

Waterborne Biopolymer Dispersions for Barrier Paper Coatings

by

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AUTHOR'S DECLARATION

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

STATEMENT OF CONTRIBUTIONS

Chapters 2–4 of this thesis are adapted from published or submitted manuscripts in which I am the first author. Professor Tizazu Mekonnen is the corresponding author and sole co-author on each manuscript. For each manuscript, contribution of conceptualization, methodology, and resources were shared. I contributed validation, formal analysis, investigation, data curation, writing, and visualization. Prof. Mekonnen supported writing and contributed supervision, project administration, and funding acquisition.

Chapter 2 is adapted from the submitted manuscript “**Progress in Waterborne Polymer Dispersions for Coating Applications: Commercialized Systems and New Trends**”.

Chapter 3 is adapted from the published manuscript “**Stable aqueous dispersions of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) polymer for barrier paper coating.**

Progress in Organic Coatings, 187 (2024), 108101”. Chapter 4 is adapted from the submitted manuscript “**Waterborne cellulose acetate Pickering emulsion generation mediated by cellulose nanocrystals for paper coating applications**”.

ABSTRACT

Demand for alternatives to synthetic, non-degradable, and single-use plastic packaging is continually increasing. Paper products are environmentally friendly and offer a potential solution, but typically do not meet performance demands without coating them with a polymeric film, usually polyolefins. Replacing conventional plastic coatings with biobased and biodegradable alternatives can substantially improve product sustainability. Furthermore, using water as a coating medium imparts further environmental and coatability advantages. In this thesis, the current state of waterborne coatings in industry is analyzed. Waterborne coatings are increasingly being used, containing conventional polyolefins, with the next step being to move towards more sustainable polymer options.

Two different waterborne dispersions are formed using distinct biopolymers and stabilization mechanisms. First, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) is dispersed in water via stabilization from the traditional surfactant sodium dodecyl sulfate (SDS). The dispersion demonstrates strong stability and coatability characteristics. Paper coated with the prepared waterborne PHBV dispersion exhibited strong barrier property performance relative to uncoated paper, with substantial improvements to water vapor permeability and grease resistance properties. A second study was performed in which a waterborne dispersion of cellulose acetate was formed using Pickering emulsion technique and cellulose nanocrystals. This dispersion exhibited similarly strong performance characteristics, with the coating again demonstrating strong barrier performance. Comparison to an industrially available product yielded competitive performance results as a food packaging container. Overall, the work demonstrates strong applicability of waterborne biopolymer dispersions as sustainable coating options.

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DEDICATION

I dedicate this work to my family, friends, and partner, who always believed in and supported me. I dedicate this work to my late grandpa Rene Delanghe, who I know would be proud to see who I am and my achievements today.

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LIST OF ABBREVIATIONS/NOMENCLATURE (ALPHABETICAL)

1 K	One-package
2DDSA	(2-Dodecen-1-yl)succinic anhydride
AlO₃	Aluminum(III) oxide
aq	Aqueous
ATR	Attenuated total reflectance
BPA	Bisphenol A
CA	Cellulose acetate
Ce	Cerium
CNC	Cellulose nanocrystals
Conc.	Concentration
cP	Centipoise
CTAB	Hexadecyltrimethylammonium bromide
CuPT	Copper pyrithione
DLS	Dynamic light scattering
E-coat	Electrodeposition coat
FTIR	Fourier transform infrared spectroscopy
G'	Storage modulus
G''	Loss modulus
HALS	Hindered amine light stabilizer
KOH	Potassium hydroxide
LVE	Linear viscoelastic region
MD	Machine Direction
MFFT	Minimum film forming temperature
MT	Megaton
NaCl	Sodium chloride
O/W	Oil/water
OEM	Original Equipment Manufacturer
OH	Hydroxyl
org	Organic
PBS	Poly(butylene succinate)
PDMS	Polydimethylsiloxane
PE	Polyethylene
PEO	Poly(ethylene oxide)

PHA	Polyhydroxyalkanoates
PHBV	Poly(3-hydroxybutyrate- <i>co</i> -3-hydroxyvalerate)
PLA	Polylactic acid
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
SDS	Sodium dodecyl sulfate / sodium lauryl sulfate
SEM	Scanning electron microscopy
SiO₂	Silicon dioxide
TBT	Tributyltin
TEM	Transmission electron microscopy
T_g	Glass transition temperature
TiO₂	Titanium dioxide (Titanium white)
UV	Ultraviolet
UVA	Ultraviolet light absorber
VOC	Volatile organic compounds
VW	Volkswagen
WEP	Waterborne epoxy
WPU	Waterborne polyurethane
wt. %	Weight percentage
WVP	Water vapor permeability
XCYB	‘X’ Coats ‘Y’ Bakes
ZnO	Zinc oxide
γ	Shear strain
ΔW	Weight change
η	Viscosity
τ	Shear stress
ω	Angular frequency

CHAPTER 1 – INTRODUCTION

1.1 Overview and motivation

There is an increasing focus on product sustainability, with efforts to move towards improved environmental friendliness [1]. One such product is plastic packaging, for which hundreds of millions of tons of waste are generated each year, with a significant portion ending up in landfills and leaking into the environment [2]. Paper packaging is a potential alternative, possessing satisfactory mechanical properties alongside being inexpensive and biodegradable [2,3]. However, without a coating, paper performs poorly in applications which demand high barrier properties, such as food packaging, due to its porosity and hydrophilicity [4]. Further, existing paper coatings are primarily comprised of polyolefins, contradictory to the renewability and degradability benefits of the paper [2].

The use of biopolymers offers an alternative to replace existing synthetic polymer coatings with a more sustainable material. Unfortunately, many biopolymers do not possess the required properties for this application, including water/grease resistance and film forming capabilities [5,6]. The two biopolymers used for paper coating studies in this work which do possess the aforementioned properties are poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) and cellulose acetate. PHBV is biobased, biodegradable, and is extracted directly from a wide range of organisms without the need for extensive downstream processing [7]. Cellulose acetate is renewable and widely available, with extensively studied property tunability via the acetylation process and other reactions [8–11]. As well, cellulose acetate is non-toxic and safe [9,12].

Alongside material selection, the coating method must also be selected. While flat-film extrusion is common for paper coatings, solvent casting is also extensively employed and can be used to make thinner films, using less material, and inexpensive facilities [13]. In solvent casting, the polymer is dissolved in a suitable solvent, and then cast onto a substrate and the solvent evaporated [4]. Water is very desirable for use as the solvent, due to safety attributes, availability, environmental benefit, and cost effectiveness [14,15]. However, many polymers, including PHBV and cellulose acetate, are not readily soluble in water [1]. Instead, a dispersion in water can be formed. One appealing approach is to initially dissolve the polymer in a water-immiscible organic solvent, and then combine it with a stabilizing agent and energy input to form a stable waterborne dispersion, then subsequently removing the initial organic solvent from the system [16].

Stabilizing agents can be traditional surfactants or Pickering particles, as shown in **Figure 1**. Traditional surfactants, such as sodium dodecyl sulfate and polyoxyethylenesorbitan trioleate (Tween® 85) are comprised of a hydrophilic head and hydrophobic tail, arranged to stabilize the oil-water interface [17,18]. In contrast, Pickering emulsions are stabilized with the use of amphiphilic particles, which are bound irreversibly to the interface [19].

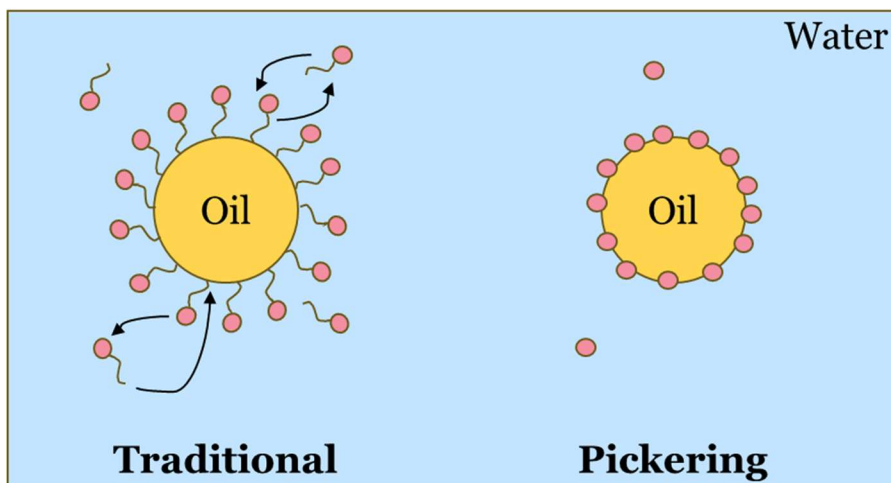


Figure 1. Simplified depiction of traditional and Pickering emulsion interfacial behaviors

1.2 Objectives

This thesis aims to investigate the formation and applicability of waterborne biopolymer dispersions as paper coatings. Two distinct systems were investigated, using two different biopolymers and two different stabilization mechanisms. Both systems underwent a thorough characterization of both the formation and stability of the dispersions and their resultant coatings on paper substrates.

Firstly, biopolymer coatings are investigated for their opportunity to displace existing polyolefin coatings, improving coating sustainability. A waterborne biopolymer dispersion is investigated as the coating medium due to enhancing system attractiveness. Therefore, the first objective for each biopolymer is to form a stable waterborne dispersion. For the first system (PHBV), a traditional surfactant (SDS) approach is used, while the second system employed a Pickering emulsion using cellulose nanocrystals (CNCs) in their native and modified form.

The second objective is to demonstrate the applicability of the waterborne biopolymer dispersions as coatings. For both systems, dispersions were tuned to evaluate their properties for stable storage and for paper coating applications. The dispersions were then coated on paper, to take advantage of the inherent properties of the polymers to overcome the weaknesses of paper as a packaging material. Successes and drawbacks to the coatings were explored, with the objective of identifying current applicability and direction for future work required to progress towards commercialization. Overall objectives of this work were to expand the number of biopolymers available to waterborne coating applications, improve understanding on their dispersion formation and characteristics, and explore and expand on waterborne biopolymer dispersion applications, particularly for barrier paper coatings as an immediate application.

1.3 Outline of thesis

Chapters of the thesis subsequent to this introduction (Chapter 1) are comprised of the following: Chapter 2 provides a literature review that focuses on the current state of industrial waterborne coatings. Existing systems and their adoption are thoroughly documented, and current and future trends are investigated to search for opportunities and predict industry decisions. Chapter 3 presents a completed experimental research work on a waterborne poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) dispersion and its application as a barrier paper coating. Characteristics and performance of both the dispersion and the coated paper are analyzed in detail. In Chapter 4, experimental research forming a waterborne Pickering emulsion of cellulose acetate is covered, including assessment of its

performance as a barrier paper coating for food packaging application. Lastly, Chapter 5 details overall conclusions and recommendations.

CHAPTER 2 – LITERATURE REVIEW¹

2.1 Introduction

Polymer coated surfaces have become ubiquitous in modern life. From house paint to food packaging, kitchenware to synthetic leathers, a myriad of products leverage the properties imparted by the polymeric coating in tandem with the substrate to provide improved material appearance, functionality, or performance [2,3,20–22]. At the same time, these coatings must remain competitive with alternative options in terms of cost, availability, environmental impact, and other pertinent indicators [20,23].

Even as a thin surface coating, polymers offer substantial advantages over non-polymeric materials. A broad range of tunable materials enables the selection of a polymer system that fulfills a wide range of color ranges, textures, and appearances, ranging from metallic luster to imitation leather, matte finish and more [24–26]. Moreover, these surfaces can be tailored to exhibit high performance in areas, such as water and vapor barrier properties (high barrier or selectively porous membranes), UV and corrosion resistance, electrical conductivity, flexibility, and impact strength, thereby enhancing the properties of or safeguarding the underlying substrate [20]. Furthermore, polymer coatings facilitate the generation of smart surfaces, providing functionalities, such as antimicrobial surfaces, actuators, and active packaging [27–30].

¹ A version of this chapter has been submitted to a peer-reviewed journal as a review article

There are multiple methods available for coating polymers onto surfaces, including extrusion, powder coating, and liquid carriers. Drawbacks associated with extrusion and other hot melt methods include high processing temperatures and handling costs due to the highly viscous polymer melt [31,32]. For some materials, like poly(hydroxybutyrate-valerate) (PHBV) and polylactic acid (PLA), extrusion methods can yield brittle films [13,33], while liquid-borne coating method allows for flexible film formation [23]. Powder coating enables the application of thin, uniform coatings without requiring an evaporation step, although it necessitates an initial melting stage for powder formation and encounters challenges such as powder agglomeration and moisture control [34]. Other liquid-free coating methods, such as press, supercritical fluid, and cold spray coating are also used in specialized applications [35,36].

When using a liquid carrier, the polymer is either dissolved in or dispersed within a suitable solvent, which is subsequently evaporated after surface coating [1]. Liquid carriers are chosen to enable evaporation at lower processing temperatures compared to other film preparation methods involving polymer melting [1]. Coating polymers from within a liquid medium offers a broad range of application methods, such as spraying, dipping, rod coating, and more [2]. Liquid coating is also preferred when functionality or multicomponent systems are involved, as it allows for self-stratification of different components [37].

Waterborne systems are preferred over organic solvents whenever possible due to their superior environmental friendliness and enhanced safety features, including reduced fire, explosion, and worker physiological risks [14,38]. It is important to note that within this

review work, ‘solvent’ or ‘solventborne’ refer to organic liquids that can act as hazardous pollutants. Initially, waterborne systems gained popularity because of their ability to achieve sufficiently high solid weight percentages (wt.%) while substantially reducing targeted emissions [14]. Higher solids percentage results in smaller equipment sizes, faster drying time, and reduced storage and transportation costs [39]. Achieving higher solids percentages in dispersions is possible because the system is no longer constrained by the amount of polymer that can dissolve in the solvent or form via reaction, as the viscosity remains relatively low as desired [40,41]. Rather than viscosity being dictated by the hydrodynamic interactions between the dissolved polymer and the solvent, the viscosity is largely dictated by particle size, and any added rheological modifiers [23,40,42,43]. While waterborne and high solids content were initially synonymous with one another [14], some applications of waterborne polymer systems now do not necessarily require high solids content to be industrially practical [3,44].

However, designing waterborne systems is still limited by several drawbacks. Chiefly, many polymer systems do not dissolve or disperse well in water and instead prefer organic solvents [45]. Additionally, water-phase polymerization of monomer to obtain waterborne polymers is not possible for many preformed polymers, including biopolymers, many of which are of interest for sustainable coatings [1]. As a result, substantial resources must be allocated to create a suitable dispersion. Additionally, while higher wt.% means lower storage and shipment costs than organic solvent systems, dry systems offer even better cost-effectiveness in this regard. Storage and shipment can also be complicated by the poor stability arising in

many waterborne systems [46]. Organic solvents are also still frequently required as part of the overall process [14,23]. Lastly, the evaporation temperature for water is often higher than its organic solvent counterparts [40]. A summary of these benefits and remaining drawbacks is provided in **Figure 2**.

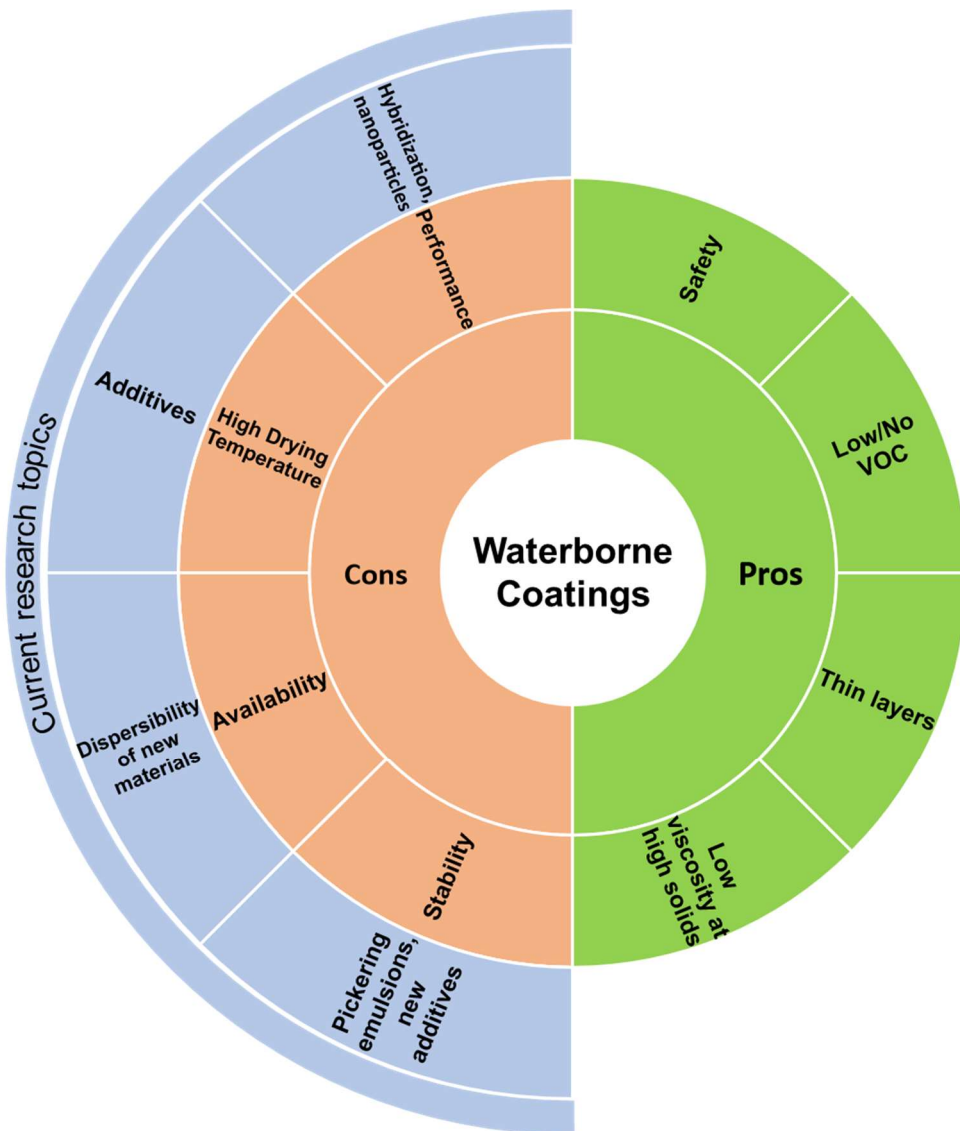


Figure 2. Benefits and drawbacks to waterborne coating systems compared to existing alternatives

While there are multiple methods available, the predominant approach for obtaining waterborne polymer dispersions of preformed polymers (not emulsion polymerizable) is through phase inversion [1]. In this process, the preformed polymer is dissolved in a suitable organic solvent, which is immiscible in water. Subsequently, water and a surfactant are added to the solution alongside an energy input. The organic solvent is then evaporated, leaving the polymer dispersed in water [23]. Although an organic solvent is still used in this process, the quantity required can be significantly reduced compared to non-waterborne processes. Moreover, it can be better controlled and recovered during the preparation process, and in some cases, it may be eliminated entirely with alternative preparation methods [14,47].

The waterborne dispersion is subsequently cast onto a substrate, and as water evaporates, the polymer particles undergo merging to form a homogeneous coated surface [1]. Initially, as water evaporates, the dispersed polymer spheres pack closely together due to the decreasing volume and start to deform to fill in void spaces. With sufficient temperature (above the minimum film forming temperature, or MFFT), the spheres coalesce, with the polymer chains interpenetrating and forming a continuous film [1,4,40,48]. It is important to note that this process is specific to dispersed polymer systems, which require spherical particle deformation and coalescence, rather than dissolved polymer systems [40]. These steps are illustrated in **Figure 3**. While the process involved for dispersed systems is more complex, it can be beneficial in tuning film morphology [49]. Different dispersed particles exhibit greatly

varying coalescence behavior, as opposed to dissolved systems, where behavior is nearly uniform [49].

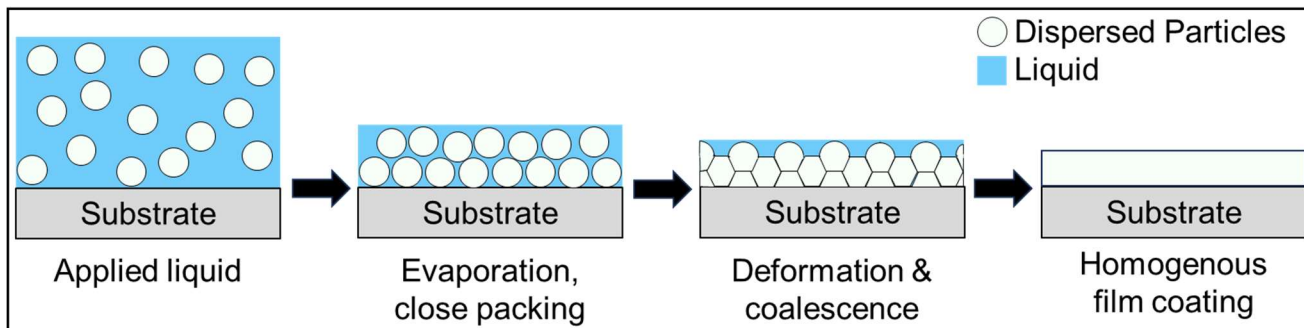


Figure 3. Process of film formation from liquid polymer dispersions

Currently, waterborne dispersions are used in place of solventborne in some of the largest use case coatings industries, including the biggest, architectural applications [14,50]. Advances in waterborne technology have also allowed their use for wood coatings, automotive, and more [51,52]. As the technology continues to advance, replacement of conventional coatings for applications, such as paper packaging [1], availability of water-insoluble polymers like polyhydroxyalkanoates [4], novel applications including smart packaging [53], and stabilization methods such as Pickering emulsions [12] will all continue the expansion of the waterborne coatings industry.

This review chapter sets out to showcase the most recent challenges and developments in waterborne polymer coatings. The latest progress in improvements to stability, breadth of materials, and industrial viability is critically reviewed. As well, current industrial uptake and the future of waterborne system advancement and adoption is thoroughly discussed.

2.2 Established waterborne polymer systems

Waterborne coatings have gained significant traction across various commercial applications, offering a multitude of benefits. They provide grease/moisture barrier properties in packaging products, mitigate moisture and microbial attack in wood finishes, and enhance corrosion resistance in metal substrates. Notably, waterborne coatings constitute the largest global class of coatings [54], and they substantially reduce the volatile organic compounds (VOC) content compared to solventborne coatings, thereby benefiting both workers and the environment [14,38]. Additionally, dispersion coatings can utilize less solid material than dry coating methods like extrusion [4]. Although formulating waterborne coatings to match the stability and performance as conventional coatings presents challenges [46], ongoing advancements are steadily enhancing their efficacy. Consequently, the market adoption of waterborne coatings is projected to continue rising in the foreseeable future [55].

2.2.1 Wood coatings

Uncoated wood, whether indoors or outdoors, is highly vulnerable to environmental damage and degradation. Factors, such as moisture, radiation, microorganisms, temperature variations, mechanical stresses, and chemical exposure can easily compromise its integrity [56,57]. The frequency and intensity of these stressors in a given environment dictate the degree of protection which must be imparted by the selected coating [56]. The biopolymers constituting wood (polysaccharides, lignin, phenolics) are particularly susceptible to degradation caused by ultraviolet (UV) and biological attack [57]. Due to the high incidence

of fungal growth, moisture control is of utmost importance [57,58]. While some wood treatments involve chemical modification of the wood or the addition of fillers, wood coatings remain the standard for providing protection [59,60].

In addition to imparting protection, wood coatings are commonly used to enhance the visual appearance of the product, and must meet consumer expectations in terms of aesthetics [56,61]. This can pose challenges, especially for applications requiring extensive protection, such as exterior products, and even more so when a clearcoat finish is desired to preserve the natural beauty of the wood [61]. Clearcoats typically allow UV transmittance through the coating to the wood substrate, leading to photodegradation and coating delamination [61]. In such cases, the coating alone may not suffice, necessitating the combination with pretreatments or other measures to stabilize the wood [61]. Extensive research has been conducted to develop successful clearcoats that do not require additional treatments, such as using silicone coatings with metal additives. However, the protective and longevity performance of these clearcoats has yet to match that of opaque alternatives [51,61].

In general, waterborne wood coatings for exterior applications are based on polyurethane, acrylic, or alkyd based polymers [51]. Polyurethane coatings exhibit strong weathering and mechanical degradation resistance [51]. Since polyurethane is incompatible with water, various waterborne dispersing methods are employed to generate waterborne systems [62]. Common industrial methods include forming a hydrophilic pre-polymer that is then polymerized in water or conducting the formation in acetone and then transferring to water when removing the acetone [62]. Less commonly, hot-melting or using a ketimine-ketazine

process are reported [62]. Acrylic solutions offer strong UV resistance, dry quickly, and possess good adhesion to wood [51]. However, they may contain micropores, which allow fungal penetration and degradation of the wood, and often require additional measures to prevent fungal growth [51,63]. Acrylic coatings are typically produced through emulsion copolymerization to form a stable colloidal dispersion in water [56]. Lastly, alkyd resins for wood coatings offer distinct benefits, including a glossy appearance and potential for auto-oxidative curing [51]. Alkyd dispersions in water can be formed either via direct emulsification or through phase inversion methods [64].

Alkyd and acrylic resins are often combined to mitigate individual disadvantages, typically utilizing water-soluble alkyds for wood coating applications [51,56]. For interior applications, where the degradative stresses on wood are much lower, protective performance is of reduced concern [44,65]. The same polymers serve as the basis of interior wood waterborne coatings, albeit with simpler formulations required [66]. Multi-coat systems are prevalent, including combinations like acrylic primers and polyurethane top-coating, or hybridized versions thereof [67]. Coating additives encompass components acting as colorants, fillers, thickeners, dispersants, UV absorbers, and more depending on the desired properties [57]. Biopolymers, such as lignin, chitin, and zein all have potential to displace some current conventional wood coatings with biodegradable alternatives [57]. However, material availability, costs, and more complex formulations act as barriers to commercial adoption [68].

Wood coatings are typically applied via spraying, brushing, or dipping methods [58].

Subsequently, the coating undergoes curing, which can involve applying heat to facilitate surface coalescence, using UV light or another reaction initiator when the system is not yet fully polymerized such as some polyurethanes, or drying at ambient conditions [56,62,69]. In addition to these conventional surface coating methods, there are alternative pressurized and non-pressurized methods available for achieving deeper penetration, such as the Bethell process and Gedrian's Bath [58]. However, these methods tend to be costly, and are generally reserved for chemical treatment and nanoparticle impregnation rather than combined with surface coating applications [58].

Unfortunately, waterborne wood coatings still exhibit numerous drawbacks. In exterior applications, water barrier properties are of utmost concern to avoid fungal growth, yet waterborne coatings tend to have higher hydrophilicity than conventional coatings [70]. Conversely, for interior applications, mechanical resistance is the most desired property, and waterborne coatings often fall short [68]. These challenges are further complicated by wood's inherent properties, such as its porosity, which leads to dimensional changes as moisture levels fluctuate. Consequently, coatings must be flexible and possess strong surface adhesion to prevent deterioration and decay over time [58]. Nevertheless, significant strides, including nanoparticle incorporation and other modifications to existing coatings or the development of novel waterborne formulations, have enabled the mitigation of these issues, offering a promising future for the continued utilization of improved waterborne wood coatings [58,68].

2.2.2 Paints

Paints encompass a vast category, characterized by diverse purposes, polymers, substrates, and coating methods. However, their primary function is always to enhance appearance and, in commercial contexts, to provide some level of protection to the underlying substrate [71,72]. Consequently, paints typically contain colorants alongside polymeric resin and other additives [72–74]. Architectural paints dominate market segment size, comprising over 50% of worldwide volume, and include both indoor and outdoor paints with ~75% of the coatings being waterborne [52,54,75]. Other significant applications include automotive, coil, and marine coatings, all of which are discussed in this work. Although numerous additional paint applications exist, such as toys and home appliances, they occupy smaller market shares and research interests, often exhibiting substantial technological overlap with the aforementioned segments [76]. For many years, the paint industry raised environmental and occupational concerns due to high VOC emissions. However, a combination of innovation and legislation has significantly reduced emissions, favoring lower VOC options like waterborne paints [14,52,77].

2.2.2.1 Automotive paints

Automotive paints represent some of the most complex coatings, with multiple distinct layers required to meet the stringent appearance, lifespan, and environmental resistance requirements which are demanded by consumers [73,78]. Automotive coatings are highly competitive among companies with consumers holding high expectations, and having been

subject to substantial environmental and worker safety regulations [54,79–81]. These factors have contributed to automotive coatings having substantial significance to the overall coatings industry (outsized beyond market share) as it has been involved in many industry innovations, from formulations to application methods [78,80]. Relevant to this work, waterborne exterior automotive paints began to be introduced in the 1980s for basecoats, with waterborne primer and clearcoats following in the 1990s [52].

Broadly, automotive coatings can be divided into exterior and interior applications, with exterior coatings necessarily undergoing much greater environmental stress [73]. Exterior metal automotive parts involve multiple layers of coating, including an initial corrosion resistant layer known as the electrodeposition coat (E-coat), followed by a primer, basecoat, and a clearcoat, applied in this order, as shown in **Figure 4** [54,82].

Dry thickness (μm)	Name	Purpose	Waterborne Market share
40–50	Clearcoat	Appearance protection, gloss	<1%
10–30	Basecoat	Color and effect	>80%
25–40	Primer	Bind E-Coat to Basecoat	>10%
20	E-Coat	Corrosion protection	100%
Pre-treated substrate			

Figure 4. Layers of a typical automotive exterior paint stack, with estimates of global waterborne market share within each standard automotive exterior coating layer [52,79,82–85]

Additional coating layers are also applied to areas for specific purposes, such as anti-chip coatings on the hood and lower body between the e-coat and primer layers, and additional rustproofing and sound deadening of the underbody [78]. Exterior plastic parts, such as bumpers and mirror shells, are frequently coated to match the appearance of their metallic counterparts, and can be coated independently of the metal components (offline), or mounted and then metal and plastic parts coated all at once (inline / online depending on at which layer the plastic and metal components are combined) [86]. In either case, the basecoat and clearcoat products are identical, as is the application equipment, such that the components

appear identical [86]. Rather, the primary difference between components is in the primer layers and initial treatment steps. For electrostatic basecoats (uncommon) only, an offline or inline (mounted after E-coating) plastic component must be coated with an electrically conductive primer or have electrical conductivity integrated into the substrate [86]. Online coated systems (mounted prior to pretreatment) must be capable of withstanding temperatures of 160–190 °C used for E-coat drying, limiting some plastics from being mounted early in the process [86,87]. While not itself a layer, there is also an initial pretreatment step. Pretreatment ensures that the surface is smooth and free of contaminants and dust, and possesses desired surface energy and tension, allowing for better coating adhesion and smooth film formation [86,88]. Pretreatment requirements are even more stringent when waterborne coatings are involved, with the current industry standard being a multi-zone water power wash and dry to avoid the introduction of organic solvents [78,86,89]. For plastic components, the pre-treatment stage may also include the use of an adhesion promoting layer, as coating adhesion is frequently the most challenging part of using coated plastic components [87].

Electrodeposition coat (E-coat)

Following pretreatment, the first coating layer applied is designed to provide corrosion resistance and is known as the electrodeposition coat or E-coat [78]. Modern E-coats overwhelmingly provide protection via barrier properties (as opposed to sacrificial or inhibitor coatings) whereby the coating blocks water, salt, and oxygen from reaching the underlying metal surface [90]. This layer also serves to enhance chip-resistance and

contributes to the overall durability of the coating stack, often working in conjunction with the primer [79,90]. Initially, anodic electrodeposition was used for coating application, but modern processes overwhelmingly use cathodic electrodeposition whereby the metal is negatively charged and the paint is positively charged [78]. The coating is applied via a dip tank, for which the car body passes through a tank (~90 °F) containing majority deionized water (80-90%), paint solids (10-20%), and some solvent [78]. The car body then enters a bake oven at 160-190 °C for 10 minutes to allow evaporation, crosslinking, and uniform film formation [78,86,87]. Solvent content is very low, below 0.5%, thus this layer is typically considered environmentally friendly from an emissions perspective [78,90]. Final coated thicknesses are around 20 μm , with the process standardized and highly reliable to the point where many manufacturers have only a single electrocoating tank / line feeding all further downstream coating lines [90]. A further benefit of the dip tank method is that internal surfaces which would otherwise be difficult to reach are also coated [78,91]. These tanks are very large, with a material turnover rate (theoretical rate of tank contents by feed material) of two weeks to six months [90].

The paint solids makeup is typical of a waterborne paint, being majority (70%) comprised of a waterborne resin and a cross-linker, with the remainder being pigment grinding and stabilizing resin, pigments, and extenders and additives, such as dispersants, stabilizers, and cross-linking catalysts [90]. The resin composition is typically an epoxy blend (such as bis-phenol) which further incorporates polyesters, polyacrylates, and polyurethanes, with rubber also occasionally included to further improve energy absorption and thus chip resistance

[90,92–96]. While any crosslinking functional group could be used, for best solubility and consistent film formation, primary amine substitution is highly preferential [90,92].

Similarly, many crosslinking agents are available, however modified polyisocyanates are currently heavily favored by industry due to their high reactivity and capability to fine-tune final film properties [92,97]. Automotive Original Equipment Manufacturer (OEM) coating is oligopolistic, with BASF, PPG, and Axalta (Dupont pre-2013 [98–100]) providing nearly all exterior coatings, and with these products highly engineered specifically for automotive applications [52].

For E-coating, their respective products are CathoGuard® (BASF), ENVIRO-PRIME® & POWERCRON® (PPG), and AquaEC™ (Axalta) [101–103]. The chemical reactions at the electrodes produce oxygen and hydrogen, which can present as bubbles in the film if the bath and / or drying temperatures are insufficient to allow for their release [90]. Other common defects include craters, pinholes, boil outs, hash marks, and “water spots”, which can be removed by sanding [78,90]. Overall, drawbacks to the waterborne approach currently employed are relatively few. Among these, the primary issues are preventing bacterial growth in the large open water tanks used for coating, the necessity and intensity of the pretreatment steps, and the high energy associated with baking the E-coat layer [79,90,92]. As the percentage of metal components replaced with polymer composites as the substrate for exterior automotive applications continues to grow, the demand for and purpose of this layer may change significantly [78,87].

Primer

A primer (or primer surfacer) is the next layer applied, and primarily serves to ensure a high-quality bond between the E-coat and the topcoat (basecoat + clearcoat) [104]. Secondly, the primer acts as another layer of chip resistance, and enhances the overall paint appearance by providing a smooth coating surface for finishing [78]. Lastly, the primer acts to block UV from reaching and delaminating the E-coat, as the topcoat thicknesses and compositions are usually insufficient for this purpose due to the focus being on final appearance [104].

Solventborne, waterborne, and powder primers are available, with solventborne still dominant worldwide but with waterborne standard in Europe and powders heavily used in the United States, due to stricter environmental and safety regulations in these markets phasing out solventborne options [96,104]. Regardless of format, the polymer content is usually acrylic, polyurethane, or polyester crosslinked with alkyoxylated melamine [91]. Powders have the advantages over waterborne of having near zero volatile content, as well as waste from overspray being able to be recycled [81]. On the other hand, waterborne systems are more easily retrofitted into existing manufacturing plants [105], as well as having thinner films and lower material usage [81]. Color of the primer is chosen to roughly match the color of the basecoat, such that a chip which penetrates to the primer is less visible [91,106]. Depending on the type of primer and application method, typical thicknesses range from 25–40 μm [79,91].

Recently, there have been successful efforts to remove the primer layer entirely by shifting its responsibilities to other layers. Beyond material savings and emission reductions from the

coating layer itself, this has the further benefit of reducing the number of “bakes” or curing steps which occurs from the current standard of 3 bakes down to 2. Note that despite 4 layers, there are only 3 bakes since with the standard process the topcoat consisting of base and clearcoats is always applied wet-on-wet then cured with a single bake [107]. The standard 4-coat-3-bake (4C3B) process as well as primerless deviations is shown in **Figure 5**. There would be substantial environmental benefit from development of widely applicable waterborne systems requiring fewer coating and baking steps [107].

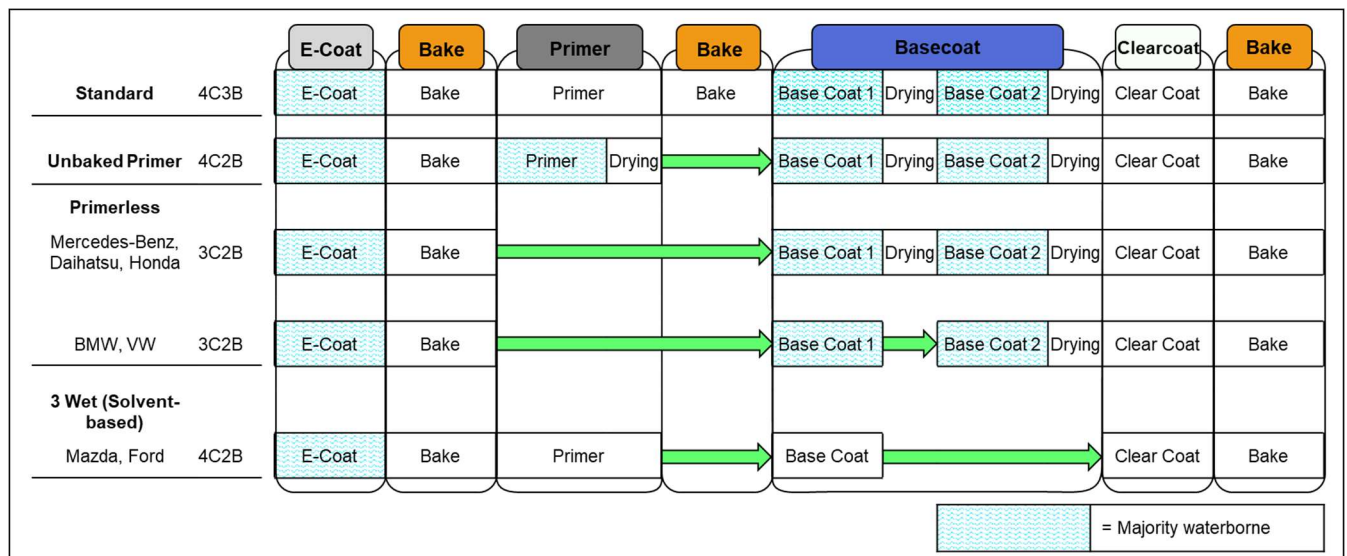


Figure 5. Standard automotive coating process and variations thereof. Steps where waterborne coatings are the dominant choice are highlighted.

A primerless system incorporating isocyanate into the basecoat to impart better chip and UV resistance has been used by Volkswagen (VW) and BMW at various plants in Mexico, Spain, the United States, the United Kingdom, and more [73,108]. Daihatsu and Mercedes-Benz have also used a 3-coat, 2-bake (3C2B) which retains drying between layers, while Mazda and Ford have employed a 4C2B solventborne system retaining the primer where each layer is

applied wet-on-wet [81]. However, these methods described have not gained worldwide adoption as they generally sacrifice the majority of the chip and UV resistance aspects imparted by the conventional primer and are thus ill-suited for high corrosion risk geographic areas, as well as having a lower lifespan before UV-caused delamination will occur [96]. As such, while as much as 50% of vehicles in economically developing regions are made without the primer layer for cost purposes [73], the focus here is on waterborne primerless systems which can compete with conventional systems in terms of performance. More recently, Honda has introduced a 3C2B system to a plant in Brazil, in which two waterborne basecoats and clearcoat are all applied and then cured in a single bake [96,107]. This method retains the increased durability and quality imparted by the primer layer, but shifts the responsibility to the first basecoat layer [96]. Defect control also becomes more difficult as the three successive waterborne layers compounds the risks of popping and sagging occurring [96]. In the standard process depicted in **Figure 5**, basecoat 1 and basecoat 2 are the same coating just applied multiple times (e.g. 2x with bell applicators or bell followed by pneumatic spray) [73]. As a result, the Honda process does have four formulaically distinct coatings similar to the standard process [96]. Further, the responsibilities of the standard primer have been shifted nearly exclusively to the new basecoat 1 layer, while conventional basecoat responsibility for color development is now solely provided by basecoat 2 [107]. Therefore, the distinction between the primer in the standard process and basecoat 1 employed in the Honda process is not clear, and the author feels the Honda process could fairly be regarded as a 4C2B system with a single-application basecoat replacing the

conventionally double-applied basecoat. Regardless, it should be recognized that the Honda technology depicted in **Figure 5** is distinct from that of Mercedes-Benz and Daihatsu, as while the process steps are the same the more recent Honda technology incorporates greater vehicle protection measures [107]. Similarly, the BMW process listed works similarly to that of Honda, shifting the responsibilities of the primer to a new basecoat 1 distinct from basecoat 2, making it also effectively a 4C2B system [108]. Also, the numbering conventions differ between publications and manufacturers, likely in part due to it being beneficial to claim any reduction in the number of coats or bakes. There are also references to 3C1B systems which ignore the 1C1B aspect of the initial E-coat, however in this paper that is always counted as a discrete step [109].

Toyota has also published research into applying the primer, basecoat, and clearcoat followed by a single bake for the three layers [109]. Toyota notes that the appearance of the single bake systems is conventionally inferior to that of the traditional 4C3B system, and so has been confined largely to economy-class vehicles [109]. To improve surface smoothness of the basecoat (and thus the basecoat / clearcoat interface) as well as the final coating appearance and quality, the glass transition temperature (T_g) of the acrylic resin should be reduced, and melamine substituted with an isocyanate hardener [109].

Basecoat

The main purpose of the basecoat is to provide the desired color and visual appearance effects to the vehicle [79,110]. Because of the high quantity of pigments and additives, basecoats are the most expensive layer in the vehicle paint stack [91]. Basecoats typically

have a thickness of 10–20 μm [79,91]. However, the thickness is dependent on the colour and incorporated effects, and how well they exhibit black-white hiding [73]. Silver and white tend to be thinner, while chromatics such as red may be as high as 30 μm [73]. Monocoat systems (single topcoat layer rather than separate basecoat and clearcoat) were the standard until 1970, and remain available in limited capacity [73,111,112]. However, they have been phased out in North America and other markets where the improved durability and appearance of the 2C1B topcoat outweighs the increase in cost [73,113].

White is by far the most popular color worldwide as it was utilized for 35% of new vehicles in 2021, the locally leading color in nine out of 10 identified major market regions, and the global lead for the past eleven years [114,115]. Despite this, white's share has been slowly declining as chromatic (non- white, black, gray, or silver) colors have increased in popularity, albeit still representing <20% of the market [114,115]. Black and gray tie for 2nd place with 19% each, with the only market where white is not in 1st place being Europe, where it is in 2nd place behind gray; at 27% for gray and 23% for white [114]. It should be noted that the large coating companies, BASF and Axalta, both classify silver as a separate category from gray; at nearly 10% of new global vehicles the combination of silver and gray would be solidly above black for 2nd place, although black retains an outsized share in the luxury vehicle segment [114,115]. While white leads in nearly all regions, its largest lead is also home to the highest automotive production volume, with just under 50% of vehicles in Asian regions having white coatings [114,115]. TiO_2 (titanium white) is overwhelmingly used as the white pigment, both for automotive and other applications, and in fact nearly 95%

of global titanium production is for titanium white [73,116,117]. However, due to photocatalytic degradation caused by unmodified TiO_2 , the TiO_2 particles are coated with layers of both SiO_2 and AlO_3 to prevent photooxidation of the coating matrix [73,118]. There are over 40,000 distinct automotive base coatings which have appeared on the market, with over 1,000 released annually [73]. The color and desired visual effect largely impacts the selection of pigments and additives rather than the resin, with insoluble pigments as opposed to soluble dyes being overwhelmingly chosen for automotive applications due to their superior lightfastness [73].

Waterborne basecoats use an acrylic and/or polyester as the main binder, as a partially cross-linked core shell emulsified polymer [73,91]. Co-binders are additional polyesters or polyurethanes, while melamine provides more cross-linking upon baking [73,91]. Shear-thinning behavior is critical (as with most paints), and for waterborne basecoats this is generally achieved by incorporating silicates [73,119]. Thixotropic behavior not only prevents defects, such as sagging, but is also necessary for proper flake orientation during drying (also aided by high volume shrinkage caused by the evaporation), and preventing settling in supply tanks [73,91,120]. However, the low-shear viscosity cannot be too high or else proper levelling of the film will not occur, so the choice and quantity of additives must be done with great care [120]. Solid basecoats can be applied as a single coat, while more complex paint effects, such as metallic paints require two coats to properly achieve the desired visual effect [81]. In the past 10 years, waterborne basecoats have overtaken solventborne options within major markets, driven by environmental regulations [121–123].

Waterborne basecoats remain a significant source of emissions, as VOC content is typically still 10–15% [73,79,124]. While the shift to waterborne paints (and other improvements) has cut automotive VOC emissions to less than 10% of the level seen in the 1970's, development of waterborne basecoats without the need for an appreciable VOC content is critical to eliminating remaining emissions [79].

Clearcoat

Clearcoats are the final layer applied, and act to both protect the appearance of the vehicle and impart a glossy visual effect [91,110]. Typical thicknesses are 40–50 μm , applied via spraying [79,91]. The clearcoat is applied directly onto the basecoat, without an intermediary baking step [91]. However, there is a brief drying / flashing stage which dries the basecoat to be as high as 90% solids content [79,85].

The clearcoat must be durable against multiple adverse conditions, including temperature, UV, abrasion, impacts, airborne pollutants, and acid rain [91,125]. As a result, durable resins must be chosen, and all formulations include ultraviolet light absorbers (UVAs) and hindered amine light stabilizers (HALS) to assist with longevity [91]. Waterborne clearcoats generally use polyester-acrylate resin which is crosslinked with melamine and/or blocked isocyanate [73,126]. Since the late 1990s, top clearcoats have employed nanosilica to improve scratch resistance and gloss retention [82].

While waterborne clearcoats were first available in 1990, as of 2008 they constituted <1% of the global clearcoat market, and remain similarly low today [73]. Instead, solventborne

clearcoating remains dominant, with powder coating capturing a small (<5%) portion, but edging out waterborne coatings as the environmentally friendly clearcoat option chosen by industry [73,85]. Isocyanate is difficult to incorporate into waterborne systems without incurring unwanted reactions or extremely short pot life, and has been among the key limitations on waterborne clearcoat development [127,128]. The high thickness of the clearcoat layer has been noted as another key issue, as a waterborne clearcoat will then require substantial energy and time for evaporation, as well as increased risk of improper curing [129,130]. Despite this, waterborne clearcoats are available on the market, and see moderate adoption in the refinishing segment [129,131]. However, regardless of whether waterborne or powder clearcoats are chosen, widespread OEM adoption will only occur if forcibly imposed via stricter emission regulations [123,129].

Automotive interiors

Interior automotive surfaces employ a variety of coatings to bestow specific appearances and textures, as well as improve durability [54]. Waterborne polyurethane (WPU) is the most employed, being used for synthetic leather surfaces, nonwoven fiber protection, and as a clear coating [22,132]. WPU is also extensively employed throughout other parts of automobiles, for example as adhesives and foams [133]. As a coating, WPU is known to provide excellent mechanical properties, as well as vital resistance to UV and weatherability [132]. Coated fibers such as those constituting floor mats are dip coated, while synthetic leathers are coated then dried (and surface coagulated) via a variety of proprietary methods such as applying acids or heat depending on the formulation and desired appearance

[22,134]. The microsphere structure of the resulting surface plays a strong role in the resulting appearance, with a smoother surface appearing glossier while a rougher surface appears matte (approximately linear relationship) [22,135–137]. Control of the surface morphology can be performed through control of crosslinking, such as through additives, as crosslinking increases roughness and thus decreases gloss, and vice versa [22,26]. Surface heterogeneity also plays a large role in gloss determination [138]. For automotive leathers, the WPU chosen is generally based on an aliphatic diisocyanate for superior long-term durability [139]. The selection of polyol (WPU's are obtained by reaction of polyol and diisocyanate) is more varied depending on the specific desired effects, with polyester, acrylic, polyether, and polycarbonate-based polyols all seeing use [139,140]. The surface coating will also incorporate acrylic emulsions, as well as typical additives such as pigments and rheological modifiers [139]. These WPU synthetic leather surfaces are also used for other products, such as furniture, clothing, and accessories, however the high weatherability and durability requirements for automotive applications makes the application of particular interest, as successful coatings can then generally be applied to other products with lesser requirements [22].

Other waterborne automotive coatings

There is interest in converting the remaining solventborne coatings still in use to waterborne counterparts, such as for engine coatings [141]. As well, there is continued innovative improvement of systems such as waterborne flaky aluminum pigments in order to suppress existing issues with corrosion (novel double-layered surface decoration) [142], addition of

nanoparticles to existing dispersions for improved performance [143,144], improvement of WPU self-healing properties [145], and invention of smart coatings which can react to varied environmental stimuli [78]. Lastly, it should be noted as well that the information presented is specifically for OEM coatings rather than refinish coatings unless otherwise specified. Refinish coatings must cure at temperatures between ambient and 60 °C, and do not have access to intensive coating processes, making waterborne applications inconsistent and expensive [123,127,146,147]. As a result, while the polymer composition of the coatings remains very similar, resin with a lower glass transition temperature may be used in order to achieve better curing [146]. Waterborne refinishing coatings are therefore much tougher to formulate as faster-drying coatings and therefore lower boiling point solvents are more desirable [146]. With that in mind, automotive refinishing shops are aware of the benefits to worker health in using waterborne coatings over solventborne, and have been seen to voluntarily switch to waterborne as they have been made more readily available [148]. As painting currently consumes 30-50% of the total energy input to the automotive manufacturing process, development of waterborne coatings which can be cured at lower temperatures would result in enormous energy savings, compounding their environmental returns [79,107].

2.2.2.2 Coil coatings

Coil coatings have the primary purpose of imparting corrosion protection to metal, particularly aluminum and steel [54]. The metal comes uncoated as coils, is unrolled and coated, then rerolled or immediately formed into the final product [54,75]. Since the coating

is applied to flat metal sheets and then formed, the coating must be highly flexible such that tight bends can be achieved without cracking or delamination [75]. As well, as mentioned, the coating must be highly corrosion resistant, have weatherability resistance for outdoor applications, and be durable [75].

Unlike architectural coatings where waterborne coatings are the majority, for coil coatings waterborne adoption is still extremely limited (<1% of market) due to relatively poor performance and higher costs, as well as operational difficulties [54,75,149,150]. The few industrial systems which do exist employ acrylic or acrylate-epoxy hybrid dispersions [54,151]. Solventborne coil coatings are conventionally polyesters (frequently siliconized), polyvinylidene fluoride (PVDF), polyvinyl chloride (PVC), and polyurethanes [54,75,150]. Each of these polymers with the exception of PVC has seen successful waterborne formulations for coil coating at lab-scale [54,149,150]. It is important to note as well that the coating performed while the sheet is flattened involves multiple stages and coatings, along with pretreatment. There is frequently a primer / basecoat as well as the topcoat, so ideally the entire system must be changed to be waterborne, increasing complexity [54]. The waterborne coatings are applied in the same manner as solventborne coil coatings, primarily via continuous rollers [54,75]. However, solventborne coil coatings are also occasionally coated using electrostatic high-speed discs [75].

2.2.2.3 Architectural

Architectural coatings are by far the largest coatings market segment, by both revenue and product volume [14,50]. Architectural coatings encompass both indoor and outdoor coatings

(especially paints) which improve the appearance of our buildings, while also providing environmental protection to the underlying substrate [72,152,153]. Waterborne coatings make up over 70% of the global architectural coatings market, driven by being the standard for interiors (the largest subsegment) [54]. Current interior architectural coatings have very low of zero VOC content [48]. While waterborne interior coatings have been available for over 60 years [54], waterborne products meeting the more strenuous performance demands of exterior environments has only been met in the past few decades [154]. The higher demands for exterior coatings include resistance to chalking, water absorbance, yellowing, acidity, abrasion, extreme temperatures, and more [152–155].

Currently, waterborne architectural coatings most commonly employ acrylic, styrene-acrylic, alkyd (hybridized, often with styrene/acrylic), polyvinyl acetate, or polyurethane polymer dispersions, with silicones occasionally added [154–159]. 5–35% of the waterborne paint is the resin by volume [72]. Pigment, extenders, surfactants, and rheology modifiers are also nearly always present in the formulation while UV absorbers, dispersants, biocides, defoamers, adhesion promoters, slip agents, and more are added as desired for the specific application [72,152]. Rheological behavior of architectural coatings is critical, as they are generally applied relatively thickly (brush / roller as opposed to spray etc.) to vertical surfaces and then dried at ambient conditions [54,72]. A general guide to the desired magnitude of shear thinning is provided in **Figure 6** [72]. As waterborne formulations are typically known for having low viscosity, without addition of a thickener the paint will be prone to issues, such as runs, drips, and sags [72]. Associative and cellulosic thickeners are

the most common thickeners for waterborne architectural coatings [54]. Due to the number of components in the formulation, the rheological characteristics are quite complex and thus formulations cannot be made via modelling alone [72]. Alongside the rheological modifier additive, the polymer particle size (smaller=more viscous) [42], the surfactant, and polymer volumetric concentrations majorly influence the resultant behavior, while factors such as the pigment have a much smaller effect [72].

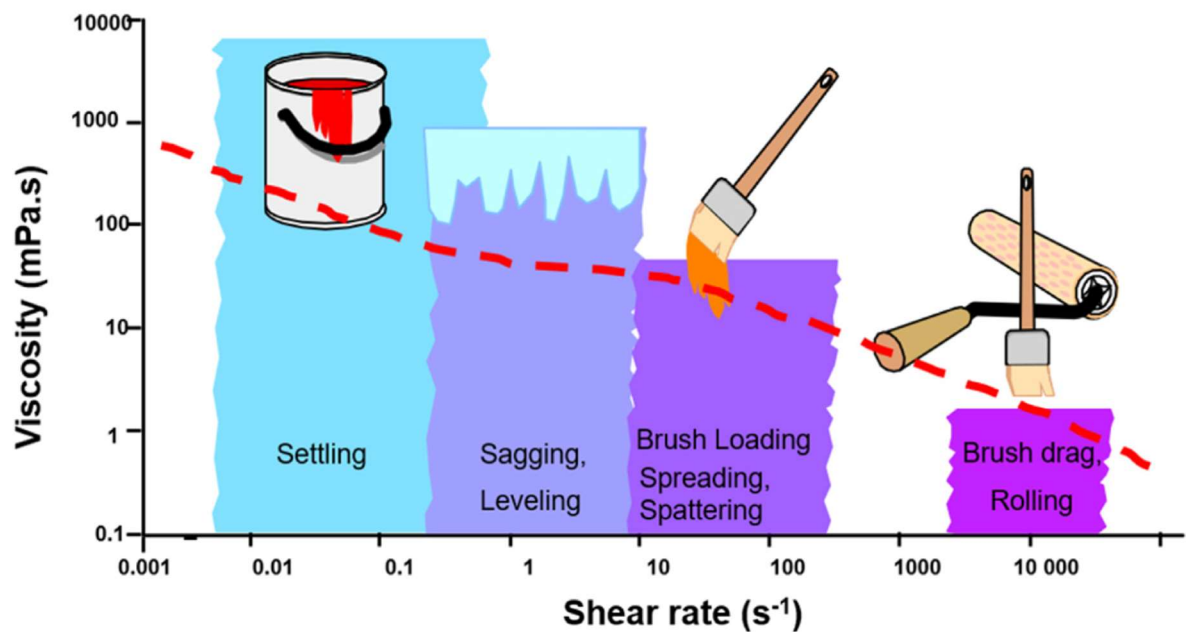


Figure 6. Desired relationship between viscosity, shear rate, and paint properties. Reproduced from Ref. [72] with permission of Elsevier © 2022

Continued innovation in waterborne architectural coatings includes complementation of a broader range of substrates (wood, stone, etc.) [152,153], better waterproofing lifespan for high demand applications such as roof sealing [156], and nanoparticle additives for improved properties, such as dirt resistance and antibacterial activity [160–162]. As the architectural coating market continues to expand and with waterborne architectural coatings continuing to

be the dominant option, further research and sustainability regulations may allow further advances, such as bio-renewable and biodegradable resins to become economically viable [48,77]. In the meantime, the very low VOC content of current architectural coatings acts as a goal for other industries still primarily using solventborne coatings [77].

2.2.2.4 Marine

For marine coatings, the most important aspects are corrosion resistance and anti-biofouling properties [54,163]. Biofouling of large ships can lead to fuel cost increases of over 40%, as well as other issues such as introduction of invasive species [164,165]. For anti-biofouling, there are two classes of coating in this space: self-polishing antifouling coatings and foul-release coatings [54,164]. Self-polishing marine coatings employ a biocide which is soluble or reactive with the water, and thus is gradually stripped off over time maintaining a relatively smooth surface [54,164]. The vast majority of these paints were acrylics incorporating tributyltin (TBT) until TBT was banned worldwide in 2008 due to its harmful environmental effects [164,165]. Now, other organometal biocides, primarily copper pyrithione (CuPT), are used, despite persisting environmental concerns [164].

Foul-release coatings are the primary alternative, using an ultra-smooth surface to stop adhesion of microorganisms to the surface [54]. Fluoropolymers and siloxanes, such as polydimethylsiloxane (PDMS), are incorporated into polymeric materials including waterborne polyurethane (WPU) [54,166]. While the PDMS provides the smooth surface, the WPU promotes substrate adhesion, has low cost, and during drying allows for migration of siloxane groups to the surface [54]. Ideally, foul-release coatings would be so smooth that

initial adhesion to the surface is halted. However, there is still some adhesion to foul-release coatings in practice [166]. Nevertheless, these adhered fouling organisms can be removed easily during cleaning [166]. As a result, this has not been a significant barrier to adoption, and adoption of foul release coatings increased from less than 1% of the market in 2009 to over 10% in 2014 [164]. The largest barrier to further increase is the high cost and requirement for frequent re-application, which can be over 100 USD/L for material alone. While such cost can be justifiable for large commercial boats spending millions on fuel per year, it is exorbitant for the recreational vessels constituting 20% of the market [164]. The other key issue with foul-release coatings is that they usually require a high amount of ship movement to effectively prevent adhesion; as a result, they are ineffective for many vessels and temporary underwater structures which remain stationary for extended periods of time [164,166]. In fact, some shipping companies that committed to adopting foul-release coatings after the 2008 ban on TBT later switched back to biocidal copper paints, such as Maersk in 2012, due to poor foul-release coating performance [164].

Some coatings newer to the market look to combine the benefits of both antifouling and foul release coatings, or otherwise improve upon the performance of siloxane-based foul release coatings. Sol-gel coatings are available which allow for extremely smooth surface finishes further hindering initial adhesion of fouling agents, allowing effective fouling prevention even for vessels at rest [164]. Other coatings employ microencapsulated biocides, which are slow-released leading to over 95% lower biocide emitted than with the traditionally water-soluble biocides [167].

Beyond the antifouling topcoat for components directly submerged in water, the primer and various fillers provide critical corrosion resistance to all marine components. The intensity of required resistance varies greatly depending on multiple factors, such as location on the interior or exterior of the vessel, fresh or salt water, or presence of the marine component in the water splash zone [168,169]. Waterborne primers and top coats based on acrylics, epoxy, and urethanes are employed, mostly for low-corrosion stress applications [168]. High-stress applications, such as ocean-submerged pipelines do not use waterborne coatings as they cannot compete in terms of resistance, durability, or cost [168]. Waterborne styrene-acrylic copolymers are also widely used commercially as metallic substrate primers, and additives such as zinc phosphate are used to promote anticorrosive properties [54,169]. In addition to ship hulls, other immersed metal components, such as pipelines and offshore platforms, require coating for anti-corrosion and biofouling resistance [166,169]. Anti-corrosion coatings are further required for any components exposed atmospherically or periodically to the marine environment, such as shipyards, metallic bridge structures, holds, and other interior areas [163,168,169].

The application and drying process of waterborne marine coatings also causes difficulties. Most shipyard components are coated and dried in the open-air to the detriment of waterborne coatings, which are highly moisture and temperature sensitive for drying [163]. This issue is compounded by the fact that shipyards are by nature generally located in areas of high atmospheric moisture, leading to slow and inconsistent drying [163]. Marine coatings are generally applied via spray, rollers, or brushes [164].

2.2.3 Packaging

Rather than just protecting the substrate, packaging coatings must additionally protect the package contents [170,171]. For food packaging, barrier property performance is critical, protecting contents from moisture and oxygen to preserve freshness [172]. Other products, such as disposable drinking cups, must add a coating to overcome the weak wet strength of paper, which would otherwise tear and fall apart [173]. Packages are frequently comprised of multiple distinct layers and/or use petrochemical-based polymers, making them destined for the landfill, even despite the otherwise biodegradable substrate in the case of paper [2,172]. While extrusion coating and lamination are most common, waterborne dispersion coatings allow for other methods, such as curtain, dip, bar, and roll coatings which have lower film thickness and thus lower dry material usage [2,174]. Packaging comprises a very high percentage of our overall plastic usage, as well as our solid waste [2,175]. As a result, biobased and biodegradable packaging options are heavily researched and factor into consumer decisions and sustainability initiatives [77,176–178].

Unfortunately, existing commercial paper packaging coatings do not extensively employ waterborne technology [174]. There are however a few in limited use, such as acrylic dispersions from BASF (e.g. Joncryl®) and Aquaspersions [179,180]. The implementation of waterborne dispersion coatings for paper packaging is a very promising area of research and is discussed in section **2.3.3**. For now, commercial waterborne packaging coatings are largely confined to the areas of aluminum coatings.

Metal drink can coatings must also protect the drink from obtaining a metallic flavor or

losing its carbonation (if applicable), while also protecting the can from corroding due to the drink acidity [76]. These coatings have been predominantly waterborne now for decades, with epoxy-acrylic copolymers with phenolic or amino crosslinkers being the common basis [76,181]. Originally, toxic bisphenol A (BPA) was used, but is now largely replaced by other bisphenols with lower or unproven toxicity [76,182]. Polyester-based, as well as a bio-based phenol coating derived from cashew shell waste have also been investigated, although the cashew option is not currently waterborne [182,183]. Waterborne varnishes for exterior coating of the metal drink cans has a much lower rate of adoption, but has grown substantially in recent years [184].

2.2.4 Other commercialized coating systems

There remain numerous other commercialized waterborne coatings, which represent smaller markets and may often be considered subsets of the discussed systems due to similarity of the technology [77]. For example, other transportation coatings such as for buses and trains have similar substrate protection and environmental exposure resistance requirements, but with differing cosmetic requirements [185]. As a result, the overall coating system is quite similar, but simplified in terms of layers and additives [185]. Aircraft and automotive refinish paints are also similar to the automotive paints discussed, with different environmental exposure requirements for aircraft and economic considerations for refinish paints [186–188].

Similarly, as touched on earlier there are countless applications for waterborne paints. Toys, agricultural equipment, appliances, helmets, cookware, gym equipment, and road markings

are a few examples which employ waterborne paints in some capacity [14,74,189,190].

Waterborne printing ink has also begun to see market uptake, mainly with waterborne polyurethanes for currently commercialized systems but with some interest in acrylic systems [191–195]. Waterborne polyurethanes are also used in adhesives [62,175], soft-touch materials such as synthetic leather [22], nail enamel [196], textile coatings [197], and more [198]. Waterborne polyurethane / acrylic hybrid systems are often used in these and similar applications where the less expensive acrylic cannot meet performance requirements on its own [194,199].

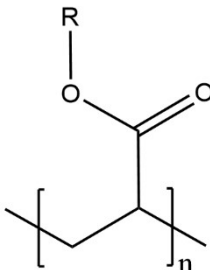
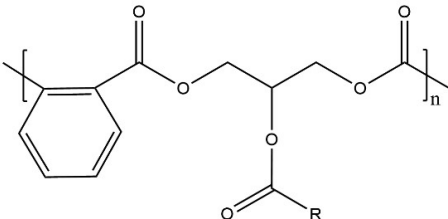
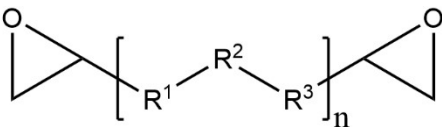
Other commercialized waterborne coating systems using a variety of polymeric systems include seed coatings [200], drug pellet coatings [201], and anti-smudge coatings [202]. Paper coatings for non-packaging purposes comprises applications, such as paperback books [74], playing cards [203], and thermal paper [204]. Emulsified asphalt, especially for the waterproofing layer of pavement structure, commonly employs styrene-butadiene latex but has also been shown to perform well using polyvinyl acetate and waterborne epoxy resin [205,206]. Lastly, polytetrafluoroethylene (PTFE) is used for a myriad of non-stick and non-reactive surfaces and is commonly coated as a waterborne dispersion [207–209]. As stated, this section is not meant to comprise an exhaustive list. Other commercial waterborne coatings exist, and as time passes and new systems are developed or become economically viable this list will continue to grow. The shift to waterborne coatings is already in full swing as solventborne coatings are continually phased out for their more environmentally friendly counterparts [55,77,210].

2.2.5 Overview of commercialized systems

A summary of currently commercialized waterborne polymers is given in **Table 1**, below.

Note that this table is not exhaustive, and only considers the main polymer resins rather than polymeric additives such as bactericides and associative thickeners [211].

Table 1. Commercialized waterborne polymer resins for dispersion coatings

Waterborne Polymer		General Unit Structure	Commercialized Applications	References
Acrylic	Polyacrylate		Wood coating, paint, adhesive, marine	[45,51,67,91,155,168,212]
Alkyd			Wood coating, paint	[51,157,213]
Epoxy	Polyepoxide		Anticorrosion (automotive, marine, aluminum can)	[90,96,168,181]

Polyester		$\left[\text{C}(=\text{O})\text{R}^1\text{C}(=\text{O})\text{O}\text{R}^2\text{O} \right]_n$	Paint	[91,214]
PTFE	Polytetrafluoroethylene	$\left[\text{CF}_2\text{CF}_2 \right]_n$	Non-stick	[207,212]
PU	Polyurethane	$\left[\text{O}\text{R}^1\text{O}\text{C}(=\text{O})\text{NH}\text{R}^2\text{NH}\text{C}(=\text{O}) \right]_n$	Wood coating, paint, synthetic leather, adhesives, marine, ink, nail enamel, textile	[22,51,54,62, 67,91,133,15 6,195– 197,215]

While waterborne polymer coatings overall are on the rise [55,77], they are not without drawbacks hindering their full adoption. Suitable waterborne systems are not currently commercially available for all coating applications, such as paper packaging [174] and some wood products [44,216]. Also, their performance, high drying temperatures, and pot stability makes them inadequate for some applications in their current technological state [40,46]. Lastly, most of the systems do not fully address sustainability concerns. High drying temperatures means high energy usage, there is often still a small amount of organic solvent, and the polymers are often not biobased nor biodegradable [14,23,40,79]. Despite all of this,

waterborne systems have demonstrated success for many applications, while improving safety and environmental characteristics [14,38,198]. As the shortcomings continue to be addressed through advancing research (as discussed in section 2.3.), waterborne polymeric coatings will continue to see increased commercial adoption and success in the foreseeable future.

2.3 The future for waterborne polymer systems

In this section, new developments and trends in waterborne systems are highlighted. A focus is given on progress towards new commercialized systems and improvements to existing systems. New methods of waterborne system formation, materials and additives, and applications are discussed.

2.3.1 New methods of formation and stabilization

As a precursor to new materials being made into stable waterborne dispersions, new methods of formation are necessary to overcome innate hydrophobicity and instability [45,46]. For existing waterborne systems the pot life remains a challenge to overcome, often retaining some level of VOC presence to provide stability and expected functionality [46,54,217].

Perhaps the most exciting trend for formation and stabilization is Pickering emulsions.

Aqueous Pickering emulsions use small solid amphiphilic particles bound irreversibly to the interface between the water and immiscible phases in order to provide stability [218].

Compared to systems stabilized using conventional surfactants, Pickering emulsions can boast reduced toxicity and cost, while greatly increasing stability [218]. Pickering emulsions

have seen an immense increase in research interest over the past 20 years. In 2000, less than 10 papers on the topic were published, in 2010 more than 100, to now over 800 papers published in 2021 [219,220]. Some successful oil-in-water Pickering systems researched for coatings include beeswax stabilized using cellulose nanoparticles for fruit coating [12,221], paraffin stabilized using cellulose nanoparticles for textile thermal regulation [222], and glycidyl methacrylate stabilized with graphene oxide for a self-healing coating [223]. Kalashnikova et al. have produced excellent images showing the Pickering particle coverage of cellulosic nanorods stabilizing the oil/water interface, as shown in **Figure 7** below [19].

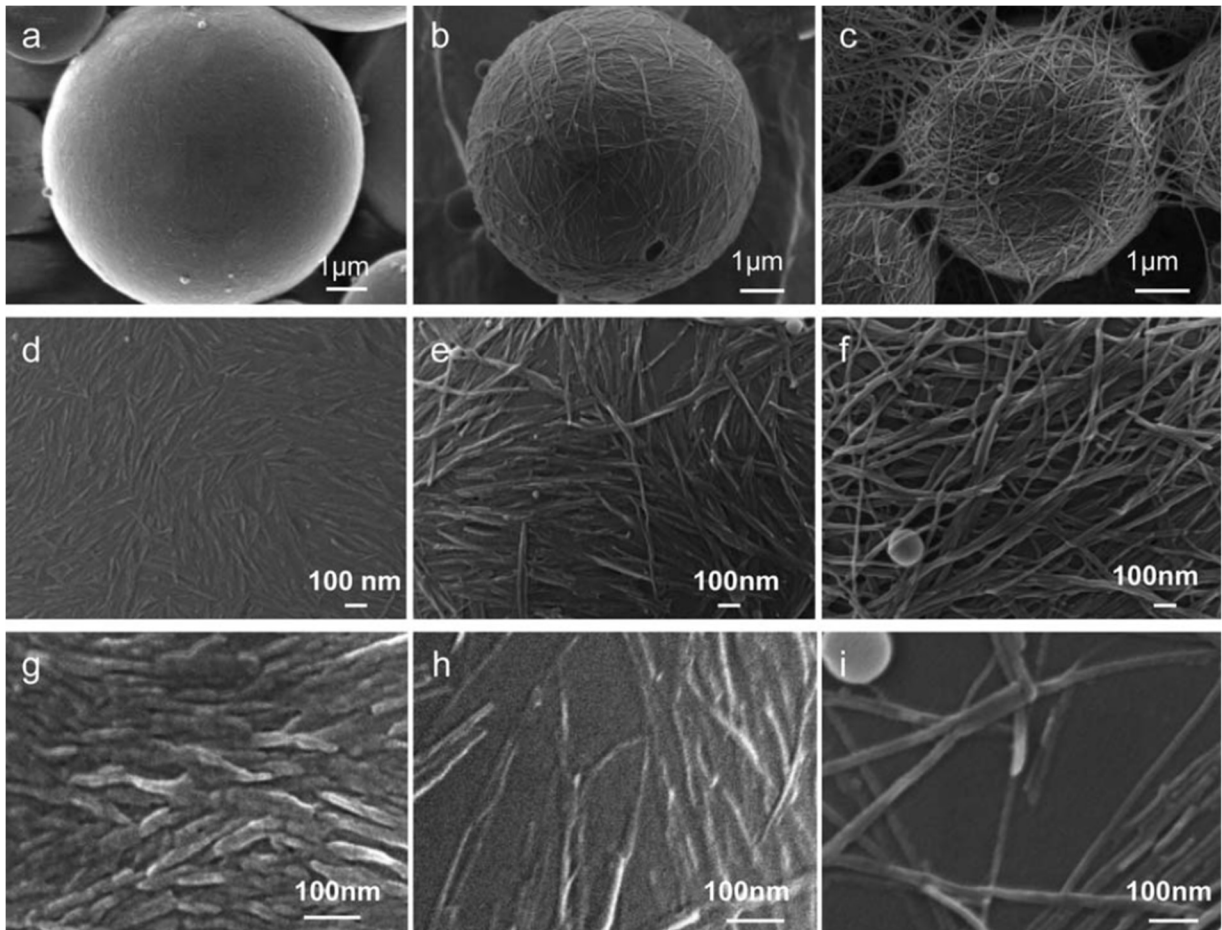


Figure 7. Scanning electron microscopy (SEM) images of polymerized styrene–water Pickering emulsions stabilized by cotton cellulose nanorods (a, d and g), bacterial cellulose nanorods (b, e and h), and *Cladophora* cellulose nanorods (c, f and i) at two different nanocrystal concentrations: 5 g/L (d–f), and 1 g/L (g and h) – revealing the coverage variation as a function of nanocrystal concentration and length. Reproduced from Ref. [19] with permission of The Royal Society of Chemistry © 2013

New methods of formation are continually investigated for reasons. Aims of this research include reduced energy requirements, improved product, allowing new materials, and solvent quantity reduction [16,45,62,224,225]. For waterborne polyurethanes, hot-melt processing and solvent-free condensation polymerization are promising methods of formation, which emit no organic solvent [62,224]. Other methods, such as radical ring-opening polymerization methods are expanding the ability to synthesize degradable polymers [226]. Emulsion polymerization-induced self-assembly mediated by reversible addition-fragmentation chain transfer was recently performed using dibenzo[c,e]oxepane-5-thione to obtain block copolymer nanoparticles directly in water [226]. Lastly, other stabilization methods seeing interest are thickeners [72,227] and the use of copolymers [228].

2.3.2 New trends in waterborne materials and additives

Of particular interest for improving current systems are the utilization of hybrid dispersions and the addition of nanoparticles to bring waterborne dispersion performance closer to that of solventborne [58,62,158]. As well, for new systems, development of waterborne dispersions of biobased and biodegradable polymers is greatly appealing to further reduce the environmental impact of polymer coatings [1].

Hybrid dispersions combine two or more polymers chemically bound together to form an improved product [157,158]. This synergy can lead to superior performance compared to individual polymers alone [158,229–231], or it can maintain performance levels while decreasing the quantity needed of the costlier polymer [194]. Many hybrid systems already see commercial use, such as the alkyd-acrylic architectural paint and acrylic-polyurethane wood coatings discussed earlier [67,157,158]. New hybridized systems include many new acrylic-polyurethane hybrids due to the flexibility of the underlying polymer formulation [194,199]. Current research on hybrid coatings includes the development of a novel one-package (1 K) waterborne non-isocyanate polyurethane-epoxy hybrid [232], improvements to the performance of polyacrylate-polyurethane hybrids [233], and numerous other projects [234–238].

Nanoparticles and other additives are of great interest to improve existing capabilities and introduce new possibilities [58,62,153,165,239–241]. Nanoparticles offer advantages, such as greater effective surface area, high stability in dispersions, and can impart unique properties not possible with conventional particles [58,242]. The possibilities are immense as both organic and inorganic nanomaterials with varying compositions, different morphologies, and more, lead to inexhaustible combinations [3,152,242]. Recently, Vijayan et al embedded ceria-zirconia nanoparticles in waterborne epoxy for marine anti-biofouling, with the antibacterial success shown in **Figure 8f** [165]. Another interesting finding is by Koyuncu et al, incorporating bismuth oxide nanoparticles into waterborne polyurethane textile coatings to provide protection against ionizing radiation, for example as a lightweight X-ray shielding

apron [243]. Incorporation of nanoparticles in waterborne epoxy for a bonded solid lubricating coating [244] and in waterborne polyurethane to improve textile puncture resistance [245] are two additional projects within this immense research space. Novel additives to enhance existing waterborne systems are similarly rife, for example adding engineered polysaccharides to natural rubber latex [246,247] and kaolin to styrene-butadiene latex [248], both to improve barrier property performance. Other additives can be critical to incorporate, such as those discussed earlier including thickeners, pigments, plasticizers, and more [52,57,72]. Of particular interest to the topics discussed in this publication are additives to reduce the drying energy requirements (directly or indirectly, such as initiators to allow photopolymerization) in order to mitigate that key drawback to waterborne systems [249–255].

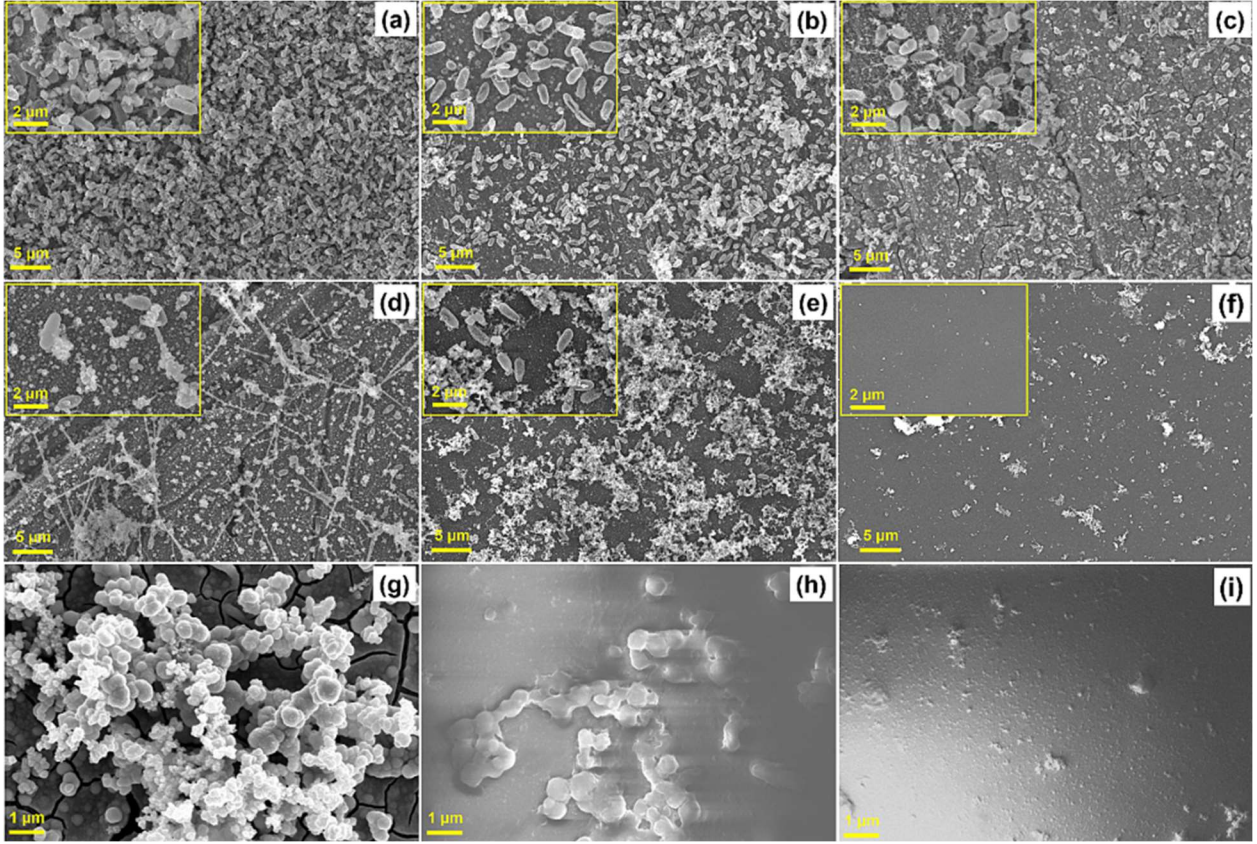


Figure 8. (a–f) SEM images of uncoated control, epoxy coated, and composites coated mild steel surface after treating with bacteria ((a) Control, (b) Epoxy (c) Epoxy and ceria (d) Epoxy with 80:20 polydopamine (PDA):ceria (e) Epoxy with 60:40 ceria:zirconium and (f) Epoxy with 48:32:20 ceria:zirconium:PDA (EPCZ)). (g–i) SEM images of uncoated control, epoxy coated and EPCZ coated mild steel surface after treating with sea water consortium ((a) Control (b) Pure epoxy (c) EPCZ). Reproduced from Ref. [165] with permission of Elsevier © 2024

Regarding development of waterborne dispersions using new polymer resins, there is particular focus on biobased and biodegradable materials to further improve the environmental benefits [23]. Pieters and Mekonnen [23] successfully dispersed the biobased and biodegradable polymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) in water (see Chapter 3). Likewise, Bramhall [4] has dispersed polyhydroxyalkanoates (PHA) in

water using a similar approach. Waterborne dispersions of both poly(lactic acid) (PLA) [1] and poly(butylene succinate) (PBS) [256] have also been reported in the literature. The waterborne PLA development may be of particular interest for practical applicability, as PLA is a mature biopolymer, and the extrusion-coated commercial paperboard products are already widely available [257,258]. Each of these works demonstrated the applicability of waterborne polymer systems on paper substrates for barrier coating purposes, a highly desirable application for waterborne biodegradable coatings as discussed further in section **2.3.3**. Additional newly developed waterborne dispersions include biodegradable polybutylene succinate [256] and biobased carnauba wax [259]. The latter, by Lozhechnikova et al [259], demonstrated applicability as a wood coating for UV exposure as shown in **Figure 9**, as well as other protective properties. Lastly, there has also been substantial work involved in bringing the performance standard of bio-based versions of the existing coatings, for example bio-based waterborne polyurethanes, up to the level of their conventional counterparts [143,198,260,261].

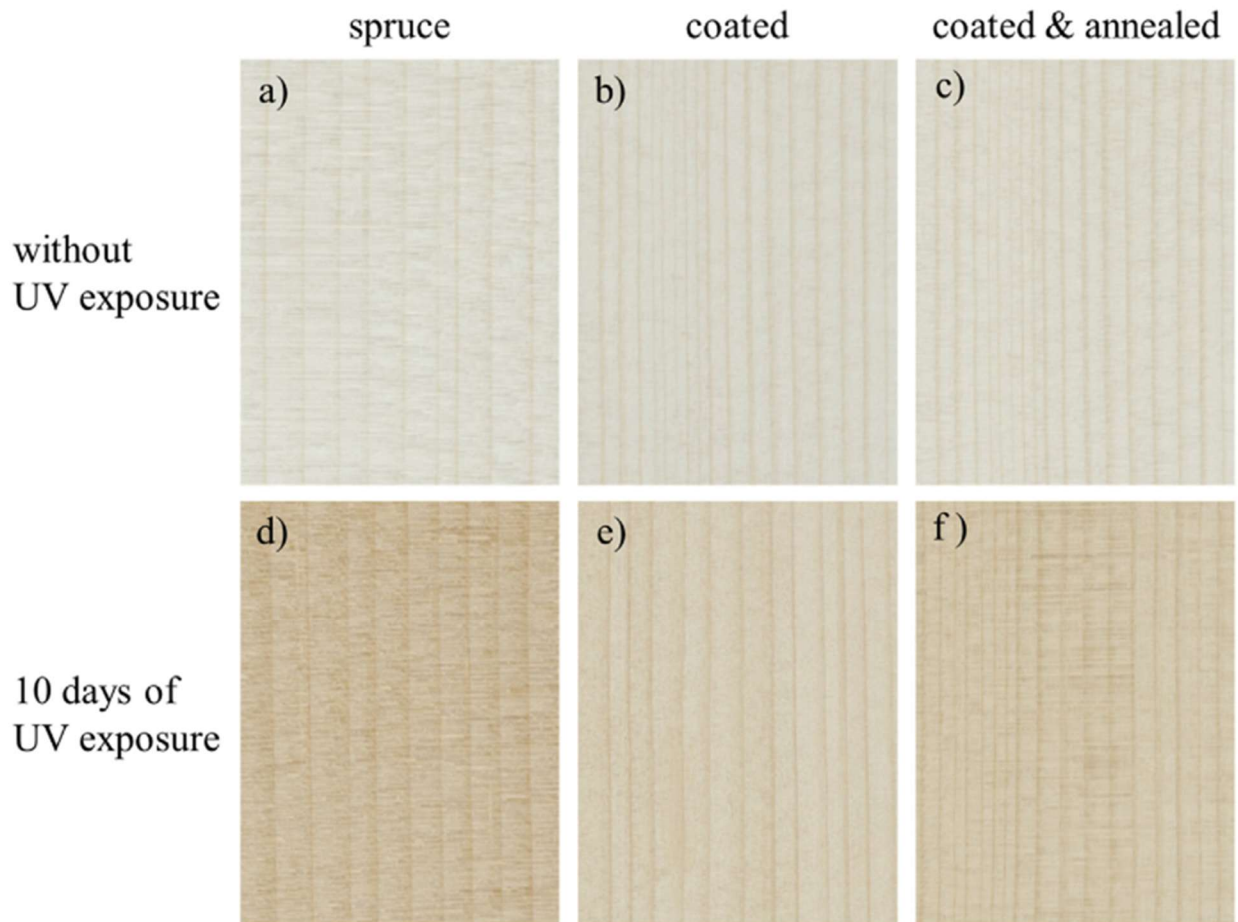


Figure 9. Photographs of original spruce (a), spruce coated with 8 bilayers ZnO/carnauba wax at 10 g/L without (b) and with annealing at 110 °C (c). Spruce (d), spruce coated (e) as well as spruce coated and annealed (f) after UV exposure for 10 days. All photographs were taken with identical camera settings and illumination. Reproduced from Ref. [259] with permission of Elsevier © 2017

2.3.3 New applications for waterborne coatings

Research into new applications for waterborne coatings can be categorized into either replacing an existing coating with more environmentally friendly alternatives or formulating new coating products. For existing applications, packaging is a key target due to the

astronomical amount of waste currently produced [2]. For new applications there is a push towards smart and active materials (including within packaging) which can adapt to and alter the surrounding environment, respectively [29,30]. Also, novel waterborne products such as chip-board coatings and hairspray are undergoing significant developments.

Paper is a very common packaging material due to being printable, biodegradable, biobased, recyclable, low cost, light weight, versatility, and more [2,256,262]. In fact, 30% of global packaging material is paper, behind only plastics (40%), and ahead of aluminum (20%) [2]. Paper's market share for packaging applications is expected to further grow as bans on single-use plastic are implemented [256]. Unfortunately, paper is porous and hydrophilic, resulting in poor barrier properties (gases, water, grease) and inferior wet strength [2,256]. Surface coatings are used to overcome these challenges [2,256]. Current barrier paper coatings use petrochemical derived coatings, which severely limits recycling and inhibits biodegradation [172]. Cost reductions play an essential role for packaging, as they are largely single-use and secondary to the main product contained within [172,263,264]. Dispersion coatings can allow for reduced material usage, reducing cost [174]. Lastly, consumer decisions and government regulations have also promoted shifts to more sustainable packaging options [77,176–178]. As mentioned earlier, there has been experimental success in creating paper packaging with biobased and/or biodegradable waterborne coatings of PLA, PHBV, other PHA's, and PBS, making the introduction of commercialized systems in this area very likely to occur in the near-future [1,4,23,256].

Other packaging products being developed include direct food coatings, smart packaging, and active packaging. Direct food coatings such as waxes can be biobased and edible, while reducing food spoilage through limiting water and gas transfer [12]. The remarkable effectiveness of these systems can be seen in **Figure 10**, in which Trinh et al used an edible Pickering emulsion of beeswax to limit spoilage of strawberries and sliced apples (as shown), as well as bananas [12]. Active packaging employs a multicomponent system, such as encapsulation and embedment in the coating matrix [265]. As an example, Ma et al embedded anti-corrosive agents within a smart pH-responsive capsule in waterborne epoxy for metal coating, with the success shown in **Figure 11** [266]. Importantly, smart packaging improves quality through the incorporation of sensors and indicators [29]. Smart packaging coatings will be similar to active packaging from the perspective of the coating, with the functionality imparted as an addition to or separate component from the primary waterborne coating itself [29,267]. Similarly, functional paints possess additional properties alongside providing protection and improved appearance to the substrate [268]. Self-cleaning, self-healing, antigrffiti, antifouling, and more are possible property additions [268], as is a specific focus on biocidal behavior [269–273]. Some of these are already commercialized for some applications, such as antifouling marine coatings as discussed earlier in this work. However, as these systems are more complex than simple barrier coatings they are currently not in widespread use and will likely see a longer timeframe for market adoption [172].

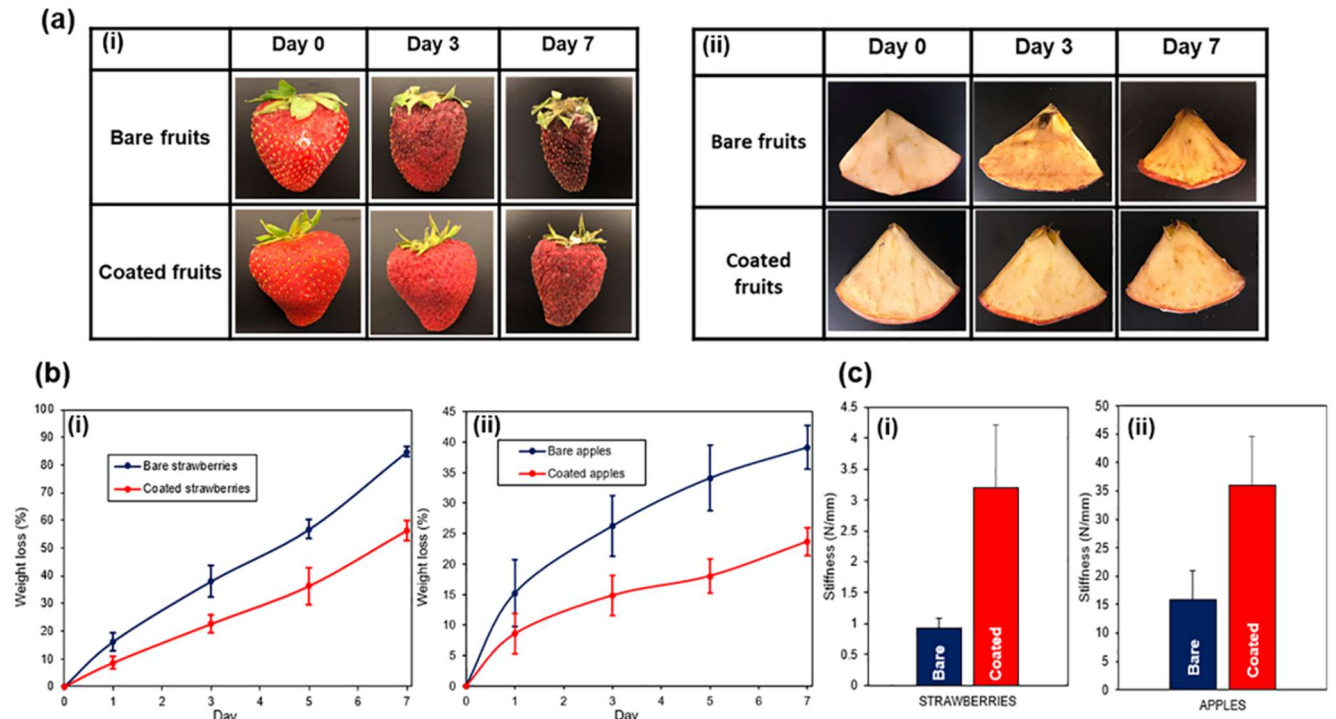


Figure 10. Effect of edible emulsion coatings on strawberries and apples. (a) Time-lapse photographs of bare and coated (i) strawberries and (ii) flesh-cut apples over 7 days. (b) Water weight loss of (i) strawberries and (ii) flesh-cut apples over 7 days, and (c) comparison between stiffness of bare and coated (i) strawberries and (ii) flesh-cut apples. Reproduced from Ref. [12] with permission of Elsevier © 2022

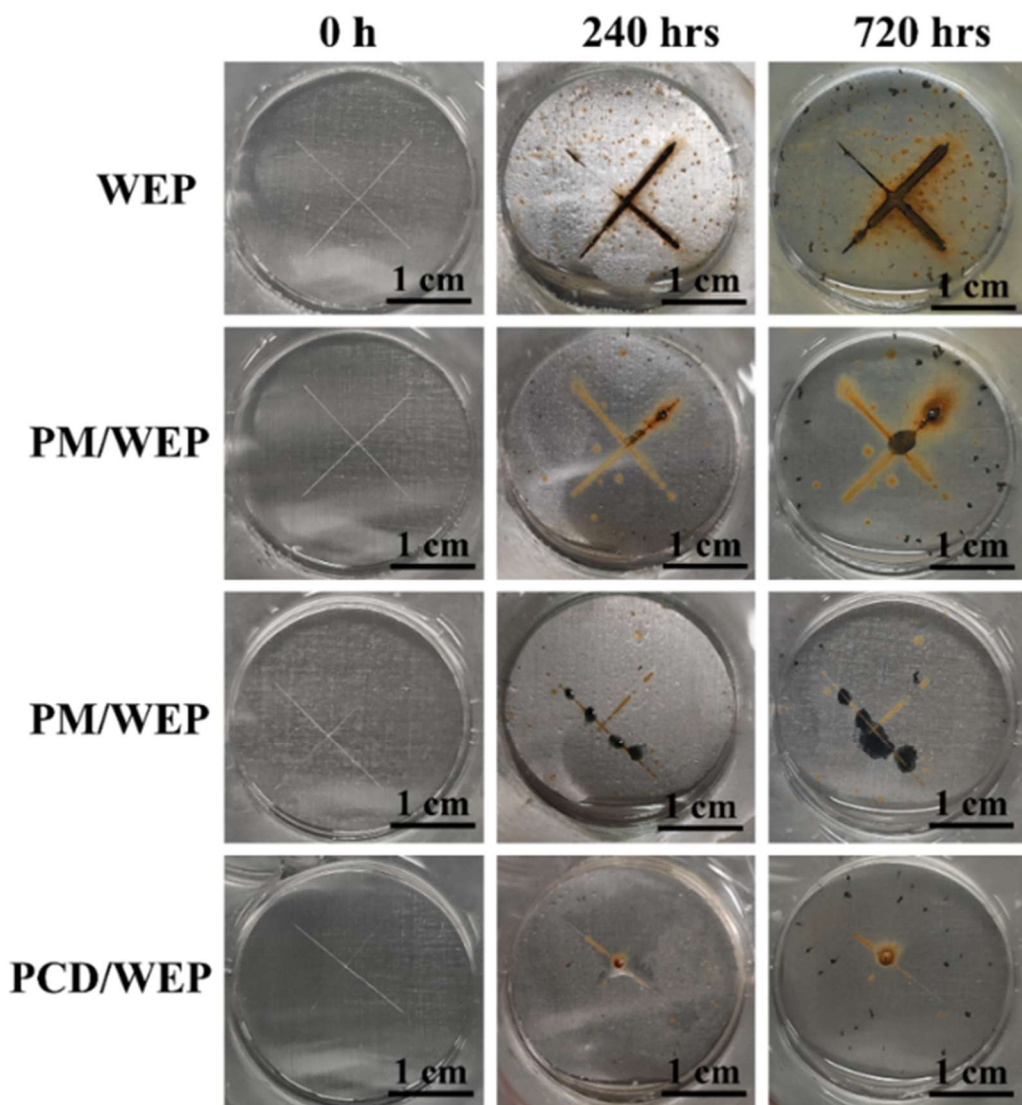


Figure 11. Visual images of blank waterborne epoxy (WEP), melamine phytate/WEP, melamine phytate with Ce(III)/WEP, and melamine phytate with Ce(III) and polydopamine/WEP of the scratch zone at 0, 240 hrs, and 720 hrs immersion stage. The area of the coating exposed to the 3.5 wt.% NaCl solution is 7.07 cm². Reproduced from Ref. [266] with permission of Elsevier © 2022

Many innovative waterborne applications are under ongoing investigation across dissimilar industries. For example, a waterborne acrylic photoresist layer for printed circuit boards has

recently been produced [274]. With the rapidly rising rate of manufacturing printed circuit boards, waterborne coatings to replace the VOC-intensive processes will be an important step to reducing the environmental and safety impacts [274]. Antistatic textile coatings [275], hair-styling products using bio-based waterborne polyurethanes prepared from castor oil [276], and slow release fertilizer coatings [277] are just a few more of the various products currently in development.

2.4 Chapter 2 conclusions

The recent adoption of waterborne systems for commercial coatings marks a promising start to the future of sustainable coatings. These systems have demonstrated broad applicability while enhancing environmental and safety characteristics through a reduction in organic solvent emissions. While hybrid systems employing multiple polymers have been used for years, their recent expanded use presents a promising avenue for potential cost-savings and addressing remaining performance issues. Furthermore, the incorporation of nanoparticles and the use of other novel additives are broadening the scope of possibilities regarding the capability and applicability of waterborne coatings.

Despite the various progresses, challenges persist. Certain systems still lack waterborne counterparts that meet acceptable standards for commercialization, notably clearcoats for outdoor applications. Additionally, issues such as pot-life, energy requirements, and the available range of systems still lags behind solventborne alternatives for many applications. Research endeavors aimed at addressing these challenges are ongoing, with emerging

stabilization techniques like Pickering emulsions seeing widespread interest. Furthermore, continuous investigation and incorporation of other additives are underway to further enhance waterborne coating performance and applicability.

Lastly, the predominant resins in use are still primarily derived from petrochemical sources. Consequently, the coatings are largely non-biobased and non-biodegradable. Moving beyond the environmental improvements achieved with waterborne systems to achieve fully sustainable coatings will be the next step, and a key challenge in the coming decades. Progress toward this transition is already underway, with the widespread adoption of bio-based waterborne polyurethanes and successful experimental applications of fully biobased and biodegradable polymers in water-dispersive formulations.

Nevertheless, these upcoming endeavors should not overshadow the significant strides made by the coatings industry toward environmental sustainability. Commercialized products must adhere to performance standards, and achieving full sustainability requires considerable time and collective effort. Waterborne systems have emerged as the standard for architectural coatings, the largest commercial coatings sector, as well as automotives, one of the sectors with the highest visibility for coatings innovation. Waterborne coatings will persist in leading environmentally conscious coating options and pioneering new coatings applications.

CHAPTER 3 – STABLE AQUEOUS DISPERSIONS OF POLY(3-HYDROXYBUTYRATE-*CO*-3-HYDROXYVALERATE) (PHBV) POLYMER FOR BARRIER PAPER COATING²

3.1 Introduction

Collectively, there has been a pronounced effort in recent years to shift towards more environmentally friendly products [1]. Currently, over 141 million tons of plastic packaging waste are generated per year [2]. Paper packaging could offer an opportunity to replace much of this waste with biodegradable and sustainable systems [2,3]. Unfortunately, while paper is inexpensive, biodegradable, and has good mechanical properties [246], it is porous and hydrophilic, necessitating the need for surface coating for food packaging and other similar applications [4]. Compounding the issue, existing surface coatings available are principally petroleum-based polymers, to the detriment of the paper biodegradability [2]. Biodegradable coated papers also have extensive applicability beyond packaging, such as paper straws [278], drug delivery [3], and slow release fertilizer [279].

Ideally, paper coatings replacing synthetic polymers with biodegradable alternatives can be made available. In particular, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) is of interest as it possesses a rare combination of suitable traits. PHBV is both bio-based and readily biodegradable under a wide range of conditions [172,280]. It also possesses excellent

² A version of this chapter has been published in peer-reviewed journal *Progress in Organic Coatings* as an experimental paper: Stable aqueous dispersions of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) polymer for barrier paper coating.

barrier properties comparable to existing petroleum-derived coatings [280,281].

Advantageously, PHBV can be produced by a range of microorganisms and be directly extracted from its biomass, unlike other common industrial biopolymers such as poly(lactic acid) that require a synthetic process to generate the final polymer [4,7]. However, PHBV is relatively expensive [282]. While it can be produced for as little as US\$2/kg [283], it is much more expensive on the market (~US\$10/kg at the time of writing this paper). Additionally, pricing of PHBV is highly variable, being tied to the geographic location of production, operating conditions, and carbon source [284]. In general, low-cost production of PHBV through investigation of the mentioned factors and others such as microorganism engineering has become a topic of substantial research in order to narrow the price gap between PHBV and traditional petroleum-based plastics [283–286]. Additionally, substantial economies of scale benefits are available for PHBV production—and projected demand is high—so there is rationale for benefit realization [283]. As a result, hopefully the cost premium associated with PHBV will cease to be a significant barrier to adoption.

Beyond the material of the coating itself, the coating method is also important. Commonly employed methods such as flat-film extrusion on pure PHBV result in a brittle film [13]. Alternatively, coatings are commonly prepared through solvent casting, in which the polymer is dissolved in solvent and then cast onto the substrate [1]. With sufficient temperature, the carrier solvent evaporates and the polymer particulates merge and form a continuous surface [4]. PHBV, like most polymers, is not readily soluble in water, instead being soluble in chlorinated and other comparable solvents which are unsafe and environmentally detrimental

[1,7,286]. The benefits of water as a safe, environmentally friendly solvent make waterborne coatings greatly appealing, even when forming stable dispersions is challenging [14]. While the prevailing method to produce waterborne dispersions is emulsion polymerization, this method is not applicable to biopolymers such as PHBV [1]. Instead, methods have been derived wherein the polymer is initially dissolved in a water-immiscible organic solvent, and then combined with a surfactant containing aqueous solution with an energy input [16]. The organic solvent is then evaporated, leaving behind a colloidal suspension of polymer in water [1]. Rheological modifiers or other stabilizers can then be added to expand the stability timeframe and increase functionality [287–289]. Unfortunately, current waterborne PHBV solutions have low solids content or poor stability [4,287]. Higher solids content reduces storage cost, energy input for evaporation, and improves film formation, provided coatability is maintained [3,39]. Furthermore, stability is a necessity for industrial applicability, in order to maintain product consistency and reduce unnecessary spoilage [289,290].

The main objective of this work was to investigate the generation of stable PHBV dispersions in water and demonstrate a potential application as a paper coating material. Different initial solvents, surfactants, stabilizers, and homogenization methods were evaluated. The resulting dispersion of PHBV in water with sodium dodecyl sulfate surfactant and guar gum stabilizer had stability and characteristics assessed through analytical techniques such as rheological study, dynamic light scattering, and microscopy. Wet mechanical properties, water vapor permeability, oil resistance, and liquid water absorbance of manila paper substrate coated with the dispersion were also evaluated to confirm barrier paper coating viability.

3.2 Materials and methods

3.2.1 Materials

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) powder, grade ENMAT Y1000 was purchased from Ningbo TianAn Biologic Material Co., China. Chloroform (99.9%), Ethyl Acetate (99.8%), Tween® 85, Hexadecyltrimethylammonium bromide (CTAB, 99.5%) powder, and Guar Gum powder (95%) were purchased from Sigma Aldrich, Canada. Sodium Lauryl Sulfate (SDS, 99%) powder was purchased from Fisher Scientific, Canada. Semi bleached colored manila paper, with a thickness of 0.26 mm and grammage of 204 g/m² was sourced from a local stationery store (Waterloo, ON, Canada).

3.2.2 Methods

3.2.2.1 Dissolution of PHBV in chloroform

Excess PHBV was dissolved in chloroform on a hot plate equipped with magnetic stirrer (at 165 °C, 1000 rpm, 1 d) under reflux, and then strained to remove undissolved solids. The resulting solution contained around 10 wt.% PHBV based on gravimetric analysis.

3.2.2.2 Preparation of PHBV dispersions using guar gum stabilizer and SDS surfactant

Distilled water was added to a glass griffin beaker, followed by the desired quantity of guar gum and SDS, as shown in **Table 2**. The corresponding amount of PHBV solution in chloroform was then added, and the solution was mixed at low (5000 rpm) followed by high speed (15000 rpm) using a mechanical homogenizer (Fisherbrand 850, USA). A stir bar was

then added, and the dispersion was stirred at 200–600 rpm on a magnetic stir plate depending on the perceived viscosity of the formulation, to allow surface disruption while keeping minimal bubble formation. The stirring continued at room temperature under fume hood suction for 2–6 h until sufficient evaporation occurred such that 10 wt.% solids content was achieved.

Table 2. Formulation design table for PHBV in water dispersions with guar gum stabilizer and SDS surfactant.

Formulation	Aqueous Phase (aq)		Organic Phase (org)
	Guar Conc. (wt.%)	SDS Conc. (wt.%)	PHBV/Chloroform volume ratio to aq phase (org:aq)
1	1	0.5	5:3
2	1	0.5	10:3
3	1	1	5:3
4	1	1	10:3

3.2.2.3 Formulation analysis

All samples from **Table 2** were analyzed with the following techniques at an interval of 1 d, 10 d, 25 d, and 50 d after preparation. No mixing was applied prior to sampling, with test specimens extracted from approximately the middle of the bulk. Samples were stored in sealed glass vials in a controlled temperature environment (18–22 °C).

Rheology

Rheological properties were analyzed using a rotational rheometer (HAAKE Mars III, Thermo Scientific, USA). Trimmed liquid samples were tested at 23 °C using a 35mm/1°

cone and plate geometry, with a gap of 0.052 mm. A waiting period of 30 s was accorded to each sample after loading before shearing, with a new sample specimen used for each test. For the viscoelastic spectra determination, the geometry was sheared from 1.0 s^{-1} to 1000 s^{-1} over 1 min using a continuous ramp. Frequency sweeps were performed over the range of 200 rad/s to 4 rad/s with constant $\gamma = 1\%$ in order to be within the linear viscoelastic (LVE) region for all samples.

Colloid particle size distribution

Dynamic light scattering (DLS) analysis was performed using a Zetasizer ZS90 (Malvern Panalytical, USA). Samples were diluted with a factor of 1:100 with distilled water, mixed via pipetting, then equilibrated for 120 s at 25 °C in the test chamber. The refractive index of the material and dispersant were set as 1.590 and 1.330, respectively. Disposable Cuvettes were used, with a 90° measurement angle. Results are presented as an average of thirty-three measurements.

Microscopy

A dilution factor of 1:10 with distilled water was used for better imaging, mixed via pipetting. A BX53M series microscope (Olympus, Japan) was used. The image lighting was adjusted in post-processing for uniformity and clarity. Particle size analysis on the images was performed using ImageJ software (NIH, USA). Colloid cross-sectional area was determined using built in functionality, and average diameter determined assuming perfect sphericity.

Solids content

Triplicates of aluminum weighing dishes containing samples had their mass regularly measured until constant mass was observed in consecutive instances, at 105 °C. The solids content was calculated using (1)

$$\text{Solids (\%)} = 100\% \cdot m_2/m_1 \quad (1)$$

m_2 is the constant mass after drying, while m_1 was the initially measured mass.

3.2.2.4 Paper coating

Manila paper substrate was coated using 10 wt.% dispersions metered using a Baker film applicator. The substrate was placed on a heated surface (140 °C). After coating and drying, the coated samples were compressed using a hydraulic press (Bench Top series, Carver, USA) with heated steel plates, at 175 °C and 1.5 MT of pressure for 1.5 min. The final overall (film + substrate) thickness was 280 µm, with a coating thickness of 40 µm.

3.2.2.5 Coating characterization

All tests below were carried out using samples in triplicate, each from a separately prepared sheet and conditioned to constant weight prior to testing. Where applicable, the coated film sides were exposed to the water or testing fluid. Uncoated comparison samples were from the same manila paper substrate as the coated samples and exposed to equivalent heating steps (140 °C for 5 min and 175 °C 1.5 MT press for 1.5 min). All tests were performed in a

temperature-controlled laboratory. All coated samples followed the formulation preparation steps of **Table 2**, formulation #2. Error bars and bands are given as ± 1 standard deviation.

Water Cobb test

Samples were prepared such that a circular area (5.5 cm in diameter) was exposed to 7 mL of distilled water contained by a clamped cylinder. After 1 minute of exposure, the sample was removed, blotted dry, and the mass was measured. The Cobb value was then determined (2)

$$\text{Cobb Value (g/m}^2\text{)} = (m_2 - m_1)/\text{Area(m}^2\text{)} \quad (2)$$

m_1 and m_2 are the sample masses before and after the test, respectively, and ‘Area’ is $2.376 \times 10^{-3} \text{ m}^2$.

Grease kit test

Twelve different standard grease solutions comprised of varying toluene, castor oil, and *n*-heptane ratios were created in accordance with Tappi T559 (compositions given in supplementary information section, **Table A4**. In ascending numerical order, a droplet of each solution was applied to the surface and wiped away after 15 s of contact. The strongest (highest number) solution that was able to be applied without causing surface staining is reported as the kit value. Higher kit values convey greater grease resistance.

Wet tensile

Test specimens were cut into 70x10 mm strips and fully submerged in distilled water for 1 min, then blotted dry. Samples were then immediately tested using a universal tensile tester

(AGS-X series, Shimadzu, Japan), with a 2.5 mm/min strain rate, 500 N load cell, and 50 mm gauge length.

Water vapor permeability

Samples were tightly sealed to cups with a mouth diameter of 5.5 cm containing distilled water. The cups were placed in a constant relative humidity environment (sealed vessel containing desiccant), and the mass was measured daily for a weeklong period. The Water Vapor Permeability (WVP) was subsequently determined through (3)

$$\text{WVP} \left(\frac{\text{mg}}{\text{Pa} \cdot \text{d} \cdot \text{m}} \right) = \frac{\Delta W \cdot l}{t \cdot A \cdot \Delta p} \quad (3)$$

Where ΔW is the weight change in mg, l is the thickness in m, t is the time (days), A is the cup mouth cross-sectional area (m^2), and Δp is the nominal partial water vapor pressure difference (1 Pa) between the two sides of the individual test samples.

3.3 Results and discussion

3.3.1 Formulation stability and characteristics

All four formulations tested had visual stability beyond 25 days (d) at room temperature (**Figure 12**). Other successful waterborne biopolymer dispersions achieved similar lab-scale stability [1], and unstable waterborne dispersions clearly display separation within this time-frame [291]. During preliminary screening, unstable formulations all displayed negative characteristics within 2 d of preparation. These characteristics included significant cloth formation on the dispersion equipment (homogenizer / sonicator), clotting on the stir bar

during organic phase evaporation, clot formation, and visual sedimentation. The successful dispersions exhibited none of these negative properties and possessed a uniform milky white appearance. There were no particles / clots visible to the naked eye, and the dispersions flowed uniformly when poured. Some bubbles could be seen and remained stable for some time due to the high viscosity at rest but could be removed through agitation. By 50 days (**Figure A1**), instability became noticeable with a thin translucent film appearing on the top surfaces of the dispersions, potentially due to coalescence [43]. Note that the volume decrease between 2 d and 25 d in **Figure 12** was due to samples taken for testing, and the differing initial volumes due to the preparation method. Since the dispersions were prepared in larger beakers and then decanted into the vials upon reaching 10 wt.% solids, dispersions beginning with a higher wt.% and initial volume created more final product. Also, the decanting process added volume inconsistency as residual product was left behind in the preparation beaker.

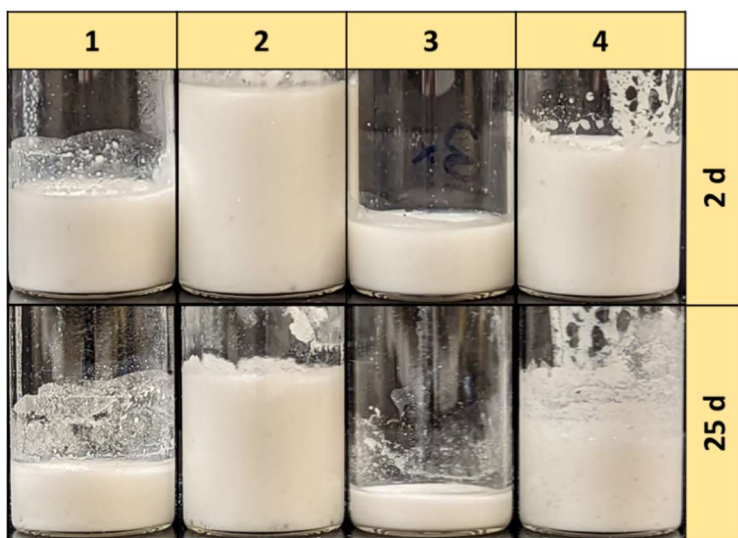


Figure 12. Stable dispersions 2 d and 25 d after preparation

Preparation of dispersions containing >10 wt.% of PHBV (**Figure A2f**) through increased time of evaporation resulted in samples passing visual stability trials but was unwieldy for other testing due to the extreme viscosity. These high wt.% samples could not be handled using air displacement pipettes and, depending on the level of evaporation, they became grainy in appearance similar to damp sugar rather than the homogeneous milky appearance observed at or below 10 wt.%. However, successful sample dilution with DI water for DLS and microscope testing may mean that preparing and distributing more concentrated dispersions and then diluting prior to use is viable for situations where the formulation is not prepared on site. Aqueous microencapsulation has been previously demonstrated on a similar (PHBV/Chloroform/Water) system [16] and may be a possible application, if sufficient solvent evaporation is performed.

Solids percentages for industrial waterborne emulsions cover a wide range of values, with high solids content acrylics surpassing 50 wt.% and seeing widespread use [39]. However, waterborne paper coatings are frequently below 10 wt.% in order to maintain slurry processability [3]. The water solubility of the polymer [45], particle size [292], storage conditions [293], and preparation method (emulsion polymerization vs solvent evaporation, etc.) [1] all play a large role in dictating the maximum achievable solids percentages. Also, gains at the formulation and application level are to be expected as the waterborne coating industry continues to mature [14,54]. Consequently, the 10 wt.% demonstrated in this work

meets current benchmarks for waterborne paper coatings and represents a promising step towards economical waterborne PHBV dispersion preparations.

3.3.1.1 Formulation components

Chloroform was chosen as the initial solvent for PHBV after a literature review and brief experimentation. While some groups have had success using ethyl acetate [294], appreciable dissolution was not obtained experimentally with the relatively highly crystalline grade of PHBV used in this study [295]. Due to the variation of bioprocesses to produce PHBV, the polymer has greater variance in properties depending on the supplier than synthetic polymers. As a result, successful solvent systems are highly dependent on the PHBV polymer input [286]. Additionally, crystalline effects are a well-known barrier to PHBV dissolution [296,297]. Thus, while ethyl acetate is highly preferable to chloroform from a safety and environmental perspective [298], and the polymer input may be modifiable to allow for ethyl acetate compatibility [297], the ease of dissolution afforded by chloroform was preferred for this study. The employment of other safe and sustainable solvents could be the subject of a follow-up investigation.

Similarly, the SDS was chosen as the surfactant after preliminary screening. Due to its chemical structure, PHBV has previously exhibited compatibility and stability with a wide range of solvents and electronic charges [299–302]. As a result, SDS, Tween 85, CTAB, and blends of SDS/Tween were tested at high, low, and midpoint concentration levels along with other screening factors (**Figure A2**). These three surfactants were chosen to evaluate the

effectiveness of cationic, anionic, and non-ionic surfactants [18,303], and their blends that are known to be capable of superior performance [304,305]. Samples containing Tween did not exhibit overnight stability and appeared translucent rather than opaque white, while CTAB created non-homogenous blends with streaks throughout. Although nano-emulsions can appear translucent or transparent [306], testing yielded the presence of negligible dry mass. SDS allowed for stable dispersions with the opaque milky white appearance expected [307]. The varied SDS concentrations used did not have a noticeable impact on visual stability. Importantly, SDS is also known to be a safe surfactant with low environmental impact relative to alternative products [17,308]. However, there is still room to improve performance and impact through exploring other opportunities such as Pickering emulsions [288,309,12]. Previously, PEO/PS block copolymers have been used successfully to stabilize PHBV in an O/W emulsion, with greater success than SDS or CTAB, albeit with higher stabilizer and lower PHBV concentration than this work [287].

Simultaneously to the above, guar gum was chosen to be the stabilizer and thickener. While starch has previously been used successfully as an aqueous biopolymer (PLA) dispersion stabilizer [1], guar gum exhibited much greater stability and superior flow properties during preliminary trials. Guar gum as a dispersion stabilizer usually amounts to <1% of the total system weight [310]. The decision to test at 1% and 2% of the aqueous phase was done as the system weight increases as PHBV is drawn into the aqueous phase, diluting the guar gum. As well, the nature and degree of the interactions between guar gum and the surfactant or polymer could have impacted the guar gum effectiveness [311,312]. It is highly likely that

other viscosity modifiers would also work as stabilizers for this system [1,313]. Other stabilization avenues such as Pickering emulsion, as discussed, can be the subject of a follow up study to potentially act as both surfactant and stabilizer. Guar gum can be farmed with lower emissions than other crops [314], is safe and consumable [310], and is environmentally friendly [315]. An interesting observation in this study is that the shelf stability of a combined guar gum / SDS aqueous system was drastically higher than guar gum alone. Combining the surfactant and guar gum together led to room-temperature stability exceeding six months, whereas guar gum in solution alone showed significant instability within one week (**Figure A3**).

Lastly, the mechanical homogenizer was selected as the dispersing equipment. Similar systems have shown success with both mechanical homogenization and ultrasonic probes [1,287], and indeed both were successful in preliminary screening. The choice to move forward with the homogenizer for this study was made due to the available equipment being able to prepare larger volumes and being used at both lab and industrial scale, easing scalability potential [316]. Unfortunately, with the homogenizer, further increasing the viscosity through additional guar gum or solids content prevented effective mixing of the system and dispersion formation as otherwise described. Manual pre-mixing, gradual gum addition, temperature, or other methods may need to be explored to achieve a satisfactory dispersion depending on equipment availability. Low-energy emulsification systems have also been garnering increased attention and may be of interest to explore in lieu of energy inefficient mechanical homogenization or sonication [317].

3.3.2 Rheological behavior

The dynamic viscosity and shear stress as a function of shear rate was evaluated to ascertain the flow behavior of the dispersions. The geometry was sheared from 1.0 s^{-1} to 1000 s^{-1} over 1 min using a continuous ramp and is shown in **Figure 13a–b**. Note that only samples 1 & 2 are plotted on **Figure 13a–c**. This was done for clarity as sample pairs 1 & 3 and 2 & 4 exhibited very similar values and overall behaviour for all figures. The full figures with all four samples plotted is available in the supporting information (**Figure A4**). In like manner, note that the **Figure 13(a)** and **(b)** data was collected simultaneously but plotted separately for clarity. The lines were prepared by plotting the average of every three data points.

Clearly, for all samples, the dynamic viscosity decreases while the shear stress increases as the shear rate is increased. The pronounced decrease in dynamic viscosity as a result of increasing shear rate represents shear thinning behavior [246]. The shear stress does not uniformly increase, however these “bumps” in the curve merely indicate the expected presence of slip surface generation [318]. Shear thinning is the expected behavior due to the guar gum addition, with the viscosity and flow curve behavior closely matching those found in literature for aqueous gum solutions [313,319]. Shear thinning is a desired trait for coating applications [2,289].

Comparing the individual samples, dynamic viscosity and shear stress both increase with time. One possible explanation is that coalescence has occurred, however, this would result in larger particles and a less viscous solution [42] rather than the observed increase in dynamic viscosity. Additionally, as seen later in **Figure 14**, this does not agree with particle

size observations. Rather, the detected decrease in large particles, potentially due to settling, could have resulted in the observed higher dynamic viscosity [42]. However, this would assume that the solids content was kept constant, which was not the case with settling and the sampling method employed. Another possibility is that the guar gum had not yet reached saturation by 1 d, and the maximum viscosity of the solution had not yet been reached. Some literature reports that the maximum viscosity of gum solutions is obtained after 2 h [310], but is highly variable and maximum viscosity may not be reached for multiple days [320]. This theory agrees with the general observation that the guar gum dominates the rheological behavior. As well, the decline in viscosity over storage time, which is reported in literature for guar gum solutions [319], could be delayed by the synergy of SDS and guar gum, as reported in **Section 3.3.1**. Moreover, the guar gum impact is confirmed by the general trends seen between samples.

Samples 2 and 4 had very close measurements to one another, and much lower dynamic viscosity and shear stress at lower shear rates than the similarly clustered data of samples 1 and 3. As samples 2 and 4 had an organic:aqueous phase ratio of 10:3, while samples 1 and 3 had a ratio of 5:3, the guar gum in samples 2 and 4 is expected to be much more diluted. The lower the concentration of guar, the lower the expected viscosity [313]. Sample 3 registered the highest viscosity and shear values, and as it had the lowest volume yield (**Figure 12**), it presumably had the highest guar concentration. With the exception of sample 3, it can also be seen that while the viscosity at low shear changes with time, the curves at higher shear rates are nearly coincident, so the shear thinning behavior was only slightly impacted [319].

Regardless, the general shear response of all samples remains consistent over time and retains the desired strongly shear thinning behavior.

Additionally, an amplitude sweep test at a constant strain of 1% was performed and depicted in **Figure 13c** to establish the deformation behavior of the formulations in the linear viscoelastic region. Note that some outlier points were removed when they were clear incorrect values. For example, the measurement for 100 rad/s of G' and G'' at 25 days for sample 2 in **Figure 13c** was removed as both the G' and G'' values showed a strong spike, measuring in the 100's of Pascals. As the values to either side and expected behavioral continuity point to the invalidity of this datapoint, it was removed. Similar to the viscosity and stress values, the storage (G') and loss (G'') moduli increase over time rather than the decrease that is typically seen in literature on similar time frames [319]. As well, the G' and G'' values are higher for samples 1 and 3 compared to samples 2 and 4, as expected for systems with increased gum concentration [289,313]. The lack of decreasing values indicates that the formulation has not substantially destabilized [319]. While guar gum systems of similar concentrations have previously reported entangled polymer behavior with a crossover point at low frequency before G' being greater than G'' through higher frequencies [313], that behavior was not consistently observed for the tested dispersions. However, Razavi and Irani found that food gum systems generally have very similar G' and G'' values at low frequencies, and that many food gum systems behave as weak gels with G' exceeding G'' at all frequencies [313]. As such, the observed behavior of G' generally being greater than G'' is in line with expectations. This behavior is compatible with various coating applications

[41,246,289]. Overall, the rheological tests support the coating applicability of the dispersions, and their long-term stability.

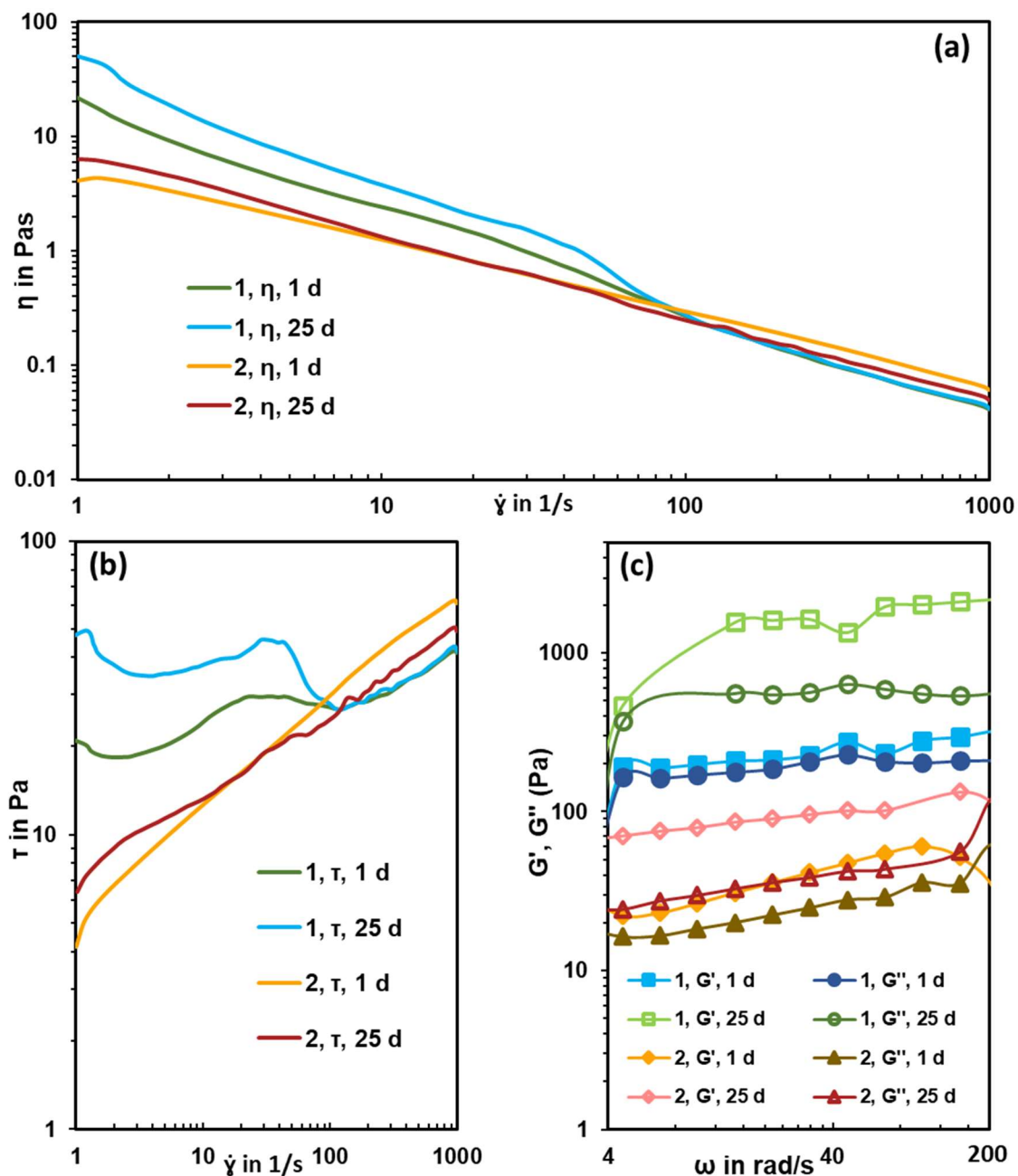


Figure 13. Rheological test results 1 d and 25 d after dispersion preparation. (a) viscosity curve, (b) flow curve, and (c) viscoelastic spectrum. Legend provides sample #, test parameter, sample age. Filled in markers indicate 1 day old while unfilled indicates 25 d.

3.3.3 Colloid particle size distribution

DLS and microscopy images were employed to assess the particle sizes and distribution of the dispersions. This data is of interest as the particle size impacts the performance of the final coating [4], and its change over time is used to assess stability [1,42]. DLS results are presented in **Figure 14**, while microscope images are shown in **Figure 15**, and particle size analysis of the microscope images in **Figure 16**. For both tests, measurements are compared at 2 d and 25 d after dispersion formation, stored at room temperature between tests. Like the rheology data, the DLS data in **Figure 14** is shown only for samples 1 and 2 to avoid overcrowding, while **Figure A5** shows all samples.

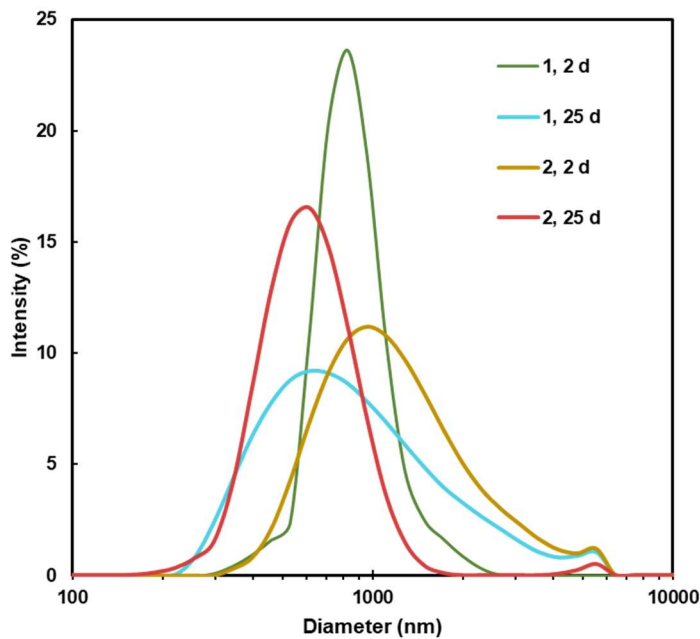


Figure 14. Particle size of prepared dispersions using DLS. Legend provides sample # and sample age.

From the DLS data, the dispersions formed narrow particle size distributions within samples and the peak frequency diameter also had low variance, falling between 600 nm and 1 μm for all samples. However, it should be noted that while the DLS data is compared to itself, the measurement's absolute values have known inaccuracies and can be misleading [321]. At 2 d, the distributions show slightly bimodal behavior, with a minority of particles present around the 5–6 μm range. However, this large-particle peak mostly disappears in the 25 d measurements, with the overall size distribution also skewing further towards smaller particles. It is possible that due to the high viscosity at rest of the dispersions, some large particles which coalesced during initial dispersion formation [316] had not yet settled out of solution. Regardless, the lack of pronounced increase in particle size from the DLS measurement indicates that there was no considerable instability of the dispersion over the 25-day evaluation time.

The data also shows high consistency between the different systems, despite differences in formulations. This is not unexpected, as previous studies on similar systems have found that the mixing equipment parameters dominate the other variables for particle size determination [287]. As all dispersions were prepared with equivalent mixing conditions, similarity among particle sizes is expected. While surfactant concentration can have a strong influence on the particle size, this effect greatly decreases and eventually ceases as the surfactant concentration reaches and exceeds a critical concentration [287]. For SDS, the relatively high concentrations used for all tested formulations resulted in the critical micelle concentration being approached or exceeded [322], so minimal variation between samples is expected.

Higher concentration than required was used due to concerns over other system components negatively impacting the SDS effectiveness [323]. Establishing the critical concentration is important and could be the subject of a follow up study to this work. As little difference in particle size between different SDS concentrations was observed, the lower SDS concentration-based formulation can be used moving forward, or potentially lowered even further.

Optical microscope images confirm the DLS results of a narrow size distribution, and of no signs of instability. The images in **Figure 15** show very little changes between the 2 d and 25 d tests. The image density between the 2 d and 25 d tests is also similar, so there was not significant settling of particles out of the dispersion. Note that the samples are diluted at a factor of 1:10, or else the density would be too high for imaging. Particle appearance is also conventional, with a visible shell / surrounding ring [16,287,288,324]. Regarding particle size, the microscope images provide an absolute particle size measurement and therefore a more accurate estimate than the DLS measurements and provide a larger than 1 μm average diameter [325]. This is larger than some other similar dispersions, but not unexpected with the differences in methodology used [1,287,316]. Particle size analysis on the microscope images using ImageJ (**Figure 16**) results in average measured diameters ranging from 2.25–2.65 μm depending on the sample. **Figure 16** data is presented using number-length mean diameter and standard deviations [325]. The particle sizes observed via microscopy are in a range which leads to further inaccuracies with the DLS size estimation, supporting the decision to use the DLS data only for overall trends while the microscope data is used for

absolute size determination [325]. While the measured average particle size is lower at 2 days than 25 days for all samples, the substantially overlapping error bars do not support a correlation between time and particle diameter [326,327], further corroborating stability. It should be noted that the reported average size is slightly underrepresented while the standard deviation is overrepresented. The optical microscope method used captured particles within a three-dimensional space, so cross-sectional size measurements were influenced by depth within the sample [328]. Nevertheless, the most important aspect is confirmation of stable particles with a narrow distribution.

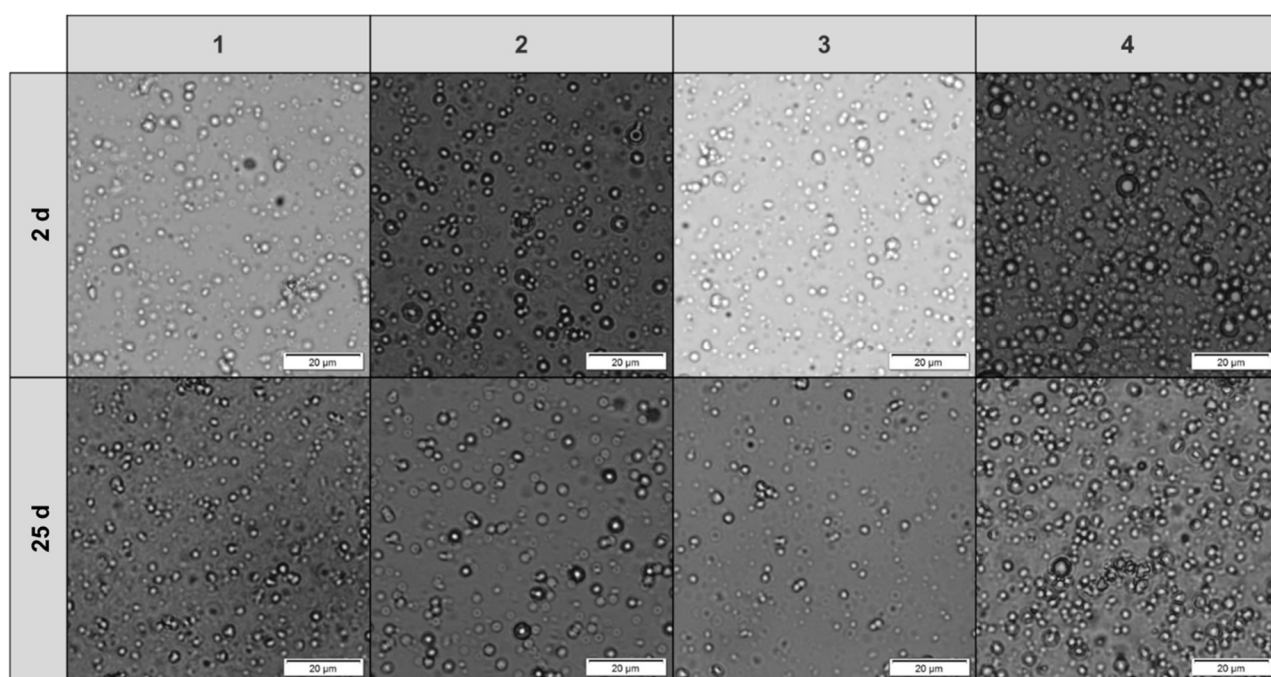


Figure 15. Optical microscope images of the four prepared dispersions at 50x magnification, 2 d and 25 d after preparation. Samples have a dilution factor of 1:10.

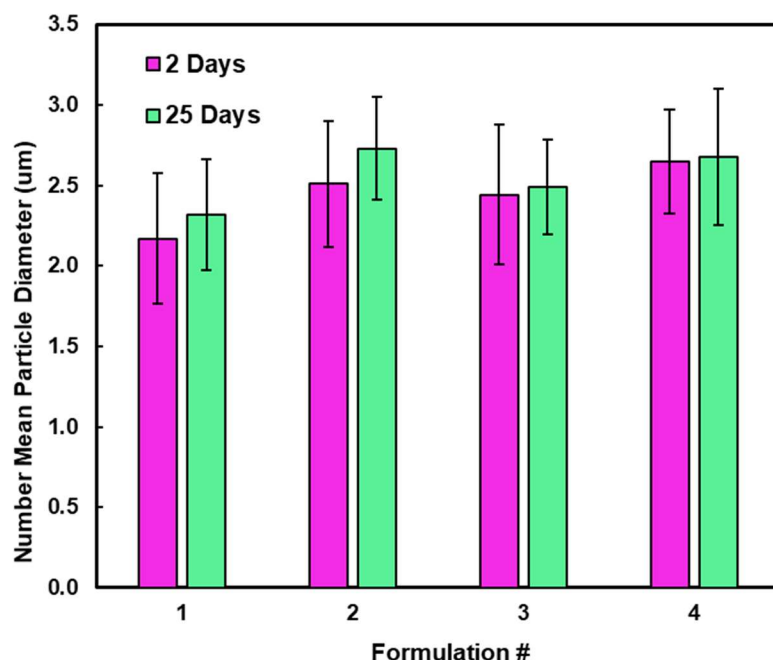


Figure 16. Particle size analysis on microscope images of the four prepared dispersions at 50x magnification, 2 d and 25 d after preparation. Samples have a dilution factor of 1:10.

3.3.4 Paper coating

PHBV dispersions were prepared as per formulation #1 in **Table 2**, coated using a Baker film applicator on manila paper at 140 °C, then pressed at 175 °C. Images of the coated paper before and after the hot compression stage are presented in **Figure 17(a)** and **(b)**, respectively. The film had excellent adhesion to the paper substrate in both scenarios, however the opaque white surface prior to compression (**Figure 17a**) had visible unevenness and porosity. This led to poor water resistance in screening trials, as expected for a PHBV film at the coating temperature used, due to the lack of full coalescence of the colloids to provide a uniform barrier film [4]. Coating and drying above 140 °C (substrate temperature)

to meet the minimum film forming temperature (MFFT) [4] led to significant degradation of the PHBV, with substantial yellowing as shown in the supporting information (**Figure A6**). Thus, the compression step was added. Here, the surface was able to be briefly exposed to the elevated temperature required – long enough to obtain a smooth and transparent film, but short enough not to cause significant polymer degradation [4]. MFFT is positively correlated with particle size [4], so different conditions may be necessary to obtain satisfactory film depending on dispersion formation conditions used.

After compression, the surface did not completely become transparent, however the plates used have imperfections and the initial coating had some variable thickness. As a result, there are visible white artifacts in the coating surface (**Figure 17b**) where the spherical particles of the coating did not completely coalesce to form a clear and continuous film [4,40]. However, the presence of these sections was not found to greatly influence the coating properties, unlike the untreated film. This result is expected to be the result of significant coalescence and polymer chain interpenetration having still occurred, albeit incomplete (so the coating surface remains partially white but became smooth to the touch). Also, longer, or more intense treatments, began to degrade the coating and/or the substrate (minor damage visible in **Figure 17b**). Delamination of the film from the substrate onto the compression plates occasionally occurred (small delamination visible in bottom, right of center, **Figure 17b**), however did not significantly occur when less than 120 s of compression at 175 °C was performed (**Figure A7**). Quality was sufficient for laboratory purposes and demonstrating

coating applicability, so optimization of the coating and treatment parameters was not rigorously performed.

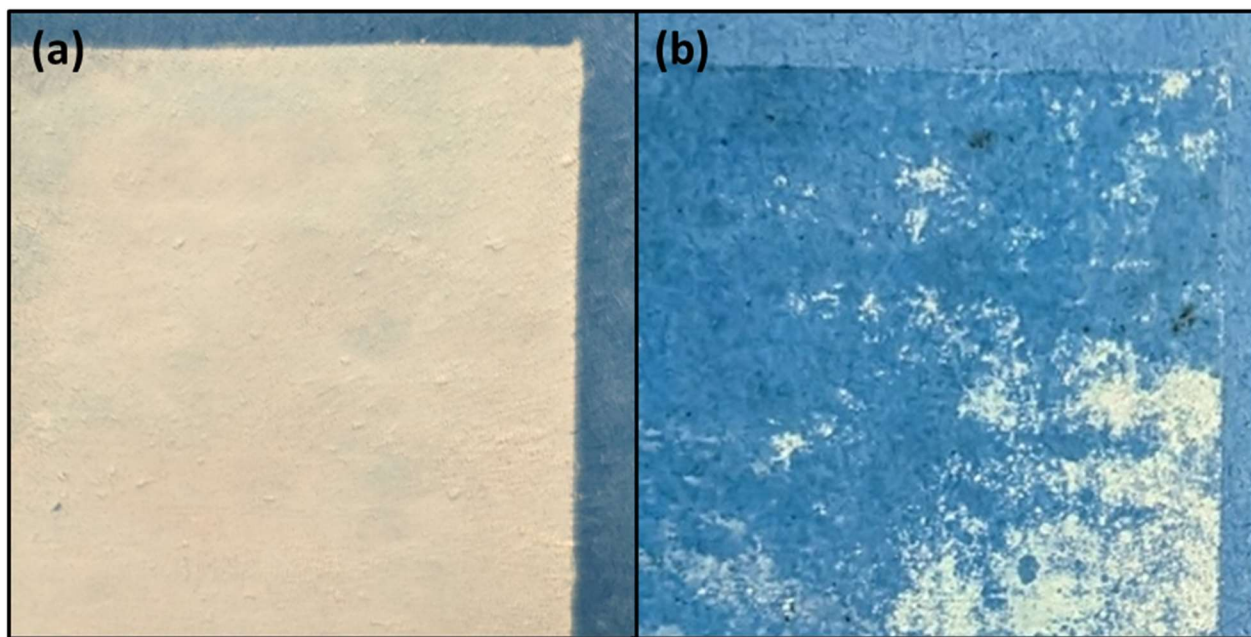


Figure 17. Coated paper as described in section 3.2.2.4. (a) after coating and drying before hydraulic compression, and (b) after hot compress. The uncoated manilla paper used has a blue color.

Printer paper was also successfully coated at the same conditions; however, it was not tested due to being less pertinent from an application standpoint (**Figure A8**). Adhesion to the substrate remained high, so other similar substrates may also have good adherence without adding pretreatment or processing steps. Furthermore, while multiple layers were used in order to provide the desired properties, the employment of higher solids content, plasticizer use, or different coating parameters can eliminate this need [3,4,13].

Formulation #1 from **Table 2** was selected as the optimal and representative formulation for the coating properties evaluation. All samples showed similarly positive rheological and particle distribution performance, and have similar formulations, so there was little differentiation available. While the SDS content may impact some properties [329], only minor effect is expected on the key properties of interest between the two loading levels [322,330]. Thus, the lower of the SDS levels is chosen. Beyond that, formulation #1 was chosen over formulation #2 due to being subjectively more favorable to coating at the lab scale. Upon scale-up, differences in required energy and material input, as well as specific rheological requirements, would also be important decision parameters [331].

3.3.5 Coating properties

The wet mechanical, water vapor permeability, water resistance, and oil resistance were evaluated as it is desirous that coatings allay inherent limitations of paper in each of those categories [2]. Other tests such as the oxygen barrier, dry mechanical, water contact angle, adhesion strength, residual surfactant and solvent, morphology analysis, biodegradability, and more were not performed, but may be of interest [2,246,280,281,332]. Correlations between the results of many of these untested properties and those that were tested can be drawn, so testing of the specific performance was not prioritized. For example, the dry mechanical properties are primarily dictated by the paper substrate [246,332], residual solvent leads to instability [1], and the water contact angle is correlated to the water Cobb test [332]. Additionally, the biodegradability and oxygen barrier properties are highly dependent on the coating materials themselves, for which great performance is expected

[2,280,333]. Lastly, the surface may be modifiable depending on the desired application. For example, if there is excess residual SDS on the coating surface, that may lead to anti-biofilm properties [329]. However, if the SDS is present to an unwanted degree, it should be removable or neutralizable during processing once it is no longer required for dispersion stability [334,335]. Overall, the purpose of the chosen tests was to assess viability of the dispersions as paper coatings, rather than to optimize the performance for a single application.

3.3.5.1 Water vapor permeability

Water Vapor barrier properties are one of the crucial aspects of packaging materials, especially for coated paper applications [2,246,281]. Resistance to water vapor transmission through the coated paper at constant temperature and relative humidity was investigated using a water vapor permeability test (WVP), displayed in **Figure 18a**. Substantially lower WVP values are noted for the coated paper compared to the uncoated paper as desired, indicating the coated paper substantially mitigates water vapor transmission. The test also shows high consistency between the tested samples, evidenced by the tight error bands, and agreeing with other tests that the coating results are highly repeatable. While the measured values for WVP are still higher than commercial packaging films [336], no impermeable control was used to benchmark leakage inherent to the testing apparatus, and the test results are known to vary greatly with changing temperature, humidity, and pressure [246]. Consequently, the best comparison is directly between the coated and uncoated samples, for

which significant improvement is displayed. These results are expected, as PHBV films are known to have good WVP properties comparable to low density polyethylene [280,281,13].

3.3.5.2 Water Cobb and grease kit

The water Cobb test is inversely correlated with water barrier performance [246], and a low water Cobb value is desirable for paper coating applications [281]. The test assesses liquid water absorbance by measuring weight change after 1 minute of direct water contact.

Uncoated paper is highly hydrophilic, and as such has a high water Cobb value [246]. In **Figure 18b**, it is apparent that the coated paper has a very low water Cobb value, drastically lower (93.5% reduction) than that of the uncoated paper, as desired. The increased resistance of the coatings to liquid water sorption is expected due to the hydrophobic properties of PHBV [281].

Contrary to the water Cobb test, a high grease kit value is desired, indicating better grease resistance [246]. This test is one of the most commonly employed methods of assessing grease resistance of paper coatings [2]. A series of 12 solutions with varying viscosity and surface tension are applied to the surface, with the highest value out of 12 which does not leave a stain reported as the kit number [332], given in **Figure 18c**. Owing to its highly porous and irregular surface, uncoated paper was stained by all solutions, so a kit number of zero is reported in agreement with other work [246,332]. By coating the surface with the PHBV dispersion, the kit number is immensely improved to a value of 9 out of 12 (**Figure A9**). A kit value of 8 out of 12 or higher is generally considered grease resistant [2], so this is

an excellent result to obtain. Furthermore, it has previously been demonstrated that the kit number can be increased by increasing the thickness of the coating layer [2] or through the use of targeted additives at low doses [246], if greater resistance is required.

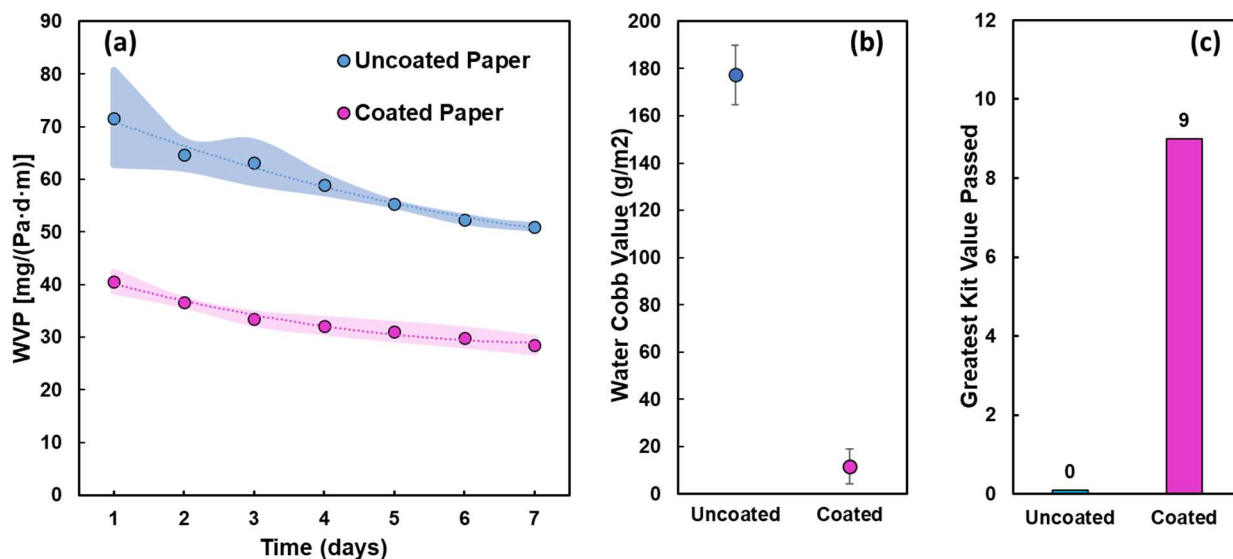


Figure 18. (a) Water vapor permeability test results, (b) Water Cobb test, (c) Grease kit comparison. Coated and uncoated samples for all tests

3.3.5.3 Wet Tensile

Wet tensile testing was performed to understand the influence of water contact on the paper's integrity, key for many packaging applications [246]. Coated samples were fully submerged in water for 1 min before undergoing tensile testing while still damp (blotted dry upon removal from water, then immediately tested), with results presented in **Figure 19**. Note that since the paper was fully submerged, with only one side coated, the paper substrate was saturated with water for both coated and uncoated test samples, rather than the coating being

able to fully impede water absorption. Clearly, the maximum stress and elongation at break were greatly improved as a result of the coating, while the Young's modulus is relatively unchanged (**Figure 19**). Maximum stress for the coated paper was roughly tripled, while the elongation at break more than doubled. Favorably, very high consistency is also evident between the tested samples. The shape of the stress-strain curves seen in **Figure 19a** is due to the nature of the paper and wet tensile test performed, and displays the expected pattern [281]. Rather than effecting sudden failure, the wet paper fibers were pulled and failed individually, thus there was gradual failure beyond the initial primary breakage. The coated surface allowed for greater stress and strain prior to failure than the uncoated surface and had a much greater number of still-intact fibers after surface breakage compared to the uncoated samples. If higher flexibility or elongation is required, multiple plasticizer additives for PHBV films have previously demonstrated improved properties [13]. Young's modulus for wet paper depends very highly on the strain rate, paper substrate, and wetting liquid, so the similar results for the coated and uncoated samples is not unexpected [337]. Overall, the coated sample performed quite well, supporting previous test results regarding paper coating applicability.

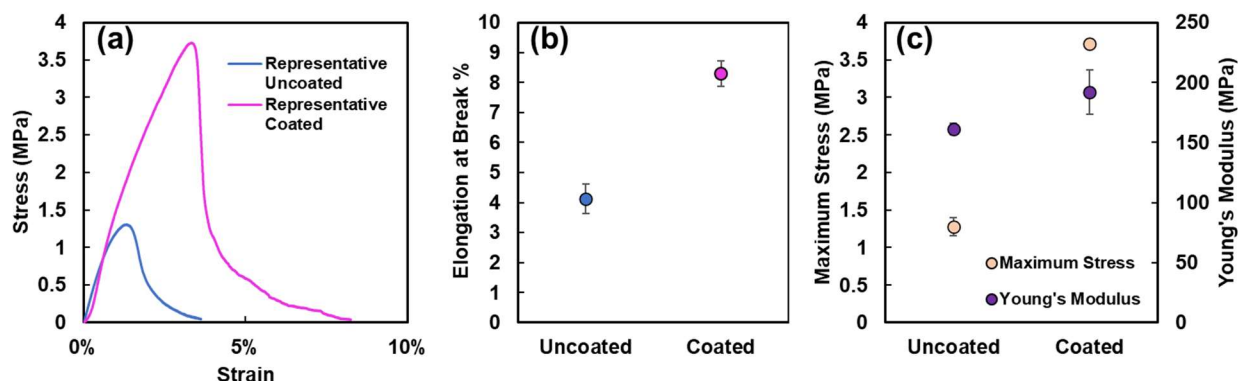


Figure 19. Wet Tensile results comparing coated and uncoated samples. (a) stress – strain curve, (b) elongation at break, and (c) maximum stress and Young’s modulus

3.4 Chapter 3 conclusions

The successful dispersion of biodegradable poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) in aqueous media with 10 wt.% solids demonstrated excellent long-term stability with favorable rheological properties for coating. Sodium dodecyl sulfate was employed for dispersion formation. However, the level within the system was not found to be overly sensitive, with changing quantity having little effect on the stability or particle size which was narrowly distributed between 600–1000 nm in diameter. Instead, the homogenization process and parameters dominated particle size determination. Strong shear thinning behavior was observed, with tunable viscosity and viscoelastic moduli through varying the guar gum quantity. Paper coated with the waterborne PHBV dispersion exhibited greatly improved water vapor barrier, wet tensile, grease barrier, and water absorption resistance properties relative to uncoated paper. This demonstrates an exciting opportunity for further development of fully biodegradable paper-based materials with high-performing barrier properties and consideration of sustainability.

CHAPTER 4 – WATERBORNE CELLULOSE ACETATE PICKERING EMULSION GENERATION MEDIATED BY CELLULOSE NANOCRYSTALS FOR PAPER COATING APPLICATIONS³

4.1 Introduction

In recent years, there has been a collective effort to shift towards more environmentally conscious products [1]. Over 141 million tons of post-consumer plastic packaging waste is currently generated each year [2]. Paper packaging is inexpensive, biodegradable, and has satisfactory mechanical properties, offering the possibility to replace much of this plastic waste with more sustainable systems [2,3,246]. Unfortunately, uncoated paper is unsuitable for food packaging and other similar applications due to its high porosity and hydrophilicity [4]. As a further impediment, currently available surface coatings are principally petroleum-based polymers, making them non-renewable and impeding biodegradability [2]. Beyond packaging, sustainable polymer coated papers can also find extensive applicability in other categories currently using conventional synthetic polymers (e.g., coffee cups, sandwich wraps, etc.) [3,278,279].

To maximize sustainability, it is of great interest to replace synthetic polymer coatings with alternatives that are both bio-based and biodegradable. Unfortunately, the list of such polymers with useful application properties, such as water/grease resistance and good film forming properties, is limited [5,6]. Cellulose-based products such as cellulose acetate and

³ A version of this chapter has been submitted to a peer-reviewed journal as an experimental research paper

cellulose nanocrystals are desirable due to their renewability and wide availability [8–10]. Additionally, both modified CNCs and cellulose acetate have the potential to be biodegradable or recyclable under certain conditions and the level of modification, such as acetylation [12,338–345]. Both cellulose acetate and CNCs are non-toxic and safe, including for food and pharmaceutical applications [9,12,346]. Furthermore, cellulose acetate is known to have respectable barrier properties, which would be advantageous for a packaging coating, with well-established modification reactions and additives to support tuning specific properties [10,11,347,348]. In particular, cellulose acetate is known to have low oxygen and water vapor permeability, capable of performance comparable to that of polyethylene [348]. Performance is known to be further improved through the addition of small particles to increase diffusion path length, and cellulose nanocrystals have previously been successfully used in other films for this purpose [11,348]. Additionally, water barrier properties can be improved through cellulose modification to decrease affinity between the polar hydroxyl groups of the cellulose and water [348,349].

Apart from the material of the coating itself, the coating method must also be considered. Flat-film extrusion is commonly employed for paper coating, but can result in a brittle film and cannot be used to make very thin films [13]. Solvent casting is also common and can overcome these issues. In this method, the polymer is dissolved into a suitable solvent, cast onto substrate, and then the solvent is evaporated [23]. Provided sufficient temperature, the polymer colloids coalesce to form a homogenous coated surface [4,40,48]. Like most polymers, cellulose acetate is not readily soluble in water, preferring solvents that are less

desirable for direct exposure and environmental release [7]. Water is appealing as it is a safe, inexpensive, and environmentally friendly solvent, and thus waterborne coatings are desirable even when forming stable aqueous dispersions is challenging [14,15].

While many synthetic polymers can be rendered waterborne via emulsion polymerization, biopolymers such as cellulose acetate cannot utilize this method [1]. As an alternative, the polymer is initially dissolved in a water-immiscible organic solvent and then combined (with energy input) with a stabilizing particle, conventionally a surfactant but more recently a solid particle so as to form a Pickering emulsion [16,19]. The chosen stabilizing agent must stabilize the interface between the polymer (cellulose acetate) and the aqueous medium [19]. CNC modification to replace some hydroxyl groups with aliphatic chains can increase CNC amphiphilicity [12]. This allows CNCs to have better balanced affinity to both aqueous and organic phases, improving stability of the Pickering emulsion [19]. Also, the aliphatic chain acts as a plasticizer, improving the properties of the resultant film coating [350].

Pickering emulsions using solid particles have been of very high interest in the past decade due to the nature of the solid particles becoming irreversibly bound to the interface [19,351]. This not only imparts greater colloidal stability, but also allows for more environmentally friendly stabilization than the use of conventional surfactants, as well as requiring low doses of the stabilizer, among other benefits [351,352]. After mixing, the organic solvent is evaporated, leaving behind a colloidal suspension of polymer in water [23]. Other stabilizers and additives, such as rheological modifiers and plasticizers, can then be incorporated if desired to expand functionality and increase stability [287–289]. Previous investigations into

waterborne cellulose acetate were successful using traditional surfactant methods, as well as using cellulose acetate as the Pickering emulsion stabilizing particle, but to the best of the authors' knowledge there has been little investigation on Pickering emulsions with cellulose acetate as the stabilized dispersed polymer [15,339,353,354]. Pickering emulsions have the added benefits of allowing higher solids content [355], reducing storage and transportation cost, evaporation energy requirements, and film formation [3,39]. Lastly, the importance of stability for industrial applicability is reiterated as being critical in order to maintain product consistency and reduce unnecessary spoilage [289,290].

The main objective of this work was to investigate the formation of stable cellulose acetate Pickering emulsions in water and demonstrate applicability as a paper coating material. Additionally, understanding the effect of CNC modification on the dispersion and coating properties was desired. Pickering emulsions of cellulose acetate in water using CNCs as stabilizer had characteristics such as stability, rheological properties, and particle size assessed. Unbleached kraft paper was coated with the Pickering emulsion, and the grease resistance, water vapor permeability, water absorbance, and wet mechanical properties were evaluated to assess barrier paper coating viability. Coated paper was compared to uncoated and a commercially available product for performance as a food takeout container packaging material.

4.2 Materials and methods

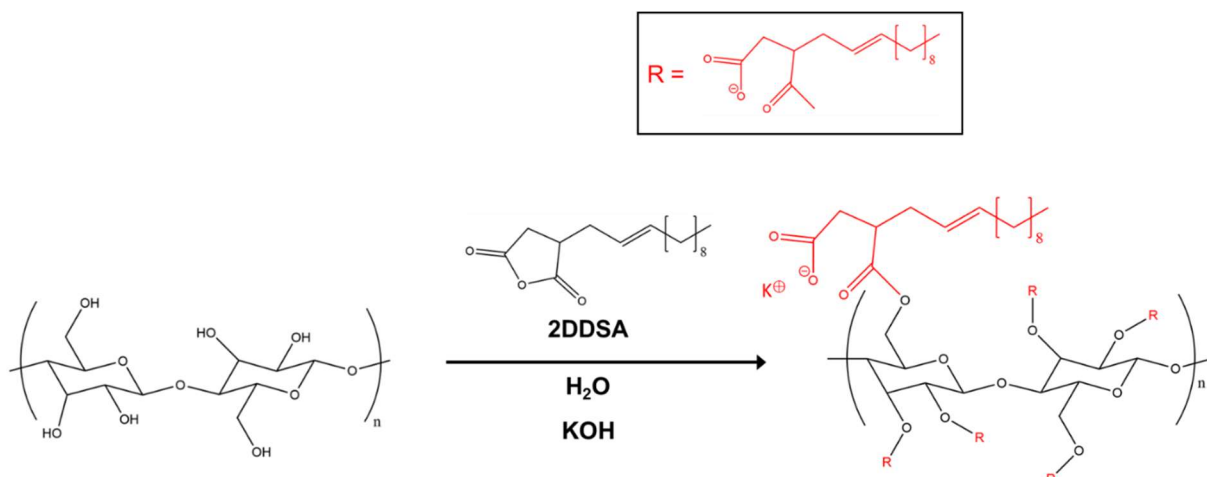
4.2.1 Materials

Cellulose acetate (CA) pellets (degree of substitution 2.2, average molecular weight 60,000 g/mol) were obtained from Eastman Chemical Company, USA. Ethyl acetate (EtAc, >99.7%), potassium hydroxide pellets (>85%), and (2-Dodecen-1-yl)succinic anhydride were purchased from Sigma-Aldrich, Canada. Cellulose nanocrystals (CNCs) (9 wt.% in water) were purchased from CelluForce, Canada. Unbleached kraft paper (chipboard), with a thickness of 0.62 mm and grammage of 440 g/m² was sourced from a local stationery store (Waterloo, ON, Canada).

4.2.2 Methods

4.2.2.1 CNC modification

CNC modification was conducted via succinylation of CNCs with the use of (2-Dodecen-1-yl)succinic anhydride (2DDSA) as depicted in **Scheme 1**. For this, 9 wt.% of never dried CNC was added to an enclosed beaker and diluted with equal volume of deionized (DI) water to halve the concentration. 0.05 mol/L KOH was added to promote favorable pH for the reaction [356,357]. 2DDSA was added at a ratio of 1 mL 2DDSA: 100 g dry weight CNC. The dispersion was subsequently stirred (600 rpm and 82 °C plate temperature) overnight. The resulting modified CNCs were stored in a refrigerator at 3 °C, alongside the unmodified CNCs.



Scheme 1. Chemical reaction of CNC and 2DDSA. Succinylation can occur at each reaction site shown (C2, C3, C6) [12,358].

4.2.2.2 Modified CNC characterization

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of the modified and unmodified CNCs were characterized using an FTIR equipped with an Attenuated Total Reflectance (ATR) crystal (Nicolett 6700, Thermo Scientific Inc., USA). Dried native and modified CNC samples were crushed into powder and directly analyzed using the ATR attachment of the FTIR under ambient conditions. Measurements were repeated on three samples for each powder, with representative curves provided.

Zeta potential

The Zeta potential (ζ -potential) of both the modified and unmodified CNCs was obtained using a Zetasizer ZS90 instrument (Malvern Panalytical, USA). CNCs were diluted to 0.1 wt.% in distilled water, then characterized at 25 °C after 30s of equilibration. Reported

values are the average of three separately prepared measurements, each consisting of 12 consecutive runs, per sample. Dispersant refractive index, viscosity (cP), and dielectric constants were set to 1.330, 0.8872, and 78.5, respectively. Clear disposable Zeta cells were used.

4.2.2.3 Preparation of CA dispersions using CNC Pickering emulsifier

15 wt.% cellulose acetate was completely dissolved in ethyl acetate on a hot plate equipped with magnetic stirrer (160 °C, 600 rpm, 1 d) under reflux. Distilled water was added to a glass griffin beaker, followed by the desired quantity of CNC or modified CNC (CNC-2DDSA) to achieve the concentration shown in

Table 3. The organic phase of CA solution in ethyl acetate was then added in the corresponding quantity. The resulting dispersion was then mixed at increasing speeds from 5,000 rpm to 20,000 rpm for constant time intervals (30 s) and speed step sizes (5,000 rpm) using a mechanical homogenizer (Fisherbrand 850, USA). Dispersions were then transferred to a magnetic stir plate, where they were stirred (600 rpm, 80 °C plate temperature). Stirring continued under fume hood suction and at ambient temperature until 10 wt.% solids was achieved via sufficient evaporation (~4 h). Prepared dispersions used 24 mL of total aqueous phase volume combined with 40 mL of organic phase.

Table 3. Formulation design table for CA in water dispersions with CNC Pickering emulsifier.

Formulation	Aqueous Phase (aq)		Organic Phase (org)
	CNC Conc. (dry wt.%)	CNC-2DDSA Conc. (dry wt.%)	CA/EtAc volume ratio to aq phase (org:aq)
1	1	-	5:3
2	0.25	-	5:3
3	-	1	5:3
4	-	0.25	5:3

4.2.2.4 Pickering emulsion formulation analysis

All dispersions prepared as per

Table 3 were analyzed using the following techniques at intervals of 1 d, 10 d, and 20 d after preparation, except for electron microscopy. Gentle mixing by inversion was applied prior to sampling, with test specimens extracted from approximately the middle of the bulk. Camera pictures were taken prior to any mixing action, and dispersions were stored in sealed glass vials away from direct light in an indoor controlled temperature environment ($\sim 22^\circ\text{C}$).

Rheology

A rotational rheometer (HAAKE Mars III, Thermo Scientific, USA) was used to analyze rheological properties. Liquid dispersion samples were trimmed and tested at 23°C using a $35\text{ mm}/1^\circ$ cone and plate geometry, and a gap of 0.0052 mm . A 30 s equilibration period was accorded after loading and before shearing for each sample, with new sample specimens loaded for each test. Viscoelastic spectra was obtained by shearing the geometry from 1.0 s^{-1} to 1000 s^{-1} over 1 min using a continuous ramp. The frequency sweeps were carried out over a range of 100 rad/s to 1 rad/s with constant $\gamma = 1\%$, selected due to being within the linear viscoelastic (LVE) region for all samples.

Microscopy

Optical microscopy was performed using a BX53M series microscope (Olympus, Japan). Image lighting and a conversion to greyscale were post-processing adjustments for uniformity and clarity. Particle size analysis was done on the optical microscopy images using ImageJ software (NIH, USA). Built-in functionality was used to determine cross-sectional area of the colloids, and average diameter was then determined assuming perfect sphericity.

Transmission electron microscopy (TEM) was also performed on the dispersions seven days after preparation, using a Talos L120C TEM (Thermo Scientific, USA). Samples were prepared prior to analysis by heating to 50 °C then diluting and vortexing. 5 µl droplets of diluted sample were then dried on Formvar-coated grids. Lastly, samples were stained with 5 µl of 1% aqueous uranyl acetate for 1 min, then the excess blotted off.

4.2.2.5 Paper coating

Kraft paper substrate was coated with two layers of the 10 wt.% dispersions metered using a Baker film applicator with a gap of 200 µm. Metered coating occurred with the substrate on a heated surface (40 °C). Subsequent to coating and partial drying (40 °C, 5 min), coated paper samples were compressed using a hydraulic press (Bench Top series, Carver, USA) with heated steel plates, at 145 °C and 1.0 MT of pressure for 45 s. The resulting coating thickness averaged 25 µm. Coated samples were produced using formulations 2 and 4 prepared as described in 4.2.2.3,

Table 3, and the above coating steps. Formulations 1 and 3 were not tested for coating.

4.2.2.6 Coating characterization

Tests described below were all carried out using triplicates of samples, each from a separately prepared sheet and equally conditioned prior to testing, with the exception of the real-world application test and scanning electron microscopy, for which only a single sample of each type was tested. The coated film surface was exposed to the water or testing fluid rather than the uncoated side, where applicable. Controls for comparison were uncoated samples from the same kraft paper substrate as the coated samples and exposed to equivalent heating steps (40 °C for 5 min and 145 °C 1.0 MT press for 45 s). Tests were all performed in a temperature-controlled indoor laboratory. Error bars and bands provided are ± 1 standard deviation.

Water Cobb test

Coated paper samples were oriented such that a circular area (3.5 cm in diameter) was exposed to 7 mL of distilled water contained by a clamped plastic cylinder. Following 1 minute of exposure, the sample was removed, the surface blotted dry, and the mass measured. The Cobb value was then determined (4)(2).

$$\text{Cobb Value (g/m}^2\text{)} = (m_2 - m_1)/\text{Area(m}^2\text{)} \quad (4)$$

m_1 , and m_2 are the sample masses before and after the test, respectively, and ' Area ' is $9.621 \times 10^{-4} \text{ m}^2$.

Grease kit test

In accordance with Tappi T559, twelve different standard grease solutions comprised of varying toluene, castor oil, and *n*-heptane ratios were created (compositions given in supplementary information section, **Table A4**). Following ascending numerical order, a droplet of each solution was applied to the coated or control surface and wiped away after 15 s of contact. The strongest (greatest number) solution that can be applied without causing permanent surface staining is reported as the kit value. A higher kit value denotes greater grease resistance.

Water vapor permeability

Samples were tightly clamped to cylindrical plastic vessels with a circular mouth diameter of 3.5 cm containing 7 mL distilled water. The cups were placed in a shared constant relative humidity environment (sealed glass vessel containing ample desiccant) at ambient indoor temperature. Mass was then measured at the same time daily for a period of 1 week. The Water Vapor Permeability (WVP) was subsequently determined as per Equation (5).

$$\text{WVP} \left(\frac{\text{mg}}{\text{Pa} \cdot \text{d} \cdot \text{m}} \right) = \frac{\Delta W \cdot l}{t \cdot A \cdot \Delta p} \quad (5)$$

Where ΔW is the weight change in mg, l is the thickness in m, t is the time (days), A is the cup mouth cross-sectional area (m^2), and Δp is the nominal partial water vapor pressure difference (1 Pa) between the two sides of the individual test samples. Note that a smaller sample diameter was used for this chapter versus chapter 3. This was done solely so that all

samples could still fit within a single sealed glass testing vessel, due to the increased number of samples for this project.

Scanning electron microscopy (SEM)

Prepared coated paper samples were analyzed using FEI Magellan 400 (Thermo Scientific, USA) and APREO 2 S LoVac (Thermo Scientific, USA) SEMs. Samples were sputter coated, and cross-sections were prepared via EM FC7 cryo-ultramicrotome (Leica, Germany) at -80 °C with a diamond knife.

Wet tensile

The test specimens were cut into 70x10 mm strips and fully submerged in distilled water for 2 minutes, then the surface blotted dry. A universal tensile tester (AGS-X series, Shimadzu, Japan) was then immediately used for testing, with a 10 mm/min strain rate, 500 N load cell, and 50 mm gauge length. Samples were all tested in the machine direction (MD) of the coating, and reported numerical measurements were obtained using samples from multiple distinctly prepared sheets.

Real-world applicability demonstration

Coating 4 as described in

Table 3 and the paper coating procedure above was prepared and folded into a 7x7x7 cm cubic box with open top, coated interior only, and sides adhered using duct tape. Similar containers were formed using uncoated paper and using a commercially coated box currently used by a local restaurant. Three orders of the Canadian dish poutine were obtained from the same local restaurant, and simultaneously transferred in their entirety to the respective containers. The tops were then covered with aluminum foil, and the container placed in a shared convection oven set to 60 °C, the minimum food-safe storage temperature [359]. Pictures of the bottoms of the containers were then taken periodically.

4.3 Results and discussion

4.3.1 CNC modification analysis

4.3.1.1 Fourier transform infrared spectroscopy (FTIR) analysis

FTIR analysis was performed to confirm the succinylation reaction between hydroxyl groups on the CNC and the 2DDSA. The FTIR spectra of both modified and pristine CNC (both dried) are presented in **Figure 20a**. The unmodified CNC showed expected characteristic peaks such as O-H stretching at 3600-3000 cm⁻¹ **(1)**, and C-H stretching at 2920-2850 cm⁻¹ **(2)**, aligning with previous studies [12,360–363].

After modification with 2DDSA, new IR peaks and modification to existing peaks occurred. A new peak emerged at 1565 cm⁻¹ **(4)**, corresponding to the asymmetric stretching vibration of the carboxyl group COO- [361]. Modification to the previously mentioned C-H stretching

peak at 2920-2850 cm^{-1} also occurred, due to symmetric and asymmetric stretching signals from the long-chain alkyl groups [360,361]. These modifications were expected, and aligned with previous similar studies on CNC succinylation or modification [12,360,361].

Lastly, the lack of a peak at 1820 cm^{-1} (**3**) is critically observed as an IR peak at 1820 cm^{-1} is associated with a closed-ring anhydride, which is present only in unreacted 2DDSA [12]. This confirms that there is negligible unreacted residual 2DDSA indicating that there is no further washing required to remove residual reagent. This then decreases the cost and complexity of the modification, and the modified CNC being stored wet means they do not need to be redispersed before use as a Pickering emulsifier. The reaction going to completion was expected as the quantity of 2DDSA added is small relative to the number of reactive sites. This is by design, as only partial substitution is desired such that the modified CNCs can display amphiphilic properties rather than completely replacing the hydrophilic O-H groups [12].

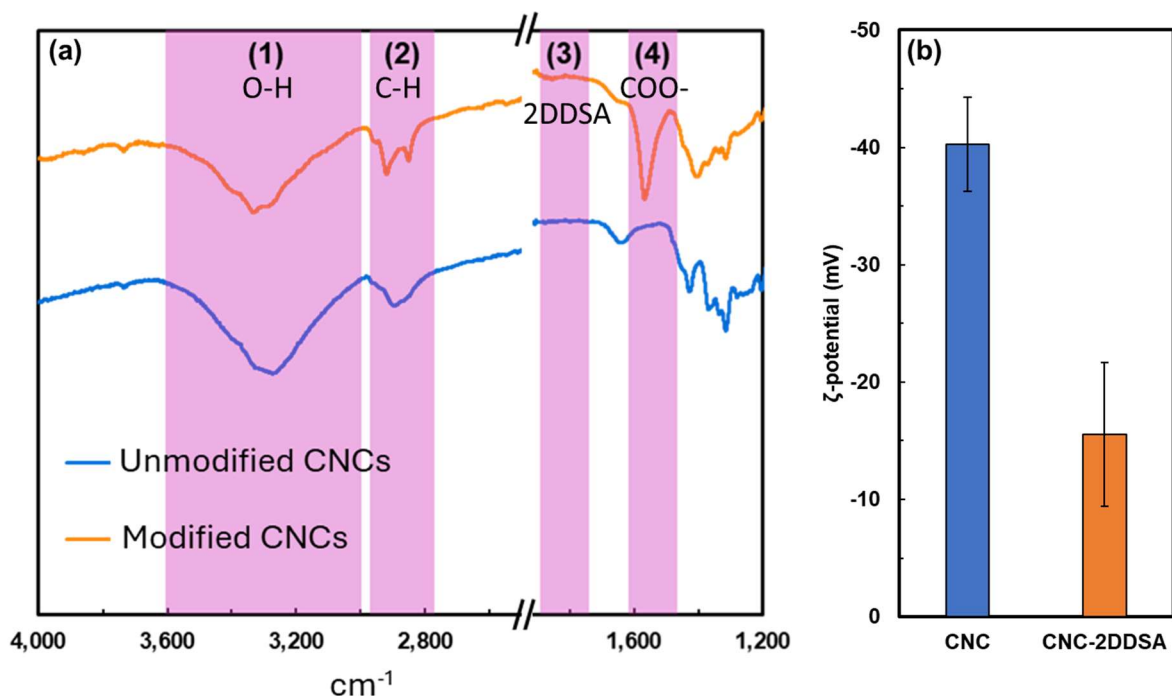


Figure 20. Analysis of 2DDSA-modified and unmodified CNCs. (a) FTIR spectra of dry CNCs. (b) Zeta potential of wet CNCs

4.3.1.2 Zeta potential

The zeta potentials of the modified and unmodified CNCs are shown in **Figure 20b**. As expected, unmodified CNCs possessed a strong negative zeta potential (-40.3 mV), with the charge increasing as a result of the 2DDSA grafting to a value of -15.6 mV [12]. This initial value is associated in part with sulfate groups generated during CNC production, while the observed increasing value is attributed to esterification [12]. Both the initial zeta potential value and that of the modified CNCs agrees with literature on similar modifications [12,360]. The changing zeta potential value supports the conclusion of successful CNC-2DDSA grafting. However, the decreasing surface electrical charge means decreased electrostatic repulsion, which could lead to increased clumping [360]. No visible aggregation was

observed on modified particles stored wet in the refrigerator for multiple months, however increased aggregation was observed when diluting samples with modified CNC relative to their unmodified counterparts. These aggregates contained weak attractive forces and were easily redispersed through vortexing, stirring, or mechanical homogenization.

The characterization experiments supported the hypothesis that the overwhelming majority of 2DDSA became grafted to the CNCs via the proposed reaction in **Scheme 1**. A subtle color change was also observed, as shown in (**Figure B1**), but overall visual appearance remained similar to the unmodified CNC.

4.3.2 Pickering emulsion formulation and stability characteristics

All four CA Pickering emulsion formulations tested were visually indistinguishable immediately after preparation, exhibiting a homogenous milk-white appearance (**Figure 21**). No aggregated particles were visible to the naked eye, and regular flow was observed when poured. However, by 20 days post-preparation at room temperature storage, sample 3 showed significant separation, and sample 1 had visible translucent clumps at the bottom of the vial. Additionally, a thin translucent film had begun to form at the top surface of all dispersions. Samples 1 and 3, which both contained the same higher concentration of CNC Pickering emulsifier compared to samples 2 and 4, demonstrated decreased dispersion stability. This suggests that the higher concentration of CNCs may promote instability, potentially through depletion flocculation [364].

Given that lower CNC loading is desirable from an economic standpoint [365], and that it also led to greater stability, samples 2 and 4 with lower CNC concentration were selected for the paper coating analysis. Further reduction of the CNC concentration was not investigated but is likely to be achievable, based on the stability observed and the presence of unbound CNC visible in the suspension under electron microscope (**Figure 24**). Although a reduction in zeta potential magnitude, and consequently repulsive force magnitude, could lead to increased flocculation, this effect was not observed in the samples. The CNC concentration was found to be the dominant factor influencing stability over the tested timeframe and values [366].

The stability of the CA dispersions over 20 days is comparable to other successful waterborne biopolymer dispersions produced at the lab-level [1]. Additionally, while formal analysis was not performed, optical microscopy and visual inspection indicated that the samples remaining stable over 20 days were still stable beyond 3 months (**Figure B2**). During preliminary screening, many unstable formulations displayed negative characteristics immediately or shortly after homogenization. Most commonly, this involves phase separation, with clearly distinct organic and aqueous phases forming right after homogenization, as well as sedimentation and creaming. Examples of separation in unsuccessful trials are shown in **Figure B3**, with all pictures within 24 h of attempted dispersion formation. The decreasing volume observed in **Figure 21** was due to aliquots removed for characterization.

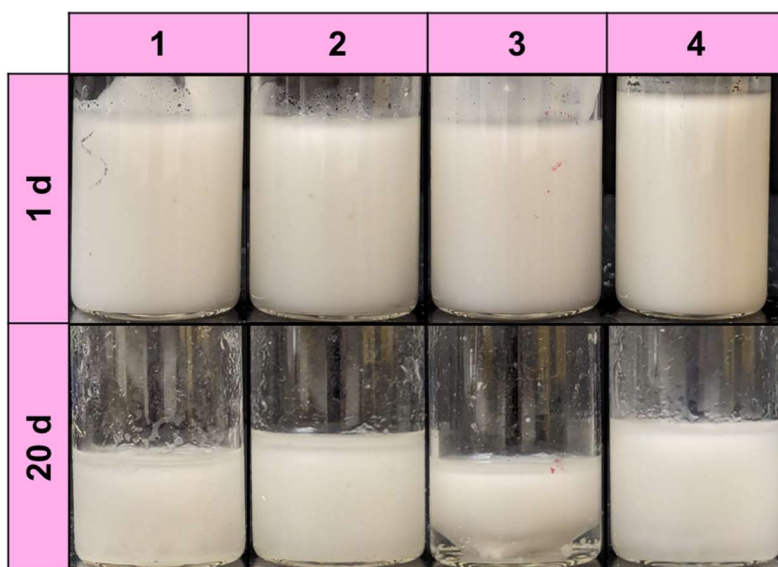


Figure 21. Stable dispersions 1 day and 20 days after preparation

Industrial waterborne emulsions and dispersions are comprised of solids fractions spanning a wide range of values. High solids content acrylics in widespread use surpass 50 wt.% solids, but waterborne paper coatings trend below 10 wt.% to allow for slurry processability [3,39]. Storage conditions, water solubility, particle size, and dispersion preparation method all impact the maximum achievable solids percentage [1,45,292,293]. Improvements to waterborne dispersion formation and application techniques are likely to result in greater benchmark solids percentages in the future [14,54]. The 10 wt.% in this work meets current industry benchmarks for waterborne paper coating, allowing for potential economic viability. The demonstrated 10 wt.% is also likely to be easily increased. The rheological behaviour of the waterborne dispersions in this study were desirable for physical coating methods [72], but modification via additives may be necessary for other methods/applications, such as curtain

coating [3,367]. Trials with increased evaporation and thus increased solids concentration (wt.%) did not exhibit a collapse of dispersion stability, and coating ability was maintained. However, dilution led to clumping and storage stability was reduced (**Figure B4**). Alternative storage conditions (e.g., lower temperature) and the addition of a rheological modifier could alleviate these shortcomings while retaining the economic advantages of a greater solids weight percentage [39,72,368].

4.3.3 Colloid particle analysis

Optical microscopy and TEM analysis were performed on the dispersions in order to confirm Pickering emulsion formation, as well as to assess the particle morphology, size, and size distributions. Particle size characterization is especially important as it both impacts the qualities of the resultant coating and is a key stability indicator [1,4,42]. Particle size distributions are presented in **Figure 22**, optical microscope imagery is displayed in **Figure 23**, and lastly TEM images are presented in **Figure 24**. Optical microscope and particle size distributions compare data observed at 1 day and 20 days after dispersion formation (stored at room temperature between tests), while the TEM images were taken 7 days after dispersion formation.

Particle size analysis (**Figure 22**) based on optical microscopy images depict a narrow size distribution and stability for dispersions 2 and 4, evidenced by low standard deviation on mean particle diameter and consistent means between 1 day and 20 day measurements. In contrast, dispersion 1 shows a large change in particle size (nearly tripling mean diameter),

while sample 3 also shows inconsistency. Data is presented using number-length mean diameter and standard deviations (distributions were approximately normal), with a minimum of 20 particles and two separate images used to obtain each result [325]. Particle sizes were determined using optical microscopy evaluation, due to accuracy issues with DLS in this particular range [321,325]. This is compounded by the presence of the CNC nanorods in the dispersion, which are not captured in optical microscopy but would impact DLS results [369].

For the optical microscopy results presented, it should be noted that the values contain some inaccuracy, such as slightly underrepresenting average size while overrepresenting standard deviation, due to the nature of optically capturing particles in a three-dimensional space [328]. However, for the purpose of this work, the absolute measurements are not critical, but rather the successful ability to compare samples across timeframes and confirm stable particle mean diameters and consistent distribution. All particles are larger than typical of an innately stable waterborne dispersion, hence the earlier recommendation of a rheological modifier to enhance stability [370]. Alternatively, the particle size could be decreased through methods such as changing the Pickering stabilizer (CNC) concentration as used in other works [19]. However, as seen in **Figure 22**, the modification of CNCs appears to be the stronger determining factor, as samples 3 and 4 both exhibit much larger mean diameter than samples 1 and 2. This is expected as a portion of the hydrophilic OH groups on the CNC have been replaced, meaning that a greater percentage of the colloid surface must be coated with CNC to provide the same interfacial stability [19].

This results in a similar effect to decreasing the concentration of stabilizing particles, and so it follows geometrically that the drop size will increase to correct for the necessary volume to surface area ratio required to form stable particles [352]. Alternatively, this effect can be stated as understanding that a greater magnitude of zeta potential will result in smaller particle size and vice versa [371]. Alteration of the mixing conditions, such as increased mixing speed or time, would also be expected to decrease the particle sizes if the employed conditions were insufficient to reach the formulation-limited minimum [287]. Regardless, the existing methods produced stable dispersions for samples 2 and 4, with a particle size amenable for coating.

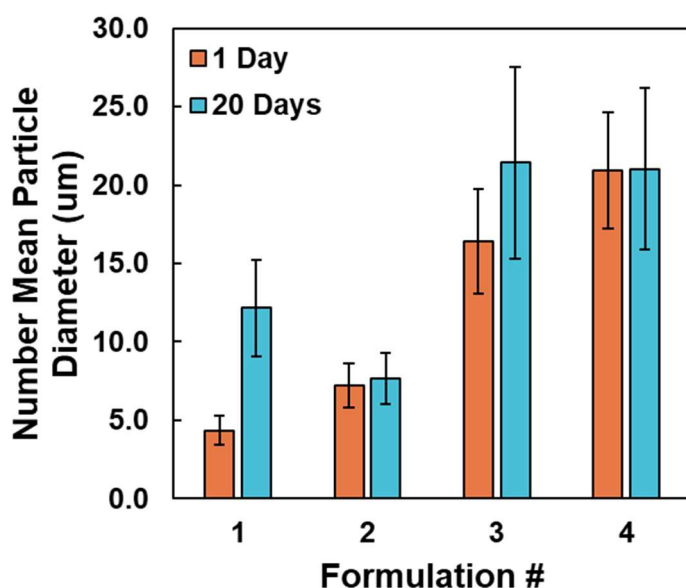


Figure 22. Particle size analysis on optical microscope images of the four prepared dispersions, 1 day and 20 days after preparation.

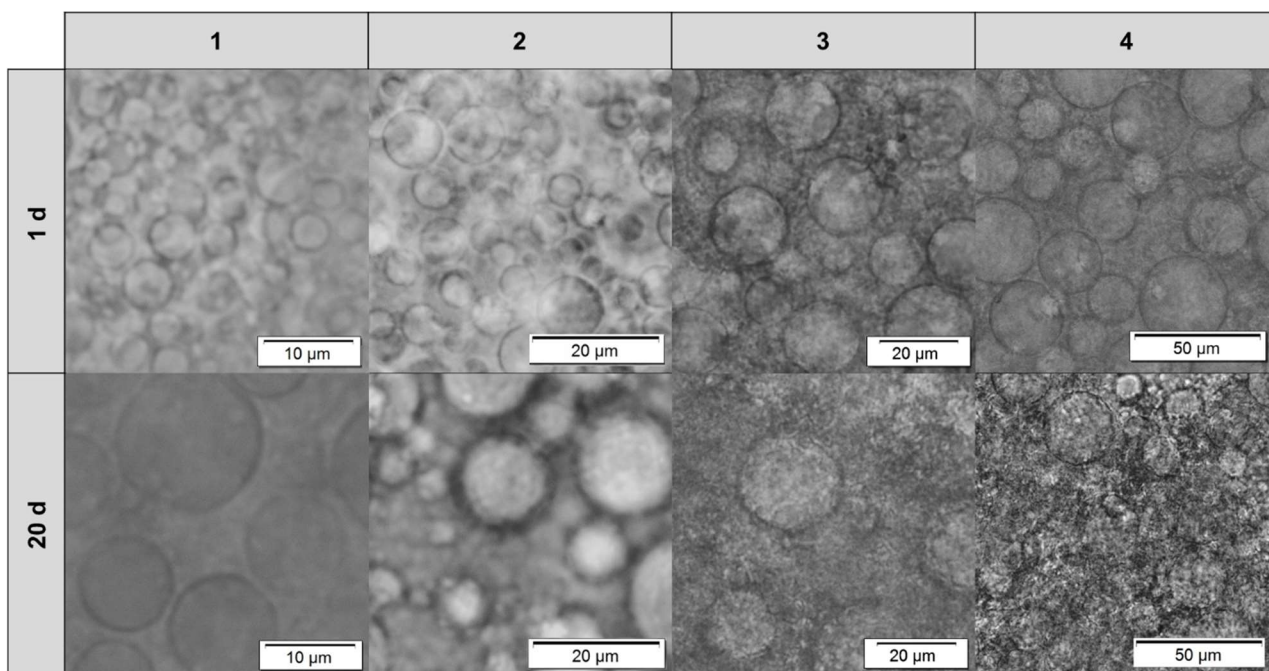


Figure 23. Optical microscope images of the four prepared dispersions at varying magnification, 1 day and 20 days after preparation. Color, brightness, and contrast adjusted.

The TEM images clearly show cellulose acetate particles stabilized by CNCs at the phase interface. This is particularly evident in images such as **Figure 24b**, where CNCs prevent contact between otherwise abutting particles. The CNCs appear to lie nearly flat along the particle surface, maximizing interfacial contact and supporting the notion that a Pickering emulsion has been formed [19]. The colloid particles appear roughly spherical as expected based on underlying kinetics [19,372,373]. For the testing method, it should be noted that the small white dots seen to varying degrees in the images (especially noticeable on **Figure 24e**) are not particles. These spots appear due to the adverse effect of the electron beam on the organic material and are not relevant for the analysis performed in this work [374].

Additionally, the samples shown have been diluted, and TEM imagery does not account for

depth [375]. TEM and particle size analysis also support the earlier hypothesis that higher concentrations of CNC promote instability, through a mechanism such as depletion flocculation. CNC modification is shown to be the determining factor for size in **Figure 22**, rather than concentration, confirming why dispersions 2 and 4 are more stable than 1 and 3. Consequently, the stabilized cellulose acetate particles likely have a saturated surface coverage of Pickering particles, with excess CNC remaining unbound in solution, visible in the TEM imagery. Overall, these images positively support the proposed stabilization mechanism of Pickering emulsion formation and provide insight into the interfacial behavior.

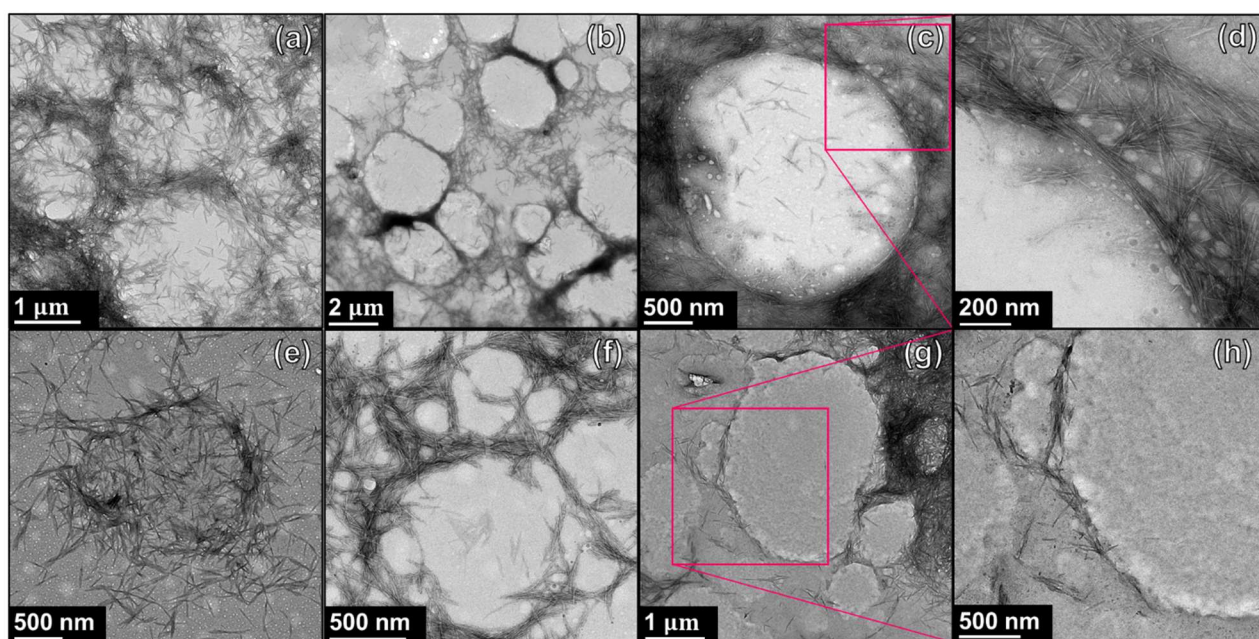


Figure 24. TEM images of formulations 1 (a), 2 (b-d), 3 (e-f), and 4 (g-h), 7 days after preparation, at varying levels of magnification.

4.3.4 Rheological behavior

Dynamic viscosity and shear stress as functions of shear rate were evaluated to determine flow behaviour of the created dispersions. As shown in **Figure 25a–b**, the samples were sheared from 1.0 s^{-1} to 1000 s^{-1} via continuous ramping over 1 min. Note that only samples 1 and 2 are plotted on **Figure 25a–c**, while the rheological behaviour of samples 3 and 4 is available in the supporting information (**Figure B5**). This split was done for clarity in reducing the quantity of overlapping data displayed on the figures, as sample pairs (1 and 3) and (2 and 4) exhibited similar overall rheological behaviour. **Figure 25(a)** and **(b)** data was measured concurrently on a single sample but plotted separately for ease of visual decipherability.

For all samples as the shear rate is increased, the dynamic viscosity decreases while shear stress increases, until high shear rates at which the peak shear stress value is eclipsed and shear stress begins to decrease. The observed decreasing dynamic viscosity associated with increasing shear rates demonstrates clear shear thinning behavior for all samples [246]. Slip surface generation is the suspected cause of the non-uniformly increasing shear stress, which is expected in these dispersions based on the large dispersed particle sizes and volume percentage [318]. Shear thinning is both the desired behaviour for coating applications and the expected behaviour for a Pickering emulsion [2,43,289,376].

Comparing the 1 day and 20 day measurements, dynamic viscosity and shear stress have increased for all samples at both the minimum and maximal values (1.0 s^{-1} and 1000 s^{-1}), with the exception of stress for dispersion 4 at 1000 s^{-1} . As shown in **Figure 22**, particle sizes

increased over time, indicating coalescence as a possible explanation for some of the observed behaviour [377]. Larger particles would generally result in a less viscous solution rather than the observed increased dynamic viscosity [42]. However, the CNC particles are not included in the particle size analysis. As the particles coalesce, the surface area drops, leading to an increased concentration of unbound CNC particles in solution if CNC particles remain solely at the CA colloid surfaces and at a constant surface density [377]. This effect may be sufficient to explain the observed behaviour, as the difference between both the samples rheological properties and particle sizes over time are fairly small. Samples 1 and 3 also have higher dynamic viscosity than their counterparts, samples 2 and 4. This further supports the importance of CNC concentration on the rheological behaviour of the solutions, as 1 and 3 contain a greater quantity of CNC.

An amplitude sweep test was also conducted, as shown in **Figure 25c**, at a constant strain of 1% to evaluate deformation behavior of the dispersions within the linear viscoelastic region. While the storage (G') and loss (G'') moduli behavior remains similar over time for samples 2 and 4, samples 1 and 3 show large deviations in behavior. These decreasing G' and G'' values for dispersions 1 and 3 indicate destabilization [378]. The erratic behavior on the 20 day dynamic viscosity and shear stress measurements for samples 1 and 3 similarly portray destabilization and non-homogeneity [379].

Overall, while acceptable for industrial coating applications, it was worse than desired, as a key benefit of Pickering emulsions is their high stability [19,380]. However, the systems contained particle sizes on the larger side for Pickering emulsions [380], exceeding the

Brownian-induced limits for unaided indefinite stability [370]. To further increase the stability time, a rheological modifier such as a gum could be added. Gum addition would increase the viscosity at rest (storage) [319], while retaining coatability [289,319]. Refrigeration and avoidance of light exposure may also enhance shelf stability by reducing energy in the system [381]. Despite the room for improvement, the samples tested, especially dispersions 2 and 4, showed long-term stability sufficient for industrial applications. Additionally, the rheological behaviour observed supports the proposed application for the dispersions as coatings [41,246,289].

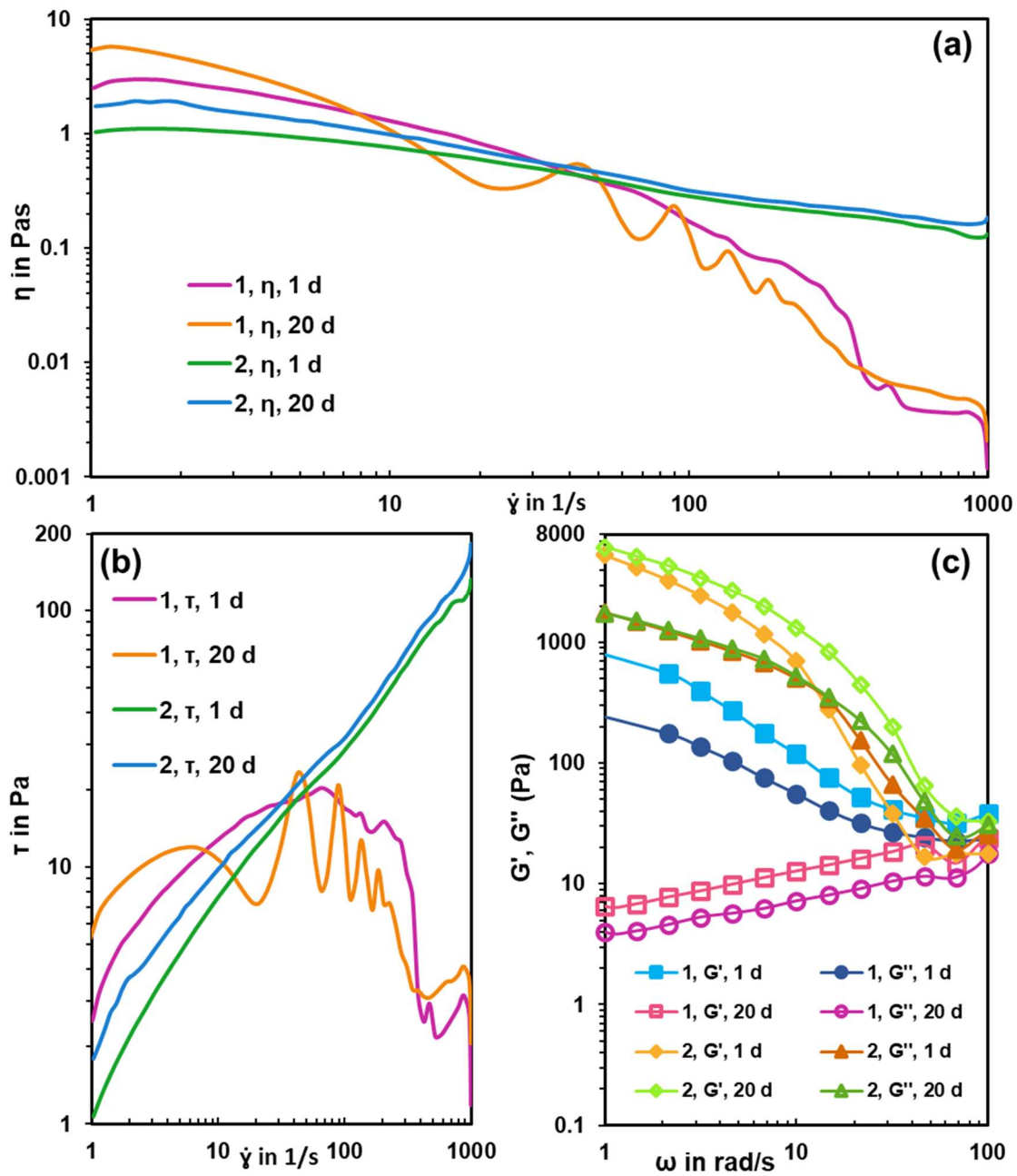


Figure 25. Rheological test results 1 day and 20 days after dispersion preparation. (a) viscosity curve, (b) flow curve, and (c) viscoelastic spectrum. Legend provides sample #, test parameter, sample age. Filled in markers indicate 1 day old while unfilled indicates 20 d.

4.3.5 Paper coating and properties

Selected cellulose acetate Pickering emulsions in water, stabilized with cellulose nanocrystals, (formulations 2 and 4 in

Table 3) were coated on unbleached kraft paper at 40 °C using a Baker film applicator, then pressed at 145 °C. The prepared coated paper made with dispersion 4 before and after being hot compressed is shown in **Figure 26(a)** and **(b)**, respectively, while coating with dispersion 2 is shown in **Figure B6**. Excellent film adherence to the paper substrate even under flexion was seen both before and after the heated compression. The heated compression was performed to briefly elevate the temperature to that of the minimum film forming temperature (MFFT), allowing full coalescence of the colloids necessary to provide a uniform film with barrier properties [4,40,48]. At the same time, the temperature, pressure, and exposure time were selected such as to not cause significant degradation of the polymer or paper substrate through preliminary experimentation [4].

The primary visual result of the thermal curing is that the film turns transparent, indicating coalescence and the formation of a continuous film (**Figure 26 and B6**) [4,40]. As well, the surface of the film became smooth, whereas prior to treatment there was visible roughness, and some small patches appearing bare where the underlying paper was visible through the deposited white coating (**Figure 26a**).

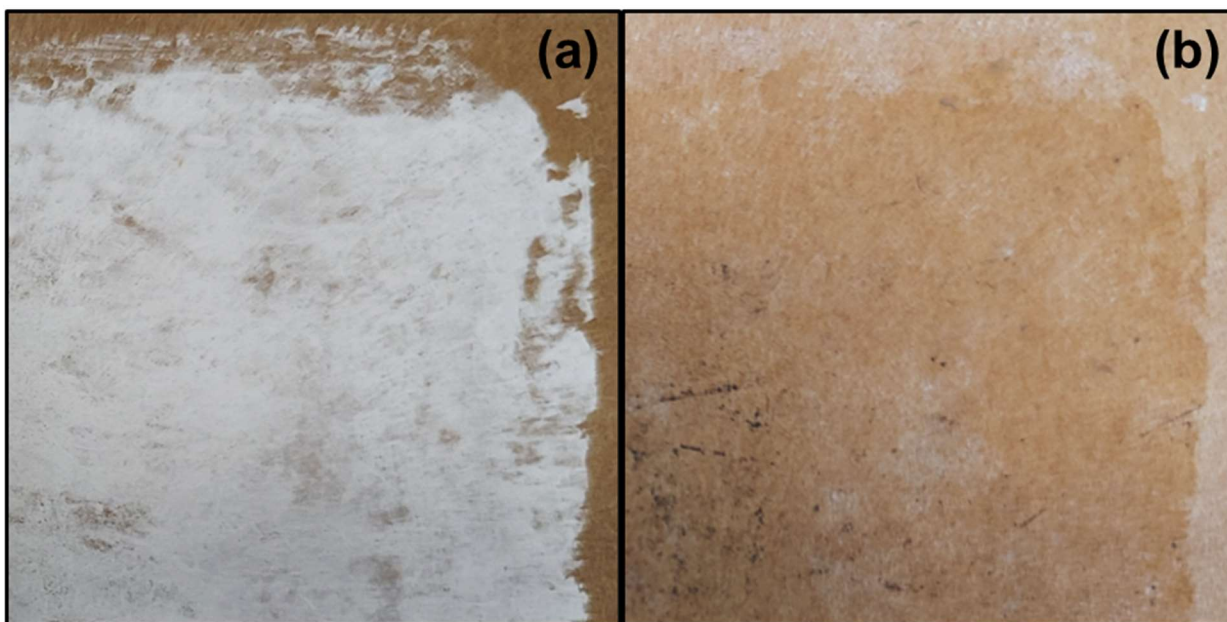


Figure 26. Paper coated with dispersion 4 as described in section 4.2.2.5. (a) after coating and drying before hydraulic compression, and (b) after hot compress. The unbleached kraft paper possesses a brown color.

Samples 2 and 4 were selected because they exhibited the necessitated stability. While both samples contain equal CNC loading, the modification of the CNCs is expected to yield some difference in coating properties, alongside the already known differing particle sizes.

The water vapor permeability, water resistance, oil resistance, and wet mechanical properties of the coated papers were then evaluated. These characteristics were selected for evaluation as they are all limitations of uncoated paper which are desirable to overcome [2]. As well, SEM was performed on both the surface and cross-sections of the coated paper in order to better understand the coating morphology. Lastly, a real-world application study was performed, using the coated paper as a container for greasy takeout food.

4.3.5.1 Coating morphology

SEM imagery of the surface and cross sections of papers coated with both dispersions is shown in **Figure 27**. From the images, it is clear that the surface of dispersion 4 using modified CNC is much smoother than the surface using dispersion 2. This is not surprising, as the decreased zeta-potential of the modified CNCs are expected to reduce the impact of repulsion forces and thus allow for smoother coalescence [366]. While a decrease in particle size is generally known to decrease MFFT, the particle diameters are of similar order of magnitude and the applied thermal curing was above MFFT for both dispersions, thus in this case it likely had little impact [366,382]. Similarly, the cross section on dispersion 4 coated paper shows smaller voids within the coating itself. Both coatings show similar thicknesses of $\sim 20\text{ }\mu\text{m}$, as expected due to the solids percentages and coating volumes being practically equal. As well, both cross-sections reveal strong adherence to the paper substrate, with no delamination visible. Based on the equivalent thicknesses but smoother and less porous coating from dispersion 4, paper coated with dispersion 4 is expected to yield superior barrier properties to that of dispersion 2 [383–385]. As well, due to the CNC modification, dispersion 4 should have reduced hydrophilicity as desired for barrier coating of paper [2].

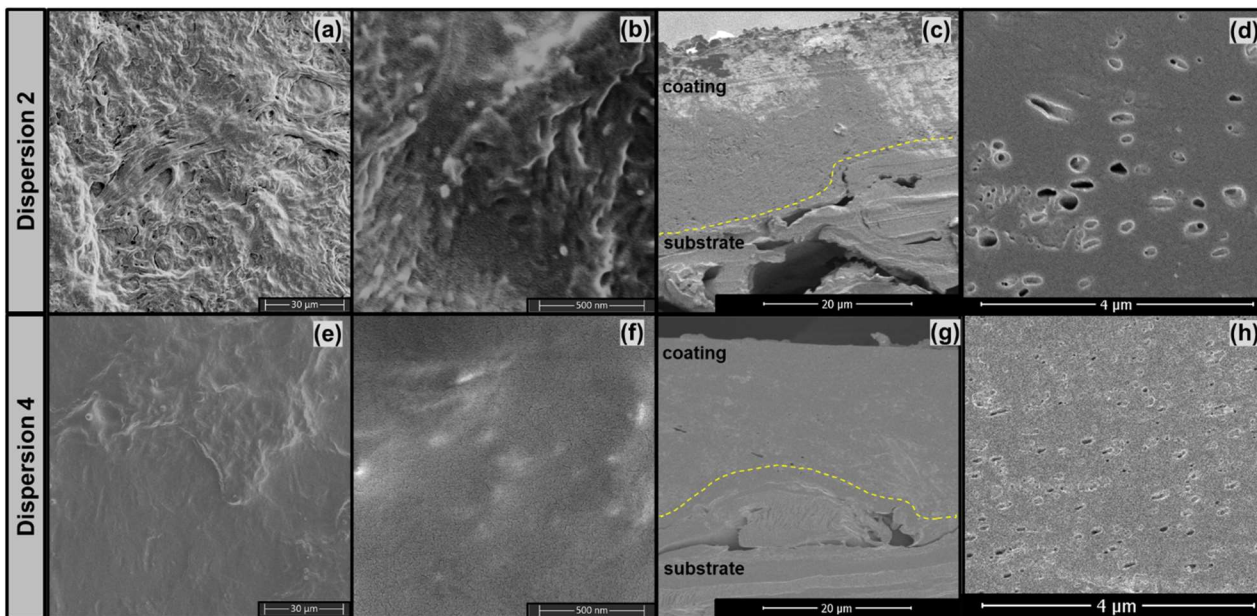


Figure 27. SEM images of surface (a,b,e,f) and cross sections (c,d,g,h) of coated papers. Dispersion 2 with unmodified CNC (a-d) and dispersion 4 with modified CNC (e-h). (d) and (h) are cross-sections solely of the coating

4.3.5.2 Water vapor permeability

Resistance to water vapor is among the most critical properties of packaging materials, and is of particular concern for applications using paper substrates[2,246,281]. Transmission of water vapor through the coated papers at constant temperature and relative humidity was measured using a water vapor permeability test (WVP), shown in **Figure 28a**. For papers coated with both dispersions, slightly lower WVP values were measured compared to uncoated paper, with the dispersion 2 coating measuring the lowest water vapor transmission. The values are as desired, demonstrating that the paper coating mitigates water vapor transmission. As well, the tight error bands show consistency within each of the samples tested and supports repeatability. Measured values were higher than literature values for

commercial packaging films, however it should be noted that high variability in the test exists [246,336]. Changing temperature, humidity, and pressure can all influence the results, as well as the lack of impermeable control used as a benchmark in this experiment [246]. As a result, comparison among the samples tested is of the greatest value, and a reduction in transmission greater than 10% is seen for both coatings tested relative to the uncoated sample. The modest improvement could be attributed to the kraft base paper substrate. Contrary to many papers which are thin and highly porous, the utilized kraft paper chosen is thick and has relatively high grammage [386]. These factors mean that the baseline transmission is much better than often seen for paper substrate, and thus a significant reduction is both harder to achieve and less critical to success.

The superior transmission performance of coating 2 over coating 4 was also unexpected, as the reduced hydrophilicity of coating 4 as well as the preferable morphology was expected to favor coating 4. However, the small particle size does favor coating 2, with the film potentially achieving better penetration into the substrate pores than coating 4 [387,388]. Alternatively, despite having larger pores in the coating visible in the SEM image for coating 2 (**Figure 27d**) compared to coating 4 (**Figure 27h**), the pores appear to be more disjoint, and may not have continuous or as large of channels allowing as high levels of transmission [387]. This latter described effect seems more likely based on the SEM morphology images and must have had a more significant effect on reducing the transmission than the mentioned factors in favor of coating 4. Lastly, it is possible that the larger pores seen via SEM and the greater hydrophilicity meant that the coating acted in a hygroscopic manner, retaining more

water than coating 4 and thus decreasing the total vapor transmission quantity [389]. This hypothesis is lent credence by the substantial water retention seen in the water Cobb test, **Figure 28b**. Overall the results are also expected as it is known that cellulose acetate has only moderate WVP properties [390]. If preeminent performance is necessary, additives could be incorporated into either the coating or the substrate itself for this specific purpose [390,391].

4.3.5.3 Water Cobb and grease kit

Low water Cobb values are desired for paper coating applications, as the value from the water Cobb test is inversely correlated with water barrier performance [246,281]. In the water Cobb test liquid water absorbance is assessed by measuring the weight change of the subject after 1 min of direct water contact. As uncoated paper is highly hydrophilic, it has a high water Cobb value [246]. The paper coated with dispersion 2 has a much greater Cobb value (**Figure 28b**) rendering the coating unusable for many applications. This observation is associated with the highly hygroscopic CNCs and the value supports the proposed notion for the WVP test that showed that the low transmission value was due to a very high water absorbance level. Contrary to the poor performance of dispersion 2, dispersion 4 shows excellent water Cobb performance. The water Cobb value for dispersion 4 exhibits greater than 60% reduction in the magnitude of water absorbed relative to the uncoated paper. This percentage reduction in water absorbance, as well as the Cobb value itself exceeds the results found in literature for similar systems [392,393].

For the kit test, a high value is preferred and indicates greater grease resistance [246]. The kit test is a widely accepted method for testing grease resistance of paper coatings [2]. 12 solutions with varying viscosity and surface tension are applied in series to the surface [332]. The highest value out of 12 which does not leave a permanent stain on the surface after being wiped away is reported as the kit number, as reported in **Figure 28c**. Uncoated paper has a surface which is highly porous and irregular, and thus is stained by all solutions and receives a kit number of zero [23,246,332]. Coating the paper with the cellulose acetate dispersions greatly improves the kit values, to 7 for dispersion 2 and 10 for dispersion 4. Kit values greater than 8 out of 12 are typically considered to be grease resistant, so the value of 10 is very promising for successful applicability of the coating [2]. It has also been demonstrated in literature that the kit number can be further increased if required through the use of specific additives or increased coating thickness [2,246]. The superior performance of coating 4 over coating 2 is expected due to the smoother surface [246,332]. One study on commercial food packaging samples found kit ratings ranging from 8–11, so the rating of 10/12 is competitive even with the disadvantages inherent to lab coating [394–396].

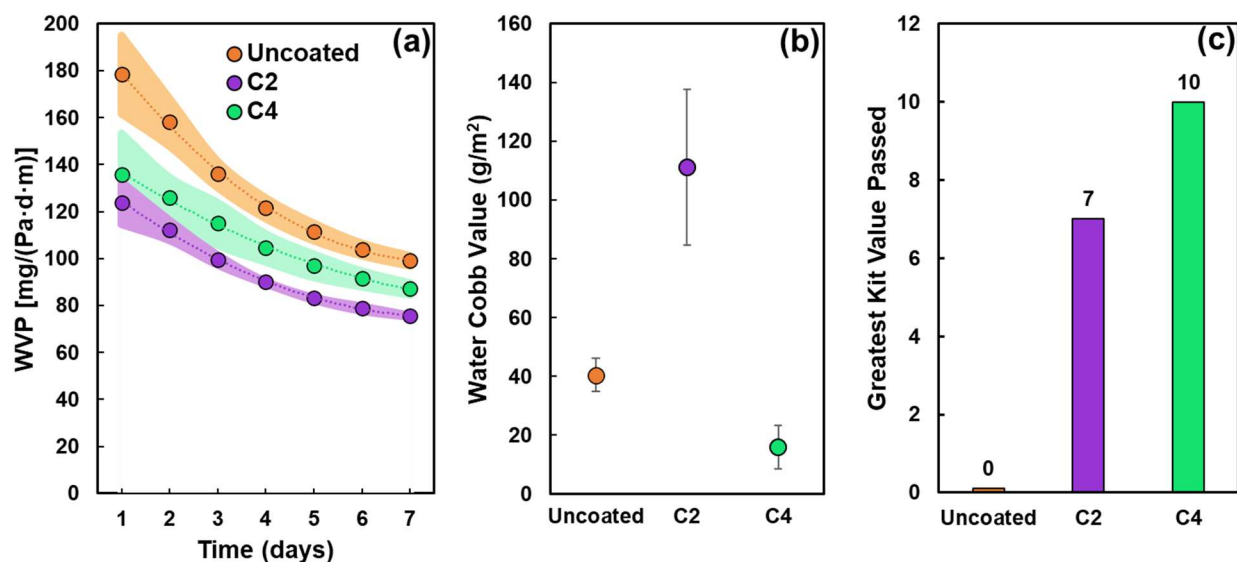


Figure 28. (a) Water vapor permeability test results, (b) Water Cobb test, (c) Grease kit comparison. Dispersions 2 and 4 as well as uncoated paper for all tests.

4.3.5.4 Wet tensile properties

Wet tensile testing provides insight into the influence of direct water exposure on the structural integrity of the paper, which is a key consideration factor for many packaging applications [246]. Coated and uncoated samples underwent 2 mins of complete submersion in water, were blotted dry, and then immediately underwent tensile testing. Results of this testing are presented in **Figure 29**. Since samples were fully submerged with only one side coated (or none), for all samples regardless of the water resistance of the coating itself the paper substrate was impregnated with water. Minor or insignificant improvement to the tensile properties was seen from either coating but, positively, no property showed a decreased performance relative to being uncoated. The greatest changes were seen for the

maximum stress and Young's modulus values of coating 2, with the elongation at break for coating 4 also showing strong improvement over the uncoated paper. It is well established that wet paper has a Young's modulus lower than that of dry paper [337]. As well, in general an increasing porosity will result in a decreasing Young's modulus as fluids have a Young's modulus of zero [397]. With this in mind, it follows that for the Young's modulus to be higher for coating 2 it is likely that the paper itself remains unaffected, with the hygroscopic coating retaining much of the moisture. This proposition agrees with the previously proposed mechanisms surrounding the water Cobb and WVP values. Regardless, the values are in line with expectations of the coating having only marginal effect on the wet tensile properties, when such a large proportion of the mechanical properties in this case will be dictated by the thick paper substrate and tensile testing parameters rather than the thinner coating applied to only one side [337]. As well, the observed stress-strain curvature is as expected for a wet tensile test on paper in which gradual failure of individual wet paper fibers is expected as opposed to simultaneous total failure [281]. Samples also showed small distributions, with high consistency between tested samples as desired. Lastly, as discussed for the other properties, alternative substrate selection and additives (such as plasticizers) can be chosen if specific tensile properties are of particular importance [13].

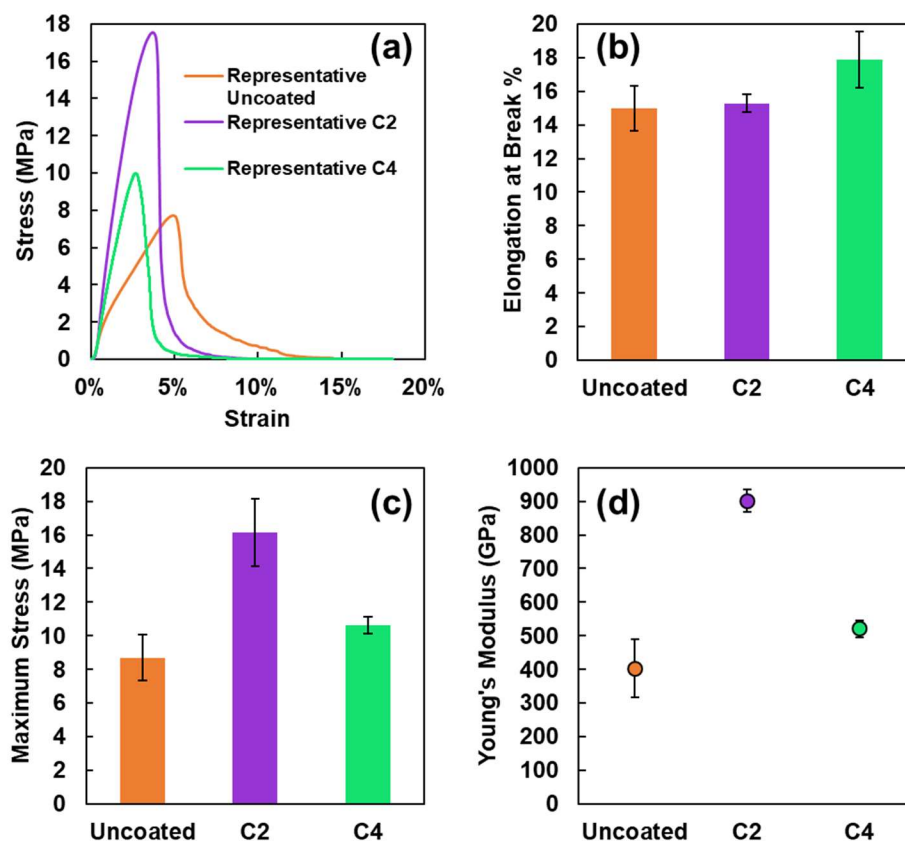


Figure 29. Wet Tensile results comparing coated (dispersions 2 and 4) and uncoated samples. (a) representative stress – strain curves, (b) elongation at break, (c) maximum stress, and (d) Young's modulus

4.3.5.5 Real-world applicability demonstration

The application depicted in **Figure 30** was performed to assess the performance of the coating for a takeout container application. This application was selected due to high interest [246,398–400], as well as its requirement for similar properties to those contained by the coating. Chief among these properties is the high experimentally determined grease resistance, with moderate improvement to the water Cobb value, as well as being more

environmentally friendly with the biobased material as opposed to many existing commercial options [246,398–400].

For the trial, the performance of a commercially available takeout container product was compared to that of a lab-prepared container using dispersion 4 and uncoated kraft paper. Each container was filled simultaneously with a full order of the Canadian dish poutine, sourced from a local restaurant. All containers were then closed and stored in a shared convection oven set to 60 °C, the safe temperature of food, and then the bottom of each container was photographed periodically. Dispersion 4 was chosen for this trial over dispersion 2 due to the experimentally superior results in the most relevant category of grease resistance, as well as much better water Cobb performance. The commercially available product appeared to be a blend of polylactic acid (PLA) and polyethylene (PE) based on FTIR analysis (**Figure B7**) [401,402].

Clearly, from the images captured in **Figure 30**, the uncoated paper performed much worse than the two coated samples and was completely saturated with grease by the end of 24 h. In contrast, the lab coated sample greatly exceeded expectations by performing as well or better than the commercially available product. This is extremely promising as there were no additional additives to the lab product to alleviate shortcomings, as well as an industrial coating generally being smoother and more homogenous, benefiting barrier properties [395,396]. As well the loci of failure are particularly positive. Whereas the commercial sample had grease spots appear on the flat bottom surface within 0.5 h and then horizontally penetrate the paper to expand, the lab-prepared sample never saw penetration through the

container base. Rather, penetration of the lab-prepared coating only occurred at the container creases, and after greater than 6 h. Note that the dark spot visible on the middle-right edge of the lab container is thermal damage from the coating hot compression and not grease, hence why it never changes in size or shape. The 90° creases used were likely too weakening for the coating without any plasticizer additive, without industrially acceptable technique (such as knife/pocket folding) and that the container was folded after complete film cooling rather than while the coating was at elevated temperature [403,404]. Reduced angles of the creases (the commercial container had no 90° creases), altering the folding method, and incorporating additives all have the potential to have made the container demonstrate zero grease penetration in the test window. Alternatively, improved morphology through industrial coating may already be sufficient to overcome the crease failure. It may also be of no consequence as this test used elevated temperature and time of exposure meant to represent the most extreme use-case, and container integrity was still uncompromised. Regardless, the test demonstrated that the coating is competitive with or exceeds existing commercial product performance.

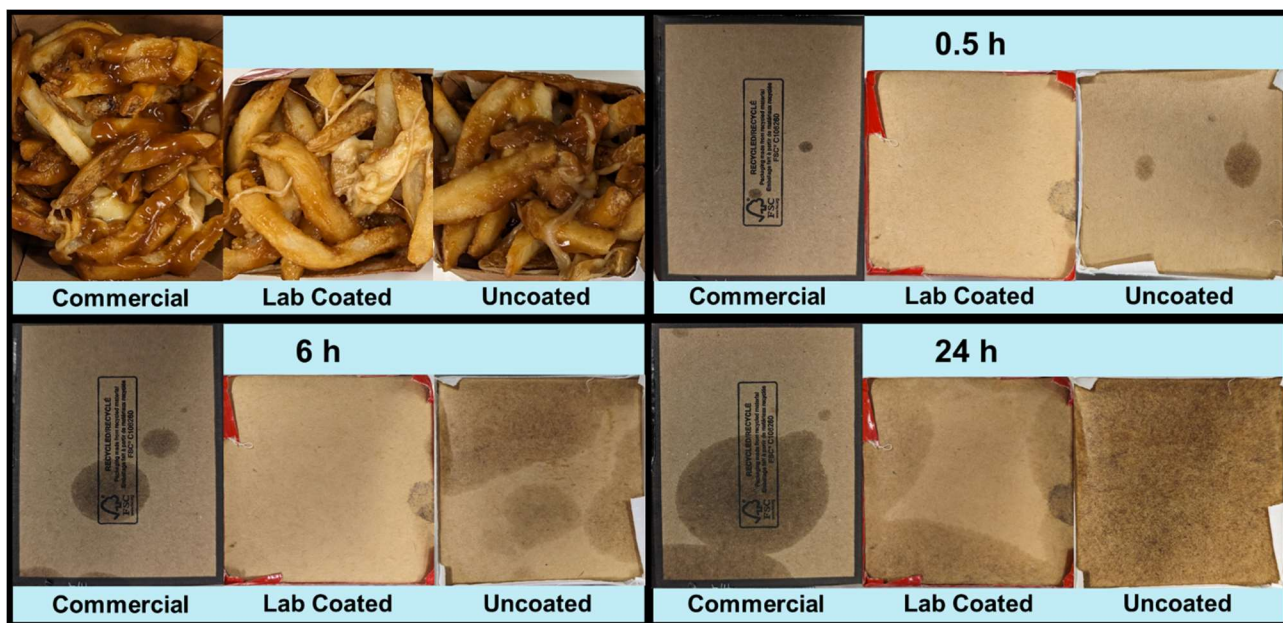


Figure 30. Coated paper application trial. Commercially available takeout container, lab prepared container using dispersion 4, and uncoated kraft paper. Stored covered in oven at 60 °C.

4.4 Chapter 4 conclusions

A Pickering emulsion of biobased cellulose acetate stabilized in water using CNCs was successfully created. The dispersion exhibited good stability and rheological properties favorable for coating applications. CNCs were used in unmodified commercially available form, as well as modified with 2DDSA for altered properties. CNC modification was a success, with the modified CNCs exhibiting lower zeta potential and hydrophilicity. The level of CNC loading into the dispersions significantly impacted dispersion rheology and stability, with lower loading levels forming more stable dispersions. However, modified versus unmodified CNC selection was the controlling factor for particle size determination. Pickering emulsion particle morphology was analyzed using optical microscopy and

formation confirmed via SEM. Paper coated with the generated Pickering emulsion demonstrated greatly improved grease resistance (kit score 10/12 vs 0/12) and water barrier performance (60% reduced Cobb value), without compromising wet structural integrity. A comparative analysis of paper coated with the aforementioned dispersion versus a commercially available product showed strong viability for potential packaging applications. This work indicates an exciting opportunity for the future of bio-based waterborne paper coatings with high barrier property performance.

CHAPTER 5 – CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

Waterborne biopolymer dispersions have substantial potential to become viable commercial products, based on industry trends towards sustainable coatings and improving availability and performance of waterborne coating products. In this thesis, two different biopolymers were investigated, with two different methods of waterborne stabilization. Both experimental projects demonstrated the successful formation of waterborne biopolymer dispersions.

Barrier paper applications are shown to be viable, with strong performance characteristics, both in improvement over uncoated paper and compared to existing commercial products.

The first system investigated was waterborne biobased and biodegradable PHBV using a traditional dispersion technique and employing SDS surfactant and guar gum stabilizer.

Long-term stability at 10 wt.% solids was observed, as were favorable rheological properties for coating applications. Paper coated with this dispersion demonstrated markedly improved barrier property performance based on measurements of water vapor barrier, wet tensile, grease barrier, and water absorption resistance compared to uncoated paper.

In the second system, cellulose acetate was dispersed in water using a Pickering emulsion technique. CNCs were used as the Pickering stabilizer, both in unmodified form and using CNCs modified via reaction with 2DDSA. CNC modification was successful in lowering the zeta potential and reducing the hydrophilicity. Paper coated with cellulose acetate and modified CNC dispersion exhibited vastly improved grease resistance, as well as substantial

improvements to water barrier performance. A trial comparing the coated product to a commercially available food container also demonstrated competitive performance and strong viability for packaging applications.

Overall, the work contained herein indicates an exciting future for bio-based waterborne coatings. While much work remains prior to commercialization, a variety of waterborne dispersions were shown to be formed with relative ease and competitive properties, while greatly improving specific sustainability aspects over current industrial systems.

5.2 Future Work

Suggestions for future research works can be divided into further work on the two systems presented, and overall work on waterborne coating systems. For the systems presented, current performance should be further investigated and tuned for selective applicability to specific applications, such as added flexibility or thermal resistance for certain packaging types. Industrial systems frequently employ numerous additives and/or modification reactions for optimal performance beyond the limited trials presented herein. As well, neither study performed a full biodegradation or compostability study. The PHBV coating is not expected to show any issues, but degradation must be confirmed, as does levels of residual chloroform. For the second project, cellulose acetate and CNCs are both known to degrade under specific conditions and levels of modification, which may not be currently satisfied. If the system is not currently biodegradable, tuning to achieve this milestone in addition to the

sustainability benefits afforded by being biobased and a waterborne system would greatly enhance the attractiveness of the system for reaching sustainability goals.

For overall work on waterborne coating systems, more biopolymers and potential applications should be evaluated, such as other PHAs and polysaccharides, but also additional classes of biopolymers such as proteins. Applications should initially focus on additional high-waste packaging applications such as deli paper. The coatings space is very broad, with substantial variety among products and opportunities for high-value innovative products. Overall, the future for waterborne coatings is bright, with promising advancement towards fully sustainable coatings.

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<https://doi.org/10.1016/j.compstruct.2004.01.024>.

APPENDIX A – SUPPORTING INFORMATION FROM CHAPTER 3

Table A4. Kit test solutions formulations

Kit Number	Castor oil (g)	Toluene (g)	Heptane (g)
1	969	0	0
2	872	50	50
3	775	100	100
4	678	150	150
5	581	200	200
6	484	250	250
7	388	300	300
8	291	350	350
9	194	400	400
10	97	450	450
11	0	500	500
12	0	450	550

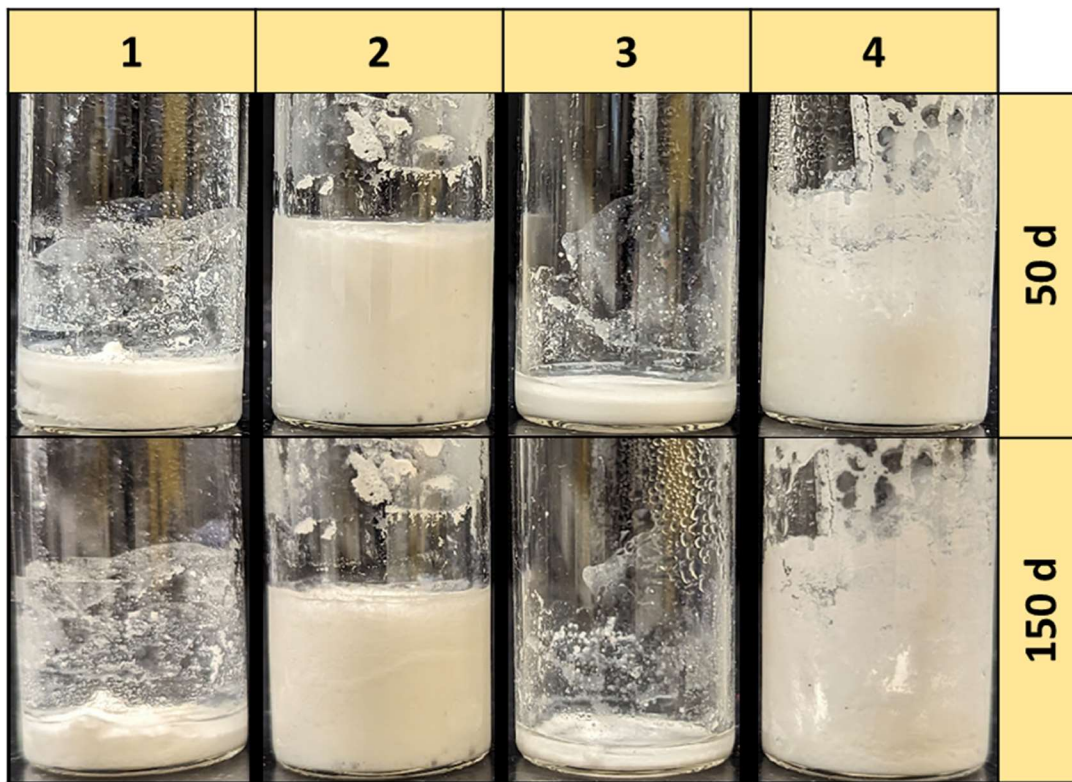


Figure A1. Dispersions 50 d and 150 d after preparation

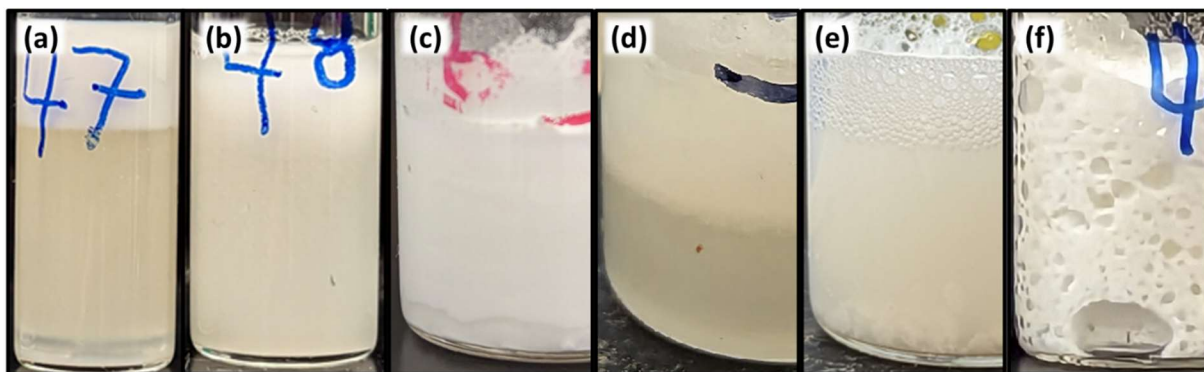


Figure A2. Dispersions prepared exploring different conditions. (a-d) in lieu of pure SDS surfactant, prepared aqueous phase concentration. (a) 2% Tween® 85, (b) 2% Tween® 85 and 2% SDS, (c) 2% CTAB, (d) no surfactant (guar gum stabilizer still used), (e) 2% corn starch in place of 2% guar gum, (f) stable dispersion evaporated to high wt.% solids

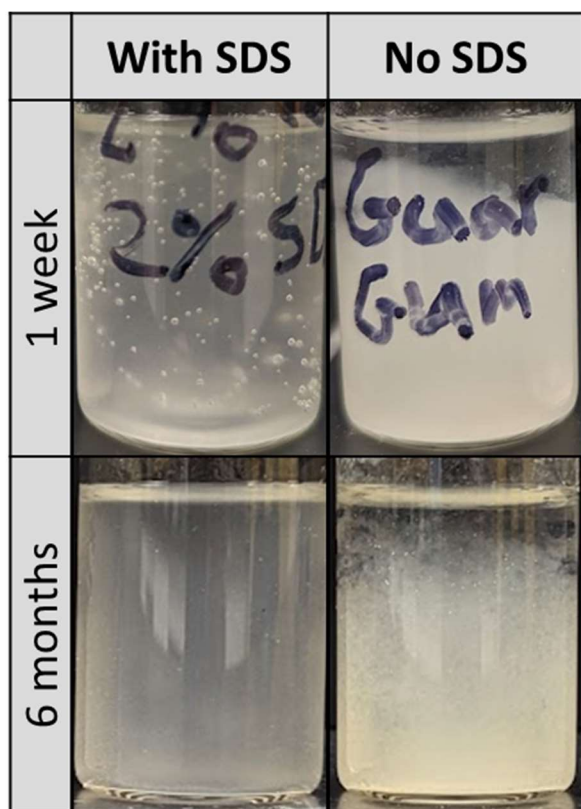


Figure A3. 2% Guar gum with 2% SDS and without, 1 week and 6 months after preparation

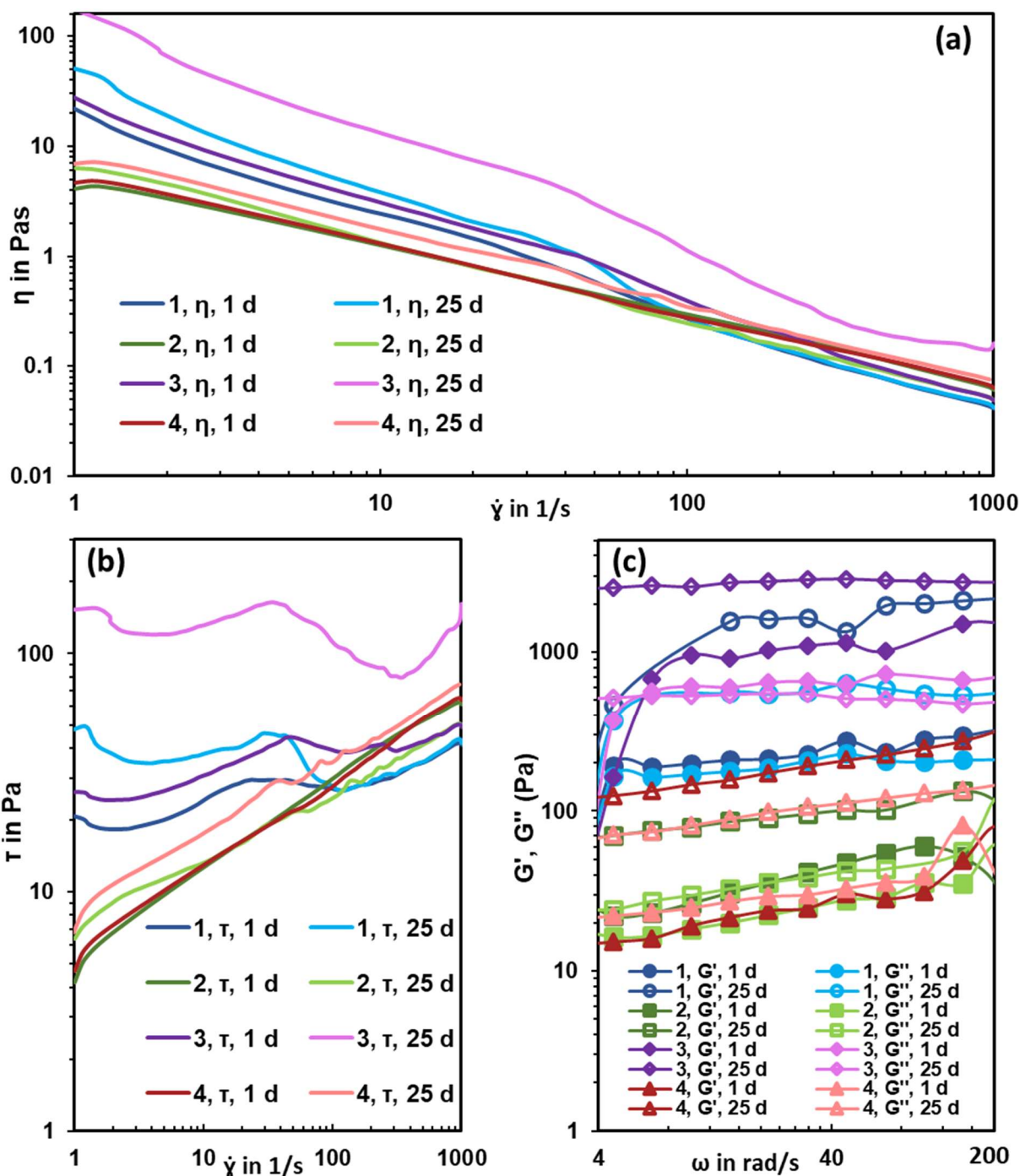


Figure A4. Rheological test results for all samples 1 d and 25 d after dispersion preparation. (a) viscosity curve, (b) flow curve, and (c) viscoelastic spectrum. Legend provides sample #, test parameter, sample age.

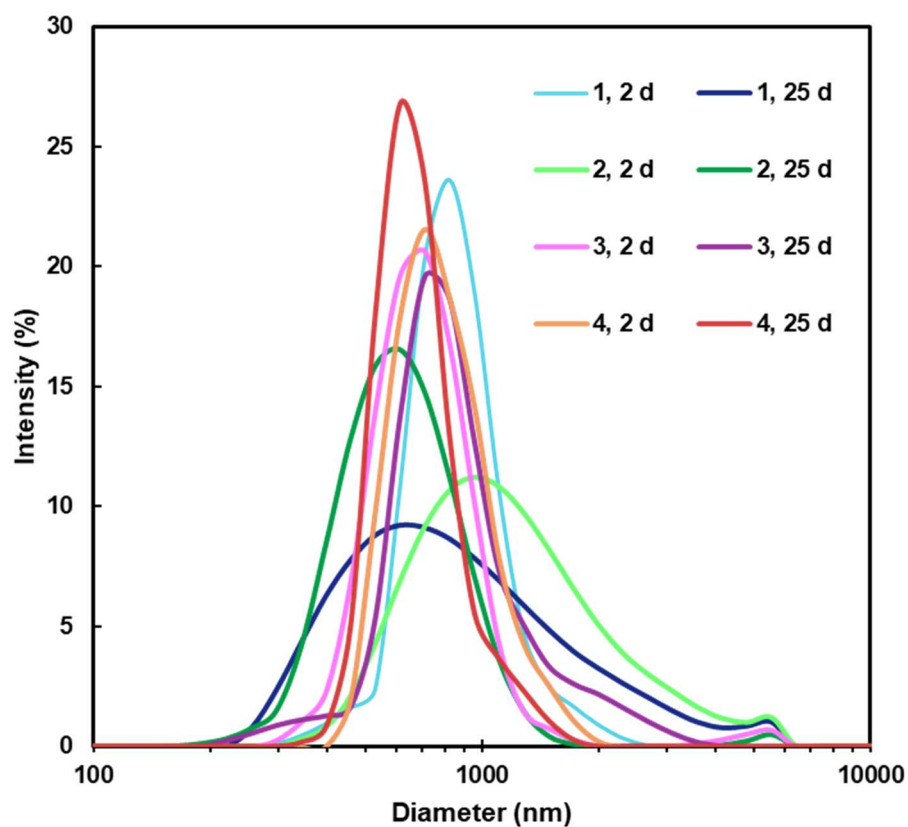


Figure A5. Particle size of all prepared dispersions using DLS. Legend provides sample # and sample age.

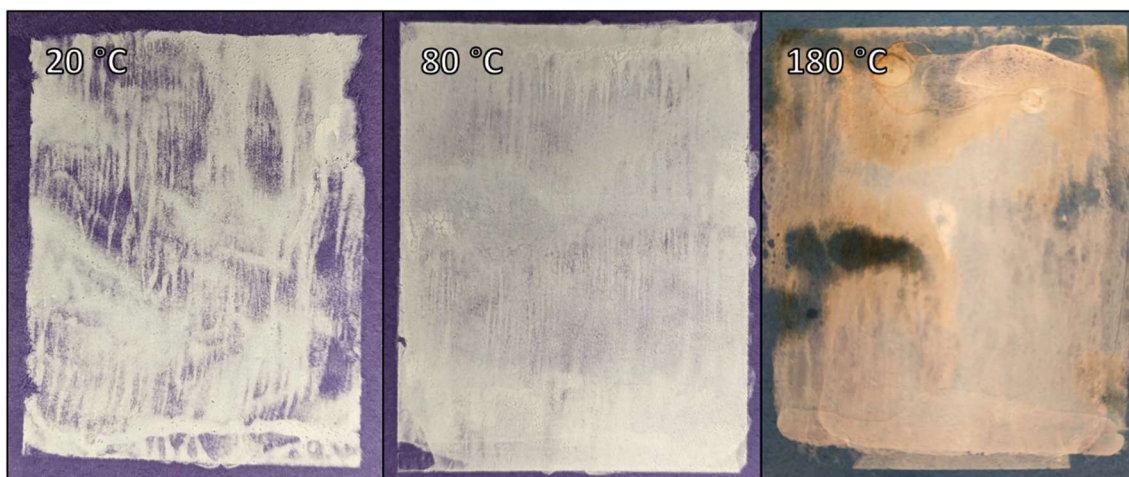


Figure A6. Effect of coating and drying temperature on surface appearance

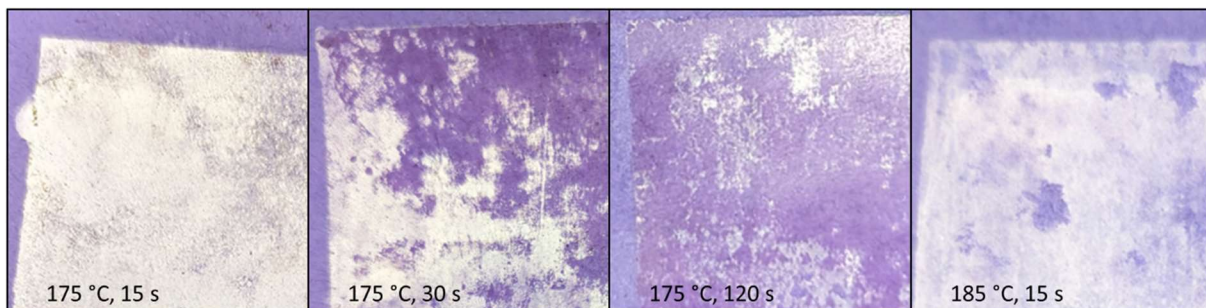


Figure A7. Effect of compression treatment temperature and time on surface appearance

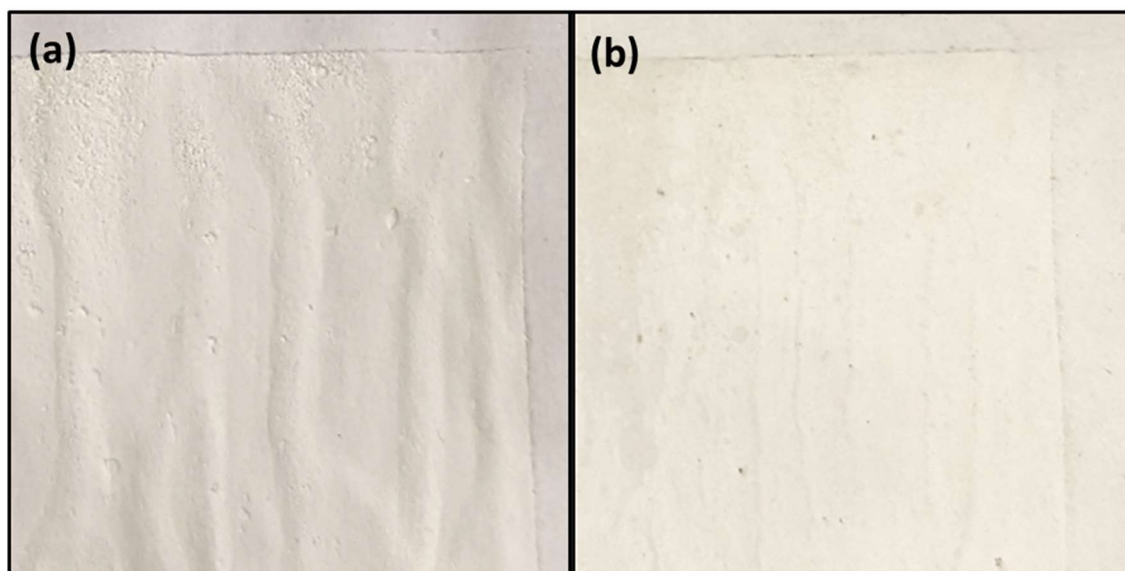


Figure A8. Coated white paper substrate (a) after coating and drying before hydraulic compression, and (b) after hot compress

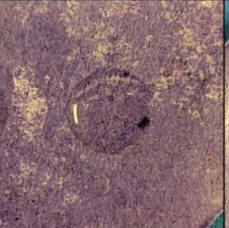
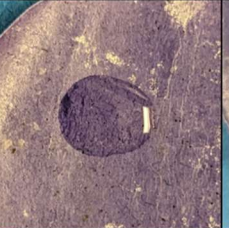
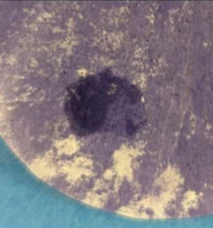
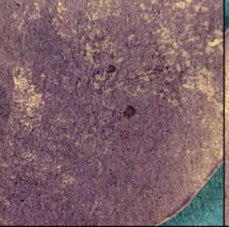
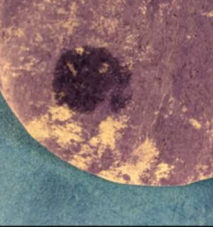
	Uncoated Paper	Coated Paper			
Kit Test Solution Number	1	1	8	9	10
Droplet on Surface					
After Wiping					

Figure A9. Grease Kit test results

APPENDIX B – SUPPORTING INFORMATION FROM CHAPTER 4

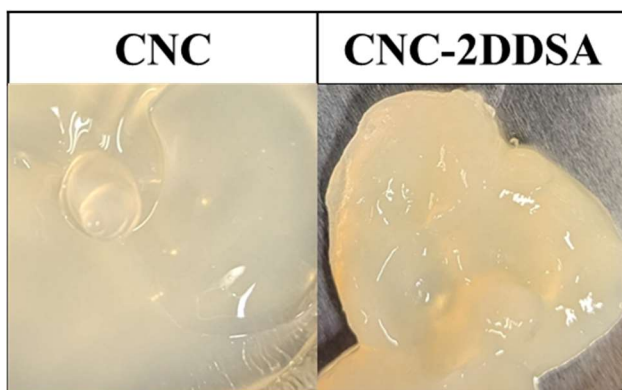


Figure B1. Modified and unmodified cellulose nanocrystals.

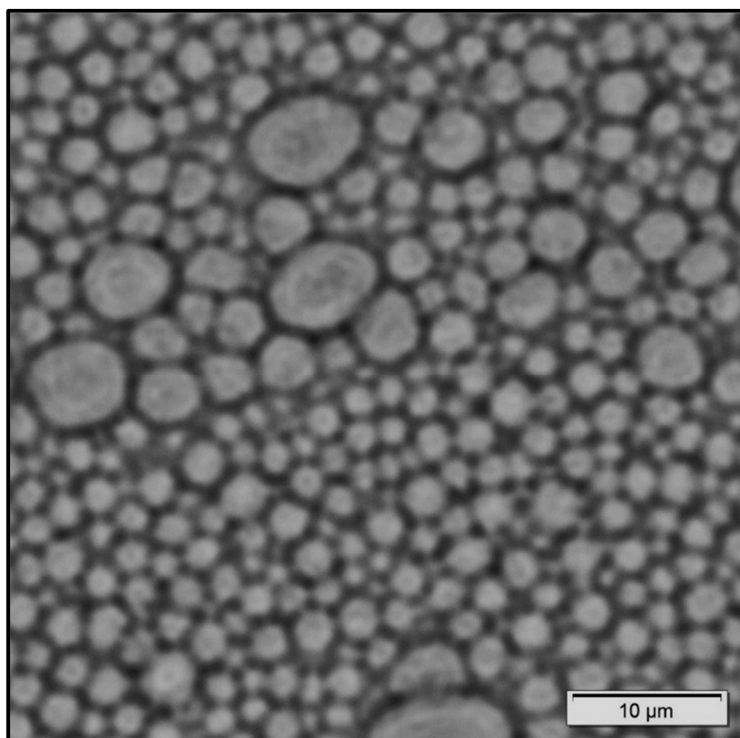


Figure B2. Dispersion sample 3 months after preparation (unmodified CNC).

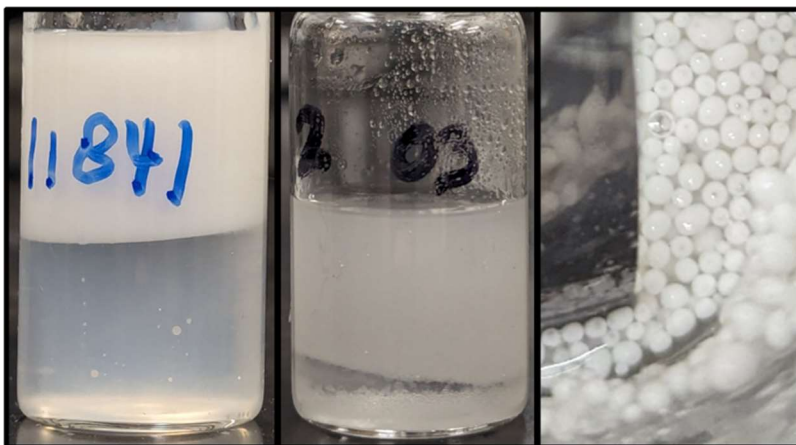


Figure B3. Examples of unsuccessful dispersions exhibiting separation behaviour such as creaming, settling, clumping. Taken within 24 hours of attempted dispersion formation.

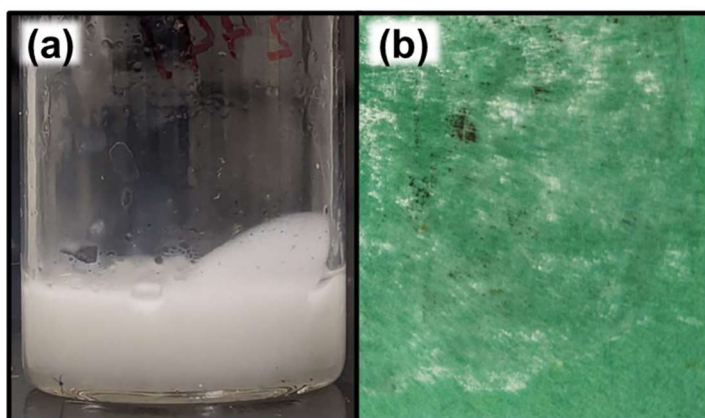


Figure B4. (a) Higher solids wt.% dispersion (~20 wt.%), (b) Same dispersion coated on manila paper

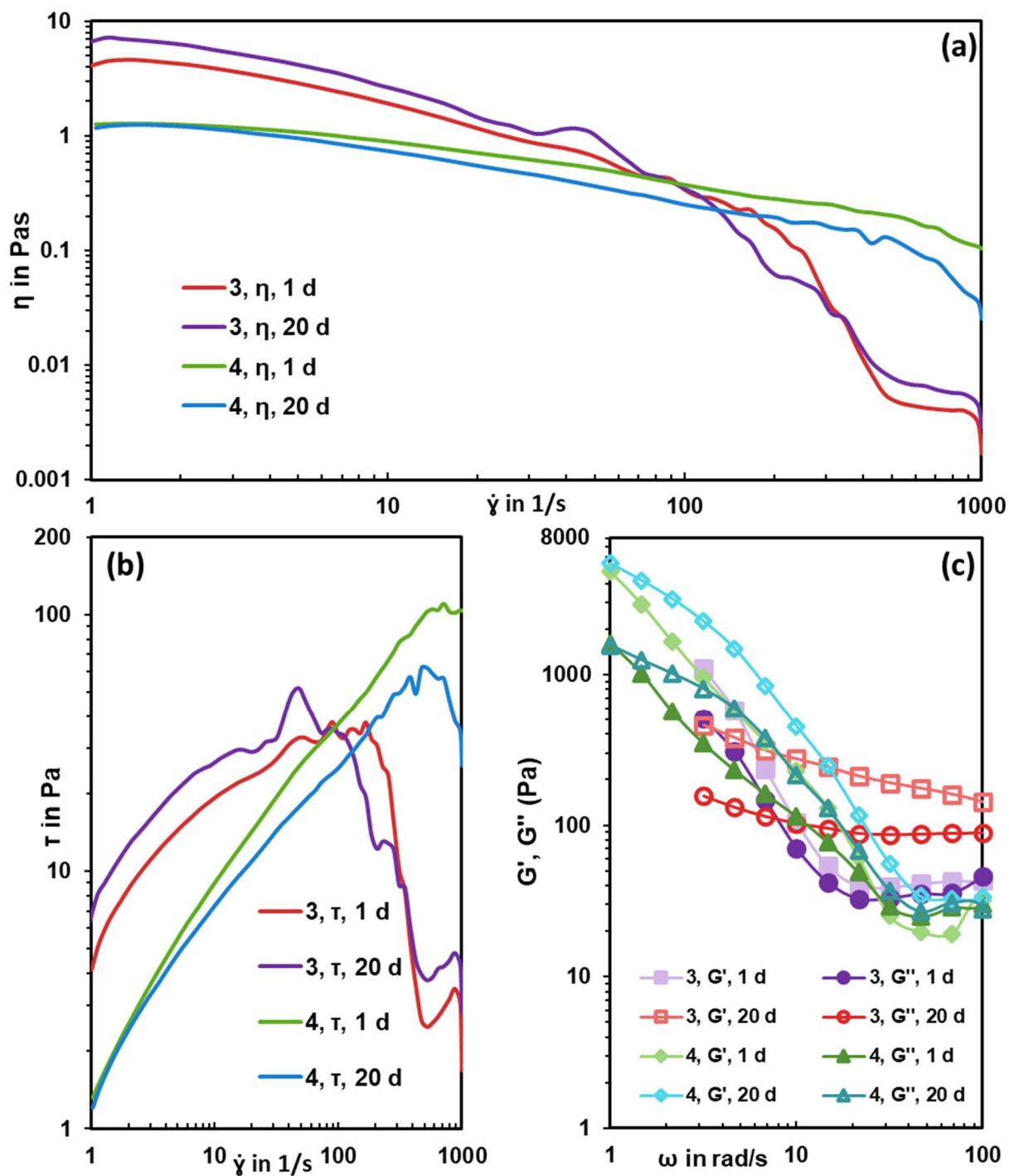


Figure B5. Rheological test results 1 d and 20 d after dispersion preparation. (a) viscosity curve, (b) flow curve, and (c) viscoelastic spectrum. Legend provides sample #, test parameter, sample age. Filled in markers indicate 1 day old while unfilled indicates 20 d.

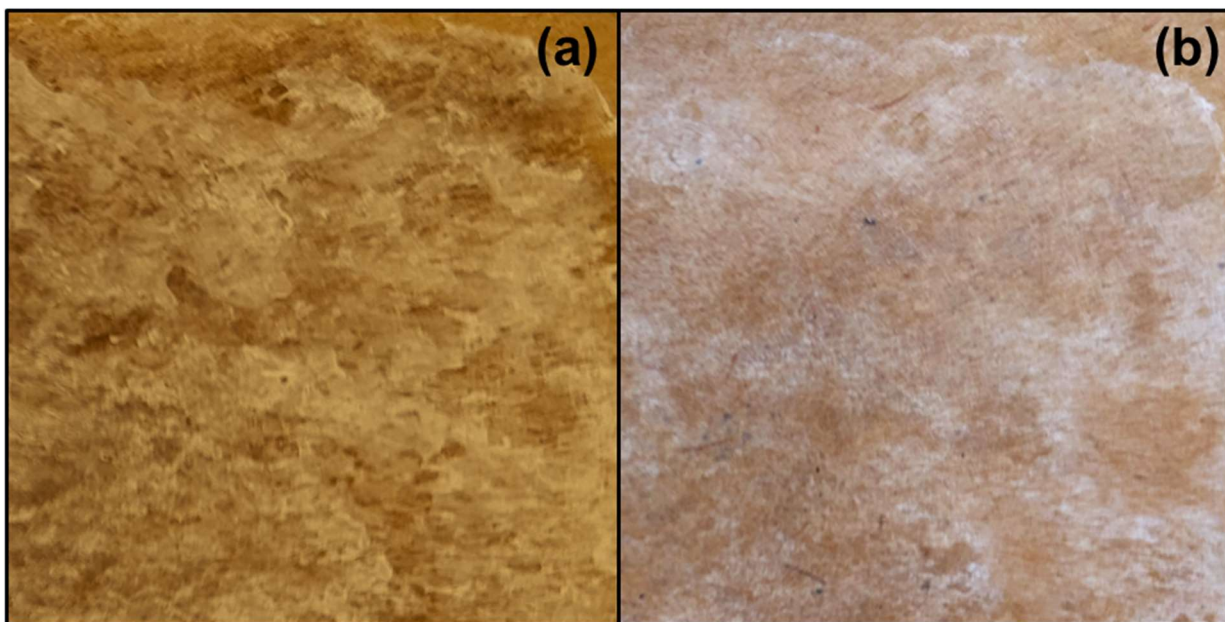


Figure B6. Paper coated with dispersion #2 as described in main body (a) after coating and drying before hydraulic compression, and (b) after hot compress. The unbleached kraft paper has a brown color.

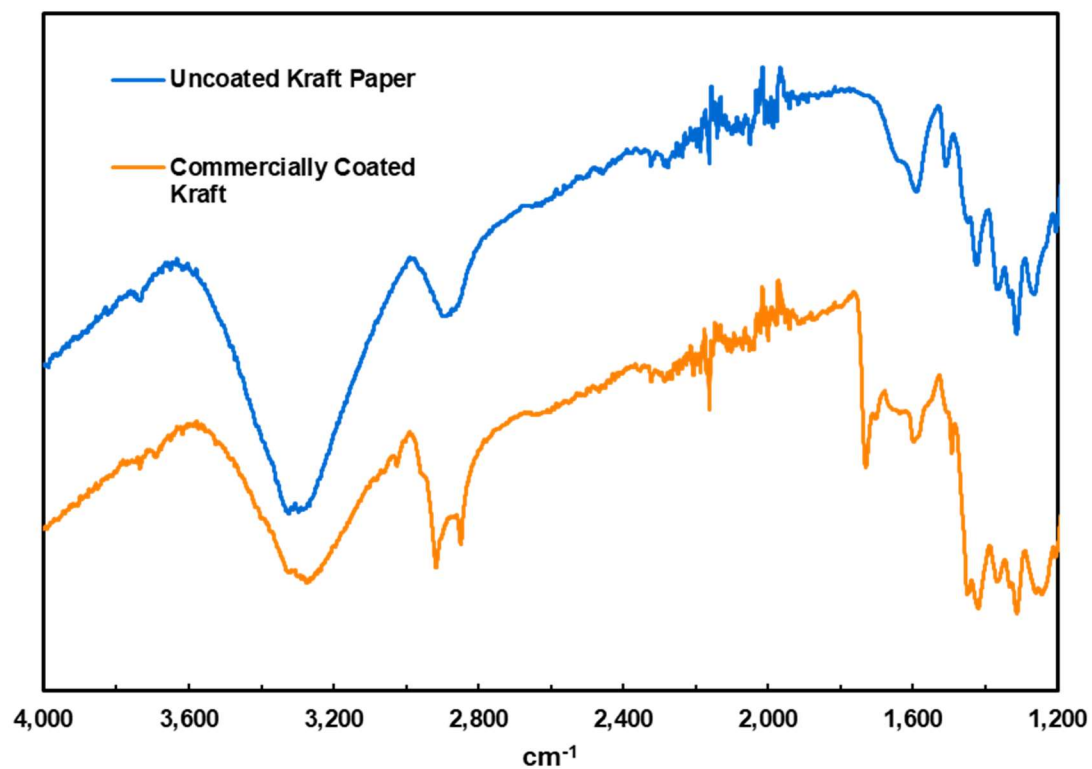


Figure B7. FTIR spectra of uncoated kraft paper and commercially available product meant for takeout container application.