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Starch-*graft*-copolymer latexes initiated and stabilized by ozonolyzed amylopectin.

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Abstract

A method is presented for synthesizing surfactant-free latexes comprising starch-*graft*-(vinyl polymer) (1) starting with a suspension of the highly branched starch amylopectin, either native or degraded, then (2) using ozonolysis to create free-radical initiation sites on this amylopectin scaffold, and then (3) adding monomer and inducing polymerization. The ozone simultaneously thins the starch and creates initiating/grafting sites on the starch from which starch-*g*-copolymer latexes can be grown. Encapsulation of starch inside hydrophobic polymer particles created by a heterogeneous free-radical polymerization process was demonstrated using energy dispersive spectroscopy (EDS), the first time the particle morphology of such a latex has been so characterized. The data unambiguously prove that low molar mass degraded starch can be encapsulated within a latex particle. The underlying mechanisms have been explored and data

quantifying rates of production of hydroperoxides by ozone, thermal decomposition of the starch hydroperoxides so formed and degradation of amylopectin by ozone are reported. The activation energy for thermal decomposition of the starch macroinitiator, determined in this work to be $125 \pm 8 \text{ kJ}\cdot\text{mol}^{-1}$, is consistent with the proposition that the initiating species are mainly hydroperoxides. Colloidally stable poly(styrene-*co*-n-butyl acrylate) latexes based on high molar mass amylopectin were developed. These were stable against electrolyte (several months in $4 \text{ mol}\cdot\text{L}^{-1} \text{ NaCl}$), with 20 % of the starch effectively grafted to the particles. Films cast from such latexes were more pliable than starch films and readily redispersed in water.

Keywords:

Amylopectin, ozone, hydroperoxide, starch grafting, paper coating, hybrid biomaterial, energy dispersive spectroscopy, styrene, n-butyl acrylate, vinyl acetate

INTRODUCTION

Starch-*graft*-poly(vinyl) copolymer latexes have the potential to improve performance in applications such as surface sizing and paper coatings over the current technology of blending starch suspensions with synthetic polymer latexes.^{1,2} Furthermore, replacement of a proportion of synthetic monomer with starch to produce a stable low-viscosity latex is desirable because of the low cost and the environmental benefits (biodegradability, renewable resource) of starch.

There is extensive literature over nearly fifty years reporting grafting of synthetic polymers onto starch and cellulose.^{3,4} The vast majority of papers have been concerned with producing hydrophobically modified starch rather than latexes. A succinct review of the reaction chemistry of starch grafting has been compiled by Athawale and Rathi.⁵ One of the first successful techniques⁶ employed ozone as a means of creating grafts. Apart from patents, there are only a few reports in the scientific literature of latex production from grafted polysaccharides;^{7,8} these latexes only contained small proportions of starch (less than a few percent) whose role in the latex is as stabilizer rather than a bulk component of the final product.

Several starch copolymer latex formulations have been patented for coating of paper or fibers.⁹⁻¹³ Brockway used peroxide and persulfate initiators to graft acrylate esters to gelatinized starch, producing latexes that improved adhesion of the starch to hydrophobic fibres.^{9,10} Kightlinger et al. produced high solids content latexes using Ce^{IV} to initiate polymerization of acrylate monomers grafted on starch,¹¹ although this method used only a low starch-to-monomer ratio and also requires the starch to be thinned to the point where tensile strength decreases dramatically. Moeller and Glittenberg claimed inclusion of polymer nanoparticles in “starch particles” or starch inclusions in polymer particles depending on the “hardness” of the synthetic copolymer composition (undisclosed mixtures of styrene, butadiene and acrylonitrile);¹² the product achieved gains in gloss but weakened the surface strength of the coating.¹⁴ Rinck et al. gave a

process for producing stable, high solids, low viscosity latexes with moderate particle size in the presence of low molar mass (MM) dextrans¹³ (dextrans have the same chemical composition and branching pattern as starch, the only difference between the two being that dextrans have lower molar masses). Although they gave no information on grafting efficiency or latex morphology, they noted that the maximum amount of high MM dextrin ($> 10^5 \text{ g}\cdot\text{mol}^{-1}$) present must be less than about 5 % or else the latex gels or coagulates. Workers at Penford Products Company have reported¹⁵⁻¹⁷ emulsion polymerization of styrene and butadiene in the presence of starch, the products presumably involving some grafting.

Nguyen et al. reported that 1,3-butadiene, which is usually considered to be relatively unreactive, grafts efficiently to highly thinned starch.¹⁵ Their preferred initiator was potassium persulfate which is used extensively to initiate homopolymerization. Furthermore, a chain transfer agent was added that will transfer radical activity to form homopolymer. This apparent contradiction may be resolved if the homopolymer (which inevitably forms under these conditions) cross-links through the residual double bonds of starch-g-polybutadiene, thereby becoming indirectly grafted to the starch. They reported high percentage grafting with total extractables less than 20 % and in some instances as little as 0.5 % on a dry weight basis. Further work by the same group at Penford¹ demonstrated the morphology of films formed from starch-g-copolymer latexes prepared according to Nguyen's patent as non-coalesced particles bound by starch, which are readily redispersed in water.

In all of the patents mentioned above very little discussion of the underlying mechanisms is given, and the only internal particle morphologies examined are those of Moeller and Glittenberg's inclusion particles.¹²

The aim of the present work is to explore processes which could encapsulate starch in latex particles, and to quantify the underlying mechanisms.

Starch macroinitiators can be formed by ozonolysis, whereby hydroperoxide groups are thought to be formed on the starch backbone.^{18,19} Addition of appropriate monomer together with thermolysis or redox activation then initiates polymerization (and therefore grafting) of synthetic polymer. Ozone has been used in this way to graft butadiene²⁰ and styrene^{6,20} to polysaccharides but not to make a latex. There may be some difficulties related to industrial use of ozone but ozone is used industrially in large scale water purification and bleaching of wood pulp. Potential advantages of such a procedure are that ozone is cheap, clean, environmentally sound and leaves no residue in the latex; indeed, its bleaching properties can remove colored impurities. Also, the oxygen-centered radicals so produced are reactive to all common monomers. However, significant degradation of the starch results from lengthy exposure to ozone. This has implications for mechanical strength imparted to the substrate in coating applications.

Emulsion polymerization is commonly implemented with a pre-formed seed, whereby second-stage polymerization is carried out by the addition of monomer and initiator to a latex.²¹ Starch from the waxy corn varieties used is almost entirely amylopectin; this is a highly branched polymer colloid which, after functionalization to form initiating sites on the starch, might function as a seed for grafting hydrophobic polymers. Native amylopectin macromolecules in water are typically 300 to 400 nm in diameter (while modified waxy starches such as StacKOTE™ 7, derived from Amioca, are about 100 to 250 nm in size). Typical “particle numbers” calculated for amylopectin macromolecules are of the order of 10^{17} L^{-1} for a 20 % solids suspension, which corresponds to those of typical latexes. This correspondence made the notion of using amylopectin macromolecules as “seed particles” most enticing. However, there is an essential difference between such a procedure and conventional seeded emulsion polymerization: the concentration of polymer within the “seed”. Taking a specific example of measurements of weight average molecular weight $\bar{M}_w \sim 2.5 \times 10^8$ and of radius gyration ~ 250 nm (in a 90 % dimethyl sulfoxide / 10 % water solution) of the same amylopectin samples by Han et al.,²² one calculates a mass fraction of polymer inside a single amylopectin molecule in solution of ~ 1 %. This compares to that inside a swollen particle in a typical seeded emulsion

polymerization of synthetic polymer of ~ 30 % mass fraction (i.e., ~ 0.3 weight fraction polymer, 0.7 weight fraction monomer).²³ Thus the polymer within an amylopectin molecule in solution is so dilute that it might function more as a scaffold or skeleton for polymerization of a synthetic monomer, rather than as a true seed.

It might be expected that, by grafting sufficient numbers of hydrophobic chains to amylopectin, conditions might be found that would make the amylopectin macromolecules (which it will be recalled are mainly water with a sparse starch skeleton) collapse in on themselves, thereby encapsulating much of the starch molecule in a hydrophobic latex particle stabilized by the unencapsulated portion of the “seed” amylopectin macromolecule and/or fragments of degraded amylopectins which would be grafted to the outside of the particle. This would have the further benefit of reducing or even removing the need for added surfactant. Obviously using starch to stabilize a latex is not novel. The points we make are (1) that it is possible to incorporate highly degraded starch *inside* the particles not merely as a stabilizer on the outside of particles and (2) that nearly all the literature is from patents and little research has been published on the mechanisms behind the patented processes. We would like to think we have shed some light on this under-reported chemistry.

EXPERIMENTAL

Syntheses

Reactions were undertaken in a 1 L Pyrex water-jacketed reactor equipped with an overhead stirrer, ports (with septa) for the addition of reagents and a fine pored diffuser to supply gas in small bubbles (O₂/O₃ or N₂ as required). The efficiency of the ozonolysis procedure depends, amongst other factors, on the bubble surface area, as mass transfer across the bubble/solution

interface is slow. The monomers used (styrene, Huntsman; n-butyl acrylate (BA) and vinyl acetate, Aldrich) had their inhibitors removed on alumina columns and were stored at 4 °C for not more than a few days before use. Monomers were purged with nitrogen for 15 minutes immediately prior to use. Iron(II) sulfate and sodium metabisulfite (Ajax Finechem, analytic reagent grade), sodium sulfoxylate (Fluka, purum), potassium persulfate (Merck), Aerosol MA-80 (Cytec) and sodium dodecyl sulfate (Aldrich) were all used as supplied.

Ozonolysis of starch.

Waxy corn starches (Mazaca, kindly provided by Penfords; Amioca and StacKOTE™ 7, kindly provided by National Starch) were gelatinized in a Siltex 175D autoclave (30 min at 120 °C) in sodium acetate buffer (pH 3.5, 0.1 mol·L⁻¹) for all ozonolysis experiments. Sodium acetate buffer (pH 3.5, 0.1 to 0.2 mol·L⁻¹) was prepared from sodium acetate (Merck, pro analysi) and glacial acetic acid (Ajax Finechem, analytic reagent grade), used as supplied. Milli-Q water (18.2 MΩ·cm⁻¹) was used throughout. Ozone was generated by electric discharge with a Yanco Industries, Canada, OL80W ozonolyzer. Aliquots of gelatinized starch (700 g) were oxidized with a stream of ozone using oxygen as the carrier gas. Standard conditions, used throughout except where indicated otherwise, were 10 °C, 7.7 % ozone by weight at 100 mL·min⁻¹.

Iodometric titration.

Starch hydroperoxide (StaOOH) determination was by iodometric titration.²⁴ Typically, a 20 mL sample of ozonolyzed starch solution was purged with nitrogen for 15 min. To this was added 100 mL of thoroughly purged H₂SO₄ (1.0 mol·L⁻¹, Aldrich), an excess of sodium iodide (1 g, reagent grade, Merck) and three drops of a 3 wt% solution of ammonium molybdate (NH₄)₆Mo₇O₂₄ to catalyze the reduction of StaOOH by iodide ions (the catalyst was necessary to achieve reasonably sharp end-points in a timely fashion). The iodine so formed was titrated with nitrogen-purged sodium thiosulfate solution (0.01 mol·L⁻¹, Aldrich) maintaining a nitrogen

atmosphere throughout. In blank titrations of ozonolyzed buffer (without starch), only insignificant amounts of non-starch peroxides (presumably H_2O_2) were detected. Higher flow rates of ozone created foaming problems, and thus $100 \text{ mL}\cdot\text{min}^{-1}$ was selected as optimum for our reactor. At this flow rate $12.5 \text{ mmol}\cdot\text{h}^{-1}$ of ozone is delivered to the reaction mixture.

Thermal decomposition of starch hydroperoxides.

For the determination of Arrhenius parameters, ozonolyzed starch solutions were purged with nitrogen and equilibrated in temperature controlled baths for 20 minutes. Samples were taken at suitable intervals (from 20 min at 58.5°C to 20 h at 30°C), hydroperoxide concentration was determined by iodometric titration and fitted with a first order exponential decay. This is something of an oversimplification as it is quite likely that several different hydroperoxides (and possibly other strongly oxidizing species as well) are formed during ozonolysis. Also, it is well known that decomposition rates of peroxides are very sensitive to rough surfaces, dust particles and trace contaminants.²⁵ One might expect these factors to create problems with rate measurements. Nonetheless, over this temperature range the decomposition data were well fitted by first-order kinetics (see for example: Figure 4).

Latex 1.

StacKOTE™ 7 (20 g) was gelatinized at 90°C for five min in $0.025 \text{ mol}\cdot\text{L}^{-1}$ sodium hydroxide solution (180 g). It was then ozonolyzed at room temperature for 23 h producing a low-viscosity clear solution, pH 3. The temperature was increased to 50°C under nitrogen purging then styrene (18 g) was added. Iron(II) sulfate solution was added (0.3 mL , $0.05 \text{ mol}\cdot\text{L}^{-1}$) followed by sodium metabisulfite (25 mL , $0.2 \text{ mol}\cdot\text{L}^{-1}$ at $0.02 \text{ mL}\cdot\text{min}^{-1}$) and maintained at 50°C for 48 h.

Latex 2.

400 mL of a 15 wt% StacKOTE™ 7 suspension in sodium acetate buffer ($0.2 \text{ mol}\cdot\text{L}^{-1}$, pH 3.3)

was gelatinized in the autoclave at 121 °C for 30 min. It was then ozonolyzed at room temperature for 44 h. The reactor was purged with nitrogen for 20 minutes before iron sulfate solution was added (0.7 mL, 0.05 mol·L⁻¹) followed by sodium sulfoxylate (0.025 mol·L⁻¹, 10 mL at 0.05 mL·min⁻¹) and styrene/BA (10 g, 50/50 wt/wt) while the temperature was increased to 50 °C. After 40 minutes a mixture of styrene (40 g) and BA (40 g) was added at 0.6 mL·min⁻¹ and maintained at 50 °C for 2 h. Potassium persulfate (0.4 g) was added and the temperature was increased to 60 °C for 14 h. To 300 g of this latex was added 30 g styrene/BA (50/50 wt/wt) and the temperature maintained at 60 °C for 4 h.

Latexes 3 – 12, based on native starch.

Waxy corn starch was gelatinized in sodium acetate buffer (0.1 M) in the autoclave at 121 °C for 30 min. The starch suspension was then ozonolyzed for 1 – 3 h as detailed in Table 1. The reaction was heated to the required temperature with nitrogen purging, monomer was added and the temperature maintained as detailed in Table 1.

Latex 13.

A 10 wt% suspension of Mazaca was gelatinized in sodium acetate buffer (0.2 mol·L⁻¹) in the autoclave at 121 °C for 30 min. The starch suspension (575 g) was then ozonolyzed for 3 h and purged with nitrogen for 1 h. *Step 1:* The reaction temperature was set to 50 °C. Styrene (0.55 g), vinyl acetate (0.55 g) and potassium persulfate (1.00 g) were added followed by iron(II) sulfate (0.1 mol·L⁻¹, 10 mL at 0.5 mL·min⁻¹). *Step 2:* The temperature was increased to 70 °C and BA was added (20 mL at 0.5 mL·min⁻¹) after which the temperature was reduced to 50 °C and held overnight. *Step 3:* The temperature was increased to 70 °C and a 50/50 wt/wt mixture of styrene and BA was added (110 mL at 110 mL·h⁻¹) and the temperature maintained at 70 °C for 2 h.

Characterization

Nuclear Magnetic Resonance.

NMR was used to quantify the effect of ozonolysis on branching density with a view to determining the propensity of ozone to attack the α -(1 \rightarrow 6) branch points or α -(1 \rightarrow 4) straight chain glucoside bonds as follows. A 14 wt% suspension of Mazaca was gelatinized and ozonolyzed under standard conditions as described above. Samples were taken at 0 h, 0 h 30, 1 h, 1 h 50, 22 h, and 44 h. 2 mg freeze-dried samples of ozonolyzed starch were dissolved overnight in 0.5 mL DMSO-d₆/D₂O 80/20 v/v at 80 °C. Quantitative ¹H NMR spectra were recorded on a Bruker DPX300 at 90 °C at a Larmor frequency of 300.13 MHz. 64 transients were recorded with a 7.9 μ s 90° pulse and a 5 s relaxation delay. The chemical shift scale was calibrated using a trisilylpropanoic acid (TSP) internal standard at 0 ppm. The temperature was calibrated using an ethylene glycol standard.²⁶ Branching levels were calculated by integration of the signal between 5.35 and 4.90 ppm for the α -(1 \rightarrow 4) and the chain ends, between 4.90 and 4.77 for the α -(1 \rightarrow 6), and subsequent division of the latter by the former.

Size Exclusion Chromatography (SEC).

Amylopectin was debranched as follows: 7 μ L (3800 units) of isoamylase (Aldrich) was added to 1 mL of starch suspension (10 wt% in 0.2 M sodium acetate buffer, pH 3.5) and maintained at 50 °C for 2 h. All ozonolyzed and debranched starch samples were injected at two different concentrations to check that there was no aggregation; the chromatograms were flow-corrected and baseline-corrected. The conditions for the SEC analysis were the following: Shimadzu LC-10ATVP pump, Shimadzu DGU-14AVP degasser, Shimadzu SIL-10ADVP autoinjector, Shimadzu CT10ACVP column oven, Wyatt Optilab DSP interferometric refractometer; Waters columns: Ultrahydrogel guard column + Ultrahydrogel500 + Ultrahydrogel250 + Ultrahydrogel125; eluent: 0.05 mol·L⁻¹ ammonium acetate set at pH 5.2 with acetic acid + 0.05 %

sodium azide; flow 0.6 mL·min⁻¹.

Energy dispersion spectroscopy.

EDS²⁷ line scans of starch-*g*-styrene latex particles were obtained on a VGSTEM (HB601, Oxford Instruments ISIS with a 1 nm probe size) by measuring the wavelength and intensity of the X-rays emanating from a line scan with a very intense electron beam across the diameter of individual particles. The only significant source of oxygen in such a system is the starch itself, and thus an “oxygen scan” across the particle reveals the distribution of starch within the particle.

Particle size and viscometry.

Particle sizes were determined either by Capillary HydroDynamic Fractionation (CHDF, Matec, CHDF1100) at 1.4 mL·min⁻¹ or by dynamic light scattering (DLS, Brookhaven BI9000AT, 35 mW He/Ne laser, 632.8 nm). Viscosities were measured on a Brookfield DVII+ viscometer with the appropriate spindle, at 100 rpm.

Ultracentrifugation.

For our purposes starch grafting efficiency is defined as the percentage of starch grafted to latex particles. This was measured by ultracentrifugation of latex (90,000 rpm for 30 minutes), with determination of the starch content of the supernatant by gravimetry. Blanks were performed on starch solutions; it was found that a very small amount of a brownish impurity precipitated but this was insignificant in terms of mass balances.

RESULTS AND DISCUSSION

Starch Ozonolysis

Hydroperoxidation of starch.

The ozonolysis conditions were varied to determine the dependence of production of hydroperoxides on parameters such as temperature, flow rate and concentration of ozone, starch type and starch concentration. The efficiency of hydroperoxide production by ozonolysis for our reactor setup under our standard conditions (10 °C, 7.7 wt% ozone/oxygen, 100 mL·min⁻¹) was 9.3 % (defined as the molar percentage of ozone converted to hydroperoxide) for the first 3 h. Thereafter, the efficiency decreased as the hydroperoxide concentration plateaued after 20 h at about 8 mmol·L⁻¹, only about twice the concentration attained in the first three hours. The effect of temperature on hydroperoxidation of starch is shown in Figure 1. Hydroperoxidation at 0 °C is less efficient than at 10 °C, possibly due to increased viscosity or decreased reactivity. At 30 °C the decrease of efficiency compared to 10 °C is at least partly due to thermal decomposition of hydroperoxides (decomposition rate constant $k_d = 5 \times 10^{-6} \text{ s}^{-1}$; see below) and decreasing solubility and half life of ozone with increasing temperature. The drop in hydroperoxidation rate at longer times is consistent with thermal decomposition. There was also an unexplained inhibition period with very little hydroperoxidation in the first 30 minutes.

The effect of initial pH on hydroperoxidation of starch is shown in Figure 2: there is a strong dependence on pH. This is to be expected as ozone is less stable at high pH due to its reaction with hydroxyl ions liberating both oxygen and hydroxyl radicals.²⁸ The mechanism is unknown and whether it is different for different pH values is beyond the scope of the present work. At low pH the production of starch hydroperoxide is relatively efficient. At higher pH it is much slower and only increases after the pH has been reduced by side reactions of ozone with starch. The rate increases with time in the high initial pH suspensions as the pH decreases throughout.

The effect of starch type and concentration on hydroperoxidation is shown in Figure 3. Production of hydroperoxides was similar for each starch type and independent of concentration with the exception that, at the highest starch concentration tested (21.5 wt%) the efficiency decreased noticeably, probably due to the effect of increased viscosity on the transport of ozone from bubbles into solution.

Thermal decomposition of starch hydroperoxides.

The thermal decomposition rate of starch hydroperoxides was measured at temperatures ranging from 30.5 to 58.5 °C as detailed above. A typical decomposition plot is presented as Figure 4 and the decomposition rate coefficients so obtained are plotted as a function of inverse temperature in Figure 5. The Arrhenius parameters (frequency factor A and activation energy E_{act}) for thermal decomposition of the starch hydroperoxide macroinitiator have been determined as $A = 1 \times 10^{16} \text{ s}^{-1}$ and $E_{\text{act}} = 125 \pm 8 \text{ kJ}\cdot\text{mol}^{-1}$. These values are consistent with the proposition that the decomposing species are mainly hydroperoxides, as typical activation energies for organic hydroperoxides²⁹ are around 130 kJ·mol⁻¹. The frequency factor is typical of that for this type of dissociation reaction.³⁰

Degradation of starch by ozonolysis.

The degradation of starch by ozone before its use as a macroinitiator in latex production was characterized by SEC and NMR. SEC traces of starch degraded over various times of ozonolysis are shown in Figure 6, together with those of two debranched Mazaca samples. Quoting absolute molar mass distributions (MMDs) of amylopectins from SEC traces is incorrect as amylopectins are highly branched and therefore there is no one-to-one relationship between hydrodynamic volume (as measured in SEC by calibration against linear standards) and MM. Therefore we have limited comment to qualitative comparisons of SEC distribution as a function of elution time. The hydrodynamic volume of the degraded starch clearly decreases with increasing ozonolysis

time (traces a to f), which is usually attributed to oxidative and hydrolytic cleavage of the glycosidic bonds.¹⁸ Castro et al. have shown that there is little difference in the MMDs of debranched amylopectin from different varieties of plants, and that the peaks in the bimodal distribution correspond to MMs of about 8,500 and 2,500 g·mol⁻¹.^{31,32} Using debranched Mazaca (traces g and h) as an SEC standard shows that amylopectin that has been ozonolyzed for more than 20 h (traces e and f) has hydrodynamic volumes much smaller than that of a linear chain of 8,500 g·mol⁻¹.

Figure 7 shows the anomeric region of ¹H NMR spectra of Mazaca starch after various ozonolysis times: (a) 0 min, (b) 30 min, (c) 60 min, (d) 110 min. The signals at 5.20, 5.15, 5.05 and 4.85 ppm arise from the α-(1→4) linkage between monomeric units, from the non-reducing ends, from the reducing ends, and from the α-(1→6) linkage (branching point) respectively.³³⁻³⁶ Increasing ozonolysis times increased the number of chain ends with respect to α-(1→4) linkages, as shown by the relative increase of the intensity of the signal at 5.15 ppm with respect to the one at 5.20 ppm. This provides evidence that chain scission is primarily at the α-(1→4) linkages, as this is the only way that more non-reducing ends may be formed. Possible oxidation of reducing ends by ozone is insignificant in amylopectin, as there is only one such group per amylopectin molecule (very small signal at 5.05 in spectrum (a)) compared to ~10⁵ non-reducing ends. Increasing ozonolysis times also leads to an increase in branching level, 2.9, 4.5, 5.0 and 4.8 for spectra (a) to (d) respectively. The precision on these branching levels is estimated at 7 %, 6 %, 7 %, 11 % from the respective signal-to-noise ratios (15.2, 17.37, 15.3, 10.8) of the signal at 4.85 ppm.³⁷ Our NMR results demonstrate that glycosidic bond scission is limited primarily to the α-(1→4) bonds in amylopectin leaving the α-(1→6) bonds intact.

Samples submitted to longer ozonolysis times (22 and 44 hours) were investigated with the same NMR method. However, they exhibited poor signal-to-noise ratios of the signal at 5.20, 5.15, 5.05 and 4.85 ppm, indicative of a significant degradation of the glucose units.

No unambiguous mechanism for the reaction of ozone with polysaccharides was uncovered in our literature searches. We have shown that (a) the degradation of starch by ozone at 10°C occurs primarily at the α -(1→4) bond as indicated by the relative increase in the formation of reducing end groups with no measurable loss of α -(1→6) signal in the NMR and (b) a significant amount of starch hydroperoxide appears to be formed as indicated by iodometry and the Arrhenius parameters determined therefrom.

Amylopectin-graft-copolymer latexes

Starch incorporation in particles of latex 1.

The starch-g-styrene latex 1 was prepared for study by energy dispersion spectroscopy (EDS). It was very polydisperse with a weight average diameter of 210 nm, determined by CHDF. Figure 8 shows an EDS line scan on latex 1 together with the corresponding electron micrograph. In the micrograph the bright region of the left half is a hole in the support film. Particles suspended over such holes are selected for oxygen EDS line scans as the support film contains oxygen. The only significant source of oxygen in such a system is the starch itself and thus, an “oxygen scan” (circles) across the particle reveals the distribution of starch within the particle. Oxygen concentration was modeled with the assumption that for homogeneous particles (solid line) the intensity of the x-rays characteristic of oxygen should be proportional to the thickness of the particles, and for core-shell (dotted line) it should be proportional to the thickness of shell the scan is passing vertically through; an elementary calculation for these simple geometries. The core-shell distributions were calculated for a shell arbitrarily occupying 30 % of the particle volume. If the starch was merely adsorbed at the particle surface, one would expect a completely different profile resulting from core-shell morphology, with peaks at the edges and a lower oxygen count towards the centre. Varying the shell thickness within physically reasonable values affects the width of the peaks at the particle edges but the curves remain qualitatively the same. The peak from 270 to 300 nm in the homogeneous model is due to a combination of factors. Firstly, the support film starts at 270 nm, its contribution can be estimated from the signal in the region where the scan passes only through the support film; then, because the large particle

“looms” over the smaller one, there is a region of 7.5 nm width centered at 285 nm over which the profile intersects both particles. Taking all this into account, it is clear that the homogeneous model is a surprisingly good fit to the line scan data while a core-shell morphology may be discounted. Thus the oxygen line scan provides very strong evidence that the starch is incorporated more-or-less uniformly throughout the particle. Unfortunately, EDS could not be utilized in this fashion to characterize latexes grown with BA and vinyl acetate, as oxygen is present in the synthetic polymers.

This latex is not a representative paper-coating latex (or pre-cursor thereof). It is a starch-g-polystyrene latex and was used to demonstrate the incorporation of starch within the particle by an EDS oxygen line scan as described above. The point of the line scan is the even distribution of oxygen (and therefore of starch) throughout the particle. The slight enrichment at the surface is unimportant and is probably due to the degraded starch at the surface stabilizing the latex.

Paper coating performances of latex 2.

The starch-g-styrene-co-n-butyl acrylate latex 2 was selected for testing because it had the targeted solids content and film forming properties desirable in a potential paper coating. It had a final solids content of 36 % (determined by gravimetry), a Brookfield viscosity of 12 cP, a weight average diameter of 148.5 nm and relative variance of 0.014 (determined by DLS). It dried to a clear, pliable film that swelled slightly in water but maintained its integrity. This latex performed poorly in paper coating tests conducted using standard protocols, with the exception of the roughness of the coated paper product which was significantly lower than for a conventional starch/latex blend. Roughness is attributed to shrinkage during drying and was one of the attributes that the grafted product was expected to improve. All the other coating properties (whiteness, brightness, gloss, wet-pick strength etc.) were outside the range of typical commercial products. This was attributed in part to the extensive degradation undergone by the starch during prolonged ozonolysis (see above). Furthermore, ultracentrifugation revealed that only about 30 % of the original starch was grafted and the free starch in the system was of low

molar mass ($<10,000 \text{ g}\cdot\text{mol}^{-1}$). Low MM starch has adverse effects on wet pick strength, which is a measure of the integrity of the coating in the presence of the printer's fountain solution. Ungrafted, low MM starch migrates and clumps in the coating resulting in mottling. Any significant fraction below about $20,000 \text{ g}\cdot\text{mol}^{-1}$ detracts from paper coating attributes.

The initial hydroperoxide concentration in *Latex 2* was 8 mM. The ozonolyzed starch solution was $0.8 \text{ mol}\cdot\text{L}^{-1}$ in glucoside units. Hence there was one hydroperoxide per hundred glucoside units ($\text{MM}=16,200 \text{ g}\cdot\text{mol}^{-1}$). Starch chains substantially below this MM are unlikely to have a hydroperoxide functionality and thus would not become grafted to latex particles. This is likely to contribute to the low percentage starch grafting in this latex and the low MM of the ungrafted fraction.

Investigation of grafting and gelation mechanisms with high MM starch latexes 3 to 13.

In the light of the preceding inferences, shorter ozonolysis times were employed and unmodified waxy starches were used, as detailed in Table 1; this was expected to reduce the amount of low MM starch in the system. Latexes 3 to 12 were prepared as described above. Well behaved latexes were readily made with starch concentrations below c^* (the concentration at which all macromolecules in solution are in contact with their neighbors), which is about 3 wt% for amylopectin in water (latexes 5 and 10). These were stable on the shelf with no sign of coagulation after more than six months.

Latexes made with native starch that had been ozonolyzed for 3 h or less at concentrations above c^* gelled after the addition of only small amounts of styrene and/or BA (Table 1, latexes 3,4,6,7,8 and 9). The gels could be redispersed with ultrasonication, producing “normal” low viscosity latex, in which further polymerization could be induced by addition of initiator and more styrene or BA, but these invariably gelled again. In a typical example, the latex 7 gel was broken by ultrasonication of 200 mL samples (Vibracell VCX750; 20 kHz, 15 min at 30 %) to

give a latex of 13 % solids with Brookfield viscosity of 150 cP. When a further 2 % styrene was added, the latex gelled again.

Native amylopectin is known to degrade under shear.³⁸ Latex 8 was prepared using a gelatinized Mazaca suspension that had been ultrasonicated prior to ozonolysis (20 kHz, 15 min at 30 %). This “latex” also gelled. Therefore it is not some effect of ultrasonication on the size or structure of the amylopectin molecule that prevents gelation. It is postulated that the gel is broken because the polymer particles are centers of relatively dense mass tethered together by strands of polysaccharide, rather like dumbbells, and as such experience the most energetic shearing under ultrasonication. The weakest link between two such particles is a single polysaccharide chain and this is easily broken by high shear. A particle may have many tethers, as would be the case when the particle was formed by the coalescence of many neighboring precursor particles. However, amylopectin has a hierarchical structure³⁹ usually denoted by “c” chains for the backbone, “b” chains for branches which are themselves branched and “a” chains which are the terminal branches (see figure 9). Hence, clusters of precursors that may coalesce into particles will ultimately have a common “b” or “c” chain between themselves and any other cluster/particle and this will be the weakest link between two particles.

The proposed mechanism for this gel formation is a slightly unusual sort of cross-linking (Figure 9). It is proposed that precursor particles are tethered to the much larger amylopectin molecules, which act like a scaffold for the synthetic polymerization step. This prevents their precipitation but does not prevent coalescence as the particle surface may be quite bare. Coalescence of precursor particles within a single amylopectin molecule would potentially lead to encapsulation of entire amylopectin molecules. However, above c^* there is a large probability that precursor particles grafted onto one amylopectin molecule could coalesce with precursor particles on an adjacent amylopectin molecule, effectively cross-linking the amylopectin molecules. Therefore it seemed that if coalescence of these precursors could be prevented gel

formation might be avoided. To this end, latexes 11 and 12 were made by adding surfactant at the beginning of an otherwise standard preparation. The latexes were dialyzed for three days with twice daily changes of water. They remained stable on the shelf for more than six months, consistent with our postulate.

The rationale behind the preparation of latex 13 was as follows (Figure 10). It involves use of vinyl acetate (VAc), which is relatively hydrophilic (solubility in water is $0.3 \text{ mol}\cdot\text{L}^{-1}$ at 50°C ⁴⁰) and has a high propagation rate coefficient.⁴¹ In *step 1* it was hoped to graft many “surface-active” chains to each amylopectin molecule. These chains would result from termination by combination of grafted chains with aqueous phase oligomeric radicals initiated by persulfate. From the aqueous phase concentrations and the reactivity ratios for VAc/styrene⁴² it is predicted that the starch radical is most likely to propagate with one or two VAc molecules, followed by a styrene molecule which effectively “caps” the grafted chain, because propagation with another styrene unit is much slower than termination and addition of a VAc unit is slower still. Simultaneously, sulfate radicals will initiate aqueous-phase oligomeric radicals “capped” with styrene. Of course it is possible for such “capped” radicals to propagate with styrene but it is well known that in persulfate-initiated styrene emulsion polymerization the entry efficiency is very low ($< 1\%$ under our reaction conditions⁴³), and most oligomeric radicals terminate by combination in the aqueous phase. In the absence of polymer particles, aqueous phase termination is even more favored, and therefore most grafted oligomers will be terminated in this fashion. This will create an entity that might be loosely described as a “unimolecular-micelle”. Carbohydrates form stable structures in solution, especially at the high starch concentrations in this work and in the model we propose the starch forms the scaffold connecting the coalesced precursor particles. Together they form a thick gel. However, we found that if the coalescence of precursor particles is prevented the latex doesn’t gel and we conclude therefore that the starch scaffold is limited to individual amylopectin molecules. The reason for adding VAc is simply to increase the length and thereby the surface activity of the grafted chains over that which one

would expect if styrene alone was used.

Step 2 grows precursor particles stabilized against coalescence by the sulfate end groups resulting from aqueous phase initiation of n-butyl acrylate by sulfate radicals. Entry by n-butyl acrylate oligomers is expected to be very efficient,²¹ thereby grafting nearly all the remaining sulfate ions to the precursor particles.

Step 3 is growth of the precursor particles within the amylopectin “unimolecular-micelle” acting as a scaffold. It was hoped that particles that are tethered closely together may be forced to coalesce as they grow by virtue of being attached via a common “b” (or even “a”) chain, while those on neighboring amylopectin molecules are repelled by the surface charge on the particles and the charge due to the sulfate grafted to the amylopectin; if *step 1* is omitted, *step 2* on its own produces a gel after the addition of only a small amount of BA, (e.g. latex 3). Such “forced coalescence” is most likely to occur towards the center of amylopectin molecules where the mobility of the growing precursor particles is most constrained.

Finally it was hoped that the surface active segments grafted to the amylopectin might be inclined to adsorb onto the growing particles, thereby collapsing the amylopectin.

The final latex prepared using this procedure was stable against electrolyte (several months in 4 mol·L⁻¹ NaCl), but only 20 % of the starch was effectively grafted to the particles. Thin films cast from this latex were transparent, though some phase separation was apparent in very thick (~1 mm) films. Films cast from this latex were more pliable than starch films and redispersed in water (over a period of a few days or very rapidly with the aid of gentle ultrasonication), yielding much the same particle size distribution as the parent latex (~150 nm). Non-coalesced particles were visible in fractured films with SEM. These observations are consistent with the mechanistic hypotheses of Figure 10.

Latex 13 is the end result of our successful understanding of the mechanism of gelation (and its

avoidance) for latexes based on undegraded starch. It was not tested for paper coating however, because the facile redispersion in water of films cast from this latex was contrary to the specifications for such films.

CONCLUSIONS

A method is described whereby highly branched starch molecules (amylopectin or modified amylopectin) can be induced to act as a scaffold to form grafts with a synthetic polymer using free-radical polymerization. The technique is to create sites on the amylopectin chains in solution which can act as macro-initiators for free-radical polymerization in emulsion. Surfactant-free, starch-*graft*-copolymer latexes can be made based on native waxy starches, which comprise highly branched amylopectin chains, with minimal degradation if the precursor particles are stabilized against coalescence at early times in the reaction. Failure to do so results in gelation of the “latex” after the addition of only a small amount of monomer, a problem reported in the literature and only overcome in the past by using highly degraded starch^{11,13} with concomitant loss of mechanical strength of the paper coating.

This is the first time that a starch-g-copolymer latex has been characterized by EDS, unambiguously proving that starch may be encapsulated inside hydrophobic polymer particles, complementing the TEM work of Moeller and Glittenberg¹². However, significant encapsulation was only achieved for low molar mass degraded starch (dextrins).

Ozone treatment of amylopectin at 10 °C introduces hydroperoxide functionality. Stable poly(styrene-*co*-n-butyl acrylate) latexes can be synthesized using ozonolyzed amylopectin as both a macro-initiator and stabilizer. Such latexes were stable against electrolyte (several months in 4 mol·L⁻¹ NaCl) but only 20% of the starch was effectively grafted to the particles. Films cast from such latexes were more pliable than starch films and slowly redispersed in water.

In the effort to optimize the process several of the underlying mechanisms have been explored and data quantifying rates of production of starch hydroperoxides by ozone, thermal decomposition rates of the starch hydroperoxides so formed and degradation of amylopectin by ozone has been reported.

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REFERENCES

1. Abell, S. In TAPPI 1992 Coating Conference Proceedings; TAPPI Press: Atlanta, 1992; pp 95-104.
2. Maurer, H. W.; Kearney, R. L. Starch-Staerke 1998, 50, 396-402.
3. Roy, D.; Guthrie, J. T.; Perrier, S. Macromolecules 2005, 38, 10363-10372.
4. Tomasik, P.; Schilling, C. H. In Advances in Carbohydrate Chemistry and Biochemistry, Vol 59; Elsevier Academic Press Inc: San Diego, 2004; pp 175-403.
5. Athawale, V. D.; Rathi, S. C. J.M.S.-Rev. Macromol. Chem. Phys. 1999, 39, 445-480.
6. Kargin, V. A.; Koslov, P. V.; Plate, N. A.; Konoreva, I. I. Vysokomolekulyarnye Soedineniia 1959, 1, 114-122.
7. Gugliemelli, L. A.; Doane, W. M.; Russell, C. R. J. Appl. Polym. Sci. 1979, 23, 635-644.
8. Bertholon, I.; Lesieur, S.; Labarre, D.; Besnard, M.; Vauthier, C. Macromolecules 2006, 39,

3559-3567.

9. Brockway, C. E. (A. E. Staley Manufacturing Company). US Patent US3,061,472, October 30, 1962.
10. Brockway, C. E.; Christman, D. W.; Estes, R. R. (A. E. Staley Manufacturing Company). US Patent US3,061,471, October 30, 1962.
11. Kightlinger, A. P.; Speakman, E. L.; Van Duzee, G. T. (Standard Brands Incorporated). US Patent US4,375,535, March 1, 1983.
12. Moeller, K.; Glittenberg, D. In TAPPI 1990 Coating Conference Proceedings; TAPPI Press: Atlanta, 1990; pp 85-91.
13. Rinck, G.; Moeller, K.; Fuellert, S.; Krause, F.; Koch, H. (Synthomer Chemie GmbH, Cerestar Holding B.V.). US Patent US5,147,907, July 10, 1990.
14. Maurer, H., 2002, personal communication.
15. Nguyen, C. C.; Martin, V. J.; Luebke, G. R.; Pauley, E. P.; Tupper, D. E. (Penford Products Company). US Patent US5,130,395, July 14, 1992.
16. Nguyen, C. C.; Martin, V. J.; Pauley, E. P. (Penford Products Company). US Patent US5,003,022, March 26, 1990.
17. Nguyen, C. C.; Martin, V. J.; Pauley, E. P. (Penford Products Company). US Patent US5,130,394, July 14, 1992.
18. Pan, G. Y.; Chen, C. L.; Gratzl, J. S.; Chang, H. M. Res. Chem. Intermed. 1995, 21, 205-222.
19. Stannett, V. T.; Fanta, G. F.; Doane, W. M.; Chatterjee, P. K. Textile Science and Technology 2002, 13, 323-347.
20. Borunsky, J. (Polymer Corp. Ltd.). Canadian Patent CA549110, November 19, 1957.
21. Gilbert, R. G. In Emulsion Polymerization: A Mechanistic Approach; Academic Press: London, 1995; pp 177.
22. Han, J. A.; Lim, H.; Lim, S. T. Starch-Staerke 2005, 57, 262-267.
23. Gilbert, R. G. In Emulsion Polymerization: A Mechanistic Approach; Academic Press: London, 1995.
24. Vogel, A. I. In A Textbook of Quantitative Inorganic Analysis; Longmans: London, 1961; pp 363.
25. Rice, F. O.; Kilpatrick, M. L. J. Phys. Chem. 1927, 31, 1507-1510.
26. Ammann, C.; Meier, P.; Merbach, A. E. J. Magn. Reson. 1982, 46, 319-321.
27. Williams, D. B.; Carter, C. B. In Transmission Electron Microscopy: a textbook for materials science.; Plenum Press: New York, 1996.
28. Schuchmann, M. N.; von Sonntag, C. Journal of Water Supply - Research and Technology - AQUA 1989, 38, 311-317.
29. Dixon, K. W. In Polymer Handbook; Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds.; John Wiley & Sons: New York, 1999; pp 43-48.

30. Gilbert, R. G.; Smith, S. C. In Theory of Unimolecular and Recombination Reactions; Blackwell Scientific: Oxford and Cambridge Mass., 1990.
31. Castro, J. V.; Dumas, C.; Chiou, H.; Fitzgerald, M. A.; Gilbert, R. G. Biomacromolecules 2005, 6, 2248-2259.
32. Castro, J. V.; Ward, R. M.; Gilbert, R. G.; Fitzgerald, M. A. Biomacromolecules 2005, 6, 2260-2270.
33. Gidley, M. J. Carbohydr. Res. 1985, 139, 85-93.
34. Andersson, L.; Andersson, R.; Andersson, R. E.; Rydberg, U.; Larsson, H.; Aman, P. Carbohydr. Polym. 2002, 50, 249-257.
35. Nilsson, G. S.; Bergquist, K. E.; Nilsson, U.; Gorton, L. Starch-Staerke 1996, 48, 352-357.
36. Peng, Q. J.; Perlin, A. S. Carbohydr. Res. 1987, 160, 57-72.
37. Klimke, K.; Parkinson, M.; Piel, C.; Kaminsky, W.; Spiess, H. W.; Wilhelm, M. Macromol. Chem. Phys. 2006, 207, 382-395.
38. Klavons, J. A.; Dintzis, F. R.; Millard, M. M. Cereal Chemistry 1997, 74, 832-836.
39. Hizukuri, S. Carbohydr. Res. 1986, 147, 342-347.
40. Yeliseeva, V. I. In Emulsion Polymerization; Piirma, I., Ed.; Academic: New York, 1982; pp 247-288.
41. Hutchinson, R. A.; Richards, J. R.; Aronson, M. T. Macromolecules 1994, 27, 4530-4537.
42. Greenley, R. Z. In Polymer Handbook; Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds.; John Wiley & Sons: New York, 1999; pp 264.
43. Maxwell, I. A.; Morrison, B. R.; Napper, D. H.; Gilbert, R. G. Macromolecules 1991, 24, 1629-1640.

Figures and tables

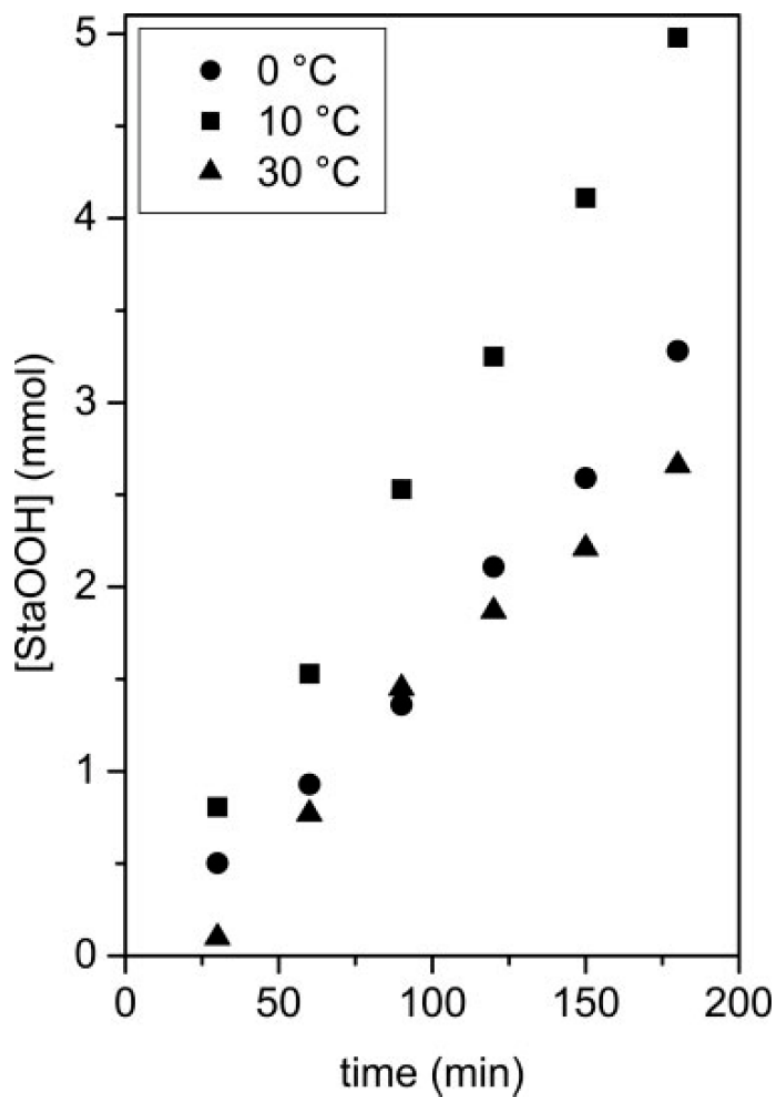


Figure 1: Effect of temperature on hydroperoxidation of starch in a 10 wt% suspension of StacKOTE™ 7 at pH 3.5.

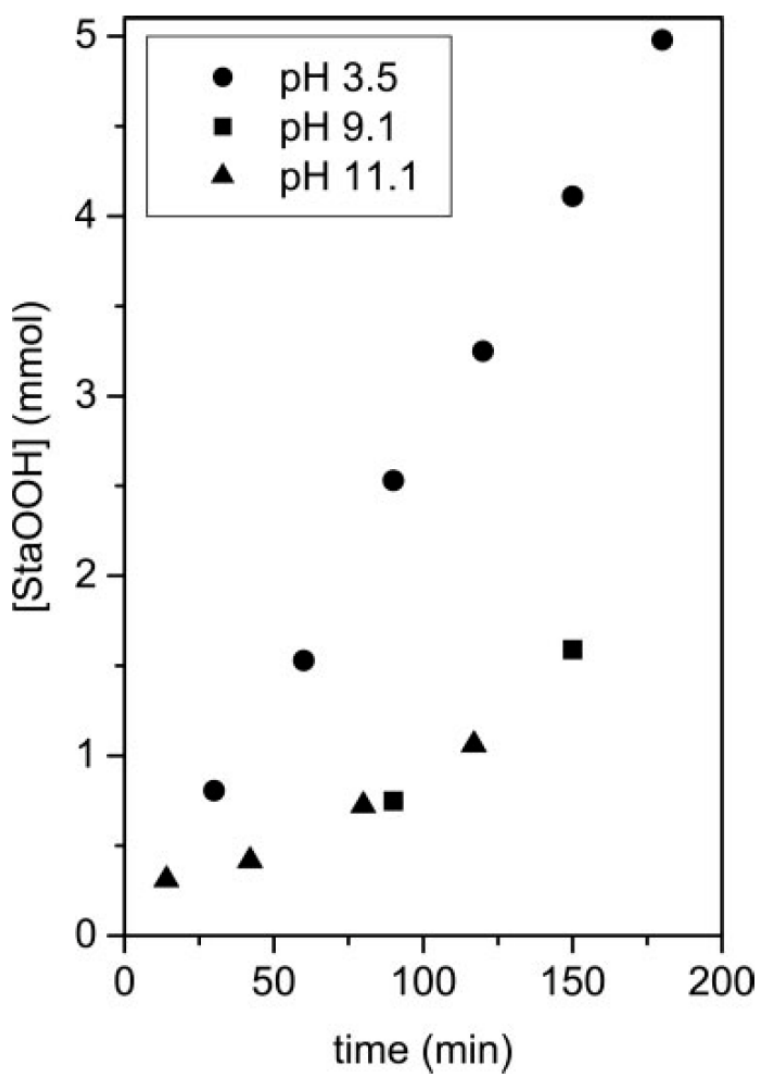


Figure 2: Effect of initial pH on hydroperoxidation of starch in a 10 wt% suspension of StacKOTE™ 7 at 10 °C. The suspension with initial pH values of 9.1 and 11.1 were not buffered; the suspension with initial pH value of 3.5 was buffered with sodium acetate 0.1 mol·L⁻¹.

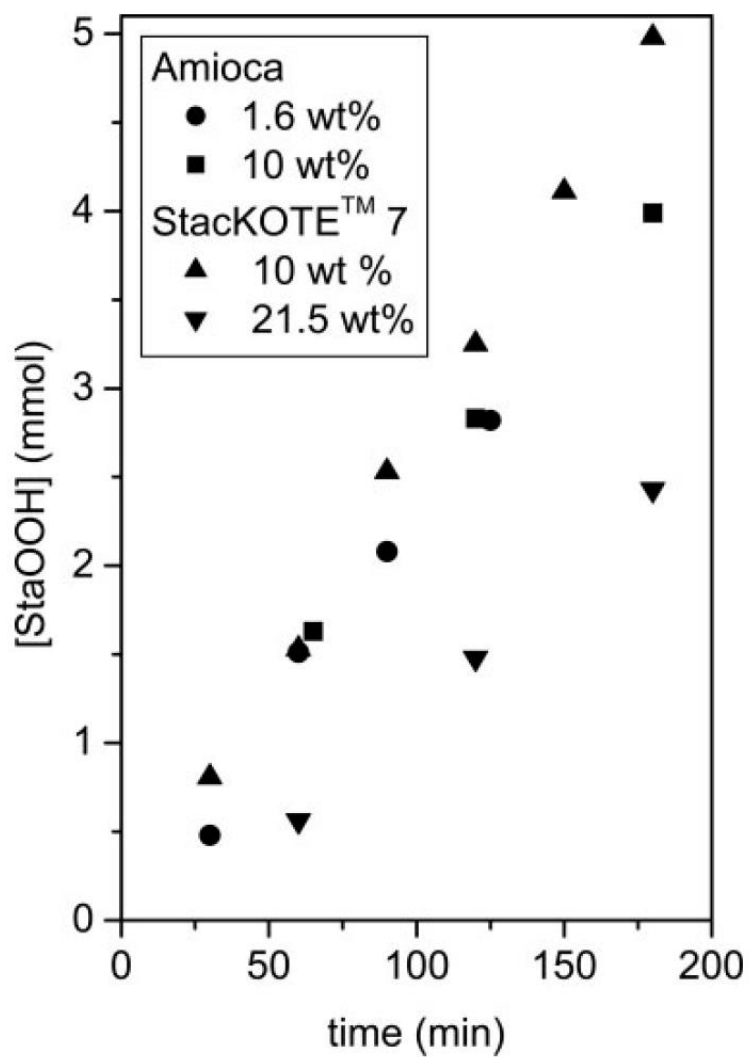


Figure 3: Effect of starch type and concentration on hydroperoxidation of starch at 10 °C and pH 3.5, in a sodium acetate buffer 0.1 mol·L⁻¹.

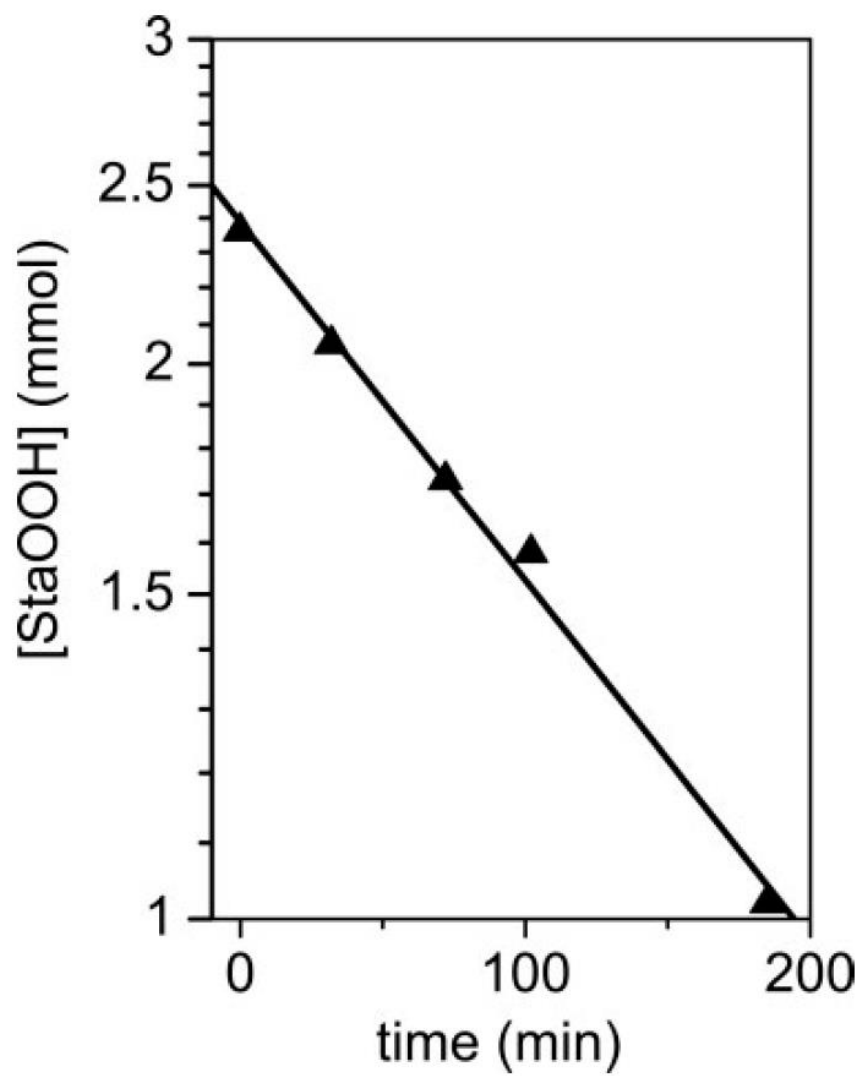


Figure 4: Starch hydroperoxide decomposition at 50°C, pH 3.5, in a sodium acetate buffer 0.1 mol·L⁻¹.

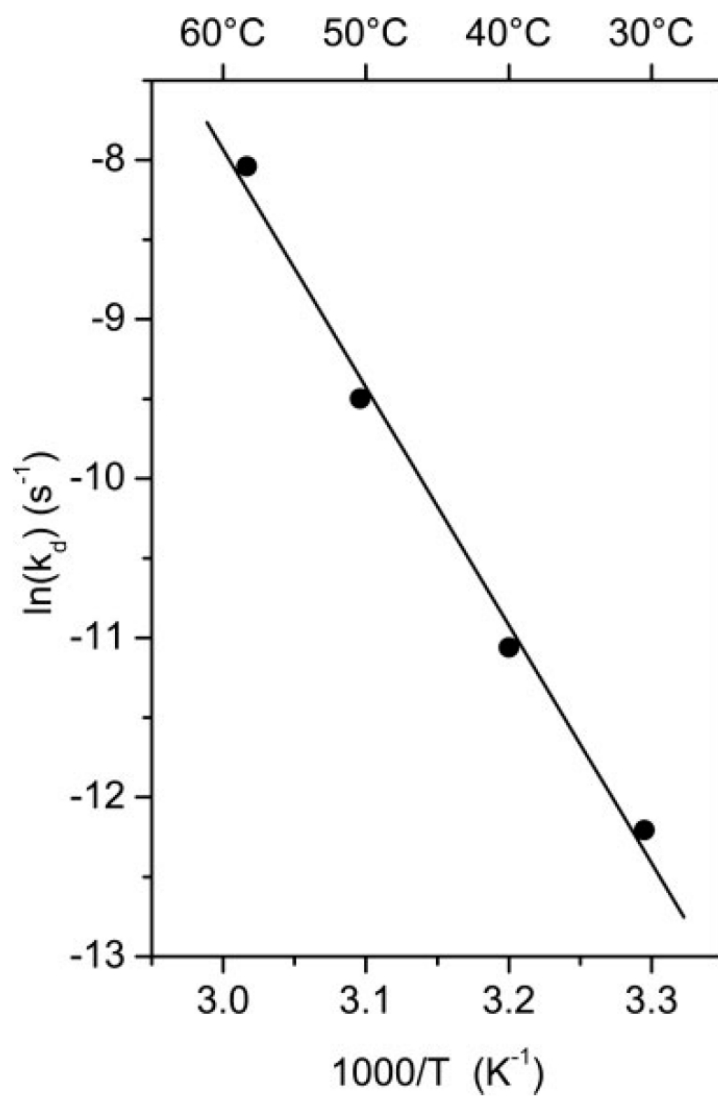


Figure 5: Arrhenius plot of thermal decomposition of starch hydroperoxides in a 1 wt% suspension of Mazaca in sodium acetate buffer 0.1 mol·L⁻¹, at pH 3.5.

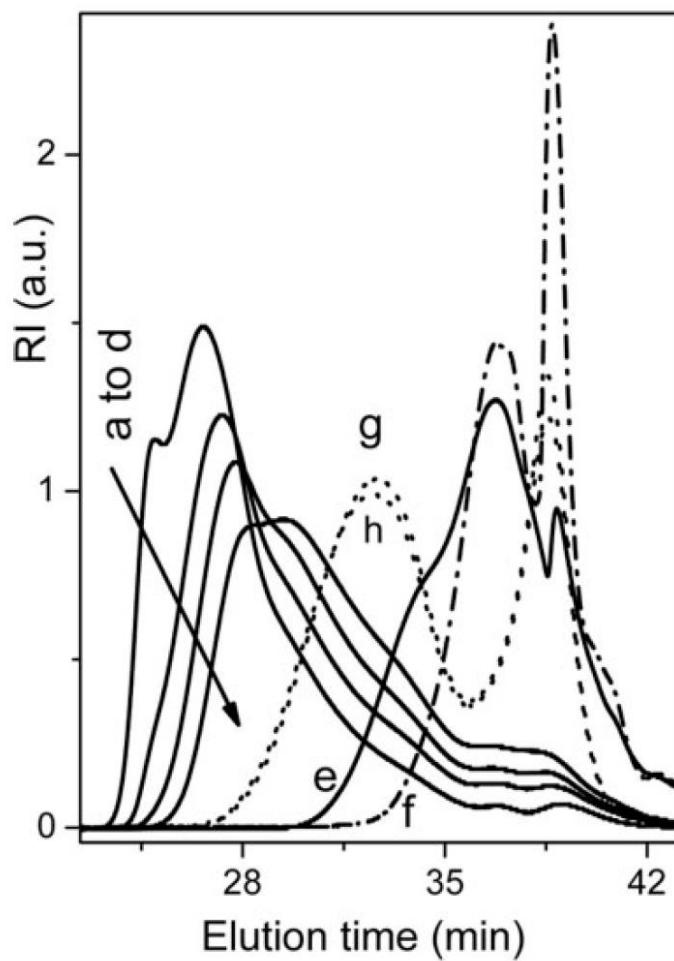


Figure 6: SEC traces of Mazaca after (a) 0 min, (b) 30 min, (c) 60 min, (d) 110 min, (e) 22 h and (f) 44 h of ozonolysis. Traces (g) and (h) are of debranched Mazaca, included for comparative purposes.

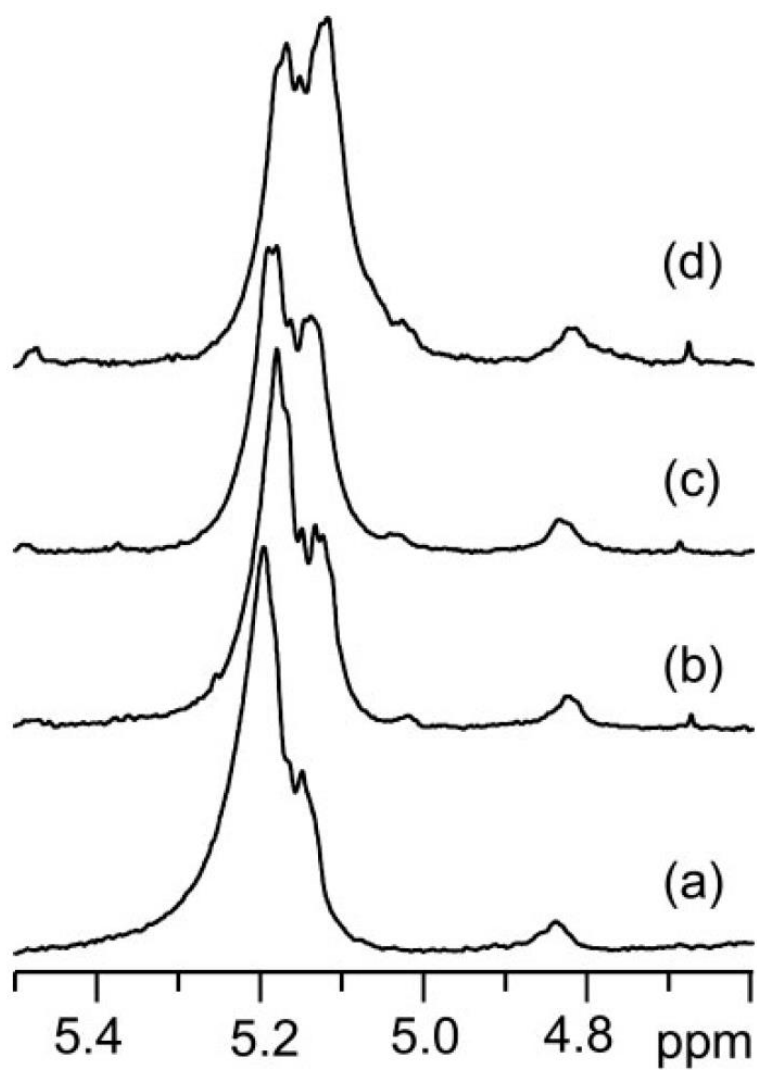


Figure 7: Anomeric region of ^1H NMR spectra of Mazaca starch recorded at 90°C in $\text{DMSO-d}_6/\text{D}_2\text{O}$ 80/20 v/v after (a) 0 min, (b) 30 min, (c) 60 min and (d) 110 min of ozonolysis.

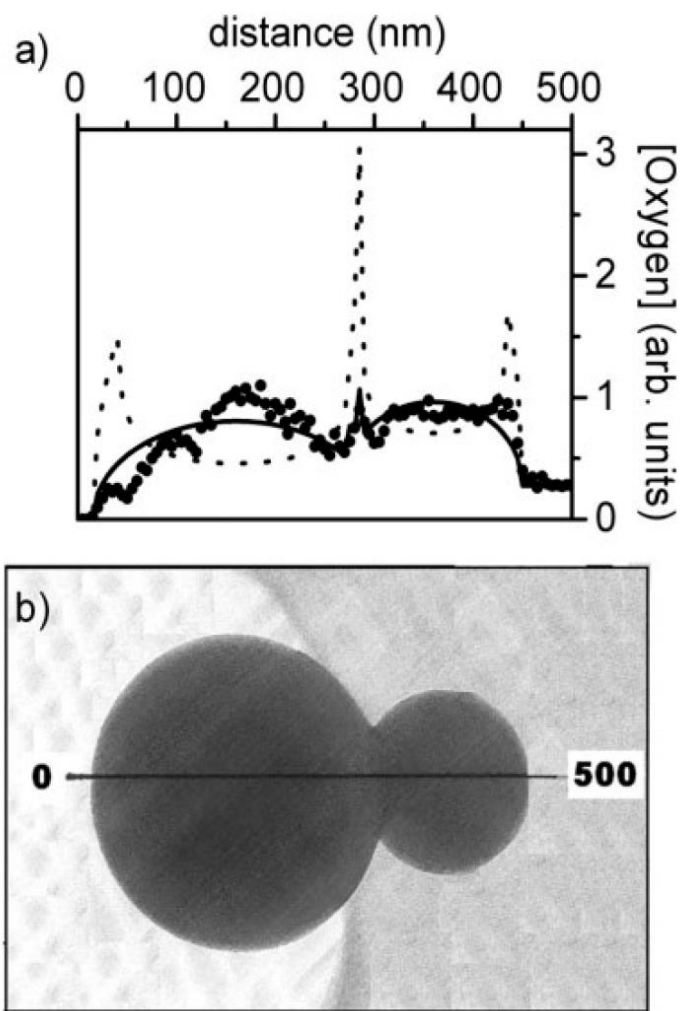


Figure 8: (a) Energy dispersion spectrum for a 1:1 starch:styrene, 12 % solids latex (Latex 1), circles: oxygen profile; solid line: homogeneous starch distribution model; dotted line: styrene core with starch shell; (b) corresponding electron micrograph.

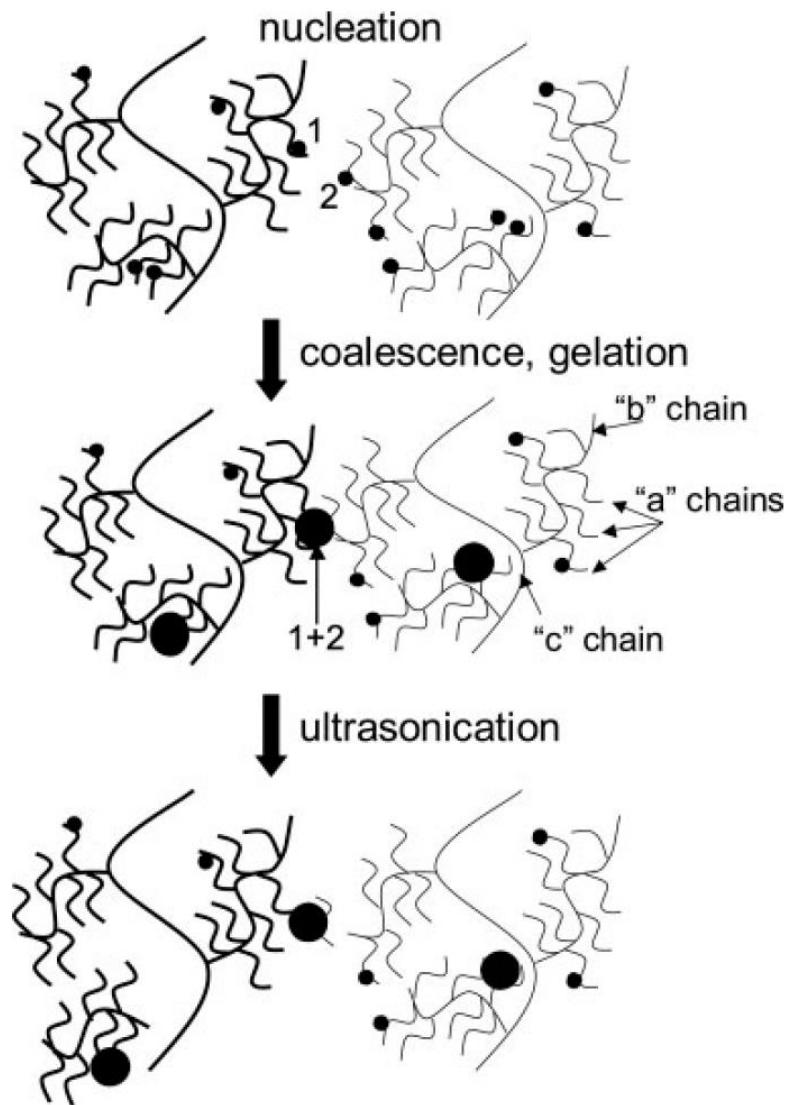


Figure 9: Schematic of amylopectin architecture and proposed gelation mechanism. Precursor particles 1 and 2 coalesce thereby cross-linking the amylopectin molecules. Typically, there are approximately 10^5 "a" chains per amylopectin molecule.

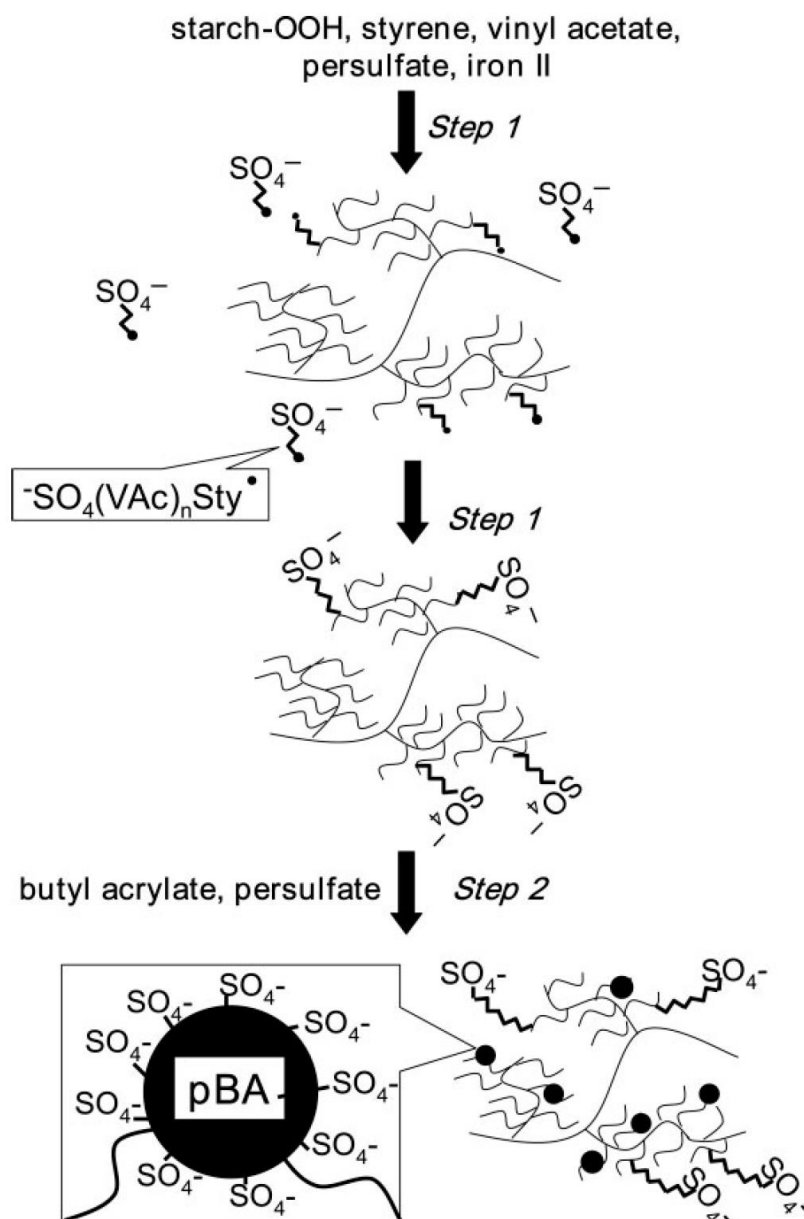
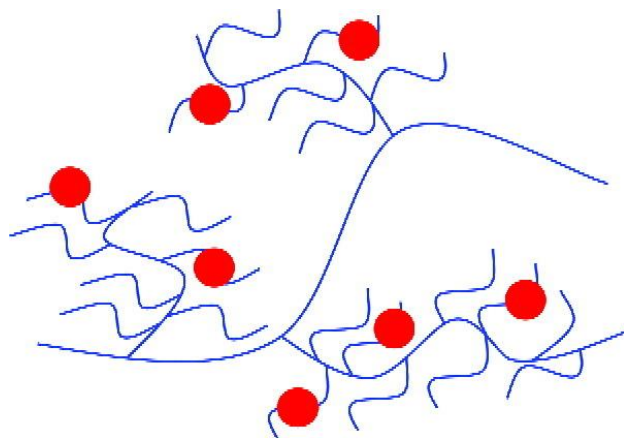


Figure 10: Schematic of *Latex 13* mechanism. Precursor particles grow and coalesce inside an amylopectin “unimolecular-micelle” acting as a scaffold.

Table 1: Latexes grown on native starch. Quantities are weight percent on a total mass basis.

Latex	starch	O ₃	Monomer(s)	Surfactant	Temp.	Duration	result
3	Amioca 9.55 %	3 h	Styrene 9.09 %	No	70 °C	3 h	gel
4	Amioca 9.25 %	3 h	1:1 styrene/BA 2.51 % initial, 10.86 % over 2 h	No	70 °C	3 h	gel
5	Amioca 1.36 %	1.5 h	Styrene 1.96 %	No	70 °C	3 h	latex
6	Mazaca 10.8 %	3 h	BA 9.09 %	No	70 °C	3 h	gel
7	Mazaca 10 %	1 h	Styrene 3.85 %	No	50 °C	4 h	gel
8	Mazaca 10 % ultrasonicated	1 h	Styrene 2.60 %	No	50 °C	4 h	gel
9	Mazaca 10 %	1 h	Styrene 1.06 %	No	50 °C	4 h	gel
10	Mazaca 2 %	1 h	Styrene 2.44 %	No	50 °C	4 h	latex
11	Mazaca 10.66 %	3 h	BA 7.89 %	AMA-80 1.5%	70 °C	4 h	latex 52 nm
12	Mazaca 11.07%	2 h	BA 7.89 %	AMA-80 1.5%	70 °C	4 h	latex 300 nm

GRAPHICAL ABSTRACT



A method is presented for synthesizing surfactant-free latexes comprising starch-*graft*-(vinyl polymer): ozone is used to simultaneously thin the starch and create initiating/grafting sites on it. Encapsulation of low molar mass starch inside hydrophobic polymer particles was demonstrated using energy dispersive spectroscopy. Colloidally stable poly(styrene-*co*-n-butyl acrylate) latexes based on high molar mass amylopectin were developed. The underlying mechanisms have been explored and data quantifying rates of production of starch hydroperoxides by ozone, their thermal decomposition and degradation of amylopectin by ozone are reported.