G, Jeio Tech Co., Ltd, Daejeon, Korea) for temperature control was connected to sample stage of the goniometer. A time series of image for droplet deposition was captured during 30 seconds at 1 image per sec. Reported contact angles (θ) are the average of the values obtained for the droplets which were placed on different positions on the food surfaces. The θ of any droplet not showing circular shape distorted by hairs or venation were discarded when analysis. Samples were cut into strip shape (about 2.5 × 0.5 cm) using blade and fixed with double sided adhesive tape on a glass slide. Droplet was deposited on the flat surface avoiding the venation or trichomes of leaves. The θ was obtained from the first image after the deposition, and equilibrium state of a droplet. In case of the θ value keeps changing or spreading on the surface, last captured image was used to calculate the θ.

2.3 Calculation of surface free energy of solid

2.3.1 Zisman method

Zisman method allows to calculate the critical surface tension (γ_c) of a liquid that form a perfect wetting, 0° of θ on the food surface (Mostafavi, 2019). This γ_c is explained as surface free energy of solid surface, but this method is applicable for low energy systems having lower than 100 mN/m surface free energy (Zisman, 1964). The γ_c of a solid surface can be calculated with at least 2 liquids with known surface tension. The cosine of the measured contact angle from different liquid droplets are plotted against the liquid surface tension (γ_{LG}) and the γ_c is estimated by extrapolation to $\cos\theta = 1$ (θ = 0°). This method can only be applied to solid surface with dispersive component (Owen, 1969).

2.3.2 OWRK method

The Owens-Wendt-Rabel-Kaelble (OWRK) method assumes that the surface free energy of solid (γ_{SG}) is composed of two components, polar component (γ_{SG}^{p}) and dispersive component (γ_{SG}^{d}). At least 2 liquids with known values of polar and dispersive components are used to calculation. In this experiment, six liquids are selected as Table. 2.1. and data from five liquids are recorded to solve Eq. (1)

$$\frac{(1+\cos\theta)\gamma_{LG}}{2\sqrt{\gamma_{LG}^{d}}} = \sqrt{\gamma_{SG}^{p}} \cdot \sqrt{\frac{\gamma_{LG}^{p}}{\gamma_{LG}^{d}}} + \sqrt{\gamma_{SG}^{d}} \qquad (1)$$

where γ_{LG} is surface tension of liquid, γ_{LG}^{d} is dispersive component of liquid surface tension, γ_{LG}^{p} is polar component of liquid surface tension, γ_{SG}^{d} is dispersive component of solid surface free energy and γ_{SG}^{p} = polar component of solid surface free energy.

2.4 Roughness

Surface roughness was evaluated by using confocal laser scanning microscopy (LEXT OLS3100, Olympus Corporation, Tokyo, Japan) at magnification 10X. Samples were cut into strip shape using blade and fixed with double sided adhesive tape on a glass slide. Obtained image (1280 x 960 µm) was analyzed with the software LEXT (Olympus Corporation, Tokyo, Japan) and at least 3 images are taken for the roughness measurement. 7 roughness parameters were selected for amplitude and distance information. Amplitude parameters are divided in profile and areal parameters which are known as two-dimensional and three-dimensional roughness respectively, height of arithmetical mean height (*Ra* and *Sa*), root mean square height (*Rq* and *Sq*), maximum height (*Rz* and *Sz*). Distance parameter is mean width of profile elements (*RSm*) composed of peak and valley. The equations of these 7 parameters are described in the Table. 2.2. To analyze the profile parameters (*Ra*, *Rq*, *Rz* and *RSm*), 3 vertical lines and 3 horizontal lines are selected from each image, and to analyze the areal parameters (*Sa*, *Sq* and *Sz*), 5 squared areas (200 x 200 µm) were selected.

Table. 2.2. Profile and areal roughness parameters evaluated.

Evaluation target		parameter	equation	Reference
Profile length	*Ra*	arithmetical mean deviation of the profile	$Ra = \frac{1}{l}\int_0^l \lvert Z(x)\rvert dx$	KS B ISO4287 (2019) ISO 4287:1997
	Rq	Root mean square deviation of the assessed profile	$Rq = \sqrt{\frac{1}{l}\int_0^l Z^2(x)dx}$	
	Rz	Maximum heigh of profile	$Rz = Rp + Rv$	
	RSm	Mean width of the profile elements	$RSm = \frac{1}{m}\sum_{i=1}^{m} Xs_i$	
Area	*Sa*	Arithmetical mean height of scale limited surface	$Sa = \frac{1}{A}\iint_A \lvert Z(x,y)\rvert dxdy$	KS B ISO25178-2 (2017)
	Sq	Root mean square height of scale-limited surface	$Sq = \sqrt{\frac{1}{A}\iint_A Z^2(x,y)dxdy}$	
	Sz	Maximum height of scale-limited surface	$Sz = Sp + Sv$	

2.5 Statistical analysis

Measured data were analyzed using SPSS 26.0 (IBM, Chicago, IL, USA). Mean differences were compared using ANOVA (one-way analysis of variance) and multiple comparison was conducted using Scheffe's test. $P < 0.05$ was considered as statistically significant. To analyze the roughness parameters, the variables were compared using nonparametric Kruskal-Wallis one-way analysis of variance with stepwise step-down post hoc test as the data didn't meet the ANOVA assumption of normality.

3. Results and discussions

3.1 Contact angle

Contact angle of 6 test liquids are measured as shown in Table. 2.3. It turned out that 2-propanol was not an appropriate liquid for measuring contact angle on the food surface because it spread after the deposition therefore contact angle detection was not possible. Similar result was found in the contact angle measurement on the broccoli leaf surface (Rich and Boaz, 2018). Among the tested samples scallion was the least wettable surface for all test liquids showing highest contact angles. Gimbap has only a few data compared to other samples because it was difficult to measure the contact angles as the surface was wet by moisture from the inner ingredients and sesame oils on the surface. Fresh materials tend to have higher contact angle than the processed food except dried laver. Dried laver showed higher contact angle than other two processed food. It may be due to the sundae and gimbap are the cooked surfaces containing high moisture contents from the inner ingredients. Diiodomethane and formamide showed low contact angle on the food surface and glycerol and water showed high contact angle on the food surface.

Table. 2.3. Contact angle (CA) at equilibrium and time for equilibrium (EQT) from the deposition

		water		diiodomethane		ethylene glycol		formamide		glycerol		2-propanol	
		CA	EQT (s)	CA	EQT (s)	CA	EQT (s)	CA	EQT (s)	CA	EQT (s)	CA	EQT (s)
PR	ad	114.90 ± 7.38	2.89 ± 1.32	75.45 ± 7.02	1.84 ± 0.77	92.33 ± 8.62	7.29 ± 5.70	103.83 ± 11.23	4.29 ± 5.24	110.21 ± 9.93	6.84 ± 6.30	N/A	
	ab	81.13 ± 9.42	7.09 ± 5.36	54.17 ± 4.45	2.20 ± 1.18	60.96 ± 5.21	9.89 ± 5.26	69.45 ± 5.05	12.84 ± 10.81	84.09 ± 4.68	14.44 ± 7.43	N/A	
SC	tail	70.64 ± 12.32	8.51 ± 5.92	51.86 ± 7.48	2.67 ± 1.69	58.25 ± 9.60	13.86 ± 4.68	44.98 ± 19.13	11.38 ± 7.71	70.14 ± 12.26	17.34 ± 8.65	N/A	
	head	84.01 ± 10.72	6.22 ± 4.93	55.49 ± 4.76	2.22 ± 1.33	66.24 ± 12.70	5.96 ± 4.42	67.00 ± 7.01	5.44 ± 5.68	90.33 ± 8.75	9.24 ± 6.76	N/A	
BP		95.62 ± 4.24	6.00 ± 3.55	62.88 ± 4.23	2.33 ± 1.41	73.26 ± 5.40	8.24 ± 5.57	81.31 ± 4.98	6.87 ± 6.04	90.57 ± 4.20	8.91 ± 4.76	N/A	
RL	ad	91.04 ± 7.97	5.93 ± 5.12	53.01 ± 6.40	4.33 ± 5.31	64.1 ± 8.07	9.76 ± 5.38	66.98 ± 11.32	16.00 ± 9.03	74.32 ± 7.20	14.89 ± 7.70	N/A	
	ab	84.29 ± 9.48	7.22 ± 4.29	54.61 ± 6.35	2.91 ± 2.46	63.02 ± 8.21	9.87 ± 4.85	59.86 ± 10.49	12.73 ± 7.07	73.32 ± 9.75	16.47 ± 8.35	N/A	
SD		59.86 ± 18.39	18.89 ± 8.68	30.76 ± 7.97	9.02 ± 4.44	38.87 ± 8.09	27.20 ± 4.04	44.74 ± 7.61	25.70 ± 6.02	47.90 ± 7.50	25.60 ± 4.88	N/A	
LV	DL	94.62 ± 11.42	4.14 ± 3.98	41.01 ± 4.11	1.78 ± 0.94	40.33 ± 3.54	5.52 ± 2.61	49.14 ± 6.45	4.73 ± 4.12	-	-	N/A	
	GB	29.48 ± 5.82	28.80 ± 0.45	17.95	9.00	28.27 ± 2.62	22.80 ± 3.56	-	-	49.21 ± 10.40	20.67 ± 3.51	N/A	

PR = perilla; SC = Scallion; BP = bell pepper; RL=red lettuce; SD = sundae; LV = laver; ad = adaxial; ab = abaxial; DL = dried laver; GB = gimbap

N/A = not applicable

Number of droplets deposited on the surface is 45 except ethylene glycol (44) and Glycerol (44) on adaxial side of perilla, ethylene glycol (30) and formamide (30) on abaxial side of red lettuce, ethylene glycol (41) and formamide (40) on sundae, water (29), diiodomethane (32), ethylene glycol (31) and formamide (26) on dried laver and water (5), diiodomethane (1), ethylene glycol (5) and glycerol (3) on gimbap.

3.2 Wettability

3.2.1 Zisman method

Zisman method was used to estimate the critical surface tension (γ_c) of six foods surfaces. In the Fig. 2.1., cosine values of contact angles of test liquids are plotted as function of the surface tension of liquid used. The extrapolation to the $\cos\theta = 1$ from measured values are expressed in the graph. When $\cos\theta = 1$, the surface tension of the liquid that can wet completely the surface is shown. laver had the highest critical surface tension (γ_c = 43.63 mN/m) among the tested foods, followed by sundae (γ_c = 35.81 mN/m) and the scallion had the lowest critical surface tension (γ_c = 6.93 mN/m), indicating that scallion is a surface difficult to be wet and laver and sundae are easy to be wet. Gimbap showed negative value (γ_c = -19.02 mN/m) this is because Zisman method counts only dispersive component of the solid surface and the polar components are not considered on the solid-liquid interface interaction, therefore, the calculated critical surface tension need to be interpreted carefully because the food surfaces including the plant surfaces have the polar component of surface energy.

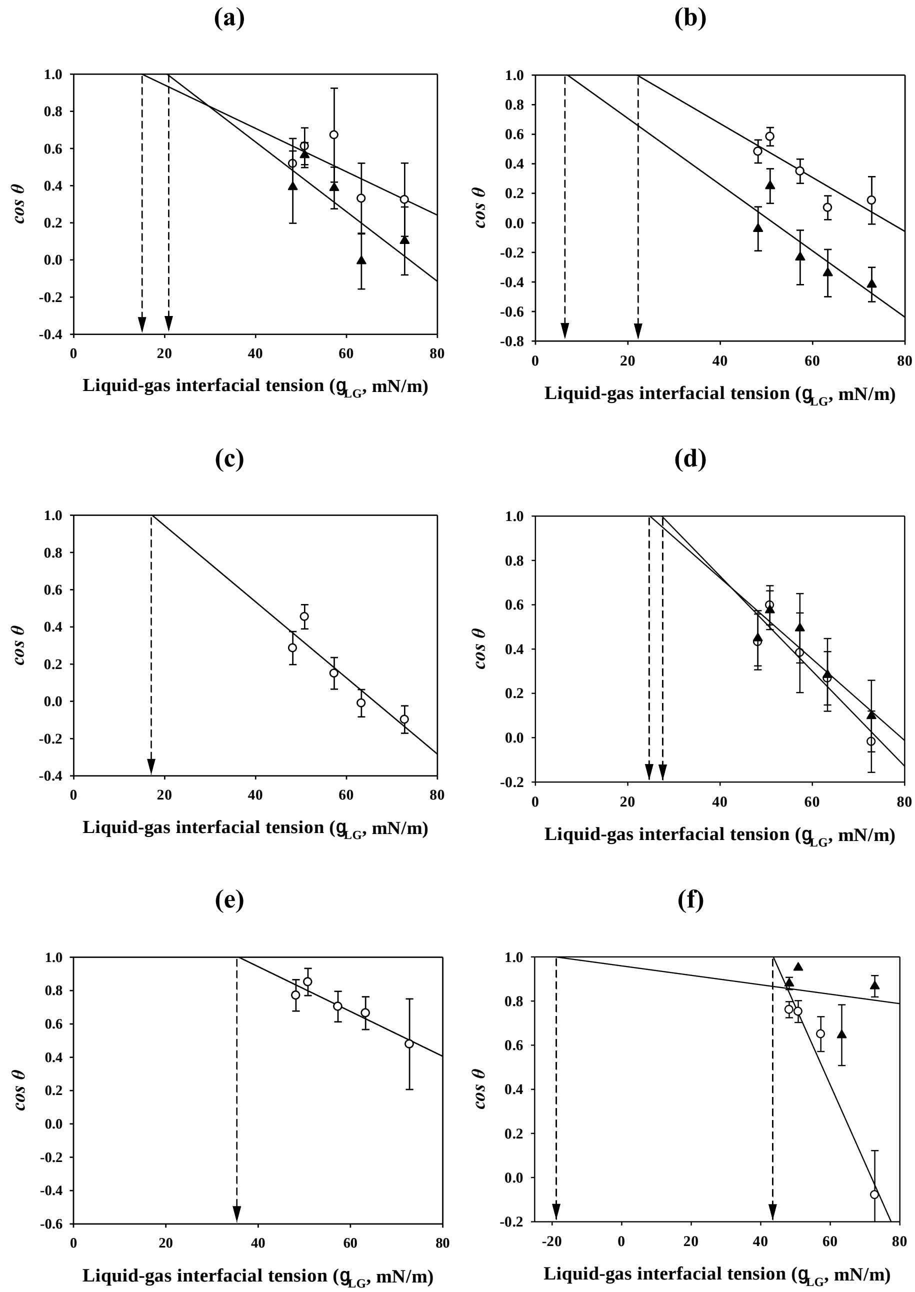
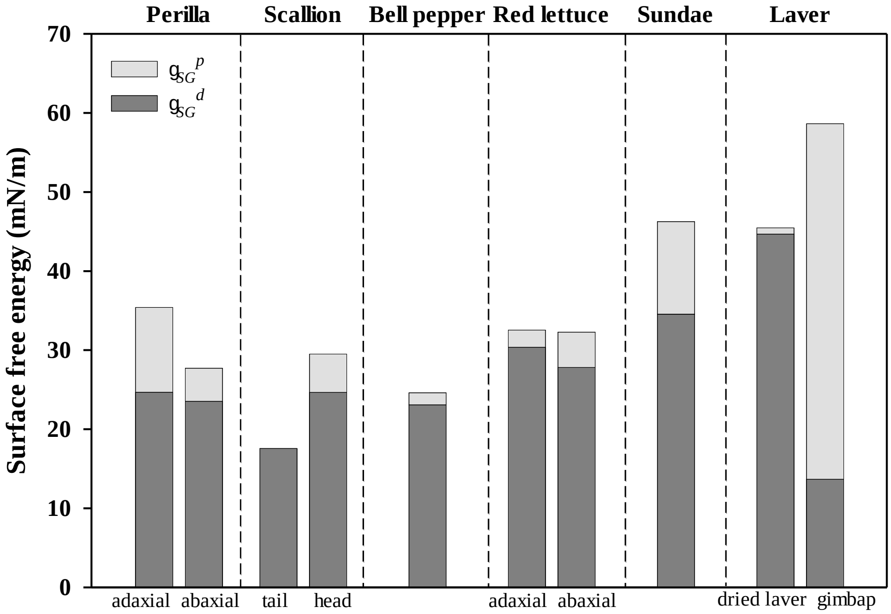


Fig. 2.1. Zisman plot to estimate the critical surface tension (γ_c) of foods. (a) perilla (○: adaxial, γ_c = 14.99 mN/m; ▲: abaxial, γ_c = 20.52 mN/m), (b) scallion (○: tail, γ_c = 6.93 mN/m; ▲: head, γ_c = 21.98 mN/m), (c) bell pepper (γ_c = 17.25 mN/m), (d) red lettuce (○: adaxial, γ_c = 27.37 mN/m; ▲: abaxial, γ_c = 24.80 mN/m), (e) sundae (γ_c = 35.81 mN/m), (f) laver (○: dried laver, γ_c = 43.63 mN/m, ▲: gimbap, γ_c = -19.02 mN/m)

3.2.2 OWRK method

Surface free energy of 6 food surfaces showed that they are composed of 70% to 100% of dispersive component which means relatively high non-polar and hydrophobic surface. The adaxial side of perilla had the highest polar component, 30% (10.72 mN/m), indicating the most hydrophilic surface and the scallion tail and laver surface had no or little polar components (0.00 and 0.14 mN/m respectively). Laver and sundae had high surface free energy of 46.33 ~ 58.71 mN/m and scallion tail had the lowest surface free energy of 17.61 mN/m. Therefore, sundae and laver surfaces can be determined as highly wettable surfaces and scallion tail as hard to wet surface. even though the result of Zisman method doesn't explain the polar interaction of the interface, both Zisman and OWRK method shows common result which is that the processed food had higher surface energy than fresh food surfaces, being more easy to wet. This difference probably comes from the damaged surface because the sundae and laver had to go through production process which includes washing, drying or heating.

Fig. 2.2. Surface free energy of foods calculated by OWRK method. Polar (γ_{SG}^{p}), and dispersive (γ_{SG}^{d}) components.



3.3 Roughness

Result of roughness of height parameters (*Ra*, *Rq*, *Rz*, *Sa*, *Sq* and *Sz*) analysis are listed in Table 2.4. And mean width (*RSm*) of surface elements is shown in Table 2.5. Amplitude roughness parameters shows that generally laver, bell pepper had lowest value in roughness and adaxial side of red lettuce had the highest value indicating that the laver and bell pepper are relatively smooth surface than other food surfaces. To be in detail, Sa shows that laver, bell pepper and scallion tail had the lowest value followed by abaxial side of perilla. Sundae and abaxial side of red lettuce had significantly bigger value than abaxial side of perilla and smaller than adaxial side of red lettuce but there was no significant difference with scallion head and adaxial side of perilla. Sq had the values laver, scallion tail bell pepper < abaxial side of perilla < red lettuce (abaxial), sundae < red lettuce (adaxial), but red lettuce (abaxial) and sundae did not show significant difference from scallion head and perilla (adaxial). In *Sz*, scallion tail, laver, bell pepper had the lowest value among tested surfaces. Perilla (adaxial) showed the lowest value. *Ra* and *Rq* showed same result in mean difference, laver and bell pepper was the smoothest surface followed by perilla (abaxial). Perilla (adaxial) is the second highest valued surface but not significantly different from sundae, red lettuce (abaxial) and scallion head. *Rz* showed that perilla (abaxial), laver and bell pepper was significantly lower than perilla (adaxial), scallion head, red lettuce (abaxial) and sundae. Red lettuce had the most high value.

In *RSm* data, 3 to 6 images are used for analysis. Scallion tail had 4 captured images but one set (3 X axis and 3 Y axis) of an obtained image is not included in analysis due to there was an abnormal outlier showing over than 400 μm. The adaxial side of perilla leaf showed lowest value among other food surfaces and the surface of scallion tail showed highest value which means that the distance of the profile elements (peak and valley) of perilla (adaxial) are tightly arranged while those elements of scallion tail are loosely arranged. Adaxial side of red lettuce leaf has the second lowest value after perilla (adaxial), and significantly lower than sundae and bell pepper, but not significantly different from the abaxial side of perilla, the abaxial side of red lettuce, laver (both dried and used for gimbap) and scallion head. Bell pepper had the second highest value following the scallion tail showing significantly higher than perilla and red lettuce, but not significantly different from sundae, laer and scallion head. Among food surfaces, both part of scallion (tail and head) showed big standard deviation (58.32 ± 30.57 and 33.23 ± 18.24 μm respectively) even though a set having outlier was not included. This may be affected by the surface pattern which is arranged in parallel as shown in Fig. 2.3. shows the food surface textures. Fresh foods have a cell pattern in polygonal shape. Scallion head has the elongated cells are displayed on the surface in parallel. Porcine intestines are the natural casing material for sundae to pack the stuffing. In processing step some crevices and deformation can be made. The relatively high standard deviation through the amplitude parameter maybe from these irregular scratches on the surface and it is also noticed in the Fig.2.3. (e).

Table. 2.4. Result of surface profile and areal roughness in amplitude parameters

		Profile parameters				Areal parameters			
		Ra **(μm)**	***Rq*** **(μm)**	***Rz*** **(μm)**	***n***	***Sa*** **(μm)**	***Sq*** **(μm)**	***Sz*** **(μm)**	***n***
Perilla	adaxial	10.39 ± 1.66 [d]	13.09 ± 2.09 [d]	82.21 ± 14.43 [b]	30	10.12 ± 1.72 [d]	12.77 ± 2.07 [d]	100.29 ± 13.04 [c]	25
	abaxial	7.75 ± 0.92 [b]	9.90 ± 1.14 [b]	63.97 ± 5.83 [a]	18	6.43 ± 1.08 [b]	8.38 ± 1.30 [b]	79.57 ± 10.02 [b]	15
Scallion	tail	8.96 ± 4.46 [bc]	10.92 ± 4.89 [bc]	64.42 ± 27.42 [a]	24	4.75 ± 1.25 [a]	6.31 ± 1.81 [a]	71.13 ± 27.01 [ab]	20
	head	11.60 ± 6.27 [cd]	14.54 ± 7.09 [cd]	93.57 ± 26.06 [b]	30	7.81 ± 2.32 [bc]	10.54 ± 2.95 [c]	111.23 ± 20.49 [c]	25
Bell pepper		5.39 ± 1.15 [a]	7.18 ± 1.47 [a]	55.63 ± 14.87 [a]	24	5.01 ± 1.49 [a]	6.62 ± 1.72 [a]	78.61 ± 17.49 [b]	20
Red lettuce	adaxial	17.56 ± 3.89 [e]	21.70 ± 4.68 [e]	118.98 ± 27.35 [c]	18	16.69 ± 5.36 [e]	20.33 ± 5.85 [e]	131.75 ± 23.71 [d]	15
	abaxial	10.46 ± 3.02 [cd]	13.55 ± 3.73 [cd]	90.33 ± 20.02 [b]	18	10.06 ± 3.49 [cd]	13.24 ± 4.55 [cd]	114.63 ± 27.65 [c]	15
Sundae		11.05 ± 6.31 [bcd]	14.06 ± 7.34 [bcd]	90.58 ± 30.72 [b]	36	9.24 ± 4.97 [cd]	12.21 ± 5.99 [cd]	108.75 ± 33.68 [c]	30
Laver	dried laver	5.14 ± 1.82 [a]	6.94 ± 2.46 [a]	52.26 ± 15.68 [a]	18	3.96 ± 1.77 [a]	5.35 ± 2.29 [a]	62.86 ± 19.59 [a]	15
	gimbap	5.20 ± 1.56 [a]	6.95 ± 1.98 [a]	57.19 ± 13.90 [a]	18	3.97 ± 1.12 [a]	5.62 ± 1.49 [a]	75.02 ± 11.44 [b]	15

Ra and Sa, arithmetical mean height; Rq and Sq, root mean square height; Rz and Sz, maximum height.

n is the number of profile (X and Y axis) used for analysis.

Data are shown as mean ± SD. Different letters on data indicate significant differences between groups ($p < 0.05$).

Table. 2.5. Result of surface profile roughness parameter for mean width of profile elements.

		RSm (μm)	*n*
Perilla	adaxial	19.80 ± 2.20 [a]	30
	abaxial	24.72 ± 3.20 [bc]	18
Scallion	hail	58.32 ± 30.57 [e]	18
	head	33.23 ± 18.24 [bcd]	24
Bell pepper		33.43 ± 10.64 [d]	24
Red lettuce	adaxial	23.10 ± 2.53 [b]	18
	abaxial	24.74 ± 4.89 [bc]	18
Sundae		28.17 ± 5.75 [cd]	36
Laver	dried laver	30.30 ± 10.81 [bcd]	18
	gimbap	25.71 ± 4.90 [bcd]	18

Data are shown as mean ± SD. n is the number of profile (X and Y axis) used for analysis.

Different letters on data indicate significant differences between groups ($p < 0.05$).

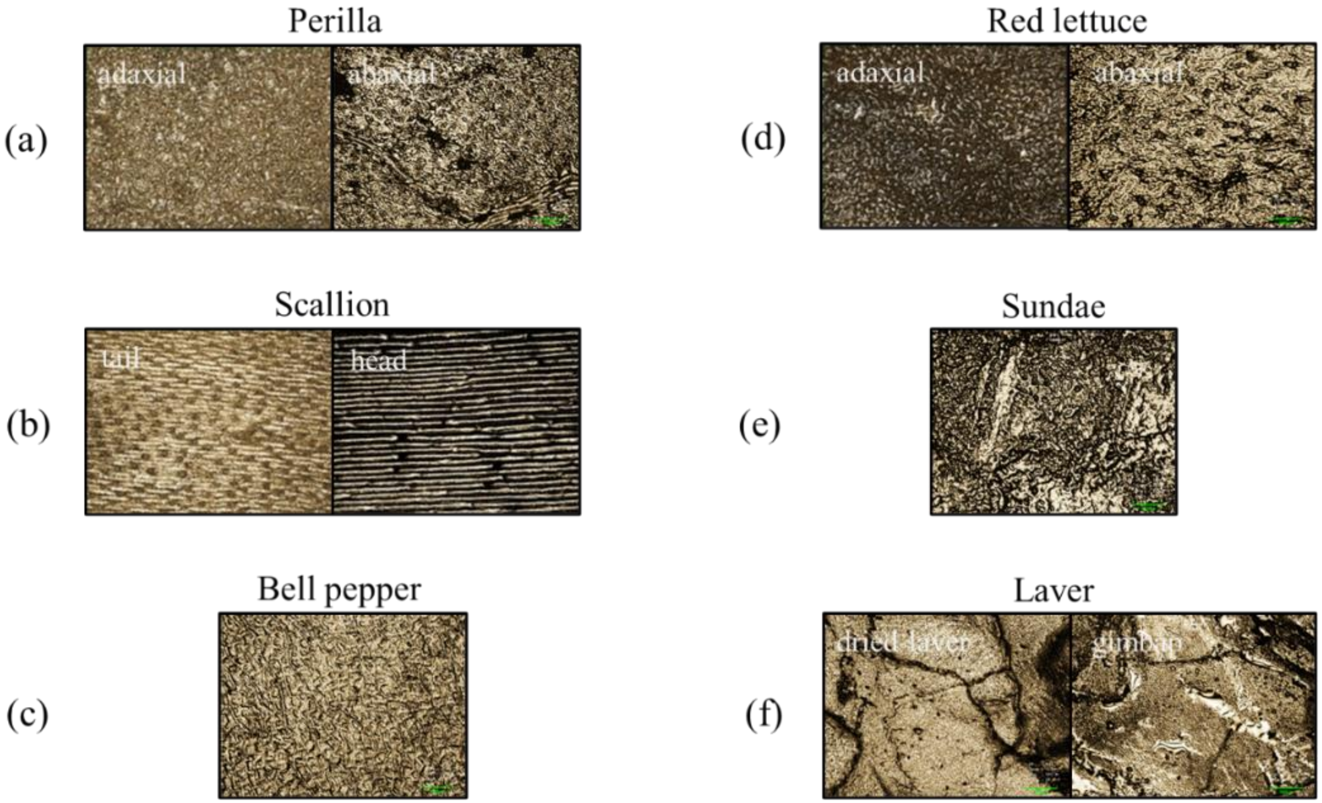


Fig. 2.3. 2D surface image (grayscale) obtained by CLSM

4. Conclusions

Surface energy and roughness of six popular food products (perilla, scallion, bell pepper, red lettuce, sundae, and laver) were analyzed. To determine the SFE, static contact angles of six liquids (water, diiodomethane, 2-propanol, ethylene glycol, formamide, and glycerol) were measured on the food surfaces and analyzed with Zisman method and OWRK method. To determine the surface roughness was analyzed with two types of parameter, amplitude and distance parameters. Profile and areal roughness of amplitude parameters, such as arithmetical mean height (*Ra* and *Sa*), root mean square height (*Rq* and *Sq*), maximum height (*Rz* and *Sz*), and mean width of profile elements (*RSm*) for distance parameter, were measured by confocal laser scanning microscopy. Laver and sundae showed high SFE (45.5 ~58.7 mN/m), while scallion tail had the lowest value (17.61 mN/m), indicating that sundae had the strongest tendency to interact with foreign matters among the tested foods and scallion tail had the lowest tendency. Sundae and perilla (adaxial) showed very high polar SFE (11.72 and 10.72 mN/m, respectively), indicating the strong tendency to interact with polar foreign matters, while scallion tail, laver and bell pepper had the lowest polar SFE (0, 0.14 and 1.54 mN/m respectively).

These results indicate that the surfaces of fresh foods have lower surface energy than processed food, being less wettable surface. The red lettuce (adaxial) showed relatively high surface roughness values, whereas the laver, perilla (adaxial), and bell pepper showed relatively low values. The results obtained in this study provide information useful to understand the surface characteristics of the six widely consumed food products.

Chapter 3

Correlation between food surface properties and adsorption of foreign matters

1. Introduction

From the previous chapter, surface energy and roughness of six widely consumed foods (perilla, scallion, bell pepper, red lettuce, sundae, and laver) are analyzed. The result indicates that the tested food surfaces are low energy surfaces and fresh foods have lower surface energy than processed food, therefore being less wettable. While processed foods, sundae and laver, showed higher surface energy so they are expected to interact more with foreign matters than fresh foods. For the roughness of food surfaces, amplitude and distance parameters were used and the result indicates that the red lettuce (adaxial) showed relatively high values in amplitude roughness value and middle in distance roughness value, whereas the laver, perilla (adaxial), and bell pepper showed relatively low values in amplitude roughness and the distance roughness were lowest in perilla and laver and bell pepper were similar to the red lettuce.

On the surface of food, many foreign matters such as chemicals and miroorganisms can be attached. Considering the circular food system, foods go through production, processing, retail and consumer stages to be finally consumed (Thakali and MacRae, 2021). The particulate matter (PM) is a term referring to mixed substances of solid and liquid (Popek et al., 2015). The composition, size and emission source vary between locations and time. The size of PM is ranging from 0.01 to 100 μm aerodynamic diameter (AQEG, 2005), and generally classified as coarse particle for diameter from 2.5 to 10 μm, fine particle from 0.1 to 2.5 μm and ultrafine particle smaller than 0.1 μm in diameter (Beckett et al., 1998; Oberdörster and Utell, 2002). It is well known that PM penetrate into the human body through respiratory tract and the particles having less than 10 μm in diameter can have impact on human health and also PM can be entered to the gastrointestinal tract by intaking contaminated food, and those PM can have adverse effects such as altering gut microbiota and immune function and development of gastrointestinal inflammatory diseases (Salim et al., 2014). However, little is known about the interactions of PM with food surface.

Chitosan is often used to from protective edible coating on the surface of fresh produce, because it is a nontoxic, biocompatible and biodegradable biopolymer having fungicidal activity and the ability to elicit plant defense responses (Ali et al. 2011 and 2012; Lin and Zhao 2007).

The objective of this chapter is to investigate the effects of the surface properties of the foods on the adhesion of PM and chitosan solution. The adhesion of PM and chitosan solution to the real food surfaces were determined by the amount of adsorbed PM on the food surface and the wettability of coating solution, respectively, followed by statistical analysis to correlate the adhesion and the food surface properties.

2. Materials and methods

2.1. Materials

2.1.1. Food surfaces

Four fresh foods, perilla (*Perilla frutescens* Britton), scallion (*Allium fistulosum* L.), red lettuce (*Lactuca sativa* L.), bell pepper (*Capsicum annum* L.) are obtained from local supermarkets and prepared as described in section 2.1.1 and 2.1.2 of Chapter 2.

2.1.2 Chitosan

Three chitosan products with different molecular weights (low, medium and high, based on the viscosity) were purchased from TCI (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) for chitosan solution. The detailed information of used products can be seen in Table. 3.1.

Table. 3.1. Specification information of chitosan used in the experiments

	Low molecular weight (5-20 mPa·s)	Medium molecular weight (20-100 mPa·s)	High molecular weight (200-600 mPa·s)
Deacetylation value	81.1%	85.6%	83.5%
Viscosity	5 mPa·s	30 mPa·s	570 mPa·s

Data is from certificate of analysis provided by TCI (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan). Viscosity measurement condition is 0.5% in 0.5% acetic acid at 20°C

2.2. Adhesion of particulate matter on food surface

The PM dispersion experiments are conducted by Food Processing Laboratory (Chung-Ang University, Anseong, Korea) and the result of PM adhesion amount data is used as variables for the statistical analysis, Spearman's correlation.

2.2.1. PM dispersion in chamber

On the surface of bell peppers, model PM (ISO 12103-1 A1 Ultrafine Test Dust, Powder Technology Inc., Arden Hills, MN, USA) was deposited using particulate matter dispersion chamber. Samples were exposed to PM at a concentration of 300 μg /m^3 in the chamber for 30, 60, 90 and 120 min to quantify the PM adhesion amount on the food surfaces. Airflow in the chamber was made by injecting N2 gas through a pipe connected to bottom part of the chamber. The PM concentration in the chamber was measured every 15 min with a particle measuring device (BQ20, Trotec GmbH, Heinsbergh, Germany) and the model PM was added with N_2 gas through a pipe connected to upper part of the chamber when the concentration was decreased. For SEM measurements, samples were collected after the PM exposure and cut into squares shape of 0.5 × 0.5 cm and attached to an aluminum plate with double side adhesive carbon tape. Then the plate was covered with the petri dish to prevent dust contamination falling from the air while it was being dried for 12 h in desiccator at 23 ~ 25°C and 25 ~ 30% relative humidity. Samples adhered on aluminum plate were attached to aluminum stub with double side adhesive carbon tape and coated with Platinum for increasing the electrical conductivity. Prepared samples were examined by Scanning electron microscope (S-3400N, Hitachi High-Tech Corporation, Tokyo, Japan) and three micrographs per 0.5 × 0.5 cm square piece were randomly selected at 500× under 10 kV acceleration voltage.

2.2.2. PM particle size measurement

Fig. 3.1. illustrates the particle size distribution of model PM analyzed by laser diffraction particle sized analyzer (1190LD, CILAS, Orleans, France) and the particle size distribution is based on the Fraunhofer theory.

2.3. Adhesion of chitosan edible coating solution on food surface

2.3.1 Preparation of chitosan solution

Nine types of chitosan solutions were made for adhesion analysis. 0.5% 1.0% and 1.5% (w/w) chitosan flakes were dissolved in 0.7% (w/w) acetic acid to make the different concentration of chitosan solution for each molecular weight. In total 10 solutions are prepared including 0.7% acetic acid and 3 different concentration of chitosan for each molecular weight.

2.3.2 Surface tension measurement

The surface tension (γ_{LG}) of prepared solutions was measured by Du noüy ring method (K100, KRÜSS GMbH, Hamburg, Germany), and each solution was measured triplicate at 20°C under atmospheric pressure. Each solution was poured into a glass vessel and the measurement was conducted according to the procedure of the tensiometer. Before every measurement, the platinum ring was rinsed by ethanol and distilled water then cleaned by flaming (Shahbaz et al., 2012).

2.3.3 Contact angle measurement

A volume of 6 ml of droplet was placed on the surface and contact angle

(θ) was measured by sessile drop method as described in the previous Section 2.2 of Chapter 2.

2.3.4 Wettability of the solution

Work of adhesion (W_a, mN/m) between the food surface and a solution and spreading coefficient (W_s, mN/) were determined according to Eqs. (1) and (2)

$$W_a = \gamma_{\mathrm{LG}}(1 + \cos\theta) \quad (1)$$

$$W_s = \gamma_{\mathrm{LG}}(\cos\theta - 1) \quad (2)$$

2.4 Statistical analysis

Data were analyzed using SPSS 26.0 (IBM, Chicago, IL, USA). Mean differences were compared by using nonparametric Kruskal-Wallis one-way analysis of variance with stepwise step-down post hoc test as the data did not meet the ANOVA assumption of normality. (Correa et al., 2015; Nahm, 2016)

Spearman's correlation coefficient was used to determine the relationship between the variables of food surface properties and the adhered foreign matter. The used variables are listed in Table. 3.2. Simple linear regression used to investigate the direction and strength of the relationship between surface properties and adhesion.

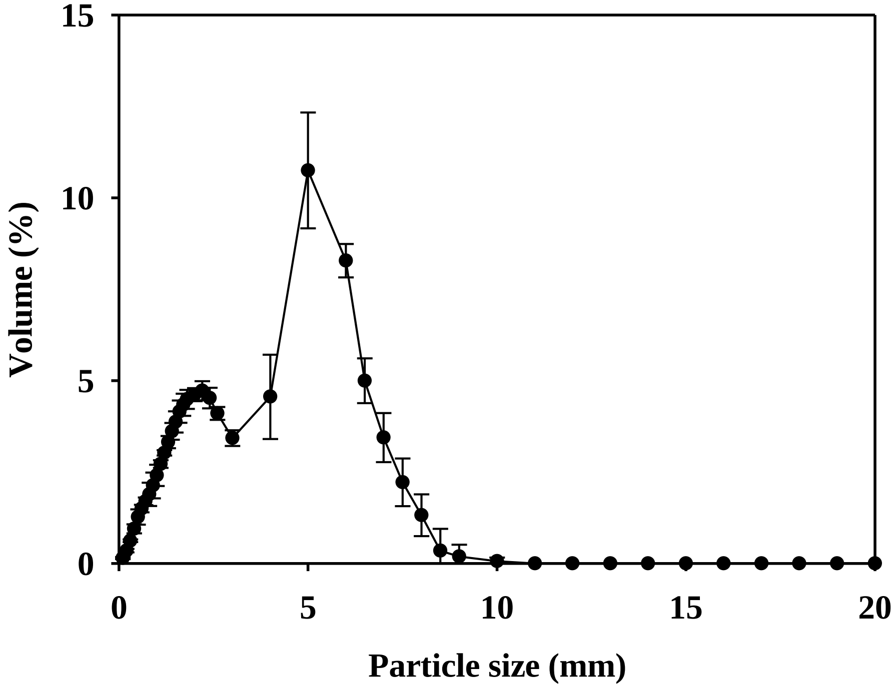


Fig. 3.1. Particle size distribution of model particulate matter (A1 Ultrafine Test Dust, Powder Technology Inc., Arden Hills, MN, USA) .

Table. 3.2. Values of surface wettability and roughness parameters obtained for perilla (adaxial), red lettuce (adaxial), and bell pepper, which were correlated to the amount of PM adhered to the surfaces of the foods

		Surface wettability parameters (mN/m)				Surface roughness parameters (μm)						
		γ_{SG}^{p}	γ_{SG}^{d}	γ_{SG}	γ_{c}	***Sa***	***Sq***	***Sz***	***Ra***	***Rq***	***Rz***	***RSm***
Perilla	adaxial	10.72	24.73	35.45	14.99	10.12	12.77	100.29	10.39	13.09	82.21	19.80
Red lettuce	adaxial	2.18	30.42	32.60	27.37	16.69	20.33	131.75	17.56	21.70	118.98	23.10
Bell pepper		1.54	23.13	24.67	17.25	5.01	6.62	78.61	5.39	7.18	55.63	33.43

3. Results and discussions

3.1. Particulate matter adhesion

The data provided by Food Processing Laboratory (Chung-Ang University, Anseong, Korea), adhesion of model PM (A1 Ultrafine Test Dust) on food surfaces is illustrated in Fig. 3.2. Perilla surface showed the least PM deposition on the surface during 2 h of exposure for 30, 60, 90 and 120 min in chamber and the PM deposition was 8.67, 11.50, 16.33 and 17.33 ($\times 10^5/cm^2$) respectively. Bell pepper was the most PM deposited surface showing about 19 to 23 times more PM than perilla for same exposure time, 161.33, 222.17, 327.33 and 396.33 ($\times 10^5/cm^2$) respectively. Red lettuce did not have as much as bell pepper but had large number of PM about 7 to 17 times more than perilla had for 2 h, 59.00, 116.83, 150.67 and 286.50 ($\times 10^5/cm^2$) respectively. The hourly increase was calculated by the slope and the PM were deposited on the perilla, red lettuce and bell pepper surfaces more PM of 6.17, 143.27 and 162.03 respectively per hour from first measurement.

Using the PM deposition data, Spearman's correlation test was used to determine the relationship with food surface properties (Table. 3.2.). In the table 3.3., Spearman's factor and numerical values are listed as a result. It revealed that between PM adhesion and surface free energy (γ_{SG}) and between PM adhesion and polar component (γ_{SG}^{p}) had negative relationship ($p < 0.01$). Also, the hourly increase of PM was negatively related with γ_{SG} and γ_{SG}^{p}. These indicate that the higher γ_{SG} and γ_{SG}^{p}, the less PM adhesion on the surface. Among the roughness parameters, distance parameter (*RSm*) which explains the mean width of profile elements had the positive relationship with PM adhesion in every exposure time and the hourly increase. This means that the wider mean width, the more PM adhesion on the surface. Spearman's correlation coefficient revealed no correlation between surface roughness amplitude parameters (Sa, Sq, Sz, Ra, Rq and Rz) and PM adhesion. Fig. 3.3., 3.4. and 3.5. illustrate the relationship between PM adhesion and γ_{SG} and γ_{SG}^{p} and *RSm* respectively.

In Chapter 2, we expected that the surface with higher surface energy or rough surface would affect the foreign matter adhesion on the food surface (Chen et al., 2017; Kranjc et al., 2018, Wang et al., 2009; Wang et al., 2014). The results of correlation coefficient are quite interesting that the surface with high surface free energy and polar component had less PM on the surface. This may be because of roughness which can has much bigger effect than that of surface free energy, so the effects are screened. The effect of *RSm* can be explained by considering the roughness feature and particle size ratio (Katainen et al., 2006; Kumar et al., 2013). There are two cases, one is that particle is much larger than surface feature, and the other is that the particle is similar or smaller than surface feature. In the latter case, adherend will be located between the peaks with more contact points and in the former case, particle adhesion is depend on the particle size as the bigger particle size will contact with more peaks. Model PM (A1 Ultrafine Test Dust) has the particle size (D90, 5.76 ± 0.20 μm) smaller than the surface feature mean width which had the range from 19.80 to 33.43 μm, therefore the particle would deposit on a space between the peaks and on the surface with higher *RSm* value, the particle can place in the deeper valley. Similar result are shown in a research of diatoms attachment on microtextured surface (Scardino et al., 2006). Significantly higher numbers of diatoms are found on the surface with the highest numbers of attachment points and lower number of attachment points resulted reduced attachment.

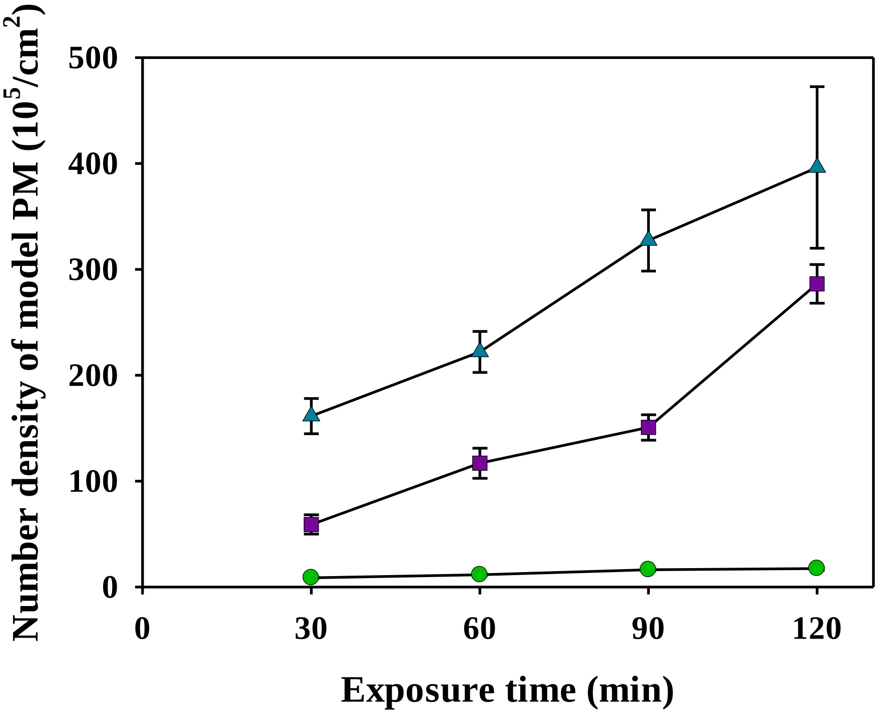


Fig 3.2. Number density of model PM (A1 Ultrafine Test Dust) deposited on food surfaces (perilla, ●; red lettuce, ■; bell pepper, ▲) during 2 h exposure in chamber. The data is provided by Food Processing Laboratory (Chung-Ang University, Anseong, Korea).

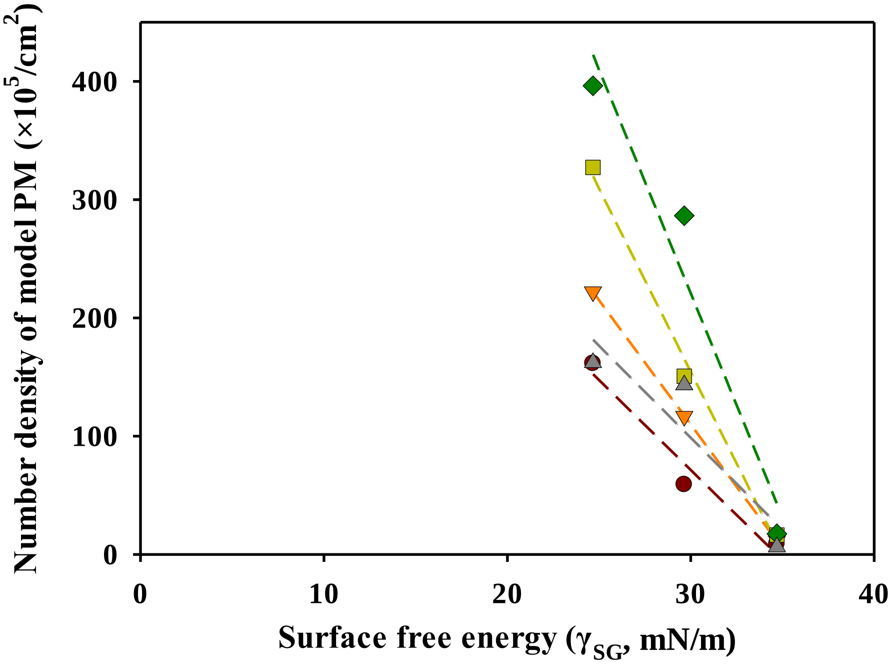


Fig. 3.3. Linear regression analysis between the total surface free energy (γ_{SG}, mN/m) of food samples and number density of model PM ($\times 10^5/cm^2$) at different exposure time (30 min, ●; 60 min, ▼; 90 min, ■; 120 min ◆; slope, ▲). γ_{SG} values: perilla = 34.70 mN/m; red lettuce = 29.65 mN/m; bell pepper = 24.67 mN/m.

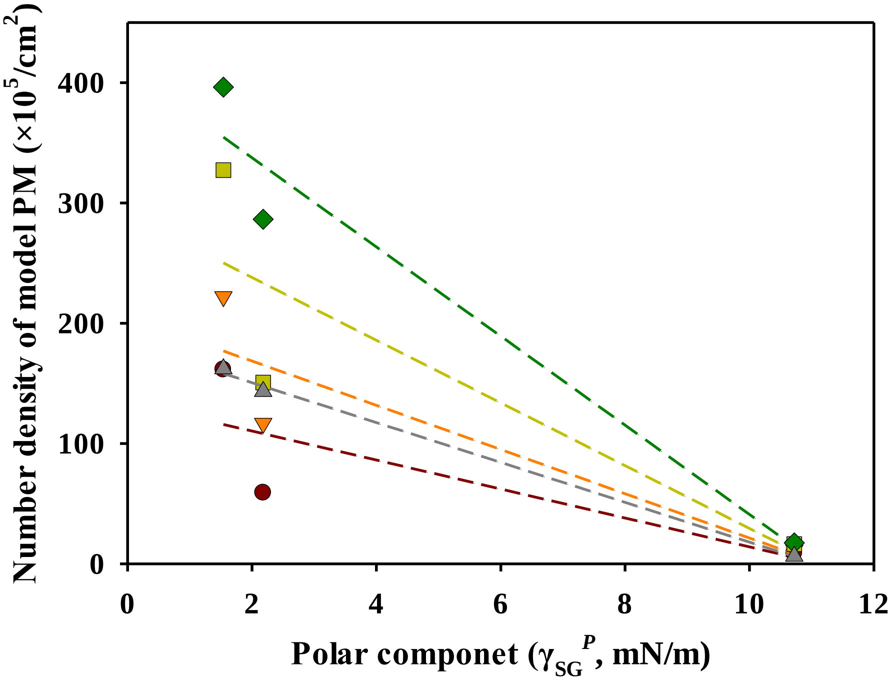


Fig. 3.4. Linear regression analysis between the polar component of surface free energy (γ^{p}_{SG}, mN/m) of food samples and number density of model PM ($\times 10^5/cm^2$) at different exposure time 30 min, ●; 60 min, ▼; 90 min, ■; 120 min ◆; slope, ▲). γ^{p}_{SG}, values: perilla = 10.72 mN/m; red lettuce = 2.18 mN/m; bell pepper = 1.54 mN/m

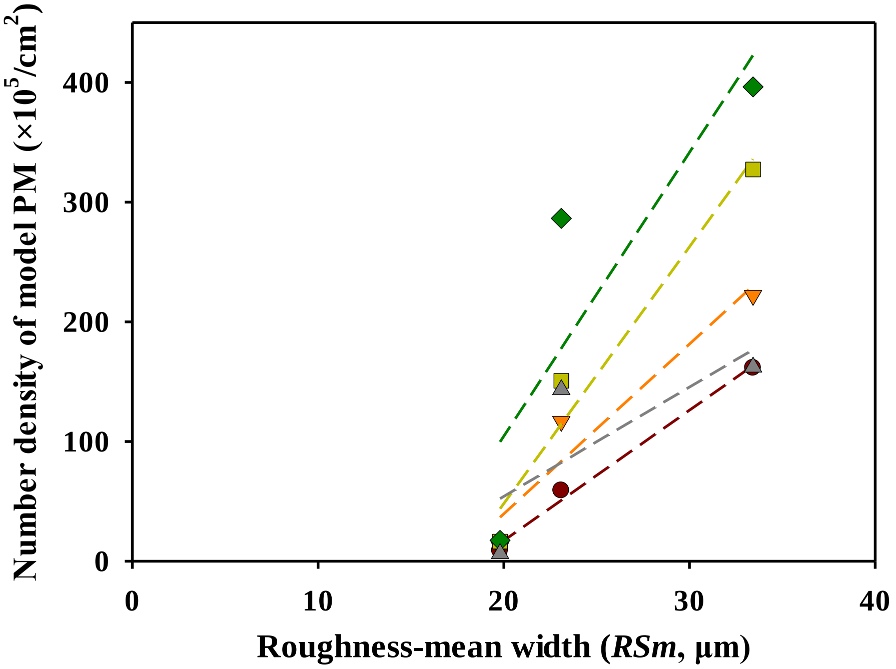


Figure. 3.5. Linear regression analysis between the surface mean width (*RSm*) parameter of food samples and number of model PM (A1 Ultrafine Test Dust) at different exposure time (30 min, ●; 60 min, ▼; 90 min, ■; 120 min ◆; slope, ▲). *RSm* values: perilla = 19.80 µm; red lettuce = 23.10 µm; bell pepper = 33.43 µm.

Table. 3.3. Spearman correlation coefficient values for factors of surface properties and particulate matter adhesion.

Factors		0.5 h	1.0 h	1.5 h	2.0 h	slope
Wettability	γ_{SG}^{p}	-1.00**	-1.00**	-1.00**	-1.00**	-1.00**
	γ_{SG}^{d}	-0.50	-0.50	-0.50	-0.50	-0.50
	γ_{SG}	-1.00**	-1.00**	-1.00**	-1.00**	-1.00**
	γ_c	-0.50	-0.50	-0.50	-0.50	-0.50
Roughness	***Sa***	-0.50	-0.50	-0.50	-0.50	-0.50
	Sq	-0.50	-0.50	-0.50	-0.50	-0.50
	Sz	-0.50	-0.50	-0.50	-0.50	-0.50
	Ra	-0.50	-0.50	-0.50	-0.50	-0.50
	Rq	-0.50	-0.50	-0.50	-0.50	-0.50
	Rz	-0.50	-0.50	-0.50	-0.50	-0.50
	Rsm	1.00**	1.00**	1.00**	1.00**	1.00**

**. Correlation is significant at 0.01 level (2-tailed)

3.2. Chitosan edible coating adhesion

3.2.1. Surface tension measurement

Table. 3.4. shows the surface tension (γ_{LG}) of water and chitosan solution (0, 0.5, 1.0 and 1.5%). The water surface tension is known as 72.8 mN/m (Janczuk et al., 1993) at 20°C. Chitosan with low molecular weight showed decreasing tendency in γ_{LG} value with increase of chitosan concentration. Medium molecular weight chitosan did not show significant difference in γ_{LG} value as the concentration increases. The γ_{LG} of high molecular weight chitosan slightly increased with the concentration. In all concentration, low molecular weight had significantly lower γ_{LG} than other molecular weight, indicating that the low molecular weight chitosan served as a surfactant to reduce the γ_{LG}.

Choi et al (2002) reported that the surface tension of 1.5% chitosan solution dissolved in lactic acid was 61.5 mN/m which is in the range of this experiment (43-70 mN/m). For a specific concentration, solution with higher molecular weight aggregates easier and more inter-molecular interaction occurs so the cohesive energy increases to larger surface tension (Gao & Wan, 2006; Zhong et al., 2019).

Table. 3.4. The surface tension of the chitosan solution. Different letters indicate the significant difference ($p < 0.05$).

Solution		Surface tension (mN/m)
Water		72.8
Acetic acid	0.7%	68.69 ± 0.61 [c]
Chitosan (5-20 mPas)	0.5%	52.36 ± 2.65 [b]
	1.0%	54.56 ± 3.13 [b]
	1.5%	43.13 ± 4.47 [a]
Chitosan (20-100 mPas)	0.5%	68.13 ± 0.96 [c]
	1.0%	67.43 ± 2.78 [c]
	1.5%	66.17 ± 1.40 [c]
Chitosan (200-600 mPas)	0.5%	69.66 ± 0.06 [c]
	1.0%	70.09 ± 0.04 [d]
	1.5%	70.43 ± 0.05 [e]

3.2.2 Contact angle measurement

Contact angles (θ) of chitosan solution reflect its wettability on different food surfaces. The result can be seen in Table. 3.5. The θ values of water, 0% (acetic acid 0.7%), 0.5% and 1.0% concentration of low, medium and high molecular weight chitosan solution and 1.5% concentration of low and medium molecular weight chitosan solution was analyzed. 1.5% high molecular weight chitosan was prepared with other concentrations but deposition of the droplet on the surface without containing any bubble inside was hard therefore 1.5% high molecular weight contact angle is not included in the data. Contact angle data were analyzed by Kruskal-Wallis test was conducted for each sample to compare the mean difference and the result showed that there are significant differences between the solutions ($p < 0.05$) except the red lettuce adaxial side ($p > 0.05$). The θ values of water and chitosan solutions showed no significant differences on the red lettuce. Post-hoc test are continued when the Kruskal-Wallis test had significant result to compare the mean differences between groups.

On the adaxial side of perilla leaf, contact angle of 0% (0.7% acetic acid) solution ($\theta = 53.71 \pm 10.53°$) was lower than water contact angle ($\theta = 70.64 \pm 12.32°$). Low molecular weight solution showed increased contact angle value from 47.16° to 90.81° as concentration increased from 0.5% to 1.5%. Medium molecular weight solution showed significantly higher contact angle at 0.5% concentration ($\theta = 73.35 \pm 14.67°$) than 0% solution ($\theta = 53.71 \pm 10.53°$) but no significant differences were found between different concentrations ($p > 0.05$). High molecular weight solution showed significantly higher contact angle ($p < 0.05$) at 0.5% concentration ($\theta = 95.59 \pm 7.86°$) than 0% ($\theta = 53.71 \pm 10.53°$) but at 1.0% it showed decreased to 56.39°, similar value of 0%

solution (θ= 53.71±10.53°). At 0.5% concentration, contact angle showed increased from 47.16° to 95.59° as molecular weight increased from low to high. At 1.0%, high molecular weight solution showed lower contact angle (θ= 56.39±9.12°) than other solutions and at 1.5%, no significant differences were found between low and medium molecular weight.

On the abaxial side of perilla leaf, there was no significant difference ($p > 0.05$) between water (θ= 84.01±10.72°) and 0% solution (θ= 82.29±6.87°). And at each molecular weight, contact angle did not increase as concentration increased. At specific concentration, only at 0.5% showed increased contact angle as molecular weight increased. At 1.0% and 1.5%, there was no significant differences between molecular weight.

On the bell pepper surface contact angle of 0% solution (θ= 90.01±4.00°) was smaller than water contact angle (θ= 95.62±4.24°). At each molecular weight, contact angle did not increase as concentration increased. At specific concentration, there was no significant difference between low and medium molecular weight but high molecular weight showed increased contact angle at 0.5% (θ= 99.32±1.53°). At 1.0%, high molecular weight showed higher contact angle (θ= 99.01±1.31°) than low molecular weight solution (θ= 92.35 ± 2.81°), but no difference was found between medium and high molecular weight.

On the adaxial side of red lettuce, there was no significant difference between solutions.

On the abaxial side of red lettuce, the contact angles of water (θ= 84.29±9.48°) and 0% solution (θ= 95.78±6.97°) did not differ from each other. Low molecular weight 1.0 and 1.5% solution had higher contact angle (θ=

95.43±4.27 and 94.61±2.48°) than that of water (θ= 84.29±9.48°) but, they did not show differences between the different concentrations. Similarly, 0.5% medium molecular weight chitosan solution showed higher contact angle (θ= 93.22±6.37°) than water (θ= 84.29±9.48°) but did not differ from 0% , 1.0% and 1.5%. High molecular weight solution showed higher contact angle values (θ = 105.51 ± 7.72° and 98.66 ± 11.04°) than water contact angle (θ = 84.29±9.48°) but no increased tendency is shown as concentration increased. At specific concentration, no significant differences were found between different molecular weight.

Through the samples, at 0.5% and 1.0% showed a tendency of increased contact angles as concentration increased which indicate that the solution were harder to spread on the surface except on the perilla surface (both adaxial and abaxial) with 1.0% concentration. The contact angle results have similar tendency as surface tension of solution became larger at higher MW and concentration except the perilla surface which might be affected by the trichomes existing on the surface leading quite big standard deviation. Ren et al (2007) reported that Randomly distributed hairs on the plant surface effects on adhesion.

Table. 3.5. Contact angle of chitosan solution on the food surfaces.

Sample		Chitosan	Contact angle (°)				
			W	0%	0.5%	1.0%	1.5%
Perilla	Adaxial	L	70.64 ± 12.32^{b}	53.71 ± 10.53^{a}	47.16 ± 9.63^{a}	92.81 ± 6.14^{cd}	90.81 ± 9.09^{cd}
		M			73.35 ± 14.67^{bc}	85.21 ± 8.11^{cd}	79.78 ± 10.21^{bcd}
		H			95.59 ± 7.86^{cd}	56.39 ± 9.12^{a}	-
	Abaxial	L	84.01 ± 10.72^{ab}	82.29 ± 6.87^{ab}	74.29 ± 6.96^{a}	91.87 ± 8.45^{ab}	86.03 ± 6.46^{ab}
		M			93.69 ± 5.77^{b}	86.59 ± 4.66^{ab}	86.92 ± 4.68^{ab}
		H			90.72 ± 8.54^{ab}	91.50 ± 6.58^{ab}	-
Bell pepper		L	95.62 ± 4.24^{bc}	90.01 ± 4.00^{a}	91.21 ± 3.65^{ab}	92.35 ± 2.81^{ab}	94.03 ± 3.00^{abc}
		M			95.23 ± 3.36^{abc}	93.29 ± 4.10^{abc}	95.02 ± 1.93^{abc}
		H			99.32 ± 1.53^{d}	99.01 ± 1.31^{cd}	-
Red lettuce	Adaxial	L	91.04 ± 7.97	88.35 ± 9.22	88.15 ± 9.02	89.30 ± 4.42	93.05 ± 5.13
		M			93.32 ± 5.33	88.02 ± 3.54	91.08 ± 5.28
		H			95.01 ± 3.54	97.72 ± 6.05	-
	Abaxial	L	84.29 ± 9.48^{a}	95.78 ± 6.97^{ab}	88.63 ± 6.33^{ab}	95.43 ± 4.27^{b}	94.61 ± 2.48^{b}
		M			93.22 ± 6.37^{b}	94.37 ± 9.83^{ab}	91.80 ± 6.06^{ab}
		H			105.51 ± 7.72^{b}	98.66 ± 11.04^{b}	-

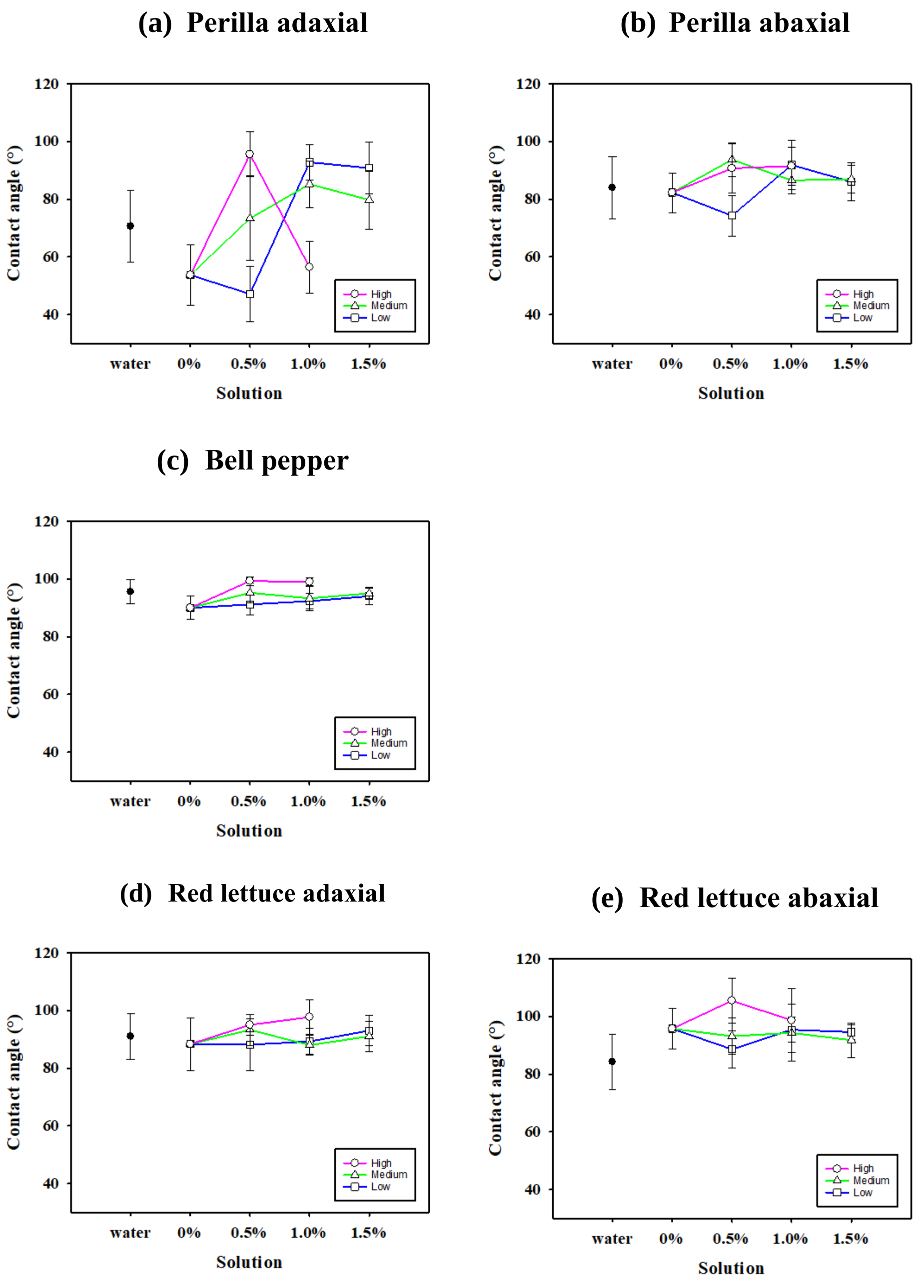


Figure. 3.6. Contact angle of chitosan solution on the food surfaces.

3.2.3. Wettability of the solution

Using the contact angle data, work of adhesion (W_a) and spreading coefficient (W_s) values were calculated and analyzed by Kruskal-Wallis test to compare the mean and post hoc test was conducted for each sample. The results can be seen in Table. 3.6. W_a is a strength between the two phases, where food surface and solution contact. The larger W_a values mean the easier wet of surface.

Except the abaxial side of red lettuce, all the samples showed similar W_a values between water and 0% solution. Red lettuce abaxial had higher contact angle values of water than that of 0%.

Adaxial side of perilla, low molecular weight solution showed decreased W_a as concentration increased, W_a values of medium molecular weight solution decreased as concentration increased and W_a of high molecular weight showed increased result as concentration increased. Abaxial side of perilla showed decreasing tendency on low molecular weight as concentration increased, but medium molecular weight and high molecular weight did not have significant differences as concentration increased.

Bell pepper also showed that W_a low molecular weight solution was decreased as the concentration increased, but medium and high molecular weight solution did not have significant differences as concentration increased. At specific concentration higher W_a values were shown at high molecular weight.

On the adaxial side of red lettuce, low molecular weight solution showed decreased W_a values as concentration increased and no significant differences were found at medium and high molecular weight. At 0.5% and 1.0%

concentration, no significant differences were found and at 1.5% concentration, low molecular weight solution had lower W_a values than the medium molecular weight.

On the abaxial side of lettuce, W_a values of low molecular weight showed decreased tendency as concentration increased and the W_a values of medium and high molecular weight solution were not significantly different. Similar to the adaxial side, at 1.5% concentration low molecular weight solution had lower Wa value than medium molecular weight solution.

The tendency was that lower concentration and lower molecular weight had higher W_a which means solid surfaces were easier to be wet. Among the analyzed surfaces, perilla had higher W_a values than other samples.

Using the wettability data, Spearman's correlation test was conducted to determine the relationship with food surface properties (Table. 3.2.). Different from the PM adhesion result, relationship between adhesion of chitosan solution and food surface property did not show a variable commonly related to wettability of solution and a few relationships are shown. The result shows that the adhesion of chitosan solution has strong positive relationship with the polar component of the surface free energy and total surface free energy of food surface which indicates that the surface with more free energy had better wettability. At medium molecular weight 0.5% solution and at low molecular weight 0.5%, medium molecular weight 1.5% and high molecular weight 1.0% roughness parameter of mean width (*RSm*) showed strong negative relationship which mean that the surface with widely arranged features had less wettability.

Table. 3.6. Work of adhesion (W_a) and spreading coefficient (W_s) values of solutions.

Sample		Chitosan	W_a					W_s				
			water	0%	0.5%	1.0%	1.5%	water	0%	0.5%	1.0%	1.5%
Perilla	**Adaxial**	L	96.39 ± 14.36ef	108.84 ± 10.61fg	87.54 ± 6.28de	51.90 ± 5.82b	42.50 ± 6.79a	-49.21 ± 14.36bc	-28.54 ± 10.61de	-17.17 ± 6.28e	-57.22 ± 5.82b	-43.75 ± 6.79bcd
		M			87.14 ± 16.49def	73.01 ± 9.47cd	77.78 ± 11.62cd			-49.12 ± 16.49bc	-61.84 ± 9.47b	-54.55 ± 11.62bc
		H			62.92 ± 9.48bc	108.48 ± 9.12g	-			-76.41 ± 9.48a	-31.69 ± 9.12cde	-
	Abaxial	L	80.25 ± 13.33d	77.85 ± 8.10cd	66.44 ± 6.03bc	52.79 ± 7.99ab	46.10 ± 4.82a	-65.35 ± 13.33a	-59.54 ± 8.10a	-38.27 ± 6.03b	-56.32 ± 7.99a	-40.16 ± 4.82b
		M			63.76 ± 6.84bc	71.43 ± 5.48bcd	69.72 ± 5.39bcd			-72.50 ± 6.84a	-63.42 ± 5.48a	-62.62 ± 5.39a
		H			68.77 ± 10.31bcd	68.26 ± 8.02bc				-70.55 ± 10.31a	-71.91 ± 8.02a	-
Bell pepper		L	65.68 ± 5.35d	68.68 ± 4.79d	51.25 ± 3.33b	52.32 ± 2.67b	40.10 ± 2.25a	-79.92 ± 5.35a	-68.70 ± 4.79b	-53.46 ± 3.33c	-56.79 ± 2.67c	-46.16 ± 2.25d
		M			61.93 ± 3.98cd	63.57 ± 4.81cd	60.38 ± 2.22c			-74.33 ± 3.98ab	-71.29 ± 4.81b	-71.96 ± 2.22b
		H			58.38 ± 1.84c	59.11 ± 1.58c	-			-80.94 ± 1.84a	-81.06 ± 1.58a	-
Red lettuce	**Adaxial**	L	71.49 ± 10.06d	70.65 ± 10.97cd	54.01 ± 8.15cd	55.22 ± 4.20b	40.85 ± 3.84a	-74.11 ± 10.06a	-66.73 ± 10.97	-50.70 ± 8.15b	-53.89 ± 4.20b	-45.41 ± 3.84b
		M			64.19 ± 6.32bcd	69.76 ± 4.17d	64.92 ± 6.08bcd			-72.07 ± 6.32a	-65.10 ± 4.17a	-67.41 ± 6.08a
		H			63.59 ± 4.29bcd	60.71 ± 7.34bcd	-			-75.74 ± 4.29a	-79.47 ± 7.34a	-
	Abaxial	L	79.91 ± 11.76d	61.82 ± 8.30bc	53.59 ± 5.75bc	49.41 ± 4.04b	39.66 ± 1.86a	-65.69 ± 11.76bc	-75.57 ± 8.30abc	-51.12 ± 5.75a	-59.71 ± 4.04c	-46.59 ± 1.86a
		M			64.32 ± 7.55c	62.37 ± 11.39bc	64.10 ± 6.97			-71.95 ± 7.55abc	-72.48 ± 11.39abc	-68.23 ± 6.97abc
		H			51.17 ± 8.99bc	59.65 ± 13.3bc	-			-88.15 ± 8.99a	-80.53 ± 13.3ab	-

L = low molecular weight; M = medium molecular weight; H = high molecular weight

Table. 3.7. Spearman's correlation coefficient values for surface properties factors related with the adhesion of chitosan edible coating solution.

Surface property		Chitosan solution	Spearman's correlation coefficient	P-value
Wettability	$\boldsymbol{\gamma_{SG}^{p}}$	M1	.900*	0.037
	$\boldsymbol{\gamma_{SG}}$	M1	.900*	0.037
Roughness	***Rsm***	L1	-.900*	0.037
		M3	-.900*	0.037
		H2	-.900*	0.037

*. Correlation is significant at 0.05 level (2-tailed)

L1 = low molecular weight 0.5%; M1 = medium molecular weight 0.5%; M3 = medium molecular weight 1.0%; H2 = high molecular weight 1.0%

4. Conclusions

To evaluate and analyze what surface properties are mainly related to the adhesion of foreign matter on the food surface, two different foreign matters are selected. First, the model particulate matter deposited on the food surface were calculated and second, the edible coating solution was used to investigate the interaction between food surface and foreign matter.

The result shows that the PM adhesion on the food surface was mainly affected by the surface microstructre, more specifically, mean width between the surface elements. The interaction between solid-solid surface, the contact area leads the adhesion force. In general, roughness reduces the contact area of two substrates interface as the adherend is attaches to the peaks, but the size of the particle needs to be considered too. If the particles are similar or smaller than surface features, this adherend can be deposited between the peaks or enter closer to the valleys thus the contact area and adhesion force can be increased.

When the adhesion of foreign matters has to be controlled, such as an efficient adhesion or a protection from contamination, surface properties are important but also the properties of foreign matters have to be considered.

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Abstract in Korean

젖음성 및 미세구조와 같은 식품 표면 특성은 외부물질(미세먼지, 농약, 미생물 등)의 식품 흡착에 주요한 역할을 한다. 외부물질 중 미세먼지로 인한 대기오염이 세계적인 이슈가 되고 있으며 미세먼지는 호흡기 질환과 심혈관 질환을 유발하여 인간의 건강을 위협하는 것으로 알려져 있다. 미세먼지는 음식 섭취를 통해 인간의 위장관에 유입될 수 있고 염증과 장내미생물군의 변화시킬 수 있다. 미세먼지는 낮은 농도에서도 장시간 노출 시 식품표면에 상당한 양이 축적될 수 있고, 이는 식품표면의 특성에 큰 영향을 받을 것으로 예상되지만, 관련 연구는 거의 보고된 바 없다. 신선식품은 부패하기 쉬워 수확 후 관리기술을 이용하여 저장 및 소매 과정에서 품질 손실을 줄이는 것이 필요하다. 흔히 사용하는 식품 포장재는 화학 합성 물질이며 분해되지 않아 환경 문제를 일으킨다. 이를 대체가능한 식용 코팅은 얇은 물질이 표면에 부착하여 장벽을 형성하고 물리적 보호 기능을 가진다.

본 논문은 표면 젖음성 및 표면 미세구조를 포함하여 미세먼지 및 식용 코팅과 같은 외부물질과 식품 표면 간의 상호작용에 영향을 미칠 수 있는 표면 특성을 조사한다. 미세먼지의 식품 표면 부착에 대한 이해는 미세먼지 상호작용 식품 표면을 분류하고 식품 체인을 조절 가능하게 하여 미세먼지에 대한 식품 안전 확보 또는 효과적인 자원 사용 및 제품 손실을 방지하는 데 유용한 지침을 제공할 수 있다.

많이 소비되는 6가지 식품(깻잎, 대파, 피망, 적상추, 순대, 김)이 분석됐다. 6개 액체(물, 다이오도메탄, 2-프로판올, 에틸렌글리콜, 포름아미드, 글리세롤)의 정적 접촉각을 측정 후 OWRK(Owens, Wendt, Rabel, Kaelle) 및 Zisman 방법을 사용하여 식품표면에너지(SFE)를 구하였다. 미세구조 정량화를 위해 산술 평균 높이(*Ra* 및 *Sa*), 제곱 평균

제곱근 높이(*Rq* 및 *Sq*), 최대 높이(*Rz* 및 *Sz*), 프로필 요소의 평균 너비(*RSm*)와 같은 진폭 및 거리 거칠기 파라미터를 공초점 레이저 스캐닝 현미경으로 측정하였다. 김과 순대의 SFE(45.5~58.7 mN/m)가 높았고, 대파 하단은 가장 낮은 값(17.6mN/m)을 보여 순대는 검사 대상 식품 중 이물질과의 상호작용 성향이 가장 강했고 대파하단은 성향이 낮았다. 적상추(앞면)는 상대적으로 진폭 거칠기가 높았고 김, 깻잎, 피망은 낮았다. 거리 매개변수는 대파 하단이 높고 깻잎(앞면)이 낮았다.

실제 식품표면에 대한 미세먼지와 키토산 용액의 흡착은 각각 표면에 흡착된 미세먼지의 양과 코팅 용액의 젖음 정도를 측정하였고, 통계적 분석을 통해 흡착과 식품표면 특성의 상관성을 확인하였다. 그 결과는 식품 표면의 미세먼지 접착이 표면 미세 구조, 더 구체적으로는 표면 요소 사이의 평균 너비의 영향을 주로 받았음을 보여준다.

본 연구에서 얻은 결과는 식품 표면 특성이 외부물질 흡착에 미치는 영향을 이해하는 데 유용한 정보를 제공하여 잠재적 위험이 되는 미세먼지 오염에 대한 식품 안전성의 확보, 효율적인 자원 사용과 제품 손실을 줄이는 데 지침이 될 수 있다.