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The Incorporation of Vinyl Modified Regenerated Starch Nanoparticles in Emulsion Polymerizations

by

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ABSTRACT

The replacement of synthetic polymers with renewable content in emulsion polymerization latexes has been a focus of research over the past several decades. Emulsion polymerization is a more sustainable way to produce polymers for films and resins. Starch is a sustainably sourced material that has proven to be extremely useful as a filler, comonomer, and property modifier for polymer latexes.

In this thesis, we attempt to incorporate high levels of starch materials into emulsion latex using waxy and dent sourced (cheaper) vinyl-functionalized regenerated starch nanoparticles (RSNPs). When fed as a batch charge, incorporation (by reaction as opposed to blending) of a grade of waxy RSNPs with 3 wt.% polymerizable sugar-based monomer (PSBM) and medium hydrophobicity (S-3-M) into the polymer matrix was 0-10 wt.% for a 15 wt.% RSNP loaded, 40 wt.% solids latex. Semi-batch feeding of the S-3-M RSNPs resulted in stable latex with the highest loadings of 40 and 50 wt.% (40 wt.% solids) with 0-10 wt.% RSNP incorporation into the synthetic particles, while 40 wt.% loading (20 wt.% incorporation) was achieved with a grade of waxy RSNPs with 6 wt.% PSBM and medium hydrophobicity (S-6-M). Strategies were developed to prepare synthetic latexes with high RSNP loadings and moderate incorporation.

Dent sourced RSNPs proved difficult to use in emulsion formulations due in part to the higher percentage of water-soluble linear amylose in the nanoparticles. To reduce the chances of coagulation and minimize the viscosity of the final latex it was important to ensure monomer starved conditions, that the only initiator feed occurred at the seed stage of the reaction (to degrade the soluble starch and prevent later stage coagulation), and that a hydrophobic tie-layer was used to assist in removal of soluble starch from the water phase. Although a successful procedure was devised for creating a dent sourced RSNP loaded latex with a viscosity of 250 cp, it was significantly longer than the procedures used with waxy RSNPs (6 h polymerization + 1 h RSNP dispersion). An additional treatment of the RSNP dispersion prior to the polymerization can lower the final latex viscosity to 100 cp.

Higher incorporation of vinyl-functionalized RSNPs may be achievable if the covalently bonded PSBM functional groups are resistant to hydrolysis, the amylose and other small MW

starches are completely removed from the water phase, and monomers with more appropriate reactivity and hydrophobicity are employed. To this end, maleic and methacrylic anhydride modified RSNPs were prepared and tested in emulsion polymerizations. The maleic anhydride modified RSNPs were successfully loaded into an emulsion latex at 15 wt.% (40 wt.% solids content) resulting in 20-30 wt.% incorporation when utilizing 2-ethylhexyl acrylate as the tie-layer monomer with 2-ethylhexyl acrylate or butyl acrylate/methyl methacrylate/acrylic acid as the shell layer.

This work presents the only comprehensive attempt to incorporate RSNPs into synthetic latexes at high loadings and solids with persulfate initiation without the need to severely reduce the RSNP molecular weight. The learning generated provides a framework for continuing research into increasing the incorporation of RSNPs into polymer particles.

RÉSUMÉ

Le remplacement des polymères synthétiques par des matières renouvelables dans les latex de polymérisation en émulsion a fait l'objet de recherches au cours des dernières décennies. La polymérisation en émulsion est un procédé plus durable pour produire des polymères pour films et résines. L'amidon est un matériau d'origine durable qui s'est révélé extrêmement utile comme charge, comonomère et modificateur de propriétés pour les latex polymères.

Dans cette thèse, nous essayons d'incorporer des quantités élevées de matériaux d'amidon dans du latex d'émulsion en utilisant des nanoparticules d'amidon régénérées fonctionnalisées par un vinyle (moins coûteuses), cireuses et dentielles (RSNP). Lors de l'alimentation en brut, l'incorporation (par réaction par opposition au mélange) d'une classe de RSNP cireux avec 3% en poids de monomère polymérisable à base de sucre (PSBM) et hydrophobicité moyenne (S-3-M) dans la matrice polymère était 0 à 10% en poids pour un latex de 15% en poids de RSNP chargé, 40% en poids de solides. L'alimentation semi-discontinue des RSNP S-3-M a entraîné un latex stable avec les charges les plus élevées de 40 et 50% en poids (40% en poids de solides) avec 0 à 10% en poids d'incorporation RSNP dans les particules synthétiques, tandis que 40% en poids de chargement (20% en poids d'incorporation) a été obtenu avec une teneur en RSNP cireux avec 6% en poids de PSBM et hydrophobicité moyenne (S-6-M). Des stratégies ont été développées pour préparer des latex synthétiques avec des charges RSNP élevées et une incorporation modérée.

Les RSNP provenant des sources dentielles ont été difficiles à utiliser dans les formulations d'émulsion en raison, en partie, du pourcentage plus élevé d'amylose linéaire hydrosoluble dans les nanoparticules. Pour réduire les chances de coagulation et minimiser la viscosité du latex final, il était important d'assurer des conditions de privation de monomère, que la seule alimentation de l'initiateur se produise au stade de la semence de la réaction (pour dégrader l'amidon soluble et éviter la coagulation ultérieure), qu'une couche d'attelage hydrophobe a été utilisée pour aider à éliminer l'amidon soluble de la phase aqueuse. Bien qu'une procédure réussie ait été conçue pour la création d'un latex chargé RSNP avec une viscosité de 250 cp, elle était significativement plus longue que les procédures utilisées avec les

RSNP cireuses (6 h de polymérisation + 1 heure de dispersion de RSNP). Un traitement supplémentaire de la dispersion de RSNP avant la polymérisation peut abaisser la viscosité finale du latex à 100 cp.

Une incorporation plus élevée de RSNP fonctionnalisés en vinyle peut être réalisable si les groupes fonctionnels PSBM liés par covalence sont résistants à l'hydrolyse, l'amylose et d'autres amidons au taux moléculaire bas sont complètement éliminés de la phase aqueuse et des monomères avec une réactivité et une hydrophobicité plus appropriées sont utilisés. A cette fin, des RSNP modifiés par l'anhydride maléique et méthacrylique ont été préparés et testés dans des polymérisations en émulsion. Les RSNP modifiés par l'anhydride maléique ont été chargés avec succès dans un latex d'émulsion à 15% en poids (40% en poids de teneur en matières solides), ce qui a entraîné une incorporation de 20 à 30% en poids lors de l'utilisation d'acrylate de 2-éthylhexyle comme monomère de couche d'attache avec du 2-éthylhexyle acrylate ou acrylate de butyle/méthacrylate de méthyle/acide acrylique en tant que couche de coquille.

Ce travail présente la seule tentative complète d'incorporer des RSNP dans des latex synthétiques à charges élevées et solides avec initiation au persulfate sans la nécessité de réduire sévèrement le poids moléculaire des particules. L'apprentissage généré fournit un cadre pour poursuivre la recherche sur l'augmentation de l'incorporation de RSNP dans les particules de polymère.

Dedication

I dedicate this thesis first and foremost to my late grandmother, *Ms. Noorieh Davoodi*, for her unwavering support and love, to my *parents* for their essential guidance and education, my *wife* for her loving hard work and support, and my *friends* for their mutual assistance and caring.

I would further like to acknowledge the *Baha'i youth* in Iran and elsewhere in the world, and beyond them all potential students, who are denied their fundamental human right to higher education.

"Regard man as a mine rich in gems of inestimable value. Education can, alone, cause it to reveal its treasures, and enable mankind to benefit therefrom."

- **Bahá'u'lláh**

Statement of Contributions

I hereby declare that I am the sole author of this thesis. I performed the polymerization experiments, polymer characterizations, and data analysis. ^{1}H-NMR analysis was carried out by the NMR Facility in the Department of Chemistry at the University of Ottawa. GPC analysis was carried out by our industrial partner, EcoSynthetix Inc.

I acknowledge Ms. Liana Martel and Mr. Anas Ettahiri for their assistance in carrying out FTIR and viscosity experiments, as well as NMR sample preparation.

I acknowledge EcoSynthetix Inc. for their in-kind work on this project through the ENGAGE, ENGAGE PLUS, and CRD grants. This work consisted of polymerizations, characterization, paper binder analysis and theoretical work referred to during consultations and not explicitly used in any of the enclosed manuscripts.

Dr. Marc A. Dubé, my thesis supervisor, provided me with guidance on research methods, standards and with editorial work on my manuscripts.

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Nomenclature

Symbols

M_L	Mass of Latex
M_M	Mass of Monomer
M_{DP}	Mass of Dried Starch and Synthetic Polymer
M_S	Mass of Starch
M_I	Mass of Initiator
M_B	Mass of Buffer
M_W	Mass of Water
D_P	Degree of Polymerization

Abbreviations

2-EHA	2-Ethylhexyl Acrylate
AA	Acrylic Acid
AIBN	Azobisisobutyronitrile
APG	Alkyl Polyglucoside
APS	Ammonium Persulfate
BA	Butyl Acrylate
BMA	Butyl Methacrylate
CAC	Critical Aggregate Concentration
CMC	Critical Micelle Concentration
CTA	Chain Transfer Agent
CTAB	Cetyl Trimethylammonium Bromide
DAC	Acryloyloxyethyltrimethyl Ammonium Chloride
DM	Dimethylaminoethyl Methacrylate
DMC	Methacryloyloxyethyltrimethyl Ammonium Chloride
DDI	Distilled De-ionized
DDIW	Distilled De-ionized Water
DLS	Dynamic Light Scattering
EA	Ethyl Acrylate
FTIR	Fourier Transform Infrared
GE	Grafting Efficiency
GP	Grafting Percentage
GPC	Gel Permeation Chromatography
HMW	High Molecular Weight
^{1}H-NMR	Proton Nuclear Magnetic Resonance Spectroscopy

IPDI	Isophorone Diisocyanate
KPS	Potassium Persulfate
MMA	Methyl Methacrylate
OSA	Octenyl Succinic Anhydride
PET	Polyethylene Terephthalate
PSA	Pressure Sensitive Adhesive
PSBM	Polymerizable Sugar Based Monomer
PSD	Particle Size Distribution
PVA	Polyvinyl Alcohol
RSNP	Regenerated Starch Nanoparticle
SDS	Sodium Dodecyl Sulfate
SEM	Scanning Electron Microscopy
SNC	Starch Nanocrystal
SNP	Starch Nanoparticle
St	Styrene
TEM	Transmission Electron Microscopy
THF	Tetrahydrofuran
VAc	Vinyl Acetate
XRD	X-Ray Diffraction

Chapter 1: Introduction

1.1 Towards a more sustainable society…

The recent increased consciousness of environmental issues and responsible manufacturing practices has had a large effect on industrial production of polymers. More research effort is being applied to developing bio-sourced and bio-degradable polymers, increasing the amount of bio-based materials being produced by 3.3 wt.% in the past 4 years.[1–3] Using the 12 principles of green chemistry as a guide, we are developing polymer processes that have a smaller environmental footprint.[4] Due to the growing demand for bio-based polymers, this project focuses on the production of latex polymers using renewable components and sustainable reaction engineering practices.

1.2 Emulsion polymerization, a greener process

Emulsion polymerization techniques can be employed to reduce the amount of organic solvent used in the production of polymer latex. Advantages of this strategy include enhanced heat transfer through the continuous water phase, the possibility to achieve high molecular weights at simultaneously high reaction rates, enhanced control over polymer morphology and structure, and a typically low viscosity final latex (regardless of molecular weight) which can be easily formed into a thin film and used for specialty applications (i.e., coatings, paints, adhesives).[5] Typical emulsion polymerization formulations include de-ionized distilled water, buffer, monomer, emulsifier (a.k.a., surfactant), and initiator. Crosslinkers, chain transfer agents, tackifiers, and fillers are often added to achieve desired end-use properties.

The study of novel emulsion polymerizations comprises three main areas of focus: polymerization process conditions, latex properties, and final product properties.[6] The primary challenge in emulsion polymerization is achieving stability in regards to limiting coagulation of polymer particles through the full range of conversion.

1.3 Renewable monomers as a way forward

Sustainability in polymer production comprises the use of bio-based renewable sources while creating safe and biodegradable materials, all within a safe and efficient polymerization process. Often these characteristics go hand in hand. Research into applications of biopolymers is intensive as there are many challenges around achieving the same high performance properties as petroleum-based polymers. As mentioned previously, polymers as particle dispersions in latex offer superior control of final product properties as well as reduction of both the amount of harmful solvents used and the amount of polymer needed to form a good film. One way to classify biopolymers is based on their method of production, as shown in Figure 1.1.[7] Biopolymers can be refined from biomass in the form of polysaccharides, proteins, and lipids (the three macro-nutrients of human beings), as other polymers from natural sources (corn starch and other agricultural/forestry crops) such as poly(lactic acid), or can be produced *in situ* by microorganisms. Most these polymers are biodegradable. Other polymers such as bio-polypropylene and bio-polyethylene are manufactured by enzymatic processing of renewably sourced material, mimic their synthetic counterparts, and are not readily biodegradable.

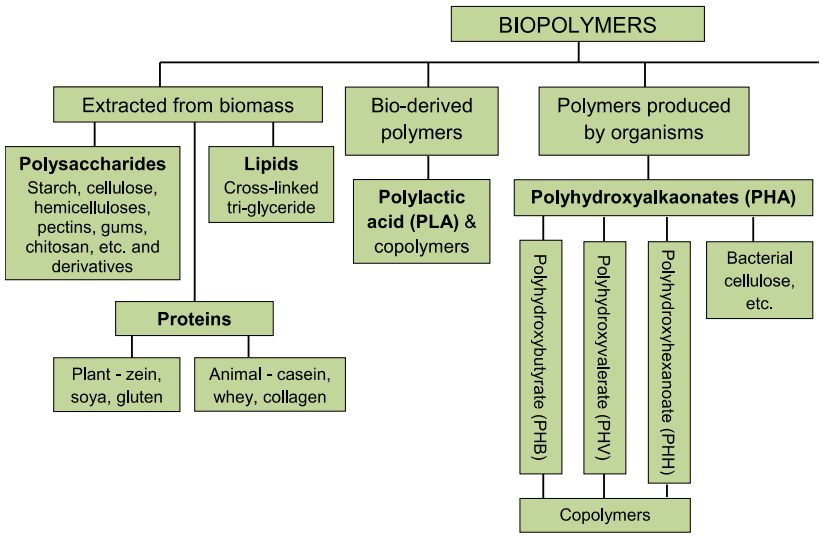

Figure 1.1 Sources for biopolymer production[7]

Due to its abundance, cost, biodegradability, and (less frequently) its chemical and mechanical properties, starch is the most commonly used biopolymer that does not have an identical synthetic counterpart. Other polysaccharides such as cellulose also share similar popularity and functionality.[8]

1.4 Polymers as Pressure Sensitive Adhesives

An important application of polymers is as films and adhesives. Adhesives are used to bond two substances together by surface adhesion and intermolecular bonds (cohesion). The adhesive polymer, as a solution or emulsion, is either applied to a rigid polymer backing to form a film, or applied directly to a contact surface (substrate). Pressure sensitive adhesives (PSA) are, in general, a class of adhesive that instantly adheres onto a surface with the application of light pressure. Because of the recent attention given to environmentally sustainable processes, emulsion polymerization has been a large focus of research because of its use of water as a suspending medium in lieu of a solvent and its allowance of greater control over the final properties of the polymer.[6] PSA formulations typically contain acrylate monomers such as butyl acrylate (BA), methyl methacrylate (MMA), acrylic acid (AA), styrene, and acrylonitrile. PSAs are evaluated for tack, peel strength, and shear strength, among other characteristics such as barrier properties. Long chain alkyl acrylates add tack to adhesive formulations, but require short chain acrylates to maintain cohesive strength. Polar groups that encourage hydrogen and other intermolecular bonding work to increase cohesion.[9]

1.5 Polymer Nano-Composites

Many applications require materials with advanced properties that cannot be satisfied using purely synthetic polymer formulations. Fillers and additives dispersed within a continuous polymer phase (matrix) can serve to effectively modify materials properties. A focus of research has been the embedding of nano-fillers (1-100 nm) in polymer matrices. Nano-fillers have been used to enhance mechanical, thermal, electrical, optical, and barrier properties.[10] In the paper

industry, minerals such as clay are the most popular filler.[11] Typically, nano-composites exhibit the most desired properties when the nano-fillers are arranged in a homogeneously dispersed and randomly oriented distribution.[10]

Incorporation of nano-fillers in water-borne emulsion polymerizations is particularly challenging because of the effect the filler has on the nucleation stage of the process, on latex stability, and the final morphology of the latex particles. Recent years have seen a large amount of research into the production of novel nano-filler composites. Typical polymer composite fillers include carbon black, clay (e.g. talc), aluminum hydroxide and other minerals.[12–15] Naturally sourced and sustainable fillers include predominantly cellulose based materials such as cotton, flax, hemp, wheat, wood, as well as starch based materials.[12,16–19]

1.6 Starch based fillers and co-monomers

Starch is a naturally occurring polysaccharide with a carbon:hydrogen:oxygen ratio of 6:10:5 consisting of amylose (linear) and amylopectin (crosslinked) chains, bound together by hydrogen bonds.[20] The largest uses of starches are in the food, paper making, and pharmaceutical/chemical industries.[21] Starch in its native form offers few benefits when compared to other synthetic and bio-based polymers.[22,23] It can provide benefits to synthetic polymer matrices after being physically and/or chemically modified to increase incorporation and compatibility. Typically, the goal of modifying native starch is to form nanoparticles, change the crystallinity, increase hydrophobicity, or introduce functional moieties.[12,13,24–31]

1.6.1 Starch Nano-particles

Nano-sized starch can be categorized into three morphologies: nano-crystals, nano-particles, and nano-colloids.[13] Because of the high level of crosslinking and surface modification required in this project, amorphous nano-particles, or regenerated (mechanically treated and crosslinked) starch nano-particles (RSNPs) are used.

Surface modification of RSNPs is often necessary to allow for desirable properties and loadings beyond ~ 3wt.%. Modification consists of substituting the hydroxyl groups of the glucose repeat units with various functional groups (reactivity: C-6 > C-2 > C-3).[28] The literature provides examples of starch modified with carboxymethyl, phosphate, fatty acid, acetyl, succinic, benzyl, acetic, propionic, octanoyl chloride, stearic, lactic, ferulic acid chloride, anhydride, alcohol, as well as various ester, ether, cationic and anionic functional groups.[11,13,28,32,31,33–35]

1.6.2 Incorporation of Starch Nano-particles in Polymer Latex

Several acrylic monomers and functionalized polymers have been successfully grafted onto and from various types of SNPs.[8,36–40] Methods for modification include dry processes, reactive extrusion, aqueous slurries, aqueous/organic solutions, and emulsions. It is notable that polymer grafted SNPs have been prepared through various emulsion techniques.

Polysaccharides have been incorporated into polymer latex via pre-emulsion feeding onto a heated slurry with sulfate/ceric initiation, as stabilizers in traditional procedures, and as a seed with batch or semi-batch monomer and sulfate/ceric/manganic initiator feeds.[39,41–57] There currently exists only one claim to a latex with core (starch) – shell (synthetic) particles created from oil-in-water emulsions or with a majority of the RSNPs incorporated within the acrylate particles.[13,57]

EcoSynthetix Corp. (Burlington, ON) uses a reactive extrusion process that converts native starch to a completely amorphous nano-particle (Figure 1.2). These RSNPs are further modified through the addition of a sugar-based vinyl monomer, and thus possess reactive double bonds and have hydrophobic/hydrophilic properties not found in most SNPs. Vinyl functionality was added to the RSNP to allow the starch to overcome its thermodynamic tendency to attract water molecules (as opposed to hydrophobic monomer). Various experimental grades have been provided for this project.

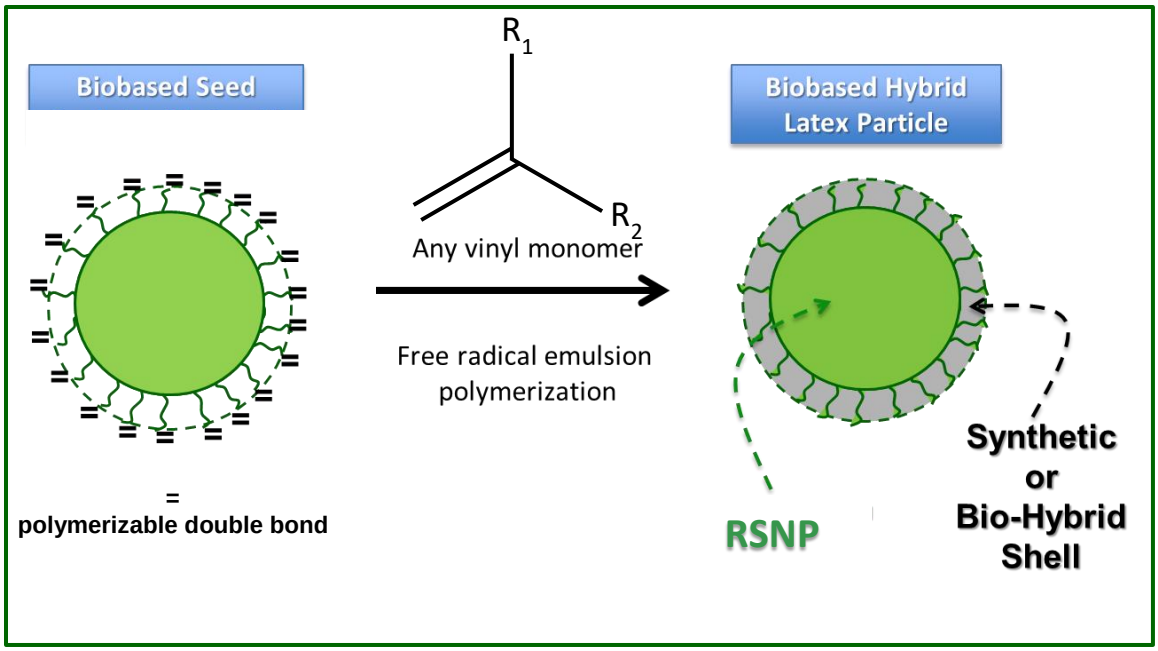

Figure 1.2 Ideal morphology of a polymerizable RSNP to increase biocontent of latex emulsions

1.7 Hypothesis and Project Objectives

We hypothesize that vinyl-functionalized RSNPs can be incorporated into emulsion polymer latexes at commercially significant RNSP loadings. 1This project comprised several research objectives, starting with the characterization of the nano-particles, the production of a stable latex via free-radical emulsion polymerization, the use of dent-sourced modified RSNPs (from yellow dent corn), and finally the testing of anhydride modified RSNPs. The underlying goal of the project was to determine under which conditions the RSNPs can be used as a co-monomer to achieve high RSNP loading and high solids content latex for industrial use. Our goal was to achieve >40 wt.% loading (wt.% of RSNPs in total solids) at >40 wt.% solids content (wt.% of solid state in total latex emulsion).

Characterization of the RSNPs consisted of determining their particle size and colloidal behavior in water and in the presence of monomer, their dispersion viscosity under various conditions, the degree of functionality, and their interaction with initiator and surfactant.

Using our knowledge of the RSNPs, free-radical emulsion polymerizations were designed to create a stable latex that included high loadings and incorporation (via chemical bonding as opposed to simple blending) of the RSNPs, preferably with core-shell morphology. The behaviour of the RSNPs during each stage of the polymerization was critical to determining if it acted as a co-monomer as intended, as a filler, or stabilizer. Special attention was placed on the polymerization procedure employed.

A cheaper sourced starch would add industrial viability to the RSNPs, and so a dent sourced RSNP was produced. Using the large amount of learning gained by using waxy sourced RSNPs in the previous stage of research, dent RSNPs were polymerized successfully to form stable latex.

Due to the persistent challenge of increasing incorporation of RSNPs into the polymer particles as opposed to increasing loading of the latex alone, a new generation of RSNPs was designed to attempt to solve the fundamental challenges that presented themselves throughout the project.

1.8 Project Challenges

The primary challenge that arose throughout the project was the incorporation of high amounts of RSNPs into the polymer particles, as opposed to only increasing loading in the overall latex. Poor incorporation led to issues during the nucleation stage of the polymerization, in regards to viscosity, and with the final film properties. The hydrophilic nature of the particles, their reactivity, and the interaction of the particles with the surfactant, initiator, and monomer in the reaction mixture all influenced the formation of highly incorporated and stable latex particles. In our attempt to induce core-shell morphology, the challenge was to ensure the hydrophilic starch was drawn into the core of the hydrophobic acrylic particles. This is contrary to the expected thermodynamic equilibrium which would draw the hydrophilic starch towards the aqueous phase on the outside of the particle (placing the RSNPs at the shell of the particle).

1.9 Learning Milestones

A set of milestones was prepared (Figure 1.3) to guide learning through the research project to ensure the proper study of the emulsion polymerization system as well as the transitioning of the new RSNPs into an industrially relevant product.

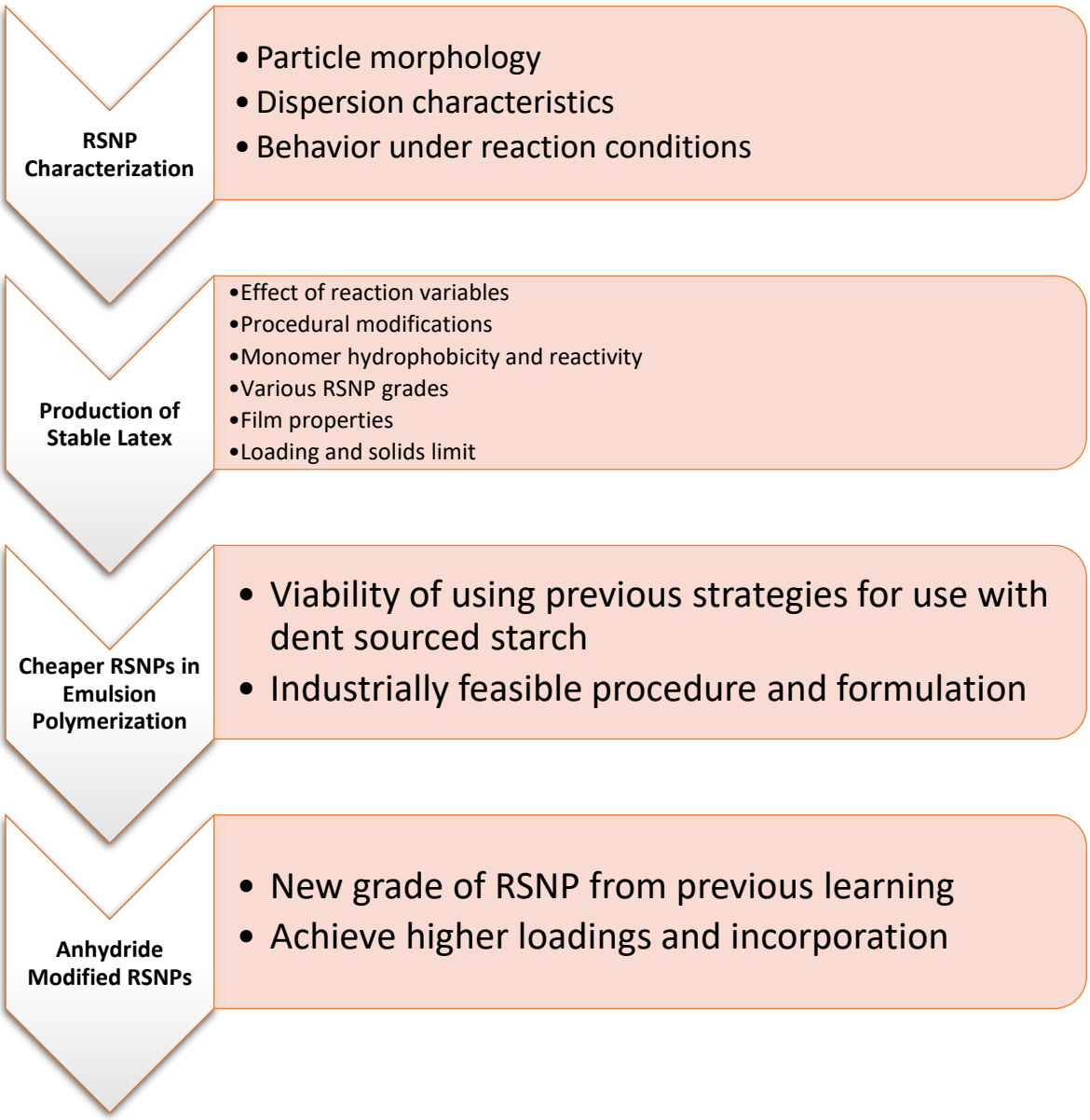

Figure 1.3 Milestones in research learning

1.10 Thesis Outline

This thesis consists of 7 chapters that present the most pertinent research work carried out during the project. Chapter 1 provided a general introduction to the project while chapter 2 (paper #1 – to be submitted for publication) provides a review of starch use in emulsion polymerizations to date. Chapter 3 details the characterization of the RSNPs. Chapter 4 (paper #2 – to be submitted for publication) presents the bulk of our work on using waxy RSNPs in emulsion polymerizations at high loadings. Chapter 5 (paper #3 – to be submitted for publication) highlights the industrial viability of using dent sourced RSNPs in emulsion polymerizations. Chapter 6 presents the work done to date in our design of newly functional RSNPs. Chapter 7 provides general discussion, future work, and conclusions for the project.

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Chapter 2: Strategies for the Incorporation of Starch in Emulsion Polymerization Latex

Strategies for the Incorporation of Starch in Emulsion Polymerization Latex

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ABSTRACT

The replacement of synthetic polymers with renewable content in emulsion polymerization latexes has been a focus of research over the past several decades. Emulsion polymerization provides a more sustainable way to produce polymers for films and resins. Starch is a sustainably sourced material that has proven to be extremely useful as a filler, comonomer, and property modifier for polymer latexes. The initiation method for grafting synthetic polymer to starch material is perhaps the most important factor in the polymerization. Several initiators have been employed: persulfate, ceric ion, permanganate, ferrous/peroxide, thiosulfate/persulfate, azo, and photo initiators. This work reviews attempts to include starch in emulsion polymerizations at various loadings and solids contents. The starch employed was in several forms including unmodified, functionalized, raw, nanosized, and low and high molecular weights.

2.1 Introduction

During the past decade, there has been a sharp increase in academic and industrial interest in the synthesis and study of sustainably produced polymeric materials for commercial applications. The identification of biopolymers for use in synthetic polymer formulations is thus of importance to the field of polymer reaction engineering[1–19]. Polysaccharides have been extensively studied and are among the most abundant, versatile, cheap, sustainably produced and commercially utilized biopolymers.[3–8,19–32] From a green chemistry standpoint, it is ideal to have the entire polymer formulation sustainably sourced and produced. One strategy is to ensure that monomers are synthesized from non-petroleum based feedstocks, or through enzymatic pathways. Fillers and property modifiers should also be sourced from natural and sustainable feedstocks when possible. Biopolymers such as polysaccharides offer naturally occurring and potentially sustainably grown materials to act as fillers and/or co-monomers for the reduction in synthetic monomer content (petroleum based or otherwise) in polymer formulations.

Starch is a polysaccharide material that contains both amorphous and crystalline regions, can be easily dispersed in water, can be physically and chemically modified, and imparts a wide range of specific properties to the copolymer depending on the starch type and its modification.[8,12,33–43] Although the use of starch materials is promising, particularly for fillers and property modifiers at low loadings, challenges persist for its use as a co-monomer. Overcoming compatibility issues between starch and synthetic polymers as well as the poor properties of starch for certain applications is essential for its use as a versatile co-monomer. The largest uses of starch are in the food, paper making, and pharmaceutical/chemical industries.[27] Commercially relevant products should be of sufficient loading and solids content (>40 wt.% for both) to make the use of starch profitable and worthwhile for a measurable impact on petroleum dependence.

This review will focus on the use of starches in emulsion polymerizations, both as fillers and co-monomers, and the strategies that have been attempted to achieve stable latex formulations. The published works described herein are limited to those where it is clear that

the nucleation mechanism of emulsion polymerizations exists, or that a similar mechanism is present that produces a stable hydrophobic oil-in-water latex. Similar graft copolymerizations that utilize polymerization techniques that are not clearly defined as emulsions are referred to throughout the review as support literature. Additionally, the scope of this work is limited to polymerization strategies and not the properties of the films and dry products resulting therefrom.

2.2 Polymerization Techniques

Several polymerization techniques exist for producing polymer latex, which is defined as a stable dispersion of hydrophobic polymer in an aqueous medium. Emulsion polymerizations, among other polymerization strategies, comes nearest to satisfying the 12 principles of green chemistry.[2] Even though sustainability is increased by incorporating starch into the polymer latex, it is important to ensure that the polymerization procedure itself, as well as the synthetic monomers used, are as sustainable as possible. The polymerization procedure should minimize the use of hazardous materials and the waste of formulation components, require lower energy input, and offer a high level of control over final polymer properties.

2.2.1 Standard Emulsion

Standard emulsion polymerizations consist of the distribution, stabilization, and polymerization of monomers (typically hydrophobic) within an aqueous phase.[44,45] Formulations typically require water, monomer, initiator, and surfactant, while fillers, and property modifiers such as chain transfer agent (CTA) and crosslinker are often added. Stage 1 of the polymerization consists of the nucleation of particles either by a homogeneous or heterogeneous mechanism (or both). A suitable initiator (typically water-soluble) provides free radicals for the polymerization of monomer in the water phase (occurs in all stages). Homogeneous nucleation occurs when un-stabilized monomer polymerizes in the water phase until a critical chain length is reached, at which point the polymer coalesces into a spherical

particle and is then stabilized by surfactant. Heterogeneous nucleation is the formation of particles by monomer swelling of surfactant micelles. Once nucleation is complete, stage 2 begins and the monomer from large stabilized droplets feed and swell the polymer particles, where polymerization continues. Oligomeric radicals in the water phase adsorb onto or are drawn into the monomer swollen polymer particles throughout stages 1 and 2. Once the monomer droplets have been depleted, stage 3 of the reaction proceeds, ideally until 100% conversion. The particle diameter and viscosity of the final latex typically range from 50 – 300 nm and 30 – 1000 cp, respectively.

2.2.2 Mini/micro-emulsion

The primary difference between mini/micro-emulsion and standard emulsion polymerizations is in the particle nucleation and growth stages. In mini/micro-emulsions, all the monomer is fed as a batch. While nucleation in emulsion polymerizations is both homogeneous and heterogeneous, nucleation in mini/micro-emulsions consists almost entirely of heterogeneous nucleation of monomer droplets with the aid of a hydrophobe.[46] The particle size in standard emulsion polymerizations changes as the nucleated particles are fed monomer from larger droplets, while in mini/micro-emulsions the particle diameter remains constant and is determined by the size of the stabilized monomer droplets at the nucleation stage. The nucleation of particles is usually carried out by ultrasound or high shear homogenization of an emulsion of monomer, surfactant, hydrophobe, and water (possibly with other additives) until a desired particle size is achieved. Mini- and micro-emulsions have particle sizes between 30 – 100 nm and 10 – 30 nm, respectively.

2.3 Starch Properties and Modification

2.3.1 Structure and Types

Depending on the source of starch (e.g., maize, wheat, potato), the number of contaminants (e.g., protein), the morphology (e.g., crystallinity), and the granule/particle size

can vary greatly. In all cases, the starch is considered non-toxic and biodegradable. Starch is originally extracted from its source in the form of microscopic granules with rings of "blocklets", each containing alternating layered lamella of crystalline and amorphous regions.[5] These regions contain two types of starch polymer, linear amylose with anhydroglucose repeat units connected by α-1,4-D-glucoside bonds, and branched amylopectin containing short branches of α-1,4-D-glucopyranose bonded polysaccharide chains at α-1,6 branch points (every ~22 repeat units).[47] There exists two possible types of crystalline allomorphs within each lamella: A-type (water molecules exist between closely packed double helixes) and B-type (water exists in the middle of a central cavity of double helixes). C-type allomorphs contain a combination of A and B-types.[5]

2.3.2 Functionalization

Modification of starch can be from functionalization of the hydroxyl groups by addition of moieties or longer chain molecules, or by "grafting from" or "grafting to" polymerization. The reactivity of the hydroxyl groups for functionalization is C-6 > C-2 > C-3.[48] These groups can be oxidized, reduced, esterified, etherified, or substituted with functional groups. The literature provides examples of starch modified with carboxymethyl, phosphate, fatty acid, acetyl, succinic, benzyl, acetic, propionic, octanoyl chloride, stearic, lactic, ferulic acid chloride, anhydride, alcohol, as well as various ester, ether, cationic and anionic functional groups.[3,26,37,48–63] Because of its hydrophilicity, in most cases starch has to be modified to increase its compatibility with synthetic polymers.[61]

2.3.3 Grafting

Both native and functionalized starch can be "grafted from" or "grafted to" using polymerization techniques.[25] A "grafting from" approach involves the initiator generating a radical on the starch backbone which subsequently reacts with a monomer and starts a polymerization mechanism. Alternatively, synthetic polymer radicals can react with the

hydroxyl groups, “grafting to” the starch backbone. Various initiators, monomers, and feeding strategies have been used to incorporate starch into synthetic polymer latexes of differing properties and morphologies.

Initiation

The types of initiator used to graft synthetic material from and to starch in emulsion polymerizations can be summarized as persulfate, ceric ion, permanganate, ferrous/peroxide, thiosulfate/persulfate, azo, and photo initiators.

Persulfates have been used in the form of ammonium persulfate, $(NH_4)_2S_2O_8$ (APS), and potassium persulfate, $K_2S_2O_8$ (KPS), for the grafting of starch with vinyl monomers according to a “grafting from” mechanism (Figure 2.1). Grafting efficiency is limited with persulfate initiation due to the favourability of homopolymerization of the acrylic monomer over radical formation on the starch anhydroglucose repeat unit. Alternatively, sulfate radicals can be formed by the redox reaction of a persulfate and thiosulfate at temperature below the dissociation temperature of KPS.[25,41,64–71]

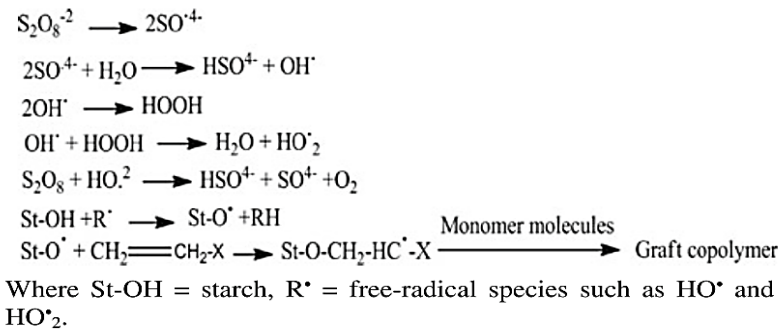

Figure 2.1 Mechanism of vinyl monomer “grafting from” starch by persulfate initiation[25]

Ceric ions (Ce(IV)) produced by ceric ammonium nitrate, $H_8N_8CeO_{18}$, and sulfate, $H_{20}N_4S_4O_{18}Ce$, have been used to produce latexes with high grafting efficiency.[25] The mechanism of ceric ion initiation is such that the ions form a complex with either the C6 carbon (Figure 2.2), C6 attached oxygen atom (Figure 2.3), C2-C3 glycol (Figure 2.4), or the C1

hemiacetal at the reducing end of the starch chains (Figure 2.5).[25,72] The most probable grafting site being the C2-C3 glycol. The complex then decomposes by abstracting a hydrogen or through the ring opening of the anhydroglucose unit, resulting in a Ce(III) ion and a radical on the starch backbone. Less likely is the chain cleaving mechanism, where the Ce(IV) ion forms a radical on the C1 carbon or the adjacent oxygen from the ether group on a non-reducing end anhydroglucose unit (Figure 2.6).

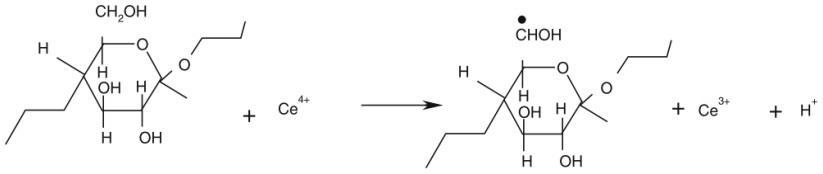

Figure 2.2 Ceric ion initiation of C6 carbon[25]

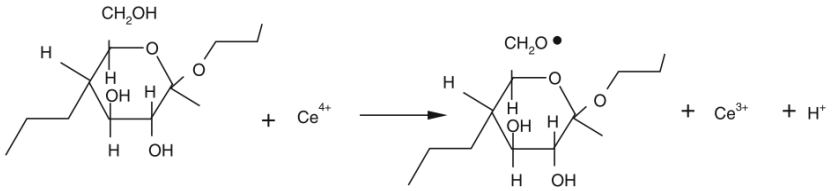

Figure 2.3 Ceric ion initiation of C6 hydroxyl oxygen[25]

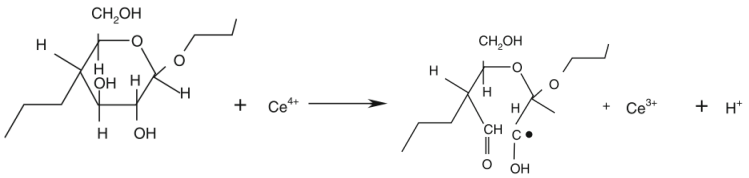

Figure 2.4 Ceric ion initiation of C2-C3 glycol[25]

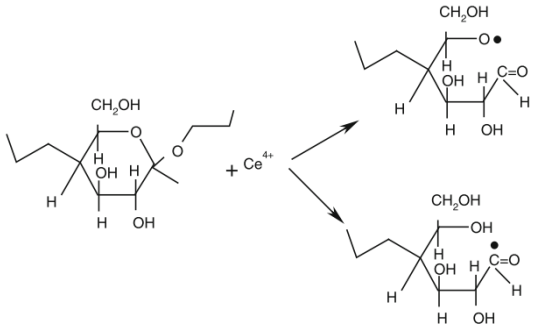

Figure 2.5 Ceric ion initiation of C1 carbon or ether oxygen in anhydroglucose unit[35]

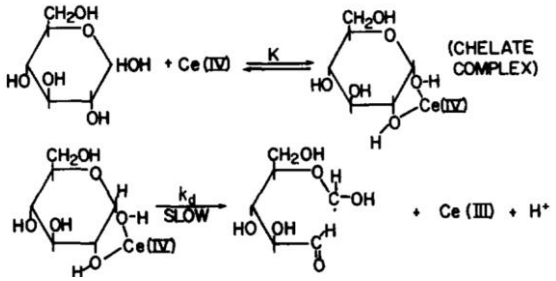

Figure 2.6 Ceric ion initiation of C1 hemiacetal at reducing end of starch chain[72]

The advantage of using Ce(IV) ions is that they do not initiate vinyl groups on monomers, greatly limiting the amount of homopolymer produced and increasing the grafting efficiency compared to persulfate initiation. A disadvantage of this type of initiator in aqueous media is the requirement of acid to avoid hydrolysis of the ceric ion.[25]

Manganese initiation using manganic pyrophosphate proceeds by the formation of a complex with the starch similar to that of ceric initiators, followed by hydrogen abstraction and radical formation on the starch backbone.[23,25,72] The initiation mechanism of the ferrous salt and hydrogen peroxide redox system is such that a hydroxyl radical is first produced by the decomposition of hydrogen peroxide by Fe^{2+}, then a radical is formed on the starch backbone by hydrogen abstraction (Figure 2.7). This initiation system, unlike ceric and manganese initiators, is able to polymerize vinyl monomers by hydroxyl free radical attack.[25,64,71,73–75]

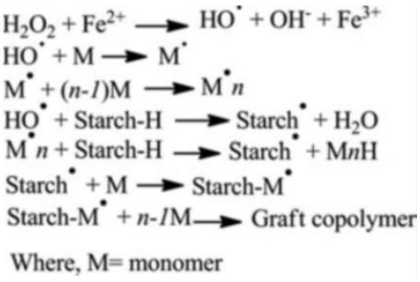

Figure 2.7 Fe^{2+} / H_2O_2 initiation of vinyl monomer or starch[25]

Azobisisobutyronitrile (AIBN) is a hydrophobic initiator that dissociates into two 2-cyanoprop-2-yl radicals capable of initiating polymerization of vinyl monomers (Figure 2.8). These radicals are theoretically capable of abstracting hydrogen from a hydroxyl group on the anhydroglucose units, thus creating a radical on the starch backbone.[25,44,76–78]

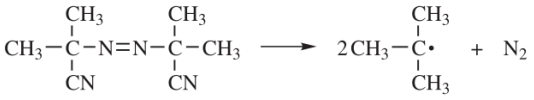

Figure 2.8 Dissociation of AIBN into 2-cyanoprop-2-yl radicals and nitrogen gas[44]

Several photoinitiators have also been employed that function by creating radicals through cleavage or electron transfer with a reducer. Submitting the initiator to a certain wavelength of radiation causes radical generation. It is also possible to generate radicals directly on the starch itself for polymerization.[23,25,79–81]

Characterization

Once grafting of the starch-synthetic monomer is complete, the grafted starch-synthetic polymer is typically purified from synthetic homopolymer by solvent extraction (e.g., Soxhlet extraction) or precipitation (e.g., centrifugation), and then characterized to determine the grafting percentage (GP %), which can be represented as a ratio (GR %) or add-on (%), efficiency (GE %) (equations 2.1 – 2.3), as well as the molecular weight and frequency of the grafted chains (equation 2.4). Confirmation of grafting can be achieved to differing degrees through FTIR and ^{13}C-NMR (starch functional groups)[41,64,68,70,73–75,82–92], SEM and TEM (morphology)[39,66–68,70,71,74,75,86,88,90–94], XRD (crystallinity)[39,74,82,83,92], acid hydrolysis, and aqueous phase analysis[93]. Grafting can be inferred by several other properties of the latex and resulting films (discussed in section 3.3.3).

$\boldsymbol{Grafting\ percentage}$
$(\boldsymbol{ratio\ or\ add-on})$

$$Grafting\ ratio\ (GR\ \%) = \frac{weight\ of\ grafted\ polymer}{weight\ of\ starch} \times (100) \quad [2.1]$$

$$Add-on\ (\%) = \frac{weight\ of\ grafted\ polymer}{weight\ of\ starch + weight\ of\ grafted\ polymer} \times (100) \quad [2.2]$$

$$Grafting\ efficiency\ (GE\ \%) = \frac{weight\ of\ grafted\ polymer}{weight\ of\ grafted\ polymer + weight\ of\ homopolymer} \times (100) \quad [2.3]$$

Once the starch is removed from the graft copolymer via acid or enzymatic hydrolysis, the average molecular weight is determined by GPC or another suitable method. Equation 2.4 calculates the number of AGU repeat units per graft of synthetic polymer:

$$\frac{AGU}{graft} = M_n of\ grafted\ polymer \times \frac{wt.\%\ of\ starch\ in\ graft\ copolymer}{wt.\%\ of\ grafted\ polymer} \times \frac{1}{molecular\ weight\ of\ repeat\ unit} \quad [2.4]$$

FTIR and ^{13}C-NMR spectroscopy are accepted methods to confirm grafting by the identification of both starch and synthetic polymer characteristic peaks in the extracted and purified starch grafted copolymer. In-line IR analysis of emulsion polymerizations can yield extremely useful information in regards to the grafting of starch at any given point in the

reaction. In cases where IR and NMR analysis are not possible due to overlapping peaks, acid or enzymatic hydrolysis are accepted as a proof of grafting.[41,64,68,70,73–75,82–92]

Transmission and scanning electron microscopy allows for the morphology of the starch and polymer matrix to be seen. Changes in structure or morphology, as well as association of starch with the synthetic polymer latex particles, can suggest a degree of grafting or at the very least, a favourable association.[39,66–68,70,71,74,75,86,88,90–94]

X-ray diffraction is useful to determine the change in crystallinity of the starch or synthetic polymer in comparison to the pure reference. Changes in crystallinity of starch towards that of the synthetic polymer or vice versa confirms grafting.[39,74,82,83,92]

Aqueous phase analysis of the polymer latex is a simple yet powerful method of determining starch incorporation in the polymer particles. The latex is centrifuged and each phase analyzed by gravimetry and NMR to determine incorporation.[93]

Latex and Film Properties

Emulsion polymerization latexes can undergo several characterization steps including the measurement of particle diameter, zeta potential, pH, conductivity, viscosity, morphology (SEM/TEM), film formation, birefringence, shelf life, paper binder properties, and grit content.[25,44,45,78,95–105]

Films produced from latexes are typically analyzed by measuring gel content[41], water solubility/swelling[73,84,106], barrier properties (gas and liquid)[84,106], glass transition temperature[64,70,82,87,91,95,107], melting point[95], thermal stability[68,70,74,82,84,85,87], opacity, contact angle[39,70,74,85], adhesive properties (shear, tack, and peel)[64,87,95,107], crystallinity, morphology (SEM/TEM)[41,70,71,84,85,89,95], tensile strength[39,41,83,94,106], elasticity[106], and biodegradability[70,71].

It is difficult to accurately predict the effect of starch on the properties listed above, as its effect will depend on many factors. Introduction of starch (in one form or another) to polymer latex has been shown, in general, to increase stabilization and viscosity as well as

increase film shear strength, Young modulus, tensile strength, abrasion resistance, fabric finishing properties, oxygen barrier properties, compatibility with certain substrates (those capable of hydrogen bonding), contact angle (hydrophilicity), biodegradability, electrical properties, and water swelling capacity, with a decrease in elongation at break and adhesive properties. Water vapour permeability and paper binder properties differed greatly depending on other factors.[4,6,7,18,21–23,25,28,34,38,39,41,43,74,108–115]

2.4 Starches in Synthetic Latex

Lowering the molecular weight of starch additives and co-monomers in emulsion polymerization increases the likelihood of latex stability and achieving an acceptable viscosity of the final latex. Low molecular weight starch, including amylose and dextrin, have been shown to be particularly conducive to being utilized in emulsion polymerizations at high loadings and solids.[64,83,87,88,95,96] Native starch has limited potential for the preparation of high solids homogeneous starch-incorporated latexes. Modification of native starch assists with its beneficial properties for emulsion polymerizations. Starches in the form of starch nanocrystals (SNCs) and starch nanoparticles (SNPs) provide the possibility of increased latex stabilization as well as improved film shear strength and higher incorporation, respectively.[27,28,60,116]

2.4.1 Native High Molecular Weight Starch

Starch that has undergone minimal physical and no chemical modification has been used in several emulsion polymerizations. Due to the type of initiator being the dominant variable in these polymerizations, studies can be organized by persulfate (Table 2.1), ferrous redox, photo, and ceric (Table 2.2) initiation.

When starch granules were used as a seed, it was found that gelatinization under high shear mixing and temperatures above 60 °C aided in reducing particle size and increasing percent grafting in polymerizations with styrene and MMA.[66,67] Successful grafting of acrylic

monomer to the granule surface will serve to breakdown any semi-crystalline regions of the particle.[68]

Table 2.1 Persulfate initiated starch-acrylic emulsion polymerizations

Ref.	Starch Type	Load.	Monomer	Solids	Feed Strategy	Initiator	Purpose
[66] [67]	Maize granules	50	St. MMA	30	Batch	$K_2S_2O_8$ (KPS)	Novel system
[106]	Tapioca (stabilizer) Maize (filler)	50	St. BA	50	Batch	$K_2S_2O_8$ (KPS)	Fabric composite
[117]	Hydrophilic Native wheat	20 7	VAc	50	/	$(NH_4)_2S_2O_8$ (APS)	Novel system
[82]	Native maize	/	VAc BA	low	Batch	$(NH_4)_2S_2O_8$ (APS)	Wood adhesive
[68]	Native potato granules	50	St.	3	Batch	$K_2S_2O_8$ (KPS)	Starch-clay nanocomposite
[84]	Native potato	33	BA MMA DAAM	/	Semi-batch	$K_2S_2O_8$ (KPS)	Coatings
[41]	Native maize (25% amylose)	65	MMA BA St.	10	Semi-batch	$K_2S_2O_8$ (KPS)	SBR latex reinforcement
[75]	Native maize	50	St.	10	Batch	$K_2S_2O_8$ (KPS) Amine activators	/
[69,70,118]	Native	10	MMA HEMA MMA MAA	10	Batch	$K_2S_2O_8$ (KPS)	Enzyme immobilization

Native starch can also be used as a protective colloid or stabilizer. Tapioca starches at low loadings were used as a protective colloid during the emulsion polymerization of styrene and BA. A maize starch dispersion was added to the final latex at loadings of 0-50 wt.% and stability was maintained.

Table 2.2 Ferrous redox, photo, and cerric initiated starch-acrylic emulsion polymerizations

Ref.	Starch Type	Load.	Monomer	Solids	Initiator	Purpose
85	Native cassava	33	St. BA DAEM HMA	30	$FeH_8N_2O_8S_2$ H_2O_2 (redox)	Novel system
79	/	/	St. BA	/	Photo-initiator	Biodegradable polymers
80	Native amylomaize Native amylopectin	30	MMA	10	None	Photo-initiation of starch
71	Maize granules	67	VAc	10	$K_2S_2O_8$ (KPS) $H_8N_8CeO_{18}$	Initiator comparison

* All polymerizations were carried out in batch

Although tensile strength decreased at 50 wt.%, no loss in properties was seen up to 20 wt.% loadings. Although the protective starch colloids could be considered to graft to a certain degree onto the polymer particles, the maize starch was added as a blend, meaning that the properties of raw starch were observed in the latex and resulting film.[106] Addition of wheat starch to as low as 3 wt.% loading during the polymerization of VAc increased the viscosity of the final latex 14-fold, while a 7 wt.% loading resulted in the formation of a solid.[117] Such loading limits for both latex stability and changes in film properties would be increased if grafting or incorporation of starch with the latex particles was sufficiently high.

Emulsifier was seen to be necessary in emulsion polymerizations with starch for polymer to be produced. When heterogeneous nucleation occurred, it was suspected that the polymeric radicals reacted with the gelatinized starch, while smaller granules and micelles increased grafting.[67] Increases in KPS concentration only affected GP and GE when the feeding strategy and monomer reactivity was such that the initiator was able to generate radicals on the starch backbone as opposed to only participating in homopolymerization. An increase in GP and GE to a maximum for a particular KPS concentration indicates grafting, while no effect of initiator on grafting indicates homopolymerization.[82,84] When more reactive monomers such as BA were

used over other monomers such as VAc or styrene, a decrease in GE and increase in homopolymer were observed.[41,82] Increases in monomer and starch concentrations tended to increase GP to a maximum while an increase in starch loading above a certain concentration also decreased polymerization rate.[75,84,119] We suspect this occurs because of the radical scavenging properties of starch, especially in an aqueous medium with hydrophilic initiator. Increases in reaction time as well as anionic surfactant concentration increased GP in general.[66] GP and instantaneous conversion can be seen to decrease and increase over long periods of time (4-10 h).[75,84]

The importance of monomer reactivity was also seen to affect GP with ferrous redox initiators. Increases in hydrogen peroxide decreased particle size while increasing conversion as expected, even in the presence of starch. Starch assisted in particle stabilization at ideal loadings and solids.[85]

Pre-illumination of a gelatinized starch seed resulted in higher GE than with illumination of the entire styrene/BA/starch emulsion alone.[79] Illumination time that gave the highest GE (2-3 h) was the same for high amylose or amylopectin starch, indicating similar photo-initiation sensitivity. Starch photo-initiation in emulsion polymerizations with MMA was successful, although conversion was <80 wt.%.[80]

As with KPS initiation, monomer conversion will decrease after a certain starch loading (33 wt.% for VAc). Sulfate groups from KPS offered early stability but high rates of homopolymerization as well as poor particle stability and zeta potential at higher conversion, while Ce initiator produced low-medium molecular weight starch-VAc amphiphilic copolymers that stabilized latex particles and were embedded at the latex surface. GE and GP were greatly increased with Ce compared to KPS (5 vs. 21.5 and 9 vs. 36 for lowest starch loading).[71]

2.4.2 Low Molecular Weight Starch

A popular and effective strategy for incorporating high starch loadings into polymer latexes at acceptable viscosities is to reduce the molecular weight of the starch. Dextrans, low molecular weight amylose, and amylase/acid degraded starch have all been employed successfully to that end (Tables 2.3 and 2.4).

Table 2.3 Dextran loaded acrylic emulsion polymerizations

Ref.	Starch	Load.	Monomers	Solids	Feed Strategy	Initiator	Purpose
[93]	Non-functional OSA $C_{17}H_{37}Cl_2NO$	25	MMA BA	40	Semi-batch	$K_2S_2O_8$ (KPS)	Novel system
[96]	α-cyclodextrin	93	/	5	Batch	$C_{12}H_{18}N_2O_2$ (IPDI crosslinker)	Water purification
[64]	Highly branched low M_W pyrodextrin	15	VAc	50	Semi-batch	$Na_2S_2O_8$ $Na_2S_2O_3$ (redox)	Novel system
[64]	Waxy maize maltodextrin	25	VAc	57	Semi-batch	$Na_2S_2O_8$ $Na_2S_2O_3$ (redox)	Novel system
[64]	Waxy maize maltodextrin	10	VAc	50	Semi-batch	$Na_2S_2O_8$ $Na_2S_2O_3$ (redox)	Modeling

α-cyclodextrin can be used as a stabilizer to form miniemulsions with hexadecane. The dextrins are then crosslinked with IPDI to form stabilized nanospheres at high loadings.[96] When used as a post-added binder, native, anionic, or cationic hydrophobic dextran resulted in limited incorporation (7, 7, and 19 wt.%), while higher incorporation (15, 27 and 27 wt.%) resulted from the addition of the dextrans in the pre-emulsion feed, supporting a conclusion of grafting when the dextran is added in situ. Cationic dextran required the use of anionic stabilizer while other types of dextran were stable as the only stabilizer with no synthetic surfactant. When starve-fed conditions were employed, a multiphase particle morphology was achieved, while all other feed strategies resulted in synthetic latex particles stabilized with a dextran shell.[93]

Factors in the preparation of a pyrodextrin seed (acid concentration, level of pre-drying, and dextrination time) were crucial for creating a monodisperse latex. When using maltodextrin with a VAc system and sulphate redox initiator, the presence of residual monomer as well as un-degraded dextran resulted in increased viscosity of the final latex. Increasing agitation as well as seed dosage of monomer increased GP and decreased viscosity supposedly due to amphiphilic graft polymer production and early micelle formation. The increase of persulfate in the seed decreased grafting due to cage effects and side reactions.[64]

Ce initiator was capable of grafting debranched amylose to the surface of monomer swollen PMMA seed latex.[86] When used as a seed stabilizer of several vinyl (BA, MMA, AA, EA,

St., 2-EHA) and cationic (DM, DAC, DMC) monomers, cationic starch showed excellent stabilizing properties at the right proportion of vinyl and cationic monomer.[114] Degraded amylose cooperatively stabilized the polymer particles along with anionic and non-ionic stabilizer, showing better stabilization than either of the surfactants alone. The synergistic effect of the three stabilizers also prevented retrogradation of the polymer latex.[95]

α-amylase has been used in conjunction with native starch as a seed with a range of monomers (2-EHA, MMA, AA, BA, and EA) and persulfate initiator in order to degrade the chains to a high enough degree that particle size and viscosity are reduced as a result of fewer large molecular weight starch chains in the water phase.

The addition of α-amylase resulted in the decrease in viscosity and particle diameter of the native starch included latex from 4300-50 cp and 632-209 nm. Particle size and viscosity increases with increased starch amount (at highest α-amylase concentration), with the viscosity drastically increasing at 30 wt.% loading.[83,87] This indicates that even with a decrease in molecular weight as a result of α-amylase, poor incorporation of the starch into the latex particle will cause an increase in viscosity at loadings under the commercially relevant concentration.

The degradation time of the α-amylase and starch seed affects the nucleation mechanism and final latex properties. The starch must be degraded to a certain point where there is a suitable amount of starch oligomers and long chains for grafting and particle stabilization, while at the same time including very small molecular weight chains or saccharides in order to maintain low viscosity in the water phase. The nucleation mechanism was concluded to begin with the grafting of starch and monomer in the water phase, the homonucleation of particles once the chain length is reached, the stabilization of the particle by synthetic surfactant, and the grafting of vinyl monomer and polymer radicals onto the new particles. Latex had good stability, zeta potential, and shelf life.[88]

Ferrous redox initiator was used along with native, anionic, and cationic starch with α-amylase. The combined stabilizing effect of cationic starch and DMC cationic monomer resulted in the most stable latex that resisted any coagulation.[89]

Table 2.4 Amylose loaded acrylic emulsion polymerizations

Ref.	Starch	Load.	Monomers	Solids	Feed Strategy	Initiator	Purpose
86	Amylose	25	MMA	25	Semi-batch	$H_8N_8CeO_{18}$	Novel system
87	Native + α-amylase	43	2-EHA MMA AA	40	Semi-batch	$(NH_4)_2S_2O_8$ (APS)	Novel system
83	Native maize + α-amylase	40	BA MMA AA EA St.	/	Semi-batch	$(NH_4)_2S_2O_8$ (APS)	Coatings
114	Cationic low M_W cassava	11	MMA EA BA 2-EHA DM DAC DMC	20	Semi-batch	$(NH_4)_2S_2O_8$ (APS)	Paper coating
88	Enzymatically degraded cassava	50	St. BA	50	Batch	$(NH_4)_2S_2O_8$ (APS)	Paper coatings
89	Native Anionic Cationic + α-amylase	2	St. BA AA DMC AP	28	Semi-batch	$FeH_8N_2O_8S_2$ H_2O_2 (redox)	Paper sizing
95	Native maize + HCl acid	70	VAc	45	Batch	$(NH_4)_2S_2O_8$ (APS)	Wood adhesive

2.4.3 Modified High Molecular Weight Starch

Native, high molecular weight, starch can be modified to impart new properties or enhance compatibility with synthetic monomer (Table 2.5).

Carboxymethylated starch was shown to be effective as a co-stabilizer with non-ionic surfactant for the miniemulsion of BA. The starch served as a coagulating agent for the polymerization of MMA due to its exacerbation of water phase polymerization and provided poor stabilization of styrene due to the limited grafting of the starch to the polymer particles due to the difference in hydrophobicity.[120]

With a ferrous redox initiator, acid modified starch was polymerized with a styrene/MMA and styrene/BA system. Styrene was shown to be a more effective grafting monomer than MMA and a worse monomer than BA. For both systems, increase in starch concentration increased both GP and GE. It is evident that with an initiator that is effective at creating radicals on both the starch backbone and vinyl monomer, a combination of low reactive (styrene) and high reactive (BA) monomer is effective (no risk of over-homopolymerization with increase of BA below a maximum).[73,74]

Table 2.5 Modified HMW starch loaded acrylic emulsion polymerizations

Ref.	Starch Type	Load.	Mon.	Sol.	Feed Strategy	Initiator	Purpose
120	Carboxymethylated	/	St. BA MMA	/	Batch	/	Miniemulsion composite nanoparticles
43	Acid modified	42	St. MMA BA	12	Batch	$FeH_8N_2O_8S_2$ H_2O_2 (redox)	Cotton yarn sizing
74	Cationic acetylated potato	20	BA St.	52	Semi-batch	$FeH_8N_2O_8S_2$ H_2O_2 (redox)	Paper sizing
90	Oxidized cassava	10	St. BA	30	Semi-batch	$(NH_4)_2S_2O_8$ (APS)	Paper coatings
64	OSA modified waxy potato	10	VAc	50	Semi-batch	$Na_2S_2O_8$ $Na_2S_2O_3$ (redox)	Wood adhesive
91	Oxidized cassava	10	St. BA	40	Semi-batch	$(NH_4)_2S_2O_8$ (APS)	Paper coating

With persulfate initiation, oxidized starch was used as a colloidal stabilizer for the polymerization of styrene/BA. A common result of core-shell morphology was achieved with starch as the shell. Particle size decreased with increasing starch concentration, while stability and zeta potential increased with grafting.[90,91] OSA modified starch with 0.01-0.04 DS was polymerized with VAc. As the DS increased, so did the viscosity of the final latex, most likely due to increased interaction between the OSA groups and the hydrophobic monomer and polymer particles. As a result, less energy was needed overall for the polymerization.[64]

2.4.4 Starch Nanocrystals (SNCs)

SNCs are hydrolyzed starch particles that are purely crystalline in structure and that act as colloidal stabilizers while imparting increased rigidity to the polymer particles and resulting films (Table 2.6).

Table 2.6 SNC loaded acrylic emulsion polymerizations

Ref.	Starch	Loading	Monomers	Solids	Initiator	Purpose
[92]	Hydrolyzed maize	50	St.	6	$K_2S_2O_8$ (KPS)	Novel system
[94]	Hydrolyzed waxy maize	10	BMA	10	$C_8H_{12}N_4$ (AIBN)	Nanocomposite
[39]	Hydrolyzed maize	15	St.	/	$K_2S_2O_8$ (KPS)	Novel system
[94]	Hydrolyzed waxy maize	10	BMA	17	$K_2S_2O_8$ (KPS)	Nanocomposite

* All polymerizations were carried out in batch

All latexes loaded with SNCs were low solids content. Due to its crystalline structure, grafting of monomers onto the SNCs was limited to the surface of the particles due to poor penetration. SNCs were polymerized with styrene or BMA in batch, with GE and GP increasing with reaction time and monomer concentration linearly, while there was a maximum with persulfate initiator concentration due to the competition of grafting with homopolymerization. Once grafting was achieved, grafted polymer chain length increase with reaction time. SNCs become amphiphilic during the polymerization and can become effective stabilizers without the need for co-surfactants to achieve stability.[39,92,94]

A miniemulsion of BMA and hexadecane initiated by AIBN was stabilized by dropwise addition of starch crystalline nanoplatelets, followed by homogenization and polymerization. Cationic surfactant assisted in bonding the platelets to the surface of the latex particles, which effectively reduced the required surfactant by a factor of 4 for equal stabilization.[94]

2.4.5 Starch Nanoparticles (SNPs)

Starch nanoparticles are fully amorphous particles that swell in aqueous media and can be easily modified for increased compatibility with synthetic monomer (Table 2.7).

Table 2.9 SNP loaded acrylic emulsion polymerizations

Ref.	Starch	Loading	Monomers	Solids	Feed Strategy	Initiator	Purpose
107	Waxy maize OSA modified	3	VAc BA	53	Semi-batch	$K_2S_2O_8$ (KPS)	Protective colloid latex
78	maize OSA-AC modified	9	St.	6	Batch	$C_8H_{12}N_4$ (AIBN)	Novel system
121	OSA-AC modified	1	St.	10	Batch	$(NH_4)_2S_2O_8$ (APS)	Novel system

Spray dried (high viscosity) and pre-gelatinized OSA modified (medium viscosity) maize nanoparticles were used as a seed with a BA/VAc charge, as well as a pre-emulsion fed semi-batch. An increase in viscosity was seen when compared to using synthetic stabilizers. Waxy maize crosslinked nanoparticles as a stabilizer for the same system showed no increase in viscosity. Compared to cellulose, protein, or PVA stabilizer, the SNPs resulted in the largest particle size.[107]

Due to their amorphous structure and potential for functionalization, SNPs provide the most promising form of starch for the creation of core-shell starch-synthetic latexes for high wt.% replacement of synthetic monomer, while retaining the beneficial properties of the purely synthetic latex. No latex reported in this work so far has claimed core-shell structure with the entirety of the starch in the core of the latex. Two recent works by Pei et al.[78,121] using OSA-AC modified SNPs shed some light on novel strategies. At low SNP loading (1 wt.%), the SNPs are shown to act as Pickering stabilizers of styrene latex particles at a pH > 8, ensuring deprotonation of the OSA carboxyl group and the creation of electrostatic repulsion. At higher loadings of 9 wt.%, core-shell (starch-synthetic) morphologies were claimed, where the

majority of the SNPs resided in the core, with some on the surface. Even at the low solids content used, we question the conclusion of core-shell structure given the following issues with the authors work: (1) styrene:SNP ratio does not fit with a predominantly starch core, (2) TEM images are not of micro-tomed particles and contrast may be altered due to the thickness of the particle, (3) the zeta potential of the particles implies that the SNPs are on the surface to a sufficient degree, (4) the absence of particle diameter evolution during the polymerization, and (5) absence of analysis of incorporation or grafting of the styrene to the SNPs (which we believe would be very high if most of the starch is in the core of the latex particles). We believe that the OSA-AC-SNPs produced represent a correct direction in the development of SNPs for core-shell morphology. The paper also provides a procedure for batch emulsion polymerizations with hydrophobic SNPs resulting in potentially high incorporated latex.

2.5 Future Directions

There exist various strategies for the incorporation of many types of native and modified starches into emulsion polymerizations. Issues still persist in regards to developing a procedure for the creation of high loadings of starch (>40 wt.%) at high solids contents (>40 wt.%) with tunable viscosity and film properties. The key to this achievement is control over the incorporation of starch into the latex particles. The higher incorporation of starch, the greater control will exist over the final latex properties while achieving commercially relevant starch and solids contents. The most promising types of particles for core-shell (starch-synthetic) latex are amorphous SNPs. It has been shown that the SNPs should be modified to include vinyl groups, as well as hydrophobic and stabilizing moieties, in order to increase compatibilization and grafting with vinyl monomers. Future work in the production of sustainably sourced polymer latex should be focussed on the use of emulsion polymerizations for creating core-shell (starch-synthetic) particles to prevent significant changes in the properties of the synthetic polymer.

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Chapter 3: Characterization of Modified Regenerated Starch Nanoparticles

3.1 Introduction

As awareness of environmental concerns has increased, certain polymer producing industries have responded by incorporating greater amounts of renewable components as fillers or co-monomers into their product formulations. This move to sustainable practice has assisted in the increase in bio-based materials produced in the global polymer industry from 1.7 wt.% in 2012 to 5 wt.% in 2016.[1–3]

Current areas of research focus include green chemistry strategies for the sustainable production of monomers from naturally occurring feedstocks (typically through extraction, enzymatic, or catalytic processes), and the production of nanocomposites with bio-based fillers.[4,5] Although the synthesis of bio-based polymers solves the problem of reliance on petroleum by-products, the problem of persistent synthetic polymers in the waste stream remains. Bio-based polymers can also be biodegradable if they decompose into their building blocks, which can then be metabolized within one year in a natural environment.[6] Due to its abundance, low cost, sustainable production, and biodegradability, polysaccharides such as starch, cellulose, chitin, chitosan, pectin, and alginate are among the most common industrially used bio-based polymers that readily biodegrade and which do not have an identical synthetic counterpart.[7–12]

Starch is a naturally occurring polymer with the chemical formula $(C_6H_{10}O_5)_n$ containing linear amylose and branched amylopectin polysaccharides. Amylose consists of α-1,4-D-glucoside bonds while amylopectin contains short α-1,4-D-glucoside chains at α-1,6-D-glucoside linkages (on average every 22 glucose units).[8] The amount of amylose can range from 70 wt.% for amylomaize to 1 wt.% for waxy maize. The raw starch granule contains both crystalline and amorphous regions, as alternating layered lamella, within “blocklets”, that are packed as rings.

The largest uses of starch in descending order are in the food, paper making, and pharmaceutical/chemical industries.[13] Starch in its native form offers few benefits when compared to other synthetic and bio-based polymers, but nanoparticle additives can be used to improve the properties of starch films.[14,15] Alternatively, starch can be used in polymer matrices after being physically and/or chemically modified for the purposes of changing the synthetic polymers properties. Typically, the goal of modifying native starch is to introduce functional moieties, form nanoparticles, change the crystallinity, or increase hydrophobicity.[8,16–23,10,24–27]

Due to their small size, high surface area to volume ratio, enhanced solubility, and functionality, nanoparticles can impart significant property modification for a polymer matrix in comparison to larger fillers. For the preparation of fillers for paper coatings for example, a primary use for starch filler, the particles must be below 10 μm for proper entrapment in the coating matrix.[28] Many polymer nanoparticles have received attention in the last two decades, including those based on or extracted directly from biomass feedstock, such as starch.[29]

Starch nanomaterials can be produced by a variety of proven methods such as fluid extraction, solvent evaporation, acid hydrolysis, enzymatic treatment, high-pressure homogenization, ultrasonication, reactive extrusion, gamma irradiation, nanoprecipitation, and emulsion-crosslinking.[17,19] Most hydrolysis methods create starch nanocrystals (SNCs) while precipitation, emulsion, and mechanical treatments produce amorphous regenerated starch nanoparticles (RSNPs) or nanocolloids. Through any of these processes, the native starch reduces in size drastically from 10-15 μm to 10-500 nm. RSNPs are of greater importance to products where a spherical particle of low density and weaker internal hydrogen bonding are required. The RSNPs can be produced in large quantities at an industrial scale with a neutral carbon footprint more easily than SNCs.[9]

Surface modification of RSNPs consists of grafting molecules to the hydroxyl groups of the anhydroglucose repeat units. The reactivity of the hydroxyl groups is C-6 > C-2 > C-3.[21] These groups can be oxidized, reduced, esterified, etherified, or substituted with functional groups. The literature provides examples of starch modified with carboxymethyl, phosphate, fatty acid, acetyl, succinic, benzyl, acetic, propionic, octanoyl chloride, stearic, lactic, ferulic acid

chloride, anhydride, alcohol, as well as various ester, ether, cationic and anionic functional groups.[28,16,20–23,10,30,24,31–33,25,34,35,26,36–38] Additionally, several acrylic monomers and functionalized polymers have been successfully grafted onto and from various types of SNPs.[7,39–48] Methods for modification include dry processes, reactive extrusion, aqueous slurries, aqueous/organic solutions, and emulsions. It is notable that polymer grafted SNPs have been prepared through various emulsion techniques.[49–51] Once modified and made sufficiently hydrophobic, the SNPs can be blended with hydrophobic polymers to form nanocomposites, or incorporated in situ via polymerization. The greater the interaction between the nanoparticles and continuous polymer phase, the lower the mechanical and thermal impact of starch will be evident in the nanocomposite.[16]

Polysaccharides have been incorporated into emulsion polymerizations via three primary techniques. One technique involves the semi-batch feed of a monomer pre-emulsion onto a heated polysaccharide aqueous slurry while initiating with potassium persulfate (KPS).[44] Another technique uses polysaccharides as a primary particle stabilizer.[52,50,46,53] The third technique includes polysaccharides in a seed followed by a typical free radical emulsion polymerization procedure.[54–56,50] All techniques result in latexes where the polysaccharide either exists as a stabilizer, is partially or fully (as a shell) grafted to the surface of the synthetic polymer particles, or is simply homogenously dispersed among pure synthetic particles within the continuous phase. There currently exists no latex with core (starch) – shell (synthetic) particles created from oil-in-water emulsions with more than a small fraction of the RSNPs incorporated into the core of the latex particles.[16]

To displace a significant amount of petroleum-based (synthetic) material from existing latex formulations, a new procedure for incorporating RSNPs that results in similar surface morphology and functionality to the purely synthetic particles and films is required. This presents a significant challenge given that a core-shell morphology where the hydrophilic component is in the core is thermodynamically unfavourable in an aqueous continuous phase. If the starch remains wholly or mostly on the shell of the particles, it is reasonable to expect both a change in the rheological properties of the latex, and the surface properties of the resulting film or coating. Bringing the starch into the core of the particles may reduce the

difference in properties between the purely synthetic latex and the latex containing RSNPs. An alternative goal would be to simply increase RSNP incorporation within the latex particle, regardless of morphology.

A novel experimental RSNP produced by EcoSynthetix is a promising candidate for the formation of the ideal morphology of core (starch) – shell (synthetic) latex particles in emulsion polymerizations. It is designed to be as a co-monomer in these polymerizations to be used with a broad range of monomers and persulfates for initiation. This paper reports on the characterization of these novel experimental SNPs as a first step in the design of seeded emulsion polymerizations.

3.2 Experimental

3.2.1 Materials

All chemicals except for Aerosol surfactants EF-800, 80-I, A-102, and WA-300 (Cytec) were obtained from Sigma Aldrich. Experimental RSNPs were provided by EcoSynthetix and used as received. These experimental grade RSNPs contain different levels and different types of a proprietary polymerizable sugar based monomer (PSBM) produced by EcoSynthetix (Table 3.1). Inhibitor was removed from n-butyl acrylate (BA, 99%) using a column packed with inhibitor remover. Once purified, the BA was stored at 4 °C. The surfactants sodium dodecyl sulfate (SDS, 99%), Tween 80, and Triton; as well as the initiator, potassium persulfate (KPS, 99%); and the buffer, sodium bicarbonate (98%) were used as received. Distilled-deionized (DDI) water was used in all experiments. Nitrogen gas was supplied by Linde Canada.

3.2.2 Particle Diameter and Distribution

Dry RSNPs were dispersed in DDI water at 50 °C for 30 min under magnetic stirring to allow for visible dispersion (i.e., no visible agglomerates). Dispersions were prepared at 15 wt.% solids. One drop of dispersion was pipetted into a cuvette with 2 mL of DDI water. The diluted

dispersion was further diluted by adding one drop into another cuvette with 1 mL of DDI water. This sample was immediately analyzed by dynamic light scattering (DLS). Particle size was measured using a Malvern Nano-S Zetasizer DLS instrument at room temperature, with an angle of 176° and a refractive index (RI) of 1.49.[57] Three measurements were made for each sample and the average was assigned as the mean Z-average size of particles. The reported average particle diameter (D_p) was the intensity-weighted average particle size.

Table 3.1 Properties of newly modified RSNPs

Grade #	PSBM (wt.%)	PSBM Hydrophobicity (Low – High)	Other Comments
S-0-hmw	0	-	No added functionality
S-3-L	3	Low	
S-0-3APG	0	-	3 wt.% alkyl polyglucoside (No vinyl groups)
S-1-M	1	Med.	
S-3-M	3	Med.	
S-6-M	6	Med.	
S-3-H	3	High	
SD-3-M*	3	Med.	

* Dent sourced starch

Note: Grade # format represents starch source - % PSBM – hydrophobicity/special formulation; e.g., S-1-M refers to waxy sourced starch with 1% PSBM and a medium hydrophobicity.

3.2.3 Viscosity

A Haake Viscotester D viscometer from Thermo Scientific was used at 100 RPM with spindle #4 to calculate the viscosity of the RSNP dispersions. 100 mL of each dispersion was charged to a 150 mL beaker with a 57 mm diameter and the spindle submerged to its notch indicator. Temperature was not changed from the experiment performed prior to viscosity measurement (60 °C unless otherwise noted).

3.2.4 Pressurized Ultrafiltration

A Millipore Amicon EMD pressurized stirred cell was used with Millipore Ultracell regenerated cellulose membranes (will exclude particles >30 nm). Maximum pressure attainable with our system was 25 psi by pressurized nitrogen gas. Each RSNP dispersion was heated to 50 °C and charged into the cell, which was then pressurized and stirred for 24 h unless otherwise noted. If at any time the solution became too viscous for transmembrane flow, the retentate was removed, reheated, diluted and recharged into the cell.

3.2.5 Surface Tension

A Krüss K12 Tensiometer with a RI01 platinum ring (ring method) and insulated vessel fixture was used to measure the surface tension of each RSNP dispersion. An immersion depth of 3 mm, measuring speed of 3 mm/min, search speed of 6 mm/min, and surface tension sensitivity of 0.005 g was used. Ten values were sufficient to achieve desired standard deviation. Each RSNP dispersion was prepared at 50 °C and 100 mL was added to a Pyrex cylinder and subsequently cooled in an ice bath to 25 °C before measurement.

3.2.6 Composition and Structure by NMR and IR

RSNP dispersions were analyzed directly using a Mettler Toledo ReactIR 45 infrared probe after background calibration and with solvent peak suppression. RSNP films were cast and then re-dispersed in D_2O or chloroform and analyzed via ^{1}H-NMR spectroscopy with a Bruker AVANCE 400 (400 MHz) spectrometer (5mm autotuning broadband probe with Z gradient, 32 scans per readout, 25 °C).

3.2.7 Emulsion Stabilization

A beaker was filled with 150 mL DDI water and 20 g BA and stirred with a magnetic stirrer. A 30 wt.% RSNP dispersion was added as a batch charge and stirred for 15 min. The

dispersion was allowed to settle for 15 min and visual confirmation of stabilization was made. Emulsion stability ranged from unstable, to semi-stable (partial phase separation), and fully stable (no phase separation). An increase in opacity indicated emulsion formation (stabilization of hydrophobic droplets).

3.3 Results and Discussion

3.3.1 Particle Size

The particle diameter of the RSNPs is required to estimate the number of the modified RSNPs making up the core of each latex particle and the thickness of the synthetic shell (if a core-shell morphology is obtained). The size of the RSNPs will also have an influence on the nucleation stage of the emulsion polymerizations, making accurate particle size determination crucial to planning appropriate procedures. Several RSNP grades were analyzed by DLS and their intensity based particle size distributions (PSDs) were compared (Figure 3.1). Most grades exhibited a bimodal distribution with peaks centered at 20 and 200 nm. Exceptions to this were S-0-hmw, which was nearly monomodal around 50 nm, and SD-3-M, which was bimodal with peaks centered at 150 and 700 nm. Z-Average mean diameters are influenced by peaks with larger intensity rather than the number of particles at a specific diameter.

Starch has a tendency to aggregate and form complexes in water. Because of this tendency, it is necessary to determine whether the peaks in the PSD represent individualized particles or aggregates of smaller ones. 15 and 5 wt.% S-3-M dispersions were filtered by ultrafiltration at 25 psi to determine the wt.% of RSNPs with diameters near the first peak at 20 nm (Figure 2.1). 40 to 50 wt.% of the particles were below 30 nm in diameter (additional tests revealed that an increased pressure difference did not draw > 30 nm particles through the membrane). The concentrated retentate had a Z-average particle diameter of 275 nm, compared to the unfiltered S-3-M diameter of 225 nm. Permeate samples were collected both immediately at the outlet of the filtration device and from a reservoir that was collecting the permeate over three hours.

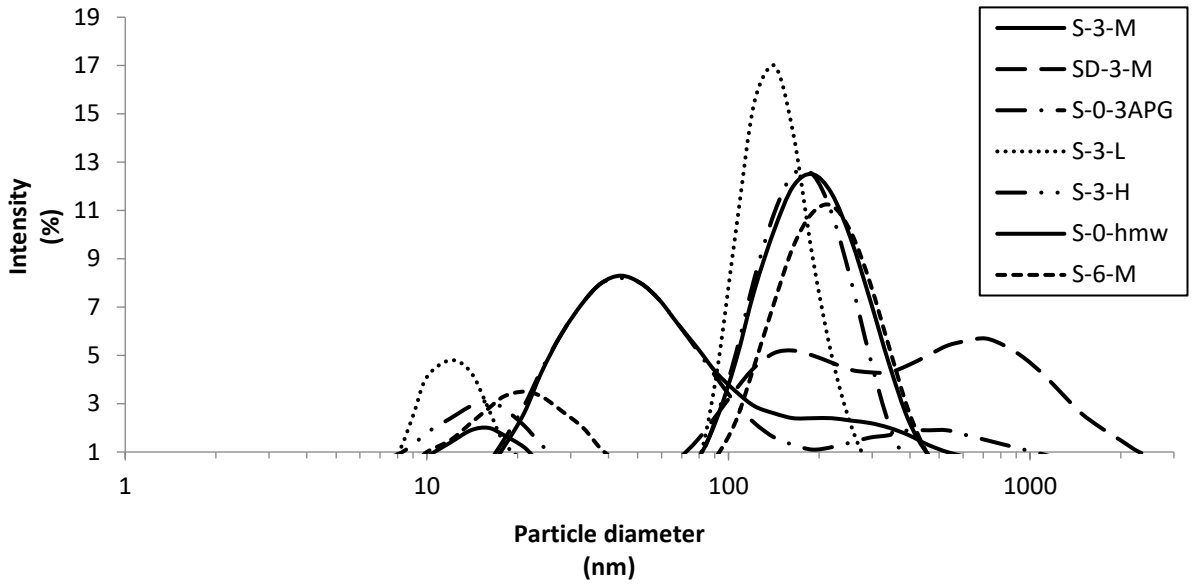

Figure 3.1 Intensity based PSDs of various RSNP grades

Samples taken directly from the filtration outlet showed only one peak at 20 nm and remained constant for at least three days. The sample from the reservoir gave an additional broad secondary peak between 300 and 800 nm (the Z-average diameter was 175 nm). Separate experiments observing the change in Z-average diameter with concentration led us to the conclusion that as the swelling or void space (which was filled with water) of the particles or agglomerates increases, so does the Z-average diameter. The secondary peak between 300 and 800 is therefore representative of loose agglomerate formation. The retentate is composed of individualized particles as agglomerates would not maintain integrity during the filtration process. We conclude that the apparent Z-average particle diameter is highly influenced by the larger RSNPs or starch aggregates. Volume based PSDs show no significant peak above 20 nm for S-3-M (and a single peak at ~800 nm for SD-3-M). This would suggest that if there are particles above 30 nm for S-3-M (60 wt.% from filtration data), then they are of a wide range of diameters (30 to 300 nm), no one size being large enough to be visible in the volume based PSDs. The presence of aggregates in concentrated dispersions would be consistent with the literature.[8,18,32,58,59] Thus, the RSNPs would be expected to aggregate under normal emulsion

polymerization conditions and would only be fully dispersed as individual RSNPs at very low concentrations (<<5 wt.%).[59] Further, the individualized RSNPs would be primarily <30 nm.

GPC analysis indicates that S-0-hmw has a higher molecular weight than S-3-M. This difference can be attributed to the addition of PSBM (which has a maleic acid group) in the S-3-M grade, which is able to degrade starch through acid hydrolysis.[8,25,44,52,60] The addition of PSBM was the only procedural difference in the preparation of S-3-M and S-0-hmw. GPC separates molecules on the basis of their hydrodynamic radius. Because no change in density of the RSNPs is expected, the observed reduction in hydrodynamic radius must be caused by a reduction in molecular weight. This would be consistent with the PSD of S-0-hmw showing a larger individualized particle peak (~ 50 nm) than S-3-M (~20 nm). In addition to PSBM, KPS also has the potential to decrease the molecular weight of the RSNPs. When separate dispersions of S-3-M and SD-3-M were mixed with KPS at 60°C, the average molecular weights decreased.

PSDs of a 15 wt.% dispersion of S-3-M at 60 °C (200 RPM anchor blade stirring) acquired over 24 h exhibited a shift of the larger peak of the PSD towards the 10 - 30 nm range. This peak returns to its original larger position upon cooling to 25 °C. The experiment was repeated at 30 °C over 24 h with no change in particle diameter after initial dispersion. Although the decrease in diameter is indicative of hydrolysis of the α-1,4-D-glucopyranose bonds that crosslink the RSNPs, this would not be consistent with our observations on particle morphology from other experiments. A more reasonable explanation would be that the increase in temperature both reduces the number of particles necessary to stabilize aggregates (lowering the critical aggregate concentration (CAC)) as well as increasing the degree of osmotic deswelling (drawing water out of the individualized particles).[61–63] Dispersions of increasing concentration were measured by DLS and were revealed to have decreasing D_p, indicating that the RSNPs are susceptible to osmotic deswelling.

Emulsion polymerization relies on surfactants to stabilize polymer particles in the nucleation and growth stages, and during storage of the final latex. Determining the relationship between these surfactants and RSNPs is essential to designing polymerization procedures. The addition of various anionic and non-ionic surfactants to dispersions of S-3-M

resulted in differences in apparent particle diameter and PDI. It is suspected that these measurements are of agglomerates formed by interaction with the surfactants. Aerosol WA-300 (anionic sulfonate/non-ionic mix with C8-C16 chain length) produced the smallest PDI while Aerosol MA 80-I (anionic sulfonate with C4 chain length) resulted in the smallest particle diameter. Anionic surfactants have a stronger ability to maintain starch agglomerate integrity than non-ionic surfactants,[58] while non-ionic surfactants tend to form micelles at lower concentrations.[64] Starch can also hydrogen bond with the sulfonate groups of the anionic surfactants.[65] This can result in the starch forming a shell around the surfactant micelles through cooperative bonding, lowering the critical micelle concentration (CMC),[55] or the surfactant surrounding the starch agglomerates through hydrogen bonding or hydrophobic effects.[64] A non-ionic surfactant could then stabilize either of the previous surfactant-starch complexes. Determining the ideal surfactant with appropriate chain length, hydrophobic-lipophilic balance (HLB), and charge is necessary to control its interaction with RSNPs.

3.3.2 Viscosity

The larger the size of hard spheres in a dispersion, the lower the viscosity due to the increased void space and decreased surface area for particle-particle interaction, assuming constant solids content. In polydisperse dispersions the maximum packing fraction will be achieved at the ratio of large:small particles that minimize the space lost between the particles. If the smaller particles are too large, too small, or too many, the maximum packing fraction will be reduced.[66] Viscosity profiles of various grades at 15 wt.% (Figure 3.2) exhibited little change in viscosity with increased temperature, with the exception of S-0-hmw which had a higher molecular weight and lower polydispersity than S-3-M as a result of no added PSBM during production. The higher polydispersity of the lower molecular weight RSNPs (as a result of 40-50 wt.% of the particle having a particle diameter < 30 nm and the remaining particles having a large range of diameters between 30 and 300 nm) gave these dispersions a lower viscosity compared to the higher molecular weight and monodisperse S-0-hmw. The slightly higher

viscosity of the SD-3-M dispersion are due to the excessively small size of the amylose portion of the particles.

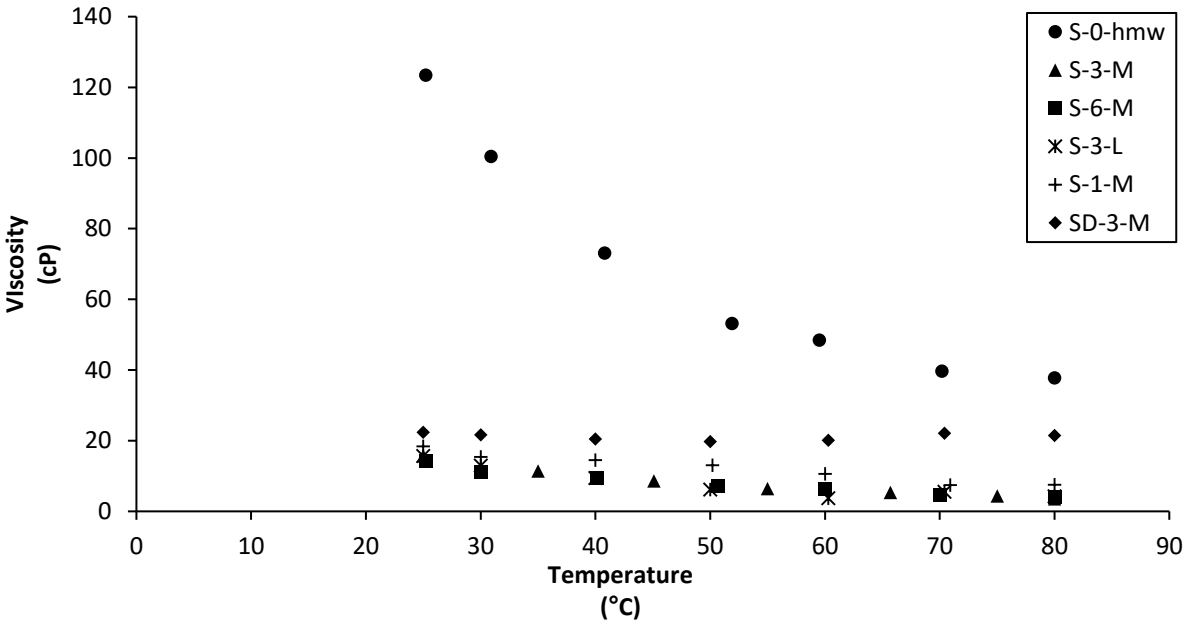

Figure 3.2 Viscosity profile of RSNP grades over range of temperatures

Viscosity measurements of dispersions of S-3-M and SD-3-M at various volume fractions were compared at 60 °C (Figure 3.3) and fitted to the Krieger-Dougherty viscosity model to determine the critical packing fraction (ϕ). The critical packing fraction is the maximum achievable amount of RSNPs in an aqueous dispersion. If the RSNP is incorporated into the synthetic latex particle during emulsion polymerization this concentration limit will increase since the water soluble starch is being removed from the aqueous continuous phase and no longer contributing to the viscosity of the latex. Since these measurements were not conducted at room temperature, it should be noted that cooling the final polymerized latex would reduce the critical packing fraction unless all the RSNPs are fully incorporated within the synthetic particles. The model did not fit the data well due to the fact that the RSNPs are not solid spheres, however the critical volume fractions of S-3-M and SD-3-M can still be used as a relative comparison. SD-3-M dispersions had a ϕ of 0.36 as opposed to 0.4 for S-3-M

dispersions, highlighting a possible challenge when attempting to load high amounts of SD-3-M into polymerization formulations.

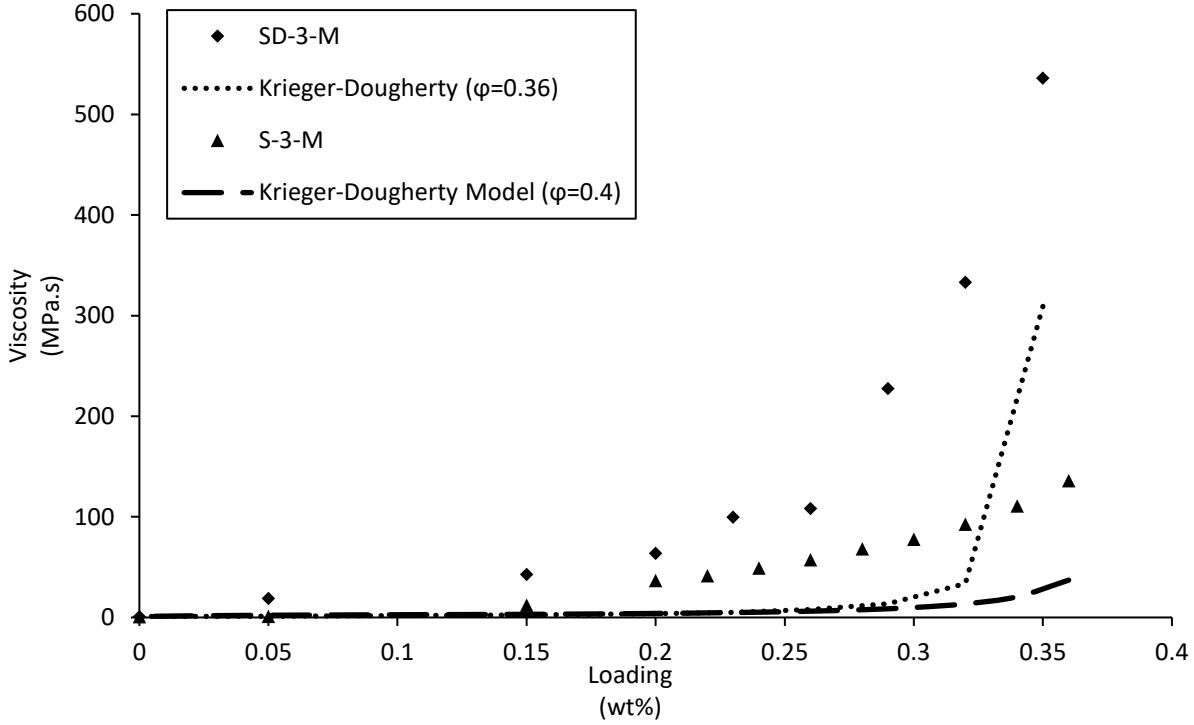

Figure 3.3 Viscosity profiles of SD-3-M and S-3-M at increasing concentrations

3.3.3 Surface Tension

The CMC and corresponding surface tension of S-0-hmw, S-3-M, and S-6-M grades were determined using a surface tensiometer (Figure 3.4). The CMC increased with wt.% of PSBM functionality, indicating that either increased PSBM functionality allows the RSNPs to form micelles or that the PSBM does not remain bonded to the particles and the change in CMC is solely dependent on the concentration of free PSBM (whose structure is that of a vinyl functionalized surfactant, or surfmer) in the dispersion.

When the surface tension is plotted against the concentration of PSBM there is less than a 0.025 wt.% difference in the CMC's of S-3-M, S-6-M and pure PSBM (Figure 3.5), confirming

the CMC is a function of free PSBM concentration. The difference in final surface tension is most likely caused by the difference in starch particle concentration. This behavior supports the theory that the RSNPs do not remain functionalized in an aqueous environment at temperatures above 30 °C. The functionality of PSBM as a surfactant is expected as it is a modified alkyl polyglucoside, and the ability of APG to be used as a non-ionic stabilizer has been previously shown.[67]

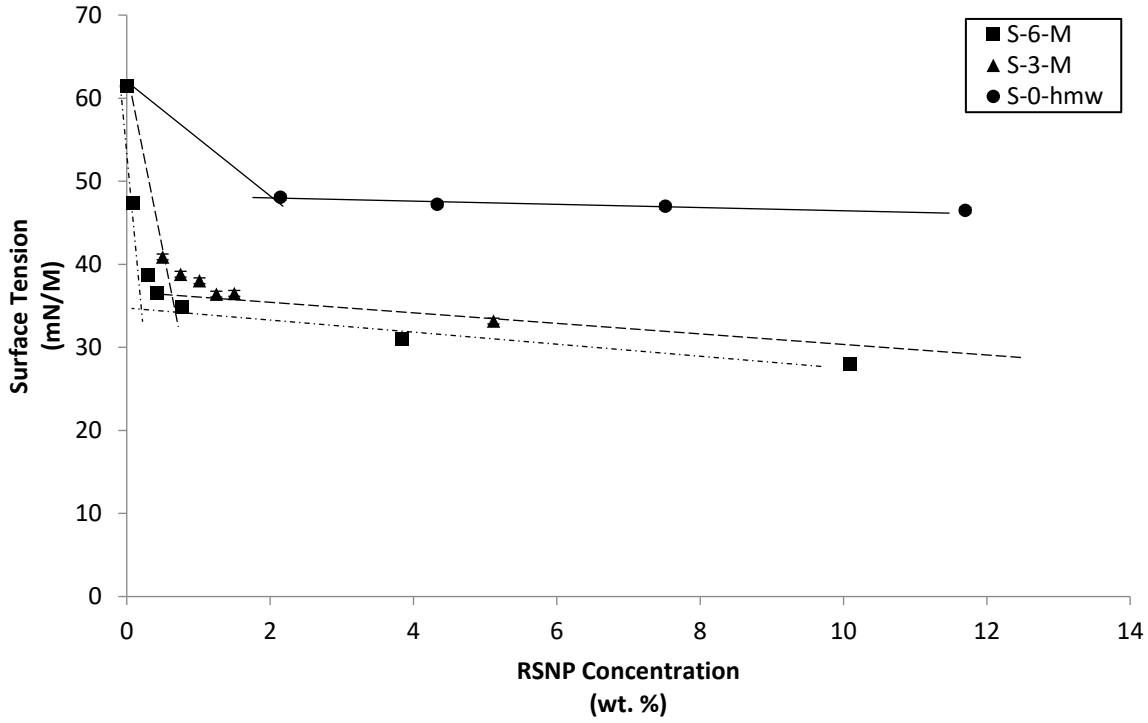

Figure 3.4 Surface tension profiles of S-6-M, S-3-M, and S-0-hmw grades at increasing concentrations with CMCs determined at crosshairs of tangent lines

The interaction between surfactant and RSNP was determined by first bringing an aqueous dispersion of surfactant to its CMC, then adding dry RSNP granules in small amounts, and finally observing the change in surface tension (Figure 3.6). The surface tension of the SDS dispersion increased with addition of S-0-hmw, S-3-M, S-0-3APG, and the permeate from the S-3-M filtration experiments. A decrease in surface tension occurred only with addition of the S-3-M retentate. The increase in surface tension is a result of SDS molecules moving from their

micelles and surrounding the lower molecular weight starch, therefore drawing SDS from the surface to the bulk in order to replace the micelles that were lost from this interaction.[55,64] The decrease in surface tension of the dispersion when retentate is added indicates that the higher molecular weight particles cause a further reduction of surface tension at the surface of the dispersion and are not attracting SDS from the micelles. The preferential attraction of SDS to the lower molecular weight starch could be explained by the creation of complexes formed by linear starch chains entangling with the hydrophobic tails of the surfactant.[21] In an emulsion polymerization the surfactant can be expected to surround the lower molecular weight starch (40-50 wt.% of total RSNP) but not the larger particles.

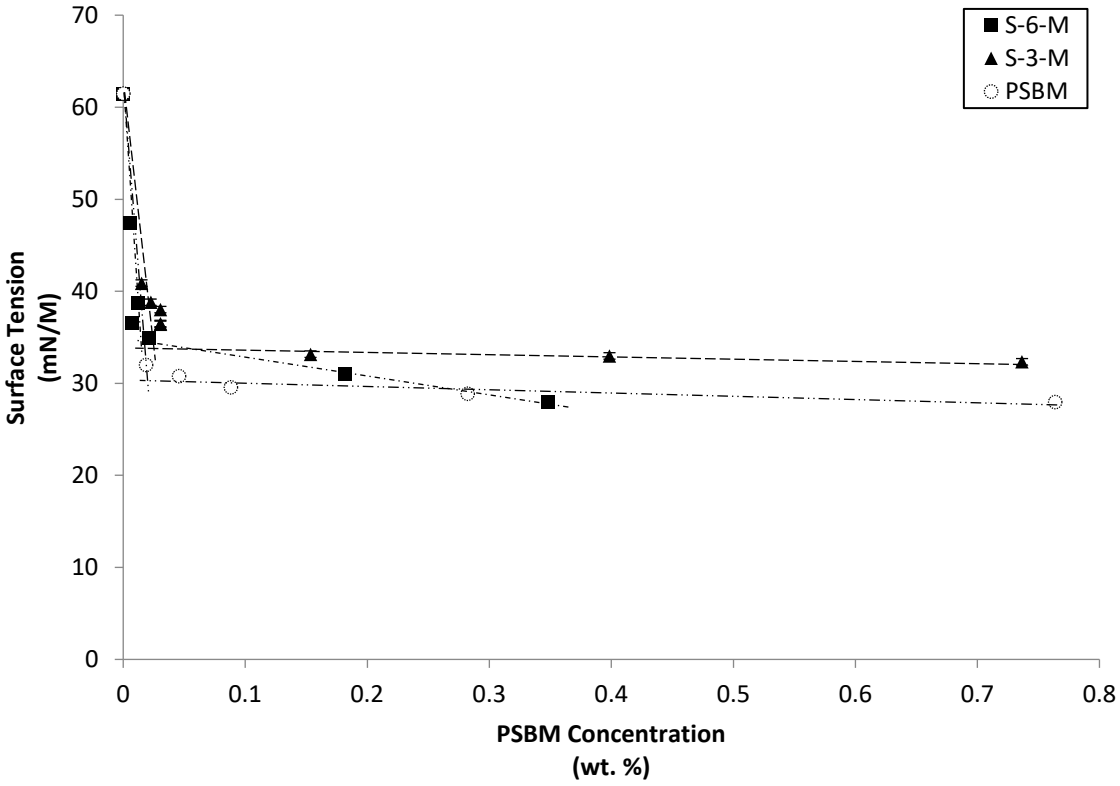

Figure 3.5 Surface tension profiles of S-6-M, S-3-M, and PSBM at increasing concentrations, plotted against PSBM concentration, with CMCs determined at crosshairs of tangent lines

All grades were able to form semi-stable emulsions of BA (indicated by increased opacity) with minor phase separation over 15 min (Figure 3.7).

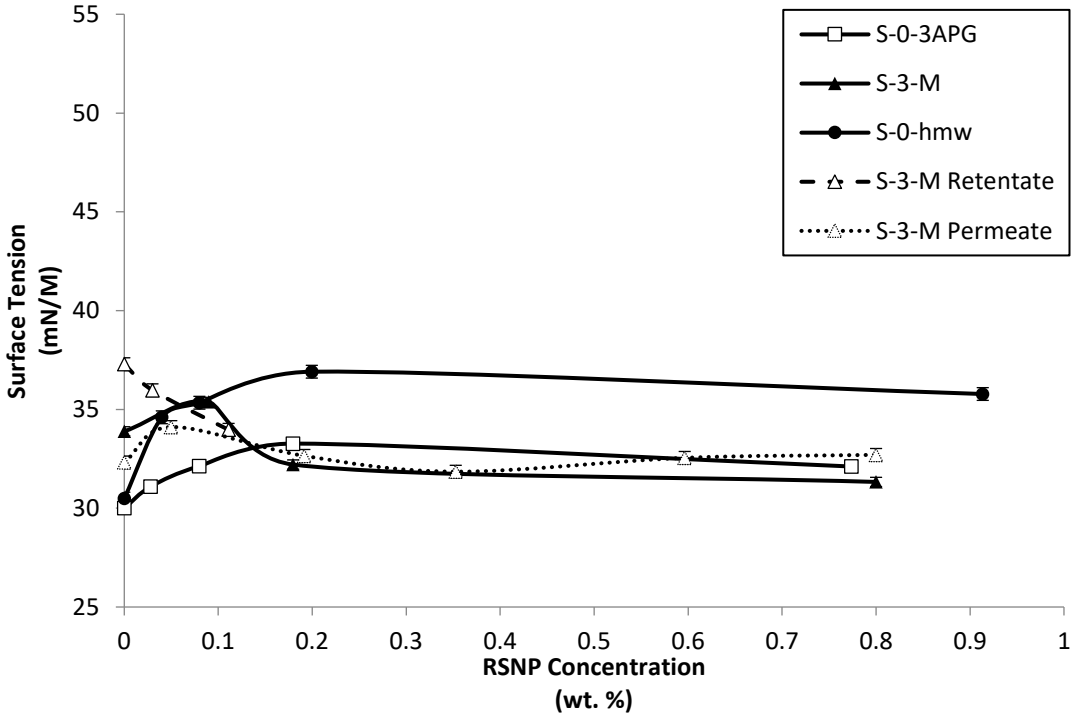

Figure 3.6 Surface tension profiles of SDS dispersions at increasing concentrations of RSNP

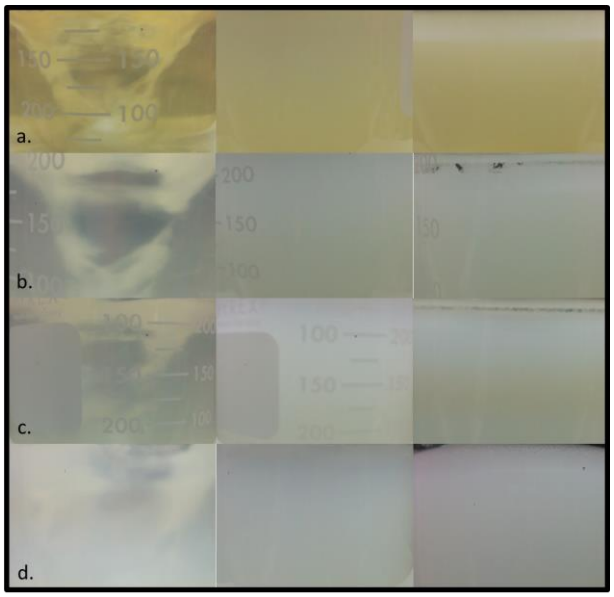

Figure 3.7 (a) S-0-hmw (b) S-3-M (c) S-6-M (d) S-3-H. From left to right column: mixing of RSNP dispersion, RSNP dispersion after being stabilized with BA, and stabilized dispersion after 15 min with visible monomer phase separation on surface.

The grade extruded with hydrophobic PSBM (S-3-H) exhibited better emulsion stability. The mechanism responsible for emulsion stability is most likely a combination of steric and Pickering stabilization.[50,52,53]

3.3.4 Functionalization

H^1-NMR and FTIR analysis of the functionalized RSNPs confirm the presence of the PSBM vinyl groups (Figures 3.8 and 3.9).

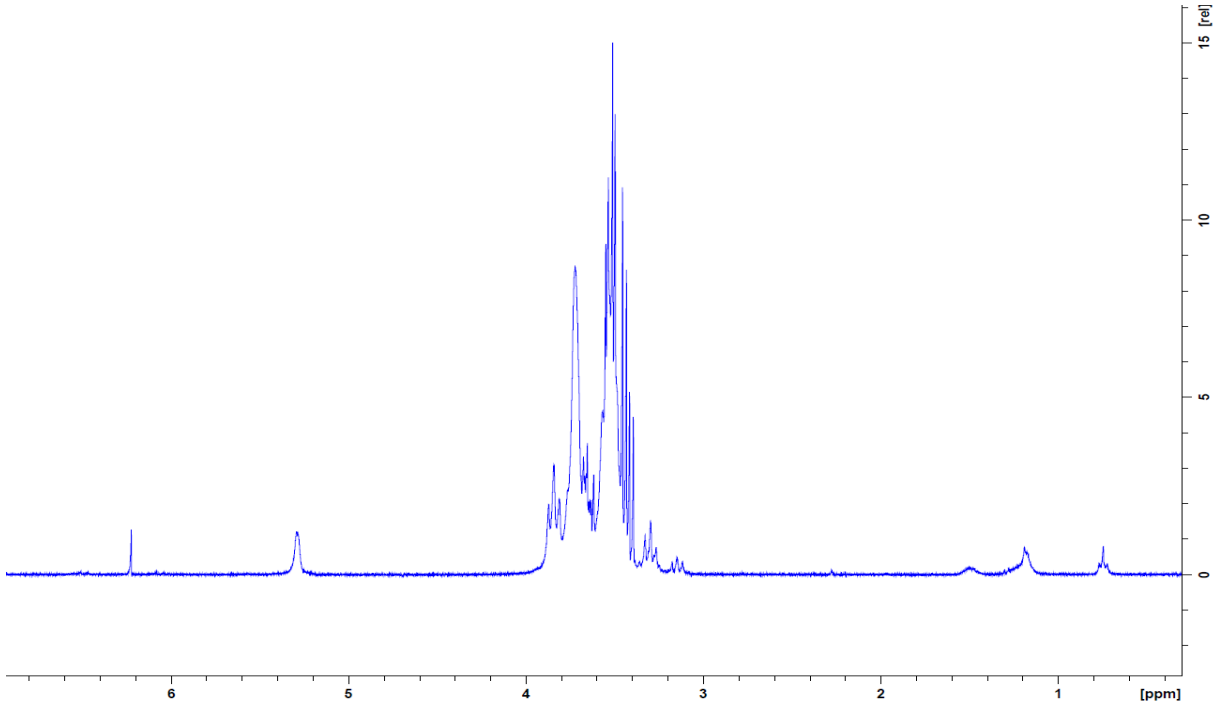

Figure 3.8 ^{1}H-NMR spectrum of S-3-M RSNPs, with the characteristic starch peaks from 3.0 – 4.0, the carbon chain of PSBM from 0.5 – 1.6, and the vinyl group of PSBM from 6.0 – 6.3

3.4 Conclusion

Z-average PD measurements were concluded to be highly influenced by larger particles and agglomerates and not representative of individualized particles. The RSNPs were also shown to associate unless kept at extremely low concentrations

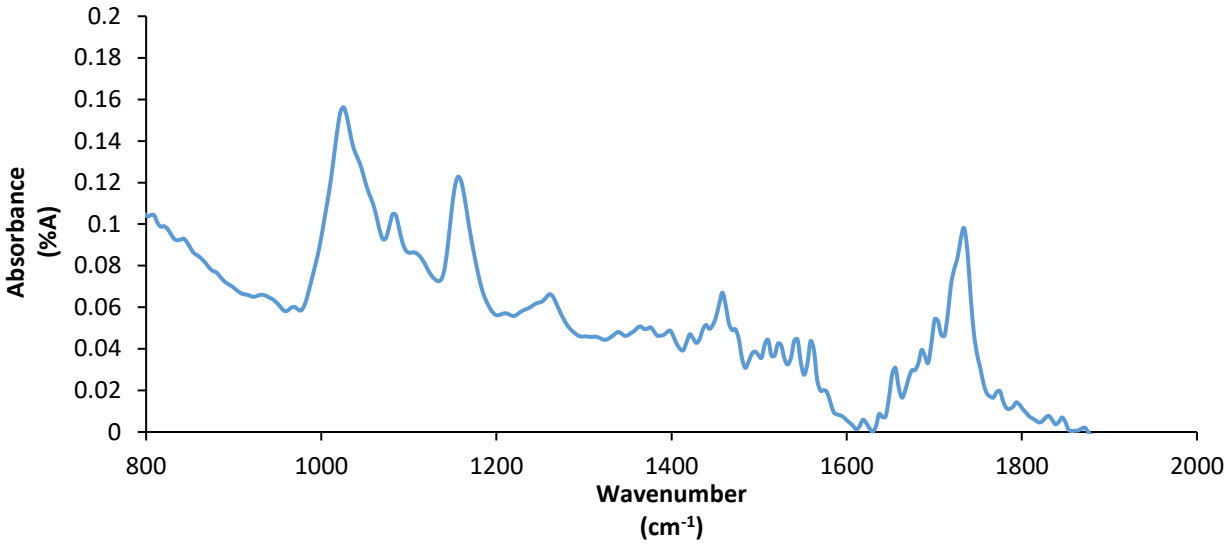

Figure 3.9 FTIR spectrum of S-3-M RSNPs, with the characteristic starch peaks from 800 – 1500, and the vinyl group of the PSBM at ~1700

(<<5 wt.%). 40-50 wt.% of the RSNPs are below 30 nm, while the larger individual particles are of diameters ranging from 30 – 300 nm. The addition of PSBM functionality to the starch particles reduces molecular weight and hydrodynamic radius. KPS also causes a reduction in the molecular weight of the RSNPs. The correct ratio of large:small particles of waxy starch sourced RSNPs contribute to their lower viscosity compared to unmodified RSNPs and dent sourced starch. The critical volume fraction is therefore larger for the S-3-M grade than for SD-3-M. Higher temperature affects the agglomerate and particle size by lowering the CAC and increasing the degree of osmotic deswelling respectively. Surfactant can be expected to surround the RSNPs in the seed stage of the polymerization, but it is unknown if this attraction will persist in the presence of hydrophobic monomer. Regardless, the RSNPs will stabilize monomer particles or at least assist in the formation of anionic micelles during the nucleation stage of the polymerization.

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Chapter 4: Novel Modified Regenerated Starch Nanoparticles for Synthetic Solid Content Reduction in Polymer Latexes

Novel Modified Regenerated Starch Nanoparticles for Synthetic Solid Content Reduction in Polymer Latexes

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ABSTRACT

Emulsion polymerization provides a more sustainable way to produce polymer latex. Newly modified regenerated starch nanoparticles (RSNPs) were used in emulsion polymerizations to prepare partially starch-incorporated latexes with reduced synthetic solids content. Incorporation of S-3-M RSNPs into the polymer matrix was 0-10 wt.% for a 15 wt.% loading, 40 wt.% solids latex. Semi-batch feeding of the S-3-M RSNPs resulted in the highest loadings of 40 and 50 wt.% (40 wt.% solids) with 0-10 wt.% RSNP incorporation into the synthetic particles, while 40 wt.% loading (20 wt.% incorporation) was achieved with the S-6-M RSNPs. Although no evidence of core-shell morphology was obtained, strategies were developed to obtain high loadings of the RSNPs within the acrylate latex. The resulting films had higher resistance to tetrahydrofuran, but poorer water resistance and adhesive properties. Higher incorporation may be achievable if the polymerizable sugar based monomer (PSBM) functional groups were permanently bonded to the RSNPs, and monomers with more appropriate reactivity and hydrophobicity are employed.

4.1 Introduction

Based on the number of publications focussing on bio-based and biodegradable polymers, the transition towards more sustainable industrial practices for the production of polymers has accelerated significantly in the past 10 years. Growth in the global production of bio-based polymers reflects this increased academic interest.[1–13] Sustainable strategies include the use of sustainably produced and bio-sourced monomers, the incorporation of bio-based fillers and components, and the use of emulsion polymerization.[14,15] Emulsion polymerization provides enhanced heat transfer by using water as a reaction medium, allows for high molecular weight products at simultaneously high reaction rates, enhanced control over polymer morphology and structure, as well as a final latex with a viscosity independent of molecular weight. The final latex can be formed into a thin film for coatings, paints, adhesives and specialty applications.

There are many applications that require materials with properties that cannot be met by purely synthetic polymer formulations. Homogeneously distributed fillers and additives throughout the polymer matrix can serve to tune the final properties.[10,16] Due to their small size, high surface area to volume ratio, enhanced solubility, and functionality, nanoparticles added to polymers form composites that yield superior properties to the original polymer matrix.[17] Nanocomposites often require a chemical retention additive to prevent the filler from leaching out of the polymer matrix after film formation.[18] Often these additives present potential toxicity and always require additional cost. Covalently bonding the filler to the polymer would eliminate the need for such additives and anchor the particles in place. If the nanoparticles acted more like a reactive comonomer than a filler, higher loading and incorporation of the nanoparticles would be possible.[16] Throughout this work, incorporation is defined as the grafting, adsorption, or otherwise permanent embedding of renewable filler/comonomer into the synthetic polymer particles.

Starch is a naturally occurring polymer with the chemical formula $(C_6H_{10}O_5)_n$ containing linear amylose and branched amylopectin polysaccharides. The amount of amylose can range from 70 wt.% for amylomaize to 1 wt.% for waxy maize. Starch can be used in polymer

nanocomposites after being physically and/or chemically modified. Typically, the goal of modifying native starch is to form nanoparticles, change the crystallinity, increase hydrophobicity, or introduce functional moieties.[11,13,16,19–29]

Starch nanoparticles (SNPs) can be produced by a variety of proven methods such as fluid extraction, solvent evaporation, acid hydrolysis, enzymatic treatment, high-pressure homogenization, ultrasonication, reactive extrusion, gamma irradiation, nanoprecipitation, and emulsion-crosslinking.[11,19] Most hydrolysis methods create starch nanocrystals (SNCs) while precipitation, emulsion, and mechanical treatments produce amorphous regenerated starch nanoparticles (RSNPs) or nanocolloids. Through any of these processes, the native starch reduces in size drastically from 10-15 µm to 10-500 nm. RSNPs are of greater importance to products where spherical particles of low density and weaker internal hydrogen bonding are required. These RSNPs can be produced in large quantities at an industrial scale with a relatively neutral carbon footprint more easily than SNCs.[12]

Surface modification of RSNPs consists of grafting molecules to the hydroxyl groups of the glucose repeat units. This modification is necessary to facilitate compatibility of the RSNPs with the polymer matrix in the nanocomposite. The literature provides examples of starch modified with carboxymethyl, phosphate, fatty acid, acetyl, succinic, benzyl, acetic, propionic, octanoyl chloride, stearic, lactic, ferulic acid chloride, anhydride, alcohol, as well as various ester, ether, cationic and anionic functional groups.[16,18,21–28,30–38] Additionally, several acrylic monomers and functionalized polymers have been successfully grafted onto and from various types of SNPs.[39–49] Once modified and made sufficiently hydrophobic, the SNPs can be combined with hydrophobic polymers to form nanocomposites. The greater the interaction between the nanoparticles and polymer phase, the lower impact of the starch on the nanocomposites mechanical and thermal properties.[16]

When the polymer matrix is hydrophobic, the hydroxyl groups of the RSNPs can disrupt the filler-matrix interactions and encourage agglomeration, causing instability either during the polymerization or during the shelf life of the final latex.[19,26,50] Nanocomposites containing starch have been shown to phase separate at loadings of 50-80 wt.%.[29] Tie-layer monomers and

compatibilizers can assist in the homogeneous distribution of RSNPs through their ability to form hydrogen or covalent bonds to one or both of the filler and polymer.[34] Crosslinkers have also been successfully used to immobilize the RSNPs within the polymer film.[22] The water absorbency/solubility of starch-containing composites is increased while oxygen permeability is decreased compared to the filler-free polymer, even at high grafting efficiency.[16,46,51] If not homogeneously dispersed and anchored into the polymer matrix, SNPs can form diffusion pathways for water at lower concentrations when compared to larger starch particles.[16]

Polysaccharides have been incorporated into emulsion polymerizations via three primary techniques. One technique involves the semi-batch feed of a monomer pre-emulsion onto a heated polysaccharide aqueous slurry while initiating with potassium persulfate (KPS).[47] Another technique uses polysaccharides as a primary particle stabilizer.[42,52–54] The third technique includes polysaccharide in a seed followed by a typical free radical emulsion polymerization procedure.[51,53,55,56] All techniques result in latexes where the polysaccharide either exists as a stabilizer, is partially or fully (as a shell) grafted to the surface of the synthetic polymer particles, or is simply homogeneously dispersed among pure synthetic particles as a blend. There currently exists no latex with core (starch) – shell (synthetic) particles created from oil-in-water emulsions.[16] In order to ensure the original properties of the synthetic latex are retained, such a core-shell structure is necessary to prevent the surface of the RSNPs from interacting with external surfaces. In other words, to maintain polymer surface properties, one wishes to conceal the RSNPs within a polymer shell.

Emulsion polymerizations generally involve (1) nucleation of monomer swollen micelles by surfactant; (2) growth of polymer particles by free radical initiation and the feeding of monomer from stabilized droplets; and (3) once the droplets are depleted, the consumption of unreacted monomer within the latex particles. Several different nucleation mechanisms may exist at the same time. All of this occurs in an aqueous medium where components such as buffer, chain transfer agent (CTA), crosslinker, and other additives are included. Seeded polymerizations use polymer particles already prepared at a known particle diameter to begin growth of a new latex. Various feeding strategies include batch or semi-batch feed of monomer pre-emulsion, initiator solution, or other additives. In order to induce a core-shell morphology

in emulsion polymerizations, it is recommended to use a lightly crosslinked seed latex, to select a shell monomer that is more hydrophilic than the seed latex or to prevent migration of shell monomer to the core. The shell stage polymerization is often accomplished using monomer-starved feed conditions. In addition, one also should ensure that the volume ratio of the seed to shell monomer is appropriate for full coverage of the seed surfaces.[57,58]

With the presence of RSNPs in the reaction mixture, several additional factors must be taken into consideration. The size of the acrylic particles in the latex affects the final film morphology due to changes in viscosity and void space and must be tailored for the specific RSNP.[50] Polysaccharide nanoparticles in general can act as steric stabilizers or protective colloids at concentrations comparable to typical anionic surfactants.[52,53] The hydrophobicity of the synthetic polymer particles will influence the stabilizing performance of the polysaccharide.

Polysaccharides will both degrade and graft to themselves in the presence of persulfate initiators.[42] Increase in KPS concentration above a minimum should not be expected to result in increased grafting of starch in emulsion polymerizations in contrast to slurries and solutions. On the other hand, reducing the size of RSNPs and latex particles has been shown to increase grafting efficiency.[46,55] Grafting efficiency increases with monomers that have low homopolymerization reaction rates. As the hydrophilicity of these monomers increases, so does their attraction to the waterborne starch.[47] Higher RSNP loading should increase grafting efficiency by increasing the chance of monomer or polymer radicals of contacting starch hydroxyl or hydroxyl radical groups.

There are no reports of oil-in-water emulsion-based latexes with core-shell morphology with the majority of the RSNPs in the core of the particles. Work by Pei et al. and Lange et al. are the only attempts found in the literature where RSNPs are used in emulsion polymerizations.[53,59,60] Other attempts to include starch in emulsion polymerizations have been in the form of high molecular weight (HMW) native starch[47,51,55,56,61–70], functionalized HMW starch[71–76], SNCs[54,77,78], or low molecular weight starch[49,71,79–87].

A novel vinyl-functionalized RSNPs was used in this work in an attempt to create a latex with high starch loading at low viscosities and surface properties similar to that of a fully

synthetic latex. Characterization of these RSNPs has been described elsewhere (Chapter 3). This paper describes several strategies to incorporate a modified RSNP into industrially relevant emulsion formulations at high loadings (25-40 wt.% incorporation).

4.2 Experimental

4.2.1 Materials

All chemicals except for Aerosol EF-800 surfactant (50 wt.% aqueous solution) (Cytec) were obtained from Sigma Aldrich. Experimental grade RSNPs were provided by EcoSynthetix and used as received. These experimental grade RSNPs contain different levels and different types of a proprietary polymerizable sugar based monomer (PSBM) produced by EcoSynthetix (Table 4.1). Acrylic acid (AA, 98%) was used as received, while inhibitor was removed from n-butyl acrylate (BA, 99%) and 2-ethylhexyl acrylate (2-EHA, 99%) using a column packed with inhibitor remover, and from methyl methacrylate (MMA, 99%) through distillation. Once purified, the BA, MMA, and 2-EHA were stored at 4°C. Sodium dodecyl sulfate (SDS, 99%), cetrimonium bromide (CTAB, 98%) surfactant, potassium persulfate (KPS, 99%), sodium bicarbonate (98%), and n-dodecanethiol (CTA, 98%), were used as received. Distilled-deionized (DDI) water was used in all experiments. Nitrogen gas was supplied by Linde Canada.

Table 4.1 RSNP properties

Grade #	PSBM (wt.%)	PSBM Hydrophobicity (Low – High)	Other Comments
S-0-hmw	0	-	Non-functionalized
S-0-lmw	0	-	Non-functionalized
S-3-L	3	Low	
S-0-3APG	0	-	3 wt.% APG (No vinyl groups)
S-1-M	1	Med.	
S-3-M	3	Med.	
S-6-M	6	Med.	
S-3-H	3	High	

Note: Grade # format represents starch source - % PSBM – hydrophobicity/special formulation; e.g., S-1-M refers to waxy sourced starch with 1% PSBM and a medium hydrophobicity.

4.2.2 Emulsion Polymerizations

Polymerizations were carried out at 60 °C in a 1 L Mettler-Toledo LabMax® jacketed stainless steel reactor equipped with an anchor stirring blade, reflux condenser, and inlets for nitrogen gas sparging, and semi-batch feeding of the monomer pre-emulsion and initiator solution. The RSNP dispersion was prepared by dispersing dried RSNP granules in an aqueous solution with buffer at 50 °C while stirring with a magnetic stirrer for 30 min or until dispersed. The RSNP dispersion was sparged with nitrogen and further dispersed at 300 rpm for 60 min. The initiator solution was charged 2 min before semi-batch feeding began. During polymerization, latex samples were taken with a syringe to measure the latex particle size and monomer conversion (by gravimetry). To prevent further polymerization, samples were quenched with a few drops of a hydroquinone aqueous solution. A typical latex formulation and procedure are outlined in Table 4.2. Every experiment reported herein was replicated.

Table 4.2 Typical latex formulation

Component	Amount (g)	wt.% of total (*phm, **phw)
Seed (Batch #1)		
New modified RSNP	30	15
Distilled, de-ionized water	212	
Sodium bicarbonate buffer	0.3	0.1**
Initiator (Batch #2)		
Potassium persulfate (KPS)	0.57	0.33
Distilled, de-ionized water	16	
Monomer Pre-Emulsion (Semi-batch)		
Sodium dodecyl sulphate (SDS)	4	2
Distilled, de-ionized water	43	
Butyl acrylate	160	95
Methyl methacrylate	9	5
Initiator Solution (Semi-Batch)		
Potassium persulfate (KPS)	1.1	0.67
Distilled, de-ionized water	29	

*phm: parts per hundred parts monomer; includes all synthetic monomer and RSNP

**phw: parts per hundred water

Our experimental design includes several feeding strategies summarized in Table 4.3. Slight modifications to any procedure are noted within the discussion.

Table 4.3 Emulsion polymerization procedures

Procedure	B #1	SB #1	SB #2
#1	KPS	KPS + pre-emulsion	KPS
#2	KPS + Surf.	KPS + pre-emulsion	KPS
#3	KPS + pre-emulsion		
#4	KPS + crosslinker	KPS + pre-emulsion	KPS
#5	KPS	KPS + pre-emulsion + RSNP	KPS

Note: All procedures use an RSNP dispersion as a seed

4.2.3 Gravimetry

Samples were left for 3 days in a fume hood to evaporate water and residual monomer. Measurements were used to calculate conversion and solids content with:

$$wt.\,\%\ conversion = \frac{M_M}{M_P} = \frac{M_L - M_I - M_S - M_B - M_W - M_{DP}}{M_{DP} - M_I - M_S - M_B - M_W} \quad [4.1]$$

$$wt.\,\%\ solids = \frac{M_{GP}}{M_L} \quad [4.2]$$

where: M_L is the mass of the latex, M_M is mass of the monomer,
M_{DP} is the mass of the starch and synthetic dried polymer, M_S is the mass of the starch,
M_I is the mass of the initiator, M_B is the mass of the buffer, and M_W is the mass of the water

4.2.4 Particle Size

Particle size was measured using a Malvern Nano-S Zetasizer dynamic light scattering (DLS) instrument at room temperature, with an angle of 176° and a refractive index (RI) of 1.49.[88] Three measurements were made for each sample and the average was assigned as the mean average size of particles. The reported average particle diameter (D_p) was the intensity-

weighted average particle size. Samples having polydispersity index values (PDI) less than 0.05 were considered to have a narrow particle size distribution. One drop of latex was pipetted into a cuvette with 2 mL of DDI water. The diluted dispersion was further diluted by adding one drop into another cuvette with 1 mL of DDI water. The sample was then analyzed.

4.2.5 pH and Conductivity

An Accumet research AR50 dual channel pH/Ion/Conductivity meter was used to measure the pH (35805-10 probe) and conductivity (13-620-155 probe) of samples. Both probes were calibrated regularly.

4.2.6 Film Formation

Films were prepared using a DIV20 wired roller on corona-treated polyethylene terephthalate (PET) backing. After each film was prepared, it was stored at 50% RH and 25 °C for 24 h. Adhesive performance was determined by conducting peel strength, tack, and shear strength testing in a temperature and humidity controlled room (25 °C and 50% RH). 180^{o} peel strength and loop tack were conducted using an Instron E3000 Instron Universal Tester and Bluehill 2 Materials Testing Software, while an in-house fabricated shear tester and Labview software was used to test shear strength. For all tests, procedures followed Pressure Sensitive Tape Council standards (PSTC, 2004), where 1” wide strips were cut from latex films (6” long for peel and tack, 5” for shear) and adhered onto stainless steel plates using a 2045 g weighted roller (4 passes for all strips), which were then mounted to the equipment. To form films for testing, latexes were applied to a 50 µm PET backing with a #50 Meyer rod (0.05 inch diameter wire wound around a 0.5 inch bar). Films were immediately placed in the control room and allowed to dry for a pre-determined amount of time. Tack samples were lowered at a rate of 1 mm/s until a 1” x 1” area of contact with the stainless steel substrate was achieved. Samples for both tack and peel measurements were removed from the substrate at a rate of 300 mm·min^{-1}.

For shear strength tests, the sample was adhered across the substrate to cover an area of 0.5” x 0.5”, and a 0.5 kg weight was attached to the loop to apply shear force.

4.2.7 Particle Morphology

Transmission electron microscopy was used to determine the morphology of the latex particles to confirm evidence of a core-shell structure and the location of the polymer with respect to the RSNP. It was performed on a Hitachi H-7000 transmission electron microscope at an operating voltage of 75 kV. Polymer latexes were diluted with DDIW and a drop of the resulting solution was placed onto a Formvar coated, 300-mesh copper grid where it was left to air dry. Dried samples were stained over a freshly prepared solution of RuO4 for 15 min prior to analysis.

4.2.9 Gel Content / Barrier Properties

The swelling index of films in water and toluene were conducted by first wrapping each sample in a hydrophilic (water barrier) or hydrophobic (gel content) membranes, weighing each sample, and then submerging them in 20 mL glass vials containing 10 mL of water or THF. Vials were sealed and left in a wrist shaker for 24 h at room temperature. Swollen samples were dried at 40 °C for 24-48 h. Dried samples were cooled and weighed. The gel content and water barrier property were calculated as the weight of the dried sample divided by the weight of the original sample.

4.2.10 Viscosity

A Haake Viscotester D viscometer from Thermo Scientific was used at 25°C and 100 RPM with spindle #4 to calculate the viscosity of liquids. 100 mL of the sample liquid was charged to a 150 mL beaker with a 57 mm diameter to be analyzed. Unless otherwise noted, samples were measured 24 h after reaction was competed.

4.2.11 Aqueous Phase Analysis

Latex was diluted to 10 wt.% solids and centrifuged at 6000 RPM for 3 h. The aqueous phase was pipetted to a vial and left to dry at room temperature. The solid precipitate (aka pellet) was left to dry in the centrifuge tube at room temperature. Gravimetric calculations were conducted and samples were prepared for NMR analysis. Incorporation was defined as the amount of starch that remained within the synthetic polymer matrix in the solid pellet.

4.2.12 Latex Composition by H-NMR Spectroscopy

Film samples were dissolved in D_2O and added to a glass NMR tube for ^{1}H-NMR analysis with a Bruker AVANCE II 400 (400 MHz) spectrometer (5mm autotuning broadband probe with Z gradient, 32 scans per readout, 25 °C).

4.3 Results and Discussion

The objective in this work was to prepare latex formulations containing a significant amount of RSNPs. A commercially significant target loading of RSNPs would be 40 wt.% based on total monomer. Ideally, the majority of the RSNPs would be incorporated into the polymer particles, but a minimum incorporation of 25 wt.% should be met. In addition, percent solids content [(polymer + RSNP)/total latex mass)] was targeted to 40 wt.%, although exceeding 50 wt.% would present a commercially desired level. To that end, a number of variables and reaction conditions were manipulated to confirm their effect on these goals.

4.3.1 Surfactant Type and Concentration

The number and size of particles in an emulsion polymerization are functions of the type and concentration of surfactant used. The number of particles affects the propagation rate of polymer radicals in the system, and thus the conversion profile. The polar head charge and size, as well as the length of the carbon chain affects the size of the micelles and how easily they are formed. SDS and EF-800 are anionic surfactants with small and large polar heads, respectively, while CTAB is a cationic surfactant.

Previously, we showed a favourable interaction between the smaller particle diameter fraction of RSNPs and surfactant, but this was not in the presence of monomer and was at room temperature (Chapter 3). In this context, favourable interaction can be defined as the hydrophobic tails of the surfactant being oriented towards the RSNPs. In an emulsion polymerization, the surfactant could form a hydrophobic layer where monomer could polymerize and form a shell. In this case, the RSNPs would act as a seed and form latex particle cores with a polymer shell. Therefore, the concentration of RSNPs would be the dominant factor in latex particle growth. Additionally, if the monomer is reacting with the RSNPs, the reaction rate should be slower due to the lower reactivity of the PSBM functional groups and the rate of reaction for acrylate grafting from starch.[44]

Polymerizations using varying surfactant types and concentrations were carried out (Table 4.4). Stable latex with viscosity <300 cp was produced with no surfactant (S3M-5), confirming previous conclusions (Chapter 3) that the RSNPs have stabilization properties and/or that the PSBM and/or low molecular weight starch hydrolyzes from the RSNP and acts as a free surfactant to stabilize the synthetic polymer particles.[89–92] Instantaneous conversion was lowest when no surfactant was used (S3M-5), and increased as surfactant concentration increased (S3M-1 and S6M-2 vs. S6M-1), as expected for a conventional emulsion polymerization (Figure 4.1). It is clear that conversion is lower when the RSNPs are present in the polymerization (A-1 vs. S3M-1, S3M-3 and S6M-1, S6M-2), either because the starch acts as a radical scavenger, that grafting is occurring, or both. Particle size was highest when no surfactant was used (S3M-5) and decreased with increasing surfactant concentration (S3M-1 and S6M-2 vs. S6M-1), again as expected for a conventional emulsion polymerization (Figure 4.1). This suggests that heterogeneous nucleation was taking place. When both surfactant and RSNPs were used, the

particle size was much higher than with no RSNPs, indicating a degree of incorporation of starch with acrylic polymer or a synergistic stabilizing effect of RSNP-surfactant resulting in larger latex particles. When SDS was used in place of EF-800, the particle size decreased and the conversion increased, as expected for a surfactant molecule with higher chain length and a smaller polar head. Film formation and adhesion testing results showed that the effects of surfactant type and concentration was as expected.

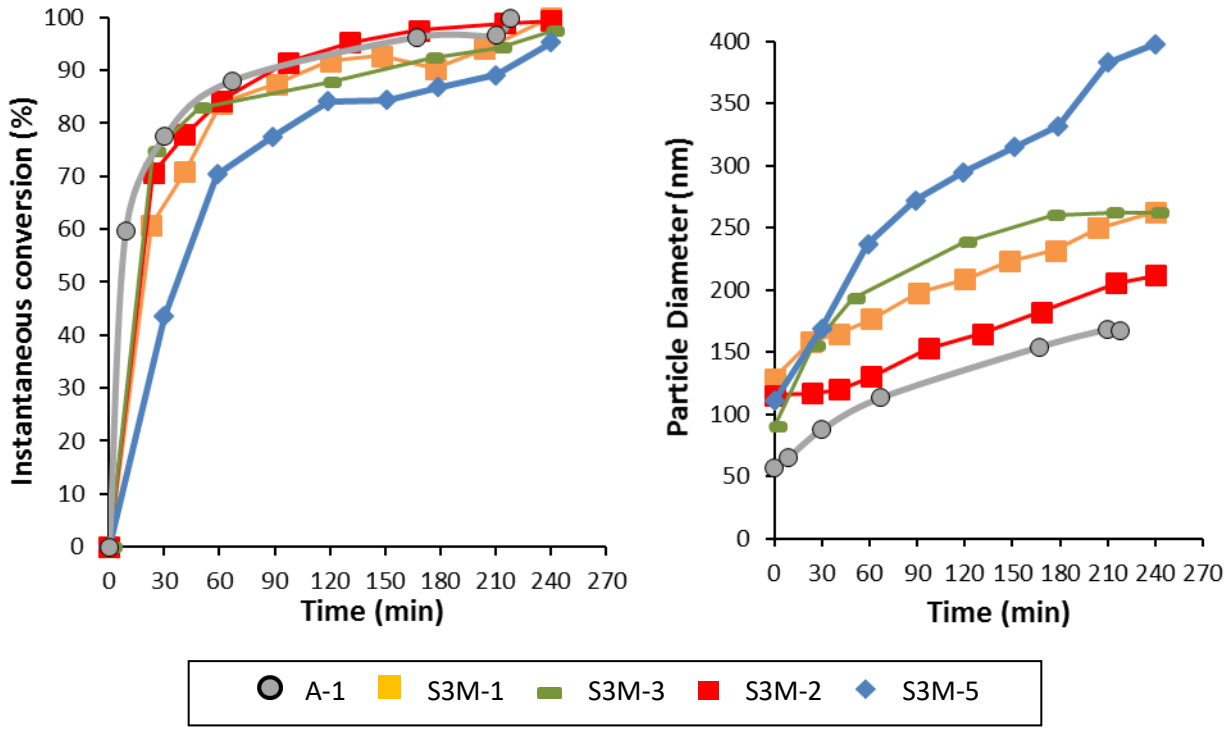
Table 4.4 Polymerizations with varying surfactant type and concentration

Run #	Surfactant Type	Surfactant Concentration	RSNP Loading	Stability and Film Formation
A-1	EF-800	2.0	0	Stable/poor
S3M-5	/	0	5	Stable/poor
S3M-1	EF-800	2.0	15	Stable/good
S3M-2	EF-800	2.7*	15	Stable/good
S3M-3	EF-800	2.0	5	Stable/poor
S3M-6	SDS	2.0	5	Stable/good
S3M-7	SDS	2.0	15	Stable/good
S3M-24	SDS/CTAB** 1:3	4.8	15	Unstable
S3M-25	SDS/CTAB** 1:1	2.4	15	Unstable
S6M-1	EF-800	2.0	15	Unstable
S6M-2	EF-800	1.0	15	Unstable

* 2.0 in pre-emulsion and 0.7% in RSNP seed, procedure #2
** CTAB in RSNP seed, procedure #2
*** Reaction conditions: BA/MMA (95/5 wt.%), 1 wt.% KPS initiator, buffered

When excess surfactant was used in the RSNP seed stage to attempt coverage of the RSNP particles (S3M-2), conversion increased and particle size decreased, indicating conventional emulsion polymerization behaviour. Compared to an identical run with no surfactant in the seed (S3M-1), particle size was lower and conversion was higher during the nucleation stage. This suggests that both the higher concentration of surfactant and the supportive behavior of the RSNPs through hydrogen bonding, induced earlier micellar formation. Thus, we can conclude that in the presence of monomer (i.e., during the feed stage), surfactant was not surrounding the RSNPs to a high enough degree to promote a core-shell particle morphology.

TEM micrographs of latex S3M-4 (Figure 4.2) seem to show RSNPs stabilizing the synthetic particles throughout the polymerization culminating with what resembled a core-shell morphology at 100% conversion. However, it is possible that as a result of sample preparation, the RSNPs dried and settled on the particles rather than being located in the core of the particle.



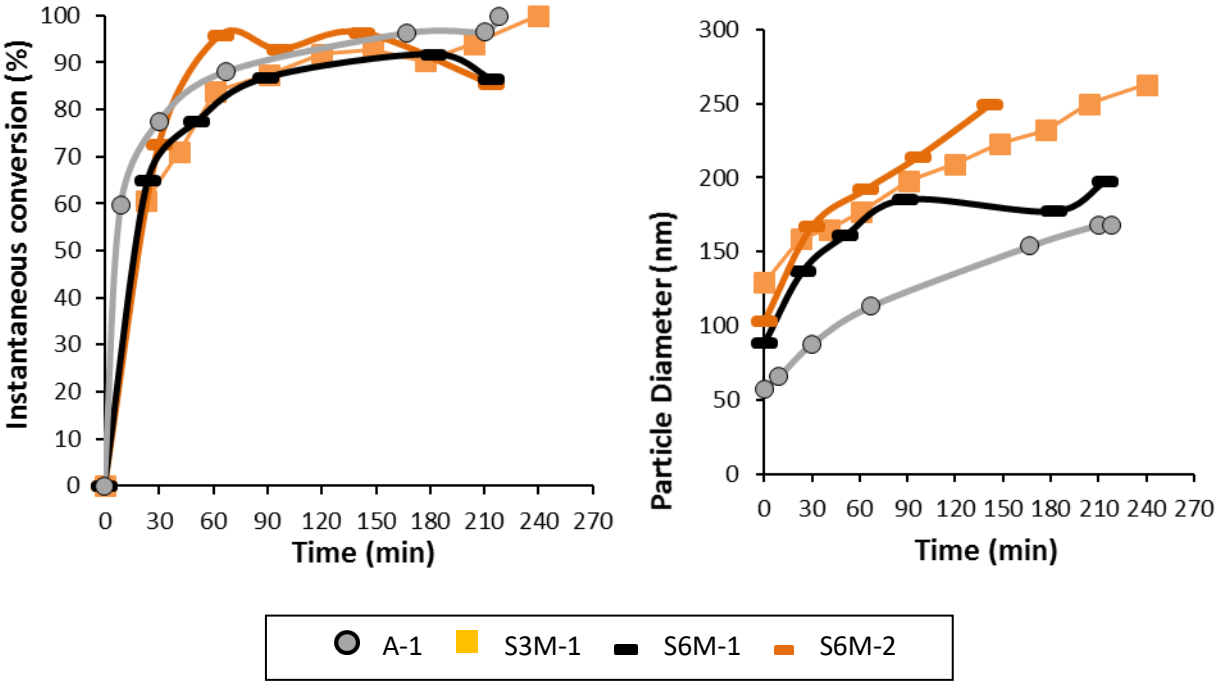
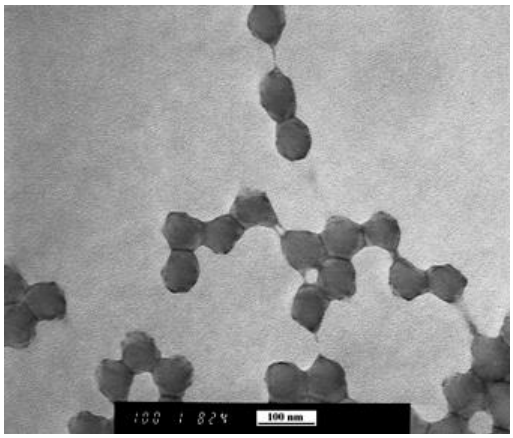
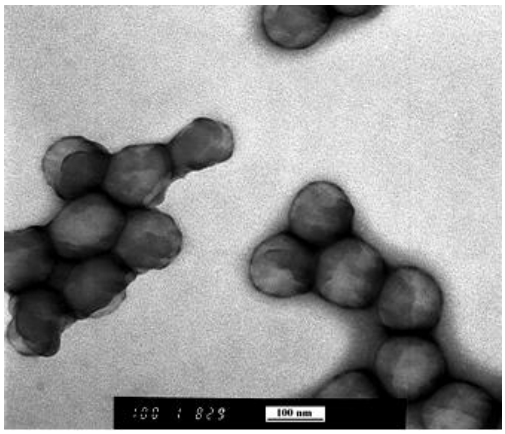


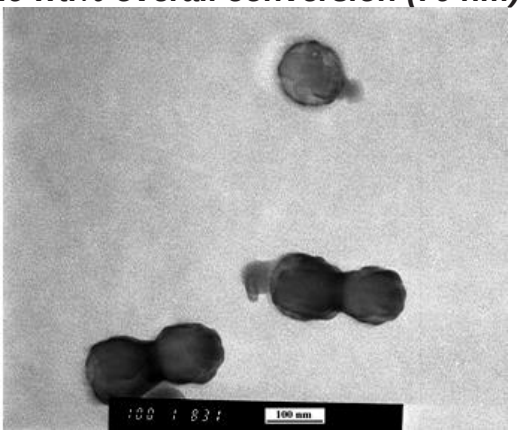
Figure 4.1 Instantaneous conversion and particle diameter of polymerizations



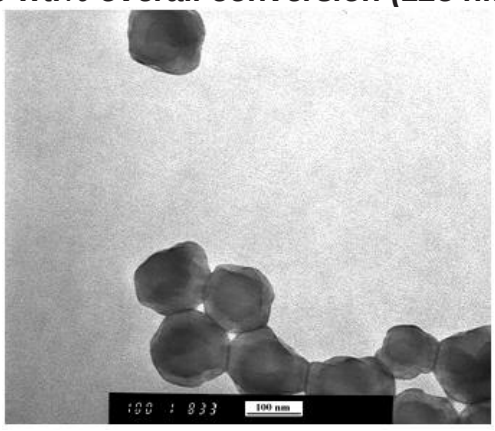
16 wt.% overall conversion (70 nm)



50 wt.% overall conversion (125 nm)



80 wt.% overall conversion (130 nm)



100 wt.% overall conversion (140 nm)

Figure 4.2 TEM micrographs of latex S3M-4. Lighter regions represent synthetic polymer whereas darker regions are RSNPs

Runs were carried out with CTAB cationic surfactant (S3M-24, S3M-25) in the RSNP seed followed by SDS in the pre-emulsion feed. This strategy aimed at forming a hydrophobic layer around the RSNP with the cationic polar head of the CTAB attracted to the electronegative polar head of the PSBM groups on the RSNPs with their tails pointed outwards. The SDS would then be attracted to the hydrophobic tail of the CTAB creating a hydrophobic layer where monomer could polymerize. These runs failed due to instability, suggesting that the PSBM heads were not sufficiently electronegative, that the PSBM molecules were for one reason or another not on the surface of the RSNPS, or that the PSBM concentration was not sufficient.

4.3.2 Initiator Concentration

An increase in initial initiator concentration in the RSNP seed stage, as well as the amount of time the KPS and RSNPs were allowed to mix (15 vs. 2 min.), resulted in a viscosity reduction of the final latex when using S-3-M RSNPs as a seed and only BA as the monomer (S3M-26, S3M-27). S3M-26 failed at 40 wt.% due to incompatibility between the monomer and the RSNP, while S3M-27 maintained stable until the run was terminated at 60 wt.% conversion. As noted previously (Chapter 3), KPS has a degradative effect on starch. Thus, the decrease in viscosity could be due to a reduction in molecular weight of water phase starch, or from increased incorporation of starch due to the increased number of hydroxyl radicals in the seed.[49]

4.3.3 Monomer Composition

Different monomer compositions of ranging hydrophobicity and reactivity were tested (Table 4.5). Polymerizations with a BA composition above 90 wt.% and hydrophilic monomers as additives (S3M-1, S3M-23, and S3M-11) produced low viscosity latex with good film

formation. The addition of AA to the reaction formulations reduced the particle diameter due to enhanced stabilizing effects. When MMA was used at a higher concentration, the viscosity increased while the quality of film formation decreased. Batch polymerizations with BA and styrene did not reach 100% conversion and resulted in slightly higher viscosities than MMA and 2-EHA batch reactions, both of which reached 100% conversion. The monomer hydrophilicity and reactivity worked in tandem to encourage the incorporation of RSNPs into the latex particles. The hydrophilicity of the monomers tended to promote association with the RSNPs and a lower monomer reactivity allowed sufficient time for monomers to react with the RSNPs. Recall that the RSNPs exhibit surfactant-like properties. A hydrophobic monomer would tend to graft to the RSNPs covering the latex particle surface while a hydrophilic monomer would lead to more grafting reactions with the RSNPs in the water phase. Thus, the presence of significant amounts of grafted materials in the water phase resulted in higher latex viscosity.

Table 4.5 Polymerizations with varying monomer composition

Run #	Surfactant Type	Surfactant Concentration (wt.%)	Monomer Composition (wt./wt.)	Viscosity (cP)	Stability and Film Formation
S3M-26	EF-800	2.0	BA	150 @ 60% conv. Unstable @ 40% conv.	Catastrophic Coagulation
S3M-27	EF-800	2.0	BA	150 @ 60% conv.	/
S3M-4	EF-800	2.3	BA/MMA 30/70	150	Stable/brittle
S3M-1	EF-800	2.0	BA/MMA 95/5	100	Stable/good
S3M-23	SDS	2.0	BA/MMA 95/5	100	Stable/good
S3M-8	SDS	2.0	2-EHA/MMA 95/5	200	Stable/poor
S3M-11	EF-800	2.0	BA/MMA/AA 93/5/2	90	Stable/good
S3M-19*	EF-800	1.0	BA	25	Stable
S3M-20*	EF-800	1.0	MMA	15	Stable
S3M-21*	EF-800	1.0	Styrene	20	Stable
S3M-22*	EF-800	1.0	2-EHA	18	Stable

* Procedure #4 at 15-20 wt.% solids and 55-60 wt.% loading

Aqueous phase analysis shows that styrene and MMA polymerizations had the greatest amount of RSNP incorporation into the latex particles (5-20 wt.%) compared to 2-EHA and BA (0-5 wt.%). Evidently, this reveals that the greatest fraction of the RSNPs resided in the water phase. These observations can be explained by higher particle surface grafting of the styrene compared to 2-EHA and BA due to styrene's lower reactivity, and the greater water-phase grafting of MMA with the RSNPs in the water phase due to MMA's hydrophilicity. To improve RSNP incorporation, it would appear that the RSNPs must associate sufficiently with the monomer, and at the same time the monomers must react slow enough to incorporate the RSNPs.

4.3.3 RSNP Type and Loading

When used as a seed, the S-3 group of RSNP grades provided the only stable latex formulations (some additional grades resulted in stable latexes when the RSNPs were not used as seeds). All of the S-3 group of RSNP grades included PSBM combined with the RSNPs at the manufacturing stage. The addition of 3 wt.% pure PSBM to the S-0-hmw seed (to mimic the same composition of S-3 group RSNPs) was also unstable. RSNPs at different PSBM concentrations (i.e., S-1-M at 1 wt.% and S-6-M at 6 wt.% PSBM) also coagulated (S1M-1, S6M-1). During the manufacturing process, the smaller amount of PSBM in S-1-M did not reduce the starches molecular weight as much as grades with 3 and 6 wt.% PSBM concentrations. The large amount of PSBM in S-6-M most likely reduced the molecular weight of the starch. However, since PSBM may not remain bonded to the RSNPs (Chapter 3), a significant amount may be added to the aqueous phase of the reaction mixture, inhibiting the polymerization rate and potentially causing secondary nucleation. The PSBM is essential for lowering the molecular weight of the RSNPs in the manufacturing process. S-0-3APG, despite including alkyl polyglycoside (APG) stabilizer as a bonded functional molecule, suffered catastrophic

coagulation due to the excessively high molecular weight of the RSNPs and the additional APG surfactant added to the reaction mixture (S03APG-1).

The hydrophobicity of the PSBM affected the particle size and viscosity of the final latex. The higher the hydrophobicity of PSBM, the greater its stabilizing strength, which resulted in smaller particle diameter and lower viscosity. The use of more hydrophilic PSBM could have increased viscosity by limiting grafting to the surface of the latex particles. The surface bonded RSNPs, instead of acting as steric stabilizers, could have interacted with other surface bonded RSNPs through hydrogen bonding, increasing viscosity.

It is likely that the effect the RSNPs have on the particle diameter is restricted to its cooperative effect of inducing surfactant micelle formation. For polymerizations using either EF-800 or SDS, the particle diameter decreases slightly with increase in RSNP loading (S3M-3, S3M-1, S3M-12 and S3M-6, S3M-7, S3M-13, S3M-14, S3M-15).

Table 4.6 Polymerizations with varying RSNP type

Polymerization	RSNP Type	Viscosity (cp)	Stability and Film Formation
0-1	S-0-HMW	/	Coagulation: Type 1*
S-0-hmw + polymerizable sugar based monomer	S-0-HMW + Polymerizable sugar based monomer	/	Coagulation: Type 1*
S1M-1	S-1-M	/	Coagulation: Type 1*
S3M-11	S-3-M	90	Stable/good
S6M-1	S-6-M	/	Coagulation: Type 1*
S03APG-1	S-0-3APG	/	Coagulation: Type 2**
S3H-1	S-3-H	100†	Stable/good
S3L-1	S-3-L	400†	Stable/poor

* Unstable latex with large coagulants
** Reaction mixture resembles cottage cheese with few non-spherical coagulants
*** Unstable latex similar to a paste with several large coagulants
**** Composition of all runs: BA/MMA/AA (93/5/2 wt.%)
† Measured immediately after latex is removed from reactor

Compared to the change in particle diameter with the increase in surfactant concentration in previous experiments (S3M-5, S3M-3, S3M-2 and S6M-2, S6M-1), it is clear that a change in surfactant concentration has a much stronger effect on particle size. If a great deal of incorporation was regularly occurring, one would expect a substantial change in particle diameter when increasing loading from 5 to 50 wt.%.

When the RSNPs were used as a seed it was not possible to reach loadings of 40 wt.% or higher with procedures #1-5. Procedure #6, where the RSNPs were fed semi-batch, allowed the latex to be loaded up to 50 wt.% (S3M-18). Although the viscosity of the latex increased with loading regardless of the way in which the RSNPs were fed, S3M-14 had the same viscosity as S3M-11 despite having twice the loading. This could be due to the ability of the semi-batch fed initiator to degrade the RSNPs that are prone to remaining in the water phase. The particle diameter of runs S3M-16 and S3M-18 were the same despite S3M-18 having slightly lower solids content, consistent with greater incorporation of RSNPs in this run. Water phase analysis however shows 0-10 wt.% incorporation for both S3M-18 and S3M-16. When the S-6-M RSNPs were added semi-batch (S6M-3), high loadings of 40 wt.% were achieved with 20 wt.% incorporation. Not only this, but the viscosity of the latex after 24 h at room temperature was lower than the identical run with S-3-M, which would be consistent with the suspected lower molecular weight of this grade due to the increased PSBM concentration during processing. This would also confirm the hypothesis that the reason earlier runs (S6M-1 and S6M-2) were unsuccessful was the increased PSBM concentration in the water phase.

Table 4.7 Polymerizations at varying RSNP loadings

Run #	Load.	Proc.	Surf. Type	Surf. Conc.	Ini. Conc.	PD	Visc. (cp)	Stability and Film Formation
S3M-3	5	1	EF-800	2.0	0.9	262	30	Stable/poor
S3M-1	15	1	EF-800	2.0	1.0	263	120	Stable/poor
S3M-5	5	1	/	0	1.0	398	20	Stable/poor
S3M-6	5	1	SDS	2.0	0.8	235	50	Stable/good
S3M-7	15	1	SDS	2.0	1.0	227	45	Stable/good
S3M-9	15	4	EF-800	5.6	0.5	146	50	Stable/poor
S3M-10	18	4	EF-800	6.3	0.6	133	/	Coagulation:

								Type 3***
S3M-11	15	1	EF-800	2.0	1.0	217	90	Stable/good
S3M-12	20	1	EF-800	2.0	1.0	210	60	Stable/good
S3M-13	27	1	SDS	2.0	1.2	202	80	Stable/good
S3M-14	30	1	SDS	2.4	1.2	180	90	Stable/good
S3M-15	40	1	SDS	2.6	1.3	163	/	Coagulation: Type 1*
S3M-16	40	6	EF-800	2.3	1.3	192	100† 500	Stable/poor
S3M-17	20	6	EF-800	3.0	1.3	/	/	Coagulation: Type 2**
S3M-18	50	6	EF-800	2.0	1.4	194	100† 800	Stable/good
S6M-3	40	6	EF-800	2	1.3	206	100† 180	Stable/good

* Unstable latex with large coagulants
** Reaction mixture resembles cottage cheese with few non-spherical coagulants
*** Unstable latex similar to a paste with several large coagulants
† Measured immediately after latex is removed from reactor
Note: Composition of runs up to S3M-11 were BA/MMA 95/5 while runs 3-16 and above were BA/MMA/AA 93/5/2

Barrier property tests show that as RSNP loading increases, the films resistance to water decreases regardless of the method with which the RSNPs were added to the latex, as the resistance to THF increased. The mechanism for increased resistance to THF is the homogeneous distribution of smaller sized starch throughout the polymer matrix and not necessarily increased grafting of synthetic monomer to the RSNPs. Resistance to THF increased with RSNP loading (15 to 30 wt.%) for films where the RSNPs were added to the latex as a seed. For films from latex where the RSNPs were added semi-batch the resistance to THF did not change from 30 to 50 wt.% loading. Films from latex using degraded, smaller sized, starch resulted in higher resistance to THF.

Films with higher RSNP content had better wetting properties than their synthetic equivalents, indicating beneficial characteristics from both the increase in viscosity and the hydrogen bonding interactions between the RSNPs and the PET backing. If grafting occurs during the polymerization, the RSNPs could also act to strengthen the interaction between particles during film formation, improving cohesive strength.

Blends of synthetic latex and a RSNP dispersion mixed at 60 °C at the same composition as polymerization S3M-1 formed opaque and heterogeneous films. This suggests a difference between blending the RSNPs with synthetic particles and including the RSNPs in the polymerization. The higher the temperature of blending and film formation, the more homogeneous and transparent the films became.

Adhesive properties dropped by 80% and 17% for peel and tack strength respectively when increasing RSNP loading from 0 to 15 wt.% RSNP in the polymerization. The reduction in adhesive properties indicates a degree of incorporation too poor to make the RSNP loaded latex useful for pressure sensitive adhesive applications without the use of additives. The shear strength of the films was significantly improved from the base case latex with 0 wt.% RSNPs, with no failure after 4 months. This is consistent with the expected increase in strength of polymer films through entanglements of the crosslinked and hydrogen bonded starch regions with the polymer matrix.[47]

4.3.4 Solids Content

If the RSNPs do not become incorporated into the latex particles and remain in the water phase, the highest solids content that could be reached was 40 wt.% solids. Beyond this limit the viscosity becomes too high to maintain stability. Strategies for increasing solids content (using an acrylic or acrylic-RSNP latex as seed or inducing a secondary particle size population) failed due to persistent water soluble starch. At 40 wt.% solids, the RSNP loading can be increased to 50 wt.%, suggesting that the amount of starch in the aqueous phase has a smaller negative impact on stability than increasing the solids content.

4.3.5 Proof of Incorporation

Aqueous phase analysis was the primary method used to confirm incorporation of the RSNPs into the polymer particles. The method is similar to that used by Bodiger et al. and less so to other precipitation methods.[46,47,83,93,94] ^{1}H-NMR analysis of the serum (water phase) was

used to determine if there was any acrylic polymer present (Figure 4.3). If acrylic polymer was present, it was either because of the low accuracy of decanting (user error), or that the grafting of starch with the hydrophobic monomer created low MW amphiphilic polymer that was compatibilized with the water phase sufficiently enough to remain there and not precipitate. ^{1}H-NMR analysis of the pellet (precipitate) showed no evidence of starch due to the inability of the solvent to dissolve both the hydrophilic and hydrophobic components of the pellet (Figure 4.4). Since the pellet material was dispersed and not dissolved in the solvent, certain components were shielded from being visible in the ^{1}H-NMR spectrum. ^{1}H-NMR analysis was thus not useful for quantitatively confirming gravimetric results for incorporation. Solid phase FT-IR analysis of the pellet was used to detect the presence of the RSNPs, although no quantitative analysis was possible (Figure 4.5).

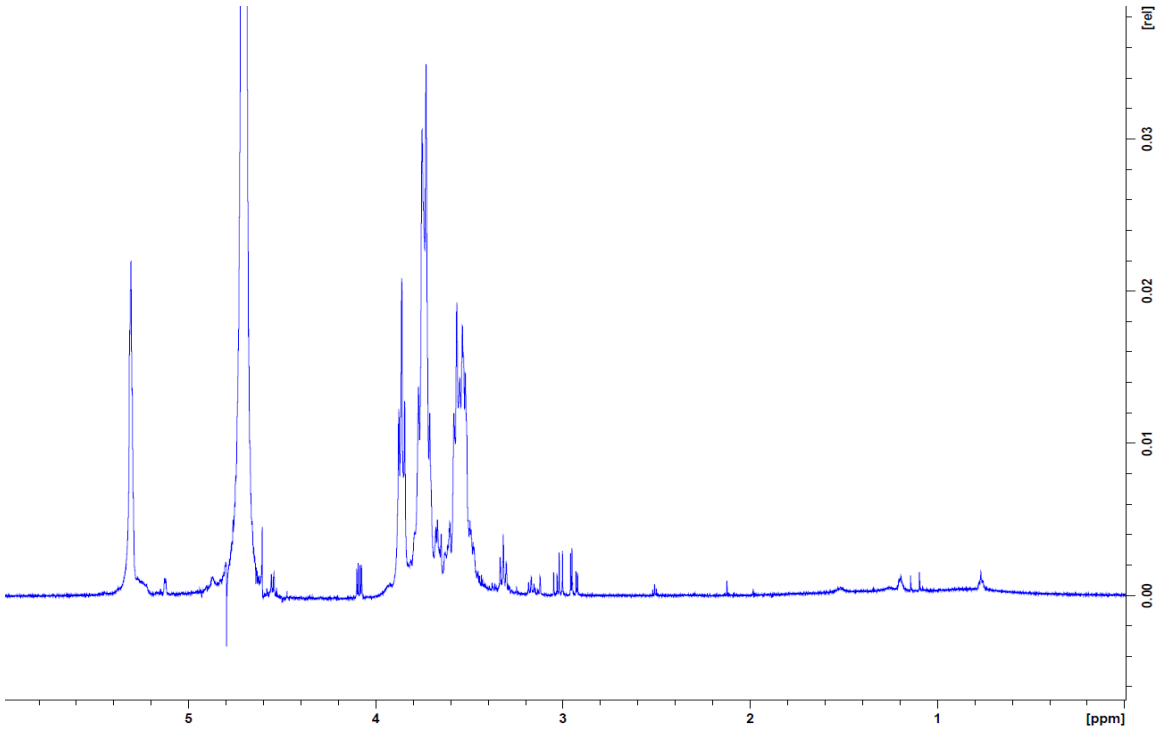


Figure 4.3 H^{1}-NMR of decanted serrum from centrifugation experiment, showing very small amounts of acrylic polymer from 0.5 – 3.0 and large amounts of starch from 3.0 – 4.0

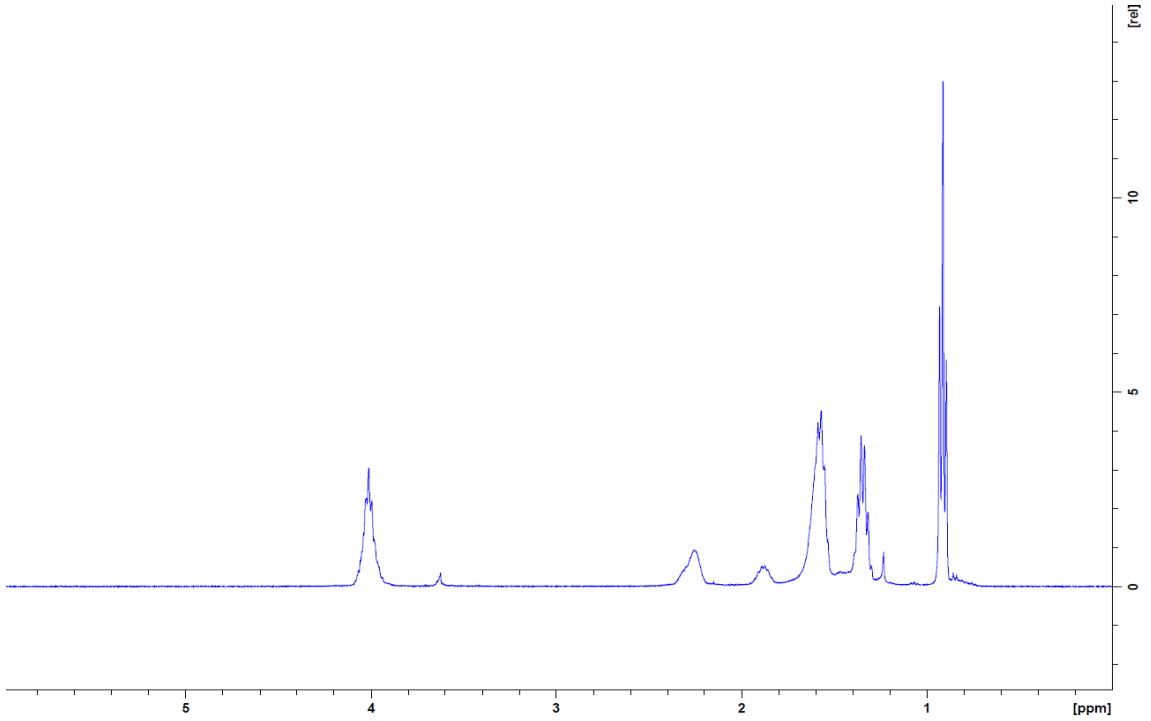


Figure 4.4 H^1-NMR of pellet from centrifugation experiment, showing no detection of starch

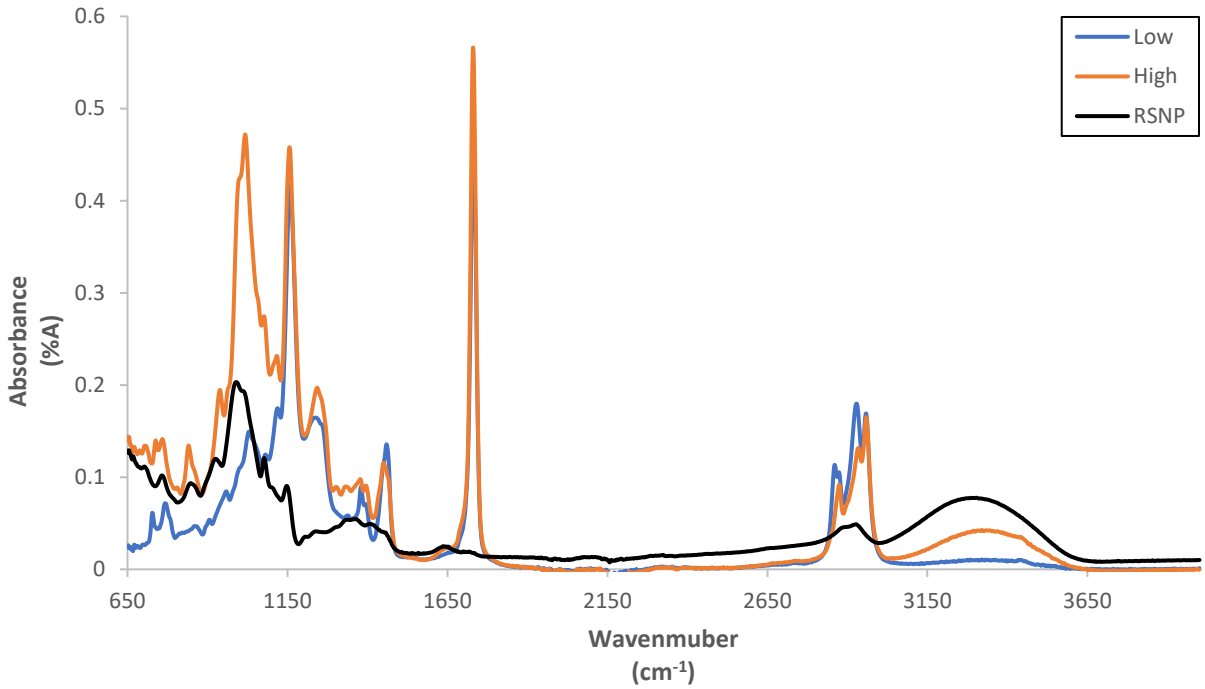


Figure 4.5 Solid FTIR spectrum of a highly and poorly RSNP incorporated latex, compared to the pure RSNP particles. The characteristic fingerprint of the RSNP can be seen at 3000 – 3500 cm^{-1} and at ~1000 cm^{-1}.

Although our values of incorporation are rather modest, grafting of starch in emulsion polymerizations using persulfates has also been shown in the literature, suggesting that grafting is possible.[55,59,60,65,83,95,96]

4.4 Conclusion

Modified RSNPs were shown to act as stabilizers, radical scavengers, and as fillers capable of incorporation within emulsion polymerization latexes. Semi-batch feeding of the RSNPs at high loadings of 40 and 50 wt.% (0-10 wt.% incorporation) were achieved via semi-batch feeding of the S-3-M RSNPs, while 40 wt.% loading (20 wt.% incorporation) was achieved with the S-6-M RSNPs. Batch runs with MMA and styrene at 50-60 wt.% loading and ~20 wt.% solids resulted in 20 and 10 wt.% incorporation.

There was no evidence of core-shell morphology in the polymerizations. The absence of this morphology was due in part to the dominance of heterogeneous particle nucleation (as opposed to dominance of the seeded particles), the inability of the surfactant to surround the RSNPs, and the cooperative stabilization enabled by the RSNPs that encouraged surfactant micelle formation. It is thought that hydrolysis of the PSBM functional groups from the RSNPs led to the presence of free PSBM in the water phase, which promoted heterogeneous nucleation and inhibited the polymerization at high PSBM concentrations.

The PSBM must be vinyl-functionalized and combined with the RSNPs during the manufacturing process lest instability occur during the polymerization. Persulfate initiators can be useful for reducing the molecular weight of the RSNPs during the polymerization, and may result in starch-starch grafting. In order to encourage RSNP incorporation and allow for higher loadings and solids, a monomer composition of the correct hydrophobicity must be chosen. This monomer must also favour polymerization with RSNPs rather than homopolymerization.

Films from latexes containing RSNPs presented good film formation (when anionic surfactant was employed in the polymerization) but poor adhesive properties. The RSNPs

added resistance to organic solvents such as THF but also made the film susceptible to swelling in aqueous environments. The smaller the size of the RSNPs, the greater the THF resistance.

Polymerizations with the newly modified RSNPs show promise and were included at high loadings (50 wt.%) and solids (40 wt.%) content. This was done without the need to reduce the molecular weight of the starch, a common strategy when high loadings of starch are being desired (Chapter 2). Increasing RSNP incorporation into the polymer particles, at these high loadings, up to commercially relevant levels remains an important target.

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Chapter 5: Dent Sourced Regenerated Starch Nanoparticles in Emulsion Polymerizations

Dent Sourced Regenerated Starch Nanoparticles in Emulsion Polymerizations

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ABSTRACT

Dent corn, a low cost source of starch, was incorporated into an emulsion polymer latex. To minimize latex viscosity and prevent coagulation a seeded, semi-batch, monomer-starved approach was used. To prevent the accumulation of water soluble starch in the aqueous phase, a hydrophobic tie-layer consisting of butyl acrylate monomer was used. In addition, an elevated initiator concentration was used in the seed stage to reduce the molecular weight of the soluble starch and promote grafting. The successful procedure yielded a latex with a viscosity of 100 cp but required a longer reaction time compared to similar procedures using a waxy sourced starch.

5.1 Introduction

A large area of green chemistry research is focussed on sustainable polymers, strategies for the production of bio-sourced monomers, and the use of bio-based fillers in nanocomposites.[1,2] Starch is among the most common industrially used, uniquely bio-based, polymers due to its abundance, low cost, and potential for sustainable production.[3–8] Starch is a hydrophilic naturally occurring polymer with the chemical formula $(C_6H_{10}O_5)_n$ containing linear amylose and branched amylopectin polysaccharides.[6] The amount of amylose is highly dependent on the source of the starch and how it is processed. Amylose amounts range from 70 wt.% in amylomaize, to 23-27 wt.% in dent maize, and 1 wt.% in waxy maize.[9] Once physically and chemically modified to form micro- or nano-particles with various functional moieties of ranging degrees of hydrophobicity, the starch can be used in polymer formulations as an additive or as a replacement for the synthetic polymer.[10,6,11–19,3,20,21]

Different types of starch nanoparticles (SNPs) can be produced by a variety of long standing methods that yield either starch nanocrystals (SNCs), regenerated starch nanoparticles (RSNPs), or starch nanocolloids.[10,12] Through any of these processes, the native starch reduces in size drastically from 10-15 µm to 10-500 nm. RSNPs are of greater importance to products where a spherical particle of low density and weaker internal hydrogen bonding are required. These RSNPs can be produced in large quantities at an industrial scale with a neutral carbon footprint more easily than SNCs.[5]

There are several sources for starch such as maize (i.e., corn), wheat, or potatoes. The source of the starch has an influence on the properties of the resulting nanoparticles due to the degree of branching (i.e., ratio of amylopectin:amylose), chemical composition (e.g., oil, protein, and other contaminants), and morphology. Starch sourced from dent corn is commercially attractive due to its lower cost compared to amylomaize and waxy maize.[22,23] Typically, dent corn has lower oil and protein contents and larger amounts of amylose compared to waxy corn. The higher amylose content tends to increase the viscosity of dent starch solutions.[22,24–27] Granules of dent starch tend to be more spherical and are more susceptible to retrogradation than waxy starch.[26,28] Dent starch tends to retain fatty acid which

interferes with papermaking equipment, making it a poorer choice for paper coating compared to waxy starch and other latexes.[22] If used as a nanoparticle in a nanocomposite (e.g., in emulsion polymerization), the challenges to its use in paper coatings could be masked, making dent a cheap alternative to waxy maize. The largest issue in using dent sourced starch in emulsion polymerization would be the high amylose content, which could increase the latex viscosity or disrupt the polymerization kinetics.

Here, vinyl-functionalized dent-based RSNPs were used as a comonomer in copolymerizations with a broad range of vinyl monomers and persulfates for initiation. Previously, waxy-based RSNPs were incorporated into polymer latex up to 10 wt.% (50 wt.% loading) and 20 wt.% (40 wt.% loading), all at 40 wt.% solids with viscosities < 400 cp. A new grade of RSNPs with identical physical and chemical modification was produced from dent maize starch as opposed to the previously used waxy maize as a way to reduce costs. The present work investigates the feasibility of using dent starch to produce the new RSNPs.

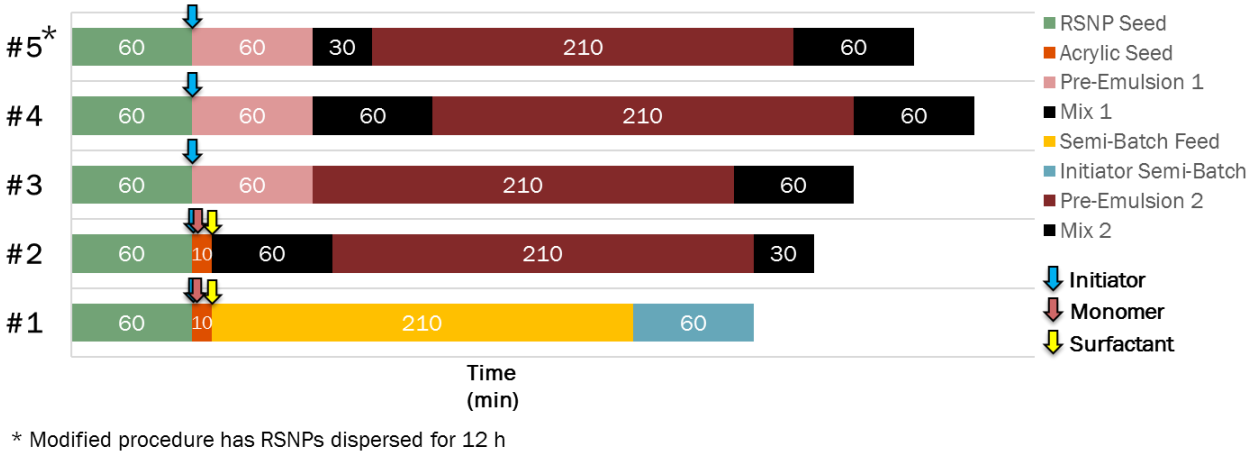
5.2 Experimental Section

5.2.1 Materials

All chemicals except for Aerosol EF-800 surfactant (50 wt.% aqueous solution) (Cytec) were obtained from Sigma Aldrich. Experimental grade RSNPs were provided by EcoSynthetix and used as received. These experimental grade RSNPs contain different levels and different types of a proprietary polymerizable sugar-based monomer produced by EcoSynthetix. All monomers, surfactant, initiator, and buffer were prepared using the procedure outlined in Chapter 3. Distilled-deionized (DDI) water was used in all experiments. Nitrogen gas was supplied by Linde Canada.

5.2.2 Polymerization

A 1 L Mettler-Toledo LabMax® jacketed stainless steel reactor was used to carry out polymerizations at 60 °C, 300 RPM, nitrogen gas sparging, and semi-batch feeding of the monomer pre-emulsion and initiator solution. The RSNP dispersion was prepared as in Chapter 3 and initiator solution was charged 2 min before semi-batch feeding began. Alternative procedures are shown in Figure 5.1, where the "acrylic seed" and "pre-emulsion 1" represent tie-layer monomers and "pre-emulsion 2" the primary feed. A tie-layer monomer is here defined as a monomer that is able to compatibilize the starch surface with the primary monomer feed. Procedure #1 represents the standard strategy for emulsion polymerization (Chapter 4). Sampling was conducted as described in Chapter 4.



* Modified procedure has RSNPs dispersed for 12 h

Figure 5.1 Alternative polymerization procedures

5.2.3 Characterization

Gravimetry, particle size (via dynamic light scattering, DLS), pH, conductivity, viscosity, aqueous phase, gel content/barrier property, and film formation measurements were conducted as described previously (Chapter 4).

5.3 Results and Discussion

5.3.1 Removal of Water Soluble Starch

The apparent particle diameter of the experimental dent RSNPs was larger than the average diameter of the waxy sourced particles (260 vs. ~100 nm) as measured by DLS. The final particle size of the successfully polymerized latexes was lower than that of the initial RSNP dispersion (140-240 vs. 260 nm). This could be because, as we noted previously (Chapter 3), the higher the degree of swelling (water content) of the particles the larger the apparent particle diameter. The increased amount of amylose in dent RSNPs compared to the waxy sourced particles could be the cause of the larger water content and therefore the higher particle diameter.

Initial attempts to polymerize with dent RSNPs failed due to a drastic increase in viscosity about three-quarters of the way through the polymerization. Due to the stabilizing effect of the starch seed, and the slower reactivity of monomer-starch grafting compared to homopolymerization, a second population of micelles/particles could have been formed during the semi-batch pre-emulsion feed, drastically increasing viscosity. Surfactant concentration was lowered in subsequent runs to prevent secondary heterogeneous nucleation. These latexes were stable until shortly after the completion of the semi-batch pre-emulsion feed, after which they coagulated. It was clear that the initiator concentration and feeding strategy were important factors in the dent RSNP polymerizations.

Initiator

Since the dent RSNPs have a higher amylose content, and that these low molecular weight starches diffuse into the aqueous phase of the reaction mixture, their interaction with the water soluble free radical initiator is important. KPS can both degrade the starch or cause hydroxyl radical formation, which could possibly lead to starch-starch grafting. The high concentration of soluble starch in the continuous phase could provide grafting sites for unreacted monomer especially after the completion of the pre-emulsion feed while the initiator continued to be fed to the reactor. This contributed to a drastic increase in viscosity

caused by the suspected presence of higher molecular weight starch-graft-acrylic polymer in the water phase.

A series of runs were carried out without a semi-batch initiator feed and all the initiator (0.5 to 1.0 wt.%) was added as a batch charge to the RSNP seed. The highest initiator concentration (1.0 wt.%) resulted in the most stable latex although coagulation (due to high viscosity) still occurred at very high conversion; this stability was attributed to the ability of KPS to breakdown the amylose in the seed when acrylic monomer was not present.

Tie-Layer

To more effectively remove the amylose from the water phase, a series of "tie-layer" monomers were fed prior to the standard pre-emulsion feed. Two positive outcomes were desired; that the tie-layer monomer would graft to the water-soluble amylose and increase its size to a critical chain length and coalesce into a sphere to nucleate a new particle, or the grafted amylose would be drawn into an existing latex particle.

Tie-layer monomers were added at the initial charge for the seed preparation stage. Both batch and semi-batch initiator feed strategies were tested, and at the completion of the seed stage, a mixing stage was used and a surfactant solution was added to stabilize the seed particles. Acrylic acid (AA), n-butyl acrylate (BA), and methyl methacrylate (MMA) were used as tie-layer monomers. Polymerizations with pure MMA and AA as tie-layer charges failed due to gel formation and high viscosity as a result of high molecular weight hydrophilic polymer in the water phase. It was concluded that AA and MMA were too hydrophilic. BA was used both as a batch charge and pre-emulsion feed during the seed stage. When used as a batch charge, the polymerization failed near the end of the run during the BA/MMA/AA pre-emulsion feed. When BA was added through a semi-batch pre-emulsion feed in the seed stage, a stable final latex was produced with a viscosity of 250 cp. In order to achieve 100% conversion without coagulation, initiator was charged exclusively as a batch at the seed stage; this was followed by a 30 minute mixing stage and then the BA/MMA/AA pre-emulsion feed. At the completion of the feed stage an additional mixing stage was used.

5.3.2 Procedural Modifications

Several polymerizations (SD3M-1, SD3M-3, SD3M-5, etc.) coagulated and formed a latex that resembled cottage cheese. For all these runs a common characteristic was high monomer concentration throughout the polymerization. The accumulation of monomer in the reaction mixture (Figure 5.2) at various initiator concentrations (0.5 – 1.0 wt.%) and feeding strategies (procedures #1 - #3) was due to the presence of amylose radical scavengers in the water phase. The presence of excess monomer droplets after the completion of the BA/MMA/AA pre-emulsion feed at the end of the reaction increases the chances of initiating these droplets and causing coagulation. This is what could lead to a latex resembling cottage cheese[29]. To reduce the risk of coagulation, mixing stages after both the tie-layer and BA/MMA/AA pre-emulsion feed were employed, as well as all the initiator being used as a batch charge in the seed stage to degrade the soluble starch (run SD3M-6, procedure #5). The optimal procedure called for a 1 h BA pre-emulsion feed (tie layer) with a 30 min mix stage, followed by a 3.5 h pre-emulsion feed of BA/MMA/AA and a 1 h mixing stage (0.85 wt.% initiator, 1 wt.% EF-800). Maximum RSNP loading with this procedure was 25 wt.% and the PD of the final latex was 160 nm. An increase in mixing time and decrease in initiator concentration (procedure #4) was not successful, confirming the necessity of 0.85 wt.% initiator as a batch charge to reduce the molecular weight of the soluble starch (as opposed to longer mixing at 60 °C in the presence of polymerizing particles).

A final adjustment to this procedure was tested where the RSNP dispersion was allowed to mix at 60 °C for 12 h in a beaker before being added to the reactor (run SD3M-4, modified procedure #5). The final latex had a PD of 200 nm and a viscosity of 100 cp. The apparent thermal degradation of the starch must have assisted the stability of the latex by reducing the molecular weight of the water soluble starches, possibly allowing them to be more efficiently incorporated into the polymer particles.

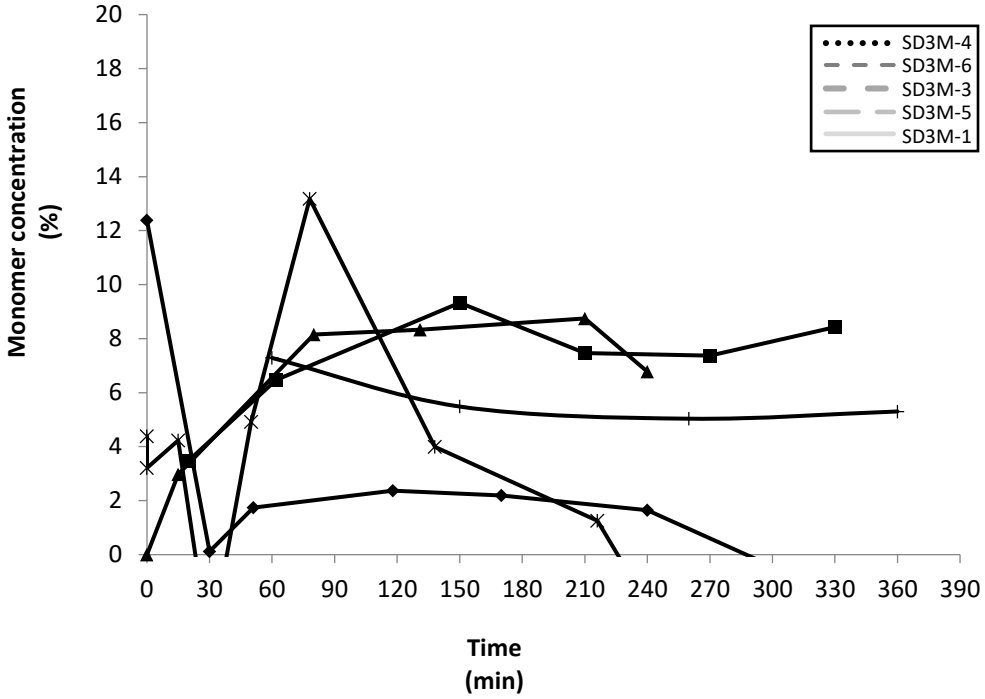


Figure 5.2 Monomer concentration in reaction mixture over the course of the polymerization (lines are not model predictions but are used solely to improve visual representation of the data)

5.3.3 Properties of Final Latex

All latexes had a brownish hue except for the ones produced with the optimal procedure, which suggests the removal of aqueous phase starches in the successful runs. Films from latex using dent sourced starch resulted in higher resistance to THF than those produced with waxy RSNPs, suggesting that the mechanism for increased resistance is the homogeneous distribution of smaller molecular weight starch throughout the polymer matrix and not necessarily increased grafting of synthetic monomer to the RSNPs. Films had no adhesive properties but were transparent similar to films made from waxy RSNP loaded latex.

5.4 Conclusion

Experimental dent sourced RSNPs contain a significant amount of amylose and other water soluble starches that move into the water phase during an emulsion polymerization. To reduce the chances of coagulation and minimize the viscosity of the final latex it is important to ensure monomer starved conditions, that the only initiator feed occurs at the seed stage of the reaction to degrade the soluble starch and prevent later stage coagulation, and that a hydrophobic tie-layer is used to remove the soluble starch from the water phase. Although a successful procedure was devised for creating a latex with a viscosity of 250 cp, it was significantly longer than the procedure using waxy RSNPs (6 h polymerization + 1 h RSNP dispersion). Including the longer heat treatment of the RSNP dispersion before the polymerization reduces the final viscosity to 100 cp but adds several hours to the procedure. Films were transparent but had no adhesive properties. The potential of dent sourced RSNPs for acrylic latex production has been proven, although the procedure is quite lengthy and may cause issues in industrial settings.

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Chapter 6: Polymer Latex Produced Using Anhydride Modified Regenerated Starch Nanoparticles

6.1 Introduction

Starch is a commonly researched polysaccharide that has potential for uses in advanced polymer materials. It can be highly functionalized and modified by physical and chemical means to form nanoparticles of various morphologies. Regenerated starch nanoparticles (RSNPs) have great potential for use in polymerizations given their highly crosslinked (and typically spherical) structure and small (<100 nm) size. Although brittle and lacking polar solvent barrier properties, the ability of the RSNPs to increase polymer film resistance to hydrophobic solvents, increasing shear strength, and reducing the amount of synthetic material needed, has been proven. Using more sustainable emulsion polymerization techniques, latexes with RSNP loadings up to 50 wt.% (10 wt.% incorporated) and 40 wt.% (20 wt.% incorporated) were previously produced using polymerizable sugar based monomer (PSBM) functionalized extruded RSNPs from EcoSynthetix Inc. (Chapter 4).

Due to the limited success of incorporating these RSNPs into the polymer particles, two new methods of functionalizing the extruded RSNPs were devised. After being produced using patented extrusion techniques, the RSNPs were modified with either maleic anhydride (dry process) or methacrylic anhydride (wet process). It was hoped that these particles would have permanently functionalized (hydrolysis resistant) vinyl groups on their surface. If the vinyl groups are indeed attached, using the knowledge of previous work (Chapters 3, 4, and 5), a procedure could be applied to effectively polymerize the acrylic monomer to the RSNPs and increase both loading and (more importantly) incorporation.

Although the abundant hydroxyl groups in starch provide for grafting sites during a polymerization, they become far more reactive if substituted with a vinyl moiety. These modified RSNPs may also have better stabilizing properties and increased compatibilization with the synthetic polymer due to added hydrophobic groups. Many organic acid anhydrides have been used in the past to functionalize starches.[1–3] Succinic anhydride with pyridine at > 100°C in an aqueous environment (alternative procedure using DMSO exists) will produce starch succinate. Octenylsuccinic modification is commonly carried out by esterification of starch with octenylsuccinic anhydride (OSA) in either aqueous, pyridine and acid chlorides, or enzyme-coupled reactions. Short chain fatty acids (acetic, propionic, and butyric anhydride) have been successfully esterified onto starch through various mechanisms at 5-50 wt.% substitution. Several other anhydrides (lauric, propionic, stearic etc.) have been successfully functionalized onto starch above 5 wt.%. Anhydride functional polymers can assist in compatibilizing starch and synthetic polymers to form blends. Maleic anhydride functional polymers have been particularly effective.[4–6] Maleic anhydride has been reacted with starch in alkaline aqueous slurries, in organic media, and in solvent-free reactions. Although these methods do not provide as high of a DS as microwave techniques, they are sufficient for this project. Because of their effective reactivity with starch, anhydrides are an obvious choice for functionalization that will resist hydrolysis in buffered aqueous media (as in the seed stage of an emulsion polymerization).

In this work, methacrylic and maleic anhydride modified RSNPs were tested as co-monomers in emulsion polymerizations. Methacrylic anhydride is able to react with itself and so polymerizations with this grade provided insight into alternative vinyl groups that do not have the unique properties of low homopolymerization rate of maleic anhydride. Maleic anhydride not only has a vinyl group that will add the required reactivity to the RSNPs, but it has the added benefit of having an extremely low reactivity with itself, ensuring no homopolymerization of the modified starch takes place.

6.2 Experimental

6.2.1 Materials

All chemicals except for Aerosol EF-800 surfactant (50 wt.% aqueous solution) (Cytec) were obtained from Sigma Aldrich. Methacrylic anhydride modified RSNPs were prepared by a wet method similar to Jiang et al. and Ačkar et al. (0.01, 0.015, and 0.1 DS).[1,7] Maleic anhydride (MAnh) modified RSNPs were prepared by a dry method similar to Vaidya et al. (0.01, 0.05, and 0.1 DS).[6] Experimental grade RSNPs were provided by EcoSynthetix and used as received. All monomers except hydroxypropyl acrylate (HPA), surfactant, initiator, and buffer were prepared using the procedure outlined in Chapter 4. HPA was used as received. Distilled-deionized (DDI) water was used in all experiments. Nitrogen gas was supplied by Linde Canada.

6.2.2 Polymerization

A 1 L Mettler-Toledo LabMax® jacketed stainless steel reactor (Chapter 4) was used to carry out polymerizations at 60 °C, 300 RPM, nitrogen gas sparging, and semi-batch feeding of the monomer pre-emulsion and initiator solution. The RSNP dispersion was prepared as in Chapter 4 and initiator solution was charged 2 min before semi-batch feeding began. Alterative feeding strategies were used as in (Chapters 4 and 5). All polymerizations were run at 15 wt.% loading of RSNPs and 40 wt.% solids content.

6.62.3 Characterization

Gravimetry, particle size, pH, conductivity, viscosity, aqueous phase, gel content/barrier property, and film formation measurements were conducted as described in a previous work (Chapter 4).

6.3 Results and Discussion

6.3.1 Methacrylic Anhydride Modified RSNPs

Dispersions with RSNP seed (15-30 wt.%) and initiator (3 wt.%) formed gels after 15-45 min under 50°C magnetic stirring. Batch and semi-batch pre-emulsion and initiator feeds, as well as a range of monomers (2-EHA, styrene, BA, MMA, HPA, and AA) were tested at 15 wt.% loading and 40 wt.% solids, with all polymerizations resulting in gel formation ~30 min into the 4 h experiments. Due to the known stabilizing properties of the RSNPs and their tendency to remain in the aqueous phase, the fact that the vinyl groups are capable to readily react with each other resulted in gel formation, regardless of the probable high incorporation of RSNPs into the polymer matrix due to the covalently and permanently bonded methacrylic anhydride groups.

6.3.2 Maleic Anhydride Modified RSNPs

Several monomer compositions and feeding strategies were employed for polymerizations with maleic anhydride modified RSNPs (Table 5.1 and 5.2). AA as a tie layer and shell monomer created a hydrogel as expected, with no grit and the RSNPs homogeneously dispersed within the polymer matrix for both DS 0.1 and 0.015 (MAN1-1, MAN015-1).

HPA resulted in no grit as a tie-layer monomer (MAN1-2, MAN1-3). For DS 0.1 RSNPs, HPA (tie-layer) with BA (shell) (MAN1-3) resulted in high amounts of grit and viscosity (leading to reversible coagulation) while HPA as a shell monomer (MAN1-2) resulted in low grit and medium viscosity. This suggests a mechanism where hydrophilic monomers reduce the amount of RSNP grit in the latex while a hydrophilic tie layer and hydrophobic shell results in high viscosity due to incompatibility and phase separation of the different polymers in the system.

Semi-batch and batch reactions with BA (MAN1-4, MAN1-5) resulted in low viscosity until the onset of reversible coagulation, indicating primarily acrylic polymerization (little grafting) which concentrated the RSNPs in the water phase, leading to reversible coagulation by high viscosity. Latexes from BA contained large amounts of grit. Polymerizations with styrene

(MAN1-7) were similar but resulted in catastrophic coagulation, possibly due to the increased incompatibility of styrene and the RSNPs.

Batch reactions with the more hydrophobic 2-EHA (MAN1-8) resulted in low latex viscosity and grit content, but with phase separation over time, indicating a certain degree of compatibility between the RSNPs and 2-EHA which could have resulted in a combination of hydrophilic (RSNP), hydrophobic (poly-2-EHA), and amphiphilic (2-EHA-grafted-RSNP) particle populations.

Using a BA seed stage and semi-batch feeding of the RSNP dispersion (MAN1-6) resulted in immediate grit formation, suggesting that grit formation is a result of interstitial placement of the RSNPs between the acrylic particles and crosslinking them together to form heterogeneous RSNP-acrylic grit.

Table 5.1 Polymerizations with MAnh RSNPs (DS 0.1)

Run #	Tie Layer	Shell	Monomer Feed Strategy	Stability	Viscosity (cp)
MAN1-1	AA		Batch**	Hydrogel	High
MAN1-2	HPA	HPA	Batch Semi-batch*	Stable Low grit	Medium
MAN1-3	HPA	BA	Batch Semi-batch*	Reversible coagulation	High
MAN1-4	BA	BA	Batch Semi-batch*	Reversible coagulation	Low until fail
MAN1-5	BA		Batch**	Reversible coagulation	Low until fail
MAN1-6	BA	***	Batch**	Catastrophic coagulation	Low until fail
MAN1-7	St		Batch*	Catastrophic coagulation	Low until fail
MAN1-8	2-EHA	2-EHA	Batch*	Stable Phase separation over time	Low

* Batch then semi-batch initiator feed
** Batch initiator charge
*** Semi-batch fed RSNPs

Note on viscosity: Low=~100, medium=~300, high=~500

For runs using the DS 0.015 RSNPs, catastrophic or reversible coagulation occurred when using hydrophilic tie-layer combined with a hydrophobic shell monomer (MAN015-1, MAN015-3). Polymerizations with HPA as tie-layer and shell monomer (MAN015-2) resulted in medium viscosity and a stable latex, similar to MAN1-2. MAN015-4 resulted in high viscosity latex similar to MAN1-3 but higher than MAN1-8, most likely due to the presence of MMA and AA. The stability and lower viscosity of 2-EHA based runs over BA and styrene may be indicative of its lower reactivity (supporting grafting rather than homopolymerization), despite its higher hydrophobicity. 2-EHA runs (MAN015-4, MAN1-8) resulted in 20-30 wt.% incorporation. The common difference between DS 0.1 and 0.015 runs where the RSNPs were used as a seed and the monomer pre-emulsion fed as semi-batch, was the drastically decreased amount of grit presence in the latex.

Table 5.2 Polymerizations with MAnh RSNPs (DS 0.015)

Run #	Tie Layer	Shell	Feed Strategy	Stability	Viscosity (cp)
MAN015-1	MMA	BA/MMA/AA	Semi-batch Semi-batch*	Catastrophic coagulation	/
MAN015-2	HPA	HPA	Batch Semi-batch*	Stable Low grit	Medium
MAN015-3	HPA	BA	Batch*	Reversible coagulation	High
MAN015-4	2-EHA	BA/MMA/AA	Batch Semi-batch*	Reversible coagulation Low grit	High

* Batch then semi-batch initiator feed
** Batch initiator charge
Note on viscosity: Low=~100, medium=~300, high=~500

It was suspected that the grit formation and increase in viscosity from runs with the 0.1 DS RSNPs were as a result of core-shell particles forming at an early stage in the polymerization. The small size of the nucleated particles (roughly each RSNP being a core) would have led to the

viscosity issues of the higher conversion latex. DLS analysis of samples taken every minute during a semi-batch fed BA/initiator polymerization show the two peaks of the RSNPs slowly merge into one peak centered at 100 nm, which is very typical of previously completed emulsion polymerizations where the RSNP is not in the core. Therefore, the theory of interstitial RSNP crosslinking and grit formation remains the most viable.

6.4 Conclusion

Methacrylic anhydride modified RSNPs caused gel formation during the emulsion polymerizations, supporting the idea that vinyl modified RSNPs cannot be used in conjunction with hydrophobic monomers. A way around this was to use maleic anhydride to modify the RSNPs to limit the reaction of the functional groups with other RSNPs. MAnh RSNPs with DS of 0.1 caused grit formation due to interstitial crosslinking of latex particles during the polymerization. RSNPs with DS of 0.015 resulted in far lower levels of grit and otherwise similar stability and viscosity results. Moving forward, a monomer with similarly low reactivity to 2-EHA but with a hydrophobicity between HPA and BA would be ideal to forming low viscosity latex with MAnh RSNPs of DS 0.015.

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Chapter 7: General Discussion and Conclusions

Drawing on the increased consciousness of issues related to sustainability and environmental responsibility, we have worked on a process for incorporating a bio-based polymer in emulsion polymerizations, using the 12 principles of green chemistry as a guide. Starch is a naturally occurring polysaccharide largely used in the food, paper making, and pharmaceutical/chemical industries that can be modified for compatibility in polymer latex. Vinyl modified RSNPs were prepared and used as a comonomer in emulsion polymerization formulations. The RSNP-synthetic composite latexes were produced using less petroleum based monomers and exhibited properties of both the synthetic and starch polymer components of the formulation.

We originally hypothesized that vinyl-functionalized RSNPs could be incorporated into emulsion polymer latexes at commercially significant loadings. Our goal was to achieve >40 wt.% loading at >40 wt.% solids content. Several research stages were necessary to achieve this important goal. First, several grades of the vinyl-functionalized RSNPs were characterized to gain insight into the polymerization procedures necessary to incorporate them into latexes. Second, emulsion polymerizations were carried out to determine the loadings and solids limits, and achievable levels of incorporation. Third, we tested the viability of using a cheaper sourced starch. Finally, anhydride modified RSNPs were prepared using the learning that was gathered during the previous research stages, and preliminary polymerizations were carried out.

Challenges in regards to incorporation of the RSNPs into the polymer particles persisted throughout this research. These challenges include the hydrophilicity of the RSNPs, even after functionalization, as well as their low reactivity with vinyl monomers under persulfate initiation conditions. Strategies were focused on overcoming the more thermodynamically favourable outcome of the starch remaining in the water phase or in the shell of the particles, rather than in their cores.

7.1 Characterization of Newly Modified Regenerated Starch Nanoparticles

The motivation for beginning a joint research project with our industrial partner was their recent development of a novel vinyl-functionalized RSNP. The new starch particles were modified with a polymerizable sugar based monomer (PSBM), in the hopes that vinyl groups were successfully covalently bound to the surface (and potentially the bulk) of the particles. The use of an existing molecule (PSBM) to bind reactive sites to the particles, which could then be dispersed in an aqueous environment for polymerization, provides an exciting possibility of introducing bio-sourced material into polymer products at high loadings. Although RSNPs have been successfully grafted (to a certain degree) in emulsion polymerizations, the kinetics of grafting synthetic monomer from the starch hydroxyl groups introduces more complexity to the reactions than when using vinyl based monomers. Our hope was to be able to use the new RSNPs as a seed for emulsion polymerizations and to limit the formulation and procedural changes to those necessary for industrial applications.

Due to the potential of starch to aggregate and form complexes in water, and the inaccuracy of the dynamic light scattering methods in analysing swollen transparent particles, experiments were conducted to get a truer sense of the behavior of the RSNPs when prepared as a dispersed seed. Filtration and DLS measurements suggest the Z-average particle diameter measurements are highly influenced by the larger RSNPs and aggregates, while the particle size distribution was a more accurate representation of the particles. The addition of PSBM in the manufacturing process resulted in a reduction in molecular weight and thus a reduction in hydrodynamic radius of the RSNPs. KPS initiator was also able to degrade the RSNPs significantly. 40-50 wt.% of the RSNPs were below 30 nm in diameter, while the remaining particles ranged from 30-300 nm with no appreciable concentration at any one diameter. The bimodal peaks of dent sourced starch were shifted to larger values of 150 and 400-1000 nm most likely due to complexing from the higher amount of amylose in the particles, or from the higher degree of swelling of the particles/aggregates. The change of particle size with concentration and temperature indicate that the particles are susceptible to osmotic deswelling and that agglomerate formation is affected by temperature, respectively.

Viscosity of unmodified S-0-hmw sourced RSNP dispersions decreased with temperature and was higher than all other grades that showed no change with temperature. This is due to the modified grades having a more favourable small:large particle diameter ratio and higher polydispersity. The critical volume fraction, determined by fitting the Krieger-Dougherty model to measured viscosity values, of waxy and dent sourced RSNPs were 40 and 36 wt.% respectively, showing the negative effect of amylose on the viscosity of the dispersions and the final latex (Figure 7.1). The increase in temperature of the RSNP dispersions influences measured particle diameter by lowering the critical aggregate concentration as well as increasing the degree of osmotic deswelling.

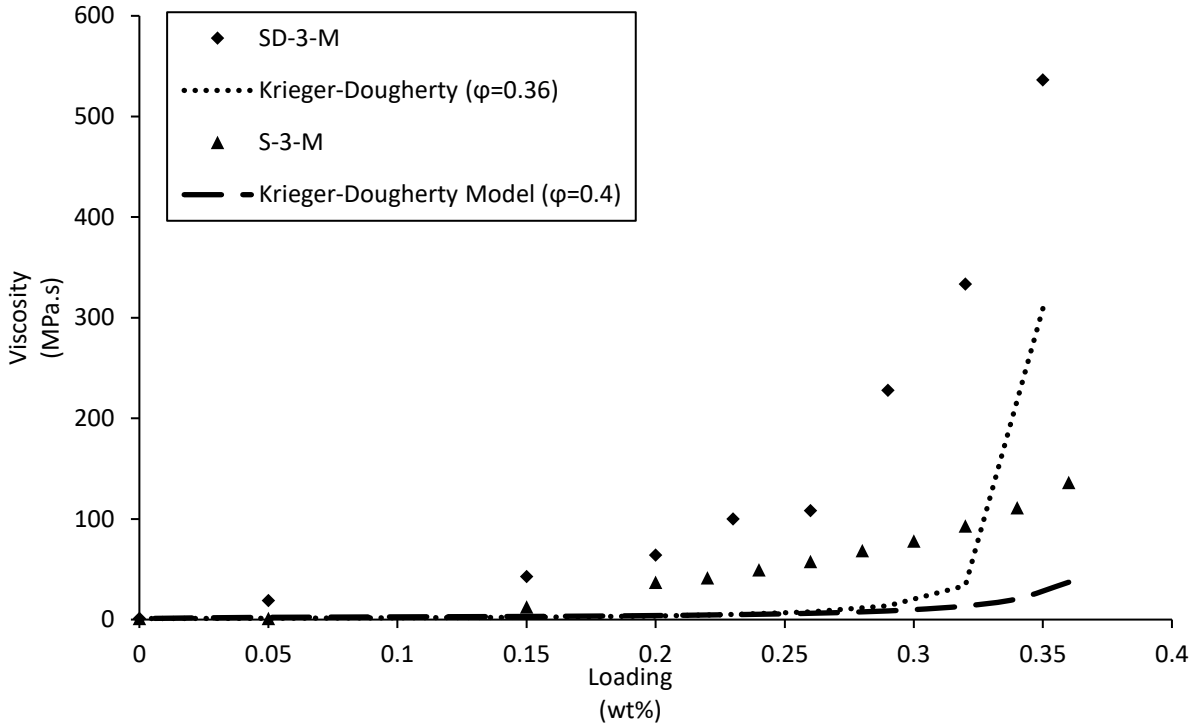

Figure 7.1 Viscosity profiles of SD-3-M and S-3-M at increasing concentrations

Surface tension results show that surfactant will surround smaller diameter RSNPs but not the larger population of particles or aggregates. The RSNPs themselves have stabilizing properties as evidenced by their ability to create emulsions with BA.

^{1}H-NMR and FTIR spectra of the modified RSNPs show the presence of PSBM vinyl groups (Figure 7.2 and 7.3).

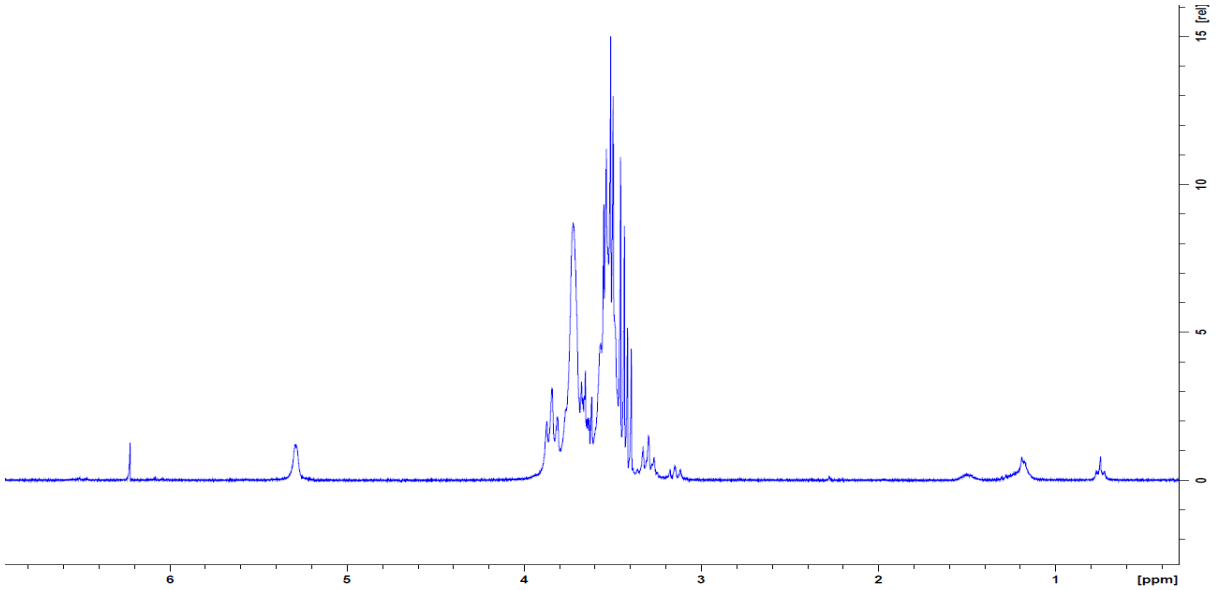

Figure 7.2 ^{1}H-NMR spectrum of S-3-M RSNPs, with the characteristic starch peaks from 3.0 – 4.0, the carbon chain of PSBM from 0.5 – 1.6, and the vinyl group of PSBM from 6.0 – 6.3

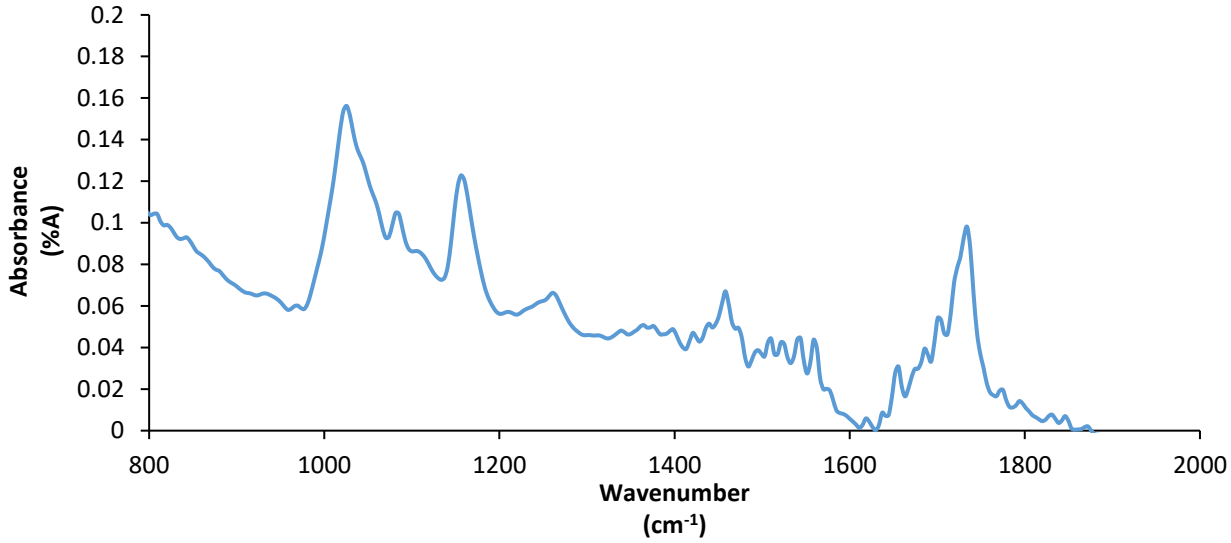

Figure 7.3 FTIR spectrum of S-3-M RSNPs, with the characteristic starch peaks from 800 – 1500, and the vinyl group of the PSBM at ~1700

7.2 Novel Polymer Latex Produced from Newly Modified Regenerated Starch Nanoparticles

Once sufficiently characterized, the RSNPs were used in emulsion polymerizations in the hope that they covalently bond and incorporate within the polymer particles, ideally as cores. An incorporation amount of 25 wt.% and loadings of 40 wt.% above 40 wt.% solids was set as a

goal for a commercially relevant product. The effect of surfactant, initiator, monomer and RSNP type and concentration on the stability of the final latex as well as the incorporation of the RSNPs into the polymer particles was studied.

Increase in surfactant concentration affected the polymerization kinetics as expected for a standard emulsion polymerization (S3M-5, S3M-1, S6M-2, and S6M-1), indicating that the RSNPs did not control the nucleation mechanism by acting as cores for the growing particles (Figure 7.4). Although a stable latex was produced with no surfactant (S3M-5), highlighting the stabilizing properties of the RSNPs, the conversion was in all cases lower when the RSNPs were present (A-1, S3M-1, S3M-3, S6M-1, and S6M-2). Lower conversion could be because by starch acting as a radical scavenger, or grafting of the vinyl monomer to the starch hydroxyl groups, or both. Particle diameter was primarily dependent on surfactant concentration, as expected, and not on the RSNP loading. Excess surfactant in the RSNP seed failed to adsorb to the particle surface once hydrophobic monomer was introduced into the system (S3M-2). Conversion was higher and particle size was lower in the nucleation stage compared to an identical run with no additional surfactant in the seed (S3M-1), suggesting cooperative hydrogen bonding between the RSNPs and surfactant, coupled with the increased surfactant concentration, inducing earlier micelle formation. Since conversion was higher in this run, it is unlikely that grafting was occurring to any high degree. CTAB was used in the RSNP seed (S3M-24 and S3M-25) in the hope that the polar heads would be attracted to the electronegative group in the PSBM while the hydrophobic tails would be directed away from the particle. SDS was then used in the pre-emulsion feed in an attempt to attract the monomer to a hydrophobic layer created by the hydrophobic tails of the CTAB and SDS. These runs led to instability, indicating a lack of charge on the PSBM group.

An increase in initiator concentration and mixing time during the RSNP seed stage resulted in viscosity reduction for several latexes (e.g. S3M-26 and S3M-27). This is most likely due to the reduction in molecular weight of the water phase starch, or from increased incorporation due to the increased number of hydroxyl radicals in the seed.

Monomers that were more hydrophilic (e.g. MMA and AA) tended to promote association with the RSNPs and those that had a lower reactivity (e.g. styrene) promoted grafting (S3M-19, S3M-20, S3M-21, and S3M-22).

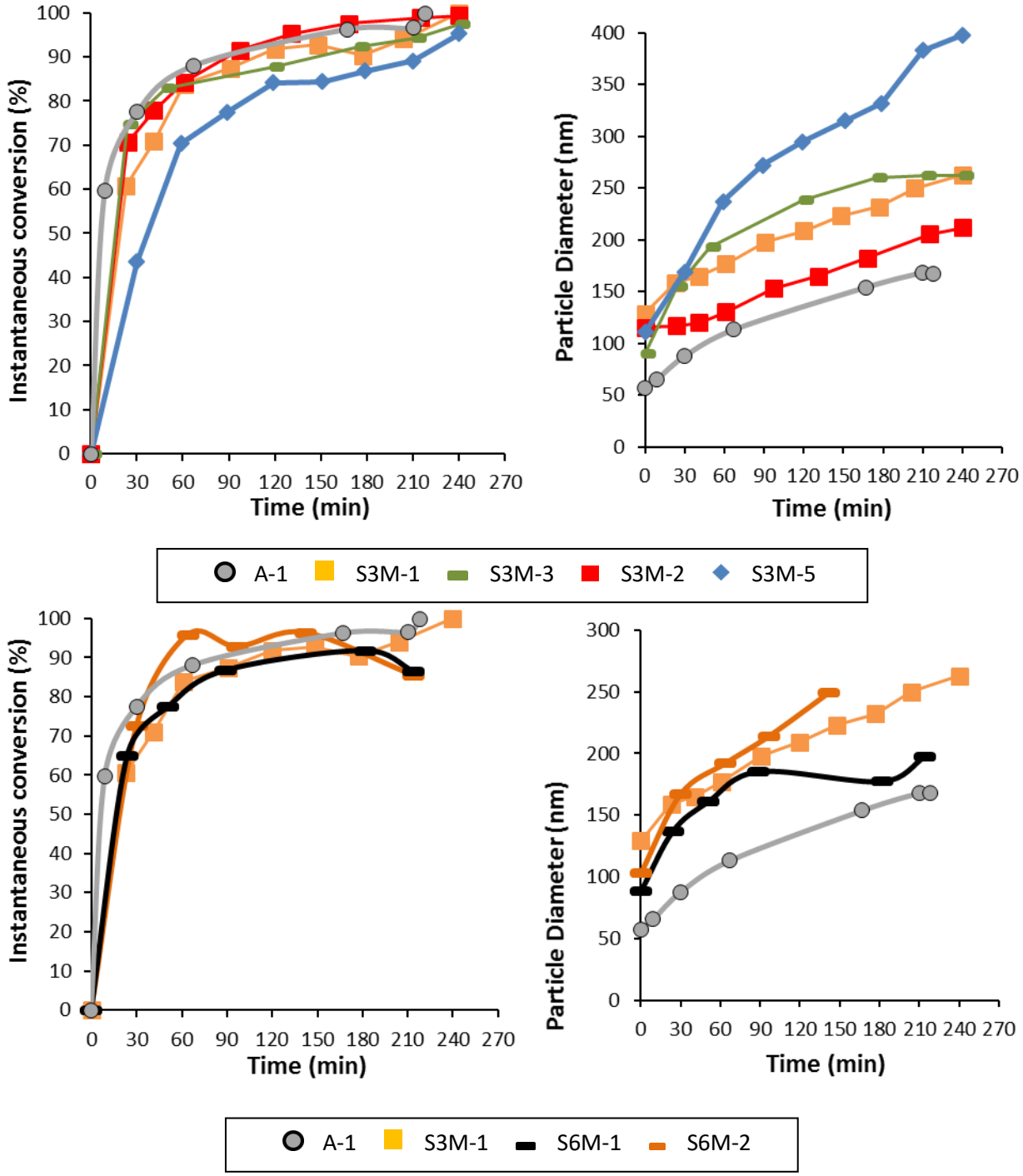

Figure 7.4 Instantaneous conversion and particle diameter of polymerizations

A hydrophobic monomer would tend to graft to the RSNPs covering the latex particle surface while a hydrophilic monomer would lead to more grafting reactions with the RSNPs in the water phase. Thus, the presence of significant amounts of grafted materials in the water phase resulted in higher latex viscosity. Aqueous phase analysis of single monomer systems showed styrene and MMA had the highest incorporation (5-20 wt.%).

Only the S-3 group of RSNPs provided a stable latex when used as a seed, while both S-3 and S-6 grades were successful (stable with lower viscosity) when fed as semi-batch. The semi-batch feeding strategy could have been favourable for incorporation due to the increased reaction time between KPS and the RSNPs, leading to degradation and/or grafting. 40 wt.% loading (~0 wt.% incorporation) of S-3-M grade RSNPs was achieved by batch feeding, while 50 wt.% (5-10 wt.% incorporation) was reached while feeding semi-batch. Semi-batch feeding of S-6-M allowed for a loading of 40 wt.% to be reached with 20 wt.% incorporation. PSBM was combined with the RSNPs during the manufacturing stage. There was instability when the components were added separately and at the same composition to the seed of the polymerization, suggesting the need for the PSBM to be added in the manufacturing process, most likely due to its ability to lower the final molecular weight of the RSNPs. During the manufacturing process, the smaller amount of PSBM in S-1-M did not reduce the starches molecular weight as much as grades with 3 and 6 wt.% PSBM concentrations. The large amount of PSBM in S-6-M most likely reduced the molecular weight of the starch. However, since PSBM may not remain bonded to the RSNPs (Chapter 3), a significant amount may be added to the aqueous phase of the reaction mixture, inhibiting the polymerization rate and potentially causing secondary nucleation. The PSBM is essential for lowering the molecular weight of the RSNPs in the manufacturing process. S-0-3APG, despite including alkyl polyglycoside (APG) stabilizer as a bonded functional molecule, suffered catastrophic coagulation due to the excessively high molecular weight of the RSNPs and the additional APG surfactant added to the reaction mixture (S03APG-1). RSNPs with more hydrophobic PSBM decreased the particle size and increased particle stability due to their increased stabilizing potential (amphiphilic structure). The use of more hydrophilic PSBM could have encouraged the incorporation of the RSNPs with the acrylic monomer, while simultaneously increasing viscosity, by limiting grafting

to the surface of the latex particles. The surface bonded RSNPs, instead of acting as steric stabilizers, could have interacted with other surface bonded RSNPs through hydrogen bonding, increasing viscosity.

When the RSNPs were added during the emulsion polymerizations and a stable, low viscosity latex was formed, the films were transparent and homogeneous. Blends of synthetic latex and a RSNP dispersion mixed at 60 °C at the same composition as polymerization S3M-1 formed opaque and heterogeneous films. This suggests a difference between blending the RSNPs with synthetic particles and including the RSNPs in the polymerization. The higher the temperature of blending and film formation, the more homogeneous and transparent the films became. Barrier property tests show that as RSNP loading increases, the films resistance to water decreases regardless of the method with which the RSNPs were added to the latex, as the resistance to THF increased. Higher THF resistance was seen for mildly degraded RSNPs. The mechanism for increased resistance to THF is the homogeneous distribution of smaller sized starch throughout the polymer matrix and not necessarily increased grafting of synthetic monomer to the RSNPs. RSNP loadings from 0-15 wt.% caused a decrease in tack and peel adhesive properties while increasing shear markedly, consistent with the expected increase in strength of polymer films through entanglements of the crosslinked and hydrogen bonded starch regions with the polymer matrix.

Aqueous phase analysis was the primary method used to confirm incorporation of the RSNPs into the polymer particles. The method is similar to that used by Bodiger et al. and less so to other precipitation methods. ^{1}H-NMR analysis of the serum (water phase) was used to determine if there was any acrylic polymer present (Figure 7.5). If acrylic polymer was present, it was either because of the low accuracy of decanting (user error), or that the grafting of starch with the hydrophobic monomer created low MW amphiphilic polymer that was compatibilized with the water phase sufficiently enough to remain their and not precipitate. ^{1}H-NMR analysis of the pellet (precipitate) showed no evidence of starch due to the inability of the solvent to dissolve both the hydrophilic and hydrophobic components of the pellet (Figure 7.6). Since the pellet material was dispersed and not dissolved in the solvent, certain components were shielded from being visible in the ^{1}H-NMR spectrum. ^{1}H-NMR analysis was thus not useful for

quantitatively confirming gravimetric results for incorporation. Solid phase FT-IR analysis of the pellet was used to detect the presence of the RSNPs, although no quantitative analysis was possible (Figure 7.7).

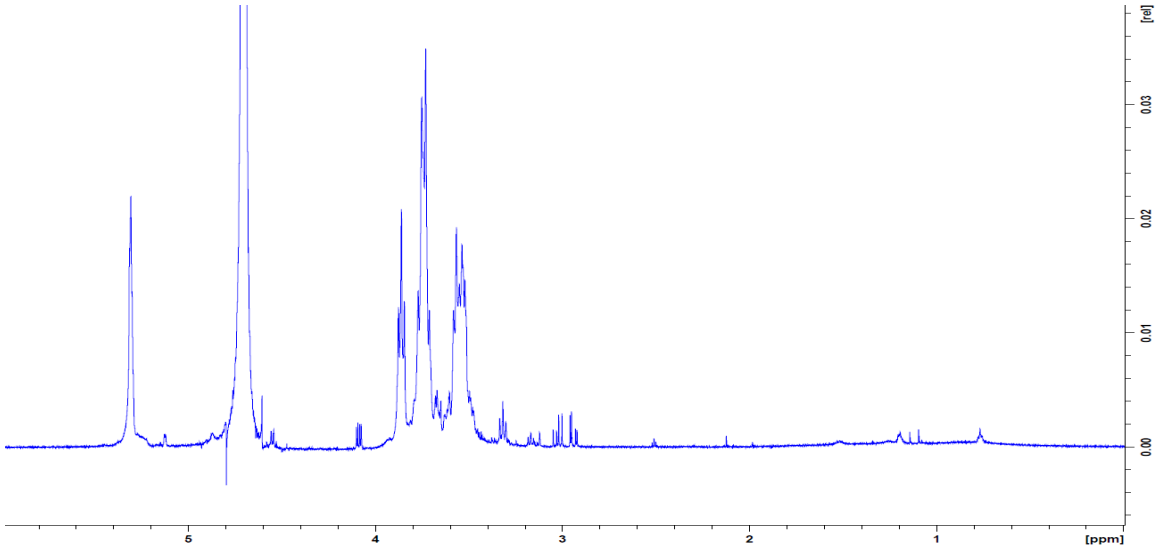

Figure 7.5 ^{1}H-NMR of decanted serrum from centrifugation experiment, showing very small amounts of acrylic polymer from 0.5 – 3.0 and large amounts of starch from 3.0 – 4.0

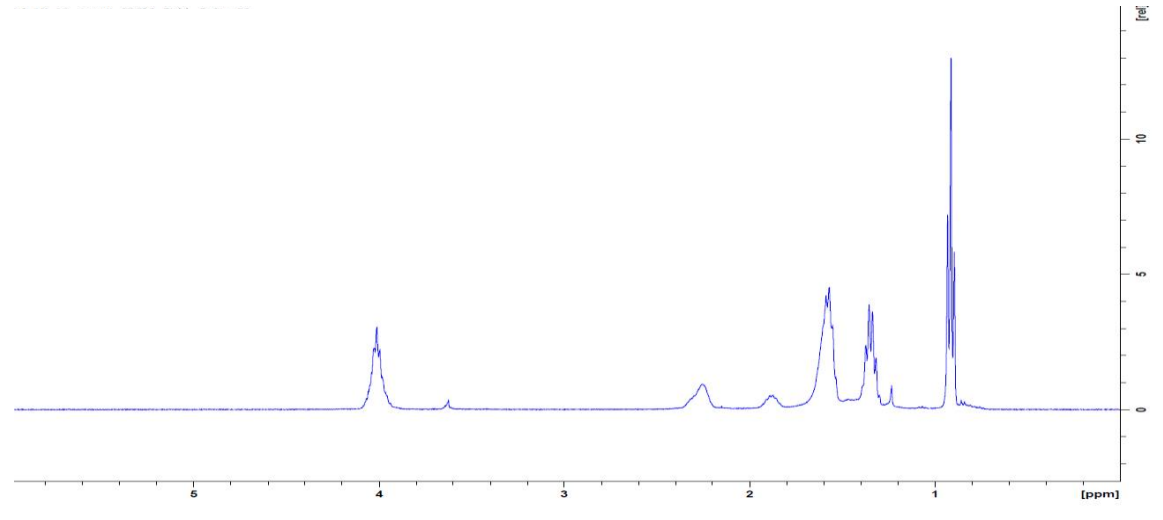

Figure 7.6 ^{1}H-NMR of pellet from centrifugation experiment, showing no detection of starch

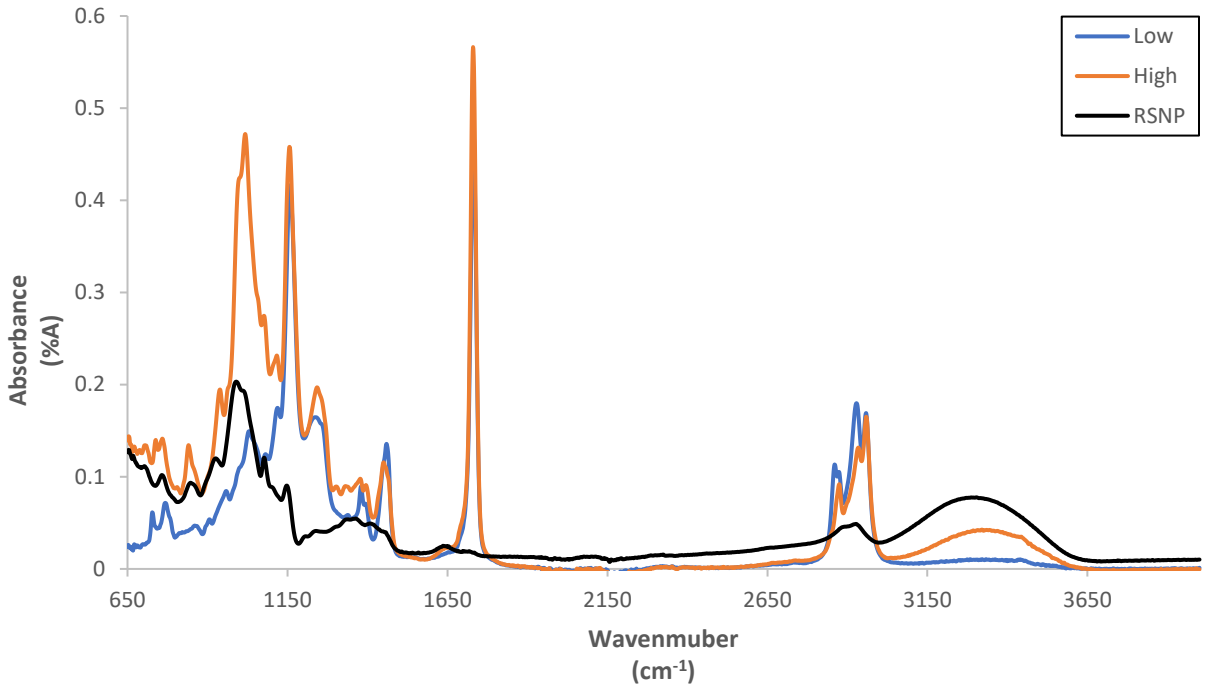

Figure 7.7 Solid FTIR spectrum of a highly and poorly RSNP incorporated latex, compared to the pure RSNP particles. The characteristic fingerprint of the RSNP can be seen at 3000 – 3500 cm^{-1} and at ~1000 cm^{-1}.

Although our values of incorporation are rather modest, grafting of starch in emulsion polymerizations using persulfates has also been shown in the literature, suggesting that grafting is possible.

7.3 The Use of Dent Sourced Starch in Emulsion Polymerizations

The primary purpose of utilizing RSNPs in emulsion polymerizations is to replace reliance on petroleum by-products. For this option to be attractive to manufacturers of commercial latex products, the use of the RSNPs must be cost effective. Dent maize offers a cheaper source of starch to produce RSNPs and was analyzed for its commercial viability.

The particle diameter of the dent sourced RSNPs was larger than the waxy RSNPs (260 vs. ~100 nm), most likely due to the increased concentration of amylose, and the higher degree of swelling (water content) in the particles (Chapter 3). Initial attempts to use the dent RSNPs as

a seed failed due to increased viscosity about three-quarters of the way through the polymerization. Once secondary nucleation was ruled out, initiator concentration and feeding strategy became our focus. KPS can both degrade starch or cause grafting by hydroxyl radical formation. Due to the high amount of amylose that diffused into the water phase, the semi-batch fed initiator could have caused excessive amylose radical formation, leading to a drastic increase in viscosity. This explains why the latex is stable until the end of the pre-emulsion feed and becomes too viscous during the initiator semi-batch feed, where the unreacted monomer and the water phase amylose could form water soluble oligomers and low molecular weight grafted polymer chains. Feeding all the initiator as a seed batch resulted in more stable latex, and was most effective at the highest concentration of 1.0 wt.%, although viscous instability occurred at very high conversion. In order to graft vinyl monomer to the amylose and induce coalescence and particle formation, or to draw the grafted amylose into the stabilized polymer particles, a series of tie-layer monomers were employed. Both batch and semi-batch initiator feed strategies were tested, and at the completion of the seed stage, a mixing stage was used and a surfactant solution was added to stabilize the seed particles. Acrylic acid (AA), n-butyl acrylate (BA), and methyl methacrylate (MMA) were used as tie-layer monomers. Polymerizations with pure MMA and AA as tie-layer charges failed due to gel formation and high viscosity as a result of high molecular weight hydrophilic polymer in the water phase. It was concluded that AA and MMA were too hydrophilic. BA was used both as a batch charge and pre-emulsion feed during the seed stage. When used as a batch charge, the polymerization failed near the end of the run during the BA/MMA/AA pre-emulsion feed. When BA was added through a semi-batch pre-emulsion feed in the seed stage, a stable final latex was produced with a viscosity of 250 cp. In order to achieve 100% conversion without coagulation, initiator was charged exclusively as a batch at the seed stage; this was followed by a 30 minute mixing stage and then the BA/MMA/AA pre-emulsion feed. At the completion of the feed stage an additional mixing stage was used. Several polymerizations coagulated to form a latex resembling cottage cheese due to unreacted monomer build up in the reaction medium, which could have caused monomer droplet initiation when initiator was fed semi-batch (Figure 7.8).

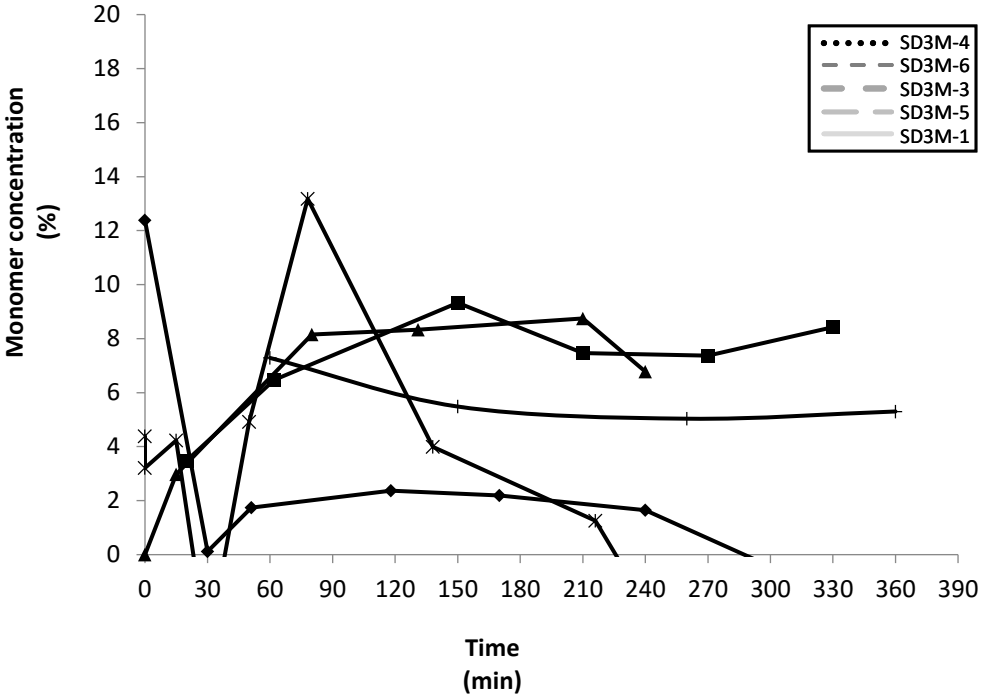

Figure 5.2 Monomer concentration in reaction mixture over the course of the polymerization (lines are not model predictions but are used solely to improve visual representation of the data)

Mixing stages were used to ensure monomer concentration in the reactor was very low. The optimal procedure called for a 1 h BA pre-emulsion feed (tie layer) with a 30 min mix stage, followed by a 3.5 h pre-emulsion feed of BA/MMA/AA and a 1 h mixing stage (0.85 wt.% initiator, 1 wt.% EF-800). Maximum RSNP loading with this procedure was 25 wt.% and the PD of the final latex was 160 nm. An increase in mixing time and decrease in initiator concentration (procedure #4) was not successful, confirming the necessity of 0.85 wt.% initiator as a batch charge to reduce the molecular weight of the soluble starch (as opposed to longer mixing at 60 °C in the presence of polymerizing particles). A final adjustment to this procedure was tested where the RSNP dispersion was allowed to mix at 60 °C for 12 h in a beaker before being added to the reactor (run SD3M-4, modified procedure #5). The final latex had a PD of 200 nm and a viscosity of 100 cp. The apparent thermal degradation of the starch must have assisted the stability of the latex by reducing the molecular weight of the water soluble starches, possibly allowing them to be more efficiently incorporated into the polymer particles. All latexes had a

brownish hue except for the ones produced with the optimal procedure, which suggests the removal of aqueous phase starches in the successful runs. Films were homogeneous and transparent although they showed no adhesive properties.

7.4 Polymer Latex Produced from Anhydride Modified Regenerated Starch Nanoparticles

Polymerizable sugar based monomer modified RSNPs were previously used in emulsion polymerizations with moderate success. Loadings of 40 and 50 wt.% (40 wt.% solids) using a complex semi-batch system were achieved with 0-20 wt.% incorporation, while single monomer batch reactions (15-20 wt.% solids and 55-60 wt.% loading) with styrene and MMA resulted in 5-20 wt.% incorporation. Our conclusion was that the particles needed to be modified with both hydrophobic and vinyl groups, with the vinyl groups covalently bonded to resist emulsion polymerization conditions to a useful degree.

Anhydride modified RSNPs were developed with methacrylic and maleic anhydride (MAnh) vinyl groups to test the viability of this type of vinyl modification. Dispersions with methacrylic anhydride modified RSNPs as a seed (15-30 wt.%) and with initiator concentration of 3 wt.% formed gels after 15-45 min under 50°C magnetic stirring. Batch and semi-batch pre-emulsion and initiator feeds, as well as a range of monomers (2-EHA, styrene, BA, MMA, HPA, and AA) were tested at 15 wt.% loading and 40 wt.% solids, with all polymerizations resulting in gel formation ~30 min into the 4 h experiments. Due to the known stabilizing properties of the RSNPs and their tendency to remain in the aqueous phase, the fact that the vinyl groups are capable to readily react with reach other resulted in gel formation, regardless of the probable high incorporation of RSNPs into the polymer matrix due to the covalently and permanently bonded methacrylic anhydride groups.

The MAnh RSNPs did not form a gel in solution with the addition of KPS, and so were polymerized with several tie-layer monomers. 0.1 and 0.015 DS RSNPs use with AA as a tie-layer created a hydrogel as expected with no grit and homogeneously dispersed RSNPs (MAN1-1, MAN015-1). HPA as a tie-layer and shell monomer tended to reduce grit content, while HPA as a seed and BA as a shell increased viscosity and produced high amounts of grit (MAN1-2,

MAN1-3). It is possible that the hydrophilicity of the HPA contributed to reducing grit (increasing compatibility with the RSNPs) while the addition of BA as a shell monomer caused an increase in viscosity due to the differences in hydrophobicity of the monomers. Semi-batch and batch reactions with BA (MAN1-4, MAN1-5) resulted in low viscosity until the onset of reversible coagulation, indicating primarily acrylic polymerization (little grafting) which concentrated the RSNPs in the water phase, leading to reversible coagulation by high viscosity. Latexes from BA contained large amounts of grit. Polymerizations with styrene (MAN1-7) were similar but resulted in catastrophic coagulation, possibly due to the increased incompatibility of styrene and the RSNPs. Batch reactions with the more hydrophobic 2-EHA (MAN1-8) resulted in low latex viscosity and grit content, but with phase separation over time, indicating a certain degree of compatibility between the RSNPs and 2-EHA which could have resulted in a combination of hydrophilic (RSNP), hydrophobic (poly-2-EHA), and amphiphilic (2-EHA-grafted-RSNP) particle populations. Using a BA seed stage and semi-batch feeding of the RSNP dispersion (MAN1-6) resulted in immediate grit formation, suggesting that grit formation is a result of interstitial placement of the RSNPs between the acrylic particles and crosslinking them together to form heterogeneous RSNP-acrylic grit. For runs using the DS 0.015 RSNPs, catastrophic or reversible coagulation occurred when using hydrophilic tie-layer combined with a hydrophobic shell monomer (MAN015-1, MAN015-3). Polymerizations with HPA as tie-layer and shell monomer (MAN015-2) resulted in medium viscosity and a stable latex, similar to MAN1-2. MAN015-4 resulted in high viscosity latex similar to MAN1-3 but higher than MAN1-8, most likely due to the presence of MMA and AA. 2-EHA runs resulted in 20-30 wt.% incorporation. The stability and lower viscosity of 2-EHA based runs over BA and styrene may be indicative of its lower reactivity (supporting grafting rather than homopolymerization), despite its higher hydrophobicity. The common difference between DS 0.1 and 0.015 runs where the RSNPs were used as a seed and the monomer pre-emulsion fed as semi-batch, was the drastically decreased amount of grit presence in the latex. It was suspected that the grit formation and increase in viscosity from runs with the 0.1 DS RSNPs were as a result of core-shell particles forming at an early stage in the polymerization. The small size of the nucleated particles (roughly each RSNP being a core) would have led to the viscosity issues of the higher

conversion latex. DLS analysis of samples taken every minute during a semi-batch fed BA/initiator polymerization show the two peaks of the RSNPs slowly merge into one peak centered at 100 nm, which is very typical of previously completed emulsion polymerizations where the RSNP is not in the core. Therefore, the theory of interstitial RSNP crosslinking and grit formation remains the most viable.

7.5 Satisfying the 12 Principles of Green Chemistry

The principles of green chemistry were developed to provide a framework for learning about green chemistry and the increased sustainability and improvement of processes and products.[1] Dubé and Salehpour examined these principles as they apply to polymer reaction engineering.[2] This project has been reviewed to determine which principles were successfully satisfied (low, medium, and high success) and whether the project as a whole contributes to sustainable polymer production practices.

Prevent Waste: Medium

The ability of the polymerizations to reach 100% monomer conversion in virtually every scenario removed the need for post-reaction residual monomer extraction, meaning that the entire monomer reagent was used in the procedure. As the solvent used for emulsion polymerizations is water and the polymerization temperature was 60 °C, very little solvent was lost during the typical 4 h timeframe where the reaction mixture was being heated. Finally, the presence of off-spec material such as gel and grit continued to be an issue due either to poor incorporation of the RSNPs or to interstitial crosslinking of the latex particles due to the high degree of grafting of the synthetic monomer to the anhydride modified RSNPs. This material would need to be removed post-reaction before the latex is to be used for film formation etc. Although this introduces a small amount of waste into the process, it is hoped that the final iteration of the RSNPs and the polymerization procedure will eliminate the need for post-production filtration.

Design Safer Chemicals and Products: High

Polymers are inherently non-toxic unless burnt or degraded by external forces. For industrially produced polymers, this is typically not an issue as the products are designed to function correctly and safely in their environments. Due to the lack of organic solvents used in emulsion polymerizations, and the inherent non-toxicity of the RSNPs, the only potentially toxic components that could be released or leached out of the polymer latex or film would be any property additives (crosslinker, CTA, plasticizer, etc.). Although none were used in the latest most successful latex, attention would need to be paid in the future if such additives were to be employed.

Design Less Hazardous Chemical Synthesis: Medium

As already mentioned, the use of water as a solvent, starch as a co-monomer, and the lack of toxic additives made our current synthesis method safer for operators and end-users. However, the use of volatile monomers and moderately dangerous initiators could cause adverse health effects if standard safety precautions are not taken or if an unexpected accident occurs.

Use Renewable Feedstock: Medium

The purpose of this project was to incorporate as much starch into industrially relevant latex formulations as possible while maintaining useful properties. Although this was to some degree successfully accomplished at high loadings, traditional monomers still comprised >50 wt.% of the feedstock. Although research into sustainable pathways of production for highly used monomers is ongoing and intense, traditional methods utilizing petroleum by-products are still favoured.

Use Catalysts, Not Stoichiometric Reagents: High

Free radical initiator was used to catalyze the polymerizations, and could drive the reaction to completion (100% conversion) even under low monomer concentration. The

removal of initiator can be challenging but it is rendered inert once the polymerization is completed, and should not be a safety risk or contribute to the toxicity of the final latex.

Avoid Chemical Derivatives: Medium

Although no modification of the acrylic monomer or polymer was conducted at any time, the RSNPs were physically and chemically modified prior to their use in the polymerizations. The use of several chemicals was necessary for the production of the desired RSNPs which could have contributed to added materials, safety risks, and potential environmental pollution.

Maximize Atom Economy: High

So long as the polymerization produces little grit and coagulum, there should be highly efficient use of all atoms in the polymerization. In this project, the presence of coagulum was extremely minimal for successfully produced latexes, while the issue of grit was persistent as previously mentioned.

Use Safer Solvents and Reaction Conditions: High

Water was the only solvent necessary in the production of the RSNPs or in their polymerization. Reaction conditions were mild at 60 °C but investigation into redox initiation (room temperature) or other catalysts should be conducted.

Increase Energy Efficiency: Medium

Due to the relatively low shear stress (200 RPM), small reactor size (1 L), and low (ambient) pressure, energy consumption was kept to a minimum. As mentioned previously, room temperature synthesis using several catalysts should be investigated.

Design Chemicals and Products to Degrade After Use: Low-Medium

The RSNP loaded latex was designed to be resistant to degradation, assuming the RSNPs are 100% incorporated into the polymer particles. In reality, incorporation was rather low, and so the existence of starch outside the synthetic polymer matrix could theoretically make the final films susceptible to biodegradation. Further testing is necessary.

Analyse in Real Time to Prevent Pollution: High

The creation of unwanted by-products besides the previously mentioned grit and coagulum, which cannot be avoided by real time monitoring, was not an issue in the polymerization system used in this project. Thus the only concern was runaway reactions and over-heating, which could have led to coagulation, soot from burning, and possible exposure of the operators to the reaction materials. Calorimetric real-time monitoring prevented this.

Minimize the Potential for Accidents: Medium

Although the degradation and burning of the latex can lead to release of harmful chemicals, the main issue in relation to accidents is with the handling of the feedstock chemicals. All of the monomers used were in liquid form, increasing the risk of spillage, and can be harmful if contacted or ingested. Initiator can also be harmful but is used as a solid and so is less likely to be ingested or spilt. The use of water as a solvent and solid and safe RSNPs reduced the overall potential for accidents during reactor preparation. Due to the reactor running at 60 °C, caution had to be taken during operation to prevent release of volatile substances.

7.6 Future Work

Several areas of focus within the scope of this research project require further attention if commercial incorporation levels are to be reached:

1. Monomer assay: Monomers of varying hydrophilicity and reactivity should be tested with the new MAnh modified RSNPs in order to determine if a particular family or specific monomer allows for high incorporation. This would allow us to create a qualitative model of monomer selection for the RSNPs that would be useful in creating future commercial formulations.
2. Hydrophobic modification of RSNPs: The vinyl-functionalized MAnh RSNPs should also be hydrophobized to increase their compatibilization with the synthetic monomer. Several small molecules should be tested at varying concentrations to determine the

best method to increase compatibility while limiting the additional materials and processes necessary for such modification.

3. Redox initiation: Due to the high selectivity of redox initiation towards monomer grafting from starch rather than monomer homopolymerization in the literature, various grades of RSNPs should be tested using various redox initiators. This may provide both higher incorporation as well as a greater range of available temperatures for polymerization.
4. Catalysts for removal of soluble starch: The literature includes several catalysts that can be used for the specific purpose of grafting small molecular weight starch (specifically amylose) to larger starches. These could be used to remove the water-phase starch at various stages of the polymerizations, reducing nucleation and viscosity issues.
5. Applications for high RSNP loaded films: Besides as pressure sensitive adhesives, films should be tested for their potential use in various commercial applications.

7.7 Final Remarks

Throughout this research project we have investigated the use of regenerated starch nanoparticles as components in synthetic polymer latex. Starch in general can be sustainably produced, is safe to handle, and is non-toxic to humans. We expected that the vinyl-functionalized RSNPs would be incorporated into emulsion polymer latexes at commercially significant RNSP loadings. Ideal conditions resulted in latexes up to 50 and 40 wt.% loading at 30 and 40 wt.% solids, with incorporation ranging from 0-10 wt.%. New MAnh modified RSNPs were able to be included at 40 wt.% loading at 40 wt.% solids at an improved 20-30 wt.% incorporation when used with a monomer of appropriate hydrophilicity and feeding strategy. Films could retain their original properties to a certain extent, while adopting the rigidity and hydrophilicity of starch. Transparency and homogeneity of RSNP loaded films were similar to their purely synthetic counterparts. The biodegradability of the films was not tested although due to the low incorporation of the RSNPs it is reasonable to assume they are susceptible to biodegradation to some degree.

We have shown in this work that RSNP loaded synthetic latex can be produced through persulfate initiation at industrially relevant loadings and solids. These latexes are stable with acceptable viscosity and their films have varying properties. Although it is difficult to compare incorporation values to the literature due to the popularity of reporting grafting efficiency and percent over incorporation, RSNP loaded latex incorporation values ranged from 0-30 wt.%. These values are expected to increase as more research is conducted into advanced incorporation strategies.

This work presents the only comprehensive attempt to incorporate RSNPs into synthetic latexes at high loadings and solids with persulfate initiation without the need to severely reduce the particles molecular weight. The learning generated provides a framework for continuing research into increasing the incorporation of RSNPs into the polymer particles and achieving core-shell morphology. Loadings at 40 wt.% solids of stable latexes were above those reported in the literature (Chapter 2). The original and new RSNPs used herein, coupled with the strategies developed throughout each stage of research, offer a way of significantly reducing reliance on petroleum byproducts as source material for synthetic latex.

References

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