Food Hydrocolloids 71 (2017) 17–25

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

Surface properties of ion-inducted whey protein gels deposited on cold plasma treated support

Konrad Terpiłowski [a], Marta Tomczyńska-Mleko [b], Katsuyoshi Nishinari [c, d], Stanisław Mleko [e, *]

[a] Department of Physical Chemistry-Interfacial Phenomena, Maria Curie Skłodowska University, M. Curie Skłodowska Sq. 3, 20-031 Lublin, Poland
[b] Institute of Plant Genetics, Breeding and Biotechnology, University of Life Sciences in Lublin, Akademicka Street 15, 20-950 Lublin, Poland
[c] Graduate School of Human Life Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi, Osaka, 558-8585, Japan
[d] Department of Food and Pharmaceutical Engineering, Hubei University of Technology, Wuchan, Wuhan, 430068, China
[e] Department of Milk Technology and Hydrocolloids, University of Life Sciences, Skromna 8, 20-704, Lublin, Poland

ARTICLE INFO

Article history:
Received 28 October 2016
Received in revised form
22 April 2017
Accepted 26 April 2017
Available online 27 April 2017

Keywords:
Whey protein gels
Cold plasma
Surface properties
Roughness
Rheology

ABSTRACT

So far no studies have been undertaken on the influence of plasma processing of different solid surfaces on the properties of subsequently formed protein coat. Calcium chloride, magnesium chloride or iron (II) chloride inducing whey protein isolate gels were obtained on glass support previously treated with the plasma at the electric voltage 160 V per 1 min. Dynamic oscillatory and ultrasound viscosity measurements, scanning electron microscopy imaging, surface roughness and contact angles measurements have been performed. Apparent surface free energy was determined using the two approaches: van Oss, Good and Chaudchury (LWAB) and contact angle hysteresis (CAH). Gels surface roughness increased with the increasing of ions concentration. Both approaches used for determination of apparent surface free energy give comparable results. When the air plasma was applied for the support activation, polar groups deposited on the surface had a greater effect on the surface wettability than roughness. Plasma treatment of glass support caused the increase of hydrophobic properties of deposited layers. Wettability properties were affected by the electron donor parameter of energy whose value increased for the samples obtained on the plasma activated supports especially the air treated ones. Plasma treatment of glass plates might have an effect on food processing, production efficiency, microbiological aspects and cleaning process of the gels deposited on their surfaces.

1. Introduction

Gels surface properties (wettability, roughness, pore size and shape) are very important in medicine, material science, food science and biotechnology. However, the data on gels surface are very scarce. Several scientists used a computer image analysis of scanning electron and laser scanning confocal micrographs to measure average roughness of gels (Chen, Moschakis, & Pugnalunin, 2006; Nayebzadeh, Chen, Dickinson, & Moschakis, 2006). In our previous research aerated whey protein gels were formed using calcium chloride, magnesium chloride or iron (II) chloride induced gelation of pre-denatured protein dispersions (Tomczyńska-Mleko, Terpiłowski, Mleko, Kwiatkowski, & Kawecka-Radomska, 2015). It was observed that the surface topography is mainly responsible for changes in the wettability. The surface properties depended on the type and concentration of the added salt. Higher cation concentration produced gels a with higher quadratic mean of the surface roughness and maximum roughness height. The contact angle of the probe liquid sample depended on the liquid surface tension components. Wettability, depending on the nature of the surface, was described for the hydrophilic surface by the Wenzel model, and for the hydrophobic surface by the Cassie-Baxter model (Tomczyńska-Mleko, Mleko, Kwiatkowski, & Kawecka-Radomska, 2015).

Surface plasma activation process became very attractive for industrial application. Cold plasma operating under low pressure or atmospheric conditions is used for relatively low temperature surface cleaning, polymer activation and deposition of coatings. The polymer layers activated by cold plasma exhibit engineered functionality with controlled surface wetting properties ranging from

* Corresponding author.
E-mail address: dairywhey@tlen.pl (S. Mleko).

http://dx.doi.org/10.1016/j.foodhyd.2017.04.032
0268-005X/

superhydrophilic to superhydrophobic (Dowling & Stallard, 2015).

Glass is the most applicable material for deposition of biological layers. It is cheap, amorphous and stable in a wide temperature range. Previously, it was used for deposition of hydrophobic layers (Terpiłowski, Rymuszka, Goncharuk, Sulym, & Gun'ko, 2015; Terpiłowski, 2015) or biological layers (Chibowski, Jurak, Hołysz, & Szcześ, 2014). Wang and He (2006) used sodium silicate glass samples activated by atmospheric pressure air plasma. They investigated different power (0–60 W) and different time of activation (0–60 s). Plasma activation time and power resulted in the increase of surface roughness calculated as the root mean square index (RMS). Yamamoto, Okubo, Imai, and Mori (2004) observed that in the glass manufacture process the freshly obtained glass plates are cooled down at an annealing temperature in the range of 454–482 °C, and during the process water can adsorb on the surface by the disrupted bonds on it. This disrupture results in single-hydroxyl, double-hydroxyl and closed hydroxyl groups appearance. On the surface there are hydrogen bonds between the polar groups and even nonthermal plasma (4–5 eV) is large enough to break the hydrogen bonds (0.2–0.3 eV). When plasma is applied, the O–OH bond with a shorter distance is divided by the electron impact and oxygen. More –OH groups appear on the surface. This process results in the decreasing water contact angle. Water is a polar liquid which interacts with surface by polar forces. The water surface tension at 20 °C is 72.8 mJ/m^2 of which 51.0 mJ/m^2 include polar interactions (Fowkes, 1964). The increase of air atmospheric plasma power causes the decrease of water contact angle (Wang & He, 2006). Generally, air plasma removes organic contaminants from the glass surface and hydrophilizes the surface. Ting, Rosario, Lee, Ramos, and Tumlos (2014) coated the plasma activated glass with silicone oil. For plasma activation they used the microwave atmospheric plasma power of 600 W at 10 s activation. Argon was injected as the central gas, with nitrogen as a shroud gas. After plasma treatment they observed decreasing of water contact angle from 37.6° ± 1.6° for the untreated to 5.0° ± 1.3° for the plasma-treated. Based on the AFM technique they found that the RMS value increased almost 4 times. On the FTIR spectra the untreated glass surface showed peaks corresponding to the Si–O–Si, Si–O$^-$ and CH_2 bonds. After plasma surface activation similar peaks were found except for CH_2. This can be treated as contaminants removal from the hydrocarbon surface.

Surface properties of food products (e.g. wettability, hydrophobicity, stickiness to the surface) have great influence on food processing, production efficiency, microbiological aspects and cleaning process. Determination of the hydrophilic/hydrophobic character of solid surface was extensively used in food, pharmaceutical, textile and paper industry for wettability studies, which may be a convenient parameter providing information about surface properties (Wiącek, 2015). Surface properties of biofilms with respect to roughness, hydrophobicity, protein adsorption, biofilm retention, and community composition of the retained bacteria, can influence food spoilage and pose a hazard to consumers. Fewer bacteria were retained on the sol-gel coated surfaces compared to the rougher steel surface (Tang et al., 2011). Newly engineered structures, characterized by high specific surface area and high porosity, have been widely researched for biomedical and food applications (Steyaert, Rahier, Van Vlierberghe, Olijve, & De Clerck, 2016). So far no studies have been undertaken on the influence of plasma processing of different solid surfaces on the properties of subsequently formed protein coat. We have chosen glass plates as the most popular and cheapest surface employed in many applications. It has very often a contact with different food products.

Table 1
Types of investigated whey protein gels.

Added salt	Prot. conc. % (w/w)	Salt conc. mM	pH
$MgCl_2$	7.0	20; 30	7.34
$CaCl_2$	8.0	20; 30	6.68
$FeCl_2$	7.5	10; 30	6.68

2. Materials and methods

2.1. Materials

Whey Protein Isolate (WPI) (88.0% protein) was purchased from Arla Foods Ingredients (Viby, Denmark). The WPI protein content was determined following methodology for total nitrogen (Kjeldahl).

2.2. Glass support preparation

Microscope slides 76 × 26 mm were used (Comex, Wroclaw, Poland). Before plasma activation glass plates were cleaned by methanol in the ultrasounds bath for 15 min and then rinsed with Milli-Q water and dried at 50 °C. After drying the glass plates were kept in the desiccator.

Plasma activation was performed in the low pressure plasma system Pico from Diener Electronic, Germany. The plates were placed on the sample shelf and the system was adjusted to a pressure of 0.2 mbar. Then the gas flow air or argon (Air Products, Warsaw, Poland) was set at 22 sccm (standard cubic centimeters per minute). The plates were treated with the plasma at the electric voltage 160 V for 1min. In order to remove the gaseous products, the chamber was purged with air for 10 s. To open the chamber it was necessary for the atmospheric pressure to be placed inside.

2.3. Preparation of protein solution and ion-induced gels on the glass support

The WPI dispersions were made by hydrating in distilled water at 22 °C for 30 min using a magnetic stirrer. The pH of the native protein solution was 6.68. For some samples the pH of the dispersions was adjusted to 7.34 (the average value between 6.68 and 8). The dispersions were heated in water bath for 30 min at 80 °C and then cooled down immediately. Calcium chloride or magnesium chloride or iron (II) chloride was added to obtain the concentrations 10, 20 or 30 mM in the final product (see Table 1). Immediately after the salt addition, the solutions were stirred for 10 s at 100 rpm using Compact Digital Lab Mixer (Cole-Parmer, Montreal, Canada) and poured on the glass plates to obtain a 1 (±0.1) mm thick layer (it was checked using a micrometer screw gauge). The plates were stored for 20 h at 7 °C, equilibrated at 21 °C for 2 h and subjected to determination of their surface properties. The rest of the ion-induced gel was used for other measurements.

2.4. Dynamic oscillatory measurements

After adding salt solutions to the pre-heated protein dispersions and stirring for 10 s at 100 rpm using Compact Digital Lab Mixer (Cole-Parmer, Montreal, Canada), the dispersions were poured on the serrated plate of the RS300 rheometer (ThermoHaake, Karlsruhe, Germany). Rheological properties were investigated using a serrated parallel steel plate geometry (35 mm diameter, 2 mm gap size) to limit the sliding effects. The gelation process was monitored for 600 s at 1 Hz and 0.01 strain. The gels stored overnight were analyzed using frequency sweeps in the 0.1–10 Hz range at 0.01strain (linear viscoelasticity region).