ACS APPLIED MATERIALS & INTERFACES

Research Article

www.acsami.org

Water-Wettable Polypropylene Fibers by Facile Surface Treatment Based on Soy Proteins

Carlos Salas,[†,‡] Jan Genzer,[§] Lucian A. Lucia,[†] Martin A. Hubbe,[†] and Orlando J. Rojas[†,§,⊥,*]

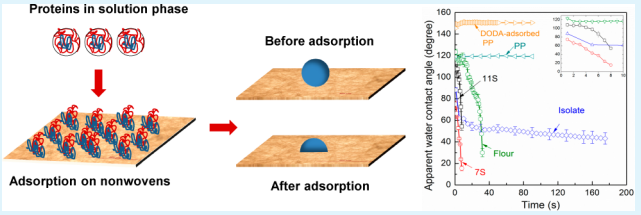
[†]Department of Forest Biomaterials and [§]Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27695, United States

[‡]Department of Chemical Engineering, Universidad de Los Andes, Mérida 5101, Venezuela

[⊥]School of Chemical Technology, Department of Forest Products Technology, Aalto University, 00076 Aalto, Finland

Supporting Information

ABSTRACT: Modification of the wetting behavior of hydrophobic surfaces is essential in a variety of materials, including textiles and membranes that require control of fluid interactions, adhesion, transport processes, sensing, etc. This investigation examines the enhancement of wettability of an important class of textile materials, viz., polypropylene (PP) fibers, by surface adsorption of different proteins from soybeans, including soy flour, isolate,glycinin, and β-conglycinin. Detailed investigations of soy adsorption from aqueous solution (pH 7.4, 25 °C) on polypropylene thin films is carried out using quartz crystal microbalance (QCM) and surface plasmon resonance (SPR). A significant amount of protein adsorbs onto the PP surfaces primarily due to hydrophobic interactions. We establish that adsorption of a cationic surfactant, dioctadecyldimethylammonium bromide (DODA) onto PP surfaces prior to the protein deposition dramatically enhances its adsorption. The adsorption of proteins from native (PBS buffer, pH 7.4, 25 °C) and denatured conditions (PBS buffer, pH 7.4, 95 °C) onto DODA-treated PP leads to a high coverage of the proteins on the PP surface as confirmed by a significant improvement in water wettability. A shift in the contact angle from 128° to completely wettable surfaces (≈0°) is observed and confirmed by imaging experiments conducted with fluorescence tags. Furthermore, the results from wicking tests indicate that hydrophobic PP nonwovens absorb a significant amount of water after protein treatment, i.e., the PP-modified surfaces become completely hydrophilic.



KEYWORDS: *soy proteins, surface modification, polypropylene nonwovens, protein adsorption, wettability, wicking*

INTRODUCTION

Commodity products are required to be stable and resistant to chemical, physical, and biological agents, which is important in their performance and life cycle.[1] Polymeric materials, in general, possess good mechanical and chemical properties that allow their use in many industrial and household applications. However, one drawback of most commonly used polymeric materials is their low surface energy resulting in low water wettability.[1,2] To overcome this latter issue, different surface modification procedures have been evaluated, including plasma treatment,[3,4] corona discharge,[3] flame treatment,[1,3] UV light irradiation,[5,6] electron beam,[7] ozone treatment accompanied with surface grafting[5] and protein adsorption followed by polymer grafting.[8,9] In addition, surface modification by adsorption of surface active agents has been applied.[1,10] These treatments have successfully "activated" the surface for further attachment of other molecules for the express purpose of improving hydrophilicity, and reducing the adhesion of biomolecules that can cause surface fouling.

Polypropylene (PP) has been studied intensively because of its relevance in textiles/fabrics, diapers, filters, and medical implants. Associated applications require high wettability, good adhesive properties, and in the case of medical implants, resistance to protein fouling.[11]

Exposure of hydrophobic polymeric surfaces to protein solutions leads to biofouling. This is an undesirable effect especially in surfaces such as those involved in biomedical devices. This drawback can, however, be turned into an advantage to endow hydrophobic PP with functional groups that could serve as a platform for the introduction of further functionalities. This has been in fact a premise of some of our recent work,[9] which takes advantage of the more than 20 amino acids with specific polar and nonpolar functionalities in proteins. Adsorption of proteins onto solid surfaces is a dynamic process affected by several factors related to the structure of the protein, the solid substrate, and physical-chemical variables.[12,13] The protein adsorption process is driven by different interactions, including but not limited to hydrophobic effects, hydrogen bonding, van der Waals interactions, and electrostatic forces that, in turn, affect the

Received: March 25, 2013
Accepted: June 21, 2013
Published: June 21, 2013

   dx.doi.org/10.1021/am401065t | ACS Appl. Mater. Interfaces 2013, 5, 6541−6548

way the molecules rearrange on the surface upon adsorption.[14] When proteins come into contact with a hydrophobic substrate, they adsorb readily on the surface to minimize the interfacial energy. Upon exposure to hydrophobic surfaces, proteins allow their hydrophobic residues to come close to the substrate while leaving the more hydrophilic groups exposed to the surrounding environment.[13]

Recently, protein adsorption onto polypropylene fibers was shown to provide high density of functional hydrophilic groups for further grafting of polymer brushes.[9] Lysozyme and fibrinogen were adsorbed on PP nonwovens and cross-linked on the surface by using glutaraldehyde. Such an approach for protein coating showed very good stability to different harsh treatments including sonication, heating at high temperature (85 °C), and immersion in organic solvents (for example, THF). Once adsorbed, the functional groups in the proteins allowed the grafting of poly(2-hydroxyethylmethacrylate) via atom transfer radical polymerization (ATRP); these polymer brushes were found to have antifouling properties.[9] We developed polypropylene fiber mats with antibacterial properties after adsorption of heat-denatured lysozyme, which carry functional groups that bind silver nanoparticles.[15] Similarly, the preparation of a functionalized PP membranes was recently reported by immobilization of bovine serum albumin (BSA) onto its surface.[16] The PP surfaces were treated by oxygen plasma and UV radiation, which then allowed grafting of poly(acrylic acid) residues that servedas spacers for the attachment of BSA. The BSA reduced further protein adsorption and improved wettability of the membrane.

Although several of the proteins used in our previous studies provided a proof of concept for the given applications, surface modification in an industrial scale can be limited because of the protein's cost and availability. For example, in contrast to lysozyme and fibronectin, other proteins, such as those derived from soy beans, are readily available and are inexpensive. Soy protein products that are commercially available include soy flour (protein content ca. 56%), concentrates (65% protein), and isolates (90% protein). Soybean proteins are composed of two main macromolecules, glycinin (or 11S), and β-conglycinin (or 7S).[17]

Soybean proteins have found industrial nonfood applications in the manufacture of plastics, adhesives, paper binders, composites, paint, dry strength additives in papermaking, paper coatings, and sizing agents.[18] We reported recently on the adsorption of soybean proteins on hydrophilic substrates[19] and their effectiveness[20] in modifying the surface of hydrophobic lignin and that of self-assembled (SAM) 1-dodecanethiol monolayers; both the lignin and hydrophobic SAM became hydrophilic after simple protein physical adsorption.[20] In this work, we report on a facile procedure leading to surface modification of PP fibers and PP substrates by physical adsorption of soy proteins. The performance and effectiveness of commercial soybean isolate and flour as surface modifiers of hydrophobic polypropylene to increase the hydrophilicity is compared against that of soy glycinin and β-conglycinin.

MATERIALS AND METHODS

Soybean flour (7B deffated soy flour) and soy isolate (Profam 974) were provided as a gift from Archer Daniel Midland (ADM, Decatur, IL). Soy glycinin (11S) and β-conglycinin (7S) were fractionated from defatted soy flour as described previously.[19] Polypropylene (PP) syndiotactic, phosphate buffer saline (PBS), fluorescein isothiocyanate (FITC), 2-propanol (isopropanol), and xylene were purchased from Sigma Aldrich (St. Louis, MO). Regenerated cellulose dialysis membranes (Fisherbrand 15.9 mm diameter (25 mm flat width), 12 000−14 000 molecular weight cutoff) were purchased from Fisher Scientific (Somerville, NJ).

Preparation of Thin PP Films. Ultrathin PP films were prepared according to the procedures described elsewhere.[21] Briefly, PP was dissolved in xylene (0.2 wt % solution) and heated up to boiling temperature in a small flask with reflux condenser for 2 h. PP films were prepared by spin coating. The solid supports (SPR gold sensors or QCM AT-cut quartz crystals) were preheated to 85 °C before spin coating by using an infrared lamp (250 W). A small volume (100 μL) of solution was poured on the substrate and spun at 3000 rpm for 20s.

Quartz Crystal Microgravimetry (QCM). The principles and operation of QCM have been described in detail elsewhere.[22−24] Here we used a QCM-D E4 (Q-Sense, Gothenburg, Sweden) operated in the batch mode. The Johannsmann[25] model was used to calculate the mass adsorbed onto the surface (see the Supporting Information for details).

The adsorption experiments were carried out with the PP thin films. Freshly prepared protein solutions of different concentrations (1, 10, 100, and 1000 μg/mL) in phosphate buffer (PBS) at pH 7.4 were used. The sensors were allowed to equilibrate in the buffer solution for ∼2 h prior to recording the base signals for QCM's Δf and ΔD, which were zeroed and allowed to run for 10 min before injection of the protein solution.

Surface Plasmon Resonance. Protein adsorption was also investigated by surface plasmon resonance (SPR Navi 200, Oy BioNavis Ltd., Tampere, Finland) under the same conditions used in the QCM experiments (concentration, temperature of 25 °C, pH, rinsing protocol, etc.). The thickness of the adsorbed protein layer was determined by using eq 1, and the surface excess concentration was computed using eq 2[26]

$$d = \frac{l_d}{2}\frac{\Delta\theta}{m(\eta_a - \eta_o)} \quad (1)$$

$$\Gamma = \rho d \quad (2)$$

where Γ is the surface excess (adsorbed excess of protein per unit surface area), $\Delta\theta$ is the angle shift, d is the thickness of adsorbed layer, l_d is a characteristic evanescent electromagnetic field decay, estimated to be ∼0.37 times the wavelength of the incident light (240 nm), m is a sensitivity factor for the sensor (109.95°/RIU, RIU: refractive index units) obtained by calculating the slope of a $\Delta\theta$ calibration for solutions of known refractive indices.[27] η_o is the refractive index of the bulk solution (buffer, 1.334[28]) and η_a is the refractive index of the adsorbed species (protein), which was assumed to be 1.57.[29] ρ is the bulk density of the soy protein (1370 kg/m^3), determined from specific volume data (0.73 mL/g).[30]

The contribution of water coupled to the adsorbed layer[31] was calculated from the mass determined in SPR and QCM experiments, according to eq 3.

$$\%\ \text{coupled water} = 100\frac{(\text{mass}_{QCM} - \text{mass}_{SPR})}{\text{mass}_{QCM}} \quad (3)$$

Adsorption on PP Nonwoven Surfaces. Nonwoven mats from melt blown PP fibers (5.2 ± 2 μm diameter) were obtained from the Nonwovens Institute (NWI, North Carolina State University). The PP nonwoven mats (1 cm × 1 cm, 30 g/m^2, 0.1 mm thickness) were first cleaned by immersion into 2-propanol for 20 min, rinsed with water, and then dried over at least 18 h in a laminar flow cabinet. The clean mats were then immersed first in isopropanol for 10 min, followed by a pretreatment involving immersion in 1 mg/mL dioctadecyldimethyl ammonium bromide (DODA) surfactant in 2-propanol solution during 30 min. The mats were rinsed with PBS buffer for 10 min. For adsorption experiments, the protein solutions (1 mg/mL in phosphate saline buffer at pH 7.4) were used at 25 °C. In some experiments, the proteins were denatured before adsorption by heating their solution at 95 °C during 1 h while stirring occasionally and then cooling to 25 °C before application.

PP mats were immersed in protein solution during 1 h while using magnetic stirring. Subsequently, the PP mats were immersed in buffer for 10 min followed by milli-Q water washing for 10 min. Prior to the contact angle measurements, the PP mats were dried for at least 18 h inside laminar flow cabinet to avoid contamination of the surface.

Fluorescent Labeling of Soy Proteins and Fluorescence Imaging. The labeling reaction was carried out following the procedure reported by Lakemond et al.[32] Fluorescein isothiocyanate (FITC) was dissolved in 10 wt % ethanol solution in PBS buffer pH 7.4 to yield 1 mg/mL solution. Protein solutions (2 mg/mL) were prepared and appropriate amounts of FITC were added to reach a molar ratio of 1:10 of protein:FITC. Once the FITC was added, the vials were covered with aluminum foil to keep them protected from light. The solutions were incubated for 18 h at room temperature and under mild magnetic stirring. After the 18 h period, the reaction was quenched by adding a sufficient amount of cysteine to the mixture (to achieve a molarratio of protein/cysteine of 1:12.5). This mixture was left under stirring for 4 h. Afterward, the solutions were dialyzed against PBS buffer pH 7.4 to remove unbound FITC and unreacted cysteine. An Olympus BX61 microscope (Olympus America Inc. Melville, NY) in the fluorescence mode, with an objective of 4×/0.10, was used to observe the surface of the nonwovens after adsorption of FITC-labeled soy proteins.

RESULTS AND DISCUSSION

Adsorption of Soy Proteins on Flat PP Thin Films. A high soy protein adsorption affinity toward PP is observedby the very fast initial adsorption as measured by electro-mechanical methods (time-dependent frequency shift isotherms from QCM) or optical (changes in the refractive index at the interface in SPR) measurements (cf. Figure 1a, b). The results of adsorption of soy proteins in their native conditions onto the surface of thin PP films (PBS buffer pH 7.4) studied by QCM are plotted in Figure 1a. Both soy flour and soy isolate displayed a well-defined adsorption plateau, which indicates saturation of the surface. In contrast, the QCM profiles for the 11S and 7S proteins did not plateau at the highest concentration studied (1 mg/mL). In addition, the initial rate of adsorption was very fast (note the initial steep slope in the QCM isotherm) for the flour and isolate, indicating their high affinity toward PP.

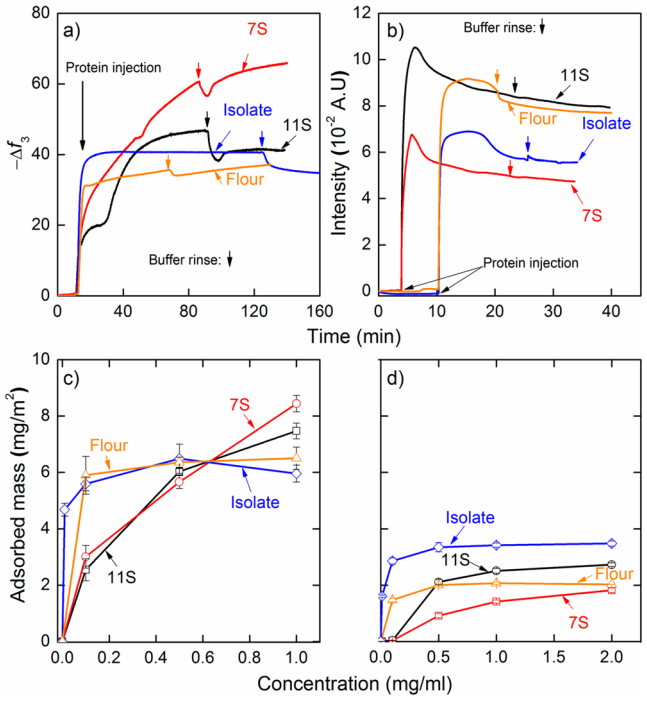


Figure 1. Adsorption of soy proteins on flat PP thin films determined by (a) the frequency shift as a function of time upon injection of 1 mg/mL protein solutions in QCM experiments and (b) changes in optical intensity (arbitrary units) signal from SPR experiments, also after adsorption form 1 mg/mL protein solution. The obtained adsorbed mass isotherms for soy proteins on flat PP thin films are also indicated from (c) QCM and (d) SPR techniques.

Adsorption studies of soybean proteins (11S and 7S) on hydrophobic self-assembled monolayers (1-dodecanethiol) indicated similar trends to those observed for PP substrates (data not shown): 11S adsorbed to a higher extent compared to 7S because of the more favorable interactions of 11S with the hydrophobic surface, which allows a tighter packing at the interface as well as the possible engagement of 11S in sulfur–sulfur associations.[20]

To evaluate the effect of hydration of the protein on their adsorption, we also monitored the process by SPR; the respective isotherms are shown in Figure 1b, d. As expected, the measured adsorbed amount was lower than that from QCM experiments(Figure 1a, c). Interestingly, each protein exhibited a different behavior when probed by QCM or SPR. These observations are explained by different hydration of the protein adlayers, as sensed by these two methods (QCM and SPR). When the hydration of the adlayers was determined by eq 3, the amount of coupled water follows the order 7S > flour > 11S > isolate (see Table 1). The same results have been observed when lignin was used as a substrate.[20] This can be related to the protein structure: 7S is a glycoprotein, whereas 11S does not have any bound carbohydrates.[33] Soy flour contains both the 11S and 7S proteins as well as soluble carbohydrates (glucose, arabinose, xylose, galactose, and sucrose)[34] that can affect the adsorption behavior and hydration. The commercial soy isolate is obtained by a different process; isolates are obtained from processing dehulled and deffated soy flour; soy isolates have a higher protein content and the proteins are precipitated at their isoelectric pH. In addition, during the process, the fiber and the sugars are removed from the product.[35] Therefore, the isolates are more hydrophobic than the flour, i.e., there are more hydrophobic amino acids exposed in the isolate than the flour. In addition, the carbohydrates and soluble fiber are removed during production of soy isolate.[35]

Table 1. Coupled Water Mass of Adsorbedsoy Protein Layersafter Exposing PP Thin Films to 1 mg/mL Protein Solutions

	adsorbed mass (mg/m^2)			
	Γ_{QCM}	Γ_{SPR}	$\Gamma_{QCM}-\Gamma_{SPR}$ (mg/m^2)	% coupled water
11S-native	7.5	2.5	5.0	66.6
7S-native	8.4	1.4	7.0	83.3
isolate	6.0	3.4	2.6	43.3
flour	6.5	2.1	4.4	67.7

The effect of thermal denaturation on protein adsorption was studied. To this end, the proteins were heated to 95 °C in PBS buffer pH 7.4 and maintained at this temperature for 1 h; the solutions were then cooled to 25 °C before running QCM experiments to acquire the adsorption isotherms (Figure 2).

Thermal denaturation promotes unfolding of the proteins by exposing internal hydrophobic amino acids to the aqueous

dx.doi.org/10.1021/am401065t | ACS Appl. Mater. Interfaces 2013, 5, 6541−6548

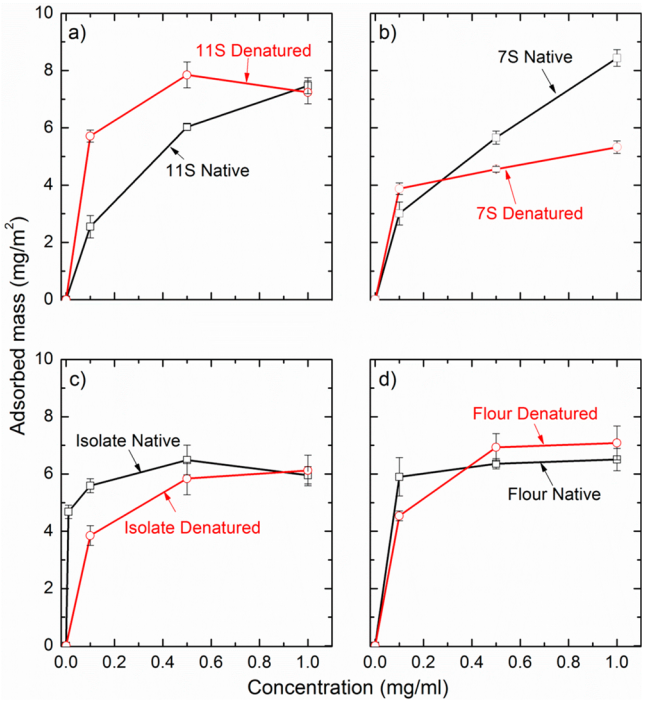


Figure 2. Adsorption isotherms for native and denatured soy proteins obtained from QCM experiments with (a) 11S, (b) 7S, (c) isolate, (d) flour.

environment. This, in turn, can promote higher adsorption onto hydrophobic substrates.[14] It was expected that compared to native proteins, protein solutions thermally treated at 95 °C would adsorb to a higher extent on the thin PP films. However, the results in Figure 2 indicate that all proteins exhibited similar adsorption upon thermal denaturation. It is possible that there is a small fraction of the protein that refolds upon cooling, as has been observed in gelation studies.[36] Although in our experiments there was no evidence of aggregation as no change in turbidity of solutions was observed by visual inspection, it is possible that the proteins aggregated upon cooling and these aggregates, with a larger effective volume, affected their packing at the interface.

Adsorption on PP Nonwovens. Adsorption of soybean proteins on the surface of PP nonwoven substrates was studied. Initially, the experiments were carried out by immersing the nonwovens immediately after cleaning into protein solutions (native or denatured). Because of the low surface energy of the nonwoven PP mats, the substrates tended to float on the protein solution even under stirring; this led to a poor contact of the PP nonwovens with the proteins which prevented effective adsorption. To overcome this issue, we carried out experiments by first immersing the PP nonwovens in 2-propanol followed by an immersion into 1 mg/mL solution of cationic DODA surfactant. This surfactant has been used in previous studies to functionalize hydrophobic surfaces using Langmuir–Schaefer deposition technique.[37] Because DODA surfactant is not soluble in water, 2-propanol was the solvent of choice because it was the same used to clean the PP nonwovens before adsorption experiments.

The adsorption of 1 mg/mL DODA surfactant solution on the surface of polypropylene thin films was studied by quartz crystal microbalance. It was observed that a thin layer of DODA surfactant adsorbed on PP after rinsing with 2-propanol (Figure 3a).

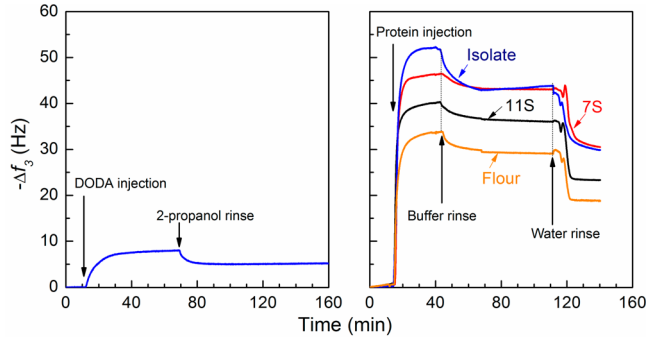


Figure 3. (a) Dynamics of DODA surfactant adsorption on polypropylene thin films measured in QCM experiments (from 1 mg/mL DODA solutions in isopropanol). (b) The adsorption isotherms for the different soy proteins (1 mg/mL) on DODA-treated PP surfaces are also shown.

The calculated areal mass of DODA adsorbed onto the surface is 0.83 mg/m^2 (1.3×10^{-6} mol/m^2). After the adsorption with DODA and further rinsing with 2-propanol, the proteins (1 mg/mL solutions) were adsorbed onto the DODA-treated PP surfaces (Figure 3b). It is worth highlighting the steep initial slope in all adsorption curves that indicates a high affinity of the proteins with the DODA-treated PP substrate.

As can be observed in Figure 3b, there is a significant adsorption of proteins on the pretreated PP surface. Some desorption upon buffer rinsing occurred as well as after rinsing with water; however, the large amount measured for the residual adsorbed proteins indicates a strong binding with the PP surface. Comparing the mass of protein adsorbed from thermally denatured solutions without preadsorption of DODA surfactant (see Table 2), different trends for each protein are

Table 2. Comparison of Adsorbed Mass on Polypropylene Surfaces (with and without DODA treatment) from 1 mg/mL solution of denatured protein

	adsorbed mass (mg/m^2)	
	No DODA pretreatment	After DODA pretreatment
11S	7.2	6.3
7S	5.3	7.6
isolate	6.1	7.6
flour	7.1	5.1

observed. Lower adsorption occurred after surfactant treatment in the case of 11S and soy flour, whereas 7S and the soy isolate displayed a higher adsorption. One reason why 11S and the flour exhibited lower adsorption is the flatter conformation of the protein molecules on the DODA-treated surface as is shown in the dissipation-frequency ($\Delta f - \Delta D$) curves in Figure 4. In addition, conformational changes (spreading) of the molecules upon adsorption can induce better coverage (tighter packing) on the surface but less mass adsorbed. The different adsorption behaviors are likely related to the structural differences of the molecules, as mentioned before in our discussion of Table 1; the isolate is more hydrophobic compared to flour, and the 7S protein tends to have a higher

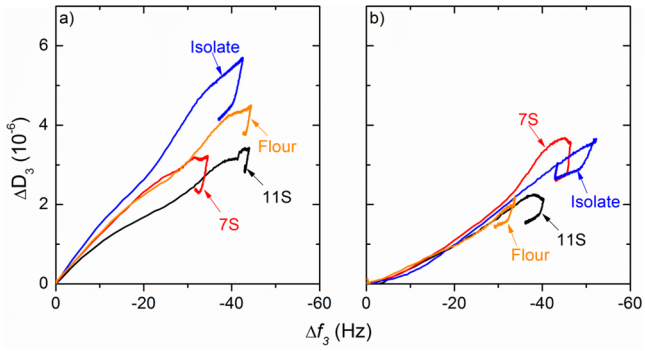


Figure 4. $\Delta D-\Delta f$ profiles for adsorption of soy proteins on polypropylene (a) without and (b) with treatment with DODA surfactant.

hydration than 11S. The trends are very similar to those observed in panels c and d in Figure 1.

The value of adsorbed mass does not provide direct information related to the conformation of the protein molecules upon adsorption. However, the QCM viscoelasticity values from the dissipation factor can provide such insight. As such, the $\Delta D-\Delta f$ curves included in Figure 4 indicate that the adsorbed proteins were more extended on PP when denatured (Figure 4a). The $\Delta D-\Delta f$ profiles upon protein adsorption on PP with preadsorbed DODA are also included (Figure 4b). The results suggest that the proteins adsorbed on PP in a flatter conformation when the DODA surfactant was present. This is reasonable because the proteins are expected to be negatively charged at the pH studied (isoelectric pH of ~4.5).[29,38] Therefore, when the PP surface was coated with cationic DODA surfactant, the cationic sites were available for electrostatic interaction with the negatively charged amino acids of the proteins. This could also promote a more uniform distribution of the protein molecules on the surface.

Water Contact Angle. Evaluation of the surface characteristics after adsorption was carried out by water contact angle (WCA) measurements. WCA was measured on quartz crystals coated with PP before and after protein adsorption (Table 3). The results indicate a significant decrease in WCA after protein adsorption. This supports the effective use of soy proteins to modify hydrophobic surfaces.

Table 3. Water Contact Angle Results for Adsorption of Denatured Proteins onto Polypropylene Thin Films after Treatment with DODA Surfactant

	water contact angle (deg)		
	before protein adsorption	after protein adsorption	WCA reduction. (deg)
11S	106 ± 2.0	27 ± 2	79
7S	105 ± 1.2	31 ± 0.2	74
isolate	105 ± 3	45 ± 1	60
flour	105 ± 2	33 ± 3	72

The decrease in WCA after adsorption of native proteins on smooth PP films without DODA treatment produced a reduction in contact angle of ~67° after adsorption of 11S, 7S, and soy isolate, whereas a reduction of contact angle of 43° was obtained after adsorption of soy flour. By contrast, the results in Table 3 indicate a higher reduction in contact angle by treating the PP surface with DODA followed by adsorption of denatured proteins. To further explore this observation, we carried out experiments using PP nonwoven samples under similar conditions of temperature, pH, and protein concentration (1 mg/mL). WCA as a function of time after adsorption of each protein studied under native and denatured conditions can be observed in Figures 5 and 6, respectively. It is worth

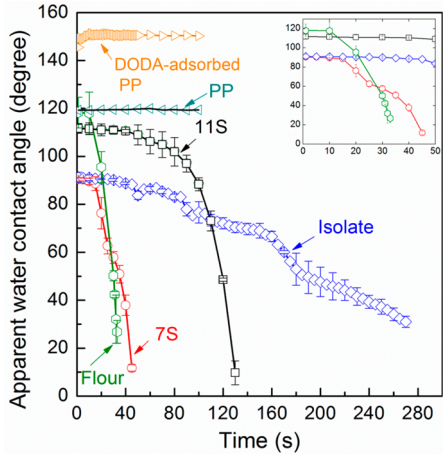


Figure 5. Time-resolved evolution of the water contact angle upon adsorption of native proteins on the surface of DODA-treated polypropylene nonwovens. Inset corresponds to the initial 50 safter water drop deposition.

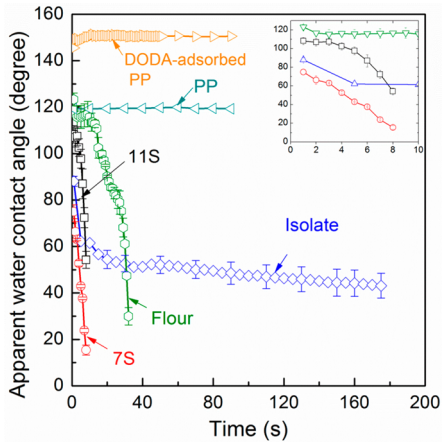


Figure 6. Time-resolved evolution of the water contact angle upon adsorption of denatured proteins on the surface of polypropylene nonwovens. Inset shows initial 10 s of the experiments.

mentioning that PP surfaces and DODA-treated PP surfaces did not display any change in WCA over time. Furthermore, DODA-adsorbed PP had a higher contact angle compared to the bare, untreated PP surfaces. The contact angle images of these surfaces after the respective treatments are supplied in the Supporting Information.

The adsorption behavior of native and denatured proteins on PP nonwoven mats is expected to be different than that discussed for smooth thin films. In fact, protein adsorption onto PP nonwovens (without DODA treatment) did not produce a change in contact angle as was the case of the flat PP films. A dewetting of the nonwoven surface when immersed in aqueous solutions (hydrophobic effect) occurs because of the low surface energy of PP, which in turn affects the diffusion of the protein from the bulk across the boundary layer surrounding

dx.doi.org/10.1021/am401065t | ACS Appl. Mater. Interfaces 2013, 5, 6541−6548

the substrate. The hydrophobic amino acids inside the protein interact favorably with the PP surface, but the tight arrangement of water molecules around the hydrophobic substrate imposes a high energy barrier that limits adsorption. To surmount this issue, we made different attempts to improve the contact between the nonwoven mats and protein in solution during the adsorption process. This included: (1) immersion of the nonwovens in isopropanol, rinsing in water followed by immersion in the protein solution, and (2) immersion of nonwovens in aqueous solutions of nonionic surfactants (Tween 80, Triton X-100 and others) followed by immersion in the protein solution. However, none of these treatments produced a change in wettability of the PP nonwoven. The surface tension lowering effect by immersion in either isopropanol or surfactant solutions may help; but if the proteins adsorb they do it forming patches on the surface. This is not the case if the nonwoven was pretreated with DODA surfactant: the hydrophobic tails of this surfactant were able to anchor strongly on the surface and it also provided cationic (head) groups that interacted with the protein molecules.

After adsorption of proteins onto DODA-treated nonwovens, a relatively high initial WCA was observed; however, a rapid increase in wettability occurred after a few seconds, until the water droplet was completely absorbed by the solid. The reduction in WCA after adsorption of 7S and the commercial soy flour was noticeable; the samples after adsorption of these two proteins displayed the largest increase in surface wettability over a short period of time. Although there are many variables affecting the WCA, including the surface roughness, porosity, surface composition, and surface area, the observed reduction in WCA did not occur when neat PP nonwovens were tested (advancing and equilibrium contact angles of 130° were measured). Additional measurements were carried out for nonwovens that were immersed in 1 mg/mL DODA solution in isopropanol and rinsed 10 min with isopropanol followed by buffer rinsing. In this case, the WCA did not change even after 5 min observation. Therefore, it is clear that the change in wettability was due to the adsorption of the soy proteins. Previous attempts to use the protein as a platform for further polymer grafting on the surface have shown that after adsorption onto nonwoven PP substrates 7S and 11S proteins performed similar to fibrinogen and lysozyme, producing a change of contact angle of ~30°.[9] However, the pretreatment with DODA followed by proteins adsorption is noted here to provide an effective, remarkable reduction in WCA and increased wettability.

WCA data for the PP nonwovens after adsorption of thermally denatured proteins are shown in Figure 6. All samples displayed an improved wettability compared to the case of native protein, this highlights the effect of unfolding of the protein molecules after denaturation, exposing hydrophobic groups that engage in hydrophobic interactions with the PP substrate.

Wicking Test. Evaluation of the ability of the PP nonwovens to absorb water after treatment with soy proteins was carried out by wicking tests using a DCA 312 Cahn balance (Thermoscientific, Newington, NH). Samples of given dimensions were suspended with a wire and immersed (3 mm below the surface) in the probing liquid. The mass uptake was monitored by the microbalance until the weight was stable or until a preset time; the latter was chosen in this case and set to 300 s. The neat PP nonwoven before and after treatment with DODA solution did not display any measurable amount of water absorption. The results of water uptake per unit mass of substrates after protein adsorption was followed during 300 s and presented in Figure 7.The results indicate a different,

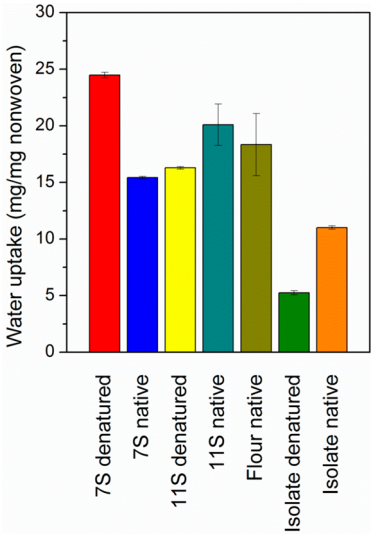


Figure 7. Results of water uptake (during 300 s) by polypropylene nonwovens carrying preadsorbed soybean proteins. The case of PP carrying denatured flour is not included because it did not adsorb any water. Likewise, bare PP and PP with preadsorbed DODA did not absorb water.

behavior for each of the proteins (either in the native or denatured state). The denatured flour protein did not absorb water, although it displayed a high wettability as far as WCA tests. The isolate samples exhibited a relatively low value of water sorption. In all cases, there was a high amount of water sorbed, reaching a limit of 25-fold of the mass of the substrate. Overall, it was possible to provide hydrophilicity properties to PP nonwovens after preadsorption of DODA surfactant followed by adsorption of soy proteins. This is not possible if each of the treatments is conducted separately. These results for PP nonwovens correlate well with the QCM experiments discussed in earlier sections and confirm the high affinity of the proteins with hydrophobic PP.

Fluorescence Analysis. Fluorescein isothiocyanate labeled soy proteins were adsorbed onto the surface of PP nonwoven substrates after preadsorption of DODA following the same procedure that was used for unlabeled proteins. The images shown in Figure 8 indicate that the soy proteins in the native state adsorbed onto the surface, but the fluorescence signal was very weak if compared to the signal of denatured proteins. This observation correlates with previous results and confirm that denatured proteins adsorbed on the surface.

In summary, results from the different analyses support that PP was successfully modified by physical adsorption of soybean proteins (especially if thermally denatured), which formed adsorbed layers that remained stable after rinsing. This methodology is proposed as a facile and inexpensive alternative for surface modification of PP fibers or PP fiber mats.

CONCLUSIONS

The adsorption of different soy proteins was investigated and the results highlighted the important protein structure–function relationships. Adsorption of proteinson flat PP model films correlated well with results for porous PP

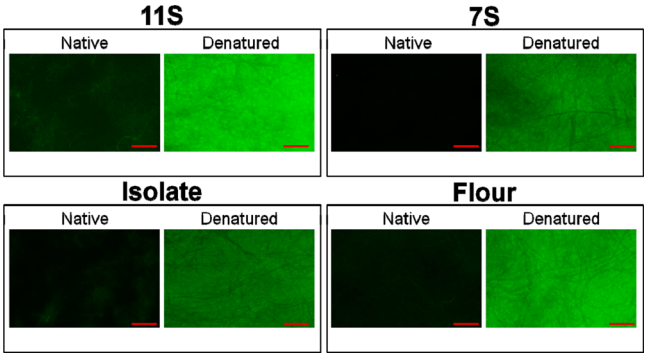


Figure 8. Fluorescence microscopy images for DODA-treated nonwoven substrates after adsorption of soybean proteins in native or thermally denatured conditions. All images are shown at the same exposure of 1/50 s. Objective 4×/0.10. Scale bar corresponds to 500 μm size.

nonwoven mats: A higher adsorption of denatured proteins was promoted after pretreatment of the surface with DODA surfactant. A flat conformation of the adlayers was observed to occur for flat PP films as determined by QCM dissipation measurements. This suggests a better coverage of the surface by the soy molecules; this was also confirmed by the fluorescence experiments, where the denatured proteins displayed a higher fluorescence. Overall, physical adsorption of soy proteins onto hydrophobic PP provided a remarkable change in the wetting behavior of the system without the use of harsh treatments that can affect the bulk properties of the material. The present approaches underline a facile, simple method to significantly modify hydrophobic surfaces with renewable, easily accessible, and inexpensive biopolymers.

■ ASSOCIATED CONTENT

Supporting Information

The Johannsmann model, used to calculate the adsorbed mass, and contact angle images of nonwoven surfaces. This material is available free of charge via the Internet at http://pubs.acs.org

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ojrojas@ncsu.edu. Tel. +1-919-5137494.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are thankful for funding support provided by the United Soybean Board (USB) under project numbers 0426 and 0490. We are also grateful to the Nonwovens Institute in North Carolina State University for providing PP nonwoven samples. Dr. Orlin Velev, Department of Chemical & Biomolecular Engineering at NC State University is thanked for granting us access to fluorescence microscope. Dr. Robina Hogan (Omni Tech International, Ltd.) is gratefully acknowledged for helpful discussions. Samples of soy flour from ADM were received as a gift.

■ REFERENCES

(1) Knaus, S.; Nennadal, A. *Macromol. Symp.* **1998**, *127*, 257−263.
(2) Chung, T. C.; Lee, S. H. *J. Appl. Polym. Sci.* **1997**, *64*, 567−575.
(3) Chan, C.-M., *Polymer Surface Modification and Characterization*; Carl Hanser Verlag: Munich, Germany, 1994.
(4) Liu, Z.-M.; Xu, Z.-K.; Wang, J.-Q.; Yang, Q.; Wu, J.; Seta, P. *Eur. Polym. J.* **2003**, *39*, 2291−2299.
(5) Huang, J.; Murata, H.; Koepsel, R. R.; Russell, A. J.; Matyjaszewski, K. *Biomacromolecules* **2007**, *8*, 1396−1399.
(6) Yamamoto, K.; Miwa, Y.; Tanaka, H.; Sakaguchi, M.; Shimada, S. *J. Polym. Sci., Part A* **2002**, *40*, 3350−3359.
(7) Krause, B.; Voigt, D.; Häußler, L.; Auhl, D.; Münstedt, H. *J. Appl. Polym. Sci.* **2006**, *100*, 2770−2780.
(8) Goli, K. K.; Rojas, O. J.; Genzer, J. *Biomacromolecules* **2012**, *13*, 3769−3779.
(9) Goli, K. K.; Rojas, O. J.; Özçam, A. E.; Genzer, J. *Biomacromolecules* **2012**, *13*, 1371−1382.
(10) Liu, X.; Wu, D.; Turgman-Cohen, S.; Genzer, J.; Theyson, T. W.; Rojas, O. J. *Langmuir* **2010**, *26*, 9565−9574.
(11) Krishnan, S.; Weinman, C. J.; Ober, C. K. *J. Mater. Chem.* **2008**, *18*, 3405−3413.
(12) Lundström, I. Models of protein adsorption on solid surfaces. In *Surfactants, Adsorption, Surface Spectroscopy and Disperse Systems*; Lindman, B., Olofsson, G., Stenius, P., Eds.; Springer: Berlin, 1985; Vol. *70*, pp 76−82.
(13) Nakanishi, K.; Sakiyama, T.; Imamura, K. *J. Biosci. Bioeng.* **2001**, *91*, 233−244.
(14) Norde, W. Driving Forces for Protein Adsorption at Solid Surfaces. In *Biopolymers at Interfaces*, second ed.; Malmsten, M., Ed.; Marcel Dekker: New York, 2003; pp 21−43.
(15) Goli, K. K. *Functional Coatings Based on Denaturation and Adsorption of Proteins*. PhD Dissertation, North Carolina State University, Raleigh, NC, 2012.
(16) Zhang, C.; Jin, J.; Zhao, J.; Jiang, W.; Yin, J. *Colloids Surf., B* **2013**, *102*, 45−52.
(17) Murphy, P. A., Soybean proteins. In *Soybeans: Chemistry, Production Processing, and Utilization*; Johnson, L. A., White, P. J., Galloway, R., Eds.; AOCS PRESS: Urbana, IL, 2008; pp 229−267.
(18) Schmitz, J. F.; Erhan, S. Z.; Sharma, B. K.; Johnson, L.A.; Myers, D.J. Biobased Products from Soybeans. In *Soybeans: Chemistry, Production Processing, and Utilization*; Johnson, L. A., White, P. J., Galloway, R., Eds.; AOCS PRESS: Urbana, IL, 2008; pp 539−612.
(19) Salas, C.; Rojas, O. J.; Lucia, L. A.; Hubbe, M. A.; Genzer, J. *Biomacromolecules* **2012**, *13*, 387−396.
(20) Salas, C.; Rojas, O. J.; Lucia, L. A.; Hubbe, M. A.; Genzer, J. *ACS Appl. Mater. Interfaces* **2012**, *5*, 199−206.
(21) Song, J.; Liang, J.; Liu, X.; Krause, W. E.; Hinestroza, J. P.; Rojas, O. J. *Thin Solid Films* **2009**, *517*, 4348−4354.
(22) Ward, M. D.; Buttry, D. A. *Science* **1990**, *249*, 1000−1007.
(23) Rodahl, M.; Kasemo, B. *Sens. Actuators, B* **1996**, *37*, 111−116.
(24) Rodahl, M.; Kasemo, B. *Sens. Actuators, A* **1996**, *54*, 448−456.
(25) Johannsmann, D.; Mathauer, K.; Wegner, G.; Knoll, W. *Phys. Rev. B: Condens. Matter* **1992**, *46*, 7808−7815.
(26) Jung, L. S.; Campbell, C. T.; Chinowsky, T. M.; Mar, M. N.; Yee, S. S. *Langmuir* **1998**, *14*, 5636−5648.
(27) Fei, S. *Affinity Interaction between Hexamer Peptide Ligand HWRGWV and Immunoglobulin G Studied by Quartz Crystal Microbalance and Surface Plasmon Resonance*. PhD Thesis, North Carolina State University, Raleigh, NC, 2010.
(28) Orelma, H.; Filpponen, I.; Johansson, L.-S.; Laine, J.; Rojas, O. J. *Biomacromolecules* **2011**, *12*, 4311−4318.
(29) Peng, I. C.; Quass, D. W.; Dayton, W. R.; Allen, C. E. *Cereal Chem.* **1984**, *61*, 480−490.
(30) Badley, R. A.; Atkinson, D.; Hauser, H.; Oldani, D.; Green, J. P.; Stubbs, J. M. *Biochim. Biophys. Acta, Protein Struct.* **1975**, *412*, 214−228.
(31) Höök, F.; Kasemo, B.; Nylander, T.; Fant, C.; Sott, K.; Elwing, H. *Anal. Chem.* **2001**, *73*, 5796−5804.
(32) Lakemond, C. M. M.; de Jongh, H. H. J.; Hessing, M.; Gruppen, H.; Voragen, A. G. J. *J. Agric. Food. Chem.* **2000**, *48*, 1985−1990.
(33) Koshiyama, I. *Cereal Chem.* **1968**, *45*, 394−404.
(34) Eldridge, A. C.; Black, L. T.; Wolf, W. J. *J. Agric. Food. Chem.* **1979**, *27*, 799−802.

(35) Deak, N.; Johnson, L. A.; Lusas, E. W.; Rhee, K. C. Soy Protein Products, Processing, and Utilization. In *Soybeans: Chemistry, Production Processing, and Utilization*; Johnson, L. A., White, P. J., Galloway, R., Eds.; AOCS PRESS: Urbana, IL, 2008; pp 661−724.
(36) Damodaran, S. *J. Agric. Food. Chem.* **1988**, *36*, 262−269.
(37) Liu, X.; Goli, K. K.; Genzer, J.; Rojas, O. J. *Langmuir* **2011**, *27*, 4541−4550.
(38) Kinsella, J. *J. Am. Oil Chem. Soc.* **1979**, *56*, 242−258.