Starch nanoparticle incorporation in latex-based adhesives

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ABSTRACT

Starch nanoparticles (SNPs) are chosen as renewable alternatives to partially replace petroleum-based monomers and produce bio-based latexes for adhesive applications. To maintain adhesive performance, SNPs are modified (i.e., via increasing cross-link density, vinyl functionalization, and adjusting hydrophilic/hydrophobic balance) to facilitate their incorporation into the latex particles. The modified SNPs are then polymerized in a semi-batch emulsion polymerization at 60 °C, and yield low viscosity latexes with up to 17 wt% SNP loading and 42 wt% solids. TEM/STEM imaging is performed and reveals the presence of a core-shell particle morphology. This is supported by comparing the adhesive properties of SNP-containing latex films from an *in situ* preparation vs. a blend of acrylic latex with SNPs. The results suggest that the modified SNPs were largely encapsulated into the latex particles rather than in the aqueous phase or at the latex particle/water interface.

1. Introduction

The use of renewable feedstocks in polymer formulations has drawn increasing attention among researchers and industry, as it is an important part of sustainable polymer product development [1–3]. Despite the availability of numerous renewable building blocks, polymer products made from renewable feedstocks often result in significant performance property changes [3–6]. Nevertheless, it is indeed possible to achieve comparable or even better properties when advanced polymer chemistry and engineering techniques are applied [1,3,7].

Starch is a polysaccharide existing in many plants (e.g., potato, wheat, corn) and is non-toxic, biodegradable, low-cost and abundant [8–10]. Native starch consists of two macromolecules: amylose, which contains mostly linear α-D-(1 → 4)-glucan units, and amylopectin, which is composed of branched α-D-(1 → 4)-glucan with α-D-(1 → 6) linkages at the branch points [11]. Depending on the source of starch, the amylose and amylopectin composition varies; for instance, corn starch contains about 0–70 wt% amylose, while amylose content in potato starch ranges from 12 to 20 wt% [9,12,13]. Starch molecules are densely packed in semi-crystalline granules, which may have various sizes (diameter from 1 to 100 μm), size distribution (e.g., mono-, bi- or tri-modal distribution), and shapes (e.g., spherical, plate) [10,14]. To date, starch has been widely used in the food industry, in paper coatings, adhesives and biomedical applications [8,15].

Developed starch morphologies such as starch nanocrystals and starch nanoparticles (SNPs) have the potential to open pathways towards materials with new and exciting properties [9,16–18]. SNPs with varying properties, such as shape and crystallinity, can be produced via hydrolysis of native starch using acids or enzymes, as well as physical treatments (e.g., reactive extrusion, ultrasonication and irradiation) [14,16,17]. Various modification methods (e.g., cross-linking, hydrophobization, anionic/cationic charging, vinyl functionalization) can be performed on SNP surfaces to tune the hydrophobicity of SNPs, introduce functional groups and alter their behavior [17,19–21].

SNPs have been applied in composite materials as nano-fillers to improve mechanical and barrier properties [22], as stabilizers for emulsion systems [23,24], as drug delivery carriers [25,26], or as binders in paper [14]. In addition, SNPs can be grafted with vinyl or acrylic monomers (e.g., butadiene, methyl methacrylate), as well as some polymers, to enhance their compatibility with hydrophobic matter [25,27,28]. More recently, SNPs modified with functional groups were used as Pickering stabilizers and/or monomers in emulsion polymerization to make starch-based latexes [29–32]. Pei et al. showed that latexes could be prepared with only up to 9 wt% SNP loading (based on total polymer mass) and with relatively low solids (6–10 wt %) due to compatibility issues between the hydrophilic starch and hydrophobic synthetic polymers [29,30]. In our previous work, various grades of SNPs with loadings as high as 50 wt% (based on total polymer

mass) were used to produce stable latexes, but the challenge remains to completely incorporate the SNPs into the latex particles [32]. In the present context, incorporation refers to SNPs that are encapsulated or chemically bound to acrylic polymer as opposed to free SNPs or starch molecules in solution.

SNPs were chosen to replace petroleum-based monomers to produce SNP-containing latexes for adhesive applications. Due to their hydrophilic nature, SNPs tend to reside in the water phase or, less likely, at the particle-water interface. Thus, to maintain the adhesive properties of an acrylic latex film, one would prefer to have the SNPs well incorporated into the latex. In other words, unless the SNPs are encapsulated in the particle cores by acrylic polymer, or at least partially covered with the acrylic polymer, the SNPs will interfere with adhesion to a substrate [33,34]. To achieve this, we modified the SNPs to promote their incorporation into latex particles. We are exploring three potential levers to improve compatibility between the hydrophilic SNPs and the hydrophobic vinyl monomers: (i) cross-linking, followed by (ii) attachment of vinyl groups to the SNP surfaces, and subsequent (iii) polymerization of a "tie-layer" of a moderately hydrophilic monomer to the SNP surfaces. Sodium trimetaphosphate (STMP) was chosen as a non-reversible cross-linker as it is nontoxic and commonly used in the food industry to produce starch phosphates [35–37]. A functionalized sugar-based monomer (FSM), was used as a source of vinyl groups to attach to the SNP surfaces. The FSM provides an additional bio-based component added to the latex formulation. Furthermore, the FSM shows a very low tendency to homopolymerize but reacts more readily with other vinyl monomers [38,39]. Butyl vinyl ether (BVE) was then added as a "tie-layer" monomer, because it has an appreciable water solubility compared to other hydrophobic monomers, and is prone to copolymerize with other monomers rather than homopolymerize [40–42]. The "tie-layer" monomer is expected to act as a bridge between the SNPs and the other more hydrophobic monomers. The cross-linked and functionalized SNP cores were then incorporated in a semi-batch emulsion polymerization to produce stable SNP-based latexes for adhesive applications.

2. Experimental section

2.1. Materials

Experimental grade SNPs and functionalized sugar monomer (FSM) were supplied by EcoSynthetix Inc. (Burlington, ON). Sodium trimetaphosphate (STMP) was used as cross-linker, sodium bicarbonate ($NaHCO_3$) was used as buffer, and 1 M hydrochloric acid (HCl) and sodium hydroxide (NaOH) pellets were used to adjust pH. FSM was used to functionalize the SNPs. Butyl acrylate (BA, 99%), methyl methacrylate (MMA, 99%) and acrylic acid (AA, 99.5%) were used as the main monomers, butyl vinyl ether (BVE) as a "tie-layer" monomer, potassium persulfate (KPS, 99%) as initiator, EF-800 (49–51 wt% aqueous solution) as surfactant, and hydroquinone (HQ) as inhibitor. All of the chemicals above were purchased from Sigma-Aldrich, with the exception of EF-800, which was provided by Cytec Industries. Distilled deionized water (DDW) was used throughout this project. BA was purified using an inhibitor removal column, and all other chemicals were used as received. Nitrogen gas (GR4.8, Linde Canada) was used to purge the reactor to remove oxygen.

2.2. Increase cross-link density of the SNPs

All SNP modifications and subsequent polymerizations were conducted in a 500 mL RC1e glass reactor (Mettler-Toledo) equipped with a Hastelloy stirrer set, two semi-batch feeding pumps, a pH probe and an inlet for nitrogen sparging. To begin, the cross-linking of SNPs with STMP was conducted using an aqueous solution reaction as described in the literature [37,43,44]. SNPs were dispersed in DDW while mixing (300 rpm) and heating to a desired temperature (25–60 °C). Once the

Table 1
SNP cross-linking reaction conditions.

Run	STMP (wt.%)	$NaHCO_3$ (wt.%)	pH
1.1	0.1	1	10
1.2	1	1	10
1.3	0.1	3	10
1.4	1	3	10
1.5	0.1	1	11
1.6	1	1	11
1.7	0.1	3	11
1.8	1	3	11

SNPs were fully dispersed and the temperature set point was reached, $NaHCO_3$ was added to the dispersion and the pH of the solution was adjusted to different target values using NaOH and HCl solutions prior to the addition of the STMP cross-linker. After a desired reaction time (0–8 h), the cross-linking reaction was stopped by adjusting the pH of the reaction mixture to 6.5 using HCl solution. The solution was then cooled to room temperature and characterized. A series of experiments were conducted to tune the cross-linking reaction conditions (Table 1).

2.3. Functionalization of SNPs

Functionalized sugar-based monomer (FSM) was used to functionalize the cross-linked SNPs. FSM is a proprietary water-soluble macromonomer, and contains glucose (hydroxyl groups) and polymerizable double bonds (maleic acid end groups) in its structure. The FSM was chemically bounded to the SNP hydroxyl groups as an added step in the STMP crosslinking procedure, prior to the final pH adjustment. The FSM was added to the cross-linked SNPs and reacted for an additional hour, and then the pH was adjusted to 6.5. This approach, allowed the FSM to be added directly to the SNP dispersion immediately after the cross-linking reaction with no additional processing required.

2.4. Synthesis of SNP-based latexes

The cross-linked/functionalized SNPs were added to a standard semi-batch emulsion polymerization formulation at a 15 wt% SNP loading (relative to total polymer weight) and 40 wt% solids content (Table 2). The polymerization process started with the preparation of the cross-linked and functionalized SNPs as per the procedure outlined below (Table 2: initial charge). During the heating process, the reactor

Table 2
Standard emulsion polymerization formulation.

Component	Amount	
	(g)	(phm[a])
Initial charge		
SNP	21.0	15.0
DDW	151.2	66.0
$NaHCO_3$[b]	0.4	0.3
Initial initiator charge		
KPS	0.4	0.3
DDW	11.6	8.3
Monomer pre-emulsion		
EF-800	5.5	3.9
DDW	27.8	19.9
BA	110.9	79.3
MMA	5.4	3.9
AA	2.5	1.8
Initiator solution		
KPS	0.9	0.6
DDW	20.0	14.3

[a] Parts per hundred parts monomers (including SNP, BA, MMA and AA).
[b] Buffer added only for non-modified SNPs.