

Advances in the Use of Protein-Based Materials: Toward Sustainable Naturally Sourced Absorbent Materials

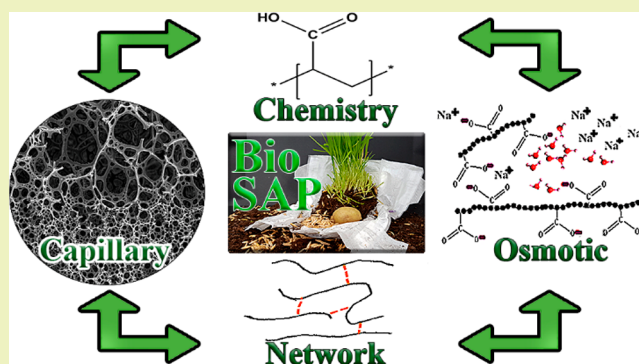
A. J. Capezza,^{†,‡} W. R. Newson,[‡] R. T. Olsson,[†] M. S. Hedenqvist,[†] and E. Johansson^{*,‡}

[†]School of Engineering Sciences in Chemistry, Biotechnology and Health, Fibre and Polymer Technology, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

[‡]Department of Plant Breeding, SLU Swedish University of Agricultural Sciences, SE-230 53 Alnarp, Sweden

ABSTRACT: Superabsorbent polymers (SAPs) are important in the health-care and personal care industries. Products like bed pads and diapers improve the comfort and sanitary conditions for people all over the world, with SAPs reaching yearly production volumes of ca. 2 million tons. However, recent sustainability issues have questioned the high negative footprint of polymers from nonrenewable resources. Biomacromolecules, especially when functionalized, have properties that make them an attractive alternative for the production of biobased SAPs. Proteins are a particularly interesting alternative due to their high variability and because of their relatively low price, being available as side streams from the agricultural industries. Due to the harsh extraction conditions, these side stream proteins are not competing with the food industry and alternative source-effective uses are advantageous in a circular bioeconomy. As the properties of a SAP material come from a combination of neutralized functional groups to promote polar liquid uptake and intermolecular cross-links to prevent dissolution, proteins offer unique opportunities due to their variability in polymerization. An increased understanding of the protein characteristics and how these can be tuned through functionalization is therefore a prerequisite for the successful development of a commercial biobased SAP that utilizes industrial and nontoxic wastes toward more sustainable products. This review focuses on proteins as biomacromolecules with relevant characteristics for superabsorbent functions, and discusses the opportunities that they may offer toward sustainable SAPs utilizing nontoxic chemicals and following the green chemistry principles.

KEYWORDS: Superabsorbent, Polymer, Protein, Sustainability, Absorption, Functionalization



INTRODUCTION

The industrial production of superabsorbent polymers (SAPs) is a fast growing area due to the use of SAPs for liquid retention in personal care and hygienic products,¹ and SAPs have many other applications including pharmaceuticals, tissue engineering, active hydrogels and daily care products.^{1–4} The SAPs in these products consist of a polymeric carbon chain backbone with, e.g. hydroxyl, carboxylic acid, amide functional side groups. The backbones are held together by a few covalent cross-links (ca. 8×10^{-4} cross-links/mol), which lead to an insoluble and expandable 3D network structure.^{3,5,6} The functional side groups consist of weak polyelectrolytes, so that in solution they can be either charged or uncharged, depending on the pH of the solution.^{6–8} These characteristics result in SAPs having the potential to both absorb and retain liquids such as (i) water, (ii) saline solution, and (iii) body fluids. An absorption of pure water of up to thousands times its own weight has been reported for SAPs, although the absorption of ionic liquids (typically 0.15 M NaCl) is normally in the range of 10–100 g/g.^{6,9} The most commonly used SAP is partially neutralized sodium poly(acrylic acid) (PAAc) derived from petroleum.^{4,5,10} PAAc is favored compared to other useful hydrophilic SAPs (e.g., polyacrylamide

poly(ethylene oxide), poly(vinyl alcohol)), mainly due to its efficiency, low cost and low toxicity. The advances in technologies for producing SAPs have in recent decades meant that hygienic products have become thinner and less expensive while retaining their high absorption performance.^{4,11,12}

Despite the fact that the current petroleum-based SAP materials show beneficial functional properties, their negative impact on the environment is becoming an increasing concern.^{13–16} This has led to a search for alternative and sustainable biobased polymers; cellulose, gelatin, chitosan, hyaluronic acid, etc., have been thoroughly evaluated for their properties as biosuperabsorbent gels.^{13–15,17–21} Among these, polysaccharides are, to our knowledge, the most extensively studied alternative. Also, several of these naturally sourced polymers already play an important role in the biological, agricultural and pharmaceutical industries.^{13,22–26}

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Proteins have been less studied in this context, but are currently gaining greater attention as biobased SAPs since they are natural polymers that show high hydrophilicity.^{14,15,20,21,27–29} Treated (mainly denatured) and functionalized proteins, e.g. fish protein isolates, with nontoxic reagents, have reported a water uptake capacity of ca. 500 g/g.^{28,30–32} Proteins are often found as side-streams from the agricultural and food industries, e.g. from starch extraction and bioethanol production, thereby providing a sustainable, inexpensive and reliable feedstock.^{33–35} Reported prices for protein concentrates, e.g. vital wheat gluten are ca. 0.80–1.22 EUR/kg (compared to 1.13–1.50 EUR/kg for PAAc).

Proteins are amino acids held together by covalent peptide bonds.³⁶ The molecular weight and amino acid composition of proteins vary considerably between different types,³⁷ this means that proteins as a material source are chemically more heterogeneous than synthetic polymers and also other naturally occurring polymers such as polysaccharides (mainly having hydroxyl side groups unless treated). The large variability among and within the proteins presents a challenge in materials manufacture.³⁸ However, the same characters contribute with valuable opportunities to steer and finely tune properties and reaction mechanisms of proteins, contributing to their potential use in absorbent materials with special swelling properties.^{31,39} Previous work has shown that porous and solid materials based on proteins have the ability to absorb water to an extent similar to that of synthetic SAP.^{28,31,33,34,40}

In this Perspective, we focus on the use of proteins as a base for sustainable absorbent materials and their use as SAPs, and we collect available information related to background mechanisms of the functionality of SAPs. We describe the proteins as macromolecules, and compile information about different protein sources evaluated for their usability as SAPs. We stress the needs for focusing on proteins from agricultural and food industrial side streams, to avoid competition with food production and to determine sustainable use of such streams. Information is included showing how the functionality of the proteins has been used to tune the physicochemical properties of the materials as superabsorbents. The latest advances of absorbent protein-based material are compiled. Thereby, we are closing the loop by summarizing the challenges and opportunities of using industrial side streams as a source for functionalized protein-based materials contributing economic, social and environmental sustainability by replacing petroleum-based SAPs.

■ PHYSICO-CHEMISTRY BEHIND LIQUID ABSORPTION IN A POLYMER

The properties of a SAP originate from two chemical features. First, the liquid absorption properties of the SAP are due to its high content of neutralized functional groups, e.g. carboxylic acid groups.^{14,20} These carboxylic acid groups consist of one carbonyl group ($-\text{C}=\text{O}$) and one hydroxyl group ($-\text{OH}$) (Figure 1), resulting in a net negatively charged structure that at a certain pH enables polar liquid uptake (water), while repelling each other leading to an expansion of the SAP. Thus, the SAPs have a pH-dependent polyelectrolyte behavior, where the pH determines the degree of repulsion in the SAP network, which in turn affects the degree of absorption.^{4,5,41–43} Second, a three-dimensional expandable polymer network is created by intermolecular cross-links and this prevents the SAP from dissolving in the liquid.⁴⁴ The approximate cross-link density required to maintain the structure of the network depends on

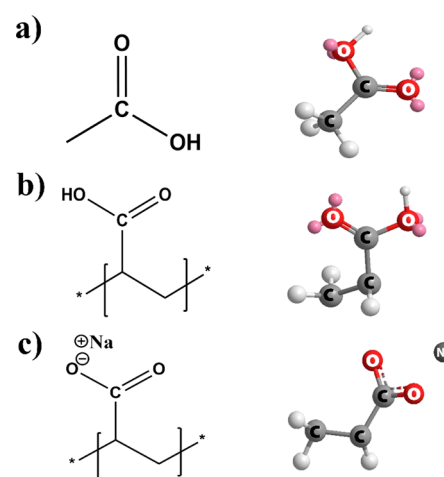


Figure 1. chemical structure (left) and a 3D representation (right) of (a) formic acid as the simplest carboxylic acid, (b) poly(acrylic acid) and (c) sodium-neutralized poly(acrylic acid). The pink spheres represent lonely electron pairs.

the SAP, but an average of 0.0008 cross-links/mol-chain has been reported for synthetic SAPs.^{3,5,6} A low cross-link density provides a high polymer network flexibility, allowing large expansion of the SAP because the chains by nature are repelling each other through the electrostatic forces from the carboxyl groups.^{4,45}

To increase the rate of liquid absorption in the polymer network, the charged functional groups are normally neutralized by the addition of alkali such as sodium hydroxide (Na^+OH^-).^{4,5,43} The presence of counterions (typically Na^+) in the SAP results in a chemical potential between the surface of the sodium-neutralized polymer chain and the added liquid.^{3,6,45–49} These additions thus influence the absorption kinetics, and allow a fine-tuning of the SAPs swelling properties.^{4,46,50–53}

The mechanisms behind changes in absorption kinetics by neutralization are based on a liquid uptake to balance the osmotic pressure. The contribution of the osmotic pressure to liquid absorption is explained by the van't Hoff Law (eq 1):

$$\Delta\Pi_{\text{ion}} = RT\left(\sum C_{\text{gel}} - \sum C_{\text{solution}}\right) \quad (1)$$

According to this law, the greater the difference between the total amount of ionic species in solution (C_{solution}) and in the gel (C_{gel}), the higher is the osmotic contribution (Π_{ion} in atm).^{54,55} A schematic representation of a partially neutralized synthetic SAP network is shown in Figure 2.

Parameters such as the functionality and concentration, molecular size, cross-link type of the polymer and the polarity of the solvent also influence the SAP functionality, e.g. its liquid diffusion behavior and swelling mechanisms.⁵⁶ The porosity of the SAP (e.g., open or closed pores) is known to influence liquid diffusion, where open pores have been shown to give a faster initial absorption than closed pores or solid structures.^{57–59} Capillarity has been shown to be the main mechanism governing the initial volumetric flow of water within the porous SAP structures,^{29,33,34,58} where the minimization of energy due to the surface energy of the liquid, causes the liquid to move toward inner sections of the material. Laplace's Law for capillary pressure (C in Pa) given by⁶⁰

$$C = \rho gh = 2\sigma/r \quad (2)$$

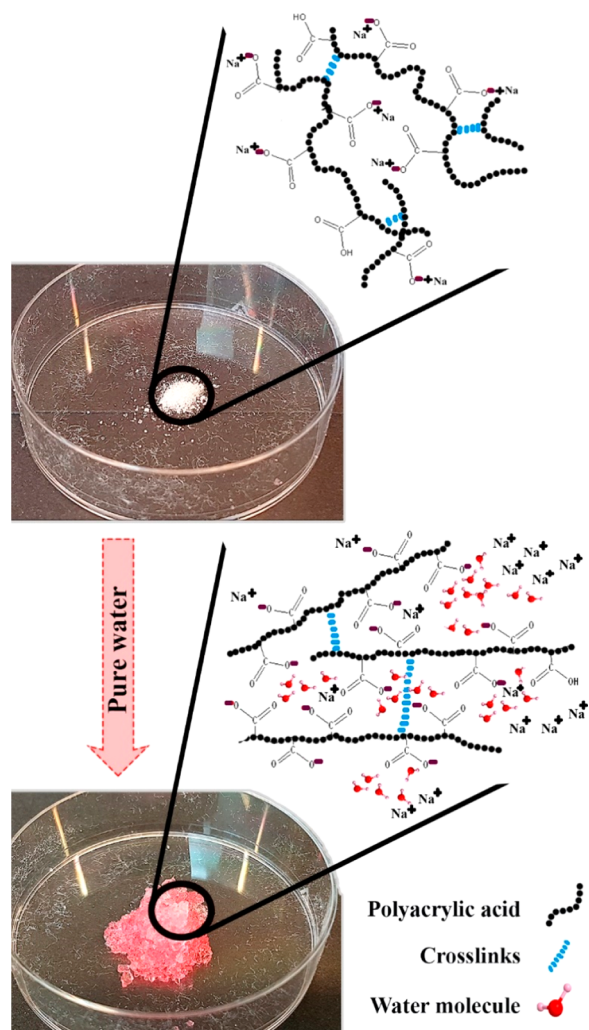


Figure 2. A sodium-polyacrylate network scheme. The development of an osmotic pressure is partially illustrated with the release of Na^+ ions when the SAP is exposed to water.

where σ is the surface tension (N/m), g is the gravitational acceleration at the surface (m/s^2), h the height of the capillary (m), r the radius (m) and ρ is the density of the liquid (kg/m^3).

The flow of a solvent (Q in m^3/s) through a polymeric porous matrix is given by Darcy's Law:^{61,62}

$$Q = -\frac{K_d A \Delta P}{\mu L} \quad (3)$$

where A is the cross-sectional area of the pores (m^2), μ the viscosity of the liquid (Pa·s), K_d the intrinsic permeability of the material (m^2) and ΔP the pressure difference between the ends of the flow section (Pa) of length L (m) in the material.

The swelling of an SAP thus proceeds as follows (i) water diffuses into the material, giving rise to an immediate deformation within the polymer network, (ii) the Na^+ concentration is gradually diluted by the addition of the liquid, and the SAP becomes charged and expands through repulsion, (iii) the process of swelling continuous until equilibrium is reached. To describe the equilibrium swelling ($\Pi = \Pi_{\text{mix}} + \Pi_{\text{def}} = 0$), the Flory–Huggins mixing (Π_{mix}) and rubber network parameters (Π_{def}) are taken into consideration, leading to^{55,63–65}

$$\begin{aligned} v_a \Pi / RT &= v_a \Pi_{\text{mix}} / RT + v_a \Pi_{\text{def}} / RT \\ &= [-\ln(1 - \phi) - \phi - \chi \phi^2 + \phi / N \\ &\quad (0.5 - (\phi_0 / \phi)^{2/3})] \end{aligned} \quad (4)$$

where v_a is the molecular volume (m^3/mol), R the gas constant ($\text{m}^3 \cdot \text{atm} / \text{K} \cdot \text{mol}$), χ the interaction parameter, N the number of molecules, and ϕ_0 and ϕ are the polymer volume fractions in the dry and swollen states, respectively. The solvent–polymer interaction contribution in eq 4 is highlighted in bold text (Π_{mix}).

Typical standard tests used to measure the swelling capacity of absorbent and superabsorbent polymers are free swelling capacity (FSC), centrifuge retention capacity (CRC) and absorbency under load (AUL), where the grams of liquid absorbed per gram of dry polymer (g/g) under various conditions are measured.^{66,67} To determine the FSC, the material is sealed in porous plastic “tea-bags” and the swelling at different times is measured. To study the water binding properties of the material while removing most of the water trapped between particles, the swollen SAP is centrifuged (i.e., 3 min at 250 g) over a porous support of glass beads and the CRC determined. Lastly, the AUL is determined by swelling the SAP in a cylinder having different weights placed on top, which generates pressures on the material, e.g. 0.08 bar, causing loosely bound water to be forced out.^{66,67}

■ PROTEINS

Proteins are among the most important biomacromolecules on Earth,⁶⁸ having fundamental functions in the human body as well as in other living organisms.⁶⁹ Physical and chemical tasks in which proteins are actively involved include biological transportation, enzymatic catalysis and formation of structural tissues.^{68–70} Unique material characteristics can be formed by the proteins, such as the remarkable mechanical strength to flexibility ratio in spider silk which can be stronger than steel,⁷¹ and in bacterial flagella that form microscopic motors.^{72,73} In contrast to many reactive polymers, proteins have the important ability to re- and depolymerize, forming molecular macrostructures of relevance in both food items and materials science.⁷⁴ Plant proteins also play a fundamental role in the processing of food items, e.g. in building the elastic network in dough and pasta,^{37,75–77} and in other applications to produce biobased materials.^{33,34,78–84}

The formation of useful material structures is however related to the type, composition, molecular weight, etc., of the particular protein and also to the processing conditions applied.^{80,85–87} The amino acid structure of the protein and its ability to form macromolecular complexes not only influences the inter- and intramolecular interactions within the polypeptide, but also determine the field of application of the protein.⁸⁸

A chain of amino acid residues, linked together by peptide bonds form the primary structure of the protein,^{69,70} but the amino acid residues differ depending on the functional group attached to the α -carbon within the amino acid. The composition and order of the amino acid residues as well as the chain length contribute to the structural conformation of the protein.⁸⁹ A total of about 20 different amino acid residues are commonly found in the chains of plant proteins, leading to a considerable heterogeneity.^{89–91} This heterogeneity means that proteins have unique and complex structures, but also challenging properties as building blocks for use in polymer processing.⁹²

Control over the primary structure of the protein chain and of the physical and chemical surroundings during processing is crucial since the proteins form secondary conformational substructures due to chain folding, which is determined by the intraprotein and interprotein hydrogen bonds combined with other interactions, under given processing conditions. An example is the folding of the amino acid chain, leading to the formation of α -helices and β -sheets of the protein,^{93,94} but to minimize the conformational energy of the protein, covalent and noncovalent interactions are formed based on secondary structures, and a 3D-structure known as a tertiary structure is formed.^{70,94} In fact, many of the macroscopic physical and chemical properties of proteins are due to their tertiary structure.⁹⁵ In addition, due to the presence of several different interactions, protein chains complexes between different proteins are frequently formed under favorable surrounding conditions.⁹³ These complexes are known as quaternary structures stabilized by covalent and noncovalent bonds giving rise to a large scale macromolecular 3D-structure.^{70,94,95}

In the substructure, the chemical structure of the amino acid residues, including the double bond of the carbonyl group (C=O) with its resonance structure and the $-C-N$ bond with physical features that resemble a double bond, give rigidity to the protein chain.^{70,84} The energy required to change the conformational state of a protein is therefore typically greater than that required by other natural macromolecules, e.g. polysaccharides, and the glass transition temperatures (T_g) of proteins are above room temperature.^{70,84} The consequential brittleness of a protein-based material can however be reduced by the addition of a plasticizer (e.g., glycerol), to make their processing easier while maintaining their mechanical properties.^{80,84,87,90} The chemistry and physical properties of a protein can thus be fine-tuned through additives, thermal treatment, and purification procedures,^{74,88,96} making proteins very promising as inexpensive materials with a potential to replace petroleum-based polymers in SAP applications.^{20,97}

■ POTENTIAL OF NATURALLY SOURCED MOLECULES FOR THE PRODUCTION OF BIOBASED SAP

To increase water absorption in natural polymers so that they can be used as SAPs, one solution has been to add carboxylic acid to the polymer chain, since the water uptake has been shown to be related to the amount of $-COOH$ in the biopolymer.^{4,5,20,28,31,32,39,98} Several routes have been adopted to incorporate carboxylic acid moieties onto the biomolecular chain, including physically mixing the additives with the biomolecule and/or promoting chemical reactions to modify the naturally occurring macromolecules. Through such methods, carboxymethylated cellulose (CMC) in a suspension can be cross-linked with epichlorohydrin to form a gel that is able to swell ca. 1000 g/g of water after 1 week.^{22,99} Insoluble cellulose can also be oxidized by the addition of nitroxyl radicals (TEMPO) to incorporate carboxylic acid units throughout the main polysaccharide chain,^{100,101} and covalent linkages between succinic anhydride (SA) and cellulose have been achieved using lithium chloride (LiCl)/*N*-methyl-2-pyrrolidinone (NMP) solutions and similar reaction media¹⁰² as illustrated in Figure 3. Although several authors have been able to demonstrate superswelling properties of functionalized biomacromolecules in water, there is little information available regarding the absorption of saline solutions. Information regarding SAP-related quality tests such as centrifuge retention capacity (CRC)

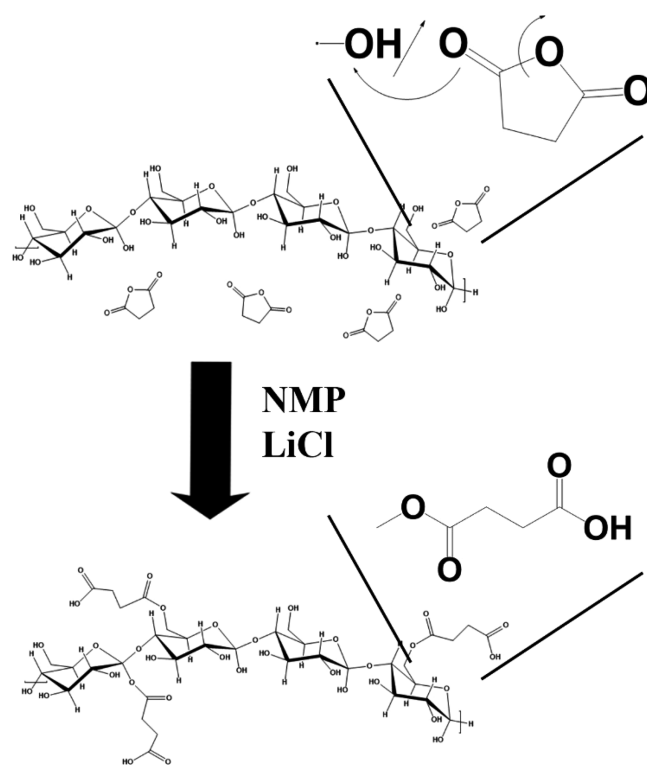


Figure 3. Suggested carboxylation of hydroxyl groups in polysaccharides.

and absorbency under load (AUL) is lacking, and it is not clear whether or not these materials fulfill SAP requirements.

It is also clear that in addition to the need for a larger water-uptake capacity, certain mechanical properties are required in the swollen state for biomacromolecules to be useful as SAPs.⁴ Here, chitin, the second most abundant polysaccharide in nature, is an interesting candidate, with a high gel strength.¹⁰³ Chitin can be chemically deacetylated to form chitosan, possessing both amino ($-NH_2$) and hydroxyl groups ($-OH$),¹³ both of which have been shown to graft to other highly reactive molecules, such as acrylic acid monomers (AAc).¹³ Combining this grafting with the additions of nanoclays such as montmorillonite (MMT),^{104,105} to enhance the mechanical properties resulted in a natural polymer with superabsorbent characteristics.

Proteins have not been studied to the same extent as polysaccharides, and few studies have been reported concerning the grafting of synthetic monomers onto protein-based materials or their composites,^{106–110} and it is difficult to find a study where a fully natural-sourced SAP is disclosed. A synthetic monomer such as acrylic acid, grafted onto a polysaccharide or protein to reproduce the swelling behavior of PAAc polymers cannot be claimed to be a naturally sourced SAP, but as a partly biobased composite or hybrid. Table 1 summarizes the most relevant work on polysaccharides and the reports where protein-based materials have been utilized.

■ PROTEINS AS A NATURAL SOURCE FOR SAPS

Several of the major groups of plant proteins are available as coproducts/side-streams at a reasonable price from agricultural and industrial processes, e.g. wheat gluten protein from wheat starch production, potato protein concentrate from potato starch production, brassica oilseeds and cottonseed protein concentrates from oil seeds extraction.^{34,78,80,97,98} Among the

Table 1. Sorption Properties of Superabsorbent Natural Materials, with a Focus on Those That Are Protein-Based^a

Raw material	Technique	Chemistry	Free swelling in water, 0.9% NaCl	Swelling time	ref.
L-Aspartic acid	Condensation and ring opening polymerization of L-aspartic acid (amino acid) to produce polyaspartic acid (poly amino acid)	Condensation polymerization	400, 125	24 h	116
Cellulose	Cellulose extracted from cotton and dissolved in LiCl/NMP solvent + DMAP and SA	Esterification of the hydroxyl groups	400 ^b , 100	48 h	102
Sodium CMC/hydroxyethylcellulose ^b	Cross-linking of CMC to HEC using DVS	N/A ^h	(pH 7) 110, N/R ^h	24 h	117
Soy protein/CMC	EDTAD-treated protein mixed with 10% CMC and cross-linked with EGDGE	Acylation and bridging with CMC network	N/R, 12.4 ^c	30 min	40
Soy protein	EDTAD-treated protein cross-linked with glutaraldehyde	Acylation	110, 25	25 h	39, 40
Soy protein	Succinic anhydride and EDTAD treatment	Acylation	3500% ^d , NR	24 h	35, 115
Fish protein	EDTAD-treated protein cross-linked using endogenous sulfhydryl groups	Acylation	526, 12.3	25 h	98
Collagen g-poly(AA-co-NaAA)	AA polymerized onto collagen protein using potassium persulfate and N,N'-methylene bis(acrylamide) (MBA) as cross-linker	Hybrid	210, 38	90 min	15
Collagen g-poly(AA-co-AAm)	Acrylamide and AA polymerized onto collagen using potassium persulfate and MBS.	Hybrid material with 5.6 wt % montmorillonite	952, 70	2 h	118
Cottonseed protein ^e	AA polymerized onto cottonseed protein and MBS	Graft polymerization	300, 50	24 h	119
Silk sericin protein g-(AA-co-AAm) ^f	Acrylamide and AA polymerized onto silk sericin protein	Graft polymerization	2150, 98	20 min	120
Wheat gluten	Denaturation and foaming of wheat gluten through lyophilization	N/A	32, N/R	50 h	34
Wheat gluten	Reaction of citric acid with wheat gluten in vacuum conditions at 120 °C	Acylation	78 ^g , N/R	2 h	121

^aThe free swelling is given in g water/g dry polymer, unless otherwise specified. ^bThe values correspond to a NaCMC/HEC ratio of 3:1. ^cAUL value according to EDANA ERT 442. ^dWeight increase compared to reference sample. ^eThe values correspond to a cottonseed protein content of 10 wt % based on AA content. ^fThe values correspond to a AA/AAm (1:0.7 monomer mass ratio) of 23 wt % based on silk sericin content. ^gThe water uptake data were obtained by using a moisture analysis equipment. ^hN/R and N/A stand for Not Reported and Not Applicable, respectively.

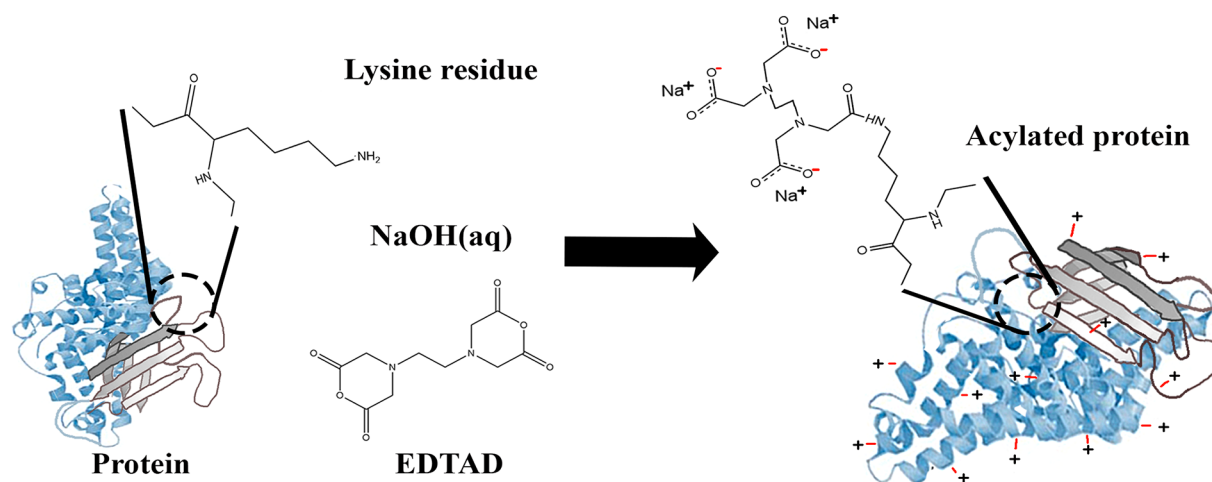


Figure 4. Functionalization of lysine groups in proteins using EDTAD. The protein structure shown is a schematic illustration of a protein secondary structure.

plant proteins, wheat gluten (WG) is among the most extensively evaluated with regard to functionality and opportunities as a suitable macromolecule for biobased applications.^{34,37,82,83,86,87,89,97,111,112} WG has been evaluated as a material for antimicrobial, electrically conductive, flame-resistant and water-absorbant properties.^{34,97,113} The water absorption of insoluble WG has been reported to be of the same magnitude as that of several functionalized natural sourced SAPs encountered in the literature.^{35,114,115} It has also been demonstrated that materials based on brassica oilseeds and potato proteins, with glycerol as a plastiziser, are mechanically stronger than other comparable biobased products.^{78,80} The heterogeneity of proteins together with their abundant availability, and unique properties, create opportunities for the

production of inexpensive multifunctional protein-based materials, although their inhomogeneous structure/reaction sites can also make them more challenging than polysaccharides to chemically and/or physically modify for SAP applications.^{14,20,28,34,40,97,98,107,111,112}

FUNCTIONALIZATION OF PROTEINS FOR IMPROVING WATER AFFINITY

A range of different experimental routes have been evaluated to modify the water affinity/absorption properties of protein-based materials.^{20,35,115,121,122} Chemical functionalization of protein materials is widely described, and both wet and dry chemistry have been applied.^{21,28,35,39,40,98,115,121,122} Among these, the radical grafting of synthetic acrylic acid/poly(acrylic acid) units

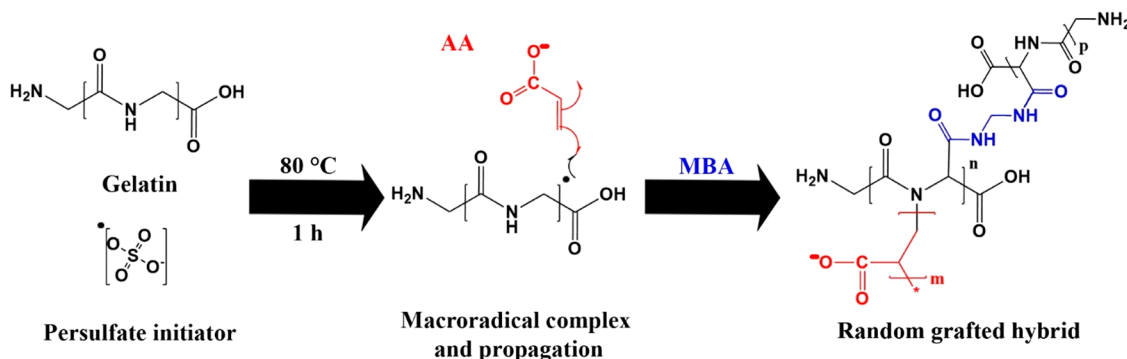


Figure 5. Graft-polymerization of acrylic acid monomer (AA) onto a protein backbone (e.g., gelatin) cross-linked with MBA.

onto protein macromolecules has been investigated as one possible route.^{15,48,84,106,107,119,123} To modify the absorbent capacity kinetics in the materials and to strengthen the gel structures, the cross-linking type and density have been varied with both treated and nontreated protein-based materials.^{15,30–32,75,80,106,124,125} Single or combinations of several of the described routes have resulted in semi-interpenetrated networks (IPN) or the establishment of biobased composites with considerable water-swelling properties.^{108,126–129} For the chemical functionalization, the hydroxyl (–OH) and amine (–NH₂) groups within the proteins are used for the inclusion of acyl groups (–COR) in the protein through acylation with anhydride reagents.^{21,28,30–32,35,39,40,98,115,121,130–132} The inclusion of the acyl groups in the protein contribute to the formation of an ester/amide bond and a pendant carboxylic acid moiety, as illustrated in Figure 4.

Soy and fish proteins are the most explored proteins for chemical functionalization via acylation. In both cases, EDTAD has been reported to be a useful reagent for acylation, and the functionalization of the proteins has been reported to contribute to water-absorbent properties.^{21,28,30–32,35,39,40,98,115,131,132} The acylation mechanism has been described as a condensation of the EDTAD salt on the lysine residues in the protein (–NH₂), leading to the formation of stable amide links.²⁸ The functionalization of proteins with EDTAD results in a ring-opening of the highly reactive furodianeone group present in the initial dianhydride, resulting in three available –COOH groups per each attached EDTAD molecule from each lysine group within the protein, as shown in Figure 4. The functionalization of proteins using EDTAD or other similar compounds is expected to contribute to an increase in the amount of carboxylic acid groups within the proteins. An increase in carboxylic acid groups results in an increase in the total net charge of the protein, leading to an electrostatic repulsion in solution, and thereby to an increase in water absorption.^{21,39,40,98,127,131,133} The EDTAD has an advantage as a functionalization agent since the residual salts present after the acylation process have a low toxicity.^{134,135} The functionalization of proteins with EDTAD is normally carried out under alkaline conditions (pH > 11) with thermal pretreatment (60 °C for 30 min) to promote maximum reactivity of the lysine groups (pK_a = 10.4)^{133,136} at the same time as the protein is denatured and deaggregated. EDTAD-functionalization of soy and fish protein resulted in the free swelling absorption of ca. 300 and 540 g/g (pure water), respectively.^{21,98} The mechanisms behind the increase in water absorption were shown to be an increase in the content of COO[–] groups and a depletion of the lysyl groups from lysine moieties. The success of the functionalization of soy and fish

proteins can be ascribed to the high lysine content and mild extraction process that these proteins show compared to proteins from other sources.^{137–140}

The protein concentration in solution and the amount of dianhydride agent added are important factors for the EDTAD functionalization of proteins. A large amount of the reagents and/or a high protein concentration lead to an excessive formation of cross-links^{28,40} which impair the water swelling properties of the material. The properties of the material can thus be controlled by careful selection of the amounts of protein and EDTAD, and by the reaction time.^{21,28,30–32,39,40,98,131,132} A low lysine content in a protein may, however, be a drawback since the chemical modification has been shown to occur as a condensation reaction of the EDTAD with lysine residues in the protein. Hence, the lower the lysine content in the protein, the lower is the content of carboxylic acid groups that can be added. Some of the major agricultural/food-based protein side-streams that can be obtained, e.g. canola and wheat gluten proteins, contain ca. 32 and 82% less lysine than soy or fish protein, respectively, which may impair the reaction efficiency on these substrates.^{137–141}

Succinic anhydride (SA) has previously been used to functionalize polysaccharides, e.g. cotton cellulose, cellulose nanocrystals (CNC) and mercerized nanocellulose (MNC) to increase their water absorption and remove heavy metal ions.^{102,142,143} SA may also be an attractive reagent for acylation of proteins due to its low cost compared to other acylation agents and its potential to be synthesized from biobased resources.^{115,144,145} Acylation via succinic anhydride has not, however, to our knowledge, been used to increase the water absorbency of protein-based materials. Only differences in mechanical properties and protein solubility have been evaluated, and this is also the case for palmitic acid chloride.^{146–148}

Besides EDTAD and acylation treatment of proteins in the wet state, protein-modification has also been carried out in water-free systems, where the condensation of reagents such as citric acid, sulfuric acid and phosphoric acid onto wheat gluten powders has been achieved in the absence of water.^{121,122,149} In principal, an acidic solution has been added to a protein and the mixture has then been dried and heated to above 120 °C for, e.g. 30 min under vacuum. It has been reported that the chemical reactions give rise to a change in the net charged groups of the proteins by the inclusion of –COOH groups and that this increases the free swelling capacity,^{121,122} but a comparison of these results with those of synthetic SAPs is not possible since the free swelling capacity in these studies was not determined by

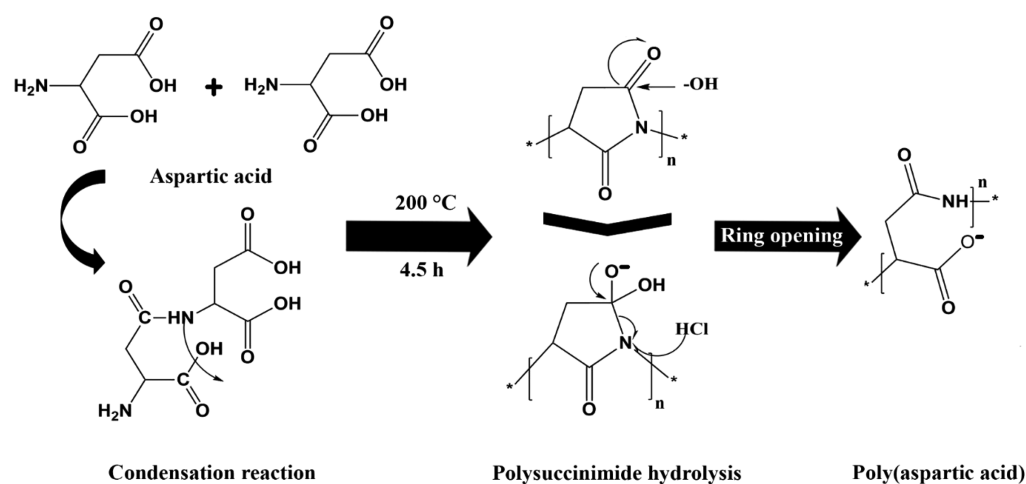


Figure 6. Polycondensation reaction and ring-opening polymerization of polysuccinimide from the condensation of aspartic acid monomer.

applying the tea-bag method, following the Edana NWSP 240.0 standard.

Synthetic acetate groups have been grafted onto proteins to increase their water-swelling properties.^{14,20} Graft-polymerization of acrylic acid (AA) and acrylamide groups (AAM) have been reported on cotton seed protein,^{107,119} silk sericin protein¹²⁰ and gelatin^{15,17,106,108–110,123,127,150–152} as the polymeric backbone. The reactions include cross-linking of the protein with *N,N'*-methylene bis(acrylamide) (MBA), a common cross-link agent used for the synthesis of SAP (see Figure 5 showing grafting to gelatin).^{4,5} The grafting resulted in an uptake of water and 0.9 wt % NaCl solution of 200 to 2100 g/g and 80 g/g, respectively.¹⁵ The highest absorption was achieved for silk sericin protein,¹²⁰ the grafting being performed using a combination of AA, AAM and silk protein, the best formulation being 6:4:1 (mass ratio). For radical polymerization to occur, 8 mmol/L of potassium persulfate (KPS) as initiator and 2.5 mmol/L of MBA as cross-link agent were used. The reaction was carried at 55 °C for 6 h.¹²⁰ The reason for the high swelling of these hybrid protein-based materials was not however discussed and the synthetic fraction constituted ca. 85 wt % of the hybrid material (protein <15 wt %). Chemically modified biobased EDTAD protein materials thus appear to be a more attractive alternative to petroleum-based SAP material than protein grafting.

Post-treatment after functionalization includes cleaning off the unreacted salts, concentration and drying. Cleaning has been carried out by dialysis of the suspension against fresh water,^{28,35,115} or by acidic precipitation of the protein followed by a washing process²⁸ using ethanol or acetone.^{31,132} Cleaning with ethanol or acetone resulted in an increase in the water absorbency of soy and egg-white albumin, respectively.^{31,132} Both lyophilization and oven drying at mild temperatures (ca. 50 °C for 12 h) have been reported as drying procedures.^{28,35,40,115,133} The extensive need for cleaning and the initial low concentration of protein-treated systems have been considered to be drawbacks for the scaling-up of such systems.

Combined High Water Retention under Mechanical Stress. To enhance both the water retention and the mechanical properties of biobased SAPs, polysaccharides and proteins have been mixed, e.g. carboxymethyl cellulose (CMC), with gelatin. These mixtures contributed both swelling and mechanical strength, although no synergy was detected, and each individual polymer retained its own intrinsic proper-

ties.^{29,40,129} Another approach is to prepare semi-IPNs as a single solution to obtain a greater synergy. In the formation of semi-IPNs, a cross-linked polymer is normally mixed with a non-cross-linked polymer, followed by the *in situ* cross-linking of the later.^{116,153,154} This method enhances the structural features of the network, giving rise to high water retention even under mechanical stress, which is lacking in neat IPN systems.^{154–156} Most of the literature suggesting semi-IPNs relates however to the preparation of limited amounts of hydrogels for drug-delivery applications. These semi-IPNs thus contain a substantial amount of synthetic polymer since the area of use does not require the development of large-scale inexpensive biobased SAP materials. An approach using solely naturally sourced materials to create the semi-IPN was presented by Damodaran et al.,⁴⁰ mixing EDTAD-treated soy protein with an anionic polysaccharide (e.g., alginate), and achieving an absorption under load (AUL) in 0.9 wt % NaCl solution and a centrifuge retention capacity (CRC) of 8 and 19 g/g, respectively. These values represent an improvement in the water retention properties of ca. 35% compared with the noninterpenetrated systems.⁴⁰ Semi-IPN structures have also been created by the polymerization and cross-linking of homo poly(amino acid) systems; polysuccinamide has for instance been used to produce a polysuccinamide/polyaspartate composite,⁴⁷ and amino acid monomers have been condensed into the homogeneous polypeptide. Aspartic acid, for example has been stepwise condensed in the presence of phosphoric acid under reduced pressure, resulting in a poly(amino acid) material and the achievement of a carboxylic acid pendant group on each monomer unit.¹⁵⁷ The charged structural features in the polymer are thus tuned to resemble those of synthetic SAP, and the reported free swelling capacity (FSC) in pure water was ca. 400 g/g.^{116,154} The suggested reaction mechanism is illustrated in Figure 6.

Cross-Linking of Protein-Based Absorbent Materials.

For a SAP not to dissolve in a liquid during the absorption test a three-dimensional cross-linked network is a prerequisite. The level of cross-linking is thus an important factor in naturally sourced SAP materials. The cross-linking process in protein-based absorbent materials has been studied from different perspectives: (i) the type of cross-link used,^{158–161} (ii) the cross-linking reagent,^{1,20,162,163} (iii) the reaction conditions,^{164,165} and (iv) the cross-link spacing and density.^{33,166}

Aldehydes are the reagents most commonly used to cross-link protein-based materials.^{34,97,163} Glutaraldehyde (GA) in particular is known to effectively cross-link polypeptide chains, providing a fast reticulation reaction in proteins, in both the solid and the wet state.^{33,167–170} It is also inexpensive and less toxic than other cross-linkers,^{33,34,97,141,165,171} and has been reported to be the best cross-linking agent in EDTAD-acylated soy and fish protein-based absorbent materials.^{21,28,30–32,39,40,98,131,132} A suggested cross-linking reaction given by glutaraldehyde is shown in Figure 7, but although glutaraldehyde is reported to be

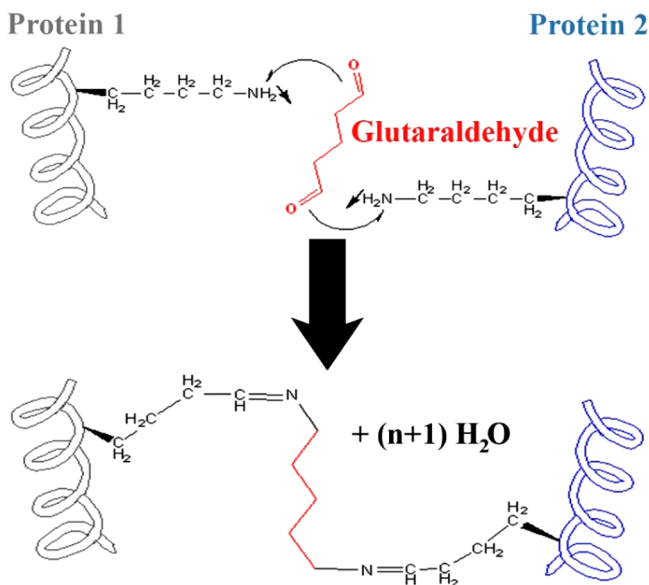


Figure 7. Cross-linking of protein through the lysine group using GA.

highly reactive, it is also known that its reactivity mostly targets specific amino acid groups, e.g. lysine.¹⁶³ Because the acylation of proteins occurs mainly through the lysine group, a balance in the extents of acylation in the protein must be considered when using GA as the cross-linking agent. GA also shows an ability to self-polymerize in storage and different alkaline conditions, giving rise to a distribution of cross-linking lengths when reacted with proteins.¹⁶⁸

Another method for cross-linking proteins is to use bifunctional diamines, as suggested by Newson et al. The commercial diamine Jeffamine EDR-176, has been evaluated for increasing in network polymerization of proteins while keeping attractive mechanical properties.^{79,172} Similarly, *N,N*-methylene bis-(acrylamide) (MBA) has been used to cross-link and form the network of protein-based absorbent materials grafted with AA.^{15,84,106,107,119} Another work reports the AUL absorption of 9.8 g/g of 0.9 wt % NaCl solution for an EDTAD-modified soy protein/CMC hybrid cross-linked by 1 wt % ethylene glycol diglycidyl ether (EGDGE).²⁸ This EGDGE-cross-linked is better than several of the other mentioned reagents due to its low toxicity. In addition, a nonhazardous cross-linking mechanism used for protein-based materials is enzymatic catalysis.^{76,173–177} Transglutaminase, i.e. a divalent calcium enzyme, is among the enzymes preferably used for cross-linking proteins. It forms intramolecular bonds and triggers the formation of γ -glutamyl- ϵ -lysine bridges,¹⁷⁸ which are stronger than disulfide bridges in proteins.^{76,162,178} There are, however, to our knowledge, no reports showing the effect of enzymatic cross-linking in SAPs based on proteins. For cellulose,

divinylsulphone (DVS) has been reported to be an alternative to MBA.^{117,166,179} The risk of traces of DVS in absorbent materials, however, introduces environmental and health concerns due to the toxicity of DVS, and epichlorohydrin has therefore been evaluated as alternative.⁹⁹ Natural-sourced absorbent materials based on cellulose have been obtained with epichlorohydrin as cross-linking agent, resulting in an FSC of 100 g/g.^{22,99,159,180,181} No literature has yet reported on protein-based absorbent materials where epichlorohydrin was used, but epichlorohydrin could have a potential use in protein cross-linking for SAPs in the same manner as for solid proteins.^{182,183}

In addition to the use of cross-linking agents for the network formation of the proteins, self-polymerization of proteins through disulfide reactions has been reported for, e.g. casein, milk protein and wheat gluten proteins. The gelation and degree of polymerization of proteins have been modified by changing the processing temperature and thermal handling of the proteins.^{37,97,98,184} The possibility to tune the degree of self-polymerization of proteins by changing the reaction parameters, e.g. temperature, is an important route for the development of nontoxic protein-based absorbent materials.

A recent emerging strategy for cross-linking in SAPs (both synthetic and biobased) includes the use of nanofillers that are capable of forming a network. Several investigations have evaluated the use of graphene oxide (GO) and nanoclay and have demonstrated an increase in the mechanical properties of the gel while maintaining its swelling capacity.^{29,185–192} Collagen grafted with acrylic acid monomers and 5.6 wt % of montmorillonite showed both an increase in mechanical strength and an enhanced water retention capacity of 950 g/g.¹¹⁸ The dual effect of improving both the mechanical and swelling properties of the material, is the result of a highly ionized surface area of the nanoclay, which gives rise to an important osmotic pressure. An increase in clay content above the percolation threshold decreases the degree of swelling, following the same course as chemical cross-linking. The particle–particle interactions provided by the nanofiller are therefore considered to provide a network restriction of the same nature as covalent cross-links.^{118,188,192}

■ MORPHOLOGICAL ASPECTS OF PROTEIN-BASED MATERIALS WITH REGARD TO WATER ABSORPTION

The morphological features of protein-based materials responsible for their water-absorbent properties are often not considered in investigations on protein-based SAPs. Tailoring of the morphologies and channel structures has been shown to promote swelling capacity, by increasing the capillary forces in the material or by increasing the surface area of particles present in the material.^{33,34,193,194} Several swelling kinetics parameters, e.g. equilibrium swelling, absorption rate and diffusion efficiency, may be altered merely by changing the final structure of the material without involving any chemical processes.^{195–199} Examples where the morphological structure affects the absorption efficiency are commonly foams, where the liquid absorption is dominated by capillary mechanisms.^{33,34,88,197,200} A difference in pore sizes have also shown to affect absorption properties.^{33,34} Differences in pore size and pore size distribution have resulted in materials which are suitable for different applications, e.g. pH-sensitive drug delivery systems, tissue engineering, blood, oil spills and plasma absorption, etc.^{133,201–208} In addition, different coatings and different

process treatments of cellulose and protein-based foams have been shown to influence the absorption of liquids with different polarities (e.g., water and/or oil).^{33,34,209,210} In this context, proteins combine foam stability and viscoelasticity with biocompatibility, making them outstanding in tailored foam structures.^{77,88,211–214} Wheat gluten foams have been evaluated for their structure, absorption and swelling properties, with absorption and water swelling of ca. 32 g/g.³⁴ Because of the large porosity of the material, resulting in capillary effects, the absorption process occurred quickly. Mildly processed gluten proteins showed water swelling kinetics and attractive mechanical properties, suitable for sponge-type applications.³³

■ POTENTIALS AND CHALLENGES FOR PROTEINS AS ABSORBENT MATERIALS

Although absorbent protein-based materials have been produced by a variety of techniques, currently produced biobased SAPs still do not fulfill all the requirements for competing with petroleum-based SAPs. The main challenge is to produce a protein-based absorbent material with adequate swelling properties to compete with the petroleum-based SAP without the need for a petroleum-based additive such as AA. To use a petroleum-based monomer together with a biobased polymer to achieve absorbent properties is not a sustainable solution for the production of a “green” SAP. Another important challenge is to develop chemical functionalization protocols that can be regarded as being of a generic nature and useful for a more general group of proteins. Generic protocols are of great value in for instance, the evaluation of protein side-stream production from the agricultural industry, e.g. wheat gluten, and not those directly extracted from certain crops. One concern regarding the use of proteins as raw materials for daily care applications, which has not been investigated nor considered so far, is possible allergenicity issues.

■ COMPETITION WITH FOOD PRODUCTION

The use of agricultural resources, e.g. wheat, oat, soy bean, etc., as feedstock for the production of biobased materials may raise the concern that these resources are needed for the production of human and animal food. A protein feedstock for fabricating biobased SAP may actually compete with food production.³⁷ However, several protein concentrates are available as side-streams obtained from different industrial processes, today used for less profitable products or as feed.^{34,37,75,78–80,82,83,97,111–113,184} Their potential use as an alternative to the unsustainable synthetic SAP would contribute to a sustainable bioeconomy, through the exchange of a unsustainable product and through a higher monetary value of the industrial side-streams. Such an exchange toward a more sustainable feedstock for the SAPs production is not expected to require much greater resources than a similar exchange toward the use of an alternative petroleum-based feedstock.²¹⁵ However, drawbacks may be seen for the use of biobased feedstock through processing/compounding modifications as, e.g. the addition of alkaline substances, depolymerization additives, denaturation agents such as urea, etc.^{215–217} Therefore, we see a possible transformation of SAPs production as a sustainable route, especially targeting side-stream protein concentrates, contributing also to increased economic return.

■ PROCESSING

From an industrial perspective there is a desire to produce biobased materials with a material functionality comparable to that of current petroleum-based products, with little or no modification to the presently utilized equipment, and production lines, and storage avoiding microorganism formation.^{215–218} This perspective has focused on sustainable and functional properties and the formation of biobased SAPs compared with current available conventional SAP alternatives. For the industrial production of protein-based materials, the literature reports processing techniques such as extrusion,^{219–222} compression,^{78–80,83} injection molding,^{223,224} and solvent casting,^{225–227} etc. The literature also shows that in wheat-gluten-based materials, the formation of microorganisms can be limited by the addition of nontoxic antimicrobial agents (e.g., Lanosol) to these biomaterials during their preparation.³⁴ This shows that processing methods are currently available that allows the production of protein-based SAPs. Limited information is available as to production costs and sustainability of protein based SAPs as related to currently used petroleum-based SAPs. If side stream sources of proteins are used for the bio-SAPs and their production is mainly striving at mimicking physiochemical characters of the petroleum-based SAPs, production of the protein-based SAPs can hardly be less sustainable in terms of water and energy use than that of petroleum-based ones.

■ CHARACTERIZATION

This Perspective paper shows clearly that the free swelling capacity (FSC) is by far the most commonly applied test used in evaluating the SAP properties of biobased materials for comparisons with currently used SAPs. FSC provides information on the liquid absorption, in both pure water and salt solutions (from the dry material) without any mechanical solicitation.^{4,5} However, as the basic swelling characteristics of SAPs are described, FSC is combined with the measurement of absorption under load (AUL) and centrifuge retention capacity (CRC) for petroleum-based versions.^{4,5} More advanced techniques such as AUL involve the application of a load to the dry material to study the absorption capacity under pressure,^{4,5,228} while CRC contributes with information about the liquid binding within the gel network.^{3–5,229} These comparisons of the different swelling properties is lacking in the literature comparing biobased and petroleum-based SAPs and requires a stronger focus in the future to enable better performance comparisons.

■ CONCLUSIONS

This Perspective summarizes the status of knowledge on superabsorbent protein-based materials (SAPs) and presents the different functionalization mechanism so far reported, which are paving the way toward more environment-friendly SAPs. Attention is given to the heterogeneity of proteins in their reactive groups, not present to the same extent in other naturally sourced polymers like polysaccharides, which contributes to unique properties but also requires molecular modifications and tuned processing conditions in order to determine the material's absorption capacity. So far, protein-based superabsorbent gels showing water and saline free swelling capacities of up to ca. 500 and 12 g/g, respectively, have been fabricated which is within the range of synthetic SAPs. One of the more promising functionalization route, where no synthetic monomers/poly-

mers are used, is protein acylation, which occurs mainly between lysine groups ($-\text{NH}_2$) in the protein by means of nontoxic reagents. Proteins derived from inexpensive industrial side-streams, e.g. wheat gluten and potato protein, are suggested as sustainable protein sources for the use of production of SAPs. Such protein side-streams represent a promising feedstock for future biobased SAPs both because of their high availability and no competition with the food market. Challenges with these protein sources are their generally low lysine content, challenging the reactions protocols herein compiled. Future work therefore need additional focus on the functionalization steps to tune the characteristics of interest from these protein sources. Furthermore, the characterization of the protein based SAP properties need to be further evaluated applying AUL, CRC, better saline FSC, etc., Additional and full-scale life cycle analyses is another need to evaluate whether it may be verified that the protein-based SAPs are a sustainable alternative to petroleum-based SAPs currently used.

AUTHOR INFORMATION

Corresponding Author

*E. Johansson. E-mail address: eva.johansson@slu.se.

ORCID

A. J. Capezza: 0000-0002-2073-7005

W. R. Newson: 0000-0003-4949-7567

R. T. Olsson: 0000-0001-5454-3316

M. S. Hedenqvist: 0000-0002-6071-6241

E. Johansson: 0000-0003-2351-5173

Notes

The authors declare no competing financial interest.

Biographies



Antonio J. Capezza is currently a Ph.D. student at KTH Royal Institute of Technology, Stockholm, Sweden and SLU Swedish University of Agricultural Sciences, Alnarp, Sweden. He received his Material Engineer degree from Universidad Simon Bolivar, Caracas, Venezuela, in 2016. He participated in a master exchange program in Macromolecular Materials in KTH Royal Institute of Technology in 2015. His research is focused on sustainable absorbent materials obtained from plant proteins as well as novel material applications using industrial side-streams.



William R. Newson is currently a researcher at SLU Swedish University of Agricultural Sciences, Alnarp, Sweden. He worked in Canada and U.S.A. as an industrial researcher in polymer processing and property improvement through molecular orientation. He received his Ph.D. from SLU in 2015, where he worked with the fabrication of biobased materials from protein side-streams. His current research is focused on food protein production from alternative sources, sustainable natural polymers and the efficient use of bioresources, especially agri-process residuals.



Richard T. Olsson is currently an associate professor at KTH Royal Institute of Technology, Stockholm, Sweden, Polymeric Material division. He received his Ph.D. from KTH in 2007, where he worked on microwave absorbing nanocomposite materials. He performed his postdoctoral studies at the CSIC (IATA), Spain, with a focus on sustainable nanomaterials. He is currently editor of Scientific Reports and has a research focus on nanocomposite materials and inorganic/polymeric interfaces as well as sustainable material engineering for future novel applications.



Mikael S. Hedenqvist is currently a professor at KTH Royal Institute of Technology, Stockholm, Sweden, where he is heading the Polymeric Materials division. He received his Ph.D. from the same institute in 1995. He was a postdoctoral scholar in the group of Professor Richard Boyd at the University of Utah, USA. He is editor of *Polymer Testing* and his research interests include transport and electrical properties of polymers, polymer degradation and stability, composites and foams, processing, modelling and biobased polymers (including protein and starch materials).



Eva Johansson is currently a professor at SLU, the Swedish University of Agricultural Sciences, Alnarp, Sweden, where she is heading the Plant Product Quality division. She is also program director for C4F, the crops part of the strategic Swedish research area TC4F (Trees and Crops for the Future) and of SLU Grogrund – Center for breeding of food crops. She received her Ph.D. from SLU in 1995. Her research interest is to understand how breeding, cropping and processing of suitable plant materials can be combined into biomass for sustainable food and industrial products.

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