Aqueous Carbon Black Dispersions Prepared with Steam-Jet-Cooked Corn Starch

James A. Kenar,[1] Frederick C. Felker,[1] George F. Fanta[2]

[1]*Agricultural Research Service, National Center for Agricultural Research Utilization, Functional Foods Research, U.S. Department of Agriculture, 1815 North University Street, Peoria, Illinois 61604*
[2]*Agricultural Research Service, National Center for Agricultural Research Utilization, Plant Polymer Research, U.S. Department of Agriculture, 1815 North University Street, Peoria, Illinois 61604*

Received 14 September 2011; accepted 9 December 2011
DOI 10.1002/app.36645

ABSTRACT: The utilization of jet-cooked waxy and normal corn starch to prepare aqueous dispersions of hydrophobic carbon black (CB; Vulcan XC-72R) is reported. Blending into aqueous jet-cooked dispersions of starch followed by high-pressure homogenization produced stable aqueous CB dispersions. The dispersed CB particles were shown to have starch adsorbed onto their particle surfaces. The adsorbed starch imparted hydrophilic properties to the CB, and after extensive washing to remove dissolved and loosely bound starch, the CB particles remained well dispersed in water. Thermogravimetric analysis, Fourier transform infrared spectroscopy, acid and enzymic starch digestion experiments, and microscopy (light and transmission electron microscopy) were used to characterize the starch-coated CB particles. The method described herein demonstrates a simple, effective, and environmentally friendly method for preparing aqueous CB dispersions. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: carbon black; dispersions; polysaccharides; renewable resources; TEM

INTRODUCTION

Carbon black (CB) is a generic term for an important family of intensely black, finely divided amorphous carbons prepared on an industrial scale by the thermal cracking or decomposition of petroleum oil feedstocks.[1,2] CB is mainly used as a reinforcement filler for rubber and other polymers, in plastics for its antistatic, conductive, and UV-protective properties, and as an important pigment in ink, toner, coating, and packaging applications.[1,3–5] CB can be classified into three main classes of highly polydisperse particles, namely, primary, aggregate, and agglomerate particles.[1,2] Primary CB particles are the smallest in size, having typical diameters of 10–75 nm, and do not usually exist as discrete particles. These primary particles are fused together to form secondary larger aggregate structures that typically range in size from 200 to 1000 nm. The three-dimensional aggregate morphology of the fused primary particles constitutes the actual basic units of CB and represents the main dispersible elements of CB. Finally, interparticle attractions between these aggregates weakly bind them with one another to form larger clusters of agglomerates, which range to sizes exceeding 1000 nm.[1]

The demand to reduce pollution from volatile organic compounds has led to the development of aqueous-based CB products.[6–9] Because of CB's highly hydrophobic nature and its predisposition toward interparticle van der Waals attractions, the wetting and dispersion of CB into water is difficult and tends to cause CB particle aggregation and produce unstable aqueous dispersions that greatly limit utility.[9–11]

To disperse CB into aqueous media, several fundamental approaches have been reported: (1) the oxidative chemical modification of CB particle surfaces to introduce hydrophilic polar moieties,[6–8] (2) the use of traditional amphiphilic molecules (low-molecular-weight surfactants or higher molecular weight surface-active polymers) to wet and disperse CB,[4,11,12] (3) the suspension of CB in water with a surfactant followed by encapsulation by either precipitation or emulsion polymerization techniques,[9,13–15] and (4) the grafting of polymer chains onto the CB particle surfaces via radical polymerization techniques.[16–20] These methods each have advantages and drawbacks associated with their implementation and result in CB dispersions having a wide range of CB particle sizes, anywhere from 10 nm to 1 mm.[9]

Starch is an important and abundant natural feedstock for both traditional food and industrial applications.[21] Native starch exists as discrete granules that range in diameter from 1 to 100 μm and is

---

Correspondence to: J. A. Kenar (jim.kenar@ars.usda.gov).

Journal of Applied Polymer Science, Vol. 000, 000–000 (2012)

composed of two polymers consisting of D-glucose repeating units, amylose, and amylopectin. Amylose is essentially a linear polymer consisting of $\alpha[1\rightarrow4]$-linked glucan, whereas amylopectin has a much higher molecular weight and has a branched structure containing $\alpha[1\rightarrow6]$ branching links. The amylose-to-amylopectin ratio within a starch granule varies with the botanical origin of the starch. For example, normal corn starch contains approximately 20–30% amylose and 70–80% amylopectin, whereas waxy corn starch contains nearly 100% amylopectin.

Although starch granules do not dissolve in water at room temperature, many interesting and useful properties of starch are exhibited when the granular structure of starch is disrupted by mechanical and thermal means, such as gelatinization and high-temperature cooking. When aqueous starch slurries are heated, only limited solubility of the starch is observed, and a major portion of the starch remains as highly swollen granules and granular fragments. Although starch may be dissolved by the heating of water slurries in an autoclave at temperatures greater than 100°C, starch solutions for commercial applications are generally prepared by a continuous steam-jet-cooking process, as first described by Coppock,[22] in which a water slurry of granular starch is pumped through a hydroheater, where it is instantly heated with high-pressure steam under high-temperature, high-shear conditions.[23,24]

Although unmodified starches are generally recognized as having little or no surface activity, they are routinely chemically modified to make effective emulsifiers.[25,26] For example, several researchers have examined the adsorption of modified starches onto hydrophobic mineral surfaces, such as talc and kaolin, to reduce the hydrophobicity of these materials and allow the separation of lower value minerals from more valuable minerals by flotation.[27–29] Additionally, unmodified starches have been used to stabilize aqueous CB dispersions for printing inks, whereby surfactants have also been used to first disperse CB; the starch functions primarily as a thickener and serves as a binder for the CB pigment.[5,30]

We have studied jet cooking under excess steam conditions of aqueous mixtures of starch with water-immiscible oils and lipids to prepare new starch–lipid compositions.[31–36] Previous studies have shown that the high temperature and intense mechanical shear of the excess-steam-jet cooking process not only substantially solubilizes the starch components but simultaneously forms micrometer-sized oil droplets that do not coalesce because a thin film of adsorbed starch forms at the lipid–water interface of these composites.[31,34] Interfacial starch formation is best explained by a process that has been referred to as *prewetting*. Prewetting, summarized in an earlier publication,[36] occurs when starch is dissolved in a thermodynamically poor solvent (i.e., water), and the accumulation of starch at the lipid/water interface leads to a reduction in the interfacial tension.

More recently, we have expanded this concept and have shown that thin starch coatings can be deposited onto other hydrophobic surfaces, such as polyethylene (PE), to impart hydrophilic properties.[37–39] To further examine the possibility of depositing unmodified starches onto the surface of other types of hydrophobic materials, the deposition of starches onto the surface of CB to impart hydrophilic characteristics was examined. Herein, we report our results concerning the adhesion of starch to CB particles in aqueous jet-cooked solutions of normal and waxy corn starch and describe a simple aqueous dispersal medium for CB.

EXPERIMENTAL

Materials

Normal unmodified food-grade corn starch and waxy corn starch (waxy no. 1, 1350) were obtained from Tate and Lyle (Decatur, IL) and had apparent amylose/amylopectin ratios of 25 : 75 and 0 : 100, respectively. Percentage moisture was determined by the vacuum drying of the starch samples at 100°C, and all weights of the starches are given on a dry weight basis. Vulcan XC72R CB was obtained from Cabot Corp. (Billerica, MA). This CB was reported by Cabot to have the following specifications: specific area = 253.1 m^2/g (ASTM D 1510), dibutylphthalate absorption = 171.7 mL/100 g (ASTM D 2414), and percentage volatiles = 0.9% (ASTM D 1509). All other chemicals were used without further purification.

Preparation of the jet-cooked starch/CB compositions

Normal or waxy corn starch (50 g) was dispersed in 1000 mL of deionized water, and the dispersion was passed through a Penick & Ford laboratory model steam-jet cooker (Penford Corp., Cedar Rapids, IA) operating under excess steam conditions. The temperature in the hydroheater was 140°C, the steam line pressure was 65 psig (550 kPa), and the steam back pressure was 40 psig (380 kPa). The pumping rate of the aqueous starch dispersion through the jet cooker was about 1 L/min. About 1300 mL of the hot jet-cooked dispersion was collected in a preheated 2-L stainless steel Waring blender container. Typically, the percentage of solids in the collected starch dispersions was 3.50 wt % (as determined by freeze drying). The difference in solids content from the calculated amount in the uncooked slurry was caused by the dilution of the cooked dispersions by the condensed steam.

Cabot Corp. (Billerica, MA) Vulcan XC72R (5.0 g) was slowly added and stirred into the hot starch dispersion, and then, the mixture was blended for 2 min at high speed. The mixture was then passed through a Panda 2 K high-pressure homogenizer (Gea Niro Soavi, Hudson, WI) equipped with a stainless steel water-jacketed feed hopper. Homogenizations were carried out at 90°C at a pressure of 630 bar. A center cut of the homogenized material was collected and subsequently fed through the homogenizer two more times at 630 bar in the same manner. A center cut of the third-pass material was collected in a glass beaker and allowed to cool to room temperature for later examination.

A control run with only CB and water was prepared by the blending of Vulcan XC72R (5.0 g) in hot deionized water (1300 g) collected from the steam-jet cooker into the Waring blender container. This mixture was then passed through the homogenizer in the same manner as described previously.

Centrifugation and washing of the aqueous starch/CB dispersions

A weighed amount of the cooled aqueous starch/CB dispersion was diluted fourfold with deionized water. The samples were gently stirred and then centrifuged at room temperature for 1 h with a Beckman J2–21 ME centrifuge (Palo Alto, CA) equipped with a JA-10 rotor rotating at 10,000 rpm and an RCF (relative centrifugal force) of approximately 17,000 xg. The supernatant (saved for starch analysis) was decanted from the precipitated starch/CB pellet. The compacted starch/CB pellet was taken up in deionized water (~ 100 mL) and dispersed by the transfer of 15-mL aliquots to a Pyrex dounce homogenizer (model 7725, 0.15-mm clearance, Corning, Lowell, MA) and movement of the homogenizer plunger up and down 10 times. The resulting starch/CB dispersion was collected and then centrifuged at 1000 rpm for 15 min (ca. 1300 xg) in a Beckman GS-6KR centrifuge to remove remaining residual compacted CB particles. This washing process was repeated five times to provide starch/CB dispersions free from excess starch and large compacted CB particles. After the fifth washing, the final precipitated starch/CB pellet was taken up in a small amount of deionized water and homogenized with the dounce homogenizer. The aqueous dispersion was divided into two portions; one fraction was stored wet, and the other fraction was freeze-dried for further analyses.

Measurement of D-glucose in the supernatant washings

The total starch residue in the supernatant samples was determined with a total starch assay kit from Megazyme International Ireland, Ltd. (Wicklow, Ireland). Amyloglucosidase from *Aspergillus niger* (300 units/mL, catalog no. A7095) was purchased from Sigma-Aldrich (St. Louis, MO). The amount of residual starch contained in the supernatants obtained from washing the starch/CB pellets were measured in duplicate as D-glucose. A solution containing 3.0 mL of supernatant, 4 mL of sodium acetate buffer (200 m*M*, pH 4.5), and 100 μL of amyloglucosidase (20 units/mL) was heated for 30 min at 50°C. The resulting solution was cooled and diluted as needed, and an aliquot was assayed spectrophotometrically at 510 nm for glucose with the Megazyme D-glucose assay procedure (glucose oxidase/peroxidase, (GOPOD) format; Megazyme International Ireland). Full details about the assay were contained in the kit instructions, and the measurement procedure was followed as described.

Treatment of the starch/CB dispersions with amyloglucosidase

The washed aqueous starch/CB dispersions were treated with amyloglucosidase to enzymatically remove starch bound to the CB particles. Ten mL of aqueous starch/CB dispersions (ca. 0.22–0.39 wt % solids) was diluted fourfold with 40 mL of distilled water. In a 2-oz glass bottle, 15 mL of the starch/CB dispersion, 20 mL of sodium acetate buffer (200 m*M*, pH 4.5), and 116 μL of amyloglucosidase (3.0 units/mL in 200 m*M* sodium acetate buffer, pH 4.5) were mixed together. A control experiment containing 15 mL of the starch/CB dispersion and 20 mL of sodium acetate buffer but containing no amyloglucosidase was also prepared. The bottles were sealed and placed into a 50°C water bath and periodically monitored. After 2.5 h, the CB particles in the bottle containing the amyloglucosidase had agglomerated and precipitated, whereas the control showed no signs of precipitation. The reactions were allowed to proceed for 17 h and were then cooled to room temperature. The supernatant from the amyloglucosidase-treated samples were decanted, deionized water (50 mL) was added to the remaining precipitated CB, and the mixture was gently stirred with a magnetic stirring bar. The mixture was centrifuged on a Beckman GS-6KR centrifuge at 3000 rpm (ca. 2000 xg) for 30 min. The supernatant was removed, and the precipitated CB was washed again with deionized water (50 mL). After centrifugation at 3000 rpm (ca. 2000 xg) for 30 min and removal of the supernatant, the remaining CB precipitates were dried on a Teflon watch glass for thermogravimetric analyses (TGAs).

Treatment of the starch/CB dispersion with 0.1*N* HCl

The washed aqueous starch/CB dispersions were treated with 0.1*N* HCl to hydrolyze starch bound to the CB particles. Accordingly, 10 mL of aqueous starch/CB dispersions (ca. 0.22–0.39 wt % solids) were diluted fourfold with 40 mL of distilled water. In a 2-oz glass bottle, 15 mL of the starch/CB dispersion and 15 mL of 0.1*N* HCl were mixed together. A control experiment without HCl and containing 15 mL of the starch/CB dispersion and 15 mL of deionized water was also prepared. The bottles were sealed, placed in an oven preheated to 95°C, and allowed to heat for 17 h. After the allotted time, the acid-treated sample had precipitated, whereas the control starch/CB dispersion containing no HCl remained dispersed. After the sample was cooled to room temperature, the supernatant from the HCl-treated sample was decanted, deionized water (50 mL) was added to the precipitated CB, and the mixture was gently stirred with a magnetic stirring bar. The mixture was centrifuged on a Beckman GS-6KR centrifuge at 3000 rpm (ca. 2000 xg) for 30 min, the supernatant was removed, and the precipitated CB was washed again with deionized water (50 mL). After centrifugation at 3000 rpm (ca. 2000 xg) for 30 min and the removal of the supernatant, the remaining CB precipitates were dried on a Teflon watch glass for TGA.

Light microscopy

Aqueous dispersions of the starch/CB dispersions were observed with a Zeiss Axioskop light microscope (Carl Zeiss, Inc., Thornwood, NY) with bright-field or phase-contrast optics. Representative fields were photographed with a Nikon D100 digital camera (Nikon Corp., Tokyo, Japan).

Transmission electron microscopy (TEM)

Washed samples (1 μL) of the starch/CB dispersions were applied directly to carbon films on 200-mesh copper grids and allowed to air dry. Untreated CB (0.25 g) was dispersed in chloroform (50 mL) by sonication with a 750-W Autotune Series high-intensity processor (Cole Parmer Instruments, Vernon Hills, IL) equipped with a 0.5-in. diameter probe at 100% amplitude for 30 s. One microliter was transferred to a carbon film grid with a glass/stainless steel syringe to avoid solvent leaching from a plastic pipette tip. Specimens were examined with a JEOL 2100 LaB_6Cryo transmission electron microscope operating at 200 kV. Images were obtained with a Gatan UltraScan 2kx2k charge coupling device camera (Gatan, Inc., Pleasanton, CA).

Fourier transform infrared (FTIR) spectroscopy

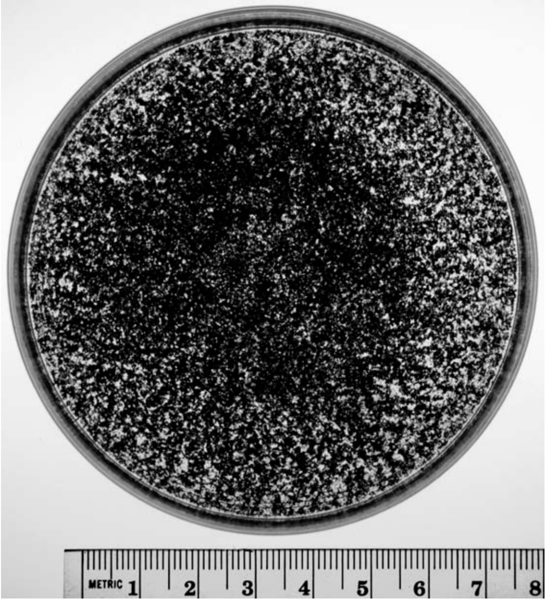

Figure 1 Large aggregates (~ 0.1–1 mm in diameter) formed after three passes of neat CB in water through a homogenizer with no starch.

FTIR spectra were recorded as KBR pellets on a Thermo Nicolet Nexus 470 FTIR system (Madison, WI) with a scanning range of 650–4000 cm^{-1} for 32 scans at a spectral resolution of 4 cm^{-1}. The KBr pellets were prepared by the blending of approximately 1 mg of sample with 250 mg of KBr and then mixing in a Crescent Wig-L-Bug amalgamator Model 3110B (Crescent Dental Mfg company, Lyons, IL) for 15 s. The KBr disks were pressed at 20,000 psi for 2 min with a 12.5-mm die. Spectra were taken immediately and analyzed with Nicolet Omnic software by subtraction of the background KBr spectrum.

TGA

Thermogravimetric curves were obtained on a 2050 TGA instrument (TA Instruments, New Castle, DE) under an air atmosphere with a flow rate of 10 mL/min. Dried samples (≤10 mg of powder) were heated from 20 to 900°C at a heating rate of 10°C/min and held isothermally for 3 min at 900°C. The TGA data were plotted as temperature versus weight percentage from which the component composition and onset and final decomposition temperatures could be obtained.

RESULTS AND DISCUSSION

Preparation of the starch/CB dispersions

Figure 1 shows the results of an attempt to disperse neat CB (3.8 wt %) in water by high-pressure homogenization in the absence of jet-cooked starch. The hydrophobic CB particles agglomerated in the aqueous dispersion to give large particle clusters up to 1 mm in diameter, which were visible without

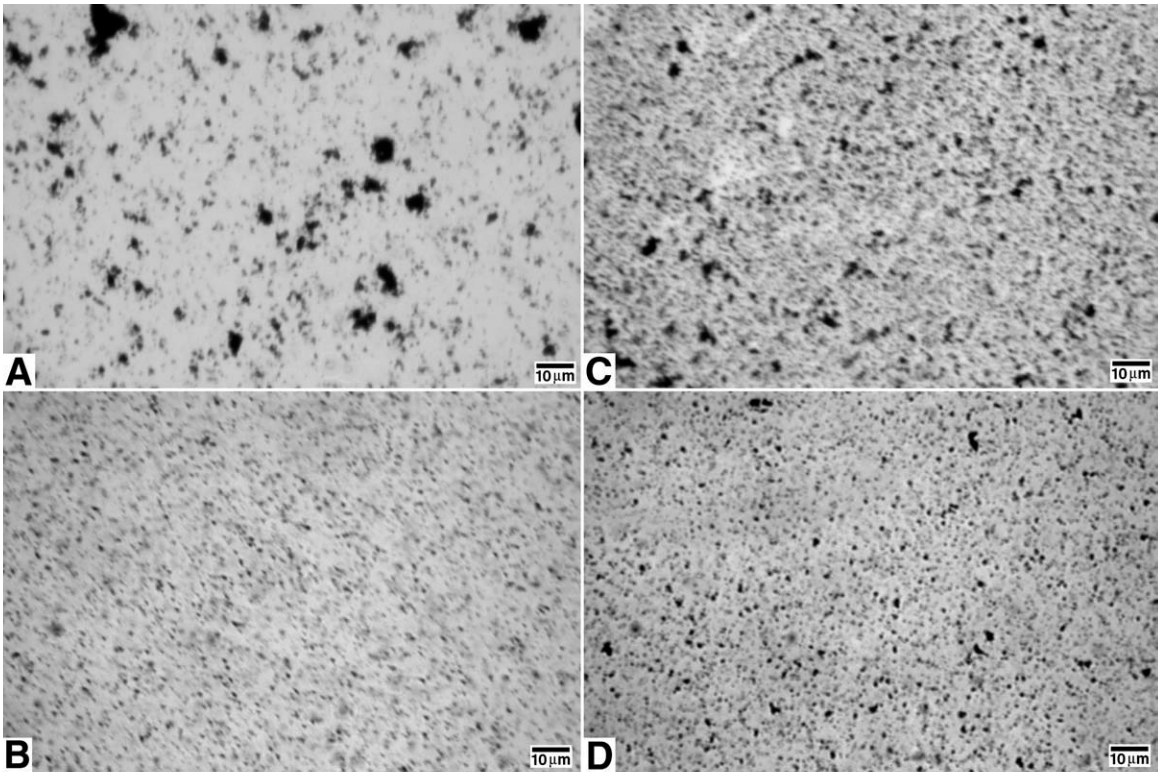

Figure 2 Bright-field light micrographs of the CB/normal starch dispersions (A) just after three passes through a homogenizer and (B) after five water washes and (C) CB/waxy starch dispersions just after homogenization and (D) after five water washes.

magnification and immediately precipitated from solution. When CB was blended into the jet-cooked aqueous dispersions of either normal or waxy corn starch at a 1 : 10 ratio of CB to starch and the resulting CB dispersions were subsequently homogenized under high pressure, well-dispersed CB particles were obtained. Observation of these dispersions by light microscopy immediately after the homogenization process showed CB particles ranging from the submicrometer level up to approximately 10 µm in diameter with both varieties of corn starch [Fig. 2(A,C)]. Figure 2(B,D) shows the dispersions after five washings and redispersing with the dounce homogenizer. This treatment apparently reduced the size of the larger clusters, and the resulting stable dispersions with both starch types were more uniform, with clusters in the 1–3-µm range After standing for 3 months at room temperature, the 1 : 10 CB/waxy starch preparations exhibited some settling of the CB particles. However, these particles were easily redispersed with only gentle agitation, and the particle size remained similar to that of the freshly prepared material [Fig. 2(D)]. In contrast, after standing for 1 day at room temperature, fragments of gel were observed in the normal corn starch/CB dispersions by microscopy (Fig. 3), and CB particles appeared to be trapped within the gel matrix. Distribution of the CB particles changed from uniform to heterogeneous, with areas rich in CB particles (which moved together when the sample flowed) and a background with few or no CB particles. Gel formation was probably due to retrogradation of the amylose present in the normal corn

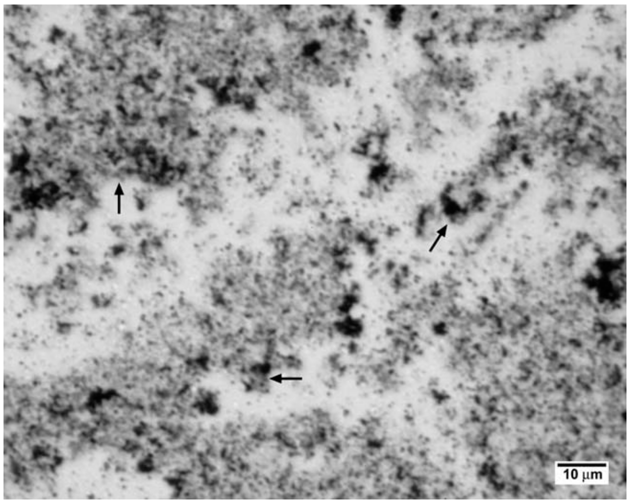

Figure 3 Bright-field light micrograph of a CB/normal starch dispersion after standing overnight with the formation of gelled regions entrapping CB particles shown with clearer regions between them. The arrows indicate gel fragments of various sizes in which the CB aggregates were embedded.

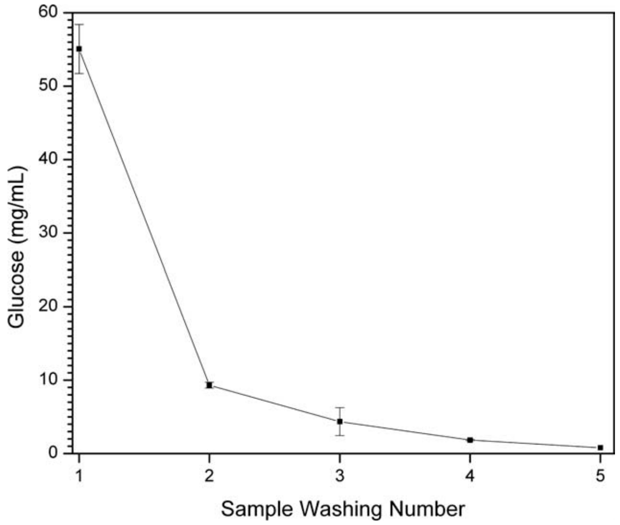

Figure 4 Glucose remaining in the wash supernatants as the waxy starch/CB dispersions were progressively washed with water to remove excess and loosely bound starch.

starch because gel formation was not observed with waxy starch, which contained no amylose. Even though the CB/normal cornstarch dispersions had formed very small gelled regions, they did not precipitate, and the dispersions remained uniformly black.

To determine whether starch had adsorbed onto the surface of the CB particles, similar to the prewetting observed with oil droplets, an experiment was carried out with waxy corn starch (to avoid gel formation), and the excess starch used during the preparation of these dispersions was removed by repeated water washing of the CB particles. Waxy starch consists of water-soluble amylopectin, which does not retrograde and is easily removed by repeated water washing. Control experiments were carried out with the jet-cooked waxy starch to confirm that the waxy starch did not precipitate from the dispersion during centrifugation to collect starch-coated CB. As shown in Figure 4, the total starch remaining in the supernatant, measured as glucose, decreased with progressive washing and was quite low after five washings; this indicated that essentially all soluble or loosely bound starch was removed from the CB particles. The resulting washed CB particles did not agglomerate but remained dispersed in water [as shown in Fig. 2(D)]. The absence of agglomeration of the washed CB, even after prolonged storage provided evidence that starch had adsorbed onto the surfaces of the CB particles and inhibited interparticle adhesion.

TEM of the washed CB/normal starch dispersions revealed typical aciniform aggregates [Fig. 5(A)], many of which were in the same size range seen in the light micrographs [Fig. 2(B)]. With this technique, aggregates ranging from about 0.1 μm to more than 1 μm were observed. Commonly seen in these samples was a relatively electron-lucent material appearing to coat the particles. The coating was irregular in thickness, and the outer contours of the coating did not closely follow the topography of the carbon primary particles themselves. Often, the coating was of such abundance that the structure of the spherical carbon particles was largely obscured [Fig. 5(B)]. Also observed superimposed within the clusters were elongated strands of material connecting the coated particles and appearing to be continuous with areas of the coating. At the edge of some clusters, the coating was more conspicuous, and individual primary carbon particles appeared to be embedded in a thicker amorphous matrix [Fig. 5(C)]. A small cluster of isodiametric particles fortuitously situated on the substrate film revealed an electron-lucent space separating the primary carbon particles and a typically appearing material coating them [Fig. 5(D)]. This suggested the possibility that the particles adhered to each other and formed the cluster after they were coated with starch.

The coating material observed on the washed CB/waxy starch dispersions examined by TEM was generally thinner and less conspicuous than that observed with the normal (amylose-containing) starch (Fig. 6). A similar difference in apparent coating thickness between normal and waxy starch was observed with coatings adhering to oil droplets in jet-cooked starch/oil composites.[36] Nevertheless, it could still be seen surrounding the carbon particles [Fig. 6(A)]. A continuous layer of coating material appeared to bridge between adjacent clusters [Fig. 6(B)]; this suggested that during the coating process, smaller clusters may have formed connections promoting the establishment of networks of clusters and resulting in larger aggregates than were originally present in the source CB. In one such bridge, one of the more distinct strands of material was observed and appeared to be continuous with the coating layer of the particles from adjacent clusters [Fig. 6(C)]. These elongated strands were often seen superimposed within areas of more crowded regions of aggregates [Fig. 6(D)].

To confirm the interpretation that the amorphous starch formed a coating over the CB aggregates visible by TEM, the neat CB used in these experiments was dispersed in chloroform and examined (Fig. 7). The same aciniform aggregates were seen as in the starch-coated samples, but the appearance of the CB was quite different. Clusters with both large (ca. 50 nm) and smaller (10–20 nm) primary particles were observed [Fig. 7(A)]. The uncoated particles formed electron images composed mainly of superimposed circular objects (interpreted as spherical). The gray level at any given point was determined by how many particles were in the electron-beam path [Fig.

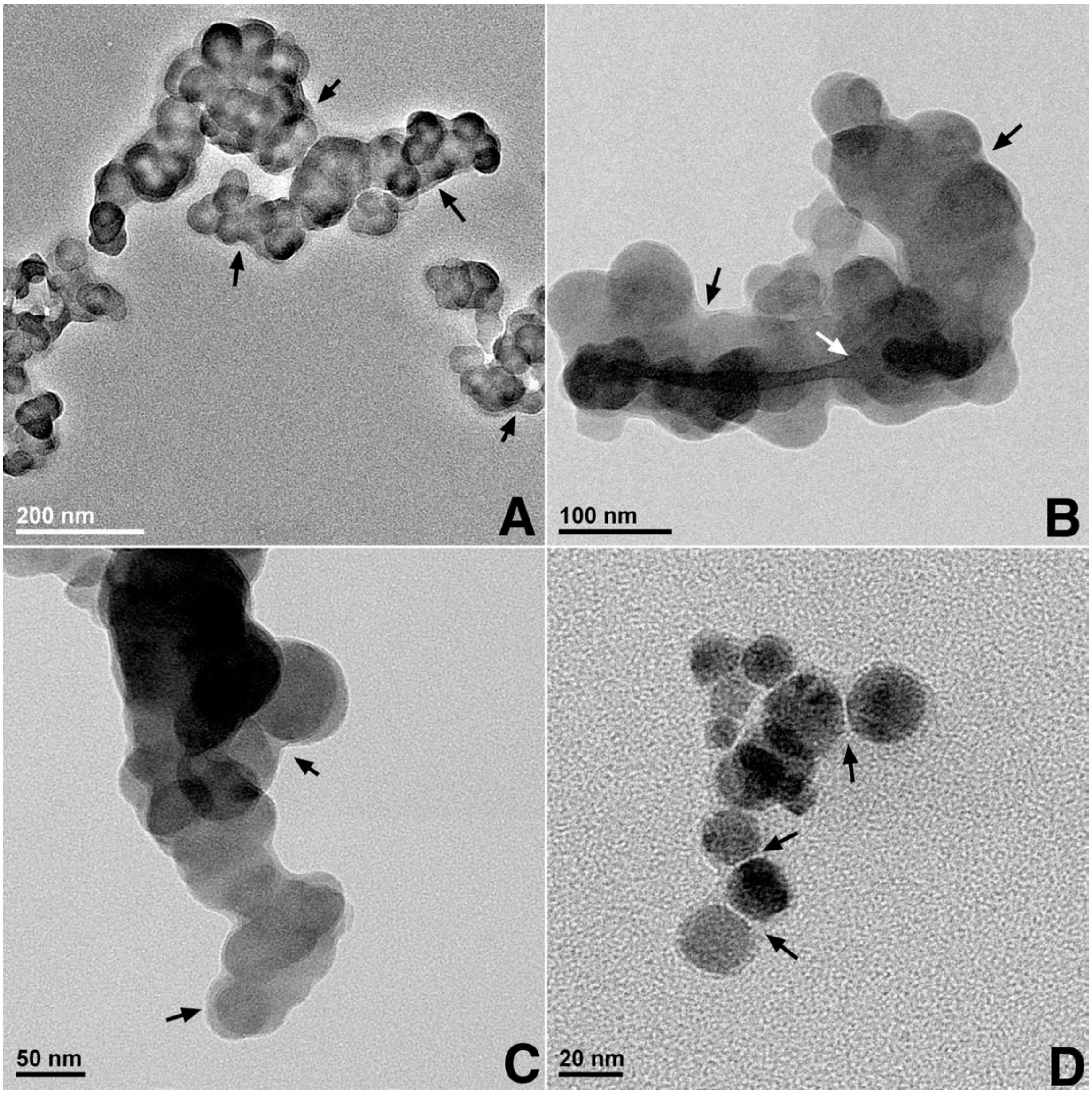

Figure 5 TEM micrographs of the CB/normal starch dispersions: (A) material apparently coating aciniform aggregates of primary carbon particles (arrows), (B) thicker coating partially obscuring the carbon particle morphology (dark arrows), with a strand of material stretching between the coated particles (white arrow), (C) smaller particles embedded within thicker coating matrix (arrows), and (D) small cluster of smaller particles showing coating and space between the particles (arrows).

7(B)]. Unlike images of the starch-coated samples (Figs. 5 and 6), the inside corners of particle clusters were sharp and geometric, and the overall appearance of clusters was much simpler and clearer. A characteristic pattern of concentric striations could be seen in most particles, which was more obvious in smaller primary particles [Fig. 7(C)]. This feature of the primary particles was largely obscured in the samples of the CB/starch dispersions, presumably by the presence of the adhering starch material. The larger uncoated CB aggregates frequently contained open spaces within the cluster structure, with regions of background-level illumination visible [Fig. 7(D)]. Such open areas were not visible in the CB/normal starch or CB/waxy starch dispersions; again, this suggested an effect of the adhering starch material.

To confirm the presence of adsorbed starch, portions of the water-washed starch/CB particles were freeze-dried and were then examined by FTIR between 1300 and 800 cm^{-1}. As shown in Figure 8, both the waxy and normal corn starch/CB compositions showed characteristic starch absorption bands at 1147–1149, 1078, and 1020 cm^{-1} that were not present in the untreated CB. The peaks at 1147–1149 cm^{-1} were attributed to the C—OH hydroxylic bond stretching, whereas the peaks at 1078 and 1020 cm^{-1} were representative of the C—O—C ether-bond

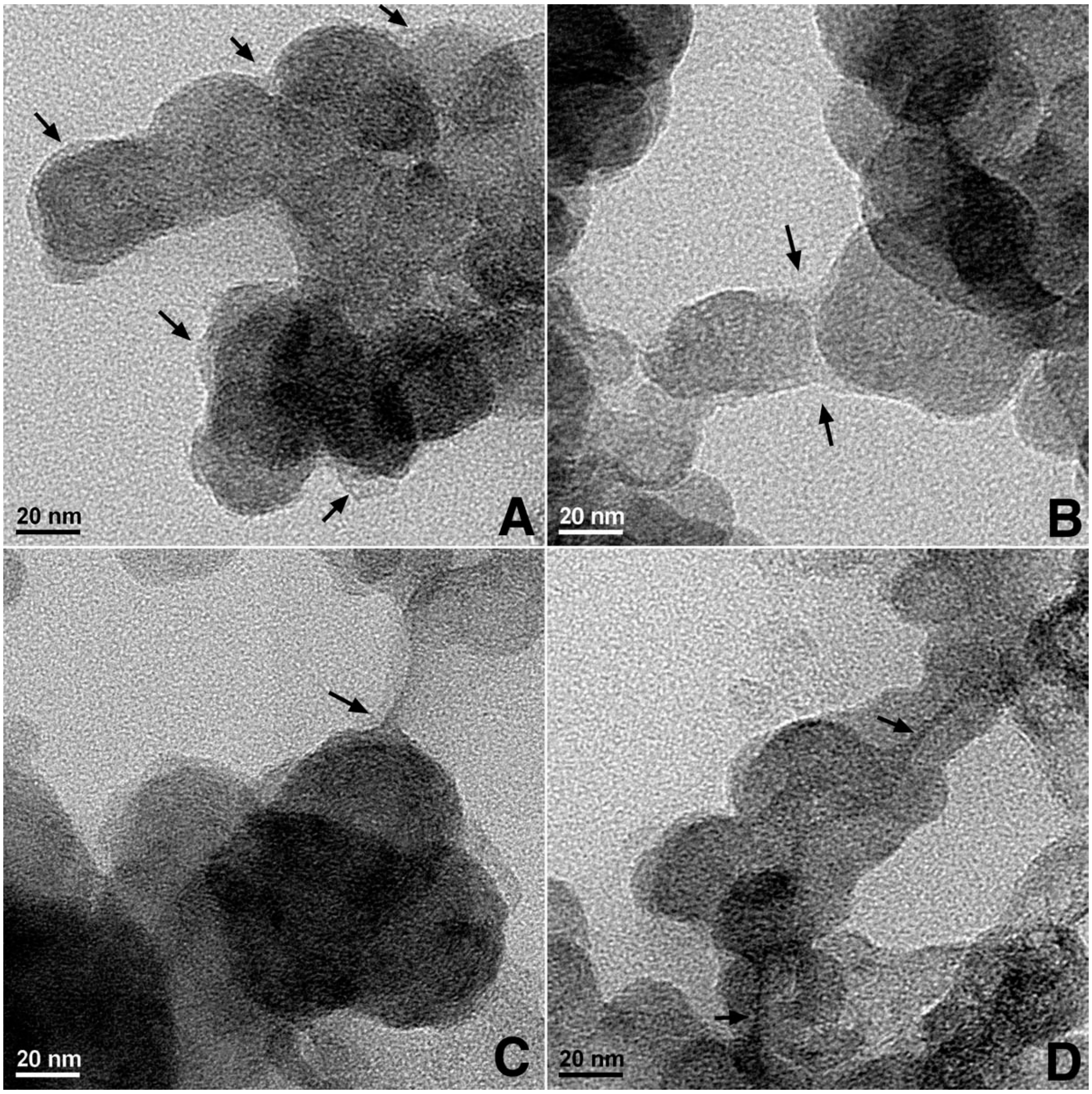

Figure 6 TEM micrographs of the CB/waxy starch dispersions: (A) thin coating material surrounding a cluster of smaller CB particles (arrows), (B) continuous layer of adhering material apparently connecting or bridging adjacent clusters (arrows), (C) darker strand of material spanning between two clusters and continuous with a coating layer (arrow), and (D) strands of material connecting particles within typically superimposed images of the particles in clusters (arrows).

stretching of the anhydroglucose ring.[40] None of the aforementioned starch bands in the starch/CB particles shifted their position significantly relative to the corresponding bands in the spectra of the pure waxy and normal corn starch, and these observations suggested that the frequencies observed for the starch adsorbed onto the CB surface arose from similar types of vibrational modes. However, in the region between 975 and 800 cm^{-1}, absorption intensity differences were observed between the pure starches and the starch/CB compositions. The waxy and normal corn starches showed medium-intensity peaks at 850 and 925 cm^{-1} attributable to equatorial C_1—H deformation and ring vibrations, respectively,[41–43] whereas in both the waxy and normal corn starch/CB compositions, these peaks were significantly diminished. It has been suggested by researchers examining the interaction of dextrin and starch with minerals[43] and metal oxides[44] containing hydrophilic groups that starch and dextrin interact with the surface moieties of these materials through chemical reactions and hydrogen bonding to form surface complexes that force a change in the glucopyranose ring conformation and result in the disappearance of the ring vibrations at 925 and 850 cm^{-1}. Furthermore, Pavlovic and Bandao[42] suggested that chemisorption between starch and iron atoms in hematite caused the 850- and 925-cm^{-1} starch band

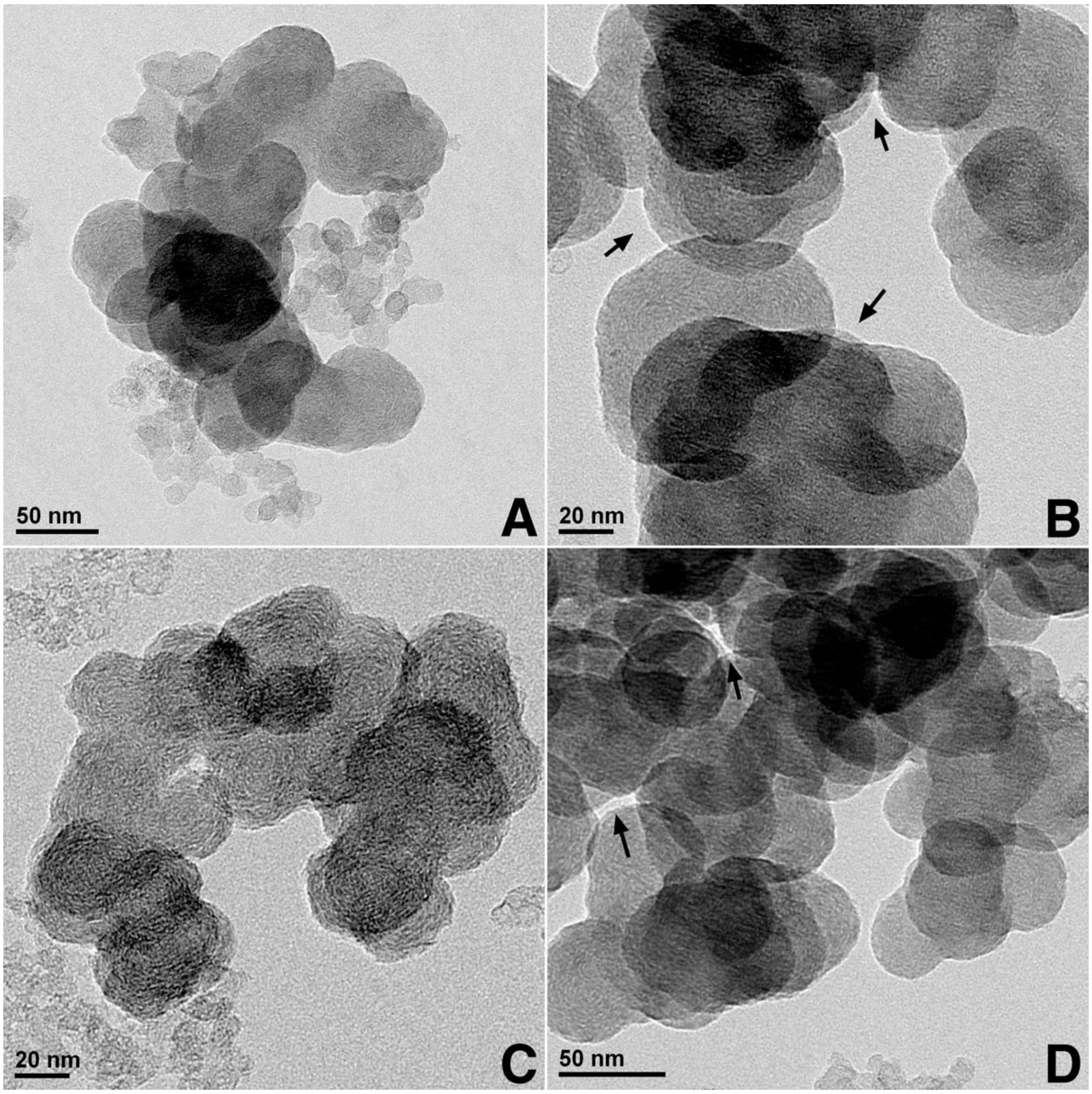

Figure 7 TEM micrographs of neat CB applied to a carbon film substrate as a chloroform dispersion: (A) aciniform clusters of large and small carbon particles, (B) clusters showing clean particle surfaces and sharp, angular appearance of overlapping particle edge images (arrows), (C) cluster of smaller particles showing characteristic internal concentric striations, and (D) larger cluster revealing open spaces with background illumination visible within clusters (arrows).

positions to shift. However, in our starch/CB compositions, we could not use these explanations to account for the diminished intensity of the 925- and 850-cm^{-1} bands because the surfaces of the CB particles were hydrophobic and did not contain hydrophilic groups. As a possible explanation, it is well known that amylose can undergo a random-coil-to-linear transition to produce helical amylose inclusion complexes with hydrophobic materials, such as long-chain fatty acids, whereby the hydrophobic inner core of amylose accommodates the hydrophobic tail of the fatty acid. For the hydrophobic surface of CB, amylose and/or amylopectin may adopt a conformation such that their hydrophobic groups are located toward the CB surface, whereas the hydrophilic groups interact with the aqueous phase. A similar mechanism could account for the adsorption of starch from the water solutions at lipid/water interfaces and onto the hydrophobic surfaces of the PE films. The conformational changes in starch associated with this process could have given rise to the observed IR spectra for the starch/CB compositions.

The TGA profiles of the normal and waxy corn starches, pure CB, and the thoroughly washed and dried waxy and normal corn starch/CB compositions shown in Figure 9 were consistent with the FTIR results. CB exhibited a single decomposition temperature at approximately 660°C, whereas the waxy and normal corn starches exhibited two

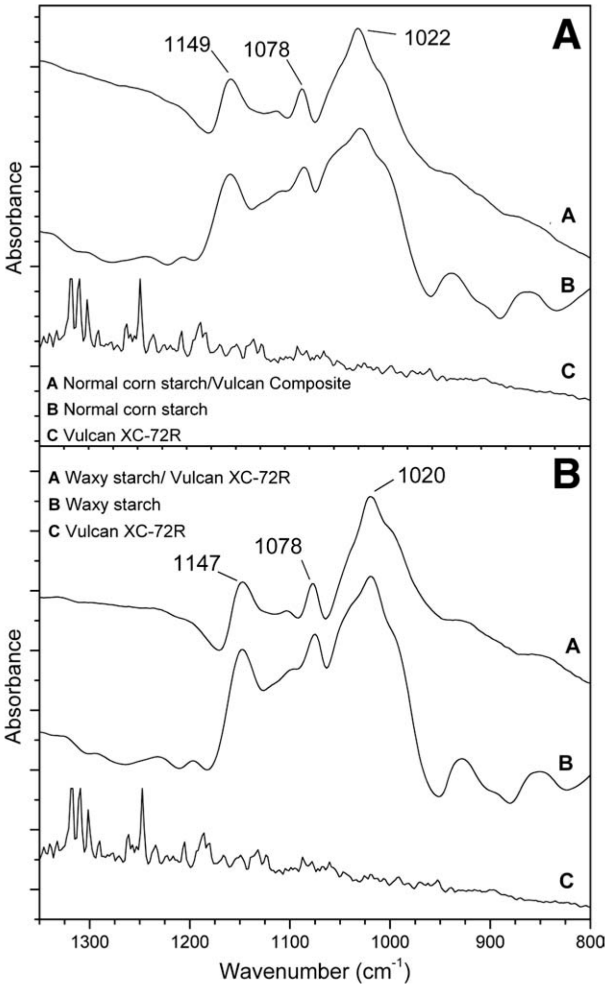

Figure 8 FTIR spectra of (A) washed and dried normal corn starch/CB and (B) washed and dried waxy starch/CB.

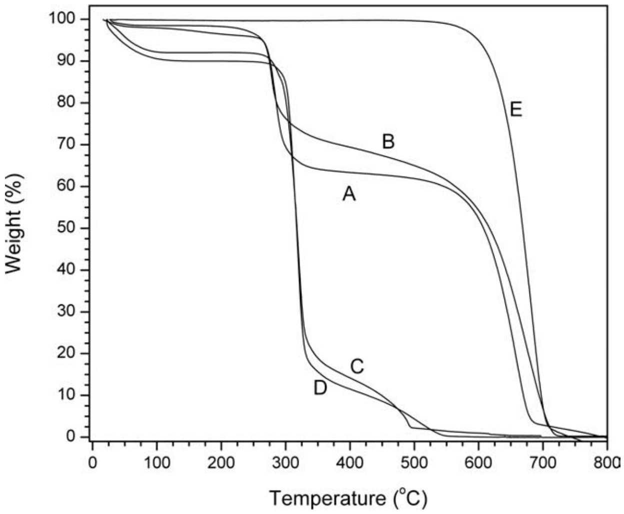

Figure 9 TGA profiles of (A) washed and dried waxy corn starch/CB, (B) washed and dried normal corn starch/CB, (C) pure waxy corn starch, (D) pure normal corn starch, and (E) pure Vulcan XC-72R CB.

decomposition temperatures at approximately 315 and 425°C, respectively. Additionally, in the waxy and normal corn starch samples, there was also an 8–10 wt % mass loss observed between 50 and 100°C due to adsorbed water. For the waxy and normal corn starch/CB compositions, an initial weight loss due to the volatilization of water at 50–100°C was similarly observed and was followed by two major decomposition temperatures, which were observed at approximately 275 and 625–650°C and corresponded to the starch and CB components, respectively. After we corrected for the water present in the waxy and normal corn starch/CB

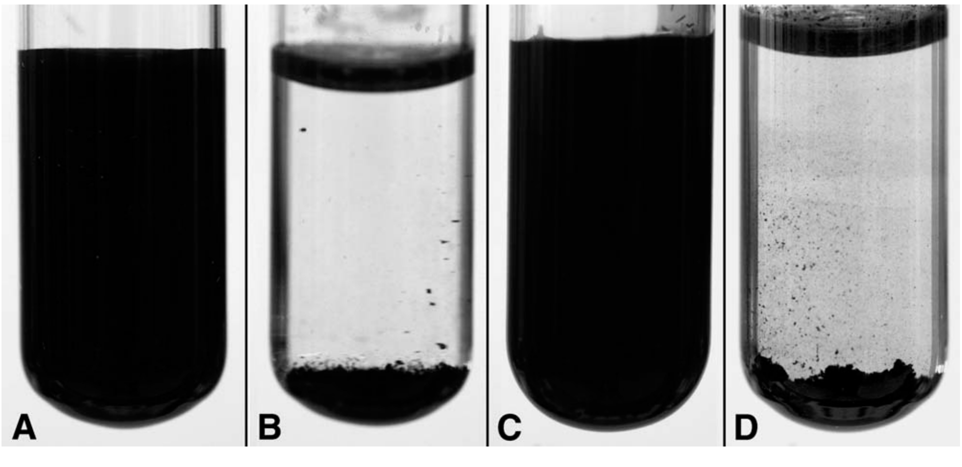

Figure 10 Photographs of the washed waxy starch/CB dispersions treated with HCl acid and amyloglucosidase: (A) washed waxy starch/CB dispersion control heated at 95°C for 15 h, (B) washed waxy starch/CB dispersion treated with 0.1*M* HCl and heated at 95°C for 15 h, (C) washed waxy starch/CB dispersion control treated without enzyme buffer only and heated at 50°C for 17 h, and (D) washed waxy starch/CB dispersion treated with 0.035 units of amyloglucosidase heated at 50°C for 17 h.

compositions, the calculated amounts of starch adsorbed onto the CB particles were 36 and 30% of the sample weight for the waxy and normal corn starch compositions, respectively.

To further examine the effect of adsorbed starch on the stability of the aqueous dispersions of starch/CB compositions, we used amyloglucosidase digestion and hydrochloric acid hydrolysis to remove starch from the CB surface. As shown in Figure 10(B,D), after treatment with either acid or enzyme, the CB agglomerated and precipitated from the dispersion in large clumps. In control treatments carried out by the heating of the sample without HCl or with enzyme buffer but no amyloglucosidase, the CB particles remained unchanged and dispersed uniformly [Fig. 10(A,C)]. After hydrolysis, the agglomerated CB particles from the waxy CB hydrolysis experiments were collected, washed, dried, and analyzed by TGA to determine the extent of starch removal. As shown in Figure 11, TGA showed that the amyloglucosidase and HCl treated samples contained approximately 16.4 and 14.8 wt % starch, respectively. Although treatments with amyloglucosidase and HCl did not remove all the starch from the CB particles, enough of the adsorbed starch was removed to disrupt the integrity of the starch coating; this allowed the CB particles to agglomerate and precipitate.

To determine whether solid matter consisting of retrograded or precipitated starch particles was responsible for or contributed to the detection of starch in the washed starch/CB dispersions, sample fields were examined by both phase-contrast and bright-field microscopy (Fig. 12). The bright-field images revealed only CB, as unstained starch is not visible using standard Kohler illumination. If present, starch precipitates, retrograded particles, or spherulites would only be visible with phase-contrast optics. Fields observed under bright field revealed no additional objects when they were switched to phase contrast. The similarity of the particle number and location seen by both methods provided evidence that the starch detected by chemical, enzymic, or physical means was associated with or more likely attached to the CB aggregates.

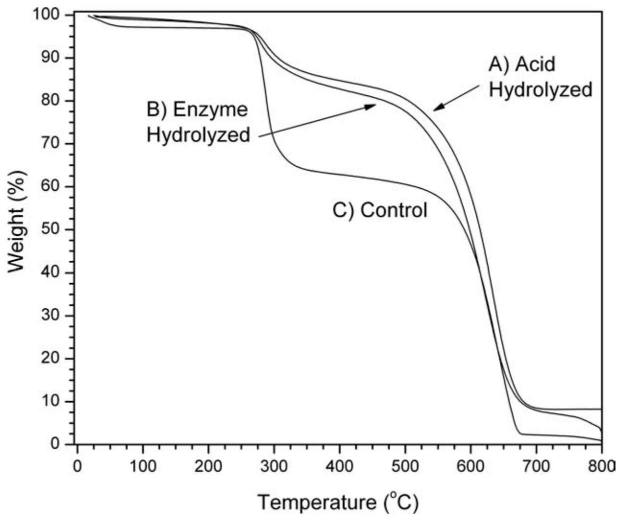

Figure 11 TGA profiles of (A) washed waxy corn starch/CB hydrolyzed with HCl, (B) washed waxy corn starch/CB hydrolyzed with amyloglucosidase, and (C) thoroughly washed waxy corn starch/CB used as a control.

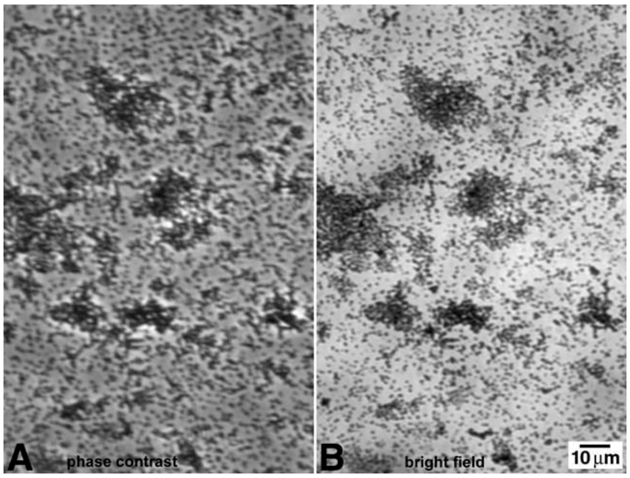

Figure 12 (A) Phase contrast and (B) bright-field images of the same field of a sample of the washed CB/normal starch dispersion. The same arrangement of objects in each image indicates that no starch particles were present, which would appear as additional particles with phase contrast optics.

CONCLUSIONS

Starch was adsorbed onto the CB particle surfaces when CB was homogenized in hot, jet-cooked dispersions of normal corn starch or waxy corn starch. The amounts of adsorbed starch after the removal of loosely bound starch from the CB particles by water washing varied from about 30 to 36 wt % when 1 : 10 CB-to-starch ratios were used. These coatings of adsorbed starch imparted hydrophilic properties to the CB particles, prevented particle agglomeration, and allowed the CB to be readily wetted and dispersed into water. Removal of the starch coatings from the washed CB particles by acid or enzymatic hydrolysis caused the particles to agglomerate into larger clumps and precipitate from solution. The deposition of starch onto hydrophobic CB surfaces could be explained by a process referred to as prewetting, which takes place when starch is dissolved in a thermodynamically poor solvent (i.e., water) and when the accumulation of adsorbed starch at the hydrophobic/hydrophilic interface leads to a reduction in interfacial tension. Although numerous methods for altering CB particle surfaces to make them more hydrophilic have been described, the method described in this study provides a simple and green method for producing aqueous CB dispersions. We are currently investigating end-use applications for these starch/CB compositions.

The authors thank Jeanette Little for performing the starch assays and Wacek Swiech for assistance with TEM. TEM was carried out in the Frederick Seitz Materials Research Laboratory Central Facilities, University of Illinois, which are partially supported by the U.S. Department of Energy under grants DE-FG02-07ER46453 and DE-FG02-07ER46471.

References

1. Dannenberg, E. M.; Paquin, L.; Gwinnell, H. In Kirk–Othmer Encyclopedia of Chemical Technology, 4th ed.; Kroschwitz, J. I., Howe-Grant, M., Eds.; Wiley: New York, 1992; p 1037.
2. Donnet, J.-B.; Bansal, R. C.; Wang, M.-J. Carbon Black: Science and Technology, 2nd ed.; Marcel Dekker: New York, 1993.
3. Kobayashi, T. Prog Org Coat 1996, 28, 79.
4. Ridaoui, H.; Jada, A.; Vidal, L.; Donnet, J.-B. Colloids Surf A 2006, 278, 149.
5. Trubiano, P. C.; Cohen, A. Y. U.S. Pat. 4,310,356 (1982).
6. Karl, A.; Kalbitz, W.; Kleinhenz, H.; Tauber, G. U.S. Pat. 6,503,311 (2003).
7. Li, D.; Sun, G. Dyes Pigments 2007, 72, 144.
8. Papirer, E.; LaCroix, R.; Donnet, J.-B. Carbon 1996, 34, 1521.
9. Tiarks, F.; Landfester, K.; Antonietti, M. Macromol Chem Phys 2001, 202, 51.
10. Li, H.-Y.; Chen, H.-Z.; Sun, J.-Z.; Cao, J.; Yang, Z.-L.; Wang, M. Macromol Rapid Commun 2003, 24, 715.
11. Lin, Y.; Alexandridis, P. J Phys Chem B 2002, 106, 10834.
12. Sis, H.; Birinci, M. Colloids Surf A 2009, 341, 60.
13. Casado, R. M.; Lovell, P. A.; Navabpour, P.; Stanford, J. L. Polymer 2007, 48, 2554.
14. Li, H.-Y.; Chen, H.-Z.; Xu, W.-J.; Cao, J.; Yaun, F.; Wang, J.-R.; Wang, M. Colloids Surf A 2005, 254, 173.
15. Xu, W.; Chen, H.; Li, H.; Wang, M. Colloids Surf A 2005, 266, 68.
16. Lee, C.-F.; Yang, C.-C.; Wang, L.-Y.; Chiu, W.-Y. Polymer 2005, 46, 5514.
17. Li, W.; Xie, Z.; Li, Z. J Appl Polym Sci 2001, 81, 1100.
18. Liu, T.; Jia, S.; Kowalewski, T.; Matyjaszewski, K.; Casado-Portilla, R.; Belmont, J. Macromolecules 2006, 39, 548.
19. Yang, Q.; Wang, L.; Xiang, W.-D.; Zhou, J.-F.; Tan, Q.-H. J Polym Sci Part A: Polym Chem 2007, 45, 3451.
20. Huang, J.; Li; Q.; Bao, Y.; Wu, C. e-Polymers 2009, 088, 1.
21. Bemiller, J. N.; Whistler, R. L. Starch Chemistry and Technology, 3rd ed.; Academic: Burlington, MA, 2009.
22. Coppock, P. D. U.S. Pat. 2,202,573 (1940).
23. Klem, R. E.; Brogly, D. A. Pulp Pap 1981, 55, 98.
24. Winfrey, V. L.; Black, W. C. U.S. Pat. 3,133,836 (1964).
25. McClements, D. J. Food Emulsions Principles, Practices, and Techniques, 2nd ed.; CRC: Boca Raton, FL, 2005.
26. Nilsson, L.; Bergensthäl, B. J Agric Food Chem 2007, 55, 1469.
27. Husband, J. C. Colloids Surf A 1998, 131, 145.
28. Järnström, L.; Lason, L.; Rigdahl, M. Colloids Surf A 1995, 104, 191.
29. Mierczynska-Vasilev, A.; Ralston, J.; Beattie, D. A. Langmuir 2008, 24, 6121.
30. Apostol, S.; Catena, R.; Simoni-Truncellito, J.; Chudolij, A.; Flores, A. M. A.; Mathew, M. C.; Mora, L. U.S. Pat. Appl. 2007/0289486 (2007).
31. Eskins, K.; Fanta, G. F.; Felker, F. C.; Baker, F. L. Carbohydr Polym 1996, 29, 233.
32. Eskins, K.; Fanta, G. F. U.S. Pat. 5,676,994 (1997).
33. Eskins, K.; Fanta, G. F. U.S. Pat. 5,882,713 (1999).
34. Fanta, G. F.; Eskins, K. Carbohydr Polym 1995, 28, 171.
35. Fanta, G. F.; Felker, F. C.; Shogren, R. L. Carbohydr Polym 2001, 46, 29.
36. Fanta, G. F.; Felker, F. C.; Eskins, K.; Baker, F. L. Carbohydr Polym 1999, 39, 25.
37. Fanta, G. F.; Felker, F. C.; Shogren, R. L.; Salch, J. H. J Appl Polym Sci 2002, 84, 1781.
38. Fanta, G. F.; Salch, J. H.; Felker, F. C.; Shogren, R. L. J Appl Polym Sci 2009, 114, 1840.
39. Fanta, G. F.; Felker, F. C. U.S. Pat. 6,709,763 (2004).
40. Cael, J. J.; Koenig, J. L.; Blackwell, J. Biopolymers 1975, 14, 1885.
41. Barker, S. A.; Bourne, E. J.; Stacey, M.; Whiffen, D. H. J Chem Soc 1954, 171.
42. Pavlovic, S.; Bandao, P. R. G. Miner Eng 2003, 16, 1117.
43. Weissenborn, P. K.; Warren, L. J.; Dunn, J. G. Colloids Surf A 1995, 99, 11.
44. Liu, Q.; Laskowski, J. S. J Colloid Interface Sci 1988, 130, 101.