



Surfactant-free hybrid latexes from enzymatically hydrolyzed starch and poly(butyl acrylate-methyl methacrylate) for paper coating

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ABSTRACT

The use of starch as renewable resource to produce eco-friendly hybrid latex has received an increasing attention in industrial application. In this work, enzymatically hydrolyzed starch-graft-poly(*n*-butyl acrylate-*co*-methyl methacrylate) (ES-g-P(BA-MMA)) latexes were synthesized by seeded surfactant-free emulsion polymerization. A complex initiation system was used to enhance the grafting efficiency. The mechanisms of initiation and graft copolymerization were discussed. The ES-g-P(BA-MMA) latexes were characterized by Fourier transform infrared spectroscopy, dynamic light scattering, transmission electronic microscopy (TEM), and differential scanning calorimetry. The effect of reaction condition on graft copolymerization was investigated. The evolution of particle morphology was revealed by the TEM. The ES-g-P(BA-MMA) latexes were used as binders for paper coating. The strength-related properties of coated paper were evaluated. The results showed that the folding resistance and picking resistance were improved. All the other properties were at least equally good as in the reference sample. The crosslinked ES-g-P(BA-MMA) latex was more effective in improving properties. The folding resistance and wet tensile strength index were enhanced significantly by 29.5% and 36.6%, respectively. This study provides an alternative choice for paper coating to develop coated paper with better properties.

1. Introduction

Polyacrylate (PA) latex is one of the most widely used families of polymeric binders owing to its excellent properties and applications [1–4]. In paper and board industry, PA serves as binder for its brightness and aging resistance. Because of the higher cost of PA latex, the latex is usually used in mixtures with modified starch to adjust the rheology and water retention. Starch is by far the least costly binder; therefore, coating formulations strive to add as much modified starch as possible [5]. However, the mixtures of PA latex with modified starch cause latex migration and nonuniform porosity, resulting in dusting, picking, and print mottles [6,7].

Graft copolymerization is an important method to improve material properties. Graft copolymers have the possibility of combining the positive properties of each polymer phase, avoiding their drawbacks and have found applications in many fields. Published studies have proven that the starch graft copolymers have an advantage over the mixtures of synthetic latex and modified starch [8,9]. The graft copolymer can be utilized at the high temperature of size press operation and do not scale on hot drier cans. Although there have been some reports on the graft

modification of starch for papermaking, less attention has been paid to the starch graft copolymer aimed at paper coating.

In our previous work [10,11], cassava starch was modified by oxidation or enzymatic hydrolysis to obtain starch solution with low viscosity at high solid concentration. The starch copolymer latexes were prepared using persulfate as initiator. The result copolymer displayed good colloidal stability and narrow size distribution, but a low degree of grafting level limited their application.

Choice of initiator is of great importance in graft copolymerization reaction. Among redox initiators, cerium salt is the most efficient initiator for starch graft copolymerization [12,13]. Cerium salts can form efficient redox systems in the presence of organic reducing agent. However, the high price of cerium salts limits their wide use.

In this work, a complex initiation system of cerium sulfate and potassium persulfate was used to enhance the grafting level and reduce the amount of expensive cerium salts. The objective of this study was to prepare enzymatically hydrolyzed starch-graft-poly(*n*-butyl acrylate-*co*-methyl methacrylate) (ES-g-P(BA-MMA)). The mechanisms of initiation and graft copolymerization were discussed. The ES-g-P(BA-MMA) copolymer was characterized by Fourier transform infrared (FTIR),

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transmission electronic microscopy (TEM), dynamic light scattering (DLS), and differential scanning calorimetry (DSC). The effect of reaction condition on graft copolymerization was studied. The ES-g-P(BA-MMA) latexes were tested as binders for paper coating. The strength-related properties of coated paper were investigated.

2. Materials and methods

2.1. Materials

Native cassava starch (17% amylase) was provided by Lufeng Starch Ltd. (Guangxi, China). α -Amylase from *Bacillus licheniformis* with activity of 3000 units/mL was obtained from Jiahe Biotechnology Ltd. (Shanghai, China). Potassium persulfate, cerium sulfate, methyl methacrylate (MMA), *n*-butyl acrylate (BA), *N,N'*-methylenebisacrylamide, and chloroform were purchased from Yongda Chemical Reagent Co., Ltd. (Tianjin, China). Commercial P(BA-MMA) latex, ground calcium carbonate, oxidized starch, and kaolin were supplied by RizhaoKumho Jinma Chemical Co., Ltd. (Rizhao, China). All other chemicals were analytical grade and used as received.

2.2. Preparation of enzymatically hydrolyzed starch

The enzymatically hydrolyzed starch (ES) was prepared using the method described previously with modification [14]. A typical procedure is as follows: native cassava starch (100 g, dry basis) was dispersed with distilled water (617 mL) in a three-necked round bottom flask equipped with a mechanical stirrer and reflux condenser. Calcium acetate (0.1 g) and α -amylase (15 U/g, based on the dry weight of starch) were added to the flask. Then the mixture was heated at 80 °C for 15 min with constant stirring. After hydrolysis was completed, the α -amylase was inactivated by adjusting the pH to 3.0 with glacial acetic acid.

The starch hydrolysates were centrifuged at 3000 rpm for 30 min. The precipitated products were washed with ethanol and then dried in a vacuum oven at 50 °C to achieve constant weight. Finally the dried products were milled into powder and sieved with a 100-mesh sieve.

2.3. Preparation of ES-g-P(BA-MMA) latex

The uncrosslinked PBA seed latex was prepared by surfactant-free emulsion polymerization at 80 °C, using cerium sulfate and potassium persulfate as complex initiators. The ES (8 g, dry basis) and distilled water (60 g) were introduced into a four-necked round bottomed flask equipped with a mechanical stirrer, a nitrogen gas inlet, and a reflux condenser. The mixture was then heated at 80 °C for 30 min. Subsequently, BA (6.4 g) was added with vigorous stirring under nitrogen atmosphere. After the flask contents were cooled to 50 °C, 1.0 mL of a solution of cerium sulfate (0.1 M) and potassium persulfate (0.0675 g) were added. The mixture was allowed to react for 3 h at 50 °C.

The crosslinked PBA seed latex was prepared under the same conditions except that the *N,N'*-methylenebisacrylamide (0.04 g, 0.5% based on the weight of dry starch) was used as crosslinking agent and added with the monomer BA.

The swelling of the uncrosslinked or crosslinked PBA seed particles by MMA was undertaken for 24 h at ambient temperature. The monomer MMA was allowed to diffuse completely into the PBA seed particles. After the reaction mixture was bubbled with nitrogen gas for 30 min, 2 mL of a solution of cerium sulfate (0.1 M) and potassium persulfate (0.135 g) were added and the mixture was allowed to react for 4 h at 50 °C. Finally, the ES-g-P(BA-MMA) latex was cooled to room temperature and filtered.

To optimize graft level, the monomer ratio and initiator concentration were varied to investigate the effect on graft copolymerization.

2.4. Characterization

2.4.1. Determination of graft level

The ES-g-P(BA-MMA) latex was precipitated, filtered, and washed with ethanol. The residue was dried under vacuum at 40 °C until constant weight was achieved. The dry residue was then made free from homopolymer by Soxhlet extraction using chloroform for 24 h [15]. The grafting percentage (GP) and grafting efficiency (GE) were calculated using the Eqs. (1) and (2).

$$GP = \frac{W_2 - W_1}{W_1} \times 100\% \quad (1)$$

$$GE = \frac{W_2 - W_1}{W_3} \times 100\% \quad (2)$$

where W_1 , W_2 , and W_3 represent weights of ES, product after Soxhlet extraction, and monomer, respectively.

2.4.2. Particle size and distribution

The particle size and distribution were measured by DLS using a Malvern Zetasizer nano90 with a detection angle of 90°. The samples were diluted with deionized water to appropriate concentration before characterization.

2.4.3. TEM

The morphology of latex particle was studied by TEM (JEOL JEM-2100 TEM, operated at 200 kV). A drop of dilute latex was casted on a carbon-coated copper grid and dried at room temperature. To observe the particle morphology clearly, the latex particles were stained with phosphotungstic acid before TEM characterization.

2.4.4. DSC

The glass transition temperature (T_g) of latex particles were studied by DSC. Appropriate amount of dried sample was weighed into aluminum sample pan and sealed hermetically. The sample was tested by a NETZSCH DSC 204F1 system at a heating rate 10 °C/min from –50 to 100 °C under a nitrogen atmosphere.

2.4.5. FTIR

The FTIR spectra of the graft copolymers were recorded on a Bomem Hartman & Braun MB spectrometer at a resolution of 4 cm⁻¹ in the frequency range 4000–375 cm⁻¹. The specimens were prepared by grinding samples together with KBr and then pressed into a disc.

2.5. Application in paper coatings

The starch graft copolymer latexes were tested as binders in coating mixture to compare with the mixture of P(BA-MMA) latex and oxidized starch. The details of coating formulation are shown in Table 1. In

Table 1
Coating formulations for paper coating.

Ingredients	Coating mixture 1	Coating mixture 2	Coating mixture for reference
Ground calcium carbonate	80	80	80
Kaolin	20	20	20
Uncrosslinked ES-g-P(BA-MMA) latex	12		
Crosslinked ES-g-P(BA-MMA) latex		12	
Poly(BA-MMA) latex			8
Oxidized starch			4
Lubricant	0.5	0.5	0.5
Insolubilizer	0.5	0.5	0.5
Rheology modifier	0.2	0.2	0.2
Dispersant	0.05	0.05	0.05

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