

Poly(vinyl alcohol) composite films with high percent elongation prepared from amylose-fatty ammonium salt inclusion complexes

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ABSTRACT: Amylose inclusion complexes prepared from cationic fatty ammonium salts and jet-cooked high amylose starch were combined with poly(vinyl alcohol) (PVOH) to form glycerol-plasticized films. For the octadecylammonium salt complexes, elongation was significantly higher than the PVOH control when the amount of complex incorporated was from 20% to 70%. For the dodecyl- and hexadecylammonium salt complexes, elongation was significantly higher than PVOH films for 20% to 40% incorporation of cationic complex. Tensile strength declined with increasing levels of amylose-ammonium salt complex, and surface hydrophobicity (contact angle) was significantly higher than PVOH films. Microscopy showed no phase separation or phase inversion, suggesting intimate mixing due to ionic interactions between cationic ammonium salt complexes and the hydroxyl groups of PVOH. The high elongations of these films and increased water contact angles are marketable advantages, along with the lower cost and increased biodegradability of the starch-based component. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44110.

KEYWORDS: blends; compatibilization; hydrophilic polymers; polysaccharides; properties and characterization

Received 5 April 2016; accepted 22 June 2016

DOI: 10.1002/app.44110

INTRODUCTION

Poly(vinyl alcohol) (PVOH) is a non-toxic, biodegradable, film-forming polymer that has many commercial applications, such as textile sizing agents, films with high oxygen barrier properties, paper coatings, and food packaging materials.¹ Incorporation of starch into these films would be advantageous because of the more rapid biodegradation of starch,² which would reduce the build-up of plastic waste in our landfills. Starch is also less expensive than PVOH and would provide an economic advantage despite any additional processing costs needed to obtain starch derivatives that are compatible with PVOH and do not detract from its properties. Starch has been extensively studied as a component in biodegradable plastics and films because it is inexpensive, annually renewable, and rapidly biodegradable. Since plastics and films prepared from pure starch do not have the strength, flexibility, and ease of processing required for many applications, starch has been blended with polymers such as PVOH to overcome these disadvantages.^{3,4}

The large number of publications related to starch-PVOH composites is a good indicator of the commercial interest in these composite films. Starch-PVOH films have been prepared from wheat starch,⁵ corn starch,^{6–10} and other starch varieties,^{11–15} and methods for improving the compatibility between starch and PVOH and evaluating their film properties have been reviewed.^{3,4} A common feature of these earlier investigations is the method of preparing the aqueous starch dispersions used to prepare the composite films. Although granular starch was gelatinized by heating in water at 95–100 °C, starch granules are not completely dissolved under these conditions, and swollen starch granules and granule fragments would still be present in the heated dispersions. Moreover, precipitation of amylose due to retrogradation^{16,17} would also occur when the starch dispersions were cooled during the preparation of cast films, and this could adversely affect film properties.

In the process of steam jet cooking, which is widely used by the starch and paper industries, aqueous dispersions of granular starch are pumped through a hydroheater in which the starch

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granules are instantly dissolved by heating with high temperature steam under high shear conditions.¹⁸ In the presence of water soluble, complex-forming ligands, such as fatty acid salts and the acid salts of fatty amines, helical inclusion complexes are formed in which the hydrophobic hydrocarbon chain of the fatty ligand enters the hydrophobic central cavity formed by the amylose helix.^{19,20} Complexes formed from the water soluble sodium salts of fatty acids²¹ and the HCl salts of fatty amines²² are water soluble, and the complexes can therefore be dried and then re-dissolved by heating in water. Unlike solutions of starch where the amylose component has not been complexed with a water-soluble ligand, these water soluble complexes do not retrograde and precipitate from the cooled solutions like uncomplexed amylose.

In a previous investigation,²³ we described the preparation and properties of composite films obtained by combining water solutions of PVOH with solutions of water-soluble, anionic amylose inclusion complexes prepared from jet cooked high amylose starch and the sodium salts of dodecanoic (C_{12}), hexadecanoic (C_{16}), and octadecanoic acid (C_{18}). We observed that the tensile properties and elongation of these films were far superior to films prepared in a similar manner from uncomplexed waxy corn starch. Having shown this with complexes with ligands bearing anionic head groups, for which ionic interactions between the complexed starch and PVOH are not a factor, it seemed possible that using ligands with cationic head groups would introduce the opportunity for ionic interactions with the slightly negatively charged hydroxyl groups of PVOH. This investigation was therefore carried out to determine whether further improved properties would be observed for composite films prepared in a similar manner from cationic amylose inclusion complexes prepared from the HCl salts of dodecylamine (C_{12}), hexadecylamine (C_{16}), and octadecylamine (C_{18}). The objectives of this investigation were: (1) to prepare water soluble amylose inclusion complexes from jet-cooked high amylose starch and solutions of the three fatty ammonium salts and determine the properties of these complexes, (2) to prepare films containing varying percentages of PVOH and the three amylose-ammonium salt complexes, and compare the tensile properties of the three series of cast films, and (3) to compare the properties of films prepared from the cationic ammonium salt complexes with the properties of films previously prepared²³ from anionic amylose-fatty acid salt complexes with the same carbon chain lengths.

Neither dissociation of the complexes nor hydrolysis of starch occurred during preparation of the complexes or films. Using cationic amylose-fatty ammonium salt complexes instead of the corresponding anionic amylose-fatty acid salt complexes resulted in PVOH composite films with significantly higher percent elongation (%E) and slightly lower tensile strength (TS) and Young's modulus (YM). Surface hydrophobicity (contact angle) was significantly higher than 100% PVOH but not as high as films made with the anionic complexes. These results, along with the lack of phase separation or phase inversion during drying, are consistent with ionic interactions between cationic ammonium salt complexes and the hydroxyl groups of PVOH, which significantly influence film properties.

EXPERIMENTAL

Materials

High amylose corn starch with a reported amylose content of 68% (determined by iodine binding)²⁴ was obtained from Cargill, Minneapolis, MN; dodecylamine (98%), hexadecylamine (98%), and octadecylamine (97%) from Sigma-Aldrich, St. Louis, MO; PVOH (MW 133,000, 99 mole % hydrolyzed) from Polysciences, Warrington, PA; and glycerol (Certified A.C.S.) from Fisher Scientific, Pittsburg, PA. The moisture contents of starch (9.4%) and PVOH (3.9%) were determined by weight loss after drying under vacuum for 4 h at 100 °C.

Preparation of Amylose-Fatty Ammonium Salt Complexes

The procedure used for steam jet cooking was the same as previously reported.²¹ A dispersion of 50.0 g of high amylose starch in 900 mL of water was passed through a Penick & Ford (Penford Corp., Englewood, CO) laboratory model steam jet cooker operating under excess steam conditions (hydroheater temperature 140 °C, steam back pressure 380 kPa (40 psig), steam line pressure 550 kPa (65 psig), and pumping rate 1 L/min).¹⁸

Solutions of the HCl salts of fatty amines were prepared by dispersing 2.6 g of fatty amine in 100 mL of solution with an HCl concentration equal to that required to convert the amine to its ammonium salt. This weight of fatty amine was equal to 7.5% of the weight of amylose in 50.0 g of high amylose corn starch. The acidified amine dispersions were then heated to 90 °C to obtain clear solutions. The hot solutions of fatty ammonium salts were then added to the hot starch dispersions, and the dispersions were slowly stirred for 1 min and then cooled in ice water to 25 °C. The amylose-ammonium salt complex was then isolated by freeze-drying. The amylopectin component of high amylose corn starch was not separated from the amylose complexes, since removal of amylopectin would not be practical in a commercial process.

Water solubility of the freeze-dried amylose-ammonium salt complexes was determined by heating dispersions of 2 g of complex in 98 mL of water to 80 °C followed by cooling in ice water to 25 °C. The cooled dispersions were centrifuged for 1 h at 10,000 rpm (15,317 g) in a Sorvall Legend centrifuge equipped with a Fiber-lite F14-6X250 rotor (Thermo Fisher Scientific, Hanover Park, IL). Pellets were washed with 50 mL of fresh water and centrifuged again. The percentages of water insoluble materials based on the weights of freeze-dried settled solids were 8.0%, 1.1%, and 0.5% for the complexes prepared from the HCl salts of dodecylamine (C_{12}), hexadecylamine (C_{16}), and octadecylamine (C_{18}), respectively.

Preparation of Films from Mixtures of PVOH And Amylose-Fatty Ammonium Salt Complexes

PVOH and freeze-dried amylose-fatty ammonium salt complexes were dissolved in water at concentrations of 2% (dry basis), and the stirred dispersions were heated to 80 °C. The solutions were then immediately cooled in ice water to 25 °C. Amylose-ammonium salt complexes are acidic (pH of a 2% solution of the C_{16} complex was 3.6), so an experiment was carried out to determine whether acid hydrolysis of complexed amylose occurs under the conditions used to dissolve the complexes for film preparation. The C_{16} ammonium salt complex

was dissolved as described above, and the viscosity of the solution was determined using an ARES LS1 rheometer (TA Instruments, New Castle, DE) with 50 mm titanium parallel plate geometry. The sample was then reheated to 80 °C and stirred at 100 sec⁻¹ for 1 h using an AR 2000 rheometer (TA Instruments, New Castle, DE) with concentric cylinder geometry. This rheometer was used to reheat the sample because the container could be sealed to avoid loss of water that would affect the observed viscosity. The viscosity of the reheated and cooled solution was then determined at 25 °C and 100 sec⁻¹ using the ARES LS1 rheometer as described above and compared with the measurements obtained with the AR 2000 rheometer. The experiment was run in duplicate, and the viscosity was determined in triplicate with the ARES LS1 rheometer. The *t*-test analysis showed that there was no significant difference in the viscosities of the initially prepared sample and the sample that was stirred at 80 °C for 1 h, indicating that amylose was not hydrolyzed under the conditions used to dissolve the freeze-dried samples.

Various portions of 2% solutions of PVOH and amylose-ammonium salt complex were combined to obtain a series of 100 g solutions that contained amylose complex and PVOH in ratios of 100:0, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, and 0:100. Glycerol (0.4 g), a commonly used plasticizer for starch, was added to give glycerol concentrations of 20% based on total polymer solids, and entrapped air was removed by applying vacuum to the solutions at room temperature. The dispersions were then poured into a 12.5 × 17.8 × 0.4 cm rubber frame on a glass plate coated with BYTAC non-stick adhesive film (Saint Gobain Performance Plastics, Poestenkill, NJ), and the dispersions were allowed to dry at room temperature.

X-ray Diffraction

X-ray diffraction analysis was performed by Texray, Laboratory Services, Argyle, TX, using the same procedure described previously.²³

Tensile Testing of Film Samples

Films were stored for five days at 23 °C and 50% relative humidity (RH) before testing. Tensile strength, Young's modulus, and % elongation were obtained using an Instron Universal Testing Machine, Model 4201 (Canton, MA) according to the ASTM D638 Type V testing procedure (crosshead speed 10 mm/min, gauge length 7.62 mm, load cell 1 kN or 100 N). Significant differences between film properties were determined using an analysis of variance (*n* = 5) and Duncan's multiple range test (*P* < 0.05).

Measurement of Contact Angles

Solutions of PVOH and the C₁₆ amylose complex were prepared at concentrations of 2% as described for the films prepared for tensile testing, and glycerol was added in amounts equal to 20% of the dissolved polymers. To obtain cast films with flat surfaces for contact angle determinations, 2 mL of each solution was transferred with a pipette to a 57 × 14 × 1 mm wax frame affixed to the surface of a 25 × 75 × 1.0 mm glass microscope slide coated with BYTAC adhesive film (Saint Gobain Performance Plastics, Poestenkill, NJ). The solutions were air dried at room temperature. Measurements were conducted using

axisymmetric dropshape analysis on a FTA-200 automated goniometer (First Ten Angstroms, Portsmouth, VA) with fta32 v2.0 software, using the procedure described previously.²³ The contact angles reported were those observed at 60 sec (mean of five measurements ± standard deviation).

Microscopy

Film pieces were taped onto microscope slides and enclosed in a sealed Petri dish containing a small piece of moistened filter paper to provide humidity and dry iodine crystals, which stained the films with iodine vapor. Stained films were observed and photographed with a Zeiss Axioskop light microscope using an Axiocam ICc 3 digital camera (Carl Zeiss, Inc., Thornwood, NY). For scanning electron microscopy (SEM), small pieces of the upper surfaces of the dried films were sputter-coated with gold and examined with a JSM-6010LA SEM (JEOL USA, Peabody, MD).

RESULTS AND DISCUSSION

Preparation and Characterization of Starch Complexes

When the freeze-dried complexes were dissolved in water for film preparation, the amount of insoluble material remaining in the solutions was largest for the C₁₂ complex (8.0%), whereas smaller amounts of insoluble material (1.1% and 0.5%) were observed when the complexes were prepared from the C₁₆ and C₁₈ ammonium salts. The relatively high percentage of insoluble material obtained for the C₁₂ complex could be caused by less complex formation due to the lower molecular weight and increased water solubility of the C₁₂ fatty ammonium salt.²⁰ A lesser amount of complex formation could result in retrogradation of partially complexed amylose, and could thus account for the increased percentage of water insoluble material observed.

X-ray diffraction patterns of the freeze-dried, water soluble products (Figure 1) showed similar 6₁V reflections at 7.5°, 12.5°, and 20° 2θ confirming the formation of amylose inclusion complexes from the three fatty ammonium salts.²⁵ The scattering pattern of the 8.0% water insoluble fraction isolated from the solution of the C₁₂ complex prepared for film casting (not shown) also showed 6₁V reflections similar to those shown in Figure 1(A) for the water-soluble fraction. Figure 2 shows the X-ray diffraction patterns of films prepared from 100% PVOH, 50:50 mixtures of PVOH and the three amylose-ammonium salt complexes, and the three amylose-ammonium salt complexes in the absence of PVOH. Comparison of the diffraction patterns in Figures 1 and 2 show that the freeze-dried complexes remained intact and were not adversely affected when dissolved in hot water, blended with PVOH, and allowed to dry to form composite films.

PVOH composite films prepared from the C₁₆ ammonium salt complex were stained with iodine vapor to determine whether the amylose complex and PVOH components of the dried films separated into distinct phases, as previously observed for PVOH composite films prepared from the amylose-sodium palmitate complex.²³ Films prepared from the C₁₆ ammonium salt complex were used as representative examples of these composite films, since the C₁₆ carbon chain is approximately midway between the chain lengths of the other two fatty amine salts

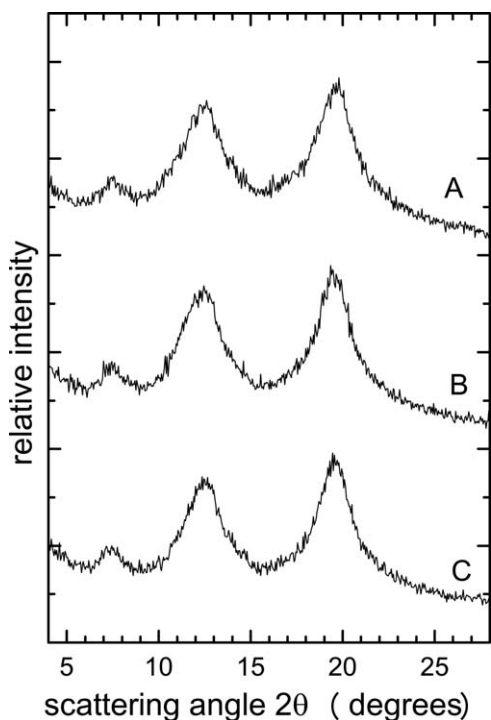


Figure 1. X-ray diffraction patterns of starch complexes prepared with (A) dodecylammonium chloride (C12), (B) hexadecylammonium chloride (C16), and (C) octadecylammonium chloride (C18).

used. Microscopic examination of films exposed to iodine vapor revealed uniform staining with no evidence of phase separation or starch-rich areas. This observation is in marked contrast to films prepared with the amylose-sodium palmitate complex, in which distinct starch-rich domains were seen from 20% to 60% content of the sodium palmitate complex (Supporting Information, Figure S1).²³ This lack of phase separation of the amine salt complex indicates a more intimate mixing of PVOH and the amylose complex, and suggests that ionic bonding of the cationic amine salt complex with the hydroxyl groups of PVOH and starch immobilizes the complex and prevent its coalescence into starch-rich domains upon film drying. Although it was observed with the sodium palmitate complex that the starch-rich domains remained strongly associated with PVOH and co-stretched with PVOH without separation to provide enhanced elongation,²³ the more intimate mixing and ionic bonding that takes place between the cationic amylose complexes and the hydroxyl groups of PVOH results in composite films with even higher values for % elongation as described below.

Films prepared from 100% PVOH, 100% C₁₆ ammonium salt complex, and 100% sodium palmitate complex that were simultaneously stained with iodine vapor are shown in Figure 3. The films prepared from PVOH, the ammonium salt complex, and the sodium palmitate complex were pale yellow, medium pink, and dark blue, respectively. The pink color of the vapor-stained film prepared from the ammonium salt complex was unexpected, since the amylose-sodium palmitate complex showed the dark blue staining typically observed for amylose. The difference in color may be due to the different ionic charges of the head groups of the two complexed ligands. With the anionic sodium

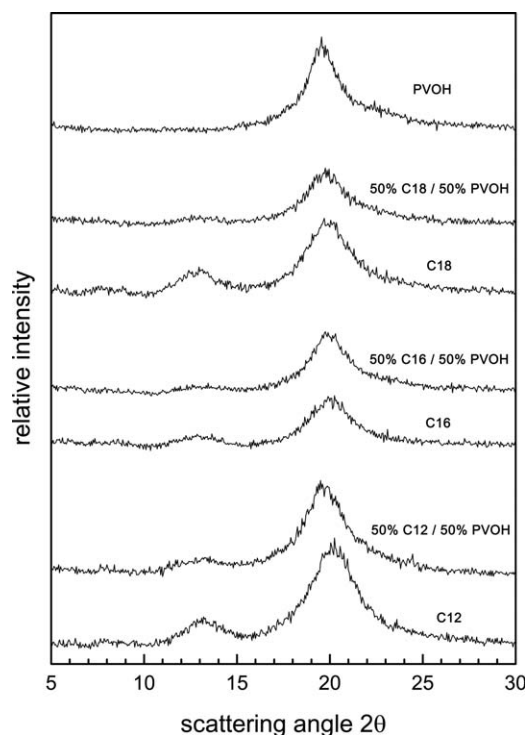


Figure 2. X-ray diffraction patterns of films prepared from PVOH, amylose-dodecylammonium chloride complexes (C12), amylose-hexadecylammonium chloride complexes (C16), amylose-octadecylammonium chloride complexes (C18), and 50:50 mixtures of PVOH and the three complexes.

carboxylate head group, the complexed sodium palmitate would be held within the amylose helix solely by the interaction of the hydrophobic alkyl chain with the hydrophobic interior of the amylose helix, and the negative charge of the head group would to some extent be repelled by the slight negative charge of the hydroxyl groups of starch. The anionic sodium carboxylate complex could thus be more easily displaced by the polyiodide

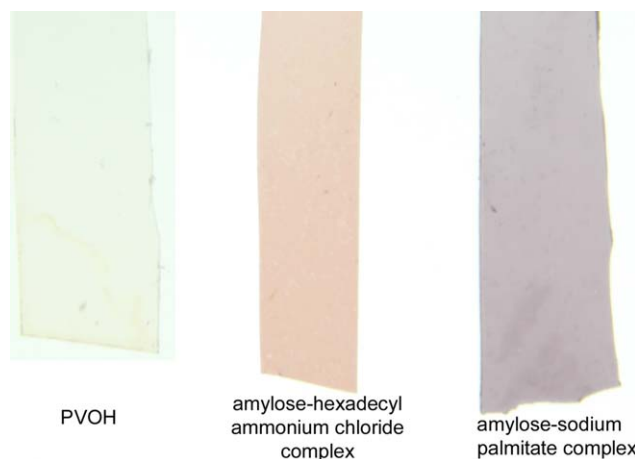


Figure 3. Light box photograph of iodine vapor stained films prepared from PVOH, 100% amylose-hexadecylammonium chloride complexes, and 100% amylose-sodium palmitate complexes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

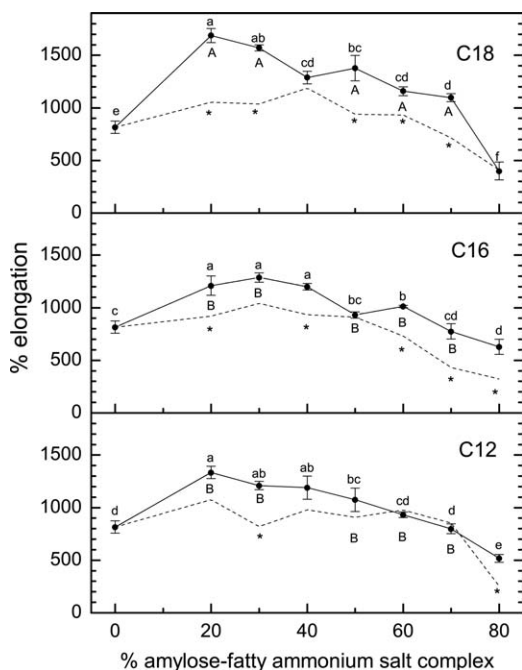


Figure 4. Percent elongation of films prepared with PVOH and increasing content of amylose-fatty ammonium chloride complexes (C18, C16, and C12). Lower case letters designate significant differences among the levels of each complex type (horizontally). Upper case letters designate significant differences between ligands at each incorporation level (vertically). Dashed lines represent corresponding data obtained previously²³ for the analogous carboxylic acid salt complexes (sodium stearate, palmitate, and laurate) for comparison. Asterisks designate significant differences (based on *t*-tests) between the cationic (solid lines) and anionic (dashed lines) ligands at each point.

forms of dissolved iodine, including the longer polyiodides that impart the blue stain.^{26,27} However, with the C₁₆ ammonium salt complex, ionic association between the cationic head groups and the hydroxyl groups of starch would make the complexed ammonium salt relatively immobile and could thus inhibit its separation from the amylose helix. This could result in fewer long, empty zones in the amylose helix, and more abundant shorter helical zones available for binding with the shorter polyiodide chains, which would impart more of a red color to the complexed amylose.^{26,27}

PVOH composite films prepared with 20% and 50% of the C₁₆ ammonium salt complex were also examined by SEM, and the morphologies of the film surfaces were compared with those of the PVOH-sodium palmitate films prepared previously²³ with the same percentages of amylose complex. Although protrusions were observed on the surfaces of films prepared from the sodium palmitate complex, films prepared from the ammonium salt complex (Supporting Information, Figure S2) were smooth, and no protrusions were observed, in agreement with the absence of phase separation observed by light microscopy.

Tensile Properties of PVOH Composite Films

Values for percent elongation (%E), tensile strength (TS), and Young's modulus (YM) of PVOH composite films prepared from the C₁₈, C₁₆, and C₁₂ cationic amylose-fatty ammonium

salt complexes are shown in Figures 4–6, respectively. The dashed curves in these figures show the tensile values previously obtained for films prepared in the same manner from anionic amylose-fatty acid salt complexes with the same carbon chain lengths.²³ Differences between the tensile properties of films prepared from cationic and anionic complexes are likely due to differences in the manner in which these two types of complexes bind to PVOH and to each other when aqueous solutions of the polymers are allowed to dry. When composite films are prepared from anionic fatty acid salt complexes, hydrogen bonding between the negatively charged amylose complexes and PVOH, which also has a small negative charge density,²⁸ will take place slowly as the concentration of the combined polymer solution increases due to evaporation of water at room temperature. This slow evaporation, coupled with the anionic repulsion between PVOH and the amylose-complexed fatty acid salt, allows the two components to separate before separation is inhibited by the increased viscosity of the aqueous solution. In contrast to the anionic fatty acid salt complexes, ionic bonding between the complexed cationic ammonium salt and the anionic hydroxyl groups of PVOH can take place in dilute water solutions, and this would inhibit the separation of the two polymers as the combined solutions are allowed to slowly dry.

Values for %E as high as those shown in Figure 4 for the films prepared from the ammonium salt complexes have not been previously reported for PVOH composite films prepared from starch-based products. For example, cornstarch dissolved by stirring at 90–100 °C was combined with PVOH up to 10% starch yielding films with up to 230%E versus 200%E for pure PVOH.⁶ Nanocrystals obtained from pea starch only slightly increased %E of PVOH from 710%E to about 740%E at 5% incorporation, while higher levels of nanocrystals and all levels of native pea starch granules resulted in decreased %E.¹¹ In the present study, %E more than double the value of the PVOH control (1687%E vs. 815%E) was observed with 20% incorporation of the C₁₈ ammonium salt complex, and for many of the films, the %E of the PVOH-ammonium salt complexes exceeded the %E of the control film prepared from 100% PVOH. These high %E values, relative to those previously observed for films prepared from anionic fatty acid salt complexes²³ may be attributed to the stronger ionic bonding between PVOH and the cationic amine salt complexes. The highest values for %E were obtained for the series of films prepared from the C₁₈ ammonium salt complex, and the largest increase in %E was observed for the film prepared from an 80:20 mixture of PVOH and complex. The highest %E values for the films prepared from the C₁₈ complex could be due to the fewer number of cationic ammonium salt groups in this complex, since the same weight of fatty amine was used to prepare the three complexes, and the C₁₈ complex has the highest molecular weight. Fewer cationic amine groups in the complex would reduce the ionic association between the complex and PVOH (relative to the shorter chain-length ligands), and thus give more flexibility to the films and enhance their ability to stretch without breaking. The ability of the films to stretch without breaking could also be enhanced by the higher molecular weight of the complexed C₁₈ carbon chain.

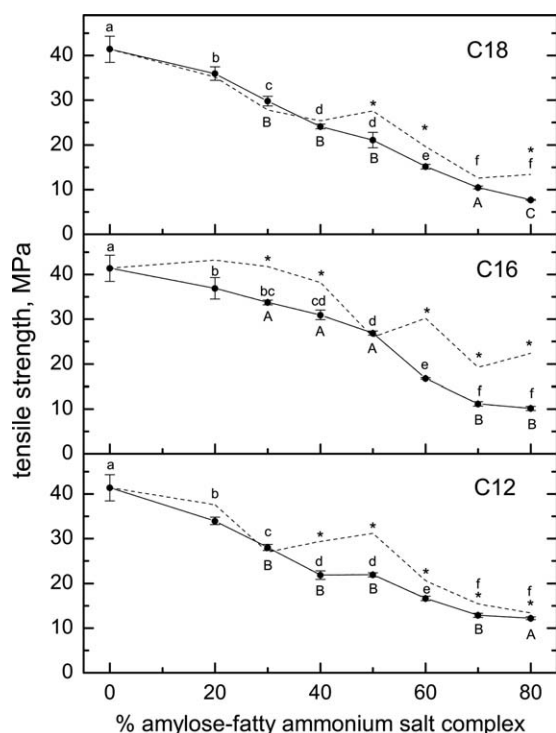


Figure 5. Tensile strength of films prepared with PVOH and increasing content of amylose-fatty ammonium chloride complexes (C18, C16, and C12). Lower case letters designate significant differences among the levels of each complex type (horizontally). Upper case letters designate significant differences between ligands at each incorporation level (vertically). Dashed lines represent corresponding data obtained previously²³ for the analogous carboxylic acid salt complexes (sodium stearate, palmitate, and laurate) for comparison. Asterisks designate significant differences (based on *t*-tests) between the cationic (solid lines) and anionic (dashed lines) ligands at each point.

Figure 5 shows that the TS of films prepared from the cationic amylose-ammonium salt complexes was in most cases lower than the TS of comparable films prepared from the anionic fatty acid salt complexes,²³ and declined steadily with increased percentages of the ammonium salt complexes. These results are consistent with the higher %E values for films prepared from the ammonium salt complexes because their increased ability to stretch before breaking results in a thinner film when it does break. As observed for the anionic complexes prepared from the sodium salts of fatty acids,²³ the highest tensile strengths were observed when the composite films were prepared from the ammonium salt complex with the intermediate carbon chain length of C₁₆. The C₁₆ complex has a greater number of cationic ammonium groups than the C₁₈ complex due to its lower molecular weight, and can therefore ionically bond more tightly to PVOH to give the higher tensile strengths observed. Although the C₁₂ complex should theoretically have the greatest number of cationic ammonium groups, as discussed earlier, the increased water solubility of the C₁₂ ammonium salt and the shorter chain length could cause it to be less tightly bound within the hydrophobic interior of the amylose helix, which could have a negative effect on tensile strength.

As observed for the films previously prepared from anionic amylose-fatty acid salt complexes,²³ Figure 6 shows that the YM values for the films prepared from the cationic ammonium salt complexes increased with increasing percentages of complex; however, these values were lower than those observed when the films were prepared from fatty acid salt complexes. Since the YM pertains to the initial, linear phase of the stress-strain curve before plastic deformation takes place, the lower YM values reflect the elasticity of these films before the yield point is reached. Typically, PVOH films have a much lower YM than the somewhat stiffer, more rigid starch films, and therefore an increase in YM with increasing content of the starch complexes would be expected. However, the YM increases more rapidly at higher levels of incorporation of the sodium carboxylate complexes (dashed lines, Figure 6), while the increase is more gradual with the ammonium salt complexes (solid lines). This difference may be related to the phase separation and phase inversion, which occurs with films prepared from the anionic carboxylate complex. Instead of the lower half of the curve increasing slowly with a sudden increase to higher values when the starch complex becomes the continuous phase, with the ammonium salt complexes there is no phase inversion because of the more complete mixing of the two components, and the single phase composition

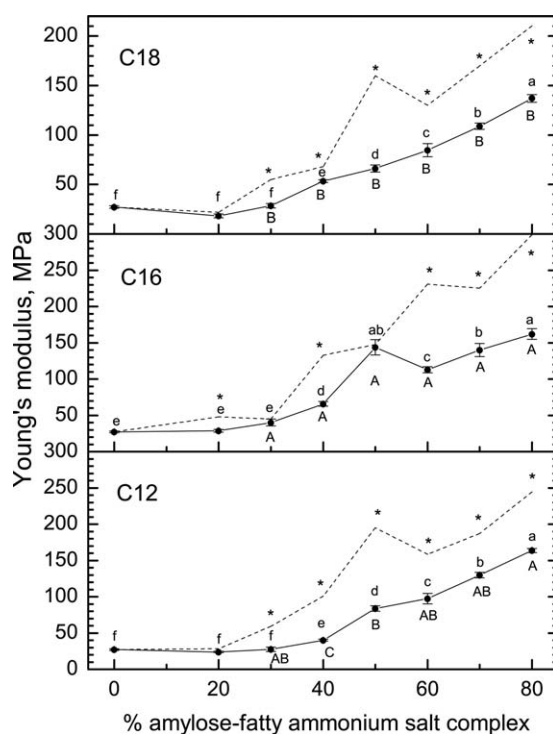


Figure 6. Young's modulus of films prepared with PVOH and increasing content of amylose-fatty ammonium chloride complexes (C18, C16, and C12). Lower case letters designate significant differences among the levels of each complex type (horizontally). Upper case letters designate significant differences between ligands at each incorporation level (vertically). Dashed lines represent corresponding data obtained previously²³ for the analogous carboxylic acid salt complexes (sodium stearate, palmitate, and laurate) for comparison. Asterisks designate significant differences (based on *t*-tests) between the cationic (solid lines) and anionic (dashed lines) ligands at each point.

Table I. Contact Angles of Dried Films and pH of Mixtures of Solutions of Amylose-Hexadecylammonium Chloride Complexes and PVOH

| % Complex | % PVOH | Contact angle, degrees ^a | pH |
|-----------|--------|-------------------------------------|------|
| 0 | 100 | 34.8 ± 7.3 ^e | 6.30 |
| 20 | 80 | 54.4 ± 6.4 ^d | 5.63 |
| 30 | 70 | 65.8 ± 3.5 ^b | 5.47 |
| 40 | 60 | 77.9 ± 1.9 ^a | 5.60 |
| 50 | 50 | 79.7 ± 0.8 ^a | 5.02 |
| 60 | 40 | 77.6 ± 0.9 ^a | 4.79 |
| 70 | 30 | 75.1 ± 3.1 ^a | 4.54 |
| 80 | 20 | 59.7 ± 0.7 ^c | 4.23 |
| 100 | 0 | 50.3 ± 4.3 ^d | 3.61 |

^aContact angle measured after 60 sec ± SD. Values followed by different superscript letters are significantly different based on Duncan's multiple range test ($P < 0.05$).

of these films retains more of the lower YM property of PVOH as the percentage of complex increases.

In summary, much higher %E values of PVOH composite films prepared in this study from cationic amylose-ammonium salt complexes were observed compared to the %E values previously observed for films prepared from waxy corn starch,²³ anionic amylose-fatty acid salt complexes,²³ and the starches from various plant sources listed in the introduction. The lower values for TS observed in this study would need to be weighed against the advantage that these films provide with respect to higher elongation, lower YM, and to the more rapid biodegradation and potentially lower cost due to the presence of the starch-based component.

Surface Hydrophobicity of Films

The surface contact angles of water droplets applied to films cast from mixtures of PVOH and C₁₆ ammonium salt complex with ratios from 100:0 to 0:100 are shown in Table I. The film cast from 100% PVOH was the most hydrophilic film with a contact angle of 34.8°. The contact angle increased from 54.4° to 79.7° with increasing content of ammonium salt complex from 20% to 50%, and then remained essentially the same until dropping to 59.7° at 80% complex. The film prepared from 100% complex had a contact angle of 50.3°. These results are quite different from those observed for the series of films made with increasing contents of amylose-sodium palmitate complex,²³ in which the contact angle increased from 31.7° for the PVOH control to 85° for films prepared with 20% sodium palmitate complex, and the values remained in the 80–89° range all the way up to 100% complex. This difference in the response pattern can be attributed to the different effects of pH on the two ligands with opposite charges on the head groups. The PVOH solution had a pH of 6.30, and increasing the ratio of ammonium salt complex resulted in progressive acidification of the mixture to pH 3.61 (Table I). The increase in pH with increased proportions of PVOH in the solution would therefore cause a partial conversion of the cationic ammonium salt head group of the complex to the uncharged amine form, which is more hydrophobic. At higher proportions of the complex, the

pH is low enough for the complexes to remain in the cationic ammonium salt form, which is apparently more hydrophilic than the corresponding sodium palmitate complex as revealed by the higher contact angles observed in the former series of films.²³ In contrast to the ammonium salt complex, solutions of sodium palmitate complexes are more alkaline than PVOH solutions (pH 8.2 for a 2% solution of the complex), and therefore the reduction in pH due to blending with a PVOH solution is not great enough to convert the sodium palmitate head group to the water insoluble free acid. Consequently, the contact angles remain high at all levels of complex incorporation.

As noted above, films cast from 100% amylose-hexadecyl ammonium chloride complexes were more wettable (lower contact angles) than those cast from 100% amylose-sodium palmitate complexes.²³ This may be a result of the difference in the ionic charge of the head groups of the respective ligands. When a solution of the amylose-sodium palmitate complexes dries down, the amylose complexes separate from the amylopectin component (that was originally present in the high amylose starch used to prepare the inclusion complex) to form relatively hydrophobic aggregates.²³ Such phase separation has been demonstrated with both synthetic mixtures of amylose and amylopectin solutions^{29,30} and with dissolved starch granules³¹ and was attributed to incompatibility between the two starch structures. Moreover, when this phase separation occurred, it was observed that the amylose-rich phase was above the amylopectin-rich phase. This phenomenon is consistent with the high contact angles observed at a wide range of PVOH:amylose-sodium palmitate complex ratios on the upper surface of the films.²³ However, when the complexes have a cationic head group, as with the ammonium salt complexes, the ionic interactions that take place in solution between the head groups and both amylose and amylopectin may interfere with the mobility of the starch during drying, resulting in a more random, diffuse distribution of the amylose complexes and amylopectin. If we assume that amylopectin is more hydrophilic than the ammonium salt complex, this explanation is consistent with the observation of lower contact angles with the cationic ammonium salt complex than with the anionic carboxylic acid salt complex, as well as the lack of phase separation in films prepared from the cationic complexes.

CONCLUSIONS

Films prepared from mixtures of PVOH and water-soluble amylose-fatty ammonium salt complexes exhibited higher values for % elongation than control PVOH films or those prepared with mixtures of PVOH and amylose-fatty acid salt complexes. They exhibited slightly lower tensile strength and Young's modulus. Surface hydrophobicity as revealed by water droplet contact angles was much higher than PVOH films, but not as consistently high at all incorporation ratios as films prepared with fatty acid salt complexes. Microscopy revealed no apparent phase separation or phase inversion with cationic amylose-ammonium salt complexes in contrast with that observed with anionic amylose-fatty acid salt complexes. These observations are consistent with a more intimate mixture and inhibition of phase separation resulting from ionic interactions between the cationic head groups of the ammonium salt complex and the slightly

negative hydroxyl groups of both amylose and PVOH, in contrast with the repulsion of anionic amylose complexes and those polymers. The improved elongation properties of these films suggest that these PVOH composite films would have marketable advantages in some areas of application as well as imparting lower cost and increased biodegradability due to the high percentage of the starch-based component.

ACKNOWLEDGMENTS

The assistance of Gary Kuzniar with testing of physical properties is gratefully acknowledged.

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