

Composites of Starch and Poly(ethylene-co-acrylic acid). Complexing between Polymeric Components

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Synopsis

Extrusion-blown film prepared from a semidry mixture of starch and poly(ethylene-co-acrylic acid) (EAA) cannot be sharply separated into its polymeric components by selective solvent extraction, and the two polymers have the outward appearance of being compatible. Also, the starch portion is resistant to enzyme attack, and starch domains are not visible by SEM. Further studies were therefore made on the starch-EAA system to determine reasons for the apparent compatibility between the two polymers, and evidence for polymer complex formation was obtained. Combination of aqueous ammonia solutions of starch and EAA led to an increase in viscosity, and a coprecipitate of starch and EAA separated from solution. Moreover, solvent extraction would not separate physical mixtures of starch and EAA prepared from aqueous solutions. Although both the linear (amylose) and branched (amylopectin) components of starch formed an apparent complex with EAA, a low molecular weight starch fraction and a high molecular weight dextran (a polysaccharide with α -(1 \rightarrow 6) linked glucopyranosyl units) did not. These observations support the theory that a helical inclusion complex is formed from starch and EAA, which is similar to the well-known complexes produced from starch and fatty acids.

INTRODUCTION

Composite systems containing starch and poly(ethylene-co-acrylic acid) (EAA) have been under investigation at the Northern Regional Research Center for a number of years, and Otey and co-workers have published a series of papers in which preparation and properties of these composites are described.¹⁻⁴ Starch sells for about 10-15 cents per pound, and it is perhaps the most abundant and lowest-cost natural polymer on the market. It is also completely biodegradable. Applications for extrusion-blown starch-EAA films originally centered on agricultural mulches, i.e., biodegradable films used to cover fields of high-value crops to suppress weed growth, to retain soil moisture, and to promote rapid germination by raising soil temperature. About 125 million pounds of polyethylene is currently used in the United States per year for this application, with a projected growth to 190 million pounds by 1990. Since films of this type must be removed from the fields and disposed of at a cost of \$100 or more per acre, the factor of biodegradability introduced by the presence of starch would be an important asset. Current interests in enhancing biodegradability in plastic bags and packaging and also in conserving our petrochemical-

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based resources by blending with annually renewable, natural polymers has further expanded the potential fields of use for composites of this type.

High levels of starch can be compounded successfully with EAA in the presence of either aqueous ammonia or aqueous alkali. Both starch and EAA are dispersible in these solvent systems and can thus be intimately mixed. This approach provided the first known thermoplastic polymer system containing high levels of gelatinized starch that could withstand the strain associated with extrusion blowing and yield quality films. Extrusion-blown starch-EAA films containing about 40% starch are uniform, flexible, transparent, and have good physical properties. There appears to be excellent compatibility between EAA and starch. Standard ASTM tests showed that blown films supported the growth of microorganisms if starch levels were about 40% or higher.² Compatibility between EAA and starch was similarly reported by Maxwell,⁵ who used blends of the two polymers in solution as water-resistant paper sizes. Maxwell also observed that addition of an aqueous ammonia solution of EAA to a water solution of starch resulted in a pronounced viscosity increase. Although polyethylene shows no compatibility with starch and gives poor quality films when extrusion blown under conditions used with EAA, Otey^{2,4} found that it was possible to incorporate polyethylene into a composite of starch and EAA and still get good film properties. Polyethylene films containing granular starch have been reported by Griffin⁶; however, these films contain low levels of starch and assume a paperlike consistency at starch levels approaching those used by Otey.

Otey and co-workers⁴ have suggested that compatibility between starch and EAA might result from hydrogen bond formation between EAA carboxyl groups and the hydroxyl substituents of gelatinized starch, although interactions between the two polymers were not examined in detail. Because of the commercial importance of these composites as biodegradable polymers, we have undertaken a study of EAA-starch interaction, and some of our initial experiments are described in this report. Evidence will be presented to support a theory that starch and EAA form a complex similar to known helical inclusion complexes formed between starch and fatty acids.

EXPERIMENTAL

Materials

EAA was Primacor 5981 from Dow Chemical Co. This polymer contains about 20% acrylic acid by weight and has a melt index of 300, M_w of about 18,000, and M_n of about 7000.⁷

Unmodified cornstarch (Globe 3005) was from CPC International. Amioca waxy cornstarch (amylopectin) and Avebe potato amylose were from National Starch and Chemical Corp. Acid-modified starch was Star-Dri 1 from A. E. Staley Mfg. Co., and M_n by membrane osmometry was 46,000. Dextran samples were industrial grade from Sigma Chemical Co. Average molecular weights of the two samples (reported by the manufacturer) were 266,000 and $5-40 \times 10^6$. Glucoamylase was Diazyme L-100, and α -amylase was Taka-Therm from Miles Laboratories.

A low molecular weight starch fraction was prepared by stirring 46.4 g (dry basis) of Stalex 90 acid-modified starch (A. E. Staley Mfg. Co.) in 500 mL of water overnight at room temperature. Insoluble solid was separated by centrifugation, 200 mL of ethanol was added to the supernatant, and the precipitated solid was again removed by centrifugation. The supernatant was freed of ethanol by dialysis against distilled water, centrifuged to remove traces of suspended solid, and freeze dried to yield 18.6 g of low molecular weight starch ($M_n = 5400$ by vapor phase osmometry).

Starch-EAA Blown Film

Film was prepared by Otey et al.,⁴ who mixed and extruded into strands the following formulation:

Unmodified cornstarch:	6.35 kg dry basis (40%)
EAA:	7.14 kg (45%)
Urea:	2.38 kg (15%)
Water:	1200 mL
Concentrated NH_4OH :	1320 mL

The extrudate was then extrusion blown into film with a thickness of about 1.7 mil and a lay-flat width of 12 in. Experimental details are given in Ref. 4.

Analyses

Scanning Electron Microscopy (SEM). Samples were mounted on aluminum stubs with double-sided tape and were coated with a 200 Å layer of gold-palladium (60-40) alloy. Samples were then examined and photographed in a Hitachi ISI scanning electron microscope.

Molecular Weights. Vapor phase osmometry and membrane osmometry of starch samples were carried out by Arro Laboratory, Joliet, IL.

Percentage EAA by Weight Loss on Hydrolysis. Accurately weighed samples of starch-EAA (0.2-0.5 g) were heated under reflux for 1.5 h in 50 mL of 0.5 N hydrochloric acid. Acid-insoluble fractions were separated by filtration, washed with water and with ethanol, and dried under vacuum. Infrared spectra of isolated polymers showed only weak polysaccharide absorption. Percentage EAA by weight was calculated from weight loss on hydrolysis, assuming 10% residual carbohydrate in the polymer.

RESULTS AND DISCUSSION

Initial experiments centered on an extrusion-blown film containing 40% starch, 45% EAA, and 15% urea prepared by Otey et al.⁴ on a pilot scale. Urea was used to enhance starch gelatinization at low water levels and low temperatures. As a first step in the examination of this film, a weighed sample was exhaustively extracted with water at room temperature. Recovered polymer amounted to 84.4% of the original weight, indicating that only urea had been

dissolved. A similar extraction at room temperature with 1 *N* sodium hydroxide, which is a commonly used solvent for starch, also removed little else beside urea. The starch component is therefore resistant to aqueous solvents at room temperature.

Portions of film (water-extracted to remove urea) were next treated with a glucoamylase and also with a high-temperature α -amylase to determine whether the starch portion could be degraded by these enzymes and then removed by water extraction. Digestion with glucoamylase was carried out for 45 h at 50°C and with α -amylase for 24 h at 90°C; however, in neither experiment was a significant amount of starch removed. In a control experiment, an extrusion-blown film prepared from a graft copolymer of starch and poly(methyl acrylate), containing about 50% starch, was digested with glucoamylase under identical conditions to give complete removal of the starch component. The starch portion of our starch-EAA film is thus less susceptible to enzyme attack than the starch portion of a graft copolymer.

Portions of film were finally allowed to stand for 20 h in either 6 *N* or 12 *N* hydrochloric acid to determine whether starch could be hydrolyzed and removed under these conditions. Room temperature was used so treated films could be examined by SEM without the danger of heat-induced changes in morphology. Digestion with 6 *N* hydrochloric acid removed 33.6% of the original film, whereas a 43.4% weight loss was observed in 12 *N* acid. Since part of this weight loss is due to extraction of urea, a significant amount of carbohydrate still remains in both films. No voids were observed in the 12 *N* acid-treated film when examined by SEM at 20KX (Fig. 1), even though about 70% of the starch component had been removed. Polysaccharide domains in the original film are therefore not large enough to be observed at this magnification.

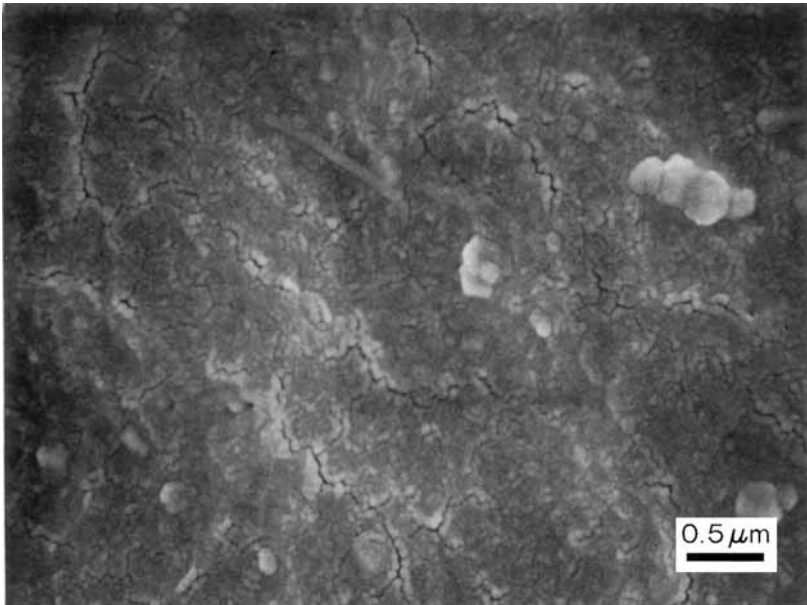


Fig. 1. Starch-EAA blown film after treatment for 20 h at room temperature with 12 *N* hydrochloric acid. Photographed at 19.9KX.

We next attempted to separate extrusion-blown film samples into their EAA and starch components by organic solvent extraction, after first washing out urea and then converting carboxylate salt substituents in the EAA portion to carboxylic acid by soaking in 0.025 *N* hydrochloric acid. EAA is readily soluble at about 75°C in a ternary solvent system composed of 15 : 15 : 70 (by weight) 1,1,2-trichloroethane : isopropanol : toluene, whereas starch is soluble in dimethylsulfoxide (DMSO) at this same temperature. Extractions were carried out on both air-dried and water-wet films [experiments 1 and 2 (Table I)] to take into account the possible formation of anhydride crosslinks when the film is allowed to dry in the acid form. In both experiments, a significant fraction, containing both starch and EAA, remained insoluble in both solvents and was a highly swollen gel in DMSO. Also, the DMSO-soluble fraction from the wet film extraction contained 5% EAA that had been carried over with the starch component. A scanning electron micrograph at 20KX of the film used in experiment 2 after extraction of unbound EAA with ternary solvent but before treatment with DMSO (Fig. 2) showed that the remaining EAA-containing starch was in the form of submicron-sized spheres.

The failure of enzymes to digest the starch component and the inability of good solvents for EAA and starch to cleanly separate extrusion-blown film into its component parts suggested interaction and/or bonding between the two components, but the mechanism of interaction was still not clear. In addition to assuming a complex between the two polymers, the data could also be explained by chemical bonding between starch and EAA. Extrusion blowing is a heat- and shear-intensive process, and the possibility exists not only for graft copolymer formation via chemical reaction between hydroxyl and carboxyl substituents but also for block copolymer formation by combination of macroradicals generated by shear-induced degradation. A series of experiments was therefore carried out to acquire evidence pertinent to these possibilities.

TABLE I
Extraction of Starch-EAA Films with Ternary Solvent^a and DMSO

Experiment	Film	Weight percent of original film		
		Soluble in ternary solvent (starch content) ^b	Soluble in DMSO (% EAA)	Insoluble (% EAA)
1	Extrusion blown, dry	45 (0)	25 (0) ^b	30 (12)
2	Extrusion blown, wet	48 (trace)	36 (5)	16 (9)
3	Cast from aqueous NH ₃ ^c	39 (0)	26 (11)	35 (11)
4	Cast from aqueous NH ₃ -NaOH ^d	43 (0)	13 (trace) ^b	44 (20)

^a Ternary solvent: 15 : 15 : 70 (by weight) 1,1,2-trichloroethane : isopropanol : toluene.

^b Estimated from infrared spectrum.

^c 1 : 1 weight ratio of starch : EAA.

^d 1 : 1.25 weight ratio of starch : EAA.

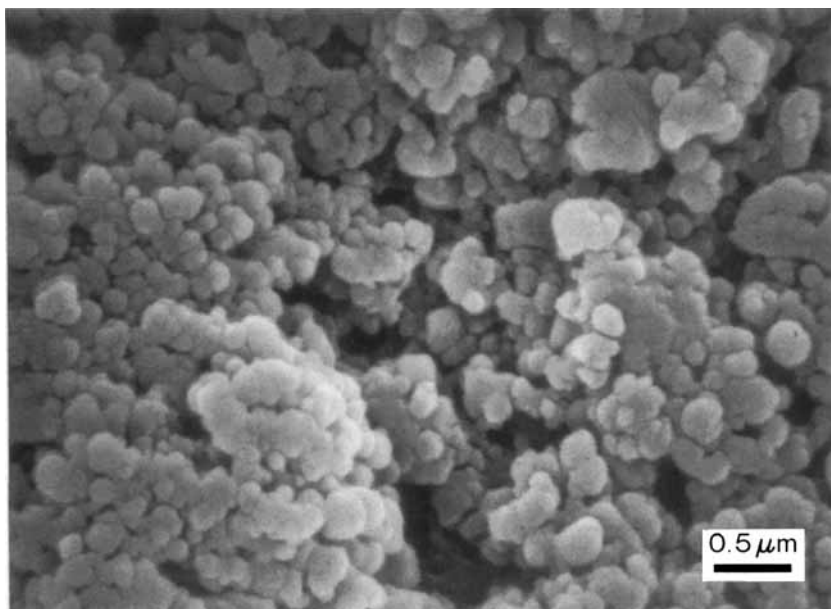


Fig. 2. Starch-EAA blown film after extraction of unbound EAA. Photographed at 20.4KX.

A physical mixture of corn starch and EAA was prepared by combining the following two polymer systems: (1) a solution of 2.5 g of EAA in 25 mL of 50 : 50 (vol) concentrated NH_4OH : water and (2) a dispersion obtained by heating (75°C) 2.5 g of starch in 50 mL of the same solvent [experiment 3, (Table I)]. In agreement with Maxwell,⁵ we observed an increase in viscosity when the two systems were combined. The mixture was allowed to air-dry, the resulting film was converted to the acid form, and the moist film was next extracted with ternary solvent and with DMSO by the same procedure used for extrusion-blown film. This physical mixture also could not be separated into its components by solvent extraction, indicating that high temperature and shear are not necessary for interaction between starch and EAA. To ensure that starch was completely soluble when the physical mixture with EAA was prepared, a similar experiment (experiment 4) was carried out with starch dissolved in 1 *N* sodium hydroxide. Solvent extraction gave results similar to experiment 3.

Because viscosity increases were observed by both Maxwell⁵ and ourselves when starch and EAA were combined, this phenomenon was investigated in more detail (Table II). When equal weights of starch (dissolved in 1 *N* sodium hydroxide) and EAA (dissolved in aqueous ammonia) were combined at a total concentration of 2 g in 70 mL, the Brookfield viscosity of the mixture was 1840 cP. Control experiments in which (1) EAA solution was combined with 1 *N* sodium hydroxide and (2) starch solution was combined with aqueous ammonia produced viscosities that were lower by over an order of magnitude. Although dilution with water to about 500 mL produced only slight turbidity in the two control solutions, the starch-EAA mixture was highly turbid, and centrifugation followed by water washing afforded 1.4 g of insoluble polymer containing 42%

TABLE II
Combination of Starch and EAA Solutions. Viscosity and Product Composition.
Comparison with Controls

Component A	Component B ^a	Brookfield viscosity ^b (cP)	Insoluble product ^c
1 g starch in 50 mL of 1N NaOH	1 g EAA in 20 mL of aqueous NH ₃	1840	1.4 g (42% EAA)
50 ml 1N NaOH	1 g EAA in 20 mL of aqueous NH ₃	20	None
1 g starch in 50 mL of 1N NaOH	20 mL of aqueous NH ₃	52	None

^a Aqueous NH₃ was prepared by combining equal volumes of concentrated NH₄OH and water.

^b Run at 30 rpm with number 3 spindle.

^c Isolated by diluting the mixture with water to about 500 mL, centrifuging, water washing, and freeze drying.

EAA. An adduct between starch and EAA will thus precipitate from solution by simply mixing aqueous alkaline solutions of the two components. Since it is difficult to visualize a rapid chemical reaction between the two polymers under such mild conditions, these data provide evidence for complex formation.

To determine whether starches having a lower molecular weight than unmodified starch would also form complexes of this type, we prepared a low molecular weight ($M_n = 5400$), cold water-soluble starch fraction and studied its behavior with EAA. Contrary to unmodified starch, an aqueous ammonia solution of this starch fraction produced little or no increase in Brookfield viscosity when combined with a solution of EAA [Table III (experiment 1)]. Moreover, when the mixture was allowed to air-dry and the resulting film was extracted with water, a clean separation of starch and EAA was obtained. Good separation was also observed when the aqueous mixture was acidified to pH 2.5 (experiment 2), since EAA precipitated as a flocculant solid whereas starch remained in water solution. Results were not greatly different when the low molecular weight starch fraction was dissolved in 1 N sodium hydroxide (experiment 3). These experiments show that no EAA complex is formed from starch with a molecular weight as low as 5400.

We next ran a similar series of experiments with a commercial, warm water-soluble, acid-modified starch of intermediate molecular weight ($M_n = 46,000$). Although little or no increase in viscosity was observed when aqueous ammonia solutions of EAA and acid-modified starch were combined [Table III (experiment 4)], complexing evidently occurred, since water extraction of the resulting air-dried film did not give sharp separation of components. About 30% of the starch remained in the water-insoluble fraction, whereas about 8% of the starting EAA was held in water solution by starch. As a control experiment, an aqueous ammonia solution of acid-modified starch was allowed to air-dry in the absence of EAA, and the resulting film was extracted with water under identical conditions. All but 8% of the starch dissolved in water at room temperature. Acidification of an aqueous ammonia solution of EAA and acid-modified starch (experiment 5) gave soluble and insoluble fractions with roughly

TABLE III
 Combination of EAA Solution^a with Starches of Different Molecular Weights. Viscosity and Water Extraction of Composites

Experiment	Starch and solvent ^b	Brookfield viscosity of blend (cP) ^c	Dry before extraction	Acidify before extraction	Water-insoluble fraction	Water-soluble fraction
1	$M_n = 5400$; 1 g in 55 mL aqueous NH_3	2.6	Yes	No	0.90 g (0 starch)	0.94 g (0 EAA)
2	Same as Experiment 1		No	Yes	0.99 g (0 starch)	0.8 g (0 EAA)
3	$M_n = 5400$; 1 g in 55 mL 1N NaOH	5.8	Yes	Yes	0.95 g (0 starch)	Not determined
4	$M_n = 46,000$; 1 g in 55 mL aqueous NH_3	4.0	Yes	No	1.24 g (25% starch)	0.72 g (11% EAA)
5	Same as Experiment 4		No	Yes	1.24 g	0.82 g (14% EAA)

^a EAA solution prepared by heating 1 g EAA in 20 mL of a 50 : 50 (vol.) mixture of concentrated NH_4OH and water.

^b Aqueous ammonia prepared from 50 mL water and 5 mL concentrated NH_4OH .

^c Run at 30 rpm.

the same compositions as those observed in experiment 4. In another control experiment, acid-modified starch gave no precipitate when a water solution was acidified under identical conditions. Experiments in Table III thus show that starch molecular weight must be above some critical (but as yet unknown) value before complexing with EAA will occur.

To help understand the nature of the starch-EAA complex, experiments were carried out to determine (1) whether another polysaccharide with a structure different from starch would also form a complex and (2) whether branching in the starch polymer influences complexing ability. Aqueous ammonia solutions of EAA were thus combined with solutions of dextran (a microbial polysaccharide), waxy cornstarch (which is composed of highly branched amylopectin), and amylose (the linear fraction of starch). Table IV gives Brookfield viscosities of these mixtures as well as the weight and composition of the precipitated polymer complex isolated by dilution and centrifugation.

Although dextran is a poly (glucopyranose) like starch, the two polymers are structurally different. In starch, α -(1 \rightarrow 4) linkages between glucopyranosyl units cause the polymer chains to assume a helical configuration,⁸ whereas no such configuration is possible with dextran because the predominant linkage between glucopyranosyl units is α -(1 \rightarrow 6). The α -(1 \rightarrow 4) linkage found in starch is apparently critical for complex formation because combined solutions of dextran (MW 5-40 \times 10⁶) and EAA exhibit little or no increase in Brookfield viscosity. Moreover, dilution and centrifugation yields a negligible weight of insolubles. In contrast, large viscosity increases are observed with both branched (amylopectin) and linear (amylose) components of starch, and over half of the combined weight of the two polymers separates from the mixture upon dilution and centrifugation. Although Table IV shows that differences in complexing indeed exist between the linear and branched components of starch, branching is apparently not a critical factor in complexing ability.

To further document differences in complexing ability between dextran and starch, aqueous ammonia solutions of dextran (MW 266,000) and EAA were

TABLE IV
Complex Formation between EAA^a and Different Polysaccharides

Polysaccharide ^b	Brookfield viscosity ^c	Insoluble product ^d	
		Weight (g)	Weight percent EAA
Dextran (MW 5-40 \times 10 ⁶)	7.7	0.015	
Amylopectin	3940	2.5	42
Amylose	1426	2.5	31

^a EAA solution was prepared by heating 2 g of EAA in 40 mL of a 50 : 50 (vol.) mixture of concentrated NH₄OH and water.

^b 2 g polysaccharide in 75 mL aqueous ammonia. Dextran was dissolved in water at room temperature. Amylopectin and amylose were steam-jet cooked. Concentrated NH₄OH was then added in a volume ratio of 1 part NH₄OH to 10 parts polysaccharide solution. Brookfield viscosities before mixing with EAA solution: dextran (46 cP), amylopectin (14 cP).

^c Run at 30 rpm.

^d Isolated by centrifugation after diluting with about 1 L of aqueous ammonia. Samples washed with aqueous ammonia and freeze dried.

combined and allowed to air-dry, and the resulting film was then extracted with water as in experiment 4, Table III. In contrast to the film from EAA and acid-modified starch ($M_n = 46,000$), dextran and EAA could be separated by water extraction. The infrared spectrum of water-insoluble EAA showed only trace absorption in the 1000 cm^{-1} region for polysaccharide, and the soluble dextran showed no carbonyl absorption for EAA. A mixed solution of dextran and EAA was also cleanly separated by acidification to pH 2.5 under the conditions of experiment 5, Table III. Although comparable experiments with EAA and dextran (MW $5\text{--}40 \times 10^6$) were not as clean cut due to the higher molecular weight and lower water solubility of this particular dextran sample, a sharper separation of components by water extraction was observed than for acid-modified starch-EAA mixtures.

CONCLUSIONS

Experiments suggest that starch and EAA associate to form a complex when the two polymers are mixed under alkaline conditions, and this complex helps promote compatibility between the two polymers, for example, during the extrusion-blowing experiments carried out by Otey et al.²⁻⁴ Our results cannot be explained simply by chain entanglement since interaction to give both a viscosity increase and a coprecipitate occurs immediately upon mixing dilute polymer solutions. The low molecular weight of EAA (M_n about 7000) provides an additional argument against this explanation. It is also difficult to explain our results by hydrogen bonding or van der Waals forces between the two polymers since interactions of this type would be nearly identical with starch and dextran.

Even though we have no direct proof for a helical inclusion complex, formation of a structure of this type is a reasonable explanation because it is well known that starch forms such complexes with a number of different compounds. The characteristic blue complex resulting from addition of iodine-potassium iodide solution to starch has been known for over 150 years,⁹ while fractionation of starch into its amylose and amylopectin components by selectively complexing amylose with butanol was first published in 1942 by Schock.¹⁰ In 1946, Mikus et al.¹¹ presented evidence for the helical structure of amylose-fatty acid inclusion complexes, and numerous publications devoted to complexes of this type have since appeared in the literature. Complexed amylose exhibits a characteristic V pattern when examined by X-ray diffraction.¹² The helical macromolecule formed from repeating α -(1 \rightarrow 4) glucopyranosyl units has its hydrogen atoms located inside the helix, thus giving the helical cavity a hydrophobic surface necessary for compatibility with guest molecules. In amylose-fatty acid complexes, the starch helix typically has six glucopyranosyl units per turn; and each turn amounts to 8 Å along the helix axis.¹² Although complexing with amylopectin can similarly take place by way of the outer branches of the polymer,¹³ complexing is inhibited by the shorter length of these outer branches as compared with amylose. Reduction of starch molecular weight by treatment with acid or enzymes should inhibit complex formation even further.

EAA used in this study is a random copolymer containing 20% acrylic acid by weight, and this composition roughly corresponds to that of a $C_{23}\text{--}C_{24}$ fatty acid. Karkalas and Raphaelides¹⁴ showed that amylose formed complexes at

pH 12 with the potassium salts of fatty acids having chain lengths up to C₂₂, and their research does not suggest that complexing would be inhibited with fatty acids of higher molecular weight. Since the structure of the EAA polymer may be viewed as a number of fatty acid repeating units linked together through carbon-carbon bonds, crosslinking could theoretically take place if a molecule of EAA complexes with more than one polysaccharide molecule. Crosslinking in this manner could account for the instantaneous viscosity increases and the formation of precipitates observed when solutions of the two polymers are combined.

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

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