Comparative cleaning tests with modified protein and starch residues

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ABSTRACT

The cleanability of food contact surfaces is determined by surface characteristics and the properties of the soiling material. Effects of selected physicochemical parameters of biopolymer soils on the removal from stainless steel were studied using a laboratory flow cell system with continuous removal measurement and, additionally, gravimetric detection. The results show the potential for improving cleaning processes on the basis of structural properties of the biopolymers. A higher cleaning efficiency was achieved when surface energy and cationic charge of the polymers was lower, indicating that adhesive interactions (van der Waals forces of attraction and electrostatic forces) between surface and polymer play a dominant role. The effects of pre-heating treatments of the soils, inducing molecular changes, on removal behavior were however not significant. The results indicate that a holistic view of product and process design is useful to develop efficient cleaning protocols.

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1. Introduction

Cleaning is essential to ensure hygienic food production and process performance. To improve efficiency of the cleaning of either heated or unheated surfaces, the knowledge of the specific soil properties that affect the performance of cleaning processes is essential. The understanding how organic soils respond to cleaning assists to finding decisions concerning cleaning fluid and method (Fryer and Asteriadou, 2009; Wilson, 2005).

To execute efficient cleaning, adhesive and cohesive bindings of a soil onto contact surfaces must be overcome with minimal energy. The mechanisms of particle or polymer removal are influenced by the physicochemical properties of the soiling material and can be explained by thermodynamic and electrostatic fundamentals (Fourche, 1995; Michalski et al., 1997; Visser, 1995). According to the DLVO theory, total interaction energy comprises Lifshitz–van der Waals attractive forces, and attractive or repulsive electrostatic forces. Van der Waals interactions itself depend mainly on the Lifshitz–van der Waals (LW) surface free energy of the soil, and the electrostatic interaction is controlled by its electrokinetic potential. In contrast to electrostatic forces, van der Waals contributions are insensitive to pH variation and electrolyte concentration in aqueous systems (Al-Amoudi and Lovitt, 2007; Zhao and Liu, 2006). Contact area effects, depending on soil particle roughness and morphology, play an additional role in polymer/surface interactions (Bobe et al., 2007; Liu et al., 2006).

Several physical and chemical processes that alter the structure of organic soils may influence adhesion to contact surfaces. For example, acidification leads to systems with a higher cationic charge and hydrophobicity, which increases attractive forces so that removal becomes more difficult (Lopez et al., 2010; Stanga, 2010). Mauermann et al. (2009) reported a decrease of cohesive interactions within the soil and between soil and surface when surface and protein or starch-based soils have the same electrical charge. Itoh et al. (1995) explained electrostatic interactions between β-lactoglobulin and stainless steel by modified amino or carboxyl groups. For several starch types, Prochaska et al. (2007) showed that polar carboxyl group substitution resulted in enhanced surface activity and was accompanied by a viscosity decrease, especially at pH < 4.0. Drying removes water from a substrate and leads to changes such as volume reduction, solids redistribution and polymerization. Closer packing increases cohesive forces in films and makes removing and dispersing soils more difficult (Jonhed et al., 2008; Stanga, 2010). Additionally, LW surface free energy γ^{LW} of the soil will change. In context with tomato paste removal from stainless steel, Liu et al. (2006) reported on an adhesive strength of $\gamma^{LW} = 29.2$ mJ/m^2 for the unbaked system, and of

$\gamma^{LW} = 30.6$ mJ/m^2 for tomato paste baked onto the steel. Detry et al. (2011) revealed an influence of the drying rate on starch granule adherence, which was attributed to physico-chemical wetting mechanisms. Exposure to more than 60 °C also causes structural changes. It was reported that, when globular proteins undergo shape changes through denaturation, the exposure of hydrophobic sites leads to insolubilization. Surface hydrophobicity affects shape and compactness of adhering aggregates at soiling and their interfacial behavior during cleaning (Sava et al., 2005; Rabe et al., 2011). Goode et al. (2013) observed a significant temperature-induced increase in adhesion forces between whey protein and stainless steel. When starch is gelatinized in water, colloidal solutions of high viscosity are obtained, in which the internal structures of the granules undergo considerable changes (Ratnayake and Jackson, 2006).

The need to study and optimize cleaning has contributed to the development of specialized research techniques including flow cells, micromanipulation devices, or fluid dynamic gauging (Gordon et al., 2014). To evaluate soil adherence to surfaces, the residual soil mass after applying washing or cleaning protocols on solid surfaces can be determined (Handojo et al., 2009; Michalski et al., 1997). Flow cells were applied for comparative investigation of the cleaning behavior of different soils (Detry et al., 2009; Otto et al., 2014). Sensitive and rapid spectroscopic techniques may be used to continuously assess the amount of polymers removed from stainless steel, or in cleaning solutions (Boyd et al., 2001; Fickak et al., 2011).

Several studies concerning the removal of several types of food soils were performed to investigate effects of surface modification treatments at different scale level, to determine properties of cleaning agents, or to develop or to monitor cleaning techniques (e.g., Boxler et al., 2013; Jeurnink and Brinkman, 1994; Saikhwan et al., 2006; Otto et al., 2011; Wallhäußer et al., 2012). The cleaning mechanism is also influenced by type and properties of the residues which are to be removed. A general relationship between soil characteristics and cleaning energy is given by Fryer and Asteriadou (2009) who developed the cleaning map to classify cleaning problems. However, little work has been done to extend the classification matrix to cohesive solid soil residues. This article demonstrates effects of selected modification procedures of starch and protein on the cleaning result. The parameters analyzed were the electrokinetic potential, surface free energy and conformational changes of a range of polymer residues treated by various process conditions such as acidification, drying and heating.

2. Materials and methods

2.1. Materials

The test specimens had a surface roughness ≤0.8 μm, which is generally recommended for being used in the food industry (Gerhards and Schmid, 2013). The coupons from electropolished stainless steel 316L (40 × 20 × 1 mm^3) were washed in 1% NaOH under sonication (15 min, 45 kHz, 160 W), rinsed in deionized water and dried on filter paper. Other surface properties of the steel coupons are: surface free energy, 38.3 mJ/m^2; isoelectric point, 4–5 (Mauermann et al., 2009).

Milei 80 whey protein (Milei GmbH, Leutkirchen, Germany), soy protein (Vegacon 90, Nutrition-Factory Alphacaps GmbH, Augustdorf, Germany), native waxy corn (WC) starch (Maisita 21.000, Agrana Stärke GmbH, Aschach, Austria) and oxidized potato (OP) starch (Aganadyn 20.050) were selected as model polymers. Moisture was determined by drying at 105 °C to constancy (ISO, 1996), fat content was determined by the Soxhlet method (ISO, 1994), and protein by the Kjeldahl method (ISO, 2005) using

conversion factors of 6.25 for whey protein and 5.71 for soy protein. Ash was determined by incineration (ISO, 2007), and carbohydrate content was calculated as remaining difference to 100%. The amylose content of starch was analyzed using the concanavalin-A binding method (Yun and Matheson, 1990) with a commercial test kit (Megazyme Ltd., Bray, Ireland) (Table 1).

2.2. Soiling material preparation and modification

Based on suggestions from literature (Boyd et al., 2001; Detry et al., 2011), each powder was suspended in deionized water at a concentration of 1% (w/v). After stirring for 12 h at room temperature, 100 μL liquid soil (thus containing 1 mg polymer) was pipetted onto a 2 cm^2 area of the steel coupons and dried at 55 °C for 1 h.

In addition to this standard soiling procedure, modified polymer residues were prepared by changing pH and/or drying temperature, or by pre-heating the polymer suspensions to mimic processing conditions. pH adjustment was done with 0.5% HCl (pH 3), or with 0.5% NaOH (pH 9). To simulate thermal exposure, the soil films on the coupons were dried at 90 °C for 1 h. Heat-induced modification of the polymers prior to soiling was achieved by heating the suspensions in a water bath to 82 °C for 2 min.

2.3. Characterization of test soils

2.3.1. Electric properties

Streaming potential and isoelectric point (IEP) of acidified or alkalized polymer suspensions were determined using a PCD 03 pH particle charge detector (Mütek, Herrsching, Germany; Mohammed et al., 2000). After filling 20 mL 1% (w/v) polymer suspension into the teflon cell, the streaming potential was induced by a plunger oscillating in the sample cell. Measurement temperature was 21 °C. pH was adjusted by 0.1 mol/L HCL or 0.1 mol/L NaOH in 0.05 mL/min steps with an automatic titration device (Metrohm AG, 702 SM). The potentials (mV) were recorded in duplicate together with suspension pH by PCD-Titration software 1.6. In the titration curve the polymer IEP refers to pH at a streaming potential of zero.

2.3.2. Thermodynamic properties

Contact angles of polymer films were determined by a modified Wilhelmy plate method using a digital DCAT11 tensiometer (Dataphysics, Filderstadt, Germany; Stiller et al., 2004). The stainless steel coupon was coated on both sides with thin coherent films by sequential pipetting of 100 μL polymer suspension on each side and subsequent drying at 55 °C or 90 °C for 1 h. The plate was attached to the instrument's microbalance (accuracy: 0.01 mg) and immersed into α-bromonaphthalene (α-BN) at 2 mm/min. The contact angle θ (°) was calculated from the wetting force F (mN) by $\cos\theta = F/\gamma L$ where γ is the surface tension of α-BN (44.4 mJ/m^2) and L (m) is plate perimeter. From the average contact angle cosine of the apolar α-BN, the Lifshitz−van der Waals component of the surface free energy γ^{LW} (mJ/m^2) of dry soil films was calculated using $\gamma^{LW} = 11.1 \times (1 + \cos\theta)^2$ (Zhao et al., 2004). Analysis was done in 10 replicates.

2.3.3. Thermal properties

Thermal properties of the biopolymer soil residues were analyzed in duplicate by differential scanning calorimetry (DSC) from 20 to 110 °C at a heating rate of 10 K/min using a DSC Q200 with hermetic aluminum pans (TA Instruments, Eschborn, Germany). The soils were detached from coupons by placing them in 10 mL deionized water in a T480/H-2 ultrasonic bath (Elma GmbH, Singen, Germany) for 1 h and subsequently concentrated with an