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Pectin-based Biodegradable Water Insoluble Films

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SUMMARY: Aqueous solutions of pectin, an acidic polysaccharide which occurs in various natural products, was cast into clear films. While the films were flexible enough to be used as wrapping materials, their strength and resistance to water were inferior to presently used commercial films. However, precast films immersed into aqueous solutions of multivalent cations became insoluble in water and depending on the ions became stronger in tension. Tensile strength increased to levels comparable to, or in the case of calcium, copper(II) and zinc, greater than those of some commercial wrapping materials

Introduction

Synthetic wrapping materials, e.g. polyethylene and polypropylene, are relatively inexpensive and for most applications possess good physico chemical properties, e.g., tensile strength and appropriate transmission rates for water vapor, oxygen and carbon dioxide. However, the increasing use of synthetics creates environmental problems since their biodegradation requires many years$^{1)}$. Improved biodegradability of packaging materials can be acquired by chemical modification and dilution with more degradable components$^{2)}$. Alternatively, the packaging function could be provided with biodegradable polymers. These biopolymers do not always possess satisfactory physico-chemical properties, but can be modified to a limited degree without affecting biodegradibility. Naturally, the starting biopolymer should be readily available and inexpensive in order to compete with the present commercial products, such polyethylene.

The use of synthetic polymers also increases the demand for dwindling oil resources and negatively impacts trade balance. Agriculturally derived polymers, e.g., polysaccharides and proteins are domestically produced, potentially abundant as surplus or waste and their biodegradation does not increase greenhouse gases

One of these biopolymers, pectin, is currently available from the waste of apple and citric juice processing and from sugarbeet waste from sugar processing. It is a polysaccharide

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containing small amounts of neutral sugars, but its major component is D-galacturonic acid with (1-4) α linkages. Its molecular weight is around 100,000 Dalton depending on its origin. A percentage of the carboxyl groups may be present in esterified form as indexed by the degree of esterification (DE), which is defined as the percentage of total carboxyl groups esterified. Pectin is characterized as high methoxy, HM (DE>50) or low methoxy, LM (DE<50), but the percentage can be changed by deesterification.

The presence of free carboxylic groups is the key factor for the improvement of the physico-chemical properties of pectin films. It was reported almost fifty years ago that the reaction of calcium with pectin resulted in a film-like material the ôtendernessö of which decreased with the methoxy content of the pectin$^{3-5)}$. This is not surprising since acidic polymers can readily form ionomers with suitable multivalent cations. However, when the aqueous solutions of these two components are mixed, in most cases immediate gel formation occurs dependent on factors e.g., concentration, temperature, pH, etc. Aluminum and copper are used to precipitate pectin from aqueous solution in its production$^{6)}$. While gel formation by pectin is important in food applications$^{7)}$, it is difficult to obtain uniform transparent wrapping films once gels are formed. Therefore, precast and dried water-soluble pectin films were dipped into multivalent cation solutions under appropriate conditions to assess the possibility for and degree of improvement to their physic-chemical properties.

Experimental

Materials. The pectin was the product of Tic Gums Inc. with a designation of LM32, lot no. P4073 with a 32% degree of esterification. The amount of amidation was not known, but in commercial pectins it is normally in the range of 15-20%. The following multivalent cations were used as the aqueous solutions of their reagent grade chloride hydrates: aluminum, calcium, cobalt(II), copper(II), iron(II), magnesium, nickel(II) and zinc

Preparation of pectin films. While pectin is watersoluble when mixed with water it forms globules. Therefore, 1.5 g of pectin was wetted first with 25 ml of ethanol and then mixed with 270 ml of water and 0.6 g of glycerin. The mixture was stirred for 30 minutes to obtain complete dissolution, and then poured into a 10x10 cm^2 frame and dried in an electrophoresis gel dryer under an air flow at 55°C. Dry films were obtained in 3-4 hours. The thickness of the films, measured by a micrometer, varied between 0.15-0.25 mm.

Treatment with multivalent cations. For most of the experiments, unless otherwise noted, the dry films were dipped into a 5% solution of the multivalent cationic solution for 5 minutes, then air dried between filter papers for 24 hours.

Dissolution. Dried films (1.3x 1.0 cm^2) were suspended in 10 ml of distilled water, an excess amount relative to the original solution, and visually checked at regular intervals for dissolution.

Measurements. The dried films were visually inspected for integrity and uniformity. Fragile films were discarded. The acceptable films were cut into 1.3x10 cm^2 ribbons. Tensile strength of the films was measured in quintuplet by INSTRON Model 4502 Series H3033 at a relative humidity of 50% and temperature of 25°C according to ASTM D1004-94a. The rate of water vapor transmission was measured by a modified ASTM-E96-80 procedure using circular samples of two inches of diameter and mounted on Plexiglass test cells8).

Results and Discussion

Pectin is water soluble and its solution can be cast to form a clear film. However, without further treatment the watersoluble film readily degrades and dissolves within 10-20 minutes if suspended in water. However, immersion of these films into multivalent cation solutions for 30 minutes increased the subsequent time for dissolution, depending on the cation. For instance, Ca^{++} treated films did not dissolve even after 2 weeks (Table I)

This is understandable if we consider that there are two competing steps when the pectin film is submerged into multivalent cation solutions. On one hand, water penetrates into the film, loosens the attraction between the polymer chains and starts the dissolution. At the same time, however, the multivalent cations penetrate the film and establish increased bonding between the polymer chains. If the second step is faster than the first one, the bonding fortifies the film before it dissolves. Obviously, the rate of diffusion and the success of ionic stabilization is determined by solution properties and concentration of the ion. Based on the result of our earlier work with alginic acid where a 5% concentration resulted in good protection against dissolution9), all experiments with pectin were carried out at the 5% level. After 5 minutes, with the exception of magnesium, each multivalent ion treatment resulted in a film at room temperature with reduced solubility. Table I summarizes dissolution data for

TABLE I. 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

the films obtained after immersion in 5% multivalent cationic solutions. Interestingly, Mg^{++} did not provide any significant improvement. This is in agreement with the report of other researchers that Mg^{++} does not form a stable eggbox structure with pectin$^{10)}$.

In our experiments with alginic acid$^{9)}$ extended dipping time had no effect on the dissolution, but did increase tensile strength. For calcium a marked increase was observed during the first two minutes of immersion. After two minutes the tensile strength continued to increase at a smaller rate until 30 minutes, when the effect was saturated. Therefore in all further experiments a 30 minute dipping time was used.

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 (3-3.5 times). The calcium-treated films were almost twice as strong as a reference cellulose acetate film. Not surprisingly treatment with divalent cobalt, iron and nickel ions had also increased the tensile strength of the pectin films: but only a 2.0-2.2-fold increase. Dipping the dry pectin films in aluminum and magnesium chloride solutions had very little if any strengthening effect on the film. Table II 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 was calculated for each of the treatments and the change in this constant from the constant for the untreated film. These differences, Δk,

TABLE II. 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

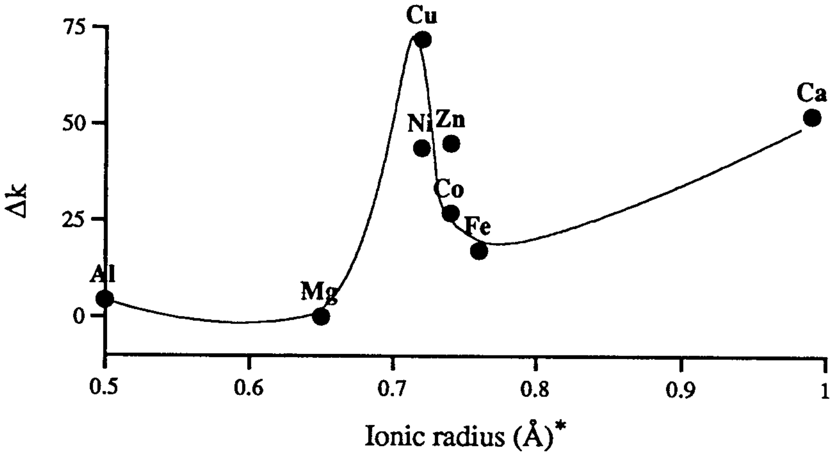

Fig. 1. Young modulus vs. crystal ionic radius.
* Lange's Handbook of Chemistry. John A. Dean (ed.), 12th edition, McGraw-Hill Book Company, New York, 1979, Table 3-10, pp. 3-120 to 3-125

were 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 increases and a very specific effect in the range of an ionic radius of 0.72-0.76 Å. The specific effect may arise because of the presence of structural passages through which ions of about 0.75 Å radius may penetrate to the ligand holes in which 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 helix11). 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 helices12). 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 minutes, after one hour 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 two days. These results suggest that water in the partially dry matrix mobilizes the polymer structure. As water is removed, the helices condense upon 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.day.kPa. This would provide additional advantage for pectin-based films vs synthetic ones in applications where moisture control is important.

Conclusion

Pectin films readily react with multivalent cations making them not only water insoluble, but also resistant to water vapor transmission. 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.

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