

Films from Mixtures of Viscose and Alkali High-Amylose Corn Starch

INTRODUCTION

Cellulose and amylose are both natural linear polymers of D-glucose, and to some extent their physical and chemical properties are similar. Viscose, made by xanthation of cellulose, is coagulated in mineral salt and acid solution to produce cellophane, whereas amylose in alkaline solution, without prior xanthation, can be coagulated similarly to give clear, strong, flexible films.¹⁻⁴ The high cost of the latter polysaccharide obtained by fractionation of corn or potato starch, however, eliminates it as a raw material for nonedible packaging film. Recent commercial availability of the more economical high-amylose corn starch of 71% apparent amylose content⁵ with promise of future reduced cost suggested an exploratory investigation of this product for the preparation of nonsupported films. In attempts to coagulate this starch in alkaline solution by acidification, we obtained only extremely tender, wet films which fragmented on further treatment.

A possible way to improve the wet strength of high-amylose corn starch films for additional processing is to add various proportions of viscose to the alkali-starch solution prior to coagulation. Satisfactory films obtained from mixtures of viscose and alkali high-amylose corn starch would be expected to have potential for packaging after appropriate coating to obtain water resistance. Furthermore, production of such films, particularly those containing high starch-to-cellulose ratios, would require much less carbon disulfide than that used in regular cellophane manufacture with consequent reduction of costly xanthation facilities. This note describes the preparation and some of the properties of films containing 3% and 65% of high-amylose corn starch in admixture with regenerated cellulose.

EXPERIMENTAL

The high-amylose corn starch of apparent 71% amylose content used was commercial Amylon-7 obtained from National Starch and Chemical Corporation, Plainfield, N. J. The product had an intrinsic viscosity of 1.09 in 1*N* potassium hydroxide⁶ from which \bar{M}_w was calculated to be 379,000 according to the viscometric relation of Cowie:⁷

$$[\eta] = 1.18 \times 10^{-5} (\bar{M}_w)^{0.89}.$$

This value is in good agreement with a reported molecular weight of 334,000 determined by light scattering.⁸

The cellulose used for viscose preparation was Cellunier Q produced by Rayonier Canada Limited, Port Alice, B. C.

Alkali High-Amylose Corn Starch. With continuous agitation 35 g of high-amylose corn starch containing 10.9% moisture was sifted into 120 ml of water and after 30 min, 24.5 ml of 5*N* sodium hydroxide solution was added. The straw-colored solution contained 17.02 wt-% of starch (dry basis) and 2.68 wt-% alkali.

Viscose. Twenty-six grams of air-dried cellulose (moisture 5.3%) was steeped in 825 ml of 18 wt-% sodium hydroxide at room temperature. After 1.5 hr the cellulose was cut into 0.5-in. square pieces, steeped 2.5 hr more, then pulped in a blender, and returned to the steeping tray for another hour. The pulp was next filtered under vacuum on a Buchner funnel and pressed with a rubber dam until the weight of the residual alkali cellulose was three to four times the weight of the original air-dry cellulose. The pressed mat was shredded manually and aged overnight at room temperature in a closed 1-l, three-necked, round-bottomed flask equipped with a mechanical stirrer. Carbon disulfide (13 g) was then added dropwise to the alkali cellulose in 5 min with stirring and cooling in an ice bath. Within 30 min the mass turned a deep orange color

and xanthation was continued for 2 hr at room temperature. The closed system was cooled in an ice bath and placed under vacuum for 10 min to remove carbon disulfide vapors. Next 160 ml of 1*N* sodium hydroxide solution was added dropwise to the xanthated mass in 35 min and the cold mixture stirred continuously for 4 hr. The resulting solution containing 9.25 wt-% of cellulose (dry basis) was stored at 5°–10°C from 3 to 5 days for ripening.

Films. Films were prepared from homogeneous mixtures of ripened viscose and alkali high-amylose corn starch in weight ratios of cellulose to starch of approximately 1.6:1 and 0.5:1. The mixtures were composed of 150 g of viscose and 50 g of alkali starch solution and 112 g of viscose and 112 g of alkali starch solution, respectively, which were deaerated under vacuum for 3 to 4 hr, cast on stainless-steel plates, and drawn with a 6-in. casting blade having 0.030-in. clearance for coagulation to film. The gel coatings on the plates were coagulated for 5 to 10 min in a bath at 50°C, and during regeneration in a second bath, films were stripped from the plates for further treatment. The composition of the baths and the processing sequence of the coatings are shown in Table I.

The wet films were air dried at room temperature and then equilibrated at 50% relative humidity and 25°C for 5 days before testing.

TABLE I
Processing Sequence of Coatings

Procedure step	Composition of solutions	Solution temp, °C
Coagulating	20% Na ₂ SO ₄ + 1% ZnSO ₄ + 2.5% H ₂ SO ₄	50
Regenerating	12% H ₂ SO ₄	50
Washing	tap water	50
Desulfuring	10% Na ₂ S	50
Washing	tap water	50
Bleaching	2.5% NaClO	25
Washing	distilled water	25

TABLE II
Properties of Films^a from Mixtures of Viscose and Alkali High-Amylose Corn Starch

High-amylose corn starch content of film, %	Tensile strength, psi		Mullen burst, psi	MIT fold 1.0 kg load	Elongation, %
	Dry	Wet ^b			
65	9,079	1,022	45	1,992	6
38	10,482	2,603	72	3,467	7
0 (100% viscose)	11,236	4,253	49	1,128	11
0 (cellophane) ^c	13,000 (MD)		41	2,740 ^d	14
	7,800 (TD)		—	10,080 ^d	13

^a Slightly hazy, unplasticized films 1–2 mils thick.

^b Dry substance of the wet films was about 40%.

^c Unplasticized and uncoated commercial product. Data from manufacturer.

^d At 45% relative humidity.

RESULTS AND DISCUSSION

Alkali high-amylose corn starch solutions were compatible with viscose at the concentrations used. Gel coatings on the stainless-steel plates were easily processed in

baths that simulated those utilized in cellophane manufacture except for a coating that contained a cellulose-to-starch ratio of 0.2:1 which rapidly disintegrated during regeneration.

As shown in Table II, the dry strength and fold properties of films from the mixtures compared favorably with those of films from commercial cellophane production and from laboratory-prepared viscose. Wet strength of the films was not determined immediately after coagulation or regeneration. However, values obtained after soaking $1/4$ -in. strips of air-dried films in water at room temperature for 5 min showed that wet strength was inversely proportional to the high-amylose corn starch content of the films. No detectable transmission of oxygen was observed during 24 hr at 25°C and 50% relative humidity⁹ with films from the mixtures and with the film prepared from viscose alone.

The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

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