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Complexes of starch with telechelic poly(ε-caprolactone) phosphate

R. L. Shogren

Plant Polymer Research Unit, National Center for Agricultural Utilization Research, Agricultural Research Service, US Department of Agriculture, 1815 N. University St., Peoria, IL 61604, USA*

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The interaction of starch with poly(ε-caprolactone) having end-linked phosphate groups (PCL phosphate) was studied in order to determine if aliphatic polyesters could form inclusion complexes with starch similar to those formed from amylose and fatty acids. Normal cornstarch co-jet cooked with aqueous PCL phosphate solutions formed highly viscous gels on cooling, whereas jet-cooked starch solutions had low viscosities. Solutions of waxy maize starch had low viscosities after jet cooking either with or without PCL phosphate, while high amylose starch formed gels with or without PCL phosphate. Essentially all amylose precipitated from a dilute solution upon addition of PCL phosphate solution. After extraction with a solvent for the PCL phosphate, about 0·1 g PCL phosphate remained bound per g of amylose. X-ray diffraction and CP/MAS C-13 NMR studies showed that the PCL phosphate/amylose complexes adopt a semi-crystalline, V-type helical inclusion structure.

INTRODUCTION

There has been much interest recently in the utilization of gelatinized starch for single-use biodegradable plastic items (Stepto & Tomka, 1987; Roper & Koch, 1990; Lai & Kokini, 1991; Wiedmann & Strobel, 1991). However, starch alone or in blends with other hydrophilic polymers can be very water sensitive. Previous work at this laboratory has shown that starch and poly(ethylene-co-acrylic acid) (EAA) can be extrusion processed into films and molded items having fair mechanical properties and moisture resistance (Otey *et al.*, 1980). The partial compatibility of these very dissimilar polymers results from the formation of helical, V-type inclusion complexes similar to those formed from amylose and fatty acids (Fanta *et al.*, 1990; Shogren *et al.*, 1991*a*, *b*). EAA interacts favorably with the hydrophobic interior of the amylose helix and displaces water molecules to the more hydrophilic exterior of the helix. Because EAA biodegrades extremely slowly (Imam *et al.*, 1992), it would be desirable from the standpoint of environmental protection to find a substitute for EAA that would biodegrade more rapidly.

Poly(ε-caprolactone) (PCL), is a linear synthetic polyester having the repeating structure $[-(CH_2)_5COO-]_n$. Hydroxyl groups are present at both ends of the polymer chain because polymerization of ε-caprolactone is normally initiated with a diol. Such polymers having unique functional end groups are termed telechelic. PCL is readily degraded by microorganisms on land and in the ocean (Lisuardi *et al.*, 1992; Nishida & Tokiwa, 1992), but is quite hydrophobic and incompatible with starch. Therefore, in order to increase the hydrophilicity of PCL diol sufficiently to permit entry into the aqueous starch phase, chemical modification of the PCL would be necessary. This paper describes modification of the hydroxyl end groups of a low molecular weight PCL diol to phosphate groups and the interaction of the modified PCL with various starches and amylose.

EXPERIMENTAL

Materials

PCL diol, nominal molecular weight 2000, was obtained from Polysciences, Inc. A polymer of this size was

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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.

chosen since previous studies have shown that aromatic polyesters with carboxyl end groups formed stable emulsions in water when molecular weights were below 2500 (Cuirassier *et al.*, 1989). Pearl cornstarch was Buffalo 3401 from CPC, high (70%) amylose cornstarch was amylomaize VII from American Maize-Products and waxy maize starch was amioca from National Starch and Chemical. Corn amylose was prepared by the method of Schoch (1945). Phosphorus oxychloride ($POCl_3$, 99%) was from Aldrich Chemical Co.; other chemicals were reagent grade.

Synthesis of PCL phosphate

In a typical reaction, 400 g of PCL diol (0·4 mole hydroxyl) was heated to 50–60°C in a 1·5 liter resin flask equipped with a thermometer, water-cooled condenser, motorized stirrer, nitrogen inlet, dropping funnel and heating mantle. After purging with nitrogen, 68 g (0·44 mole) $POCl_3$ was slowly added with stirring to the melted PCL. The reaction was allowed to proceed overnight. The molten mixture was then poured into 700 ml of 2 M $NaHCO_3$ at 50°C with stirring. The resulting paste had a pH of approximately 7·5. The paste was diluted with 2 liters of distilled water to give a fluid dispersion, precipitated with 2 liters of ethanol, extracted with water (to remove sodium phosphate) and air-dried. Alternatively, the paste was first air-dried and then extracted with water and again air-dried. The yield was typically 70–80% based on the recovered polymer weight.

Viscosity of jet-cooked starch-PCL phosphate pastes

A Penick & Ford steam jet cooker operated at 65 psi line and 40 psi back pressure (141°C) was used. In the jet cooking process, a stream of high-velocity, high-pressure steam mixes turbulently and intimately with an incoming stream of starch slurry, which rapidly gelatinizes and disrupts the starch granules (Klem & Brogly, 1981). Cornstarch, amylomaize VII and waxy maize starch were jet cooked individually and with 10% added PCL phosphate (dry-weight basis) and then cooled to room temperature over 30 min. Viscosities were measured at 25°C with a Brookfield Synchroelectric Viscometer, model LVT, using spindle no. 4 for cornstarch and amylomaize and spindle no. 2 for waxy maize. Starch solids contents were approximately 5% after cooking as determined by vacuum drying at 110°C for 2 h.

Preparation of amylose/PCL phosphate complexes

Amylose solutions (4%) were prepared by magnetic stirring of amylose in 1 M NaOH for 1 h at room temperature. These solutions were then diluted with distilled water to 0·25% amylose concentration, titrated with 1 M HCl to pH 7 and heated to 90°C. The required volume of hot (80°C) 1% PCL phosphate dispersion was added to the hot amylose solution to prepare mixtures having PCL phosphate/amylose ratios (w/w) of 0·1/1, 0·25/1, 0·5/1 and 1/1. Precipitates appeared on cooling and were allowed to settle overnight. Precipitates were collected by centrifugation and were air-dried. Samples were placed in stainless steel vials with two stainless steel balls; the vials were cooled in liquid nitrogen and then were shaken with a Wig-L-Bug amalgamator (Crescent Dental Mfg.) to pulverize the samples. Amorphous amylose was prepared by dialyzing and then lyophilizing a 0·1% amylose solution prepared as described above. All samples were equilibrated at 50% relative humidity at 23°C in a constant temperature/humidity room prior to NMR and X-ray analysis. To extract loosely bound PCL phosphate, a portion of the complex (50 mg) was first swelled in methanol/water 1/1 for 1 h then stirred with 20 ml chloroform/methanol/water 10/10/1 for 1 day and centrifuged.

Analytical methods

X-ray powder diffraction analysis was performed with a Philips 1820 diffractometer operated at 40 kV, 30 mA with graphite filtered CuK_α radiation and a theta compensating slit. Data was acquired in 0·05 degree two theta, 4 s steps. CP/MAS C-13 NMR spectra were obtained using a Bruker MSL-300 spectrometer. Samples were spun in zirconia rotors at approximately 3400 Hz. Pulse widths, mix times and delay times were 7 μs, 0·5 ms and 5 s, respectively. FTIR spectra were obtained with a Mattson Polaris instrument operating at 4 cm^{-1} resolution. Samples (1 mg) and 300 mg of KBr were pulverized by shaking with two stainless steel balls inside a steel vial and were then pressed into a disc. Compositions of the PCL phosphate/amylose complexes were determined by comparison of the ratios of the areas of the PCL $C = O$ stretching vibration (1700–1800 cm^{-1}) to the amylose C-O stretch (950–1210 cm^{-1}) after subtraction of the PCL contribution to the C-O stretch. Areas were measured by cutting and weighing. A calibration curve was constructed from analytical data for starch/PCL phosphate mixtures of known composition.

RESULTS AND DISCUSSION

Characterization of PCL phosphate

The phosphorus content of purified PCL phosphate was 2·1% as determined colorimetrically after $Mg(NO_3)_2$ ashing, reaction with ammonium molybdate, hydroquinone and sodium sulfite (Williams, 1984). The same phosphorus content was also found in a PCL phosphate sample synthesized with a 2-fold molar excess of $POCl_3$ over that required to completely esterify the PCL hydroxyl groups. This suggests that derivatization is complete using a small excess of reagent. The data are consistent with a molecular weight of 2900 for the PCL phosphate and about 2600 for the base PCL diol (after substracting the weights of the phosphate end groups.)

FTIR spectra of PCL phosphate and unmodified PCL diol were obtained from film solutions cast onto a ZnSe disc and are shown in Fig. 1. No carboxylate stretching vibration (1550–$1600\,cm^{-1}$) is noted, suggesting that little hydrolytic degradation of the PCL occurred during the reaction with $POCl_3$. Note also the decrease in intensity of the O-H stretching band at $3450\,cm^{-1}$ for the PCL phosphate. At least part of the residualO-H stretching band is due to water bound to the phosphate groups as vacuum drying causes a decrease in its absorption intensity.

PCL phosphate can be dispersed in water when heated above the melting point of the PCL (50°C). These dispersions are stable for weeks at room temperature.

Viscosity of starch-PCL phosphate pastes

Double logarithmic plots of viscosity *versus* spindle rotation rate for jet-cooked cornstarch with and without added PCL phosphate are shown in Fig. 2. The jet-cooked cornstarch/PCL phosphate mixture was gel-like on cooling and had a viscosity about 70 times larger than cooked cornstarch alone at 30 rpm. The viscosity of the PCL phosphate suspension alone was not measurably different from water (1 cp). Viscosity data for jet-cooked waxy maize with and without PCL phosphate are shown in Fig. 3. Viscosities of the waxy maize starch/PCL phosphate mixtures were only three times higher than waxy maize starch alone. This suggests that PCL phosphate complexed strongly with the amylose component of cornstarch to form a three-dimensional network, while PCL phosphate and amylopectin interacted only weakly. The data in Fig. 4 show that amylomaize VII and PCL phosphate also form highly viscous mixtures. Amylomaize VII solutions, however, also exhibit high viscosities on cooling due to retrogradation. Previous work (Miles *et al.*, 1985) has shown that a rapid phase separation of amylose from water followed by a slower crystallization of amylose to the B form produces junction zones and the observed gelation. Similarly, amylose-PCL phosphate complexes can crystallize into the V-form (see below), giving rise to a network.

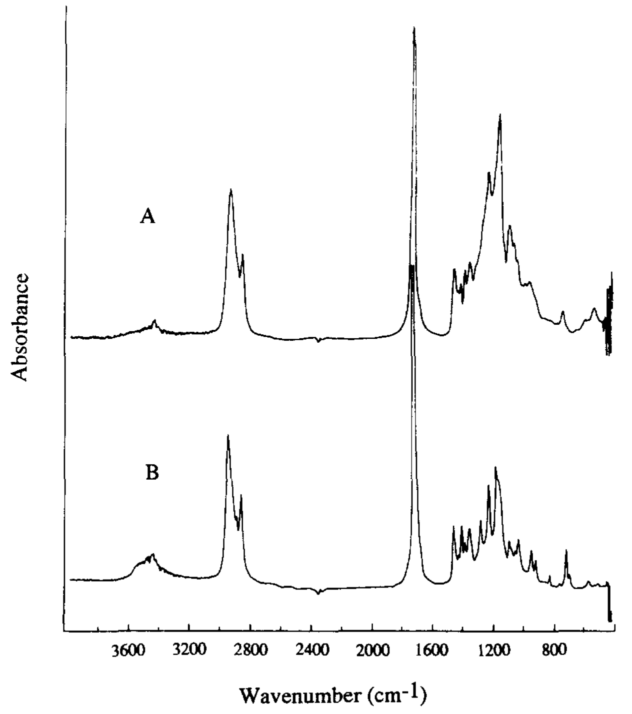

Fig. 1. FTIR spectra of poly(ε-caprolactone) phosphate (A) and poly(ε-caprolactone) diol (B).

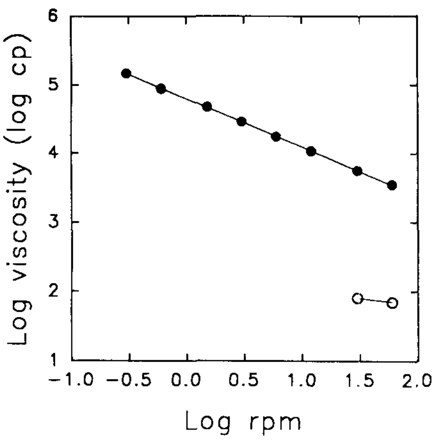

Fig. 2. Brookfield viscosities (25°C) of jet cooked normal cornstarch, 4·4% (○) and co-jet cooked normal cornstarch, 4·8% and PCL phosphate, 0·5% (●)

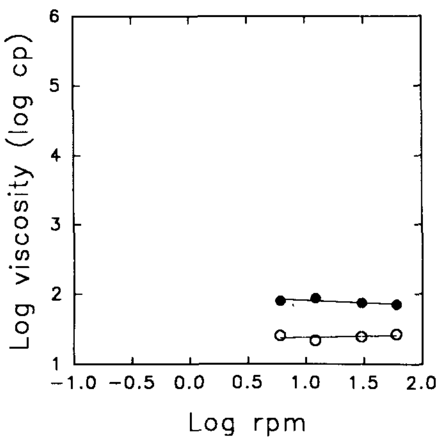

Fig. 3. Brookfield viscosities (25°C) of jet-cooked waxy maize starch, 5·0% (○) and co-jet cooked waxy maize starch, 5·0% and PCL phosphate, 0·5% (●).

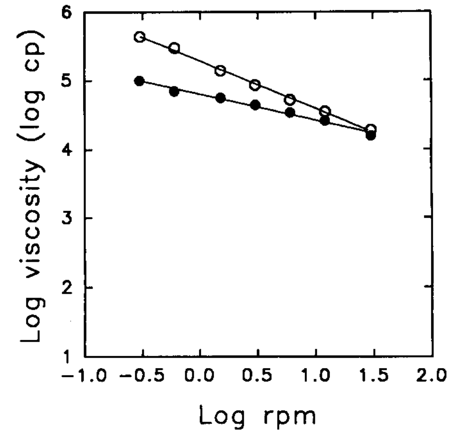

Fig. 4. Brookfield viscosities (25°C) of jet-cooked amylomaize VII, 5·2% (○) and co-jet cooked amylomaize VII, 5·1% and PCL phosphate, 0·5% (●).

Characterization of amylose/PCL phosphate complexes

In order to study the structure of the complexes in more detail, mixtures of pure amylose with various amounts of PCL phosphate were prepared. Table 1 presents the compositions of both the initial solution mixtures and the precipitates obtained after cooling the mixtures. When 0·25 g or more PCL phosphate is added per g of amylose, more than 99% of the amylose precipitates as an insoluble solid. These precipitates contain PCL phosphate and amylose in a weight ratio (g PCL phosphate/g amylose) of 0·22–0·33/1. After extraction of the 0·33/1 precipitate with chloroform/ methanol/water 10/ 10/1, a solvent for the PCL phosphate, the precipitate contained 0·1/1 PCL phosphate/amylose.

X-ray powder diffraction scans of the above precipitates as well as amorphous amylose and PCL phosphate are shown in Fig. 5. The amylose/ PCL phosphate complexes have two strong diffraction maxima at 12·4 and 19·6 degrees two theta, respectively. These correspond to $d = 7{\cdot}1$ and 4·5 Å and are similar to the 200 and 310 reflections obtained for fatty acid/amylose complexes (Mikus *et al.*, 1946). Such complexes were indexed using an orthorhombic unit cell having $a = 13{\cdot}6$, $b = 23{\cdot}7$ and $c = 8{\cdot}1$ Å (Zobel *et al.*, 1967). The amylose chains assume a 6_1 left-handed helical conformation (designated V) with the fatty acid occupying the helix interior (Zobel, 1988). Our X-ray data strongly suggest a similar conformation for the amylose/PCL phosphate complexes in which the PCL occupies the amylose helix interior. The broad width of the diffraction peaks in Fig. 5, similar to those observed for complexes of amylose with EAA (Shogren *et al.*, 1991*b*), implies that the crystallites are rather small. Assuming typical bond angles and lengths (Karkalas & Raphaelides, 1986) for PCL in a zig-zag configuration, one can calculate a theoretical weight ratio of 0·11/1 PCL/amylose in the complex. This agrees well with the experimental ratio of 0·1/1 found for the complex after extraction of loosely bound PCL.

Table 1. Composition of amylose/poly(caprolactone) phosphate complexes precipitated from solution mixtures

PCL phosphate/ amylose in solution mixture (w/w)	PCL phosphate/ amylose in precipitate (w/w)	Amount of amylose precipitated (%)
0·1/1	0·13/1	75
0·25/1	0·22/1	99
0·5/1	0·33/1	99
1/1	0·23/1	99

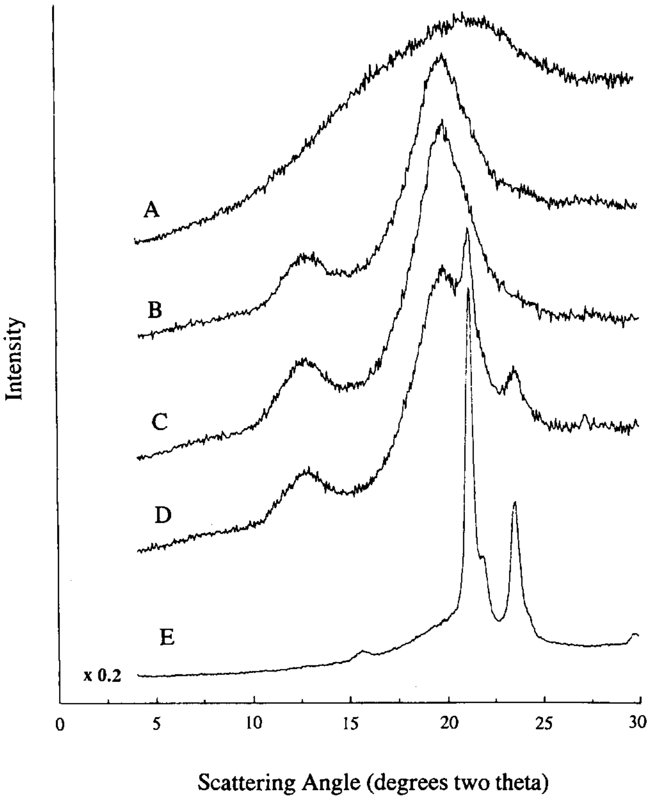

Fig. 5. X-ray powder diffraction scans of amorphous amylose (A), PCL phosphate/amylose 0·13/1 (B), PCL phosphate/ amylose 0·22/1 (C), PCL phosphate/amylose 0·33/1 (D) and PCL phosphate (E).

A diffraction scan for pure PCL phosphate is also included in Fig. 5 for comparison. Neither of the two strong peaks associated with the PCL (two theta = 1·3, 23·6) are evident in scans for the PCL phosphate/ amylose 0·13/1 and 0·22/1 complexes. This suggests that the PCL phosphate interacts strongly with amylose and is not free to crystallize.

CP/MAS C-13 NMR spectra of PCL phosphate/ amylose complexes, amorphous amylose and PCL phosphate are shown in Fig. 6. It is apparent that the complexes have a sharp C1 resonance at 103 ppm while amorphous amylose has more prominent broad components at 95–98 ppm. Previous studies have shown

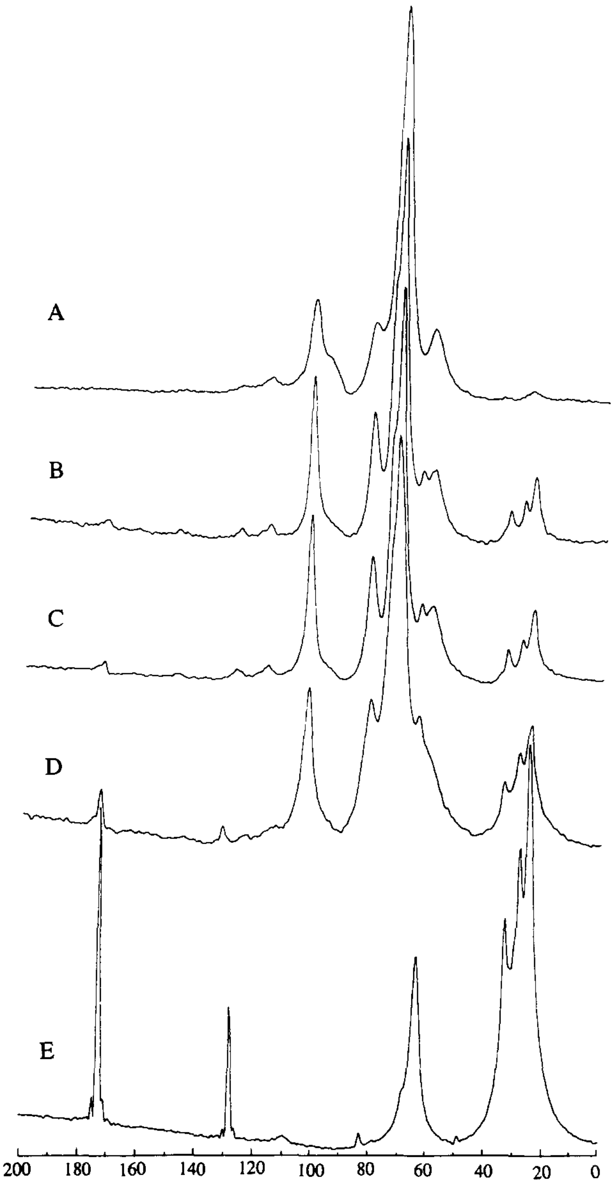

Fig. 6. CP/MAS C-13 NMR spectra of amorphous amylose (A), PCL phosphate/amylose 0·13/1 (B), PCL phosphate/amylose 0·22/1 (C), PCL phosphate/amylose 0·33/1 (D) and PCL phosphate (E).

that the resonance at 103 ppm reflects the V-type amylose structure while resonances at 95–98 ppm reflect disordered conformations (Gidley & Bociek, 1985). Thus the NMR data also support the notion of the formation of the PCL phosphate/amylose helical inclusion complexes.

These results represent the first report of the formation of an inclusion complex between a polyester type polymer and amylose. The interaction of amylose with PCL phosphate as described above may provide a mechanism for increasing the adhesion and strength of blends of these two materials in biodegradable films and molded items. Such blending is desirable to reduce the cost of the product as well as to increase tensile modulus and modify biodegradation rates. It is conceivable that such complexation might also occur between amylose and other degradable polyesters such as poly(lactides) or poly(hydroxy-butyrate-co-valerate).

Preliminary studies of ribbons extruded from amylomaize VII with 10% added PCL phosphate and 30% water at 180°C have indicated that such materials are very brittle (1% elongation at break after 4 weeks at 50% RH) compared to amylomaize VII alone (15% elongation at break). The greater brittleness may be caused by the formation of large amounts of semi-crystalline amylose V-type complexes in the ribbon containing the PCL phosphate. These complexes would be relatively well ordered, rigid and less able to absorb mechanical stresses than the more disordered, amorphous amylose.

In order to achieve good mechanical properties in these systems, the molecular weight of the polyester would probably need to be at least an order of magnitude greater than the 2000 molecular weight PCL used in the present model studies. Such higher molecular weight polyesters, even after modification of their end groups with ionic substituents, would probably not be water dispersible. However, the ends of the polyester chains might retain enough hydrophilicity to enter the aqueous starch phase with intense mixing and encourage complex formation. Alternatively, PCL containing ionic groups spaced evenly along the chain could possibly be synthesized by copolymerization. Such a polymer might have enough water dispersibility to allow complex formation and good interfacial adhesion between the starch and polyester.

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