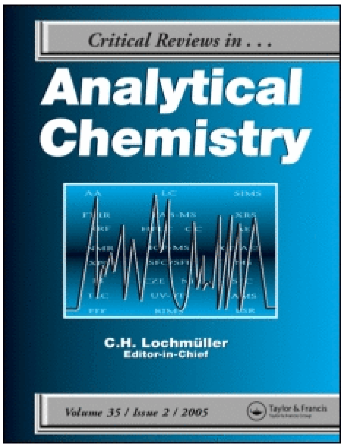

Critical Reviews in Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Biodegradable Polymers vs. Recycling: What Are the Possibilities

Attila E. Pavlath; George H. Robertson

To cite this Article Pavlath, Attila E. and Robertson, George H.(1999) 'Biodegradable Polymers vs. Recycling: What Are the Possibilities', Critical Reviews in Analytical Chemistry, 29: 3, 231 — 241

To link to this Article: DOI: 10.1080/10408349891199400
URL: http://dx.doi.org/10.1080/10408349891199400

Critical Reviews in Analytical Chemistry, 29(3):231–241 (1999)

Biodegradable Polymers vs. Recycling: What Are the Possibilities

Attila E. Pavlath and George H. Robertson

Western Regional Research Center, Agricultural Research Service, United States Department of Agriculture 800 Buchanan Street, Albany, California 94710

ABSTRACT: Synthetic, petroleum-based polymer films are extremely stable and are commonly used in agriculture, food packaging, fast-food restaurants, and on military and commercial ships. However, their attractive stability is counterbalanced by two problems. One is that petroleum polymers contribute to the demand for expensive imported oil. The other is their great resistance to biodegradation. When disposed they constitute a serious problem with very negative environmental impact. For example, the most frequently used polyethylene film takes 200 years to biodegrade. On the other hand, the use of agricultural biopolymers that are easily biodegradable not only would solve these problems but would also provide a potential new use for surplus farm production. Unfortunately, films from agricultural polymers are initially inferior to synthetic polymers mostly because of their difficult moldability and poorer physicochemical properties. However, specifically modified acidic carbohydrates and proteins with disulfide bondings may produce attractive alternatives.

KEY WORDS: biodegradable polymers, recycling, petroleum polymers, agricultural biopolymers.

I. INTRODUCTION

The most common plastics, polyethylene, polypropylene, polystyrene, polyvinyl chloride and polyethylene terephthalate are nonbiodegradable. These are produced at 10 to 15 billion pounds/year.[1] Studies on the biodegradability of these and similar polymers indicated that only polymers with a degree of polymerization, less than 500, exhibited growth of fungi in plate tests.[2–5] The only high-molecular-weight biodegrable polymers were aliphatic polyesters.

Among possible biodegradable natural polymers, starch has been most investigated. It is a relatively low-cost polymer available from agricultural surplus with potential thermoplasticity. However, it needs water for processing and the water content of the product influences its stability. Without moisture, starch will not gelatinize even at its decomposition temperature around 200°C.[6] Efforts have been made to use starch as a filler for nonbiodegradable polymers both in low[7] and high[8–9] concentrations. Some blends also incorporated autooxidant to form peroxide radicals when in contact with soil.[10,11] The results show promise for some applications.

While starch can be processed under high pressure, temperature, and moisture, starch is not a typical thermoplastic polymer. Whistler and Hilbert attributed the poor film and fiber forming characteristics of starch to the presence of the branched amylopectin fraction, which is the major component (70%) of native corn starch.[12] The thermoplasticity of starch is also affected by the addition of various inorganic salts, such as NaCl and $CaCl_2$. These additives are recommended to reduce the hydrophilicity of the final product, but they result in a higher processing temperature.[13]

Another widely available carbohydrate material is cellulose, which is biodegradable, but cannot be thermally processed, because it decomposes before melting. Chemical modifications can improve thermoplasticity but decrease biodegradability. It can be stated as a general rule that if the degree of substitution (DS) is significantly above 1.0, then no biodegradation will occur. The value of DS, which is defined as the number substituents per glucose unit, can range between zero and

3.0. This has been shown with cellulose ethers[14–16] and cellulose acetate.[17] It is theorized that steric hindrance and decreased hydrophilicity are caused by the substitutions and result in slower biodegradation.

Chitin and chitosan are polymeric amino carbohydrates that are the components of crustacean shells and insect wings. The former are available both as a waste and through harvesting of krill, a microcrustacean.[18] Both compounds are promising polymers for films due to outstanding mechanical properties and resistance to oxygen transmission. Numerous studies have been made on their reactions[19] and biodegradability.[20] The structure of chitosan can be sensitive to the degree and agents of crosslinking, interactions with salts and other components with which it is in contact, the acids used in its neutralization, and the water activity of the matrix. The structural sensitivity may be inferred by the results of the use of nonporous chitosan-based membranes for the pervaporative separation of water from ethyl alcohol-water solutions. In pervaporation the chitosan matrix effects preferential passage of water by the integration of selective adsorption from the ethanol/water solution, selective solubility within the matrix, differential diffusion through the matrix, and selective desorption to a vapor phase, which is subsequently condensed. When the pervaporative membrane is in contact with cobalt, manganese, and zinc sulfates the selectivity for water is altered by virtue of contraction of “holes” in the structure due to complex formation with the salt ions. Native (or *N*-acetyl) crosslinking in the range of 2 to 28% had no effect,[21] but crosslinking of 98% deacetylated chitosan with glutaraldehyde produced very large separation factors.[22]

Proteins are generally more expensive than carbohydrates, but are more easily biodegraded. Collagen films are used for medical applications.[23] Collagen, an animal byproduct, can be partially hydrolyzed and the resulting lower-molecular-weight polymers, gelatins, are used in food and pharmaceutical industries. Crosslinked gelatin is still biodegradable[24] and even copolymers of gelatin and polyacrylates biodegrade.[25]

Another easily available protein is casein from milk. Films made of casein have excellent mechanical properties,[26] but transmit moisture. However, when casein is combined with carbohydrates and fats, the resulting films exhibit reduced water vapor transmission characteristics.[27]

II. THEORETICAL DISCUSSION

While numerous attempts have been made using starch and a few other carbohydrates as components in various formulations for biodegradable plastics, generally the major technical problem is the need to strike a balance between stability and moldability. Water content and molecular weight are two keys to this balance. The final products should be biodegradable after fulfilling the requirements of their use; however, they must be stable during the application. The stability requires a low water content and resistance to water. On the other hand, most agricultural polymers use water as a plasticizer during molding. High molecular weight provides better stability and physical strength but decreases the moldability.

Approaches are needed for molding agricultural polymers in a low-molecular-weight form and polymerizing them after molding into stable high-molecular-weight structures. Theoretically, this may be achieved by two procedures. One is to begin with shorter linear molecular structures that contain appropriate functional groups conducive to quick polymerization to stable longer and/or crosslinked structures during the molding process. The other is to use high-molecular-weight products that contain reversible crosslinking that can be unlinked during or just before the molding process and reformed after the molding is finished.

Synthetic polymers are created by the polymerization or polycondensation of monomers which are generally stable at the moderately high temperatures required for the initiation of such reactions. The formation of polymers generally occurs through new, mostly irreversible C-C, C-O, and C-N bondings.

Most agricultural polymers are formed enzymatically through glucosidic or peptide bonding from carbohydrate and amino acid monomers and oligomers. These natural building blocks decompose at the higher temperatures used for economic, large-scale synthetic polymerization. Therefore, the polymers must be built using couplings that will occur readily at temperatures not harming the structure of either the starting materials or the forming polymers. The simplest and fastest reactions, which can couple shorter molecules into larger ones are acid-base interactions. One way to accomplish this is by reacting acidic polymers with basic ones:

$$\mathrm{HOOC{-}R{-}COOH + H_2N{-}R'{-}NH_2} \rightarrow$$
$$\rightarrow [\mathrm{{-}OOC{-}R{-}COO{-}H_3N{+}{-}R'{-}\ +\ NH_3}]_x \qquad \text{Reaction 1}$$

Another possibility is to start out with polymers rich in free carboxylic groups and convert them to ionomers using multivalent cations, for example, calcium, magnesium, or quaternary diamines:

$$\mathrm{HOOC{-}R{-}COOH + M^{++} + HOOC{-}R{-}COOH} \rightarrow$$
$$\rightarrow [\mathrm{{}^{-}OOC{-}R{-}COO^{-}M^{++}}]_x \qquad \text{Reaction 2}$$

Many carbohydrates have free acidic groups, or can be converted to contain carboxyl groups. However, basic agricultural products are less common, but some proteins could provide moldable and stable materials by Reaction 1, but there are more possible candidates for Reaction 2. Low-molecular-weight carbohydrates and/or proteins may be molded first and the surface of the molded product may be treated with multivalent cations for stability in the intended application. If greater stability is needed a process could be developed that would allow the application of these cations during molding.

Reaction 2 is applicable to the bulk of the polymers of agricultural origin even though neither basic nor acidic because most of them may be converted to polymers with free carboxylic groups through oxidation and/or hydrolysis.

Polymers formed by Reactions 1 and 2 begin with low-molecular-weight reactants, because the large natural macromolecules generally do not melt, but undergo irreversible degradation at the elevated temperatures used for molding. Therefore, in many cases the resulting products have undesirable properties. However, macromolecules with reversible weak linkages that unlink under mild molding conditions would have better thermoplasticity and the larger molecules could reform after molding. Certain common natural crosslinkings of bonds readily open and reform through reductive and oxidative processes. For example, a disulfide bond can be easily opened at moderate temperatures by simple reducing agents, for example, sodiumbisulfite, and quickly reestablished by oxidation, even by exposing to the air. Such a process is used regularly by millions of people every day for setting curls in their hair, which contains a large amount of disulfide bonds.

III. RESULTS AND DISCUSSION

A. Reaction 1 Examples

Chitosan is a polysaccharide with a structure similar to cellulose. The pure compound is the polymeric form of 2-amino-2-deoxy-D-glucose with a 1,4-β-glucosidic bonding. Chitosan solutions in 1% aqueous formic and acetic acid may be reacted with various long chain fatty acids. After evaporation, the volatile formic or acetic acid is replaced with the less volatile fatty acids and salt formation occurs. Depending on the acid, the resulting films exhibit a range of water barrier properties. The best resistance was obtained with lauric acid.[28] The film alone has moderate to good strength that can be increased by bonding to paper. Because chitosan is also used as an additive to paper to increase its strength, the film can be wetted and easily attached to a single sheet of paper or sandwiched between two sheets. Such coated paper is a potential replacement for polyethylene coated wrapping papers that are neither biodegradable nor recycylable, although the rate of water transmission is not as good as the commercial products. The successful amination of starch and other agricultural carbohydrates would provide similar starting materials.

B. Reaction 2 Examples

Transparent, flexible films were made by casting aqueous solutions of alginic acid. They were not moisture resistant and readily dissolved in distilled water within minutes. When the films were immersed in multivalent ion solutions, the crosslinking of the carboxyl groups considerably reduced the solubility of the films. However, the crosslinking was not instantaneous throughout the film. It was a function of time and concentration. The result of immersing the films in solutions of salts for varying times were compared (Table 1). When the films were immersed in these solutions competitive dissolution and crosslinking processes occurred. If the concentration of the multivalent ion is low, the first process, that is, dissolution, would be dominant. Conversely, increasing ion concentration would counteract the dissolution. A 2% concentration was not sufficient to insolubilize the films, except for copper ions. Higher ion concentrations resulted in considerably less solubility, in most cases giving films that did not dissolve in distilled water even after 3 weeks. The treatment with magnesium salt did not result in acceptable films at any concentration or treatment time. With zinc and iron, higher concentrations (10%) were needed to cause insolubility of the film.

Films were also obtained by including multivalent ions in the alginic acid casting solution, but their properties depended greatly on the concentrations and temperatures of mixing. Without addition of glycerin, these films were unacceptably fragile under all conditions. When mixing was at room temperature (~20°C), immediate gel formation occurred and no films could be cast. An increase to 50°C was needed so that the viscous solution could be poured into the frames for casting. Resulting films (Table 2) were very fragile when components were used in stoichiometric ratio. All films, with the exception of those formed from zinc, were visually opaque. The transparency increased somewhat at 75% stoichiometric ratio, but the films were still inferior. At 50% ratio only calcium, copper, and zinc gave pliable films with some opacity. Only the 25% ratio resulted in completely transparent films with all ions but aluminum. However, in each case the films readily dissolved in water within 30 min in contrast to the stable films created from water-soluble films after dipping them in multivalent ionic solutions. We hypothesize that the elevated temperature needed for keeping the mixture fluid, altered the structure of the alginic acid. This could have been by lowering the molecular weight and/or reorienting the configuration, as suggested by the lowered room temperature viscosity after heating the solutions to 50°C. Because the solubility of these films made them unacceptable for the purpose of this investigation, no further attempt was made to confirm this. Interestingly, when these soluble films (0.25 stoichiometric ratio) obtained by mixing of the components were immersed into calcium solution they became insoluble in water.

The tensile strength and elasticity of the films obtained by various methods were compared (Table 3). Treatment with calcium, at 5 and 10% concentrations, yielded the greatest increases in strength of alginic acid films. After immersing in calcium and copper, the films shrank irregularly to 50 to 60% of the original, while other ions resulted in smoother films after immersing. The effect of time also varied with the type of ions and glycerin concentration. No absolute conclusion was apparent, but a qualitative trend observed. The tensile strength quickly reached a maximum after 5 to 15 min of treatment with calcium at 5%. At 10%, the maximum was reached at shorter times and longer exposure frequently decreased the value. The addition of glycerin as a plasticizer may decrease the tensile strength, but the percentage of elongation at breakage did not necessarily increase in the same proportion and in some cases even decreased.

Pectin is another water-soluble polysaccharide that can form a clear water-soluble film. Without further treatment it dissolves within 10 to 20 min if suspended in water. However, immersion of these films into multivalent cation solutions for 30 min, just as in case of the alginate films, increased the subsequent time for dissolution, depending on the cation. For instance, Ca^{++}-treated films did not dissolve even after 2 weeks (Table 4).

Based on the tensile strength of the films, the multivalent cations can be sorted into three classes. Calcium, copper (II), and zinc provided the greatest increase in the tensile strength of the pectin film (3 to 3.5 times). The calcium-treated films were almost twice as strong as a reference cellu-

TABLE 1
Insoluble Film Formation from Na-Alginate Films Immersed in Multivalent Ion Solutions

Ion	Conc	5 min		15 min		30 min		60 min	
	%	w/g	wo/g	w/g	wo/g	w/g	wo/g	w/g	wo/g
Al	2						+		
	5	+	+	+	+	+	+		
	10	+		+		+		+	
Ca	2								
	5		+	+	+	+	+		
	10	+	+	+	+	+	+	+	
Cu	2		+		+		+		+
	5			+	+	+	+		+
	10					+	+	+	
Fe	2								
	5								
	10		+	+	+	+	+	+	
Zn	2								
	5				+				
	10	+	+	+	+	+	+	+	+

w/g = glycerin, wo/g no glycerin added.
+ homogenous, continuous and visually insoluble films.

lose acetate film. Not surprisingly, treatment with divalent cobalt, iron, and nickel ions also increased the tensile strength of the pectin films: but only a 2.0 to 2.2-fold increase. Dipping the dry pectin films in aluminum and magnesium chloride solutions had very little if any strengthening effect on the film. Table 5 summarizes the tensile strength as a function of the multivalent ions.

The effects of the different multivalent ions may be influenced by their ionic radius. Using the stress-strain data, the Young modulus, k, was calculated for each of the treatments. The change in this constant from the constant for the untreated film, Δk, was corrected for the molar concentration (assuming the effect was proportional to the concentration) and therefore are reported on a per mole of ion basis. The result is shown in Figure 1 as a function of the ionic radius of the ion. The pattern revealed suggests a generally increasing level of structure strengthening as the size of the treating ion increased and a very specific effect in the range of an ionic radius of 0.72 to 0.76 Å. The specific effect may arise because of the presence of structural passages through

TABLE 2
Visual Appearance of Films Formed from Na-Alginate and Multivalent Ion Salts Solutions

Stochiometric ratio	Ca^{++}	Zn^{++}	Cu^{++}	Fe^{++}	Al^{+++}
1.0	opaque fragile	some opacity wrinkled	opaque fragile	opaque fragile	opaque fragile
0.75	opaque fragile	some opacity wrinkled	some opacity	opaque wrinkled	opaque fragile
0.5	some opacity smooth	almost clear smooth	almost clear fragile	opaque fragile	opaque
0.25	clear smooth	clear smooth	clear smooth	clear flat	opaque fragile

which ions of about 0.75 Å radius may penetrate and in that they more effectively crosslink. The general effect may relate to the ability to crosslink between helices which are farther apart. It is possible that the peak at 0.7 may be altered to higher or lower values by changing the substrate pectin maxtrix through desterification, but this was not explored at this time. However, if this is true, then the polymer/crosslinking could be optimized in this way to obtain the best combination of properties and cost but also to meet end use requirements or restrictions regarding the nature of the crosslinking ion.

The high stability of pectin gels achieved by calcium ion has been explained by two possible structures. In each case it is assumed that pectin is present in various helical formations. However, in one structure the calcium ion provides bridges to three oxygen atoms in one pectin helix and to two oxygen atoms on an other helix.[29] In the other or "eggbox" model, the pectin helices are arranged in such way that "ligand holes" form where the calcium ion can fit and provide ionic interaction with carboxyl groups on neighboring helices.[30] While some of the effects is in the amorphous domain, both structures can adequately justify the strong bonding.

The tensile strength was greatly dependent on the moisture content of the treated film. For instance, the tensile strength of a film treated with calcium for 30 min, after 1 h of drying at room temperature between cellulose filter papers was less than that of the untreated film. Tensile strength reached the maximum 3.5-fold increase after 2 days. These results suggest that water in the partially dry matrix mobilizes the polymer structure. As water is removed, the helices condense on each other, forming additional bonds and increasing the strength of the matrix.

Water vapor transmission of a calcium-treated pectin film indicated that calcium treatment decreased the permeability from 136.6 to 44.3 g.mm/$m^2 \cdot$ day $\cdot$ kPa. This would provide additional advantage for pectin-based films vs. synthetic ones in applications where moisture control is important.

The other potential starting materials for biodegradable films are various proteins, mostly keratin, which contain cystein. These proteins, abundant in human and animal hairs, contain disulfide bonds subject to redox reactions. Such bonds, which are responsible for high molecular weights through crosslinkings, can be opened by simple reducing agents, such as sodium bisulfite. Such treatment does not affect the peptide bonds, but by temporarily opening up the crosslinking the fibers become pliable enough to form films under appropriate conditions. When wool fiber keratins were pressed at 130 to 140°C, flexible transparent films with hydrophobic surfaces were obtained.[31] Below 130°C, the resulting films had limited transparency and the original fibrous structure was

TABLE 3
Mechanical Properties of Films Formed from Na-Alginate Films by Multivalnet Ion Treatments at Maximum Load as Measured by Instron

		Concentration of ions				
Ion	Time	Glycerin	5%		10%	
	min.		Stress Mpa	Strain %	Stress Mpa	Strain %
Al	5	No	30.92	1.52		
		Yes	19.61	1.35	48.57	2.22
	15	No	37.00	1.23		
		Yes	31.00	0.96	51.67	1.40
	30	No	24.13	0.72		
		Yes	40.27	1.06	24.93	0.89
	60	Yes			23.42	1.21
Ca	5	No	71.62	3.04	96.96	3.02
		Yes	41.11	3.47	48.85	4.49
	15	No	87.32	3.52	103.20	2.83
		Yes	62.43	3.56	55.94	2.18
	30	No	65.92	3.66	88.50	2.78
		Yes	47.95	4.14	52.88	3.73
	60	No			132.40	2.59
		Yes			73.28	2.84
Cu	15	No	48.76	4.05		
		Yes	33.74	2.82		
	30	No	96.38	4.42	19.44	2.24
		Yes	19.44	2.24	53.96	3.41
	60	No			18.65	2.16
		Yes			89.78	3.28
Zn	5	No			62.69	2.35
		Yes			34.43	2.19
	15	No			79.42	2.65
		Yes			34.8	2.51
	30	No			71.72	4.19
		Yes			39.03	2.83
	60	No			64.39	1.98
		Yes			49.55	3.69

Stress denotes maximum load where test sample broke. Strain indicates percent elongation at maximum load. For untreated dry sodium alginate film these were 5.6 Mpa & 1.62% without glycerin and 6.1 Mpa & 11.8% without glycerin. Cellulose acetate and polyethylene films were 35.58 Mpa & 3.11 % and 21.28 Mpa & 153.5 % respectively.

TABLE 4
Solubility of Pectin Films

	Treatment temperature (°C)	Dissolution time (min)
None (prepared at pH=7)	25	40
	80	10
None (prepared at pH=12)	25	0.5
	80	0.3
Mg^{2+}	25	60
	80	10
Ca^{2+} and Zn^{2+}	25	>2 weeks
	80	>2 days

TABLE 5
Tensile Strength of Pectin Films as Measured on Instron*

Multivalent cation	Tensile strength (MPa)	Strain (%)
None	14.1	8.7
Ca^{2+}	52.9	2.1
Zn^{2+}	49.2	2.7
Cu^{2+}	54.1	1.9
Co^{2+}	32.4	2.7
Ni^{2+}	27.8	1.5
Fe^{2+}	26.2	3.1
Mg^{2+}	13.4	8.1
Al^{3+}	16.4	5.1

*For comparison, commercial cellulose acetate and polyethylene samples were tested by Instron using the same standard tests which resulted in 35.6MPa, 3.1% and 21.3MPA, 153.5% respectively.

quite visible, while at higher temperatures rapid browning caused by decomposition was observed.

In the case of chicken feather, which contains a less crosslinked keratin than wool, homogenous films of varying opacity were formed already at 75°C after 3 min, reaching the maximum at 110°C. A higher temperature did not result in further improvement. The pressure applied during film formation was found to be a major factor in the clarity of the resulting film up to 46.7 MPa, but higher pressures had no significant effect. The most transparent films were obtained when the feather was ground by the mixer. In other cases the films were frequently speckled with unreacted feather particles even under optimum reaction conditions.

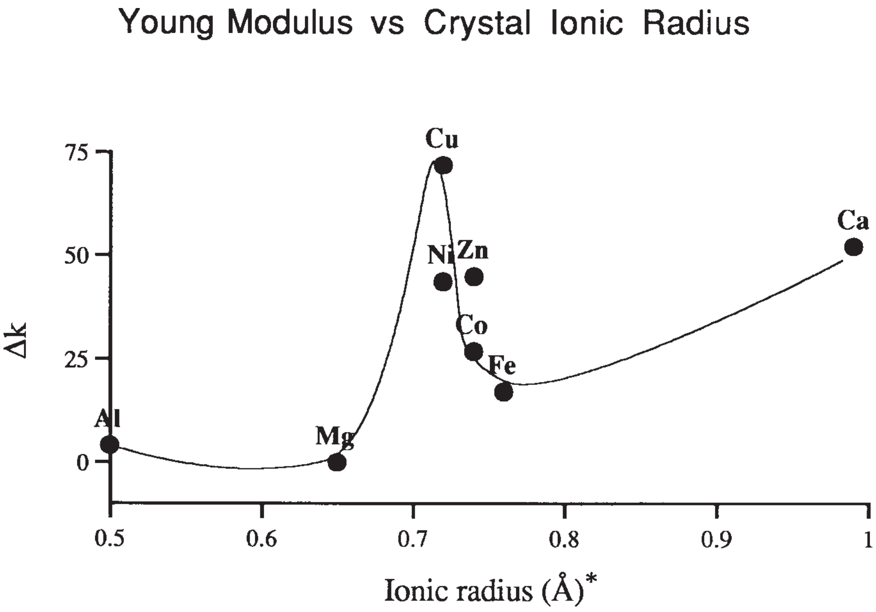

FIGURE 1

* *Lange's Handbook of Chemistry.* John A. Dean, Ed. 12th edition, McGraw-Hill, New York. 1979, Table 3-10. Pages 3-120 to 3-125.

The films obtained from chicken feather exhibited a lower tensile strength than those obtained from wool. In order to increase the strength, the addition of 10 and 20% of small wool fiber particles were tested assuming that the more highly crosslinked wool keratin would interact in its reduced form with the feather keratin. However, because the optimum conditions for wool requires a temperature of 135°C and feather starts to decompose above 130°C no usable films were obtained.

In order to overcome the problems caused by unreacted feather particles in the film, attempts were made to dissolve the feather and cast a film from a clear solution. The use of various organic-reducing agents, for example, mercaptoethanol,[32] thioglycolic acid,[33] have been reported in the literature, but these may also reduce the molecular weight of the keratin. Na_2S was also found to dissolve feather keratin, but the subsequent use of Na_2SO_3 for the elimination of the excess sulfide resulted in the formation of large amount of sulfur.[34] Therefore, economically more favorable reducing agents, such as Na_2SO_3 and $(NH_4)_2SO_3$, were investigated. It was found that both yielded 57% of the original weight of the feather, although the treatment by sulfide-sulfite mixture resulted in 74% protein solubilization. The major difference is that Na_2SO_3 and $(NH_4)_2SO_3$ were effective only at pH = 6 and 75°C, while the sulfide-sulfite mixture required only 40°C.

When the freeze-dried protein was dissolved in alcoholic ammonia with 35 to 40% glycerin to keep the film pliable, strong films were obtained after casting. However, transparency varied depending on the drying rate. It appears that when a slow drying is done at room temperature, not only is the forming film at least partially opaque but its strength also decreases significantly. The film was weaker at the opaque spots. Slow drying may allow the reformation of the native helical structure where the crosslinking is more intramolecular than intermolecular. The lack of intermolecular bonding can result in lower tensile strength.

Gluten, a wheat protein, was also converted into thin films by two methods. One was to dissolve certain fractions in aqueous alcohol and cast the forming solution into a film. The film obtained this way is transparent and it is not water soluble, but generally becomes turbid after contact with water. Films were also obtained by pressing a dough made of commercial gluten (80% protein) at temperatures of 50 to 100°C. These films were somewhat yellowish, but still highly translucent. By adding plasticizer, such as glycerin, the films were flexible and elastic depending on the amount of the plasticizer. While gluten contains much less cystein (~1%) than wool (~15%) or chicken feather (~7%), the tensile strength of gluten film was improved by adding 1% of reducing agent, such as Na_2SO_3, to the dough that opens up the disulfide bonds, and during the pressing process intermolecular crosslinking may occur. The addition of up to 10% of keratin, obtained from waste chicken feather containing a much larger amount of disulfide bond, increased the tensile strength of the film to and above that of commercial polypropylene.

IV. CONCLUSION

Alginic and pectin films, cast from aqueous solution, are transparent, but they had low strength and redissolved in water. However, when reacted with multivalent cations, they not only became water insoluble, but also resistant to water vapor transmission, and, depending on the applied ion, had higher tensile strength. Among the cations tested, treatment with calcium provides the best over all improvement in physico-chemical properties competitive with commercial, non-biodegradable films. While the exact results of the long-range biodegradability tests are not available yet, it can be safely hypothesized that the ionic crosslinking does not alter drastically the biodegradability. At worst, even though these films are water insoluble, a buried film would slowly revert to pectin through leaching. Certain proteins, for example, gluten and keratin, with disulfide bonds also formed films when they were pretreated by reducing agents and pressed at moderate temperatures. The films were translucent to various degrees, depending on the cystein content of the protein and the applied pressure. The tensile strength of these films was comparable to that of commercial synthetic films.

REFERENCES

1. Johnson, R., *J. Plastic Film Sheet.* **4.,** 155–170 (1988).
2. Potts, J. E., In: *Aspects of Degradation and Stabilization of Polymers*, H .H. G. Jellinek, Ed., New York, Elsevier, 1978, pp. 617–658.
3. Potts, J. E., *Kirk-Othmer Encyclopedia of Chemical Technology*, Suppl. Vol., M. Grayson, Ed., New York, Wiley-Interscience, 1984, pp. 626–668.
4. Potts, J. E., Clendinning, R. A. and Ackart, W. B., In: *Degradation of Polymers and Plastics*, London, Inst. of Elec. Eng., 1973, pp. 12.1–12.10.
5. Potts, J. E., Clendinning, R. A., Ackart, W. B. and Niegish, W. D., In: *Polymers and Ecological Problems*, Guillet, J. Ed., *Polymer Science and Technology*, Vol. 3. New York: Plenum Press, 1973, pp. 61–80.
6. French, D., *J. Anim. Sci.* **37(4),** 1041–1061 (1973).
7. Narayan, R., In: *Assessment of Biobased Materials*, Chum, H. L., Ed., Report SERI/TR-234-3610, Solar Energy Research Institute, Colorado, 1989 pp. 7.1–7.25.
8. Otey, F. H. and Westhoff, I&EC Products Research and Development, American Chemical Society, June, 1984, pp. 284–287.
9. Otey, F. H. and Doane, W. M., In: Proc. of Symposium on degradable plastics, Washington, D.C., The Society of Plastics Industry, Inc. 1987, pp. 39–40.
10. Griffin, G. J. L. Proc. of Symposium on Degradable Plastics, Washington, D.C., The Society of Plastics Industry, Inc. 1987, pp. 47–49.
11. Maddever, W. J. and Chapman, G. M., *Plastics Engineering*, 1989, July, 31–34.
12. Whistler, R. L. and Hilbert G. E., *Ind. Eng. Chem.* **36(9),** 796–798 (1944).
13. Huang, A. S. and Liu, X. X., In: *Biodegradable Polymers and Packaging*, Ching, C. Kaplan, D., and Thomas, E., Ed., Technomic, Lancaster, PA 1993, pp. 53–61.
14. Kasulke, U., Dautzenberg, H., Polter, E., and Phillipp, B., *Cellulose Chem. Technol.* **17,** 423–432 (1983).
15. Perlin, A. S. and Bhattacharjee, S. S., *J. Polym. Sci. Part C.* **36,** 509–521 (1971).
16. Wirick, M. G., *J. Polym. Sci. Part A-1*, **6,** 1965–1974 (1968).
17. Stutzenberger, F. and Kahler, G., *J. Appl. Bact.* **61,** 225–233 (1986).
18. Naczk, M., Synowiecki, J., and Sikorski, Z. E. *Food Chem.* **7,** 175 (1981).
19. Pavlath, A. E., Wong, D. S. W. and Robertson, G. H., In: *Polymer Encyclopedia*, Salamone, J., Ed., CRC Press, Boca Raton, 1995, Vol. 2. pp. 1230–1234.
20. Hirano, S., Tsuchida, H., and Nagao, N., *Biomaterials* **10,** 574–576 (1989).
21. Mochizuki, A., Sato, Y., Ogawara, H., and Yamashita, S., *J. Appl. Polym. Sci.* **37,** 337–584 (1989).

22. Uragami, T. and Katsumi, K., *Polymer* 31, 668–72 (1990).
23. Bogdansky, S. In: *Biodegradable Polymers as Drug Delivery Systems,* Chasin, M. and Langer, R., Eds., *Drugs and the Pharmaceutical Sciences,* Marcel Dekker, New York, 1990, 231–259.
24. Huang, S. J. et al., In: *Proc. of the Third International Biodegradable Symposium,* Sharpley, J. M. and Kaplan, A. M., Eds., Applied Science, London, 1976 pp. 731–741.
25. Kumar, G. S., Kalpagam, V., and Nandi, U. S.,. *J. Applied Polymer Sci.* 29, 3075–3085 (1984).
26. Grohmann, K. and Himmel, M., In: *Assessment of Biobased Materials,* Chum, H. L., Ed., Report SERI/TR-234-3610, Solar Energy Research Institute, Colorado, 1989, pp. 11.1–11.10.
27. Krochta, J. M., Hudson, J. S., Camirand, W. M., and Pavlath, A. E., Proc. American Society of Agricultural Engineers, Chicago, 1988, December, No. 88–6523, 1–15.
28. Wong, D. W. S., Gastineau, F. A., Gregorski, K. S. J. Tillin, S. J., and Pavlath, A. E., *J. Agric. Food Chem.* **40,** 540–544 (1992).
29. Walkinshaw, M. D. and Arnott, S., *J. Mol. Biol.* **153,** 1075 (1981).
30. Morris, E. R., Rees, D. A., and Thom, D., *Carbohyd. Res.* **66,** 145 (1978).
31. Pavlath, A. E., Lee, K. S., and Ward, W. M. *Symposium on Membranes*. I. North American Chemical Congress, Mexico City, Mexico, 1975, MACR0-20.
32. Matsuda, H., Takahashi, M., Shinoda, K., Kikyodani, S., and Inagaki, H., Japan Patent 7842281 (1976).
33. Ichikawa, R., Arai, K., and Kameda,T. Japan Patent 9291138 (1992).
34. Anker, C. A., U.S. Patent, 3,642,498, 1972.