Biomacromolecules **2007,** *8,* 3641−3645

Effect of Orientation on the Physical Properties of Potato Amylose and High-Amylose Corn Starch Films

Randal Shogren[†]

National Center for Agricultural Utilization Research, USDA/ARS, 1815 North University Street, Peoria, Illinois 61604

Received July 24, 2007; Revised Manuscript Received August 27, 2007

The effect of orientation on the properties of amylose and starch films was studied in order to determine if film strength, flexibility, and water resistance could be improved. Potato amylose and high (70%) amylose corn starch were peracetylated, cast into films, stretched in hot glycerol 1−6 times the original length, and deacetylated. Molecular orientation of potato amylose films was much higher than for high-amylose corn starch films as determined by optical birefringence. For potato amylose films, orientation resulted in large increases in tensile strength and elongation but little change in modulus. For high-amylose corn starch films, tensile strength and modulus did not change with draw ratio but elongation to break increased from about 8% to 27% as draw ratio increased from 1 to 5. Scanning electron micrographs revealed many small crazes in the drawn starch films, suggesting that the improved film toughness was due to energy dissipation during deformation of the crazes. Annealing of drawn films at 100% humidity resulted in partial crystallization and improved wet strength.

Introduction

There has been much interest in starch-based materials since starch is made from a renewable agricultural feedstock, is inexpensive, and is biodegradable.[1−9] Cushioning foams and pharmaceutical capsules made from thermoplastic starch are commercial successes that resulted from this research. Starch films are, however, rather brittle and water sensitive,[10] and this limits their usefulness for many applications. A flexible, semi-water-resistant starch film or fiber could have applications in numerous areas such as consumer packaging, personal hygiene articles, paper, etc.

Orientation is known to result in improvement in strength and flexibility of many types of polymer films and fibers.[11] In particular, Mark and co-workers[12,13] showed that orientation of lightly cross-linked, highly substituted amylose and high-amylose corn starch ethers often gave much higher tensile strengths and elongations to break. Amylose triacetate fibers also showed increases in strength after drawing.[14]

There have been several studies over the past 50 years devoted to the preparation of oriented amylose and whole starch fibers and films. Methods were developed in the 1940s and 1960s to prepare highly crystalline, oriented amylose fibers in order to determine the native crystal structures of starch. These methods included (1) acetylation, drawing in hot glycerol, then deacetylation[15] and (2) casting films from dimethyl sulfoxide (DMSO), drying, and stretching under carefully controlled conditions.[16] There have been, however, no reports of the physical and mechanical properties of oriented amylose or whole starch films prepared by these methods. The spinning of fibers from amylose and high-amylose corn starch in NaOH solution has been reported in the patent literature,[17−19] but no characterization of fiber structure or degree of orientation was reported. Extrusion of fibers composed of high-amylose and normal cornstarch plasticized with water and other additives have also been described in older and recent patents.[20−23] Again, there was no effort to characterize starch structure or orientation, and wet strength of the fibers was very low unless a large amount of cross-linking agent was added. Recently, high-amylose corn starch melts were extruded at different speeds into films and mechanical properties were measured in the machine and transverse direction.[24] Tensile strengths and elastic moduli were somewhat higher for the machine direction suggesting some orientation, but there was no independent measurement of extent of orientation. In summary, there is little published literature on the effect of orientation on the mechanical properties and water resistance of starch films or fibers.

In this work, we have studied the effects of orientation and subsequent crystallization on the mechanical properties of potato amylose and high-amylose corn starch films prepared by the acetylation, stretching, and deacetylation method. Orientation and morphology of the films were also assessed by optical birefringence and scanning electron microscopy.

Experimental Section

Materials. Potato starch was purchased from Avebe (Veendam, Netherlands). Potato amylose was purified by the method of Schock.[25] Potato amylose purity was 100% using the assay of Knutson,[26] and its intrinsic viscosity was 220 mL/g in 1 M KOH. High (70%) amylose corn starch was Hylon 7 from National Starch and Chemical (Bridgewater, NJ). Acetic anhydride (Aldrich, 99+%), dichloromethane (Aldrich, 99.6%), potassium hydroxide, and ethanol were ACS grade reagents.

Preparation of Oriented Films. Amylose triacetate and high-amylose starch triacetate were prepared using the method of Mark and Mehltretter.[27] Degree of substitution was determined to be 2.97 using the ^{1}H NMR method of Shogren.[28] The orientation procedure was adapted from Senti and Witnauer[29] as modified by Wolff[14] and is summarized below. Potato amylose acetate or high-amylose corn starch acetate, 1 g, was dissolved in 10 g of dichloromethane or 12 g of chloroform by magnetic stirring for 2 h. This solution was then cast onto glass plates covered with Teflon (Bytac, Saint-Gobain Performance Plastics, Wayne, NJ) using a 0.025 in. doctor blade and dried in a vacuum oven for 1 day at 40 °C. Films were cut into 2 × 0.5 in. strips

---

[†] Phone: 309-681-6354. Fax: 309-681-6691. E-mail: Randy.Shogren@ars.usda.gov.

10.1021/bm7008153

Table 1. Birefringence and Tensile Properties of Oriented Potato Amylose Films

draw ratio	annealing	test condition	birefringence	tensile strength (MPa)	elongation at break (%)	modulus (GPa)	toughness (MJ/m^3)
1	n	50% RH	0	59 ± 7	11 ± 1	2.8 ± 0.3	3.5 ± 0.8
6	n	50% RH	0.037 ± 0.004	101 ± 15	32 ± 7	2.3 ± 0.4	22 ± 7
1	y	50% RH	0	67 ± 7	6.1 ± 1.1	3.5 ± 0.3	2.0 ± 0.4
1	y	wet[a]		0.4 ± 0.2	14 ± 4	0.04 ± 0.01	0.0
6	y	50% RH	0.031 ± 0.004				
6	y	wet[a]		7.0 ± 0.9	31 ± 3	0.06 ± 0.02	1.1 ± 0.1

[a] Tensile properties measured after soaking in water for 30 min.

and manually stretched (with pliers) from 1 to 6 times initial length during immersion in a 171 °C glycerol bath. Deacetylation was performed in 0.25 M KOH in ethanol for 2 days at room temperature under nitrogen followed by washing with ethanol, neutralization with 0.025 M acetic acid in ethanol, and further washing with ethanol. Prior to deacetylation, films were clamped on a polypropylene sheet to avoid sample retraction and some loss of orientation.[27] For high-amylose corn starch acetates, films were deacetylated in a sealed beaker (not clamped) since these films broke if clamped. Films were dried a vacuum oven at 40 °C, then placed in 23 °C, 50% relative humidity (RH) room for 7 days prior to mechanical testing.

To induce crystallization, film samples were clamped onto a polypropylene sheet (to avoid sample contraction) and annealed for 3 days at 80% RH, 3 days at 100% RH, and 1 h in 90 °C water (2 h at 80 °C, 100% RH for high-amylose corn starch) following the prior procedure of Wu and Sarko.[30]

Tensile Testing. Testing was carried out with an Instron universal testing machine, model 4201, inside a room controlled to 23 ± 2 °C, 50% ± 4% RH Samples were cut into one-eighth in. wide strips, then tested according to ASTM D882-91 using a gage length of 1 in. and crosshead speed of 25 mm/min. Five to eight specimens were tested for each sample.

Birefringence Measurement. Oriented films were examined using an Olympus CX31-P polarized light microscope (Olympus America Inc., Melville, NY). Retardation (R) was measured using a Berek compensator (Olympus U-CBE), and birefringence was calculated as $B = R/d$ where d is the thickness of the sample in nm.

Scanning Electron Microscopy. Films were mounted onto aluminum stubs with graphite-filled tape, sputter coated with Au−Pd, and examined with a JEOL 6400 V scanning electron microscope.

X-ray Powder Diffraction. Samples were pulverized for 15 s in stainless steel vials cooled with liquid nitrogen using a Wig-l-bug amalgamator. X-ray diffraction was carried out using a Philips PW1820/1830 gonoiometer/generator (PANalytical, Bollingbrook, IL) and Cu Kα radiation. Samples were scanned from 3° to 30° 2θ in 0.05° steps at 8 s per step. Degree of crystallinity was calculated as the ratio of areas under the crystalline peaks divided by the total area (as measured by cutting and weighing).

Results and Discussion

Values of birefringence and mechanical properties for as-cast (not drawn) and drawn (6×) potato amylose films are shown in Table 1. There is no birefringence for the as-cast film since it is isotropic. Birefringence for the drawn film was 0.037. Birefringence represents the difference in refractive indices between the long and transverse directions of the film. Refractive index is related to the vector sum of bond polarizabilites by the Lorenz−Lorentz equation.[31] Since polarizabilities of bonds are different along the axis of the bond and perpendicular to it,[31] increasing birefringence of a polymer chain normally indicates increasing orientation of the chains in the direction of draw. Since previous X-ray diffraction work has shown that the method of drawing used here results in highly oriented samples,[29,30] it can be presumed that the birefringence value of 0.037 is indicative of a highly oriented amylose chain. Previous work has also indicated that amylose so treated (deacetylated in absolute alcohol) is in an amorphous state.[29]

This determination of birefringence for a highly oriented potato amylose (intrinsic birefringence) is significant because it allows the estimation of extent of orientation of starch after different processing conditions simply by measuring birefringence and comparing to the value above. The only previous report of birefringence for amylose or starch film/fibers was a recent study of amylose fibers made by solution spinning from basic solution followed by coagulation in aqueous HCl and methanolic HCl.[32] The maximum birefringence measured in this study was 0.012, suggesting incomplete orientation.

Upon orientation, tensile strength and elongation at break for potato amylose films increased by factors of about 2 and 3, respectively (Table 1). Toughness, or the area under the stress−strain curve, increased about 7-fold. Modulus, however, did not change significantly with orientation. This type of behavior is typical for oriented hard polymers such as polystyrene.[33] Yamane[32] found similar values of tensile strength (80−100 MPa) for partially oriented amylose fibers, whereas elongation at break (30−60%) and modulus (3.4−3.9 GPa) were somewhat higher than for the data in Table 1. This difference could be due in part to the fact that Yamane[32] used enzymatically synthesized amylose which is completely linear, whereas the potato amylose used in this study typically has several long-chain branch points.[34] Stress−strain curves for oriented amylose films (Figure 1) showed gradually increasing stress after yield point or strain hardening which is consistent with the high degree of orientation.

Tensile properties for wet, annealed potato amylose films are also shown in Table 1. For unoriented samples, tensile strengths when wet are very low (0.4 MPa). This is expected since water interacts strongly with the hydroxyl groups of starch, causing swelling and weakening of intermolecular hydrogen bonding. After drawing and annealing, wet tensile strengths increase to 7.0 MPa. This increase in strength reflects alignment of the potato amylose chains in the direction of testing. Although a wet strength of 7 MPa is much lower than the strength in the dry state, it is probably high enough to be useful in some nonstructural applications such as hygiene or biomedical products.

Values of birefringence versus draw ratio for oriented high-amylose corn starch films are given in Figure 2. Birefringence clearly increases with draw ratio reaching values of 0.0035 at a draw ratio of 5. This suggests that the high-amylose corn starch films had rather low degrees of orientation. Part of the reason for this is probably the approximately 20% shrinkage which occurs after deacetylation. Previous studies indicated that if amylose films were not clamped during deacetylation the resulting diffraction pattern showed less ordering.[29]

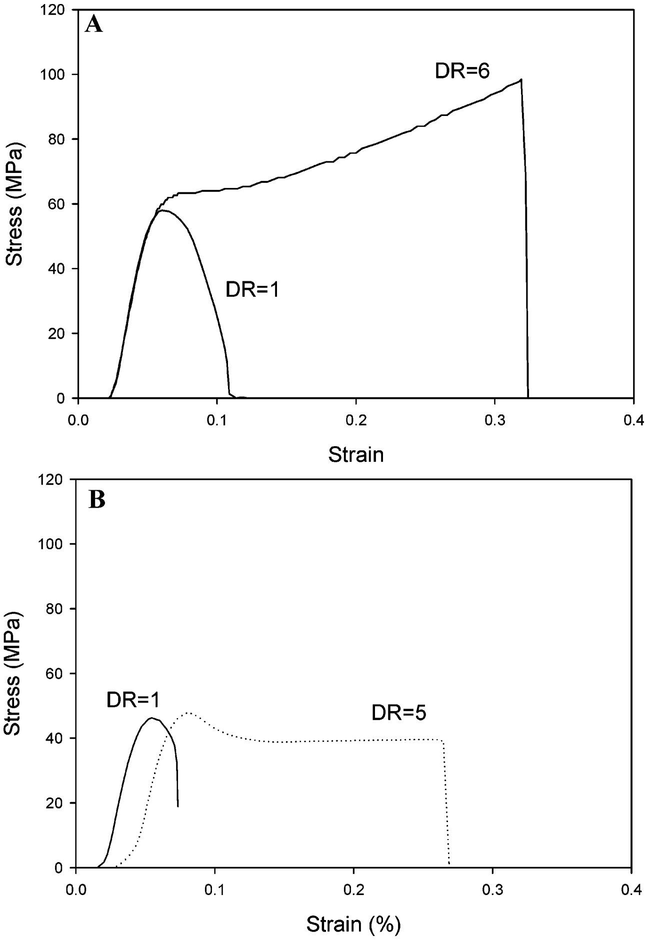

Figure 1. Typical stress−strain curves for amylose films before drawing (DR = 1) and after drawing to 6 times initial length (DR = 6) (A) and for high-amylose corn starch films before drawing (DR = 1) and after drawing to 5 times initial length (DR = 5) (B). Samples were not annealed.

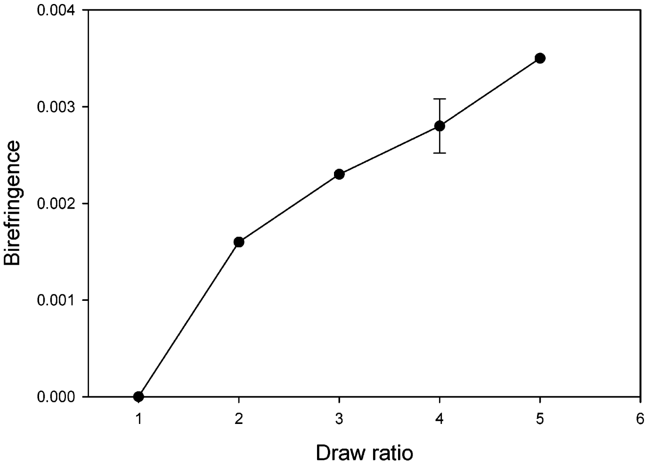

Figure 2. Effect of draw ratio on the birefringence of high-amylose corn starch films.

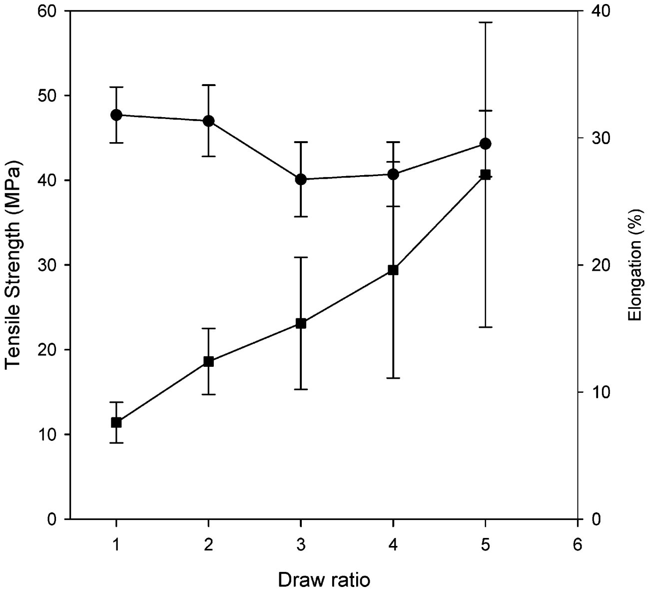

Figure 3. Effect of draw ratio on the mechanical properties of high-amylose corn starch films. Tensile strength is represented by closed circles, while elongation at break is represented by closed squares.

Another reason for the difference in orientation could be due the difference in molecular weights or branching of the potato amylose and high-amylose corn starch. The molecular weight of the potato amylose was 8.3×10^5 as calculated from the intrinsic viscosity and the Mark−Houwink equation from Cowie.[35] Potato amylose has been reported to have an average of 8−10 long-chain branches per molecule, whereas corn amylose has an average of 3 long-chain branches.[34,36] Molecular weights of the amylose and amylopectin components of high-amylose corn starch have been determined to be $1.5{-}2.8 \times 10^5$ and 1.7×10^8, respectively.[36,37] High-amylose corn starch has significant amounts (30%) of highly branched amylopectin, which would be less able to chain entangle or to crystalline while hot drawing in glycerol. With fewer of these physical cross-links, the high-amylose starch acetate may have undergone primarily viscous flow rather than orientation. Indeed, potato amylose acetate films necked down to a fairly uniform width during drawing in hot glycerol, whereas high-amylose starch acetate films had a gradual decrease in width.

Tensile strengths and elongations at break for oriented high-amylose corn starch films are shown in Figure 3. Values of tensile strength were 45 ± 5 MPa and did not change significantly with draw ratio. Similar values of tensile strength have been measured for cast and extruded high-amylose corn starch at 50% RH,[38] suggesting that the process of acetylation, casting, and deacetylation did not alter the structure and properties of the undrawn film. Elastic moduli were similar for undrawn and drawn films (1.8−2.2 GPa). Elongation to break, however, increased significantly with draw ratio, reaching 27% at a draw ratio of 5 compared to 8% for the undrawn film. Variability of elongations also increased significantly with draw ratio. This was probably due to the formation of defects such as small cracks in the drawn film. Variability in the thickness of the films also increased with draw ratio, and this would also contribute to variation in measured elongations.

Scanning electron micrographs of high-amylose corn starch films before and after drawing are shown in Figure 4. Before drawing the film surface appears to be rather homogeneous. After drawing, however, the film appears to be composed of spherical nodules about 100−400 nm in size with cracks or space between many of these. In some areas, there appears to be material connecting the spheres together. The origin of this nanostructure is not known, but it could be due to residual "blocklet" structures[39] from the starch granules. Alternatively, this could be due to swelling of the starch triacetate by hot glycerol accompanied by stress-induced void formation followed by phase separation on cooling. Similar scanning electron micrographs were observed for drawn starch triacetate films

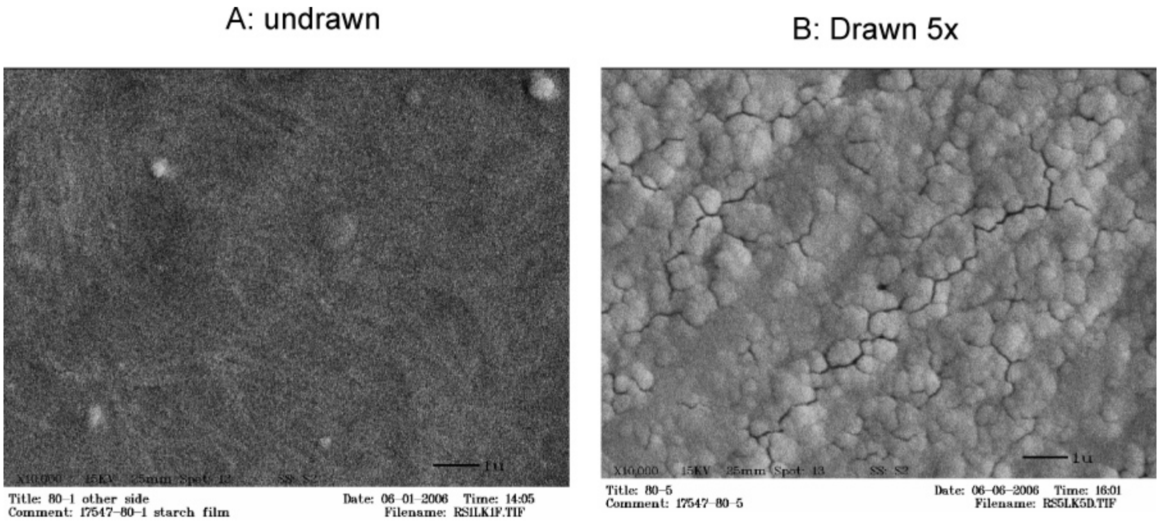

Figure 4. Scanning electron micrographs of high-amylose corn starch films: (A) not drawn, (B) draw ratio = 5. Draw direction in B is upper right to lower left.

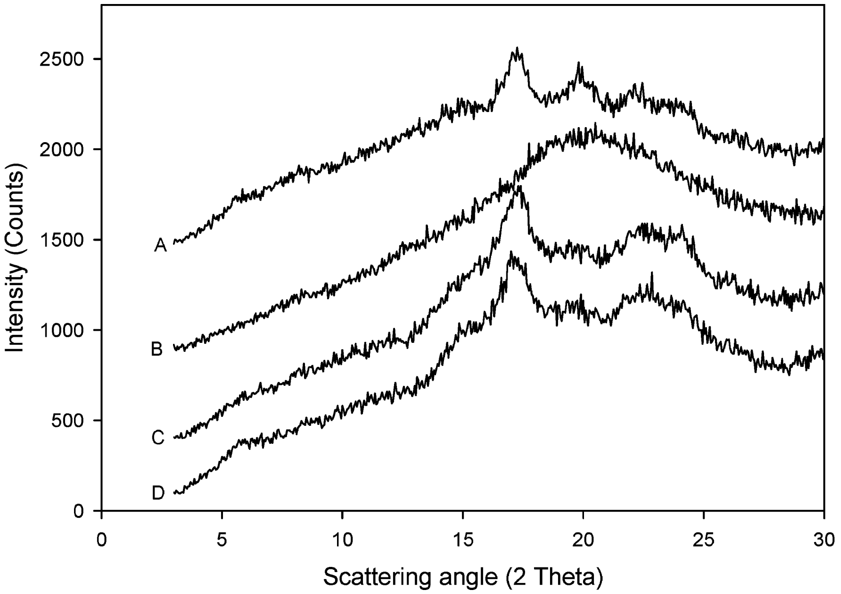

Figure 5. X-ray powder diffraction of high-amylose corn starch: native granular (A), as-cast, undrawn film (B), annealed undrawn film (C), and annealed, drawn film (D).

Table 2. Tensile Properties of High-Amylose Corn Starch Films

draw ratio	annealing	test condition	tensile strength (MPa)	elongation at break (%)	modulus (GPa)	toughness (MJ/m^3)
1	n	50% RH	47 ± 4	7.6 ± 1.6	2.2 ± 0.3	1.9 ± 0.8
5	n	50% RH	44 ± 4	27 ± 12	1.9 ± 0.3	8.9 ± 5.3
1	y	50% RH	41 ± 12	7 ± 4	2.4 ± 0.5	1.0 ± 0.5
1	y	wet[a]	0.6 ± 0.2	18 ± 8	0.014 ± 0.008	0.03 ± 0.03
5	y	50% RH	40 ± 9	9 ± 2	1.9 ± 0.4	2.7 ± 1.5
5	y	wet[a]	1.5 ± 0.2	20 ± 8	0.044 ± 0.020	0.12 ± 0.05

[a] Tensile properties measured after soaking in water for 30 min.

(before deacetylation, results not shown), suggesting that deacetylation was not the cause of the spherical morphology seen.

The mechanical behavior and morphology observed for oriented high-amylose corn starch films resembles that of “hard elastic” polymer films that have been profusely crazed by drawing.[40] Such polymers show relatively small changes in tensile strength or modulus with drawing but show large increases in elongation. The increased energy of deformation is thought to be due to formation of new lamellar surfaces on drawing as well as stretching of interlamellar filaments.[40]

Annealing of high-amylose corn starch films was carried out to determine if wet strength could be improved by crystallization. Oriented films shrunk back to their original dimensions after exposure to 100% humidity, so films were clamped on a polypropylene rack. X-ray powder diffraction scans of annealed samples are compared to samples with no annealing and native high-amylose corn starch in Figure 5. Films with no annealing are amorphous in structure, in agreement with previous work.[15,29] After annealing, the B-type crystal structure is apparent, similar to that found in native high-amylose corn starch. The degree of crystallinity was approximately 24% for both drawn and undrawn samples.

Wet and dry tensile strengths of annealed high-amylose corn starch films are shown in Table 2. The wet strength of the oriented film (1.5 MPa) was significantly larger than for the unoriented film (0.6 MPa), suggesting that orientation increases wet strength. Wet strength would, however, probably need to be increased further for such films to fill practical applications in which exposure to water is involved.

Conclusions

Highly oriented potato amylose films were prepared by an established technique (stretching of potato amylose acetate followed by deacetylation), and birefringence values for these films were measured. Such estimates for intrinsic birefringence of potato amylose should be useful in the future to assess degree of orientation for starch fibers and films prepared by other methods. Tensile strength and elongation at break both increased significantly with orientation for potato amylose films. Wet strength of annealed films also improved greatly with orientation and attained values that may be useful in practical applications. Of course, to prepare oriented amylose films or fibers on a large scale a different method of orientation such as dry or wet spinning would be needed. High-amylose corn starch films were oriented to a much lesser degree than pure potato amylose. Even so, elongation at break for high-amylose corn starch films increased substantially with orientation indicating that this is a useful method for improving the brittleness of starch films. Wet strength for annealed high-amylose corn starch increased somewhat with orientation but probably not enough for most applications. An improved, practical method for increasing the degree of orientation of high-amylose corn starch films and fibers is needed. Although the high cost of pure amylose may not be an impediment for some high-value applications such as medical products, lower cost high-amylose corn or potato starches would probably need to be used for most consumer applications.

Acknowledgment. Product names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

References and Notes

(1) Davis, G.; Song, J. H. *Ind. Crops Prod.* **2006**, *23*, 147−161.
(2) Gross, R. A.; Kalra, B. *Science* **2002**, *297*, 803−807.
(3) Bastioli, C. *Macromol. Symp.* **1998**, *135*, 193−204.
(4) Petersen, K.; Nielsen, P. V.; Bertelsen, G.; Lawther, M.; Olsen, M. B.; Nilsson, N. H.; Mortensen, G. *Trends Food Sci. Technol.* **1999**, *10*, 52−68.
(5) Swanson, C. L.; Shogren, R. L.; Fanta, G. F., Imam, S. H. *J. Environ. Polym. Degrad.* **1993**, *1*, 155−166.
(6) Belard, L.; Dole, P.; Averous, L. *Aust. J. Chem.* **2005**, *58*, 457−460.
(7) Kalambur, S.; Rizvi, S. S. H. *J. Plast. Film Sheeting* **2006**, *22*, 39−58.
(8) Stepto, R. F. T. *NATO Sci. Ser., II* **2004**, *175*, 219−240.
(9) Nabar, Y. U.; Draybuck, D.; Narayan, R. J. *J. Appl. Polym. Sci.* **2006**, *102*, 58−68.
(10) Shogren, R. *Carbohydr. Polym.* **1992**, *19*, 83−90.
(11) Seitz, J. T. Orientation and Physical Properties. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; John Wiley & Sons: New York, 1986; Vol. 16, pp 154−161.
(12) Zhao, W.; Kloczhowski, A.; Mark, J. E. *Chem. Mater.* **1998**, *10*, 794−803.
(13) Zhao, W.; Kloczhowski, A.; Mark, J. E. *Chem. Mater.* **1998**, *11*, 804−811.
(14) Wolff, I. A. J. *Ind. Eng. Chem.* **1958**, *50*, 1552.
(15) Senti, F. R.; Witnauer, L. P. *J. Am. Chem. Soc.* **1946**, *68*, 2407−2408.
(16) Zobel, H. F.; French, A. D.; Hinkle, M. E. *Biopolymers* **1967**, *5*, 837−845.
(17) Hiemstra, P.; Muetgeert, J. (Avebe) U.S. Patent 2,902,336, 1959.
(18) Hart, J. R.; Juergens, S. G.; McCormack, W. E. (Champion International Corporation) U.S. Patent 4,340,442, 1982.
(19) Eagles, D.; Lesnoy, D.; Barlow, S. *Text. Res. J.* **1996**, *66*, 277−282.
(20) Barlow, J. W.; Mumma, C. E. (Nebraska Department of Agriculture) U.S. Patent 3,499,074, 1970.
(21) Bridgeford, D. J. (Teepak, Inc.) U.S. Patent 4,226,264, 1980.
(22) Bailey, V. A.; Mackey, L. N.; Trokhan, P. D. (Proctor & Gamble Co.) U.S. Patent 6,709,526, 2004.
(23) Mackey, L. N.; Gordon, G. C.; Buchanan, L.; Heinzman, S. W.; Forshey, P. A. (Proctor & Gamble Co.) U.S. Patent 6,723,160, 2004.
(24) Yu, L.; Christie, G. *J. Mater. Sci.* **2005**, *40*, 111−116.
(25) Schoch, T. J. *Adv. Carbohyd. Chem.* **1945**, *1*, 247−277.
(26) Knutson, C. A. *Cereal Chem.* **1986**, *63*, 89−92.
(27) Mark, A. M.; Mehltretter, C. L. *Staerke* **1972**, *24*, 73−76.
(28) Shogren, R. L. *Carbohydr. Polym.* **2003**, *52*, 319−326.
(29) Senti, F. R.; Witnauer, L. P. *J. Am. Chem. Soc.* **1948**, *70*, 1438−1444.
(30) Wu, H. H.; Sarko, A. *Carbohyd. Res.* **1978**, *61*, 7−25.
(31) Bunn, C. W. *Chemical Crystallography. An Introduction to Optical and X-ray Methods;* Clarendon Press: Oxford, 1961; Chapter 8.
(32) Yamane, H. *Sen'i Gakkaishi* **2006**, *62*, P359−P365.
(33) Matsumoto, K.; Fellers, J. F.; White, J. L. *J. Appl. Polym. Sci.* **1981**, *26*, 85−96.
(34) Takeda, Y.; Hizukuri, S.; Takeda, C.; Suzuki, A. *Carbohyd. Res.* **1987**, *165*, 139−145.
(35) Cowie, J. M. G. *Macromol. Chem.* **1961**, *42*, 230−247.
(36) Takeda, C.; Takeda, Y.; Hizukuri, S. *Cereal Chem.* **1989**, *66*, 22−25.
(37) Yoo, S.; Jane, J. *Carbohyd. Polym.* **2002**, *49*, 307−314.
(38) Shogren, R. L.; Jasberg, B. K. *J. Environ. Polym. Degrad.* **1994**, *2*, 99−109.
(39) Gallant, D. J.; Bouchet, B.; Baldwin, P. M. *Carbohyd. Polym.* **1997**, *32*, 177−191.
(40) Clark, E. S. Hard-Elastic Behavior. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; John Wiley & Sons: New York, 1986; Vol. 5, pp 408−415.

BM7008153