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Effect of surface modification on starch biopolymer wettability

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ABSTRACT

The main goal of this paper was to determine wettability properties of native starch and starch modified by antibacterial solution of chitosan or lysozyme as a function of temperature and/or after plasma treatment. Contact angles for polar water (and formamide) and nonpolar diiodomethane on glass plates covered with starch film before and after gelatinization (25 °C, 37 °C and 60 °C) were measured. The surface free energy of solid (gel) was determined from the advancing and receding contact angles of these probe liquids, using the contact angle hysteresis model (CAH). The plasma treatment was immediately followed by a sharp decrease of contact angle. In the course of ageing the contact angle also decreased due to the reorientation of polar groups into the surface layer of polymer. Also a sharp decrease in negative values of W_S takes place which indicates more hydrophilic character of starch after plasma treatment. The same was after lysozyme modification but to a smaller extent. The opposite trend of changes was visible after chitosan solution treatment. The surface characterization was observed by FTIR measurements and surface topography from the profilometer images and such measurements well support the contact angle results. The arrangement of temperature, plasma treatment or biological modification can lead to improvement of starch surface wettability and stability. The obtained results open up possibilities of starch application in food, paper and packaging industries as well as in pharmacy.

1. Introduction

Starch products are the most frequently used biomaterials in many industries because they are low cost and biodegradable. Starch is one of the most widely used biopolymers in the manufacture of food industry, solid dosage, can be formulated as a filler, a disintegrant, or a binder. Besides, starch-based materials with high amylose contents exhibit good oxygen barrier functions. Amylopectin used as subcoating material improves the acidic resistance of enteric-coated pellets. Physically or chemically modified starches are used as a forming-matrix excipient and a coating material for pellets and tablets. By means of temperature modification fully or partially gelatinized starch is of great interest for the formulation of sustained release products owing to its cold water-swelling capacity and gel barrier formation. Behaviour of the layer, formed around matrices after contact with water is of significant importance also for the drug delivery profiles. Recently pregelatinized and modified starches have been described as possessing mucoadhesive properties (Ferrari et al. 1997; Guo, Heinämäki, & Yliruusi, 2002; Krogars et al., 2003; Sanchez, Torado, & Lastres, 1995).

Starch is a polymer of low rigidity. Such biopolymers possess a great strength to fracture and can be modified to obtain new products. Biological modification of starch materials causing an increase of their biocompatibility and/or antibacterial properties is based on the adhesion process, which depends on the composition and topographic nature of composites. In this paper as the biological modification the solution of chitosan or lysozyme was applied. Chitosan is a soluble form of chitin, non-toxic, biodegradable and antibacterial. Biopolymer consisting primarily of β(1 → 4) linked 2-amino-2-deoxy-β-D-glucopyranose units is currently used in separation membranes, tissue engineering, antifouling coatings, stent coatings, enzyme immobilization matrices, and as an adsorbent for removal of heavy metals from soil and wastewater. Chitosan is a commercially interesting compound because of its high nitrogen content (~7%), making biopolymer a useful chelating agent for metal ions. Many factors determine chitosan capacity of metal ions adsporption including: pH, concentration, temperature, deacetylation percent, interaction time, and chain length. If the pH is below the pK_a of chitosan (6.2–6.8), then the amines become approximately 90% protonated, resulting in a positively charged chitosan, which is a good adsorbent for anions. On the other hand, if chitosan is above the pK_a, then the deprotonated amines are a good adsorbent for cations (Cathell & Schauer, 2006; Schauer et al. 2003).

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Lysozyme is also an antibacterial substrate. Lysozymes are proteins, glycoside hydrolases, enzymes which damage bacterial cell walls by catalysing hydrolysis of 1,4-beta-linkages between N-acetylmuramic acid and N-acetyl-D-glucosamine residues in a peptidoglycan and between N-acetyl-D-glucosamine residues in chitodextrins. Lysozyme is a part of the innate immune system as a natural form of protection from gram-positive pathogens like *Bacillus* and *Streptococcus* (Sołtys, Łazarz, & Chibowski, 1997).

Starch as polysaccharide is the most commonly consumed in the human diet and is present in appreciable amounts in many staple foods, such as dips, sauce, desserts and dressing. In recent years starch, because of its unique functional properties, is used in a number of novel foods such as puddings, tortillas, processed meats, gluten-free breads and salad dressing. As a relatively cheap and commonly available substance starch is an alternative to carrier materials that for years have been applied for the microencapsulation of food components with the spray-drying method. Starch products are applied in the process of encapsulation of oils, aromas and vitamins, also as a pharmaceutical excipient. Moreover, starch is an important component in a large number of agricultural products such as tubercles, legumes, cereals and some fruits at a physiologically immature stage (Falade & Christopher, 2015; Krstonošić, Dokić, Nikolić, & Milanović, 2015; Moo-Huchin et al. 2015).

Besides its usage as a piece of numerous food products, the polysaccharide gels could be converted into films for packaging a variety of food products. Polysaccharide coatings, however, are generally less permeable to gases and more permeable to water vapour. The high water vapour permeability is due to the presence of significant amounts of hydrophilic groups in their chemical structures, particularly hydroxyl groups. These properties can be modified by employing an appropriate procedure, as suggested in this manuscript. Biological modification of starches or starch film improves their different properties. For example modification by chitosan solution develops antibacterial and antioxidant properties. Chitosan films exhibit antimicrobial activities against a variety of microorganisms. The activity is observed when food portions are dipped or sprayed with film-forming solutions of chitosan. The antimicrobial activity of a chitosan coating increases the lag phase of many microorganisms (e.g. *Staphylococcus aureus*, *Listeria monocytogenes*, *Pseudomonas aeruginosa and Enterobacteriaceae)*. Recently some authors have stated that *Aspergillus niger* was almost completely inhibited when either a film-forming solution or chitosan film at a concentration of 0.1% (w/v) was used. On the other hand, films made of chitosan and its derivatives also possess antioxidant activity, which can be attributed to the chelating action of chitosan on metal ions and to its ability to complex with lipids. The poor oxygen permeability of chitosan films also controls lipid oxidation. These properties can have a potential for the preservation of various food products, including dairy items (Sezer & Akbuga, 1999; Wu, 2005).

Incorporation of lysozyme also enhanced the antimicrobial activity. Moreover, the solutions of chitosan and lysozyme could be stored for up to 6 months without losing their antimicrobial activities against *Escherichia coli* and *L. monocytogenes*. On the other hand, increased water solubility, lysozyme release, and decreased tensile strength and elongation were observed in the films made from solutions stored at 37 °C. The results indicated that premade chitosan–lysozyme solutions may be distributed as a commercial product for coating or film applications (Noda, 1989).

Biological modification of starch surface is strictly dependent on adhesion process. Change of temperature is a possible technique to improve adhesion at the interface and wettability. By heating starch undergoes an irreversible order/disorder transition (gelatinization) in water solution. Swollen starch granules lose crystallinity after absorption of water and leach amylose (Jenkins & Donald, 1998). Starches exist predominantly in two polymorphic forms which are packed in double helices. Amylopectin is responsible for the crystallinity, whereas branched regions are amorphous (Fechner et al. 2005; Imberty, Buleon, Tran, & Perez, 1991; van Soest, Tournois, de Wit, & Vliegenthart, 1995). Different kinds of spectroscopy were used to identify and classify starches (Dolmatova, Ruckebusch, Dupuy, Huvenne, & Legrand, 1998; Dolmatova et al., 1999; Dupuy, Wojciechowski, Ta, Huvenne, & Legrand, 1997, Dupuy & Laureyns, 2002; Phillips, Pan, Liu, & Corke, 1998; Phillips, Liu, Pan, & Corke, 1999, Rubens, Snauwaert, Heremans, & Stute, 1999; Schuster, Ehmoser, Gapes, & Lendl, 2000). One technique to improve the interfacial adhesion is surface modification by plasma. Plasma treatment is mostly used for cleaning, etching, crosslinking, radical formation, surface activation and as a predeposition process. During plasma modification the commonly used gases are air, argon or nitrogen. Plasma can be described as an energetic medium composed of electrons, positively and negatively charged ions, radicals, atoms and molecules obtained by using an outer energetic source. The degree (efficiency) of etching during plasma processes depends on the density of active species and power of ion attack towards the biopolymer surface. The intensity and depth of modification arise from plasma power and exposure time. Commonly this is a few hundred Å and can reach approximately 10 nm. For materials with a weak interface like biopolymers extent of modification should be greater. Interactions of polymer surface with plasma can cause hydrogen separation from polymeric chains and free radical creation. The radicals can interact with oxygen or nitrogen from air and thus the new functional groups can be incorporated into the biopolymer surface. Also the C–C and C–H bonds can be disrupted and cross-linking by activated species of gas can be created. The H_2O plasma can be used for incorporation of hydroxyl groups on the polymer surface. Plasma containing nitrogen (N_2 or NH_3 plasma) improves wettability, biocompatibility and printability of polymeric surfaces (Barton, Bradley, Steele, & Short, 1999; Denes & Manolache, 2004; Gil'man, 2003, Hegemann, Brunner, & Oehr, 2002; Mark, Bikales, Overberger, Menges, & Kroschwitz, 1985; Paterno, Manolache, & Denes, 2002; Pitt, Lakenan, & Strong, 1993; Steen, Flory, Capps, & Fisher, 2001).

Physico-chemical changes of starch surfaces at different temperatures and biologically modified starch surface induced by air plasma are introduced in this paper. It was interesting to find how the internal structure can influence starch surface properties before and after physical and/or chemical modification. Determination of the hydrophilic/hydrophobic character of solid surface is extensively used in pharmaceutical industry for wettability studies of drug powders or textile and paper industry. Switchable wettability may be a convenient parameter providing information about starch surface properties. Modification by antibacterial substrate's film may give new applications of starch. The first studies of measuring contact angles on starch and modified starch by biological films before and after plasma treatment are reported. The obtained results are interpreted based on surface free energy and topography parameters.

2. Theoretical basis

Wettability of a solid surface can be determined relatively simply by measuring the so-called contact angle from the Young equation (Adamson, 1990):

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta \tag{1}$$

where γ_{SL} is the solid/liquid interfacial free energy. The contact angle θ is geometrically defined as the angle formed by a liquid drop