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Complexing between starch and poly (ethylene-*co*-acrylic acid)—a comparison of starch varieties and complexing conditions

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We have prepared starch-EAA complexes from different varieties of starch under a number of different reaction conditions. Water dispersions of starch at either 1 or 5% solids were combined with solutions of EAA in aqueous ammonia. Mixtures were air-dried, and the resulting composite films were then extracted with a solution of 1,1,2-trichloroethane, isopropanol, and toluene (15:15:70, by volume) to remove uncomplexed EAA. EAA content of composites after extraction was determined by FTIR. Because of its inability to form helical inclusion complexes with EAA, the microbial polysaccharide dextran was used to establish extraction conditions. Pretreatment of polysaccharide-EAA composites with methanol-water prior to extraction was essential for efficient removal of uncomplexed EAA. It was also necessary that methanol-water solutions be acidified to convert any residual ammonium carboxylate in the composite to carboxylic acid. The amount of EAA complexed by starch increased with an increase in the temperature used for gelatinization and also with the amylose content of the starch sample. Jet-cooked starch samples afforded the highest levels of complexation. Complex formation with cornstarch was not enhanced by the removal of trace amounts of lipid. Increased complexing of EAA was observed if composites were prepared at 1% as opposed to 5% solids. Under these conditions, complex formation with potato starch was about the same as that observed with cornstarch, indicating that phosphate substituents in potato starch do not influence complexing ability.

INTRODUCTION

Composite polymer systems composed of starch and poly (ethylene-*co*-acrylic acid) (EAA) have been under investigation at the Northern Regional Research Center for a number of years (Otey *et al.*, 1977; Otey *et al.*, 1980; Otey & Westhoff, 1984; Otey *et al.*, 1987). Extrusion-blown starch-EAA films containing about 40% starch are uniform, flexible, and have good physical properties, in spite of obvious differences in physical and chemical properties between the two component polymers. Composites of this type are currently receiving increased attention because of the ability of the starch component to biodegrade.

We have presented evidence (Fanta *et al.*, 1990) that the ability of the two polymers to form uniform blends is due to formation of a complex similar to known helical inclusion complexes between starch and fatty acids. Part of the evidence for complex formation was the observation that a significant percentage of the EAA could not be solvent-extracted from a mixture of the two polymers. Shogren and coworkers (Shogren *et al.*, 1991) have also obtained data to support the existence of these complexes.

Since physical properties of films and molded articles prepared from starch-EAA mixtures (and thus their practical applications) might well depend on the amount of complexation that takes place between the two polymers, the present study was carried out to compare the amount of complexed EAA in a series of starches from different plant sources, some having different amylose:amylopectin ratios. We also examined a variety of experimental conditions for the preparation

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

of starch-EAA composites to determine the influence of preparative conditions on complexation.

EXPERIMENTAL

Materials

Dextran (industrial grade, average MW 5–40 × 10^6) was obtained from Sigma Chemical Co. (St. Louis, Missouri). With the exception of extrusion-blowing experiments, cornstarch was Buffalo 3401 from CPC International, Inc. (Argo, Illinois). Extrusion-blown films were prepared from Globe 3005 cornstarch from CPC. Waxy cornstarch (Amioca) was from National Starch and Chemical Corporation (Bridgewater, New Jersey), high amylose cornstarch (Amylomaize VII) was from American Maize Products Co. (Hammond, Indiana), and potato starch was from Sigma Chemical Co. Cornstarch was defatted by continuous extraction with 95% ethanol for 3 days in a Soxhlet extractor (Schock, 1964). The extracted starch was washed with water and allowed to air-dry. Polysaccharide weights were corrected for moisture content and, except where indicated, are given on a dry-weight basis.

EAA was Primacor 5981 from Dow Chemical Co. (Midland, Michigan). This polymer, which contains about 20% copolymerized acrylic acid by weight, has a melt index of 300, Mw of about 18 000, and Mn of about 7000.

A 5% solution of EAA in aqueous ammonium hydroxide was prepared by stirring 25 g of EAA pellets in 500 ml of 50/50 (by volume) concentrated ammonium hydroxide/water in a flask equipped with a reflux condenser. The mixture was heated to 75°C, stirred at 75–85°C for about 6 h, and then allowed to cool. The slightly turbid solution was then diluted with concentrated ammonium hydroxide to a total weight of 500 g. For some experiments, this solution was further diluted to 1% by addition of water.

Jet-cooking

Jet-cooking (Winfrey & Black, 1964) was carried out with a Penick & Ford laboratory model continuous cooker operated with 70 psig line-pressure steam (Penick & Ford Ltd., Cedar Rapids, Iowa). Cooking was carried out at 140°C (40 psig steam) with a pumping rate of about 1·1 litre min^{-1}. Starch dispersion was collected in a Dewar flask to maintain the temperature of the dispersion at about 90°C.

Somewhat higher starch concentrations than those desired were used to allow for dilution of the cooked dispersion with condensed steam. This dilution factor caused some variability in starch concentration in cooked dispersions. For example, if we jet-cooked a suspension of 80 g of starch in 1200 ml of water, starch solids in the collected dispersion (determined by freeze-drying a weighed portion of dispersion) ranged from 4·5–5·3%. A suspension of 12·5 g of starch in 1000 ml of water produced a dispersion that contained 0·95–1·1% starch solids.

Dextran-EAA composites; 5% dextran solids

A mixture of 25·0 g of dextran and 470 ml of water in a stirred flask was heated for 1 h at 94–95°C, and the resulting solution was cooled to 55°C. Water was added to give a total mass of 500 g, and the solution was cooled to 25°C. Solutions of dextran and EAA at 5% solids were then combined at weight ratios of 60:40 and 80:20. Mixtures were stirred for 10 min, poured into polyethylene-lined trays, and allowed to air-dry. Dry composites were in the form of brittle films.

Dextran-EAA composites; 1% dextran solids

A mixture of 3·00 g of dextran and 297 ml of water in a stirred flask was heated to 95°C and stirred at this temperature for 15 min. The heating mantle was removed, and 200 g of 1% EAA solution was added to the hot dextran solution. The mixture was stirred for 10 min and then poured into a polyethylene-lined tray and allowed to air-dry.

Starch-EAA composites; 5% starch solids

Starch gelatinized in a stirred flask

A mixture of 25·0 g of starch and 470 ml of water in a stirred flask was heated for 1 h at either 75°C or 95°C, and the dispersion was cooled to 55°C. Water was added to give a total mass of 500 g, and the solution was cooled to 25°C. Starch dispersions were then combined with EAA solutions at 5% solids to give starch:EAA weight ratios of 90:10, 80:20, 60:40, and 40:60. Mixtures were allowed to stand with periodic stirring for 10 min and were dried in the same manner as dextran-EAA.

Starch gelatinized by jet-cooking

Suspensions of 80 g of starch in 1200 ml of water were passed through the jet-cooker, and cooked starch dispersions were collected in a Dewar flask. Hot dispersions were weighed into beakers and immediately combined with 5% EAA solutions to give starch:EAA weight ratios of 80:20 and 60:40. Mixtures were stirred and cooled to 25°C, were allowed to stand with periodic stirring for a total of 10 min, and were then air-dried in the same manner as dextran-EAA. In some experiments the starch dispersion was cooled to 25°C prior to mixing with EAA.

Starch-EAA composites; 1% starch solids

Suspensions of 12·5 g of starch in 1 litre of water were passed through the jet-cooker, and hot starch dispersions (about 200 g) were collected in a tared Dewar flask. The exact weight of starch dispersion collected was used to calculate the weight of 1% EAA solution needed to give starch:EAA weight ratios of 40:60, 60:40, and 80:20. The calculated weight of EAA solution was then added to the Dewar flask. Mixtures were stirred for 10 min with no external cooling and were then allowed to air-dry in the same manner as dextran-EAA.

Extrusion-blown starch-EAA films

Methods used were similar to the semidry mixing method reported by Otey and coworkers (Otey *et al.*, 1987). The urea-containing formulation was prepared by blending 51·3 g of Globe 3005 (moisture content 9·8%) and 69·4 g of finely ground EAA with a solution prepared from 11·6 g of urea, 9·4 ml of concentrated ammonium hydroxide, and 9·3 ml of water. The formulation prepared in the absence of urea contained 55·6 g of starch, 75·2 g of EAA, 10·2 ml of concentrated ammonium hydroxide, and 10·0 ml of water. Moist blends were passed twice, at 100°C, through a C.W. Brabender single-screw extruder equipped with a strand die having 17 holes, 1·6 mm in diameter (C.W. Brabender Instruments Inc., South Hackensack, New Jersey). The standard 2-zone mixing screw was 1·9 cm in diameter, had a 20:1 L/D ratio, and was operated at 60 rpm. Strands of extrudate were chopped in a Killion 2-in pelletizer (Killion Extruders Inc., Cedar Grove, New Jersey). Pellets from the second pass were extrusion-blown into film by passing through the same extruder equipped with a 3:1 compression ratio screw and a 12·7 mm diameter blown-film die heated at 100–110°C.

Extraction of polysaccharide-EAA composites and determination of EAA

Air-dried composite films prepared from EAA and polysaccharide at 1% solids were ground before extraction in a Wig-L-Bug amalgamator (Crescent Dental Mfg. Co., Lyons, Illinois) equipped with a stainless steel capsule and two $\frac{1}{4}$-in diameter stainless-steel ball pestles. Samples were milled for 30 s in 0·3 g portions. Extrusion-blown films and air-dried composite films prepared from EAA and polysaccharide at 5% solids were not ground but were extracted as whole films (except where indicated).

Polysaccharide-EAA films or particles (0·4–0·5 g) were allowed to soak overnight in 50 ml of either absolute methanol or solutions of 90:10, 80:20, or 50:50 (vol) methanol-water. Different methanol:water ratios were used to obtain composites with different water contents. With the exception of a few experiments carried out as controls, methanol–water solutions also contained 0·1 ml of concentrated HCl to convert all carboxylate substituents in EAA to the carboxylic acid form. This is necessary to maximize solubility of EAA in our extraction solvent. Polymers were separated by decantation or filtration, lightly blotted between filter papers, and suspended in about 40 ml of a ternary solvent solution containing 15:15:70 (by volume) 1,1,2-trichloroethane:isopropanol:toluene. Suspensions were heated for 1–2 h at 75–80°C, and clear supernatants were decanted. Polymers were given three more extractions with hot solvent and were then washed with ethanol and vacuum-dried.

EAA in solvent-extracted polymers was determined by FTIR as previously described (Fanta & Salch, 1991).

RESULTS AND DISCUSSION

Starch–EAA composites were prepared by mixing water dispersions of starch, at either 1 or 5% solids, with an aqueous ammonia solution of EAA. As in our earlier study (Fanta *et al.*, 1990), an increase in viscosity occurred immediately upon mixing. Dispersions were poured into trays and were allowed to air-dry to form clear, continuous, brittle films. Since EAA dissolves readily at about 75°C in a ternary solvent system composed of 15:15:70 (by volume) 1,1,2-trichloroethane: isopropanol:toluene, extraction with this solvent was used to remove EAA, which was either uncomplexed or only loosely bound to the starch. Unextractable EAA remaining in the composite was assumed to be complexed and was determined by FTIR (Fanta & Salch, 1991).

Experimental conditions necessary for efficient extraction of uncomplexed EAA were established by investigating composites prepared from EAA and the microbial polysaccharide dextran. Although starch and dextran are both polysaccharides composed of repeating glucopyranosyl units, the α-(1→6) linkages between these units in dextran do not allow the polysaccharide to assume the helical configuration that is necessary for complex formation. The most efficient extraction conditions for removing uncomplexed EAA from a starch composite should therefore be those that remove virtually all the EAA from an analagous composite prepared from dextran.

Previous work by Brockway (Brockway, 1964) has shown that efficient extraction of unbound polymer from a polysaccharide matrix requires the absorption of water to swell the polysaccharide and thus make it more permeable to solvent. Water was therefore added to our polysaccharide-EAA composites in varying amounts by soaking the composites prior to extraction in methanol–water solutions of different composition.

Table 1. Influence of pretreatment conditions on extraction of EAA from dextran–EAA composites

Solids used for composite preparation (%)	Physical state	Pretreatment	EAA content after extraction (%)	
			60:40 dextran-EAA	80:20 dextran-EAA
5	Film	50:50 MeOH-H_2O	8·2	5·1
5	Film	80:20 MeOH-H_2O	1·1	1·2
5	Film	90:10 MeOH-H_2O	1·4	1·4
5	Film	None	10·4	
5	Ground film	80:20 MeOH-H_2O	<1	<1
5	Ground film	90:10 MeOH-H_2O	<1	<1
5	Ground film	None	9·2	
1	Ground film	50:50 MeOH-H_2O	4·1	
1	Ground film	80:20 MeOH-H_2O	<1	
1	Ground film	90:10 MeOH-H_2O	1	
1	Ground film	100: 0 MeOH-H_2O	2	
1	Ground film	80:20 MeOH-H_2O (No HCl)	7·5	

Table 2. Influence of pretreatment on extractability of EAA from a 60 cornstarch–40 EAA composite[a] prepared at 5% solids

Pretreatment	EAA content after extraction[b] (%)
50:50 MeOH-H_2O	5·6 (9·0)
80:20 MeOH-H_2O	6·0 (9·6)
90:10 MeOH-H_2O	7·2 (10·8)
MeOH	7·5 (10·0)
None	11·5

[a] Starch cooked at 95°C. Whole film (unground) used for extraction.

[b] Values in parentheses are for film heated for 2 h in 120°C oven.

A small amount of HCl was also added to methanol–water solutions to convert any residual ammonium carboxylate in EAA to carboxylic acid. As we will show later, addition of acid is essential for efficient extraction. Dextran-EAA composites were prepared at either 5 or 1% solids under conditions simulating those to be used for composites with starch. Weight ratios of 60:40 and 80:20 dextran:EAA were used, and extractions with our ternary solvent system were carried out on whole films as well as on ground film samples.

Table 1 shows that extractability of EAA from dextran is highly dependent upon prior soaking of composites in aqueous methanol. The extraction is least efficient with no solvent pretreatment. Extractions are efficient, however, after pretreatment with 80:20 and 90:10 methanol–water, and both solvent systems allow EAA to be almost completely extracted from dextran. Treatment with 50:50 methanol–water results in high levels of residual EAA, presumably because the absorption of a large amount of water by dextran inhibits penetration by the water immiscible solvent. As expected, some improvement in extraction efficiency is realized if films are ground prior to extraction. Extraction efficiency is sharply reduced if HCl is omitted from the methanol–water solution.

The initial phase of our study of the starch-EAA system centered on composites prepared from solutions/dispersions of starch and EAA at 5% solids, and Table 2 shows the influence of the methanol–water ratio on the extractability of EAA from one such composite prepared from cornstarch. Starch was gelatinized by heating in water for 1 h at 95°C and was mixed with EAA solution at a starch-EAA ratio of 60:40. Extractions were carried out on whole (rather than ground) films. In agreement with the dextran data in Table 1, extraction was least efficient when no solvent pretreatment was used. The ratio of methanol:water, however, affected the two polysaccharides differently, since the lowest percentage of unextractable EAA with the starch product was observed with 50:50 as well as with 80:20 methanol–water. This difference in behavior no doubt reflects the lower water solubility of starch at room temperature, as compared with dextran, and therefore the reduced tendency of starch to swell and form a solvent-impermeable mass in the 50:50 methanol–water system. Differences between the two polysaccharides are immediately apparent when films are removed from 50:50 methanol–water for extraction. The dextran-containing film is noticeably more sticky and gummy.

Table 2 also shows the increase in unextractable EAA that we observe when films are heated for 2 h at 120°C prior to extraction. This increase in bound EAA might be due to heat-induced ester formation between carboxyl substituents of EAA and polysaccharide hydroxyls.

Since it was conceivable that the time period between preparation and extraction might influence not only the extent of complexation in a composite but also the chemical reaction between the two component polymers (e.g., esterification), we next investigated the effect of aging on extractability of EAA (Table 3). A

Table 3. Influence of storage time on extractability of EAA from a 60 cornstarch–40 EAA composite[a] prepared at 5% solids

Storage time[b] before extraction (days)	EAA content after extraction[c] (%)
1	5·5
3	6·0
6	5·3
14	5·3
29	5·9
42	5·9
64	5·9

[a] Starch cooked at 95°C. Whole film (unground) used for extraction.

[b] Film stored in sealed container at room temperature.

[c] Film pretreated with 50:50 methanol–water before extraction.

60:40 cornstarch–EAA composite was chosen for this study, and samples were treated with 50:50 methanol–water before each extraction. Throughout the entire testing period of 1–64 days, the EAA content after extraction remained nearly constant (5·3–6·0%).

Various gelatinization techniques for cornstarch were next examined to determine the effect on complexation with EAA (Table 4). EAA retained in the starch matrix after extraction increased as the gelatinization temperature was raised from 75 to 95°C, and this is probably a reflection of increased starch solubility at the higher temperature. We might expect that helical inclusion complexes with EAA would be more readily formed with soluble starch than with starch in the form of swollen but insoluble granules.

Since cornstarch is only about 25% water-soluble, even after heating at 95°C (Leach, 1965), jet-cooking was next investigated as a method for preparing starch dispersions. Jet-cooking (Winfrey & Black, 1964) has been used commercially for decades, and involves pumping an aqueous starch slurry through an orifice where it contacts a jet of high pressure steam. Under these high-temperature, high-shear conditions, the starch granule structure is totally disrupted, and little or no insoluble starch is found in the final dispersion. As expected, jet-cooked cornstarch afforded higher percentages of complexed EAA than cornstarch cooked at 95°C. Also, more complexing occurred when the jet-cooked starch dispersion was not allowed to cool but was mixed with EAA solution while still hot. The tendency of starch dispersions to retrograde on cooling is probably one of the factors responsible for this observation.

Table 4 also shows that starch:EAA ratios in composite films prepared at 5% solids can be varied from 40:60 to 80:20 without producing large changes in the amount of unextractable EAA. The single experiment carried out with 90 starch:10 EAA (with starch cooked at 95°C) showed an unexpectedly large EAA content after extraction; however, this result could be an artifact caused by reduced penetration and diffusion of water-immiscible solvent as compared with the other three samples in the same series. More uncomplexed EAA is present in composites prepared with 80:20, 60:40, and 40:60 ratios of starch:EAA, and voids can therefore be created in the polymer matrix as the extraction proceeds. These voids in turn can promote further solvent penetration and can thus facilitate the extraction process. Additional data relevant to this question will be discussed later.

Comparisons of EAA extractability between extrusion-blown films and composites prepared by combining aqueous solutions/dispersions of starch and EAA are also shown in Table 4. Extrusion-blown

Table 4. Influence of preparative conditions on extractability of EAA from cornstarch–EAA composites[a]

Starch gelatinization conditions	Initial starch:EAA ratio	EAA after extraction[b] (%)
75°C	60:40	3·2
	80:20	3·3
95°C	40:60	5·9
	60:40	6·6
	80:20	5·2
	90:10	9·2
Jet cook; cool before mixing	60:40	7·6
	80:20	8·1
Jet cook; mix while hot	60:40	9·1
	80:20	10·0
Extrusion (blown film; no urea)	40:60	13·5
Extrusion (blown film; urea present)	40:60	11·5

[a] Except for extruded films, composites were prepared at 5% solids.

[b] Whole film (unground) used for extraction. Film pretreated with 50:50 methanol–water.

Table 5. Influence of starch variety on extractability of EAA from cornstarch-EAA composites prepared at 5% solids[a]

Starch variety	Initial starch:EAA ratio	EAA after extraction[b] (%)
Corn	60:40	9·1
	80:20	10·0
High amylose corn[c]	60:40	14·5
	80:20	14·0
Waxy corn	60:40	5·0
Defatted corn	60:40	9·6
	80:20	11·3

[a] Starch samples were jet-cooked and mixed with EAA solution while hot.
[b] Whole film (unground) used for extraction. Film pretreated with 50:50 methanol-water.
[c] Contains 70% amylose.

films had a starch:EAA ratio of 40:60 and were prepared with and without the inclusion of urea (Otey *et al*., 1987). Blown films prepared in both the presence and absence of urea contained significantly higher percentages of unextractable EAA than the other samples in Table 4. This is not an unexpected result, since high-shear conditions encountered in the extruder would promote total disruption of starch granules, and the low water contents of these formulations during compounding would tend to maximize interaction between starch and EAA.

The influence on complex formation of the amount of amylose present in cornstarch is shown in Table 5. Starches were jet-cooked at 5% solids and were mixed with EAA at ratios of 60:40 and 80:20. Composites were treated with 50:50 methanol-water before extraction. Since amylose complexes with fatty acids, lipids, and alcohols more readily than amylopectin, it was not surprising that high amylose cornstarch (amylose content about 70%) gave higher percentages of complexed EAA than cornstarch (amylose content about 27%), and that waxy cornstarch (which contains little or no amylose) was poorest in complexing ability. The last entry of Table 5 shows results obtained with a cornstarch sample defatted by ethanol extraction. We felt that removal of trace lipids normally present in commercial cornstarch might provide new sites for complex formation; however, the increase in unextractable EAA was negligible.

The % solids concentration of polymer dispersions used to prepare our composites was investigated next. Since complexation causes a sharp increase in viscosity when dispersions of starch and EAA are mixed, it was likely that the high viscosities encountered in earlier experiments carried out at 5% solids might have had an inhibiting effect on mixing and complexation. Polymer concentrations of 1% were therefore examined. Cornstarch-EAA composites were prepared at weight ratios of 40:60, 60:40, and 80:20 (Table 6). Starch was jet-cooked, and hot dispersions at 1% solids were mixed with EAA solution under conditions (see Experimental) designed to minimize external cooling and thus maximize complex formation. As in Table 2, pretreatment with either 50:50 or 80:20 methanol-water gave the most efficient extraction of uncomplexed EAA. Omitting HCl from pretreatment solutions inhibited EAA extraction, while a two-fold increase in HCl had little or no effect on extractability.

Table 6. Influence of starch-EAA ratio and extraction conditions on extractability of EAA from cornstarch-EAA composites prepared at 1% solids[a]

Pretreatment	EAA content after extraction (%)		
	40:60 starch-EAA	60:40 starch-EAA[b]	80:20 starch-EAA
50:50 MeOH-H_2O	11·4	11·1 (9·3)	19·0
80:20 MeOH-H_2O	12·7	11·0 (10·7)	18·4
90:10 MeOH-H_2O	13·7	12·9 (11·1)	18·4
100: 0 MeOH-H_2O	14·0	12·9 (11·5)	18·4
50:50 MeOH-H_2O (No HCl)		13·8	
80:20 MeOH-H_2O (No HCl)		14·7	17·8
80:20 MeOH-H_2O (2 × HCl)		11·5	

[a] Composites prepared from jet-cooked starch. Films ground before extraction.
[b] Values in parentheses are for starch and EAA jet-cooked together.

Comparison of 60:40 cornstarch:EAA composites in Tables 6 and 5 (pretreatment with 50:50 methanol:water) shows only a small increase in complexation under the more dilute mixing conditions (11·1% EAA in the extracted product prepared at 1% solids versus 9·1% EAA for the 5% solids product). If 80:20 cornstarch:EAA composites are compared, however, those prepared at 1% solids contain almost twice as much unextractable EAA. These results can be explained in the same manner as the anomalous 90:10 example of Table 4, i.e. higher EAA content is probably an artifact caused by poor diffusion of water-immiscible solvent into the polymer matrix. Better mixing at 1% solids gives smaller domains of uncomplexed EAA and thus reduces solvent permeability by decreasing the size of voids formed during extraction. The fact that unexpectedly high EAA percentages are only observed in composites containing 20% EAA and not in those with 40 and 60% EAA lends support to this argument.

Values given in parentheses in Table 6 were obtained for a 60:40 composite prepared by passing a suspension of cornstarch in an aqueous ammonia solution of EAA through the jet-cooker (rather than jet-cooking the starch separately prior to mixing). This technique, which allows the two polymers to interact with maximum heating and mixing, did not lead to an increase in complexed EAA.

Waxy cornstarch-EAA composites were prepared at 1% solids under the same conditions as those used for cornstarch, and extraction results are presented in Table 7. As observed in Table 6 for cornstarch, the amount of EAA remaining after extraction of the 80:20 composite was about twice that remaining in the composite prepared with 40% EAA. Comparison of results in Tables 5 and 7 for the 60:40 composite shows more unextractable EAA when starch and EAA are mixed at 1% solids. One might speculate that better mixing at 1% solids allows amylopectin (which has less tendency to form helical inclusion complexes than amylose) to more efficiently interact with EAA.

Table 8 compares extraction results for 60:40 composites prepared from 1% jet-cooked dispersions of cornstarch, waxy cornstarch, high amylose cornstarch, defatted cornstarch, and potato starch. The three genetic varieties of cornstarch showed an increase in complexing ability as amylose content is increased, as observed in Table 5. Also in agreement with Table 5, removal of lipid from cornstarch gave no significant increase in complexing. Potato starch was not very different from cornstarch in its ability to form the EAA complex, indicating that chemically bound phosphate substituents in potato starch do not significantly influence complexation.

CONCLUSIONS

Complexes of EAA and starch can be prepared under a variety of experimental conditions by mixing water dispersions of starch at either 1 or 5% solids with

Table 7. Influence of starch-EAA ratio and extraction conditions on extractability of EAA from waxy cornstarch-EAA composites prepared at 1% solids[a]

Pretreatment	EAA content after extraction (%)	
	60:40 starch-EAA	80:20 starch-EAA
50:50 MeOH-H_2O	12·1	18·2
80:20 MeOH-H_2O	8·1	17·2
90:10 MeOH-H_2O	9·2	16·8
100: 0 MeOH-H_2O	8·8	16·3
80:20 MeOH-H_2O (No HCl)	17·0	

[a] Composites prepared from jet-cooked starch. Films ground before extraction.

Table 8. Influence of starch variety on extraction of EAA from 60 starch-40 EAA composites prepared at 1% solids[a]

Pretreatment	EAA content after extraction (%)				
	Corn	Waxy corn	High amylose corn[b]	Defatted corn	Potato
50:50 MeOH-H_2O	11·1	12·1	17·4	11·2	11·2
80:20 MeOH-H_2O	11·0	8·1	17·8	11·8	13·0
90:10 MeOH-H_2O	12·9	9·2	18·4	12·9	13·7
100: 0 MeOH-H_2O	12·9	8·8	18·0	13·2	13·8

[a] Composites prepared from jet-cooked starch. Films ground before extraction.
[b] Contains 70% amylose.

solutions of EAA. Extraction of air-dried composites with a solvent system composed of 1,1,2-trichloroethane, isopropanol, and toluene removes uncomplexed and loosely bound EAA. The EAA content of composites after extraction (as determined by FTIR) can be used to compare the complexing ability of various starches.

Since dextran cannot form helical inclusion complexes with EAA (because of α-(1→6) linkages between glucopyranosyl units), it can be used as a model polysaccharide to establish the efficiency of extraction. Experimental conditions that leave little or no residual EAA in a dextran-EAA composite should also efficiently remove uncomplexed EAA from analagous starch-containing materials.

Pretreatment of polysaccharide-EAA composites with methanol-water solution prior to extraction is essential for the efficient removal of uncomplexed EAA. However, the ratio of methanol:water needed to obtain maximum extraction efficiency varies with the polysaccharide used to prepare the composite. It is also necessary that methanol-water solutions be acidified to convert any residual ammonium carboxylate in the composite to carboxylic acid.

In starch-EAA composites, the amount of EAA complexed increases with increased gelatinization temperature, and therefore increased solubility and disruption of the starch granule matrix (starch gelatinized at 75°C < starch gelatinized at 95°C < jet-cooked starch). Complexed EAA also increases with the amylose content of the starch sample (waxy cornstarch < high amylose cornstarch). Removal of trace amounts of lipid from cornstarch by ethanol extraction does not significantly increase the amount of complexed EAA. In one representative composite, storage time at room temperature (i.e. length of time between preparation of composite and solvent extraction) had little effect on the amount of unextractable EAA.

Some increases in complexing of EAA are observed if composites are prepared from jet-cooked starch and EAA at 1% solids (as opposed to 5%), presumably because reduced viscosities obtained at the lower concentration permit more intimate mixing of the two polymer solutions. When prepared at 1% solids, 80:20 starch-EAA composites contain about twice as much EAA after extraction as those prepared at ratios of 60:40 and 40:60. These anomalous results are probably due to poor diffusion of solvent into the 80:20 composites because of their low EAA content. The complexing behavior of potato starch is not significantly different from that of cornstarch, indicating that phosphate substituents in potato starch do not influence complexing ability.

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