INDUSTRIAL PROTEINS AS A GREEN ALTERNATIVE FOR 'PETRO' POLYMERS: POTENTIALS AND LIMITATIONS

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Abstract: For the development of technical applications of polymers from renewable resources, various biopolymers are being studied. In this paper, the opportunities for industrial proteins on this market are discussed e.g. for use in (technical) coatings, adhesives, surfactants and plastics. The use of protein modifications for the improvement of functional properties relevant for technical applications is addressed.

INTRODUCTION

Development of novel applications of biopolymers, particularly in the field of technical applications, has gained much attention in the last years. This development is driven both by agricultural surpluses but also markedly by a market-pull from consumers, governments and, last but not least, industries. Currently, there is a growing awareness of the environmental problems associated with the use of synthetic, petroleum based polymers.

Technical applications cover a very heterogeneous and complex market ranging from e.g. coatings and adhesives to plastics and surfactants. Biodegradability of biopolymers is an issue for these applications, but more important are the *processing* and the *performance* of the biopolymers. That is, in order to obtain a suitable biopolymer based product, this should (1) be processable on the same equipment as current formulations, (2) show an equally good performance and (3) have an acceptable price [1]. Especially as biopolymers should compete with synthetic polymers, price is an important issue.

In the research for technical applications of biopolymers, emphasis has so far been on carbohydrates, particularly on starch and cellulosic materials. Mayer and Kaplan [2] published an overview of the costs, performance and availability of several biodegradable polymers such as starch, cellulose acetate, polycaprolactone, polyvinylalcohol and polylactic acid. Proteins were not included into this overview.

In general, the availability of biopolymers (over 300,000 tons/year) is sufficient to enable the development of technical applications. With regard to the costs, starch can clearly be distinguished from other biodegradable polymers. The costs of most biodegradable polymers is in the range of 3 - 6 US$/kg, whereas the costs of starch(derivatives) is around 1 US$/kg.

The market for biodegradable polymers is at this moment focussing on products in which the

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biodegradability of the products provides beneficial effects (e.g. waste-disposal, repulping). Examples of applications in which biopolymers can be used are protective coatings, packaging coatings and foams, paper coatings, adhesives, disposables produced by injection molding, surface active materials etc [2,3]. At this moment, there is already a number of biodegradable materials on the market or close to market introduction.

Research on the technical applications of industrial proteins has been limited so far. To some extent, this can be explained by the higher price of proteins as compared to some other biopolymers, especially starch. Nevertheless, as will be illustrated in the following, proteins have been and are still being used in technical applications. The disadvantage of the price is apparently more than compensated for by the performance of the proteins. Most of the applications of proteins that have been - or are being- developed are specialty products with a high added value. There are however good possibilities for the development of large-scale products based on industrial proteins. Examples of these bulk applications are (technical) coatings, adhesives, surfactants and plastics and these will be discussed in the following paragraphs.

INDUSTRIAL PROTEINS

Several industrial proteins are available for the development of technical applications. Examples are plant proteins such as wheat- and corn gluten, soy proteins, pea proteins, potato proteins, and animal proteins such as casein, whey, collagen and keratin. The costs of industrial proteins range from 0.5-4 US$/kg for plant proteins to > 4 US$/kg for animal derived proteins, although proteins derived from waste streams can be much cheaper. The amount of proteins available is sufficient for the development of technical applications. For instance wheat gluten is produced at 400,000 tons/year worldwide. Thus, based on their costs and availability, industrial proteins provide an attractive feedstock for the development of technical applications.

In developing technical applications based on industrial proteins, it is important to define specific properties of proteins that are relevant for technical applications. Especially the fact that these properties are *combined* in proteins can differentiate proteins from other biopolymers. The most relevant protein properties are listed below. Applications in which these properties can be exploited are shown between brackets.

- good processability, both in aqueous media and in the melt (necessary for all applications). Solids contents of > 30% are possible;
- good film forming properties and good mechanical properties of the films (protective coatings and packaging coatings, adhesives);
- adhesion to various substrates (coatings, adhesives);
- high resistance toward UV-radiation and oils/organic solvents (coatings);
- high barrier properties for gases such as O_2 and CO_2 (packaging materials);
- surface active properties (various surfactants);

Table 1: Examples of technical applications of proteins

Protein	Technical application
Casein	Adhesives, paper coatings, leather finishes
Gelatin	Photographic emulsions, adhesives, encapsulation
Soy proteins	Paper coatings, plywood adhesive, plastics
Corn zein	Printing inks, grease proof paper, floor coatings
Keratin	Textile, cosmetics
Wheat gluten	Adhesives, cosmetics, detergents

Table 1 gives examples of technical applications in which proteins can be and are being used [4-8]. Historically, work has mainly been focused on coatings and adhesives. Casein based labelling adhesives are still used in the bottling industries for their excellent rheological behaviour. For some applications, such as the use of gelatin as hot melt in bookbinding and as a stabiliser/binder in photographic emulsions, no synthetic alternatives have yet been found which have equally good performance for these applications. Noticeable is the use of corn protein as grease proof paper, due to its high barrier for oils and fats. A more recent development is the use of (plant) proteins in surfactants.

Besides these positive attributes, proteins have their limitations. For some applications it will be necessary to improve for instance the water resistance of the materials, or the mechanical strength (e.g. for coatings). Also the thermal stability of proteins (and other biopolymers) is limited. In recent years, ATO-DLO has paid much attention to the use of (chemical) modifications of proteins to implement the properties required for specific applications. Examples will be given below.

In short, proteins are very versatile materials, which combine many properties relevant for technical applications in one polymer. The properties depend on both the protein source (that is the amino acid composition) and on the modifications that are performed to improve specific properties.

PROTEIN MODIFICATIONS

Proteins are built up of amino acids differing in reactive groups such as $-NH_2$, -COOH, (C=O)-NH_2, -OH, -SH and imidazole. In total 20 different monomers are present. The amount of reactive groups depends on the protein source, but is maximum 50% of the total. Figure 1 gives an overview of the most important reactive amino acids and their average percentage in proteins. Due to the high amount of reactive groups, proteins are very suitable materials for modification. Modification can be physically (temperature/pressure treatment or the use of additives), enzymatical, or chemical. Especially chemical modifications provide a versatile route to adjust protein properties [9, 10]. Most preferred reactions take place under mild conditions (pH, temperature, pressure) and using cheap, industrially available reagents.

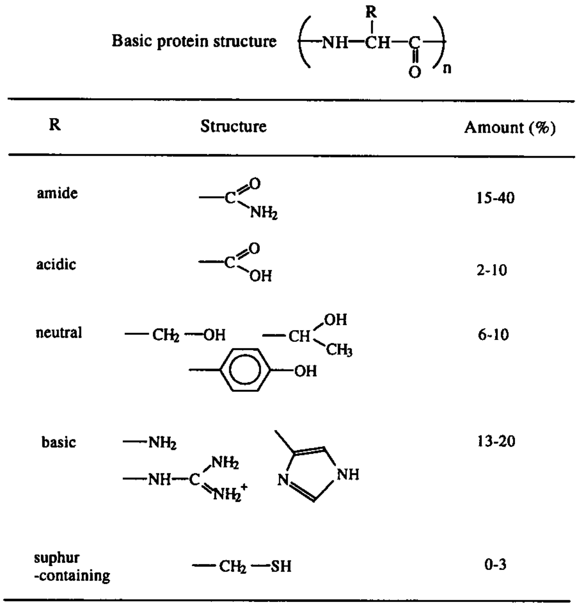

Figure 1: *Reactive amino acids in proteins*

For instance, hydrophobic alkyl groups can be introduced by reaction of the carboxylic groups present on the protein with alcohols, or by reaction of aldehydes with amine terminated residues. Conversely, additional reactive groups can be incorporated by hydrophilization of the protein. For instance, introduction of carboxylic groups can be achieved by deamidation of the amide side group of the protein. The amine group content can be increased by reaction of basic residues with imines. The specificity of the reaction depends among others on the reactants used, on the temperature and the pH of the reaction medium.

The best results often are obtained by using a two-step reaction [9]:

(1) introduction of additional reactive groups (e.g. NH_2, COOH)

(2) followed by crosslinking

Table 2 shows the effect of the two-step crosslinking approach. Non-crosslinked gluten swells > 100%, while crosslinking of native gluten with a diamine croslinker resulted in a swelling of 30%. Introduction of additional carboxylic groups resulted in a drastic increase in the effectiveness of the acid directed (diamine) crosslinker down to 2% swelling. On the other hand, the swelling percentage of Gluten-COOH upon crosslinking with the dialdehyde is increased.This crosslinker specifically reacts on amine functions and thus leaves the carboxyl groups intact.

Table 2: Swelling in water of gluten films (% surface increase) after modification and crosslinking (5 wt% crosslinker).

	Dialdehyde	Diamine	Resin
Reacts on	$-NH_2$	-COOH	all
Gluten	30	30	15
Gluten-COOH	100	2	20
Gluten-NH_2	18	40	10

By using aspecific crosslinkers like the resin (a formaldehyde resin), reacting on both carboxyl, amine and hydroxyl groups, in general the lowest swelling in water is obtained.

The choice of the modification reaction is governed by the desired effect (hydrophobization or introduction of specific reactive groups) and by the chemical composition of the protein. For instance, to increase the hydrophilicity, deamidation is most effective on proteins which contain a large amount of amide side groups (glutamine/ asparagine). A combination of modification *and* crosslinking can improve protein material properties most effectively.

APPLICATIONS

As shown in Table 1, several protein applications have already been realized. In the following, four product groups (coatings, adhesives, surfactants and plastics) will be highlighted. It will be shown how proteins properties can be adjusted for specific applications using both physical and chemical modifications. Both results obtained in our own laboratory and results derived from literature will be discussed.

Coatings

Proteins can be used for instance in protective coatings and in packaging coatings. Protective coatings are often applied from waterborne systems, while packaging coatings can also be applied by lamination using extrusion techniques. For packaging applications, the barrier properties for water vapour and gases are of prime importance. Figure 2 shows the influence of a hydrophobic additive on the water vapour permeability (WVP) of gluten coatings. The WVP was reduced by a factor of 2-5 using 7.5-20% of additive.

The permeability toward gases like oxygen and carbondioxide can also be influenced by the use of hydrophobic additives. For example, the O_2-permeability of gluten films at 91% relative humidity can be decreased from 982 to 687 amol.m/m^2.s.Pa by addition of 30% of beeswax [11]. The ratio of the permeability of CO_2/O_2 decreased from 28 to 10 after addition of beeswax.

If the water resistance or the mechanical strength of protein coatings is limiting for their application, the combination of modification (introduction of additional reactive groups) and crosslinking usually suffices (see also Table 2 for improvement of the water resistance).

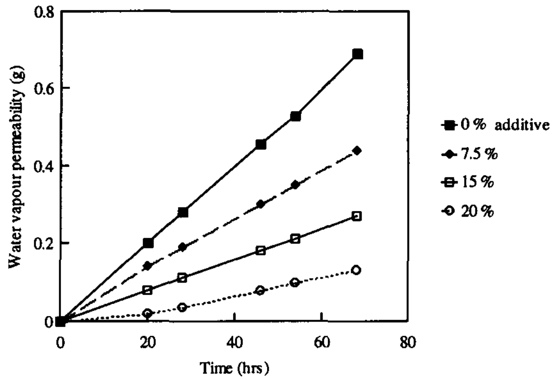

Figure 2: *Influence of a hydrophobic additive on the water vapour permeability of gluten coatings.*

Concerning protein coatings, it is shown that coating properties can be adjusted to the requirements of specific applications. One major advantage of proteins is that they can be applied from aqueous dispersions/solutions, forming a waterborne system. Therefore, proteins can comply to the trend in industry to decrease the amount of volatile organic compounds in paint systems [12].

Adhesives

For the development of adhesives, two major requirements should be fulfilled:

1) the adhesive should have a sufficient high tack. In this case both wet tack and dry bond strength are meant. Sufficient wetting of the substrate is of course another requirement.
2) the rheological behaviour of the adhesive should allow good machinability. Thus viscosity and shear dependent behaviour are of importance.

Due to the high amount of polar groups, most proteins show good adhesion to a large variety of substrates such as plastic, paper, metal and wood. By use of additives, the wet tack can be adjusted. If necessary, the dry bond strength can be improved using chemical modification like crosslinking [6]. Table 3 shows an example of how the viscosity of protein formulations can be adapted using salts which vary the solubility of the protein. The theoretically best solvent ($NaClO_4$) results in the lowest viscosity.

Table 3: *Influence of salt on the viscosity of protein formulations.*

Salt	Viscosity (Pa.s)
Na_2SO_4	8.8
$NaNO_3$	8.2
$NaClO_4$	5.6

Surfactants

A technical application based on industrial proteins which is already on the market is the use of protein based surfactants for instance in shampoos and detergents (e.g. [9]). These products are often based on protein hydrolysates which are subsequently hydrophobized. Though protein surfactants are very effective, the hydrolysates often are not optimised for their functionality. In our institute we are studying the relationship between surfactant structure and functionality by starting from hydrophobized amino acids.

Table 4 shows that amino acid based surfactants are powerful emulsifiers and foamers, with better properties than the commercial surfactant. Attachment of a hydrophobic group to an amino acid results in highly surface active substances, provided these are -COOH terminated. This product can for instance be obtained by reaction of the amino acid (glycine or glutamine) with a C_{12}- acid chloride. By reaction of the amino acid with an alcohol, only glutamine based products were obtained. This amino-terminated product did not show high surface activity.

Table 4: Emulsifying activity and foam expansion of amino acid based surfactants

	Emulsifying activity	Foam expansion (%)
Commercial	0.74	750
C_{12}-glutamine-NH_2	0.20	no foam
C_{12}-glycine-COOH	1.06	1500
C_{12}-glutamine-COOH	1.22	1100

Plastics

Protein plastics based on casein and soy protein have been known since the 1930s and 1940s [6]. By crosslinking with formaldehyde, the water sensitivity of the plastics could drastically be reduced, especially at high humidities. However, nowadays this crosslinker is not accepted anymore, so research is being performed on the use of other crosslinkers. Again, a combination of first introducing additional reactive groups into wheat gluten followed by crosslinking, can yield a 5 fold increase in the tensile strength.

Besides crosslinking, the performance of protein plastics can be improved for instance by fibre reinforcement. Protein plastics can be produced which have mechanical properties comparable to for instance polystyrene, hard PVC or ABS.

CONCLUSIONS AND FUTURE

Proteins form a class of green polymers which are very attractive for technical applications. Proteins are very versatile materials, both by source and due to the large scala of possible modifications which can be performed to tailor the properties toward the diverse requirements of technical applications. Currently, proteins are used in (expensive) high-added value market applications. In these applications, it will be a challenge to replace expensive (animal) proteins by cheaper (plant) proteins. Furthermore, good perspectives exist to increase the number of applications in which proteins can be used.

Though proteins have a high potential, more research and application work is necessary on a number of fields. Especially for the work on surfactants, it is necessary to know structure-property relationships. The interaction of proteins with water has to be studied in more detail in order to be able to avoid negative influence of water on the product properties, or even to make use of the water sensitivity of biopolymers. Also compatibility of proteins to additives and other (bio-) polymers could be a subject of research. Biopolymer science and synthetic polymer science both can benefit by exchanging knowledge and combining the fields of expertise. Examples already can be found in literature [13].

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