Chapter 6
Surface Properties of Biodegradable Polymers for Food Packaging

Z. A. Nur Hanani

Abstract Biodegradable polymers derived from biomass such as polysaccharides (starches, chitosan, and gums) and proteins (gelatin, soy, and zein) have been explored tremendously as potential food packaging materials. Their unique characteristics, for example, edible, abundance, renewable and low-cost allow these materials to be utilized in many forms such as films and coatings. However, biodegradable polymers exhibit high water vapour permeability and solubility. Functional properties of biodegradable polymers can be enhanced by blending with other polymers, lipids, surfactants, emulsifiers or other additives. Combining some polymers and additives will change the microstructure, mechanical, barrier and surface properties of films. Therefore, surface properties can influence the final applications of films and coatings. Interestingly, surface properties of polymers can be tailored using some treatment. Lack of discussion on surface properties of biodegradable films is noticeable. This chapter presents the surface properties of biodegradable films and coatings from various sources and their characterizations. Some surface treatments on films aiming to improve their characteristics and effect of the surface on active packaging are also discussed.

Keywords Surface treatment

6.1 Biodegradable Polymers for Food Applications

Nowadays, food processing involves some other treatments to prolong the shelf life of foods in the package such as freezing, irradiation, high pressure and ozone treatment. Also, the modern lifestyle and convenient options on the usage of ready to eat (RTE) meals require some further steps before consuming the foods such as microwave and oven and this indirectly may change the film surface properties and affect foods specifically.

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Synthetic polymers such as polypropylene (PP), low-density polyethylene (LDPE), high-density polyethylene (HDPE), polyethylene terephthalate (PET) and nylon have been widely used in food packaging to protect food products from physical and mechanical damages and microbiological spoilage. This scenario is due to their good performance properties such as stable, water resistance and strong. However, these materials are being utilized as food packages for short term usage despite their properties and durability that remained for a longer period. Furthermore, the recycling of these materials is impractical due to food contamination. Thus, due to environmental awareness, biodegradable materials are seen as alternatives to replace synthetic plastics which are non-biodegrade; causing some negative issues to nature. Biodegradable polymers are claimed as green materials, renewable and environmental-friendly causing this area to be tremendously exploited today.

6.2 Biodegradable Polymers

Biodegradable polymers are gaining more popularity due to the eco-friendly effect they offered, renewable, abundance and cheap. These polymers will break down and produce natural by-products such as gases (CO_2 and N_2), water, biomass and inorganic salts. Biodegradable polymers are classified into few categories depending on the sources obtained; natural biopolymers and synthetic biopolymers. Natural polymers are produced from agro-based materials such as polysaccharides (starch, cellulose derivatives, chitosan, alginate, etc.) and proteins (soy, corn, wheat, gelatin, keratins, etc.) whereas synthetic biopolymers are obtained from synthetic or natural monomers and microorganism. Biodegradable polymers can also be in combination with synthetic biodegradable polyesters (Gutiérrez and Alvarez 2017a).

Natural polymers derived from polysaccharides- and protein-based are unique since they are also edible (can be consumed together with the food) and can provide additional nutrients; giving an advantage to applying with food products (Álvarez et al. 2017). Hence, this type of polymers can be developed as films or/ and coatings. The films produced also perform good gas barrier, good mechanical properties, transparent and good carriers for active compounds such as antimicrobials, antioxidants, etc.. The main issue related to this group of polymers is the high permeability towards moisture or water (Gutiérrez and Alvarez 2017b). Great efforts are still in progress to improve the water barrier so that these materials have wider applications and can be utilised for several food types. One of the alternatives is adding hydrophobic compounds like lipids or fats to produce composites or blend films. However, incorporation of lipids to the solutions will alter the properties of films produced. Also, surface properties of the single polymer are different compared to the blends polymers (Sionkowska and Płanecka 2013).

Currently, there are high interest on developing biodegradable films, manly focused on improving mechanical and barrier properties of the materials for further applications. Only few studies focused on the improvement of surface properties of biodegradable films to enhance the characteristics of films or other surface such as paper. Surface properties are also important because they will influence the structure of films (Gutiérrez et al. 2018). However, surface properties of biodegradable polymers can be modified depending on the final applications either as coatings or films since both applications may have different purpose. Biodegradable polymers can also be used in the surface treatment of cellulose-based materials, either by coating or by extrusion/lamination (Andersson 2008).

6.3 Surface Properties of Biodegradable Polymers

Biodegradable films can be tailored based on the combination and composition of materials used which consequently, will affect the mechanical properties, water transmission rate, optical properties and also surface properties of films. Like other polymers, surface properties of food packaging polymers include wettability, sealability, printability, dye uptake, resistance to glazing and adhesion to food surfaces or other polymers (Sengupta and Han 2014). These are some of the important elements to food packaging manufacturers for maintaining the shelf life of products while ensuring good quality appearance. Furthermore, surface roughness, polarity, wettability and modification of the surface will also determine the biocompatibility of polymeric materials (Sionkowska and Płanecka 2013).

6.3.1 Wettability

Wetting is the ability of a liquid to interact with the solid surface or another fluid either maintains the interaction or penetrates the surface. Wettability is the degree of wetting due to the interaction between the fluid and solid phases. It determines the properties of polymers' surface in allowing liquid seep through and plays a crucial role in liquid coating and printing. Wettability can be determined using contact angle measurement whereby small contact angles (≤90°) indicate high wettability where as large contact angles (≥90°) indicate low wettability.

6.3.2 Sealability

Sealing involved melting of the polymer by supplying heat, followed by linking of the surfaces under pressure. Sealability determines film's ability to turn as its own bond-forming agent without requiring extra hot melt adhesive. Some materials may need less energy to be sealed, depending on the degree of materials crystallinity. Thus, temperature, time and pressure should be identified so that sufficient energy is supplied to ensure good sealability. A polymer that displays low-temperature sealability and maintains seal integrity over a broad seal temperature, dwell time and seal pressure can increase packaging line speeds, improve efficiencies and reduce seal failures (Butler and Morris 2012). However, the presence of fillers, additives or waxes may cause weaker seal due to the migration of these additives to the surface (Andersson 2008; Bracone et al. 2016; Gutiérrez et al. 2017). The–OH groups are also capable of forming hydrogen bonds and thereby provide good adhesion between different surfaces (Andersson 2008). Defects or weak spots during and after sealing may produce pathways for transportation of gases or liquids either in or out of the package (Andersson 2008).

6.3.3 Printability

Printability of polymer is the ability of the polymer to be printed without displacement of the ink. Surface properties such as smoothness, levelness, ink absorbency, gloss, etc. influence this property. Printability test can be done by using tape which will be used for lifting ink off the printed samples according to a pre-established number of peels (López-García et al. 2013). The tape is lifted off with consistent force at an angle 90° before the samples are recorded using UV-VIS spectrophotometer.

6.4 Surface Properties of Polysaccharides-Based Films

Polysaccharides have a wide range of structures, depending on the types such as starch, cellulose derivatives, chitosan, and alginate. Polysaccharides-based films possess high gas barrier due to their well-ordered hydrogen-bonded network shape (Hassan et al. 2017). However, these materials are very hydrophilic causing in high water vapour permeability. This drawback limits the usage of polysaccharides films for high moisture or semi-solid food products. To optimum the applications, they can be applied as thick films or coatings on the surface of food to absorb water, giving temporary protections to foods from moisture loss (Cazón et al. 2017). Polysaccharides films and coatings are colourless, however can change the film's colour depending on the additives or active compounds added. Mechanical property, i.e. tensile strength values of some polysaccharides based films are comparable to those values obtained in high density polyethylene (HDPE) films (Cazón et al. 2017). Highly structured polysaccharide attributes to the homogeneity of films and smoothness of the film's surface (Caro et al. 2016).

6.4.1 Starch

Starch is an agricultural biopolymer that composed of anhydroglucose. It is abundant, low price and unique. This is because starch granules vary in shape, size, structure and chemical composition depending on the botanical source (Molavi et al. 2015). The starch granules comprise two main polysaccharides; amylose and amylopectin, apart from other components such as proteins and lipids. Amylose which responsible for film-forming properties is a linear chain polymer of a-1,4 anhydroglucose units with a molecular size ranging from 20 to 800 kg/mol (Cazón et al. 2017). Meanwhile, amylopectin is a highly branched polymer of short a-1,4 chains linked by a-1,6 glycosidic branching points occurring every 25–30 glucose units and with a very high molecular weight (5000–30,000 kg/mol) (Cazón et al. 2017; Jiménez et al. 2012). Starch films are generally tasteless, odorless and transparent. However, at higher concentration, films produced tend to become whitish. Starch films that compose higher crystalline structure are less sensitive to moisture and the environmental relative humidity (Cazón et al. 2017; Molavi et al. 2015; Jonhed et al. 2008; Mali et al. 2004). Regarding surface properties, starch application increases both the roughness and the hydrophilicity of the coated surface (Andersson 2008). Films contain higher amylose content exhibits greater surface roughness (Gutiérrez and González 2016). Films with different starches have shown that glutinous rice starch and normal rice starch-based films possessed higher contact angle values than cassava starch due to higher lipid content (Phan et al. 2005). Study on the surface properties of starchy films with blackberry pulp revealed that the pulp increased the contact angle and lower surface roughness (Gutiérrez 2017a).

6.4.2 Chitosan

Chitosan is a natural polymer derived by deacetylation of chitin, the second most abundant natural polymer after cellulose (Gutiérrez 2017b). Chitosan has various applications because of its functional properties such as antibacterial activity, non-toxicity, ease of modification and biodegradability (Muxika et al. 2017). Furthermore, chitosan films are transparent and flexible and have semicrystalline structure. Chitosan addition in cassava films helps to increase the contact angle, which means improving the surface hydrophobicity of films. This is due to the hydrophobic acetyl groups present in chitosan chain, suggesting that chitosan is more hydrophobic than starch (Kampeerapappun et al. 2007). Kurek et al. (2014) also observed that larger contact angles on the chitosan surface were found compared to whey protein (support surface) of bilayer films. However, an addition of plasticizer on the chitosan films lessens water contact angle due to the water binding capacity (hygroscopicity) of plasticizers. As chitosan has highly structured polysaccharides; films produced are smooth and flat with no cracks and pores (Caro et al. 2016). However, hybrid chitosan films may have surface irregularities. Higher ferulic incorporation in the chitosan films had caused phase separation (from AFM analysis) and might be responsible for the reduction in tensile strength (Mathew and Abraham 2008). However, the authors indicated that the cross section images of SEM showed films were more compact due to the networking introduced by the acid than those control films (chitosan-starch blend) which were having discontinuous zones.

6.4.3 Pectin

Pectin is a plant cell wall polysaccharide rich in D-galacturonic acid and mostly obtained from citrus fruits or fruit processing industry waste. Films from pectin possess good hardness and adhesiveness. However, they can become rigid and brittle. The SEM images of the surface and cross-sectional of pectin films added with clove bud essential oil (CEO) showed that oil produced a dense sheet-like structure, whereas the cross-sectional images had the sheets stacked in compact layers demonstrating that CEO added uniformly in the film matrix (Nisar et al. 2018). The authors had found out that at a low level of oil (0.5%), smoother surfaces without any phase separation was observed. However, higher oil (1 and 1.5%) had caused the surface to become rough and looser texture. According to Nisar et al. (2018), the different surface morphology of films could be due to the structural changes of components of micro-emulsions during the drying process. The effect of pectin surface density on the high methoxyl pectin-based films was also investigated (Giancone et al. (2011). It was revealed that the surface density did not affect the film structure, yet, it increased the WVP.

6.4.4 Galactomannans

Galactomannans are heterogeneous polysaccharides composed of linear chains of β-(1–4)-D-mannan backbone with a single D-galactose branch linked α-(1–6) (Cerqueira and Bourbon 2011). There are three major gallactomannans used for food industry which are guar gum, tara gum and locust bean gum, mainly vary because of the different ratio of mannose and galactose. Almost similar with other common biodegradable films, galactomannans films are essentially hydrophilic. Irregular surface of galactomannans films caused the films to have higher WVP due to the presence of voids (Albuquerque et al. 2017). Furthermore, the addition of bioactive compound contributed to rougher surface and increased in the hydrophobicity.

6.4.5 Fiber

Fiber refers to edible parts of carbohydrates that cannot be digested. Natural fiber is cheap, has low specific weight, recyclable and competitive mechanical properties (Gutiérrez and Alvarez 2017c). However, fiber has poor adhesion with the matrix with the creation of voids at the interface and non-uniform dispersion (John and Thomas 2008). Modifying surface of fiber had enhanced the fiber-matrix interaction by improving the mechanical properties (Geogiopoulos et al. 2016).

6.5 Surface Properties of Protein-Based Films

Proteins are linear polymers constructed by monomer unit called amino acids through a covalent peptide bond. There are 20 types of amino acids in protein which having different chemical properties and roles (hydrophobic, polar or charged). Proteins can be classified into two types; plant proteins and animal proteins. Soy protein, corn protein and wheat protein are among the plant proteins whereas casein, collagen, gelatin and keratin are the types of extensively used animal proteins. Lactate dehydrogenase, chymotrypsin, and fumarase are the main bacterial proteins. Compared to polysaccharides and lipids, films obtained from proteins exhibit valuable characteristics for the production of food packaging as these films have good film-forming ability, mechanical properties and transparency. In fact, protein-based films have excellent oxygen and carbon dioxide barrier properties than polysaccharides-based films.

6.5.1 Soy Protein Isolate

Soy protein isolate is obtained from soy protein, a by-product from soy oil production. Hydrolyzed keratin produced from chicken feather had been used into soy protein films (Garrido et al. 2018). The findings discovered that an additional of keratin decreased the gloss significantly and enhanced the hydrophobicity. Surface hydrophobicity of protein films such as soy protein isolate, whey protein concentrate, gelatin, peanut protein isolate and sodium caseinate were also improved with the treatment of the enzyme crosslinking (transglutaminase) (Tang and Jiang 2007).

6.5.2 Gelatin

Gelatin is an insoluble protein gained by hydrolysis of collagen, a fundamental structure of animal bodies (Nur Hanani 2016). Gelatin from fish, pork and bovine have been studied greatly. The surface properties of bilayer and blend films based on bovine gelatin showed that all films have hydrophobic surface, based on the contact angle (Abdelhedi et al. 2018). Chemical reaction occured between gelatin and lactose also influenced the structure of gelatin films with tetrahydrocurcumin, causing the films to become less glossy and rougher surfaces (Etxabide et al. 2017). Deng et al. (2018) have discovered that the gelatin/zein nanofibrous film had a hydrophobic surface with 118.0°, whereas casted gelatin/zein film had a hydrophilic surface (53.5°). Addition of chitin in gelatin film also had decreased the hydrophilicity of film with film containing the highest oil had contact angle higher than 90° (Sahraee et al. 2017).

6.5.3 Zein

Zein is a hydrophobic and thermoplastic material derived from corn. Its high hydrophobicity is attributed by its high content of nonpolar amino acids. The incorporation of sugar plasticizers in zein films reduced the contact angle with higher hygroscopicity of plasticizer contributed to the higher hydrophilic due to the higher water binding capacity (Ghanbarzadeh et al. 2007).

6.6 Lipids and Other Additives

Due to the limitation on water barrier properties of starch- and protein-based films, different components mainly lipids (waxes, oils and fats) and other additives (surfactants, emulsifiers, etc.) are being added to produce composite films. Lipids exhibit excellent barriers against moisture migration. Extensive studies are ongoing considering these lipids help to enhance the water barrier of biodegradable films. Polysaccharides- and proteins-based films incorporated with lipids generally have higher mechanical properties. Nonetheless, the composite films may have higher moisture permeability than that of pure lipids (Hassan et al. 2017; Bravin et al. 2004). Higher amount of lipids used can increase gloss and decrease transparency. Meanwhile, the production of lipid based films and coating are believed to be highly effective to block the delivery of moisture due to their low polarity (Hassan et al. 2017; 104). Their hydrophobicity also causes the films to become brittle and thicker.

In general, plasticizers contribute to the decrease of contact angle of hydrocolloid films due to hydrophilicity of these materials. Higher concentration of glycerol decreases the contact angle due to the increases in the surface tension (Caro et al. 2016). In contrast, additional of plasticizers such as glycerol, sorbitol and polyethylene (glycol) in sage seed gum films had caused higher contact angle than the control films (Razavi et al. 2015). Meanwhile, calcium chloride has been used as a firming agent in mesquite gum films. The surface morphology of the films was influenced by the agent concentration, whereby the film surface became gradually rough at higher concentration (Bosquez-Molina et al. 2010).

6.7 Surface Characteristics

There are some techniques to characterize the surface properties of biodegradable polymers such as contact angle measurement, atomic force microscopy (AFM) and scanning electron microscopy (SEM). This section is not going to discuss details on each instrument. However, brief information is delivered to relate with the surface properties of biodegradable polymers.

6.7.1 Contact Angle

Contact angle is the wetting angle between the surface of the liquid and the outline of the contact surface. The analysis determines the surface hydrophobicity of polymers. Small contact angles (≤90°) occur due to spreading of the drop (molecular attraction). Meanwhile, greater angles (≥90°) occur due to the liquid becomes bead or shrink away from the solid surface. Lower contact angle indicates the films have high polarity and better bonding of adhesive. This process is a crucial index to determine the wettability of the solid phase by the liquid and establish the formation of a good bonding interface. The increase of the contact angle with water in biodegradable polymers could be due to a strong hydrogen bond inter-molecular by below of the surface of the film, i.e. the more polar sites (Lewis sites) would be affected, thus generating a decrease in the surface polarity of biopolymer-based films (Gutiérrez et al. 2016a, b; Karbowiak et al. 2006). Storage also can increase the contact angle due to the loss of moisture content and plasticizer (Suyatma et al. 2005). On the other hand, dynamic contact can reflect the degree of difficulty of coating the solid phase with the liquid in the real wetting process (Zhang et al. 2017).

Surface free energy is another parameter to discuss about the surface properties. Surface free energy (interfacial free energy) is work required to increase the size of the solid surface (work per unit area). In contrast, the term 'surface tension' is used for a liquid phase. Surface tension can be measured using some techniques depending on the nature of the liquid, the condition during the measurement and the stability of the surface. However, the contact angle is normally used to measure the surface free energy indirectly. According to Young's equation, the surface free energy can be determined using equation below:

$$\sigma_s = \sigma_{sl} + \sigma_l \cdot \cos\theta \tag{6.1}$$

where:

σ_s = surface free energy

σ_{sl} = interfacial tension

σ_l = surface tension of the liquid

θ = contact angle

In conventional plastics, polymer with high surface energy can be used as the first surface of few layers structures and requires an adhesive layer to bond to the other different layer (Butler and Morris 2012).

6.7.2 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) offers a 3D profile on a nanoscale, by measuring forces between a sharp probe (with radius less than 10 nm) and surface at very short distance (0.2–10 nm probe-sample preparation) (De Oliviera et al. 2012). The probe is supported on a flexible cantilever and the AFM tip softly touches the surface and records the small force between the probe and the surface (De Oliviera et al. 2012). The images obtained give some information about the surface roughness of films such as roughness average (R_a) and root mean square roughness (R_q). R_a, is the arithmetic mean of the absolute values of the height of the surface profile (De Oliviera et al. 2012). It is used widely because of easy to obtain. R_q is similar to roughness average, except it is the mean squared absolute values of surface roughness profile. The information delivered by AFM is beneficial to determine structural changes of the film matrix. Despite of providing high resolution at the nanoscale, this analysis is restricted due to time-consuming measurement. Smoother surface of films can also be related to the increased of the transparency as revealed by Gutiérrez et al. (Gutiérrez et al. 2016a, b).

6.7.3 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is used to determine the surface structure of polymers. The knowledge of the morphology is an important parameter to determine structural changes in the films and to predict their porosity, permeability, flexibility and resistance (Giosafatto et al. 2014; de Paula Herrmann et al. 2004). Smooth surface indicates good compatibility between compounds and the plasticizers. For cross section analysis, film with compact structure indicates the networking is developed. However, film with some porosity allows the distribution of active compound to a greater depth which in turn caused the films to release the compounds in slower rate.

6.7.4 X–Ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) can also be used to analyse the surface chemistry of biodegradable polymers. It is employed to obtain quantitative insight into the elemental composition of the surface that does not extend beyond certain depth (López-García et al. 2013). In this analysis, X-rays irradiates onto the surface of polymers in vacuum environment. The energy from the photoelectrons radiated from the surface is measured. XPS can be applied for various type of materials (conducting and non-conducting samples) by providing about the surface layer or structures.

6.7.5 Gloss Analysis

Gloss, transparency, clarity, haze, and colour are some optical properties of films. Gloss analysis is a simple method, yet its usage is not widely emphasized. Gloss analysis can directly relate to the surface roughness, with lower values indicate the surface is rougher (Garrido et al. 2018; Ward and Nussinovitch 2017). Different techniques of films manufacturing produce different surface properties. Films produced by compression moulding exhibited higher gloss values than those prepared by casting contributing to the smoother surface, as supported by SEM (Garrido et al. 2018). Also, gloss values may decrease due to the immiscibility of the polymers.

6.8 Surface Treatment

As different polymers possess various surface characteristics, therefore, it is important to have another step to alter the surface of biodegradable polymers and improve the functionality for fulfil their application. There are some techniques used to modify the surface properties such as utraviolet (UV)-light irradiation, incorporation of nano-materials, plasma surface treatment and lamination process.

6.8.1 Ultraviolet (UV)-Light

Ultraviolet (UV) radiation has been used to modify films surface properties. In the case of protein films, the radiation is absorbed by double bonds and aromatic rings of some amino acids, producing free radicals and causes intermolecular covalent bonding (Díaz et al. 2017; Rhim et al. 1999). UV treatment on film-forming solution has contributed to significant effect on the mechanical properties, colour and stability of whey protein films (Díaz et al. 2016). UV treated whey protein films also improved their puncture properties than the control (Díaz et al. 2017). UV radiation is normally applied on materials based on natural polymers for sterilisation process, whereby blended polymers may change differently than single components (Sionkowska and Płanecka 2013). Tarek et al. (2015) have studied the effect of UV-light treatment on the surface properties of plastic films for beef by determining the surface-free energy. They have found that UV-C light treatment had decreased the polymer surface roughness; however, it did not affect the surface free energy of films. UV-irradiation may cause the reduction of surface roughness of chitosan films and chitosan with silk fibroin (Sionkowska and Płanecka 2013). Surface modification using UV irradiation reduced the surface hydrophilicity and enhanced the water resistance and tensile strength of blended starch films (Zhou et al. 2009).

6.8.2 Nano Sized Materials

Packaging materials utilizing nanotechnology is also being explored and become one of the emerging areas today. Nanomaterials have high surface area and charge density. Clays, silica, nanocellulose, organic and inorganic fillers, etc. are some nanomaterials that are used to improve the mechanical and barrier properties of films. Nanofillers possess good interfacial interactions on polymer branches since they have large specific surface area and high surface energy (Nafchi et al. 2012; Kovačević et al. 2008). Chitosan nanoparticles have been added in tara gum edible films revealing that no significant difference of surface structure between films with bulk chitosan and chitosan nanoparticles (Antoniou et al. 2015). However, from cross-sectional profiles, the appearance of these two films were different whereby, nanoparticles caused the surface became rougher. Increasing the roughness had caused the contact angle of the surface also higher. In general, addition of nanoparticles had improved the hydrophobicity of film's surface by lowering the water vapour permeability and solubility. This result is in agreement with Abreu et al. (2015) whereby the incorporation of silver nanoparticles increased the contact angle significantly. Nanorod-rich zinc oxide also increased the contact angle, showing the tendency of films to absorb water decreased (Nafchi et al. 2012). The introduction of calcium montmorillonite into carboxymethyl starch films had increased the contact angle due to the clay platelets presented on the film surface (Wilpiszewska et al. 2015). In contrast, Shankar et al. (2016) claimed that adding silver nanoparticles in pectin films had caused a decrease in contact angle due to increase in roughness.

6.8.3 Plasma Surface Treatment

Plasma, the fourth state of matter is an ionised gaseous substance which if in contact with the material surface, will modify its surface properties due to the additional energy transferred from the plasma. This mechanism enables the surface to have a treatment or an alteration process to fulfil further applications such as printing, painting or laminating. It improves the adhesion properties, wettability and surface chemistry of polymers. During the treatment of polymers, energetic particles and photons generated in the plasma interact strongly with the polymer surface. Consequently, treated surface may have additional functional groups that increase the surface free energy of the polymer, enhance the printability and improve hydrophobicity through surface-chemical changes (Liston et al. 1994). This technique is an effective tool, which is convenient, quick technology, environmentally friendly and only requires low-cost processing devices (López-García et al. 2013). The polymer layers activated by cold plasma have controlled surface wetting properties, varying from superhydrophilic to superhydrophobic (Dowling and Stallard 2015). The air plasma applied on the whey protein gels had a greater effect on the surface wettability than roughness, due to polar groups deposited on the surface (Terpiłowski et al. 2017). However, a study on the effect of plasma treatment on chitosan films indicated that there were more water molecules surrounding the plasma treated sample (greater hydrophilic) and gave rougher surface compared to unmodified (Chang and Chain 2013).

6.8.4 Others

Other surface modification techniques such as silylation, acetylation, esterification and polymer grafting are also being used to improve nanocellulose composites (Zhang et al. 2018). However, most surface modification of nanocellulose use the hazardous solvents which are not preferable. Lamination of biodegradable polymers with lipids can cause to lower of WVP. Biodegradable materials can also be used in the surface treatment of cellulose-based substrates, either by coating or lamination (Andersson 2008).

6.9 Surface Properties in Active Packaging

Biodegradable polymers can act as good carriers for active compounds such as antimicrobial and antioxidant agents producing a system called active packaging. Active packaging helps to alter the package system in a positive approach as it contributes to extending the shelf life of food by inhibiting the microbial growth and delaying the lipid oxidation of some food products. Active packaging materials may have active compounds on the surface of the packaging inside the package, contributing to surface modifications of polymers.

In general, there are some research on active packaging indirectly investigated the surface properties of films. However, lack of emphasis occurred because most of the studies are keen to observe the efficiency of the active compounds in performing their role particularly for food systems. Caro et al. (2016) had developed active packaging films based on chitosan using thermal inkjet printing and found out that the efficiency of thymol as active agents is depending on few factors such as the number of oriented layers, the contact angle, the amount of glycerol used and the film type. The efficiency of thymol improved proportionally with the contact angles. However, increasing the concentration of glycerol had lowered the contact angle due to the increase in the surface tension. Meanwhile, adding active compounds in galactomannans films also improved the hydrophobicity of films despite no effect of the concentration used (Albuquerque et al. 2017).

6.10 Future Trends

Analyses on the surface properties of biodegradable polymers are essential due to their significant effects on the physical and mechanical properties. However, research on this aspect is still narrow. Some treatments to improve the surface properties can be discovered further to establish the area and can be a platform and database for future applications.

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