Aging Properties of Extruded High-Amylose Starch¹,*

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The structural and mechanical properties of extruded high-amylose and normal cornstarch were studied as a function of time and humidity to determine the suitability of high-amylose cornstarch for use in biodegradable plastic materials. After extrusion at 170°C and 20–30% moisture, high-amylose starch was mostly amorphous, with small amounts of V- and A-type crystal structures. Tensile strengths for the extruded high-amylose starch ribbons were rather stable with time (65, 50, and 35 MPa at 20, 50, and 80% RH) and were higher than those for normal cornstarch (25, 40, and 15 MPa after 84 days at 20, 50, and 80% RH). Elongations at break declined gradually with time for high-amylose starch (6, 11, and 11% after 84 days at 20, 50, and 80% RH), while rapid declines were seen for normal cornstarch at higher humidities (3, 9, and 3% after 84 days at 20, 50, and 80% RH). Differential scanning calorimetry revealed that normal cornstarch aged at a high humidity had much larger sub-Tg endotherms than high-amylose cornstarch. These endotherms reflect decreases in enthalpy and free volume which occur in amorphous polymers due to structural relaxation. It appears, therefore, that plastic materials prepared from gelatinized or melted high-amylose cornstarch should have greater strength and flexibility and slower physical aging than those prepared from gelatinized normal cornstarch.

KEY WORDS: Starch; high amylose; amylomaize; films; mechanical properties.

INTRODUCTION

There has been much recent interest in the use of gelatinized or melted starch for biodegradable, single-use items such as utensils, plates, garbage bags, planting pots, and agricultural mulch film [1-4]. One problem associated with expanded utilization of starch for these applications is the brittleness of gelatinized starch because of the rigidity of the highly hydrogen-bonded starch chains [5]. Britleness is further increased by loss of water at low humidities and by structural relaxation which occurs with time (physical aging) [6].

Normal cornstarch is a mixture of approximately 28% amylose, a linear polymer of α-1,4-linked glucose units ($M_n = 160,000$), and 72% amylopectin, a highly branched, high molecular weight ($\sim 10^6$) polymer of short α-1,4 chains (average molecular weight about 3500) linked by α-1,6 bonds [7, 8]. Cornstarch which contains a high (50-70%) apparent amylose content as determined by iodine binding is termed high-amylose starch. It is biosynthesized by a different genetic variety of corn in which certain branching enzymes are deficient [9]. High-amylose starches are very polydisperse in both molecular weight and branching frequency [8, 10-13]. Although the structure has not been completely determined, it is thought that high-amylose starches are composed of some (10–20%) linear, low molecular weight ($\sim 30,000$) amylose, a high proportion ($\sim 50$%) of “intermediate” or branched amylose having perhaps an average of six 30,000 molecular weight amylose chains.
per molecule and the remainder low molecular weight amylopectin-type molecules [8]. The amylose component of high-amylose starch has an $M_n$ of 112,000 [8]. Intrinsic viscosities of whole normal and high-amylose starch in dimethyl sulfoxide are 173 and 100 ml/g, respectively [13].

Previous studies [14-16] have shown that films cast from solutions of amylose are more flexible than films prepared for amylomaize or normal (28% amylose) cornstarch. For example, Wolff et al. [16] found ultimate elongations of 13% for corn amylose films at 50% relative humidity (RH) and 6% for normal cornstarch films. The linear amylose molecules should form more effective chain entanglements and thus have better mechanical properties than the highly branched amylopectin. Some work has also been reported showing a decrease in elongation of cast amylose films with time [15]. Cast amylose films have not been manufactured commercially, possibly because cast films are expensive to prepare.

There have been many studies on the preparation of melted or gelatinized starch by extrusion at low moisture (10–30%) and high (120–200°C) temperatures [17-26]. The crystallinity present in the amylopectin component of native starch granules is destroyed during extrusion, giving a mostly amorphous starch extrudate. Few studies of the melting or extrusion of high-amylose starch under similar conditions have been reported [27]. Recent patents describe the extrusion of high-amylose starch into expanded foam products, which are more compressible and resilient than those prepared from normal cornstarch [28-31]. Extrusion-blown films have also been prepared from high-amylose cornstarch [32]. Little is known, however, about relationships between extrusion conditions and high-amylose starch structure or whether there is any difference in the physical aging behavior of extruded high-amylose and normal cornstarch.

In this paper we have characterized the melting behavior of high (70%) amylose cornstarch at moisture contents of 12-50% using differential scanning calorimetry (DSC). The structure of high-amylose cornstarch after extrusion at 20 and 30% moisture was assessed using X-ray diffraction and DSC. The relative rates of physical aging of normal and high-amylose cornstarch were determined at different humidities.

**MATERIALS AND METHODS**

**Materials**

High (70%)-amylose cornstarch was amylomaize VII from American Maize-Products, Hammond, IN, and normal cornstarch was Buffalo 3401 from CPC International Inc., Argo, IL. These starches contained 13 and 11% moisture, respectively. Corn amylose was prepared by the method of Schoch [33]. Briefly, hot aqueous starch solutions were treated with butanol and the amylose-butanol complex precipitated on cooling. The complex was then redissolved in hot water, reprecipitated with butanol, washed with methanol, and dried.

**Extrusion of Starch Ribbons**

Prior to extrusion, samples of amylomaize and normal cornstarch were adjusted to 20 and 30% moisture and pH 6.8 by spraying the starch with dilute solutions of NaOH in distilled water using a plant mister. The amount of NaOH required (0.040 or 0.026 g NaOH/100 g amylomaize or normal cornstarch, respectively) was determined by titrating a 20% aqueous suspension of each starch with 1 M NaOH.

Moist starches were extruded using a Brabender PL2000 single-screw extruder equipped with a three-zone, $\frac{1}{4}$-in.-diameter, 30/1 barrel and a 1 × 0.02-in. die. Barrel temperatures were 150 (closest to feed zone), 170, 170, and 120 or 140°C at the die. The lower die temperature was used for starches having 30% moisture, while the higher temperature was used for the 20% moisture starches. The special high-shear, barrier-type screw used was based on an analysis of mixing sections by Rauwendaal [34, 35]. It has a fluted, 45°-angle dispersive mixing section at 13 screw diameters from the feed section. The screw mixing section is based on patents of LeRoy [36] and Gregory and Street [37]. Polymer has to flow over a barrier flight (0.18-in. width; barrel clearance, 0.020 in.) between the two inlet channels and two outlet channels. Channels have a depth of 0.125 in. and a width of 0.213 in. There is also a distributive mixing section at the die end of the screw in which the last four flights contain $\frac{1}{4}$-in. slots, two per revolution, at 45° relative to the screw axis. The screw speed was 20 rpm. Ribbons were gently pulled taut by hand on exiting the die.

After extrusion, 3 × $\frac{1}{4}$-in. tensile test strips were cut using a twin blade cutter (Testing Machines, Inc., Amityville, NY) and placed in a room controlled to 23°C and 50% RH and in desiccators containing saturated potassium acetate and ammonium chloride to give 20 and 80% RH, respectively.

**Tensile Testing**

Tensile tests of starch ribbons aged 7, 28, 84, and 170 days at 20, 50, and 80% RH were conducted using a Model 4201 Instron Universal Testing Machine. Testing was done at 50% RH so samples were removed from