

OIL- AND WATER-RESISTANT PAPER COATINGS USING LOW-COST
BIODEGRADABLE POLYMER BLENDS FOR PACKAGING APPLICATIONS

By

Aditya Nair

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ABSTRACT

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The growing environmental and health concerns over fluorochemicals coated paper and single use plastics/plastic coated paper, have led to a great interest in biodegradable and repulpable alternatives to obtain water- and oil-repellent paper substrates. The work reported herein aims at addressing these concerns by developing a fluorine-free, thermoplastic-free, and cost-effective water- and grease-resistant paper coating, using biodegradable polymers like polyvinyl-alcohol (PVOH) and starch blended with chitosan-*graft*-polydimethylsiloxane (chitosan-*g*-PDMS) copolymer. The hydrophobic and oleophobic performance of the coated paper with PVOH and chitosan-*g*-PDMS blend yielded good water-resistance (Cobb60 value: 20 ± 2.4 g/m²) and a moderate oil resistance (7/12 kit rating). Superior water and grease resistance were achieved with starch and chitosan-*g*-PDMS blend as the coating material where the Cobb60 values and kit ratings were 13 ± 0.9 g/m² and 12/12, respectively. The repulpability of the coated papers is also demonstrated in this study by washing the coating materials from the paper and repulping the pulp. This novel, inexpensive, water- and grease-resistant, environmentally friendly coating offers promising candidacy for commercial use in a myriad of applications in the packaging sector.

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This thesis is dedicated to my parents
Krishna and Jaishree Nair.
Thank you for all your support.

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Chapter 1

INTRODUCTION

1.1 Introduction

The increasing demand for sustainable packaging has re-energized the use of paper for packaging applications because paper and paperboard offer numerous sustainable benefits.¹ Paper is a low-cost, renewable, low-toxicity, and biodegradable material, thus offers a great alternative to plastics in certain applications.^{1,2} However, paper consists of long-chain cellulose molecules packed together, forming a crystalline structure with regularly distributed amorphous regions, which makes the paper substrate porous that in turn causes water absorption by capillary action.³ Moreover, the backbone chain of lignocellulose fibers consists of OH sites that make paper highly hydrophilic in nature.³ The porous structure and the presence of hydrophilic hydroxyl groups limits the use of paper in packaging and other applications, since it readily absorbs water, oil and other liquids, which leads to swelling of the fibers and in turn weakens its mechanical and physical strength.

To address the above challenges in obtaining hydrophobic paper, the industry is currently dependent on petroleum-based plastics such as Low-Density Polyethylene (LDPE), Ethylene Acrylic Acid (EAA), etc. to produce water- and oil-resistant paper through surface coatings.⁴ Alternatives for this approach are in high demand due to the limited availability of these non-renewable resources and due to their poor recyclability.³ Among other widely used coating approaches include use of Per- and polyfluoroalkyl substances (PFAS) and Bisphenol-A (BPA)-based plastics which are commonly used in food containers as an effort to impart certain functionalities in paper and improve shelf-life of food.⁵⁻⁶ The high instability of these chemicals

in the coated products leads to leaching and migration concerns that can have an adverse effect on human health and on the aquatic environments, especially landfilled leachates.⁵ Recently, Environmental Protection Agency (EPA) reported that ~26.8% of the total paper and paperboards manufactured were landfilled, mainly laminated and coated paper.⁴ Considering the fact that food and packaging containers contribute to around 45% of the waste landfilled, their leakage into the ocean and waterways ultimately lead microplastic pollution.⁷ Exposure to microplastics is perceived as serious emerging issues for all organisms including human being.⁵ As an effort to develop alternatives, researchers have focused on several materials that are bio-based (e.g., Poly Lactic Acid, chitosan), protein-based (e.g., whey protein, zein, and casein), and wax-based to develop certain specific functionalities in the paper.⁸⁻⁹ However, due to the various challenges involved in modifying these materials, maintaining water barrier properties, and the overall expensive nature of the available alternatives, there is an urgent need to develop approaches to improve the water and grease resistance of paper in a recyclable, yet cost-effective manner.

To address the above challenges, our group is actively working towards developing plastic-free, PFAS-free, cost-effective water- and oil-resistant surfaces.¹⁰⁻¹¹ A key focus is the use of benign polydimethylsiloxane (PDMS) as an alternative to PFAS because PDMS is known for imparting water and oil repellent properties while still acceptable for food contact applications.^{8, 12-13} In a recent breakthrough study, our group reported the fabrication of water- and grease-resistant coating using Chitosan-*grafted*-Polydimethylsiloxane (Chitosan-*g*-PDMS), and the coated paper was 100% recyclable by washing the coating off.¹⁴ PDMS has very low surface tension and has good hydrophobicity.¹⁵⁻¹⁴ The lack of oleophobicity in PDMS due to the non-polar nature was overcome by grafting it to chitosan, thus forming a chitosan-*graft*-polydimethylsiloxane (chitosan-*g*-PDMS) copolymer. Chitosan used in this system is a

polycationic naturally occurring biodegradable polymer derived from chitin and is known to have a structure very similar to that of cellulose and starch.¹⁶ The non-protonated polar groups of starch and chitosan would be bonded by strong hydrogen bonds with the anionic cellulose fiberfibers and will help mask the pores of the paper, thus improving its oil and water resistance.^{17,18} However, the expensive nature of the grafted copolymer and the limited availability of its components (chitosan) brought about the need to make the system economically feasible in order for it to be a viable alternative to other unsustainable approaches. This motivated us to pursue a cost-effective approach using blends of chitosan-*g*-PDMS and various inexpensive, biodegradable materials as fillers.

Firstly, polyvinyl alcohol (PVOH) was chosen as a filler for several good reasons. PVOH is inexpensive, water-soluble, readily available, and is a fully biodegradable polymer.^{19,20} Like chitosan, the structure of PVOH consists of polar hydroxyl (-OH) groups, which is critical in facilitating better miscibility of PVOH with chitosan, and also it's anchoring to cellulose (paper). In addition, PVOH is known for its excellent oxygen barrier properties and oil repellency.^{21,22} For food applications, PVOH is suitable as it is non-toxic and is used for food packaging materials that are in direct contact with the food.^{21,23} Furthermore, chitosan and PVOH impart oil repellency by efficiently masking pores on paper substrate.

On the other hand, starch has large-scale applicability in the paper coating industry primarily due to its abundant availability and inexpensive nature.⁵ The plant-based polymer consists of glucose units with plenty of hydroxyl groups, which makes the structure of starch very similar to that of cellulose and attaches well to the cellulosic fiberfibers through strong hydrogen bonds. This particular advantage makes the paper industry as the largest non-food application for starch along with other advantages that include its bio-based origin, which makes starch especially

advantageous for food contact applications as compared to the traditionally used fluorine-based coatings (PFAS) which are highly regulated by the US Food and Drug Administration (FDA).^{5,24} More importantly, the hydroxyl groups in starch facilitates modifications by substitution or oxidation reactions.⁵ It has been widely researched as a sizing agent and coating agent in the paper and paper coating industry with certain modifications that include starch-based bio-nanocomposites reinforced with clays (e.g., montmorillonite) or with cellulose nanomaterials.^{25,26} These modifications impart excellent film-forming properties, which help in enhancing the surface smoothness, mechanical properties, and oil resistance of starch-based paper coatings.²⁷ On the other hand, starch blends with polysaccharides like chitosan, alginate etc., have also been widely used as paper coatings.²⁸ Due to the aforementioned benefits, starch was the other selected material of choice for the purpose of this study and was blended with the chitosan-*g*-PDMS copolymer that was recently developed by our group.

In this work, the selected filler materials are blended with an aqueous solution of chitosan-*g*-PDMS copolymer to replace the more expensive components in the previous system and make it commercially viable.²⁹ This study reports that up to 80-90% of fillers (PVOH and starch) blended with 10-20% chitosan-*g*-PDMS imparts excellent water and grease resistant paper coating, thus offering a significant improvement cost and viability over the previously published work.¹⁸

1.2 Objectives

The main objective of this study was to develop a low-cost and fluorine-free water and grease resistant paper products. In order to achieve this, the following two objectives were pursued.

1. Analyze the effect of blending low-cost fillers (PVOH and starch) with a previously developed chitosan-*g*-PDMS coating, and determine their effect on the hydrophobic and oleophobic properties of the coated paper.
2. Validate the pulp recyclability of the coated paper through the separation of coating from the pulp, and making new paper prototypes from the recycled pulp

1.3 Hypothesis

Our hypothesis is that the addition of low-cost and biodegradable fillers such as PVOH and starch to chitosan-*g*-PDMS copolymer would impart water and oil resistance paper because the starch and PVOH will be absorbed into the porous structure of the paper similar to chitosan, while PDMS will enrich on the coating surface thus reducing the overall cost of the chitosan-*g*-PDMS coating while maintaining the intrinsic performance of the coated paper.

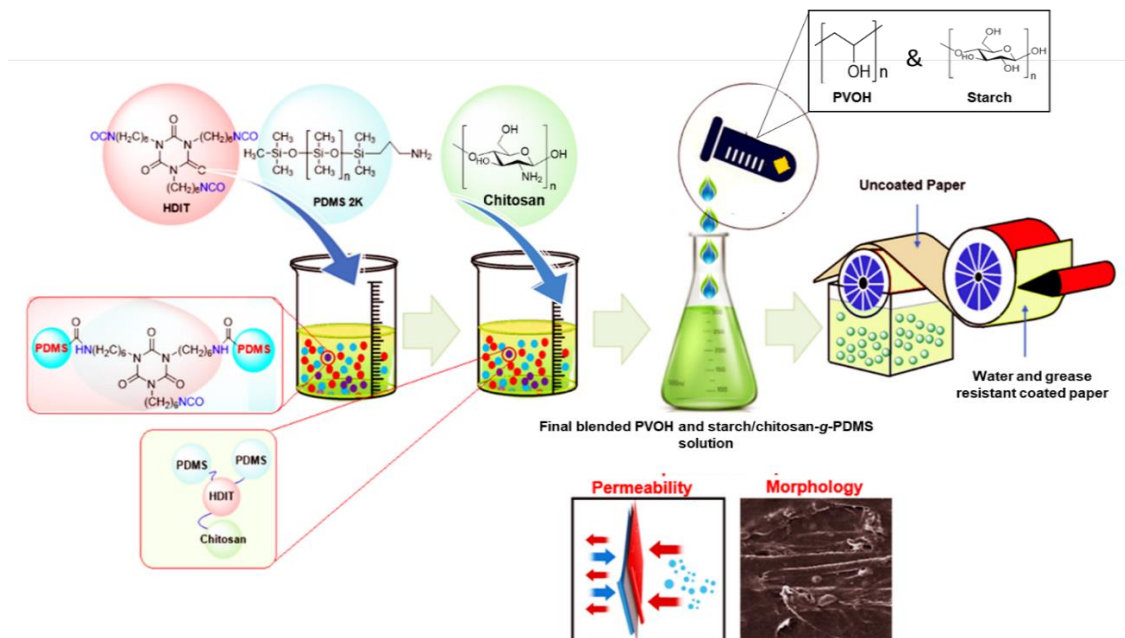


Figure 1.1 Schematic representation of PVOH and starch blended with chitosan-g-PDMS and coated on to the paper to impart water and grease resistance.

1.4 Structure of thesis

Chapter 1 describes the hypothesis and objectives of this research. The background information and literature study regarding the various coating components, including PVOH, starch, PDMS, chitosan, and the various coating approaches, are discussed in chapter 2. Chapter 3 consists of detailed information on material specifications, test methods, and equipment information used in this study. The results obtained by conducting these tests on coated papers that use PVOH as a filler are discussed in chapter 4, whereas the results obtained by using starch as a filler are discussed in chapter 5. Chapter 6 summarizes the findings discussed in the earlier chapters and discusses the future outlook for the research in this area.

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Chapter 2

BACKGROUND AND LITERATURE REVIEW

2.1 Introduction

2.1.1 Paper

Paper is a material that mainly consists of organic cellulose fibers that are interlaced together to form a flat sheet that possesses innumerable unique properties and applications. Papermaking involves simple steps that include preparation of the fiber pulp, forming of web/sheet, sizing, and smoothing. During the papermaking process, the cellulose fibers are combined with several inorganic fillers such as clay, titanium dioxide, or calcium carbonate in order to alter properties like brightness, whiteness, opacity, strength, etc. These properties allow papers to be coated, impregnated, laminated, creped, molded, and processed in many other ways. Considering these wide arrays of possible modifications, the applications of paper have only increased over the years. Paper and paperboard materials are widely used in the packaging industry due to their numerous benefits, such as good mechanical properties, lightweight, and biodegradability.³

2.1.2 Raw materials used in paper

Paper has been manufactured using different kinds of pulp, namely, mechanical pulp, which is derived by mechanical defibration of wood, and chemical pulp which is derived from chemical pulping of not only hardwood and softwood but also stems of cereals, reed, bagasse and other non-wood sources.² However, in recent years, recovered/recycled pulp has replaced the use of chemical pulp in the paper making industry due to its sustainability benefits as indicated by the

recent reports that suggest, over 40% of the raw materials used in paper are recycled paper pulp. Paper making also requires use of several fillers in order to improve the intrinsic functional properties like optical properties, smoothness, printability and to also facilitate sheet formation by filling the pores in the paper fiber matrix.^{1,2} The choice and loading of filler depend on the performance requirements of the paper and takes into consideration the general availability, costs and the targeted applications. The fillers commonly used include kaolin, which is currently replaced by calcium carbonate (CaCO_3). Calcium carbonate is often used in different forms (for example- natural ground, modified natural ground, precipitated form) to alter the brightness and opacity of the paper. Talc is another type of filler that is often used to control pitch and stickies formation that are known to hamper wood fiber processing. Other specialty pigment fillers used in the paper making process include clay, titanium dioxide, amorphous silicates and silica that are used in order to improve the properties like smoothness, brightness, opacity, printability as well as absorption properties of the paper.² Overall, a paper may contain up to 10-15% fillers, which helps in saving costs associated with paper-making while also helping internal modifications on paper. In addition to the fillers and other raw materials, the paper-making procedure also involves the addition of chemical additives like aluminum-based compounds, specialty chemicals, starch as well as bleaching chemicals. The additives used often act as binders, surface sizing agents, chelating agents, colorants, and wet-strength enhancers and comprise about 3% of the overall raw materials used in the paper.²

2.1.3 Limitations of paper

The interlaced cellulosic fibers consisting of microfibrils forms a porous structure composed of long-chain cellulose molecules with irregular amorphous regions that disrupt the crystalline structure of paper.³ (**Figure 2.1**) However, due to its porous structure, paper tends to

absorb water via capillary action, which makes it hydrophilic in nature. On the other hand, paper is comprised of lignocellulose fibers, which carry water-absorbing hydroxyl groups (-OH). Moisture tends to migrate through diffusion into the void pores as well as due to condensation and absorption into fiber cell walls due to hydrogen bonds with cellulose.²⁸ Hence, both the porous geometry and polar surface chemistry make paper unusable where direct water or liquid contact is encountered. To overcome this disadvantage, paper is often combined with coatings, typically plastics, to enhance the hydrophobicity and oleophobicity of paper.

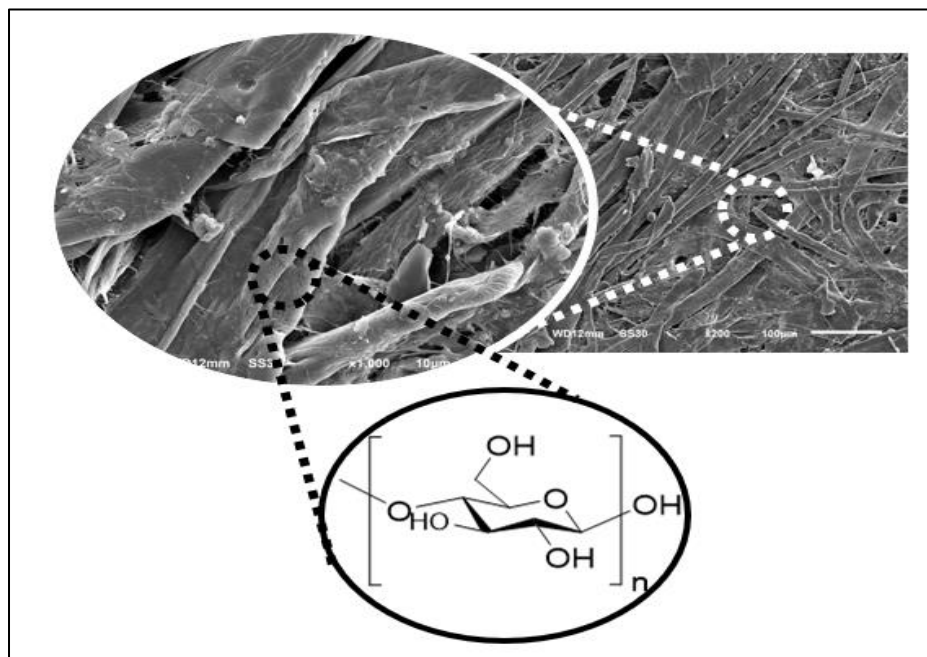


Figure 2.1 SEM (Scanning Electron Microscopy) images of cellulose fibers (resolution: 200x and 1000x) and the structure of cellulose

2.2 Current approaches for producing water and grease resistance paper substrates

2.2.1 Synthetic and bio-based film coatings

Lamination, co-extrusion, and coating are the industrial workhorse practices to impart water and oil repellency that is useful for practical applications of paper mainly due to particular

advantages in continuous production of uniform coatings with a reduced risk of pinholes and cracks.³ Extrusion coatings also offer an additional benefit of being solvent-free. Typical materials that are coated on paper using this approach include polyolefins (polyethylene), ethylene vinyl alcohol (EVOH), and polyvinylidene chloride (PVDC) that impart water and oxygen barrier properties that make the paper more suitable for food-based packaging applications.³ However, due to the complexities involved in the separation of the plastic-paper laminate, the paper loses its recyclability as well as biodegradability.^{3,28} Thus, the laminated paper ends up in landfills, from where they also leak into waterways. Due to mechanical abrasion triggered by water waves and UV exposure, the laminated plastic turns into small particles, aka microplastics, becoming high-risk for human and ecological health.²⁹ Recently, different bio-based polyester films like polylactic acid (PLA), polyhydroxyalkanoates (PHA), and polyhydroxy butyrate (PHB) have been used on industrial level paper coating. However, PLA is compostable only under controlled environment and may still pose a risk of the formation of microplastics, and PHA and PHB are expensive polymers.

2.2.2 Fluorine-based coatings

Per- and polyfluoroalkyl substances (PFAS) based coatings are often used in consumer products where good oil and water repellency is required, like sandwich wrappers, pizza boxes, paperboard cartons, etc. In addition, they are also used as a mold release agent. A number of concerns regarding the exposure to PFAS chemicals have been recently raised.⁶ A wide range of PFAS, including perfluoroalkyl sulphonates, perfluoroalkyl carboxylates, fluorotelomer alcohols and polyfluoroalkyl phosphate esters, are often used in fast food packaging that results in harmful exposure due to migration into food.³¹ The amount of migration depends on the amount, type, and chain length of the PFAS used, which varies based on the country in which it is produced and its applications.^{32,33} A recent study conducted by Laurel A. Schaider *et al.* used particle-induced γ -

ray emission (PIGE) to evaluate more than 400 packagings from fast food applications to study the presence of fluorine. Over 66% of samples were detected to contain greater than 16 nmol/cm² of fluorine.³¹ On the other hand, studies show that PFAS increases the risk of various diseases.^{6,8,34} Recent studies have raised concerns about the adverse effects of PFAS on the immune system, thus making humans more susceptible to diseases, including COVID-19.⁹

2.2.3 Latex-based coatings

Latex are water-borne plastic particles and are commonly used as a coating layer on paper substrates to enhance their repellency.⁵ However, the latex-based coated paper does not have good oil repellency. In addition, latex is often non-biodegradable (e.g., polystyrene or polyvinylidene dichloride), and thus they have a toll on the environment essentially of the same magnitude as those from laminated paper. In addition, latex coatings are more expensive than using polyethylene (PE) laminate for paper coating and face issues related to migration into food in food contact applications, thus limiting its use in the packaging industry.⁵ Numerous studies in the literature have also stated that most latex-based coating requires a coating load of 10 g/m² and above in order to produce acceptable cobb values for 1800 seconds that is often a requirement for packaging material applications.²⁹

2.3 Polyvinyl alcohol (PVOH)

2.3.1 Structure and properties of PVOH

PVOH is a polymer derived by radical polymerization of vinyl acetate followed by hydrolysis of polyvinyl acetate and consists of a backbone structure that is made up of carbon atoms.³⁵ It is known to be a water-soluble polymer that is biodegradable in both aerobic and anaerobic conditions and is a low-cost material, which is why it has been a material of choice in a

myriad of paper coating and sizing applications to make the modified paper biodegradable and economically advantageous.^{20,35} On the other hand, PVOH also offers some versatile properties (varying molecular weights: 20,000-400,000)²⁹ that depend on the chain length of the base polymer-polyvinyl acetate as well as the hydrolysis conditions, which in turn has major effects on its flexibility, adhesiveness, and solubility.³⁵ These properties help in enhancing the viscosity, film-forming properties, and strength of PVOH. Besides, a high degree of hydrolysis is known to increase the crystallinity of PVOH, which makes it an excellent oxygen barrier, while the presence of polar hydroxyl groups in the backbone chain imparts considerable oil resistance.²⁹ The presence of these hydroxyl groups and a high degree of hydrolysis also facilitates strong hydrogen bonds between cellulose and PVOH that makes it a good choice of material for surface modifications on paper. However, the presence of these hydroxyl groups also makes it hydrophilic in nature, which in turn makes it a poor barrier to water vapor, wherein a higher permeability is observed for higher humidities.²⁹ To overcome this disadvantage, PVOH is often functionalized with suitable materials via chemical reactions owing to the presence of secondary alcohol groups which also facilitates its solubility in water and other polar solvents.³⁶

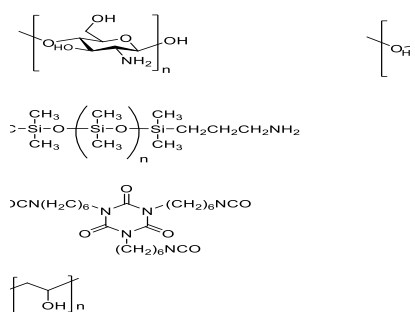


Figure 2.2 Chemical structure of polyvinyl alcohol (PVOH)

2.3.2 Applications of PVOH

The readiness of PVOH with innumerable attractive properties have compelled researchers in the packaging industry to use PVOH for coating related applications. In a study by Paralikar *et al.*, papers coated with PVOH reinforced with cellulose nanocrystals (CNCs) were observed to show an improvement in the water vapor barrier properties of paper.³⁷ The heat treatment provided in the study induced crystallization by crosslinking, which improved its resistance to permeation.^{35,37} PVOH was also combined with CNCs by a reverse gravure coating technique on polymer substrate in a similar study by Reaz A. Chowdhary and associates, which showed a considerable improvement in WVTR of the films with up to 70% CNCs in the blend.³⁸ This approach facilitates large-scale production of these coatings, especially in food packaging applications. PVOH is also known to be a non-toxic material, which enhanced its use in food packaging applications. A review of oral toxicity of PVOH was analyzed by DeMerlis and associates, which proved the above statement and reported data that supports the use of PVOH as a coating agent for pharmaceutical and dietary applications.³⁹ A novel approach by Hamdani *et al.* makes use of PVOH and Zein protein as bilayer paper coating approaches to enhance water and oil resistance of the paper.⁴⁰ This study reported a considerable smoothness in the surface of the paper proven by SEM images that produced water absorption values as low as 3 g/m² along with superior oil resistance.⁴⁰ Another study by Natthaporn Limpan *et al.* mentions the improvement in mechanical and barrier performance (WVTR) of PVOH and fish myofibrillar protein (FMP) blended films. This study also analyzed the effect of molecular weight and the degree of hydrolysis of PVOH on the properties. The reported data indicated that higher molecular weight and a higher degree of hydrolysis of PVOH lead to higher tensile strength and rigidity of the blended films.⁴¹

Aside from packaging, PVOH has also been widely used in biomedical and pharmaceutical applications.³⁵

2.4 Starch

2.4.1 Structure and properties of starch

Starch is an abundant biopolymer that is extracted from various plant sources that include potato, corn, tapioca, wheat, and recently even mango.^{3,4,29} Giving its plant-based derivation, starch a high molecular weight polymer that is composed of anhydroglucose units linked by glycosidic bonds and is made up of majorly two components- amylose and amylopectin.⁴² These two glucan polymers give starch its unique crystalline and amorphous regions with amylose being the linear polymer made up of glucose units linked together by α -1,4-glucosidic linkages while amylopectin being the highly branched molecule which is linked to the main chain via α -1,6-glucosidic linkages.^{3,29,43} Starch consists of about 75-80% highly branched amylopectin and 20-25% linear amylose chains depending on its source of extraction, which determines the amount of semi-crystallinity of starch.⁴⁴ The higher amount of amylopectin in starch typically leads to extreme branching due to strong hydrogen bonds, which restricts movements of the chains, thus making it difficult to process due to high viscosity.³ Hence, plasticizers are often used to induce flexibility and stability during processing and solubilizing starch. Starch consists of abundant hydroxyl groups and has a structure similar to cellulose, which works in favor of it being widely used in paper coating and sizing applications due to its strong hydrogen bonding of the cellulose fibers.⁴ These hydroxyl groups also facilitate a wide range of possible modifications by substitution and oxidation reactions to overcome some limitations that include its hydrophilicity, poor mechanical properties, rheological properties, and retrogradation.^{3,4}



The inexpensive and biodegradable nature of starch has influenced its applications in the paper and packaging industry. It is often used as a paper sizing agent and coating agent due to its excellent film-forming properties. The aforementioned limitations are overcome by modifications that render paper coatings with oxidized starch, acetylated starch, cationic starch, crosslinking, etc., which are efficiently used to improve water resistance, water vapor barrier properties, oil resistance, and mechanical properties of starch.^{3,45,46} Starch is also used in combination with different nanoparticles, nanocomposites and bionanocomposites mainly to improve the mechanical properties of the paper.⁴ Penggang Ren *et al.* combined starch with organic activated montmorillonite (OMMT) by processing in a twin-screw extruder to produce starch/OMMT based nanocomposites, which were used to improve the mechanical properties like the tensile strength and modulus of the paper.⁴⁷ In another study, Ivona Jankovic-Castvan and associates prepared starch-based paper coatings by modifying it with sepiolite nanoparticles. Applications of starch modified with sepiolite nanoparticles yielded approximately 20% increase in the breaking length and bursting strength of the coated papers.⁴² Excellent film-forming properties of starch are evident in a novel work by Jianfeng Xu and Huiren Hu wherein cationic starch was used in combination

with styrene acrylate-based latex as a sizing agent.⁴⁸ The film-forming capabilities of starch are also proved in a study by Dhvani Kansal et al. wherein starch was used with zein protein as a dual-layer coating approach to produce water and oil resistant paper products. Starch coatings were observed to mask the pores of the cellulosic fibers, and the dual-layer coating thus yielded water absorptivity as low as 4 g/m² along with an excellent oil resistance. The study also mentions a repulping approach which was used to successfully wash the starch/zein coating off the paper surface.⁴⁹

2.5 Chitosan

2.5.1 Structure and properties of chitosan

Chitosan is a naturally occurring polysaccharide derived from chitin, which is the second most abundant naturally occurring polysaccharide after cellulose.²⁸ Henry Braconnot was the first to isolate chitin from mushrooms back in 1811.¹⁶ Currently, the main sources of chitin include shrimp, crab shells, jellyfish, worms, and shellfish. Chitin is basically a *N*-acetyl glucosamine polymer consisting of linear monomeric units of 2-acetamido-2-deoxy D-glucopyranose attached through β -(1-4) linkages. This polymer is further deacetylated using NaOH to be converted into glucosamine units, thus producing chitosan.²⁹

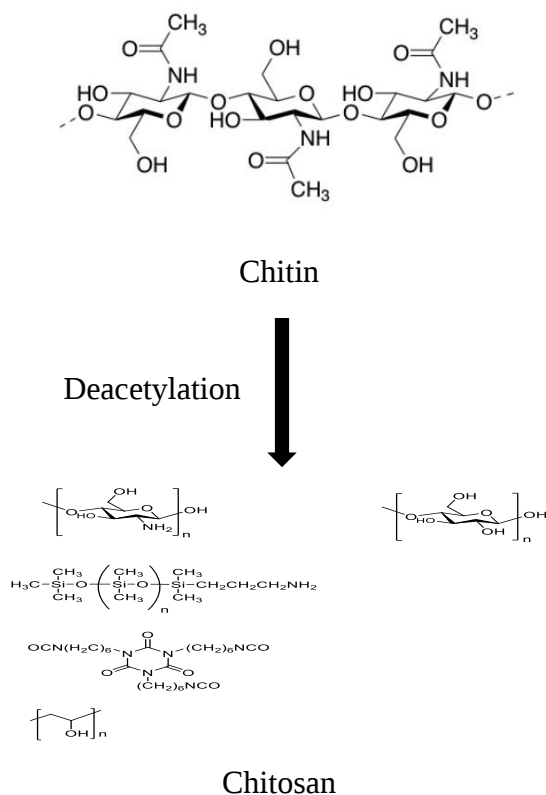


Figure 2.4 Derivation and structure of chitosan

Chitosan has gained tremendous popularity due to its bio-degradable, non-toxic nature with added benefits of having excellent film-forming properties, flexibility, transparency and semi-crystalline structure that makes it a good barrier to oxygen.²⁹ Chitosan is insoluble in water, organic solvents, and bases due to the non-protonated amino groups in alkaline or neutral medium. However, chitosan is soluble in low acid solutions like acetic acid, phosphoric acid etc. that causes protonation of the amine groups, thus making the molecule cationic.^{4,29} Due to this cationic nature of chitosan it binds well to the anionic cellulose fibers which is why it has been widely used in biopolymer paper coating applications by many researchers. Furthermore, the structure of chitosan is such that it facilitates chemical modifications due to the presence of mainly three reactive

functional groups that include the primary and secondary hydroxyl groups and the amino group on each unit.¹⁶

2.5.2 Applications of chitosan

Due to the aforementioned benefits, chitosan has been extensively used as coatings for paper and paperboard for food packaging applications. It has been particularly reported to improve oxygen, carbon dioxide and nitrogen barrier properties in a study performed by Kjellgren *et al.*⁵⁰ The excellent film-forming properties and high crystallinity imparts good barrier properties which were proven using SEM images and IR spectroscopy by Bordenave and others; that suggests that chitosan was embedded deep into the fibers of the paper and improved the water vapor barrier properties of the paper.⁵¹ Enhanced water vapor barrier and grease resistance were also reported by Weiwei Zhang and others in their bilayer coating study wherein chitosan was combined with beeswax for paper coatings which was proven to show the best properties compared to other polysaccharide coatings.⁵² Despite the excellent oxygen barrier and grease resistant properties, the water-resistance of chitosan has been noted to be insufficient, especially for food packaging applications due to the highly hydrophilic nature imparted by the presence of polar hydroxyl groups in the backbone chain of chitosan. However, the reactive groups present in chitosan opens up innumerable possibilities of chemical modifications with other hydrophobic materials to enhance the water resistance and make it suitable for many more applications.

2.6 Polydimethylsiloxane (PDMS)

2.6.1 Structure and properties of PDMS

Polydimethylsiloxane (PDMS) is a vital member of the polysiloxane or the silicones family that mainly consists of a backbone structure made up of silicon and oxygen (Si-O) having organic

moieties as a side group. Polysiloxane polymers typically possess unique physiochemical properties due to the hybrid presence of organic nonpolar functional groups and an inorganic polar backbone chain.⁵³ PDMS being one of the most studied members of the polysiloxane family, possess an inert nature, low toxicity, good thermal and oxidative resistance along with excellent water-resistant properties generating extremely hydrophobic properties.⁵³ These extraordinary properties are a result of its strength and nature of bonding of its typical side groups that impart a very low surface energy.⁵⁴ Additionally, the Si-O-Si bond angles of PDMS are incredibly flexible, and on the other hand, the Si-O bond lengths are much larger as compared to traditional C-C bonds that altogether impart flexibility into the PDMS chains, thus leading to very low transition temperatures.⁵³

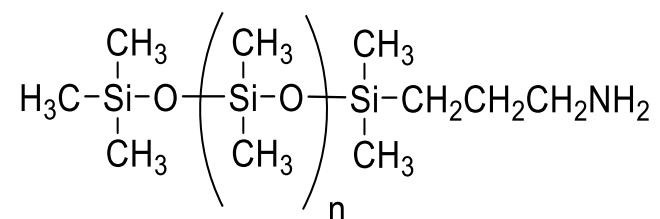


Figure 2.5 Chemical structure of polydimethylsiloxane (PDMS)

2.6.2 Applications of PDMS

These desirable unique properties of PDMS makes it apt for multiple applications that include mold-release agents, waterproof coatings, and biomedical applications. Interestingly, PDMS offers many paradoxical applications; for example: it is used as anti-foaming agents as well as foam stabilizers, it is often used as paper-release coatings as well as pressure-sensitive adhesives and as water-resistant coatings as well as de-watering agents.⁵³ In a unique study, Divya Kumar et

al. have used PDMS was used as an additive in sol-gel networks to produce to generate hydrophobic self-cleaning applications.⁵⁵ The study showed extremely low wettability proven by low water contact angles (112°) and low sliding angles ($<10^\circ$). In another study, Zhaofeng Wu and associates studied the effect of PDMS on wettability and surface morphology of waterborne polyurethane (PU) coatings. The PDMS enrichment on the surfaces led to superhydrophobic surfaces that possessed high water contact angles of 156.5° which improved the hydrophobic properties of PDMS considerably, thus making it more applicable for commercial applications.⁵⁶ Zhao Li and others have used PDMS in multiple studies to generate oil and water resistance on paper and paperboard surfaces. Combination of PDMS with melamine and chitosan was seen to reduce water absorptivity of coated papers as evident by low cobb60 values of 9 g/m^2 .^{14,17,57,58} Another study by Saadat Baksh and others proved use of PDMS and aerogel-based coatings to develop mechanically durable superhydrophobic polymeric fibrous surfaces. The results showed sliding angles as low as 5° when the substrates were coated by dipping in PDMS/toluene solution followed by electrostatic spraying of aerogel microparticles.⁵⁹ These studies prove the widespread applications of PDMS in generating hydrophobic surfaces. Besides, certain reactive groups in PDMS made it suitable for chemical modifications^{8,14,17,57} and hence was chosen as appropriate raw material for imparting water resistance to the coated paper coating.⁵³

2.7 Methods for application of coatings on a paper surface

2.7.1 Extrusion lamination

Extrusion coating is one of the most widely used and established paper coating techniques in the industry. It offers reliable, fast, solvent-free, and continuous processing of uniform thickness films, which is why it is a preferred industrial coating approach.³ The process involves melting

and extruding polymer resins in an extruder through a flat die. The molten plastic is then cast upon a paper roll, thus allowing a continuous production as illustrated in **Figure 2.6**. However, since the process involves the extrusion of molten plastic, this coating technique is restricted to coating materials with high melt stability and requires a high coating load.

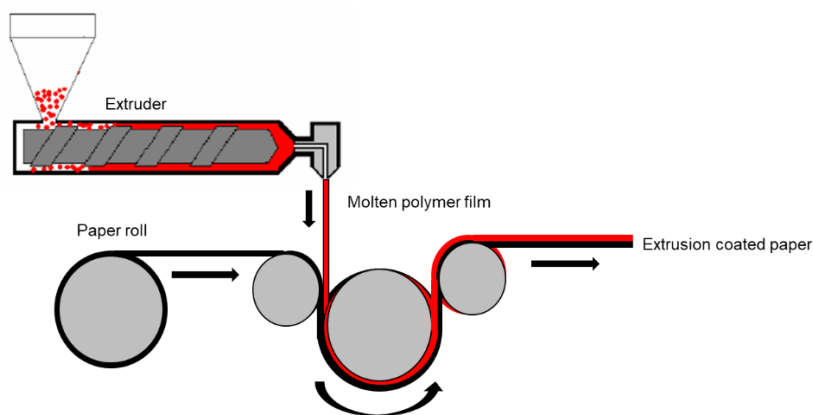


Figure 2.6 Extrusion coating process¹

2.7.2 Bar coating

A bar coating approach is generally preferred on a laboratory scale to produce a uniform coating with an even thickness and low-cost processing.³ The process involves pouring an excess viscous solution on the surface of the substrate. A cylindrical bar that consists of wires wound across it is used as a film applicator to essentially spread the coating across the paper substrate, as displayed in **Figure 2.7**. The thickness of the coating can be controlled using bars of different wire diameters that produce wet film deposits of the desired thickness. However, the process does not offer continuous processing and the thickness of the coating is restricted to the different bar diameters available.

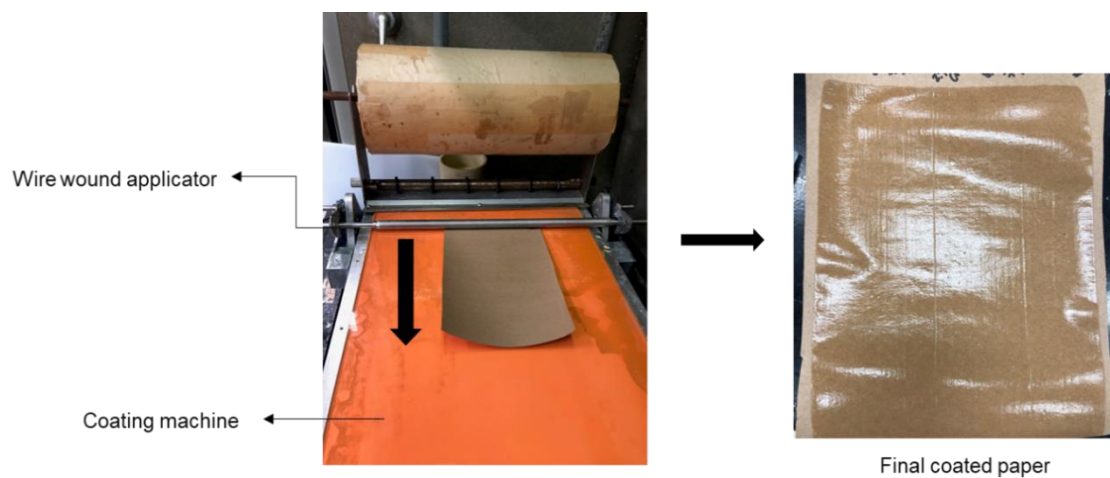


Figure 2.7 Bar coating process

2.7.3 Dip coating

Dip coating is usually preferred for the application of aqueous coating solutions onto the paper surface. This process offers a quick coating approach that involves dipping the substrate into the solution followed by drying. Some downsides of the process include no control over the thickness of the coating, which results in an uneven coating layer and a two-sided coating that complicates drying techniques.

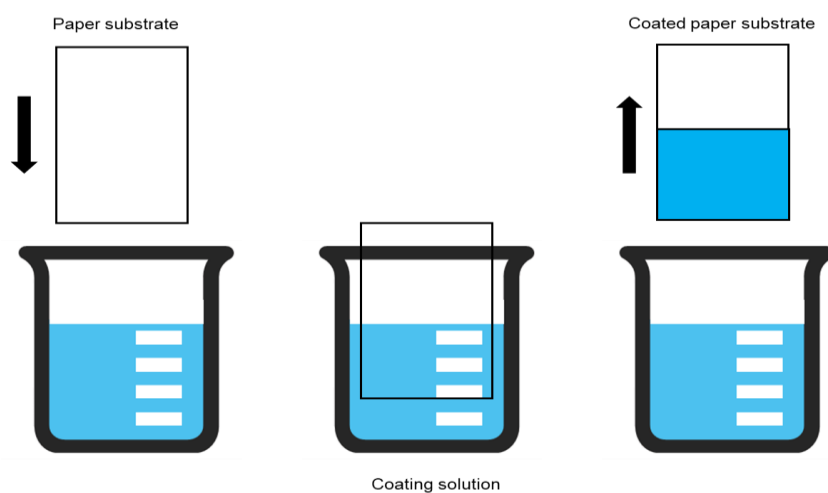


Figure 2.8 Dip coating process

2.7.4 Spray coating

The spray coating is another approach that is often used for paper coating applications for non-flat paper. The process typically involves using jet-spray nozzles to spray coating onto the substrate, as exemplified in **Figure 2.9**. This process is suitable for large-scale coating production, thus allowing continuous processing and also gives a good control over the coating load.

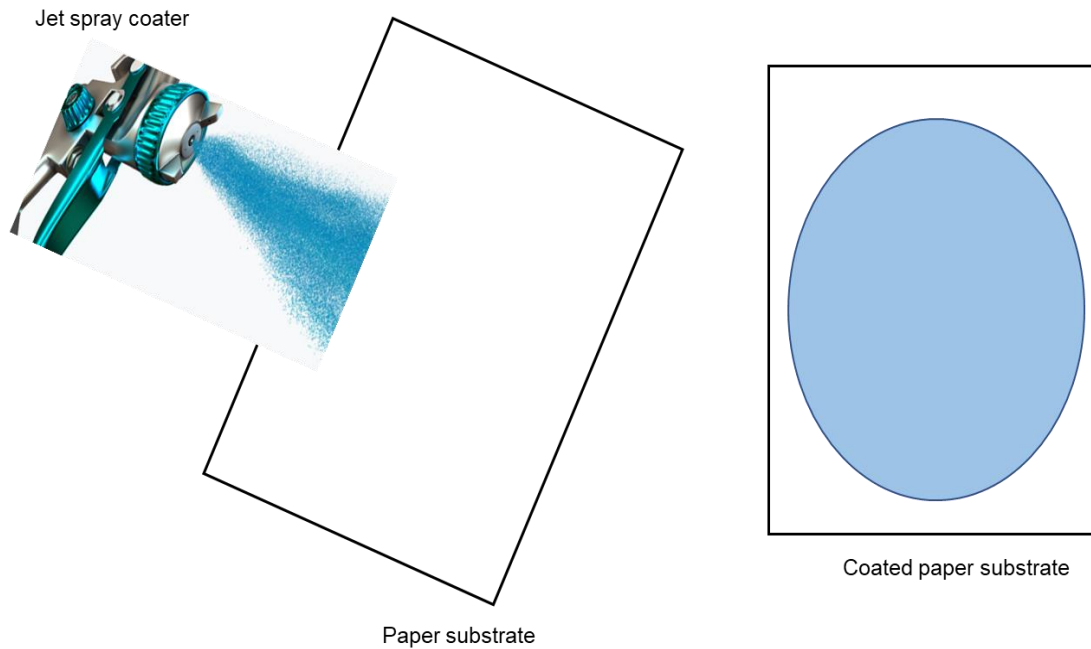


Figure 2.9 Spray coating process

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Chapter 3

EXPERIMENTAL

A version of this section is under review in Advanced Sustainable Systems and The Journal of Applied Polymer Science by Wiley.

3.1 Materials

3.1.1 Preparation of polyvinyl alcohol (PVOH) solution

PVOH solution was prepared by adding the PVOH polymer granules in cold water and further heating the mix at 80 °C until it was completely solubilized, and a clear solution was obtained. PVOH solutions with varying levels of concentrations (0.5%, 2.0%, 4.0% w/v concentration of PVOH in water) were thus prepared. For example, 4.0% w/v PVOH solution was prepared by dissolving 0.6 g of PVOH polymer granules into 15.0 mL of deionized water and stirring for 10 minutes.

3.1.2 Preparation of starch solution

First, the starch slurry was prepared by adding starch powder into de-ionized (DI) water at 20wt% starch. Then this slurry was added to preheated DI water at 90°C, and stirred for ~ 25 min until a clear starch solution was obtained. Starch solutions with varying levels of concentrations (3.0, 5.0, 7.0 % w/v concentration of starch in DI water) were thus prepared.

3.1.3 Preparation of chitosan stock solution

Chitosan stock solution was prepared in the concentration of 2.0 % (w/v) by dissolving 2.0 g of chitosan polymer powder to 96.0 mL deionized water containing 2.0 % (v/v) acetic acid,

followed by stirring for 24 hours at room temperature. Then, 5 mL of the chitosan stock solution was used to prepare the coating solution by diluting it with 0.8 mL deionized water. The final chitosan solution thus used contained 100 mg of chitosan with a concentration of ~1.7 % (w/v).

3.1.4 Preparation of polydimethylsiloxane-isocyanate (PDMS-NCO) solution

Our previous reported method was used to prepared PDMS-NCO stock solution.¹ Briefly, 26.6% w/v concentration of PDMS-NH₂ solution (133.0 mg PDMS-NH₂ in 0.5 ml acetone) was added dropwise into 13.2% w/v concentration of Hexamethylene diisocyanate (HDIT) solution (67.0 mg HDIT in 0.5 ml acetone) under constant stirring. The obtained PDMS-NCO solution thus contained 200 mg PDMS-NCO with a concentration of 20% w/v in acetone.

3.1.5 Preparation of the PVOH/Chitosan-grafted-PDMS (P/CP) coating solutions

PDMS was grafted on to chitosan by adding PDMS-NCO to the chitosan solution dropwise under stirring. CP solution containing 200 mg of PDMS-NCO in 100 mg chitosan was thus prepared.¹ For P/CP coated papers, each concentration of PVOH solution was blended with CP in four different volume ratios i.e. 90:10, 80:20, 70:30 and 60:40 as shown in **Table 1**.

Example: 5 mL of P/CP solution was prepared by adding 4.5 mL of PVOH from the pre-prepared PVOH stock solution (in all concentrations e.g., 0.5, 2.0, 4.0 wt%) and 0.5 mL of the chitosan-g-PDMS stock solution to obtain P/CP solution that contained 90% PVOH and 10% CP by volume (90:10 volume ratio).

Controls: The control papers were coated with PVOH (P) and PVOH/chitosan (P/C). For PVOH control, the papers were coated with three different concentrations of PVOH i.e. 0.5, 2.0 and 4.0% wt/v of PVOH solutions. For P/C control, the paper was coated by blending 2.0 wt%

chitosan solution and three different concentrations of PVOH mentioned above separately, while keeping the volume ratio of PVOH to chitosan as 50:50.

Table 3.1: Various formulations and blends used to coat paper substrates and their representations.

Final coating blends			
Type of coating	PVOH concentration (wt%)	Volume ratio of PVOH to chitosan-g-PDMS	Code
PVOH/chitosan-g-PDMS (P/CP)	0.5/2.0/4.0	90:10	90P:10CP
		80:20	80P:20CP
		70:30	70P:30CP
		60:40	60P:40CP
Controls			
Type of coating	PVOH concentration (wt%)	Volume ratio of PVOH to chitosan (2 wt%)	Code
PVOH/chitosan	0.5/2.0/4.0	50:50	P/C
PVOH		-	P
Unmodified paper	-	-	UM

Note: The different PVOH concentrations are distinguished by P_{0.5}, P₂, and P₄ in their code names.

For example, 90P₂:10CP denotes P/CP coated paper with 2.0 wt% PVOH solution blended with CP in 90:10 volume ratio, while 90P₄:10CP denotes P/CP coated paper with 4.0 wt% PVOH solution blended with CP in 90:10 volume ratio.

3.1.6 Preparation of the Starch/Chitosan-*grafted*-PDMS (S/CP) coating solutions

Chitosan-*grafted*-PDMS (CP) was first prepared by adding PDMS-NCO to the chitosan solution dropwise under stirring. Approximately 6 ml of water-borne solution containing 200 mg of PDMS-NCO in 100 mg chitosan was thus prepared. Finally, the starch and CP solutions prepared above, were blended together in varying levels and concentrations of starch. The increasing concentrations of starch in the S/CP solution imparted higher viscosity which in turn produced greater uniformity and increased thickness of the coating layer. The thickness of the coating in turn was observed to have an effect over the performance of the coating.^{1,2}

Example: 5 mL of S/CP solution was prepared by adding 4.5 mL of starch from the pre-prepared starch stock solution (in all concentrations e.g., 3, 5, 7 wt%) and 0.5 mL of the chitosan-*g*-PDMS stock solution to obtain S/CP solution that contained 90% starch and 10% CP by volume (90:10 volume ratio).

Controls: As controls, starch coatings were prepared in 3.0, 5.0, 7.0 % w/v concentration of starch in DI water. Starch/chitosan coating blends were prepared by blending 2.0 wt% chitosan solution with three different concentrations of starch mentioned above while keeping the volume ratio of starch to chitosan as 50:50. A detailed list of the formulations and their respective codes are displayed in **Table 2**.

Table 3.2: Various formulations and blends used to coat paper substrates and their representations.

Final coating blends			
Type of coating	Starch concentration (wt%)	Volume ratio of starch to chitosan-g-PDMS	Code
Starch/chitosan-g-PDMS (S/CP)	3.0/5.0/7.0	90:10	90S:10CP
		80:20	80S:20CP
		70:30	70S:30CP
		60:40	60S:40CP
Controls			
Type of coating	Starch concentration (wt%)	Volume ratio of starch to chitosan (2 wt%)	Code
Starch/chitosan	3.0/5.0/7.0	50:50	S/C
Starch		-	S
Unmodified paper	-	-	UM

Note: The different starch concentrations are distinguished by S₃, S₅, and S₇ in their code names.

For example, 90S₃:10CP denotes S/CP coated paper with 3.0 wt% starch solution blended with CP in 90:10 volume ratio, while 90S₇:10CP denotes S/CP coated paper with 7.0 wt% starch solution blended with CP in 90:10 volume ratio.

3.2 Methods

3.2.1 Coating Method

A 35 kraft liner paper was cut to approximately 30 cm x 20 cm and the coating solutions prepared above were coated on it using a K303 Multi Coater (RK PrintCoat Instruments Ltd, UK). About 5 mL of coating solution was used to coat the paper with a wire wound coating rod having a wire diameter of 1.27 mm (Rod number 8) that produced a wet film deposit of approximately 100 microns as per supplier specifications. The coated paper was further dried at room temperature for 24 hours and preconditioned under 23°C, 50% RH before performing any further tests.

3.2.2 Characterization techniques and testing methods

3.2.2.1 ¹H Nuclear Magnetic Resonance analysis (NMR)

¹H NMR spectra of the polymers were recorded with a 500 MHz NMR spectrometer (Agilent USA). The samples were prepared by dissolving ~5 mg in 0.5 mL D₂O/CD₃COOD.

3.2.2.2 Water absorption capacity (Cobb60 value)

The water absorption capacity of the coated paper specimens was determined as per TAPPI standard T441 om-09, using the cobb60 value test. Briefly, paper substrate was allowed to absorb water for 60 second, and the amount of water absorbed was calculated as the difference in weights of each sample specimen in triplicates before and after the test and was expressed in terms of weight of water absorbed by the specimen per unit area (g/m²).³

3.2.2.3 Grease resistance

Grease resistance of the coated paper specimens were determined in accordance with TAPPI T 559, commonly known as kit test. The kit solutions were prepared with varying amounts of castor oil, n-heptane and toluene to produce multiple levels of surface tension and viscosity (reagent number 12 being the most aggressive oil while 0 being the least). The resistance to grease was reported as an average of five kit ratings and the paper with the highest kit rating was known to have the best grease resistance.⁴

3.2.2.4 Statistical analysis

The optimum formulation for this study and the interaction of the independent variables was determined by comparing the means using analysis of variance (ANOVA) and Interaction plot features using Minitab software (version 15.1, Minitab LLC, USA). The interaction of three independent variables including the starch concentration (starch conc.), starch to chitosan-g-PDMS volume ratio (S:CP) and starch conc. and S:CP ratio together was studied against water absorptivity (cobb60 values) and oil resistance (kit rating values) as responses at a level of confidence of 5% ($\alpha=0.05$).

3.2.2.5 Attenuated total reflectance-Fourier transform infrared radiation analysis (ATR-FTIR)

A Shimadzu FTIR IR-Prestige21 spectrometer (Shimadzu Co., Columbia, MD) was used to record the infrared spectra equipped with an attenuated-total-reflection (ATR) accessory (PIKE Technologies, Madison, WI). Coated and unmodified paper were exposed to 64 scans over a wavenumber range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1} .

3.2.2.6 Thermogravimetric analysis (TGA)

TGA measurement of the coated and unmodified papers was performed using Q-50 1256 thermogravimetric analyzer (TA Instruments, New Castle, DE). A temperature range of 10-600°C was used to heat 6-10 mg of coating specimens at a constant ramp rate of 10 °C/min. The TGA analyzer was purged with nitrogen at a flow rate = 40 mL/min. The thermograms and first order derivative thermogravimetric (DTG) curve was plotted using the TA Universal Analysis software.

3.2.2.7 Material thickness, basis weight and coating load

Paper specimens were conditioned at 23°C and 50% RH before recording material thickness and basis weight. The average thickness of each specimen (expressed in µm) was measured using an auto digital micrometer (Testing machines Inc. 2 Fleetwood Ct. Ronkonkoma NY, USA) with a precision of 0.001 mm at three random locations on the paper. The final value was reported as an average of the three values. Further, the mass per unit area of the conditioned paper specimens was measured in triplicates in accordance with ASTM D646 and expressed as the basis weight in g/m² as shown by **Equation 1**. Paper samples were precisely cut into 100 mm × 100 mm and weighed on a microbalance with an accuracy of 0.0001g (Ohaus Adventurer, Ohaus corp. Pine Brook, NJ, USA). Coating loads were calculated using the difference between the average basis weights of three of coated papers and unmodified papers.⁵

$$\text{Basis weight} = \frac{\text{weight of paper specimen (g)}}{\text{area of the paper specimen (m}^2\text{)}} \quad \text{(Equation 1)}$$

$$\text{Coating load (g/m}^2\text{)} = \text{Basis weight of (coated paper – unmodified paper)(Equation 2)}$$

3.2.2.8 Scanning electron microscopy (SEM)

A JEOL 6610 SEM (JEOL Ltd., Japan) imaging system with an accelerating voltage of 15 kV was used to analyze the surface morphology of coated and unmodified papers. Samples were mounted on aluminum stubs and were further coated with 15-nm-thick gold layer using a sputtering coating machine to make the surface conductive. SEM images were obtained at a magnification of 200x.

3.2.2.9 Water contact angles (WCA) and Water vapor permeability (WVP)

In order to measure the water contact angles of the coated and unmodified papers, a 590-U1 Advanced Automated Goniometer (Ramé-hart Instrument Co., NJ, USA) was used. Three paper samples cut in 2 in. x 2 in. from random locations of the coated and unmodified paper were examined by releasing a measured water droplet (5 μ L volume) using an electronic pipette. The contact angles were recorded using a DROP image software at 30 seconds and 5 minutes intervals and the magnified images of the water droplet on the paper surface were examined in triplicates.

The water vapor transmission rate (expressed in $\text{g/m}^2\text{-day}$) of the unmodified and coated papers were obtained using an isostatic approach by using Permatran-W (Model 3/34, Mocon Inc. MN, USA). Three replicates of coated and unmodified paper specimens with a dimension of 20 mm $\times$ 20 mm were masked in aluminum sheets, such that only 0.20 cm^2 area of the paper was exposed to the water vapor under the condition of 23 $^{\circ}\text{C}$ and 50% RH. Nitrogen was used as the carrier gas and the flow rate was set to 10 SCCM. The result obtained was extrapolated to transmission rate at 100% RH and the water vapor permeability (WVP) was further calculated by using **Equation 3** expressed in $\text{g-m/m}^2\text{-day-Pa}$.

$$WVP = \frac{WVTR * \text{thickness of the coated paper}}{\text{Partial pressure difference}} \quad (\text{Equation 3})$$

3.2.2.10 Mechanical properties

The mechanical properties of the coated and unmodified papers were evaluated by performing four different tests described below in both machine (MD) and cross directions (CD). The final value was reported as an average of three values.

The tensile test was performed on an Instron 5565 Tensile testing machine (Instron, MA, USA) equipped with tensile grips and a load cell. In accordance with TAPPI T494 standard, paper specimens were cut into 1 in x 11 in size and loaded into the grips while the distance between grips was set to 7 in. Further, the specimen was stretched at a constant speed of 0.5 in./min. The resultant force required to stretch the specimen was recorded as a function of distance on an installed Bluehill software package and the maximum tensile strength was obtained in lbs/in.⁶

The edgewise compression strength of the paper was studied using Ring Crush Test as per TAPPI 822 standard. The paper specimens were cut into 0.5 in. x 6 in. dimensions and slid into a sample holder forming a circle. The force required to crush this specimen standing over its edge was recorded on a TMI crush tester (Model 1210, Instron, MA, USA) and expressed in lbs.⁷

The internal tearing force was measured as per TAPPI 414 standard using an ME-1600 Manual Elmendorf-type tear tester manufactured by Oakland instrument Co, MN, USA with a standard capacity of 1600 gf.⁸ The average tearing force required to tear two plies of paper specimen (in grams of force) perpendicular to the plane of the paper was determined using **Equation 4.**

$$\text{Average tearing force} = \frac{16 \times \text{Equipment reading}}{2} \text{ grams} - \text{force} \quad \text{(Equation 4)}$$

The bending resistance was measured using a Taber stiffness tester (Model 150-D, Teledyne Taber, NY, USA) as per TAPPI T489 standard. The paper specimens were cut into a size of 1.5 in. x 2.75 in. and an average bending resistance of five samples was recorded. The specimens were loaded into the equipment and a test length of 5 cm. was used to flex the samples to the left and right directions at an angle of 15° using a force of 500 g-cm. The average of left and right readings was used to report the bending resistance in milliNewton meter (mN.m).⁹

3.2.2.11 Repulpability

Coated paper specimens were cut into pieces and soaked in warm water for half an hour before repulping in a blender. The obtained blended fibers were divided into three parts, out of which one was left unwashed, second was washed with deionized water and the third part was washed with 1.0 vol% acetic acid. The washing process was conducted by centrifuging the slurry 3 to 5 times while removing the supernatant and adding fresh deionized water/acetic acid solution each time. The washed and unwashed fibers were further converted to recycled paper by filtering out the solutions using a mesh and flattening the damp fibers using a hot iron pad. The recycled paper samples were dried at 60°C for 1 hour before being analyzed using ATR-FTIR analysis to detect the presence of any coating.^{1,2,10-12}

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Chapter 4

RESULTS AND DISCUSSIONS - PVOH AS A FILLER

A version of this section is under review in The Journal of Applied Polymer Science by Wiley.

4.1 Characterization of coated and uncoated papers

4.1.1 ^1H Nuclear Magnetic Resonance analysis (NMR)

PVOH was commercially acquired and characterized via ^1H Nuclear Magnetic Resonance (NMR) spectroscopy. PVOH was dissolved in methanol- d_4 for ^1H NMR analysis. **Figure 4.1** (in supporting information) shows the spectra for PVOH, showing characteristic resonance at 4.0 ppm for **HC-CH₂-** protons and at 1.51-1.72 ppm for **-CH₂** protons. Chitosan-*g*-PDMS (CP) was synthesized by our reported literature method.¹ ^{13}C NMR spectrum of chitosan-*g*-PDMS was recorded in D_2O and CD_3COOD NMR solvents due to the solubility of chitosan in a slightly acidic medium. **Figure 4.2** shows the spectra for chitosan-*g*-PDMS, where the peak at -0.15 ppm indicates that PDMS has been grafted onto chitosan. The resonance from 3.25-3.75 ppm represents the **-CH** protons of the chitosan ring. The resonance at 2.9 ppm represents the **HC-NH₂** proton.

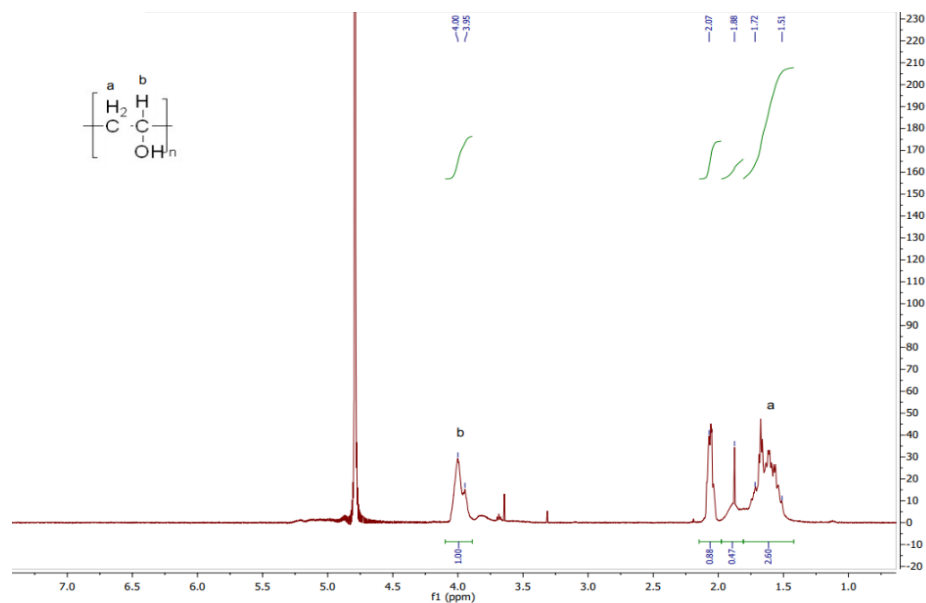


Figure 4.1 ^1H NMR of PVOH in methanol- d_4

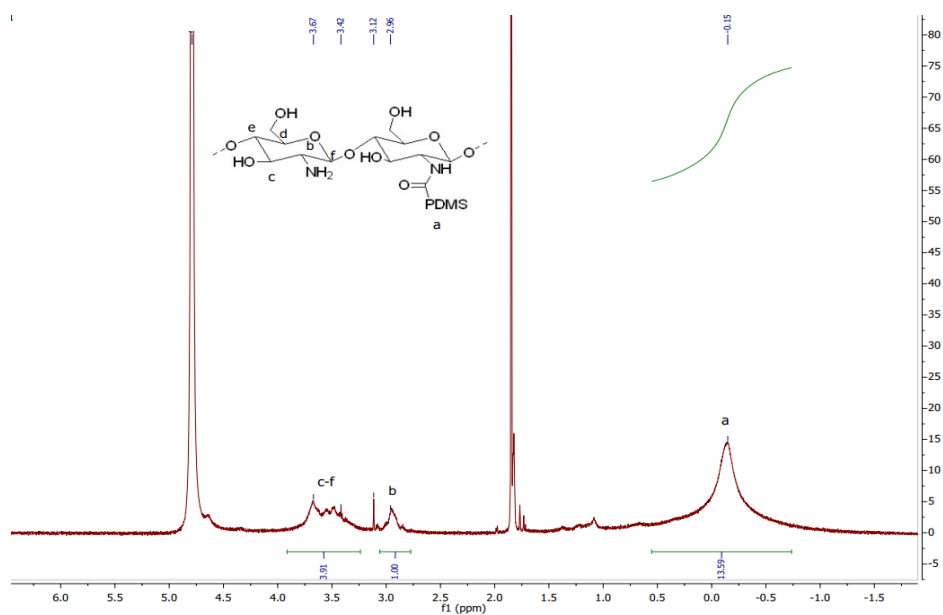


Figure 4.2 ^1H NMR of chitosan-*g*-PDMS in $\text{D}_2\text{O}/\text{CD}_3\text{COOD}$

After characterizing the coating materials via ^1H NMR spectroscopy, the coating was applied onto 35 kraft liner paper using K303 Multi Coater. The coated paper was dried at room temperature for 24 hours. Controls (e.g., PVOH coated paper (P), PVOH/chitosan (P/C) and

uncoated (UM)) were also prepared using formulations mentioned in **Table 1** and were preconditioned before analysis. Codes for each formulation are also shown in the **Table 1**.

4.1.2 Attenuated total reflectance-Fourier transform infrared radiation analysis (ATR-FTIR)

ATR-FTIR analysis of coated paper and their respective controls showed that UM paper, P-coated and P/CP coated papers have broad peak at $\sim 3300\text{ cm}^{-1}$ that represents the O-H stretching of hydroxyl groups present in cellulose (unmodified paper), PVOH and chitosan (See **Figure 4.3**). The peak at $2900\text{-}2950\text{ cm}^{-1}$ represents the sp^3 C-H stretching and the peak at $\sim 1000\text{ cm}^{-1}$ represents the C-O stretching in UM paper, P-coated and P/CP-coated paper. The ATR-FTIR analysis, as shown in **Figure 4.3**, confirmed the grafting of PDMS in the P/CP-coated paper by the presence of characteristic PDMS peaks at 1257 cm^{-1} and 790 cm^{-1} which corresponds to Si-CH₃ stretching and Si-O-Si bending vibrations in the P/CP-coated paper.^{3,4}

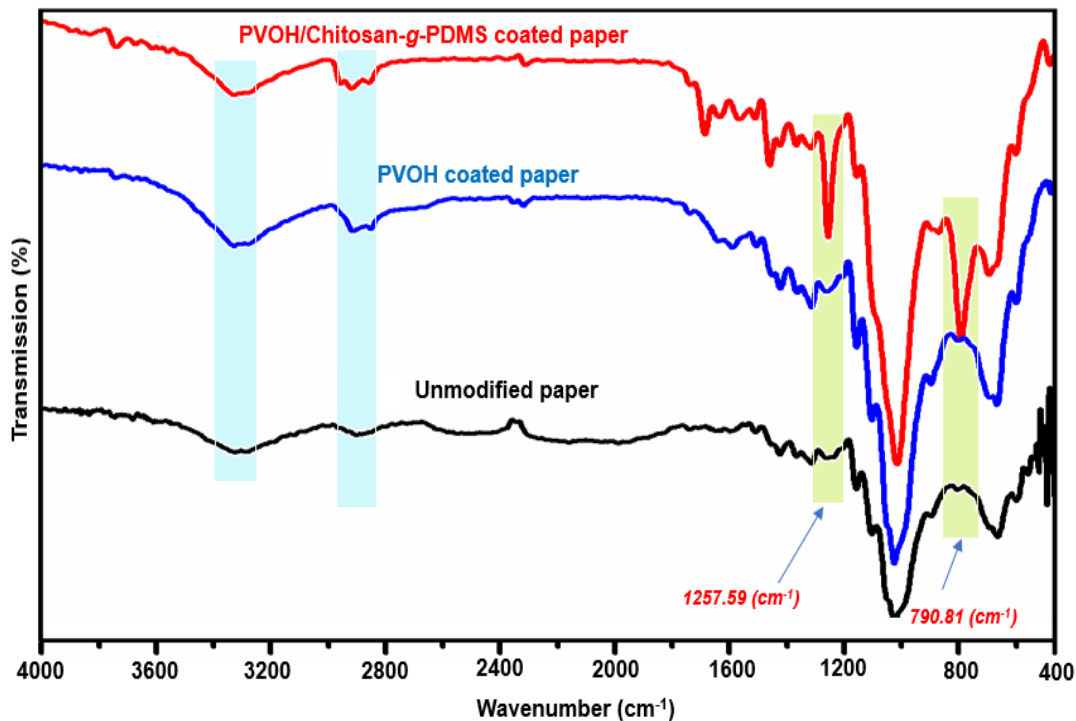


Figure 4.3 ATR-FTIR analysis of coated and unmodified papers. 64 scans were recorded for each sample using FTIR instrument.

4.1.3 Material thickness, basis weight and coating load

Basis weight, and thickness are important basic properties that highly influence the mechanical, barrier and optical properties of the paper. Therefore, selected samples were subjected to basis weight and thickness analysis as shown in **Table 4.1**. The paper thickness of UM paper was found to be $221.2 \pm 0.83 \mu\text{m}$. The paper thickness increases to $229 \pm 3.20 \mu\text{m}$ when the paper was coated with only PVOH solution and a further rise was observed when the paper was coated with different formulations of P/CP solutions. For example, as shown in **Table 4.1**, the thickness of 60P₂:40CP coated paper was $236.6 \pm 2.07 \mu\text{m}$ for which the coating load was recorded to be $2.79 \pm 2.07 \text{ g/m}^2$.

Table 4.1 Average thickness, basis weight and coating load of uncoated and coated papers

Type of paper	Material thickness (μm)	Basis weight (g/m^2)	Coating load (g/m^2)
UM paper	221.2 ± 0.8	169.9 ± 5.4	-
P ₂ - coated paper	229.0 ± 3.2	176.0 ± 6.8	0.93
60P ₂ :40CP -coated paper	236.7 ± 2.1	182.9 ± 5.3	2.79

4.1.4 Thermogravimetric analysis (TGA)

The thermal stability of the coated paper and control samples was analyzed and confirmed using the thermogravimetric analysis (TGA). **Figure 4.4 (A)** shows the residual weights for UM paper, P_{0.5}-coated paper and 90P_{0.5}:10CP coated paper when heated from 10°C to 600°C. **Figure 4.4 (B)** represents the derivative weights for UM paper, P_{0.5}-coated paper and 90P_{0.5}:10CP coated paper. As observed, the thermograms for all the three specimens were similar and thermal stability of the 90P_{0.5}:10CP coated paper till ~380 °C remained intact. This is significant as it indicates that the coated paper can be used for high temperature applications. We noticed that each component's weight loss could not be calculated precisely using these thermograms as the coating load present on the paper was significantly low compared to the weight of the paper itself. To address this challenge, the weight loss of the coating materials was calculated by first making a film of coating solutions without paper and further analyzing the film for TGA. The thermograms thus obtained from the 90P_{0.5}:10CP coated film and the CP film are shown in **Figure 4.4 (C)**, and their derivative weights are represented in **Figure 4.4 (D)**. The initial weight losses observed around 100°C-130°C were due to the loss of moisture from the films. The peak at ~400°C corresponds to the thermal

decomposition of PDMS, for which the weight loss was calculated to be 11% by weight.^{5,1} PVOH and chitosan are both known to decompose at around 280°C and 300°C, respectively, which is why a large peak at ~300°C is observed in **Figure 4.4 (D)**.^{5,6,7} It is worth mentioning that TGA gave key information indicating the thermal stability of the coating and coated paper. The weight losses for PVOH and chitosan were overlapping with that of the paper itself, which is why the coating loads were more accurately determined by basis weight method.⁴

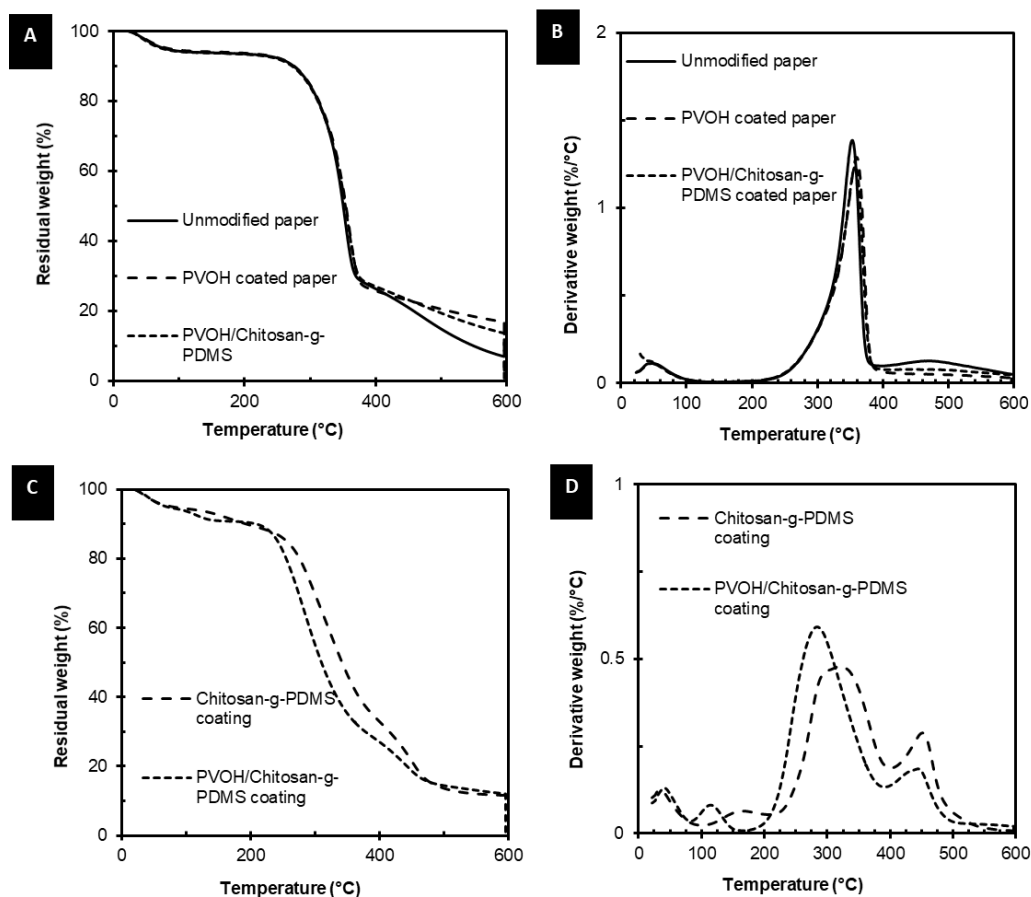


Figure 4.4. A)- Residual weights and B)- Derivative TGA analysis of UM paper, P0.5-coated paper and 90P0.5:10CP coated paper C)- Residual weights and D)- Derivative TGA analysis of coating films (CP film containing 200mg of PDMS-NCO in 100mg chitosan and 90P0.5:10CP coating).

4.2 Water and grease resistance of uncoated and coated papers

4.2.1 Cobb60 test for water absorptivity

The water-resistance of the P/CP coated papers were evaluated by testing the water absorptivity (Cobb60 value), the water vapor permeability (WVP) and the water contact angles (WCAs) of the coated papers. The effect of concentration of PVOH in chitosan-*g*-PDMS on the performance was evaluated and were compared with the properties of UM paper, P-coated and P/C coated papers as shown in **Figure 4.5**. P- coated papers showed a lower water absorptivity as compared to the UM paper. For example, the Cobb60 value for P_{0.5} coated paper was found to be $56.7 \pm 3.2 \text{ g/m}^2$ as compared to the Cobb60 value of UM paper of $66.0 \pm 1.8 \text{ g/m}^2$. This little improvement is due to the masking of paper pores; however, the cobb values were too high for P-coated paper due to the presence of hydroxyl groups on PVOH that led to hydrogen bonding with the water molecules in contact and hence shows low hydrophobicity. Interestingly, coating prepared from the P/C blend showed an improvement in the water-resistance of the coated papers. P_{0.5}/C-coated paper showed a water absorptivity of $36.0 \pm 2.3 \text{ g/m}^2$ with a decrease of 45% compared to the water absorptivity for UM paper. This was due to excellent film-forming properties of chitosan, which results in masking the pores of the paper and, thus, reducing the water absorption.⁸ The Cobb60 values were observed to further decrease in case of P/CP coated papers, which showed a decrease of 62% in water absorptivity as compared to the UM paper, with a value of $24.6 \pm 1.3 \text{ g/m}^2$ for 80P_{0.5}:20CP coated paper. This was mainly due to the hydrophobicity imparted by PDMS.⁹ For different volume ratios of P/CP such as 90P:10CP, 80P:20CP, 70P:30CP and 60P:40CP, there was no significant change in the Cobb60 values for any PVOH concentration. For example, the Cobb60 value for 90P_{0.5}:10CP coated paper was $27.8 \pm 2.6 \text{ g/m}^2$, and for 60P_{0.5}:40CP coated paper, Cobb60 value was $27.6 \pm 1.4 \text{ g/m}^2$, which were not significantly

different. The concentration of PVOH solution seemed to have no major effect on the water absorptivity of coated papers for 0.5 wt% and 2 wt% concentration for all four different volume ratios of P to CP, beyond which the water absorptivity increased significantly for 4 wt% concentration. This can be associated with polar hydroxyl groups in PVOH, which interact with water molecules and have a dominant effect at 4.0 wt% concentration.¹⁰

4.2.2 Water vapor permeability

The water vapor resistance of the uncoated and coated papers was studied using water vapor transmission rates (WVTR). Since the substrate thickness influences transmission rates, WVTR was reported as water vapor permeability (WVP) to accommodate thickness variations in the coated samples. The water vapor transmission rates for coated and uncoated papers were determined using the Mocon instrument, and the permeability values were further calculated using **Equation 2**. Three trends were observed from the WVP studies. First, coated paper has lower WVP related to the uncoated paper, mainly due to the nonporous nature of coated paper (see scanning electron microscopic images, discussed later). Second, the lower the amount of PVOH, the lower (better) is WVP since PVOH is known to absorb more water than CP. Finally, increasing the coating thickness, imparted improved WVP. A decrease of ~69% in WVP was observed for 60P_{0.5}:40CP coated paper as compared to the unmodified paper.

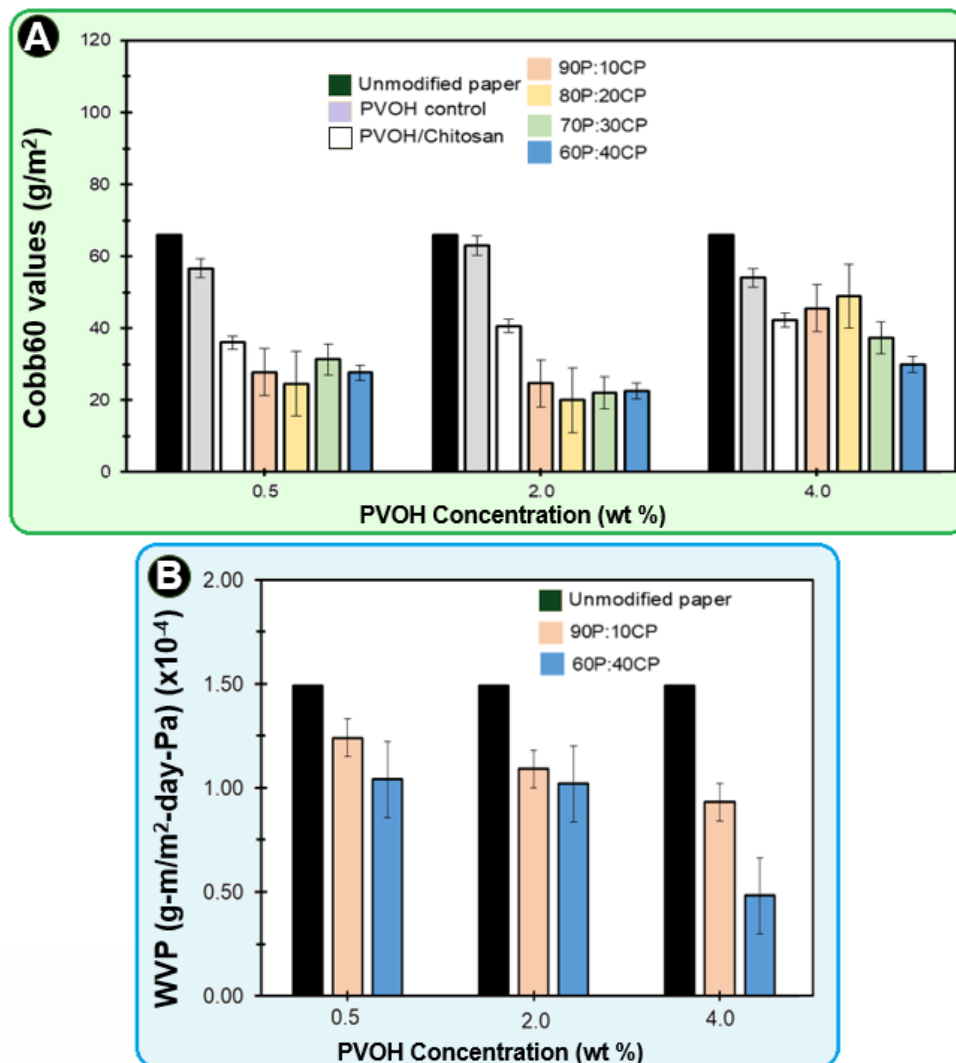


Figure 4.5 A) Cobb60 values (g/m^2) of different volume ratios of PVOH (P) and chitosan-*g*-PDMS (CP) coated papers, and different control systems of PVOH (P) coated, PVOH/chitosan (P/C) coated and unmodified (UM) papers; **B)** WVP of coated and uncoated paper at $23^\circ\text{C}/50\% \text{ RH}$. The ratios indicate weight ratios of P to CP. The control denotes UM paper.

4.2.3 Water and oil contact angles

Water resistance of the coated and uncoated paper was further investigated by performing water contact angle (WCA) measurements, as shown in **Figures 4.6A** and **4.6B**. The WCAs on

uncoated paper substrates as they absorb water too quickly.¹¹ Measurements were, therefore, performed at lapses of 30 seconds and 5 minutes at ambient conditions of 23°C and 50% RH. A surface is considered hydrophobic when contact angles are greater than 90° and hydrophilic when less than 90°.¹¹ Again, for this study, the WCAs of different P/CP coated and were compared with UM papers and PVOH coated papers, as shown in **Figure 4.6B**. As expected, the contact angle of unmodified paper was below 90° after 30 seconds and was completely absorbed by the paper within 5 minutes, which indicated poor water-resistance of the uncoated paper due to the presence of polar cellulosic materials and porous nature of the paper. For the P_{0.5}, P₂ and P₄ coated papers, the contact angles were even lower than that for the UM paper. For example, the WCA reduced from 84.00±0.8° for the UM paper to 42.2±3.2° for P_{0.5} coated paper, which further reduced to 0° after 5 minutes, as seen in **Figure 4A**. This reduction in angle for P_{0.5} coated paper can be associated to the hydrophilic nature of PVOH due to the presence of hydroxyl groups as well as the smooth nature of the PVOH coated paper as smoothness inversely affects the contact angles. The use of P/C blends was seen to impart some stability into the WCAs due to better water resistance of chitosan than PVOH. However, the contact angles were still below 90°, which indicates low hydrophobicity and higher wettability. Application of P/CP on the paper substrate imparted significant hydrophobicity by increasing the contact angle above 90° for P_{0.5}/CP and P₂/CP coated papers. This increase in water resistance corresponds to the elegant hydrophobic nature of PDMS. The contact angles for all ratios of P_{0.5}/CP and P₂/CP coating were seen to be stable and greater than 90° even after 5 minutes with the highest contact angle of 119±6.3° at 30 seconds 90P_{0.5}:10CP coated paper, as shown in **Figure 4.6A**. The contact angles for P₄ coatings seemed to be considerably lower, which is due to greater hydrophilicity imparted by a higher PVOH concentration in the coating solution. In general, for the paper coated with 4.0 wt% PVOH

concentration, the stability of the water droplet on the paper surface was poor after 5 minutes, despite the presence of CP. These results corroborate with our findings from the Cobb60 test (**Figure 4.5A**), indicating higher water absorbency and poor Cobb60 values at PVOH concentration of 4.0 wt%; thus, PVOH concentration >2wt% is counter-productive in the pursuit of higher water resistance.

Oil contact angles (OCAs) were found to be stable for all three PVOH concentrations ($P_{0.5}$, P_2 and P_4 coated papers), and the P/CP coated papers were found to show good repellency against castor oil. OCA for the UM paper was $27 \pm 2.8^\circ$ after 30 seconds, which reduced to $18 \pm 3^\circ$ after 5 minutes, thus indicating high oil absorption and low oil repellency. For P/C-coated papers with higher concentrations of PVOH, the OCA dropped to 0° after 5 minutes, which indicated low oil resistance despite the presence of active polar groups in the system. The addition of PDMS was found to significantly improve the oil resistance of the coating system. The maximum OCA was $77 \pm 2.6^\circ$ for 60 P_2 :40CP coated paper that only dropped to $73 \pm 3.1^\circ$ after 5 minutes. For P- coated and P/C- coated papers the difference in OCA from 30 seconds to 5 minutes was found to be close to 10° as shown in **Figure 4.6C**, whereas in P/CP coated papers the difference in angle after 5 minutes was not more than 5° as evident from the plot in **Figure 4.6D**. The amount of PVOH in the overall coating solution did not show any trend or affect the OCAs significantly. For example, the OCA for 90 $P_{0.5}$:10CP coated paper was noticed to be $69.5 \pm 2.2^\circ$ and was not significantly different from that for 60 $P_{0.5}$:40CP coated paper, which was $65.3 \pm 1.9^\circ$.

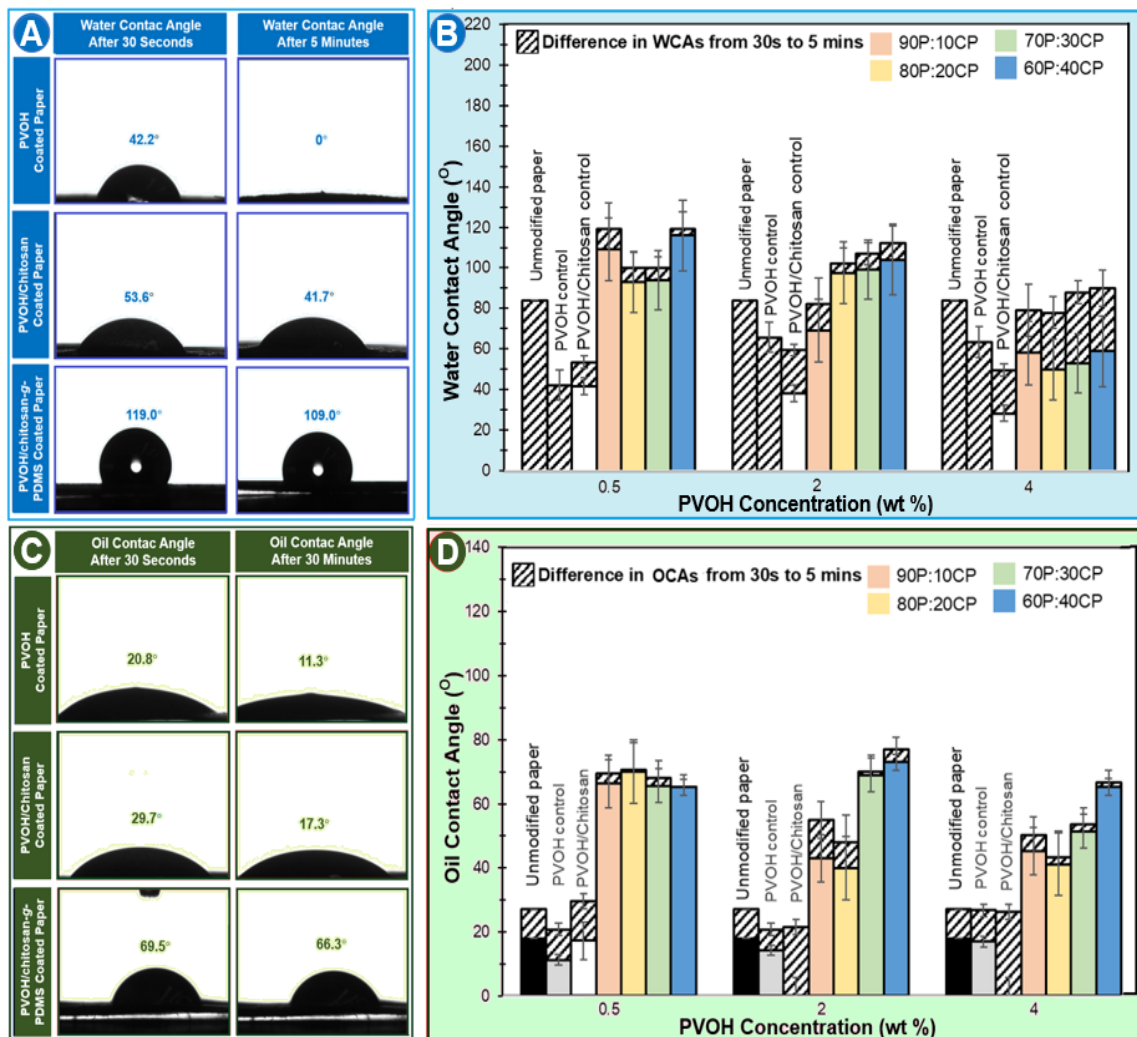


Figure 4.6 A) and C) Water (WCA) and oil contact angles (OCA) for P_{0.5}- coated, P_{0.5}/C-coated and 80P_{0.5}:20CP coated paper for 30 seconds and 5 minutes, respectively; **B) and D)** WCAs and OCAs as a function of the concentration of PVOH for UM paper, P- coated, P/C-coated and P/CP coated paper. The ratios indicate different volume ratios of PVOH (P) to chitosan-*g*-PDMS (CP) for coated papers.

4.2.4 Kit rating

Kit rating measurements were employed to evaluate the oil resistance of the uncoated and coated paper substrates. Kit ratings are expressed as numerical values between 0-12, where a

higher kit rating denotes a greater oil resistance of the specimen and vice versa ^{1,12} **Figure 4.7** represents the kit rating of the coated and uncoated paper samples as a function of different concentrations of PVOH solutions. The UM paper was seen to have a kit rating of zero, indicating no oil resistance. Coating the paper with PVOH improved the kit rating to 3.1/12 for P₂ coated paper, implying PVOH imparted some oil resistance to the paper and was further increased upon an increase in PVOH concentration. For example, the kit rating for P_{0.5} coated paper was 2.9/12, whereas for that for P₄ coated paper was 3.6/12. This increase in kit rating for PVOH coated paper is due to oleophobic nature of PVOH as well as the masking of the pores in coated paper. The addition of chitosan to PVOH improved the kit rating even further to 5/12, for P₄/C coated paper due to the very polar nature of chitosan (more OH to Carbon ration) as well as better pore masking. Additionally, introduction of CP in the coating solution was observed to further improve the oil resistance of the paper as shown in **Figure 4.7**. The kit rating was observed to further improve from 5/12 for P₄/C coated paper to 5.8, 7, 7.2, 7.6/12 for 90P₄:10CP, 80P₄:20CP, 70P₄:30CP, and 60P₄:40CP coated papers respectively. This considerable improvement in the oil resistance can be associated to the low surface energy surface created by PDMS and the masking of pores by PVOH and chitosan.^{1,3,13} Also, an increase in the concentration of PVOH in the P/CP coated papers was found to improve the kit rating which is due to better masking of the pores owing to thicker coatings. For example, it was also observed that for 90P_{0.5}:10CP coated paper, the kit rating was 3.5/12, whereas that for 60P_{0.5}:40CP was 5/12, which indicates that, increase in the amount of CP in the overall coating solution improves the oil resistance of the coated papers. A similar trend was observed for the PVOH concentration of 2.0 wt% and 4.0 wt%.

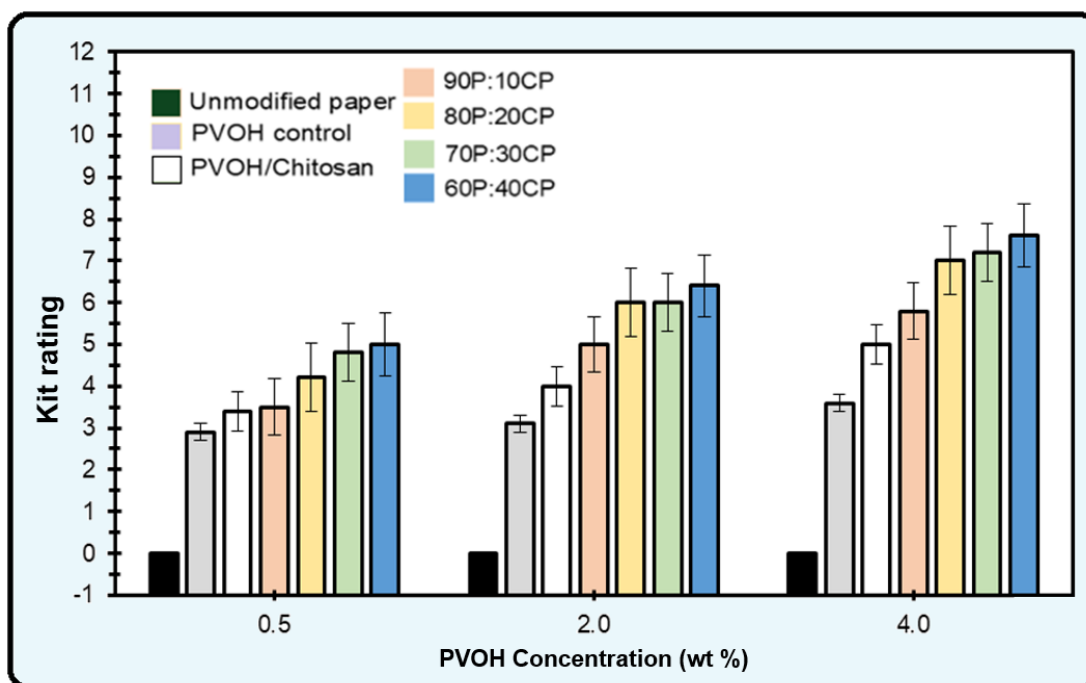


Figure 4.7 Kit rating of coated and uncoated papers as a function of PVOH concentration. The ratios indicate different volume ratios of PVOH (P) to chitosan-*g*-PDMS (CP) for coated papers. Kit rating 12 denotes maximum oil resistance and 0 corresponds to no oil resistance.

4.3 Scanning Electron Microscopy

A paper substrate consists of fibers interlaced together, thus forming a porous structure.⁸ In addition, paper surface is highly non-uniform.¹⁴ Therefore, we investigated the effect of the coatings on the surface texture of the paper using SEM analysis. The unmodified and PVOH coated papers, as seen in **Figure 4.8A** and **4.8B**, had a considerable number of uncovered pores, which lead to absorption of water and thus showed poor water resistance. However, by the introduction of CP in varying volume ratios of PVOH to CP into the formulations, the pores were masked, and the surface was proven to be smoother as shown in **Figures 4.8C** and **4.8D**. Tiny particles on the surface of the paper substrates were observed (See **Figures 4.8C** and **4.8D**), which corresponds to the phase separation of CP in PVOH matrix as the former is a minor component of the blend.

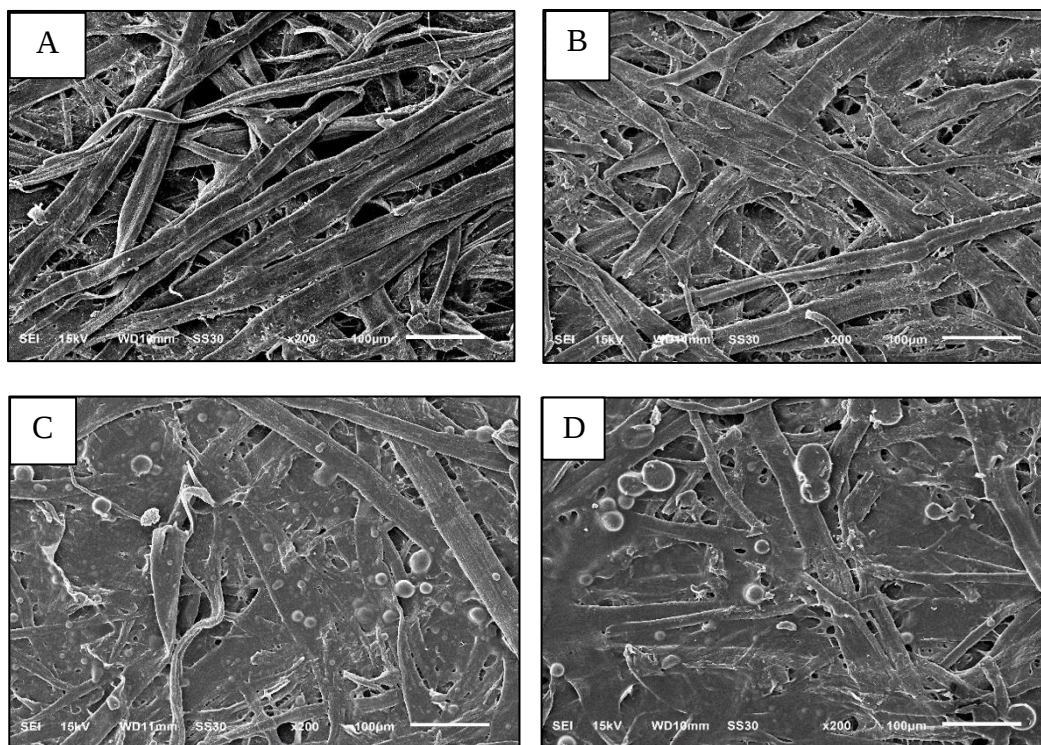


Figure 4.8 SEM analysis of: **A)** Unmodified paper; **B)** $P_{0.5}$ coated paper; **C)** $60P_{0.5}:40CP$ coated paper; and **D)** $60P_4:40CP$ coated paper.

4.4 Repulpability

The recycling of the pulp from coated paper is desirable but a challenging feat to achieve¹⁵ because plastic laminates are difficult to separate from paper. With the aim of overcoming this issue, a repulping method has been developed and successfully employed in washing off the CP coating from the paper surface.¹ This was taken further in this study to analyze the effect of PVOH as a filler in washing the optimized CP coating off the paper surface. Papers coated with of 60P₄:40CP were first blended into pulp. A portion of this pulp was converted to paper without being washed while the remaining was converted to paper after being washed with water and 1.0 vol% acetic acid solution. **Figure 4.9** shows the ATR- FTIR spectra of the washed and unwashed coated papers which were repulped. The spectra of repulped papers with a coating which were left unwashed were compared to those with coating, which were washed with water and acetic acid. The spectra of the washed papers did not seem to show typical PDMS peaks at 1255 cm⁻¹ and 790 cm⁻¹ as visible in the spectra for unwashed coated papers which proves that the coating was not present on the paper and was essentially washed off the paper surface.

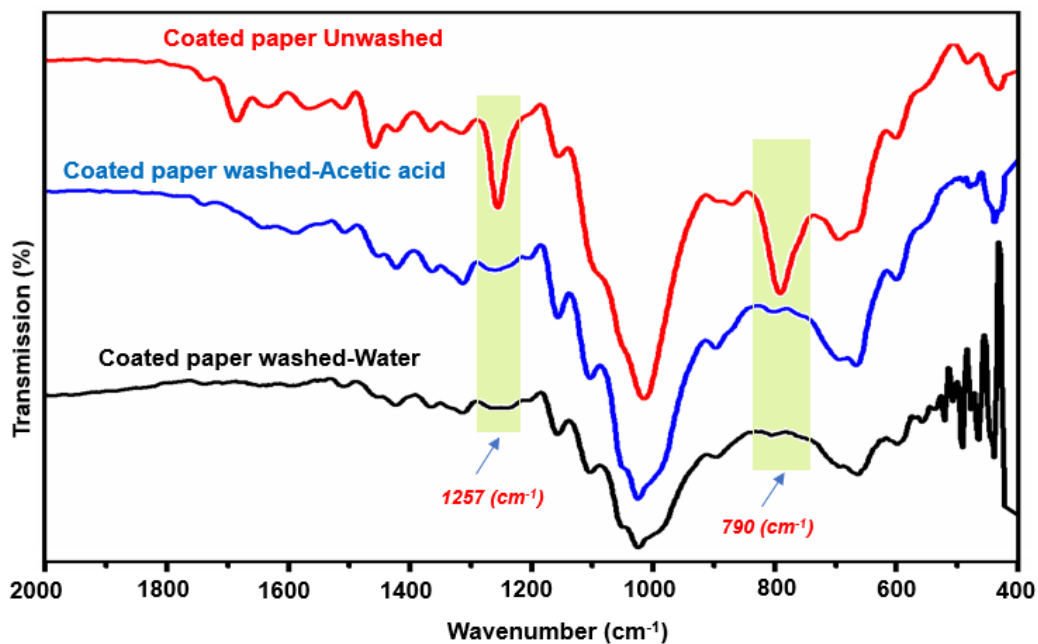


Figure 4.9 FTIR spectra of recycled papers made from fibers of 60P₄:40CP coated papers washed with 1.0 vol% acetic acid and water.

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Chapter 5

RESULTS AND DISCUSSIONS - STARCH AS A FILLER

A version of this section is under review in the journal- Advanced Sustainable Systems by Wiley.

5.1 ^1H Nuclear Magnetic Resonance analysis (NMR)

Starch was commercially acquired and characterized via ^1H Nuclear Magnetic Resonance (NMR) spectroscopy before use. **Figure 5.1 (A)** shows the spectra for starch, showing characteristic resonance at 5.39 ppm for proton labeled as *a* and a broad resonance for -CH- protons labeled as *b,c,d,e* from 3.70-3.85 ppm. The peak at 3.62 corresponds to the -CH₂- proton labeled as *f*. Chitosan-g-PDMS was synthesized by literature method.¹ **Figure 5.1 (B)** shows the spectra for chitosan-g-PDMS, the peak at -0.02 ppm indicates the grafting of PDMS onto chitosan. The resonance from 3.25-3.75 ppm represents the -CH protons of the chitosan ring. The resonance at 2.9 ppm represents the HC-NH₂ proton. **Figure 5.1 (C)** shows the spectra chitosan-g-PDMS with starch as filler. The resonance peak at 5.39 ppm confirmed the presence of starch along with chitosan. The peak at -0.04 ppm confirmed the presence of PDMS.

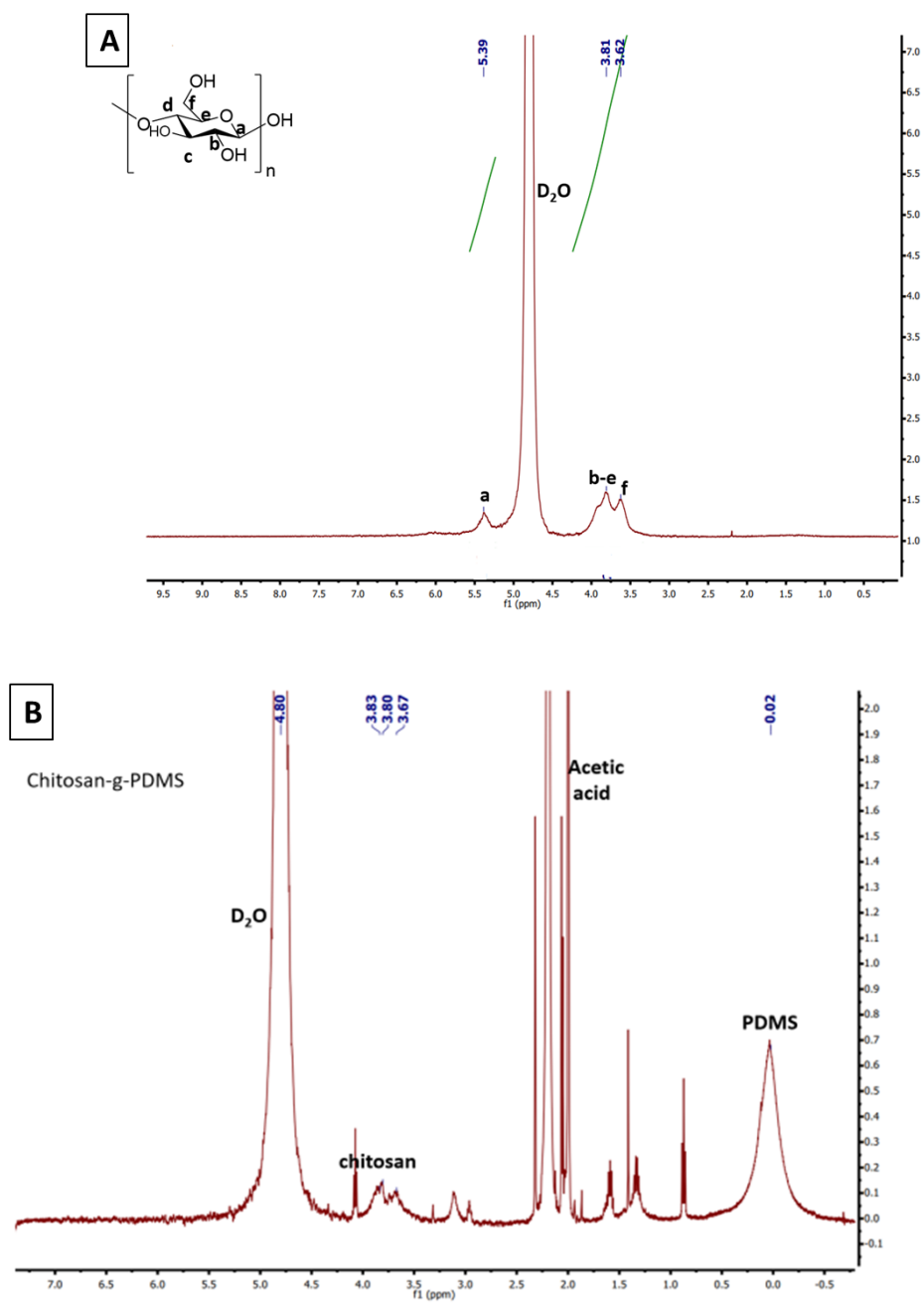
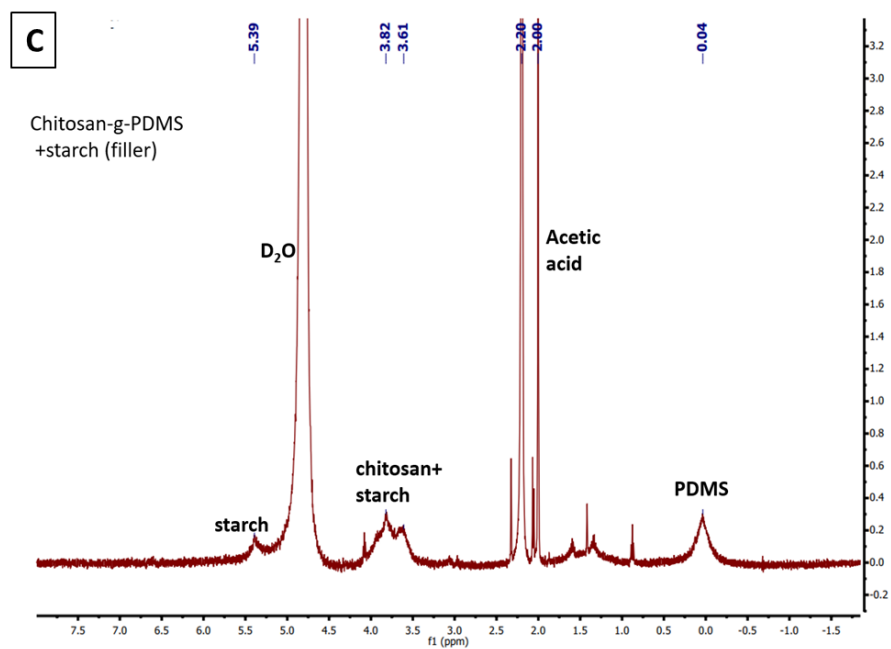


Figure 5.1: ¹H NMR of (A) starch (B) chitosan-g-PDMS and (C) chitosan-g-PDMS with starch as filler. The NMR sample was taken in D₂O

Figure 5.1 (cont'd)



5.2 Cobb60 and kit rating of coated and uncoated papers

The Cobb60 test is an excellent indication of water absorptivity and is a standard performance test for water resistance in the coating industry. Therefore, we determined the Cobb60 values of our coated papers and their respective controls (**Figure 5.2A**).² The water absorptivity of unmodified paper was observed to be $65.52 \pm 1.33 \text{ g/m}^2$, which interestingly decreased by 51% after coating with S_3 (Cobb60 value $32 \pm 0.8 \text{ g/m}^2$), and the Cobb60 value was further reduced to $30.00 \pm 0.54 \text{ g/m}^2$ for S_3/C coated paper. This improvement in water resistance can be associated with the masking of the paper's pores, as supported by our prior studies.^{3,4} The Cobb60 value of the $60S_3:40CP$ -coated paper was found to be $13.43 \pm 0.90 \text{ g/m}^2$, which showed an improvement of about 80% compared to unmodified paper. This implies that the introduction of PDMS in the coating system reduced the water absorptivity considerably, which is due to the low surface energy of the coated surface due to PDMS and the masking of paper pores by the S/CP coating (which is also supported by SEM studies as will be discussed later).^{5,6,4} We also validated that increasing the CP content in the S/CP formulation further reduces water absorptivity due to an increase in the PDMS concentration in the coating blend (**Figure 5.2A**).

The oil resistance of the coated paper and the controls was studied using the kit test as per TAPPI T559, which is a standard test used in the coating industry.⁷ The kit rating for unmodified paper was observed to be 0/12 since the paper in itself did not possess any oil-resistance. Interestingly, the introduction of starch to obtain the S_3 -, S_5 - and S_7 -coated papers yielded a considerable improvement in oil resistance as evident in **Figure 5.2B**. For example, the kit rating was observed to improve to as high as 7/12 for S_7 -coated paper. The addition of chitosan to starch further increased the kit rating of the S_7/C -coated paper to 9/12 due to the oil repellency imparted by the better film forming ability of chitosan.^{5,8-12} Meanwhile, the $90S_7:10CP$ -coated paper

showed a kit rating of 11.6/12, which again indicated that PDMS played a crucial role in imparting oil resistance onto the coated paper. The kit rating was observed to increase with a higher amount of CP in the S/CP-coated papers, with a 60S:40CP volume ratio achieving the maximum oil resistance of 12/12 due to the increase in the concentration of chitosan as well as PDMS.

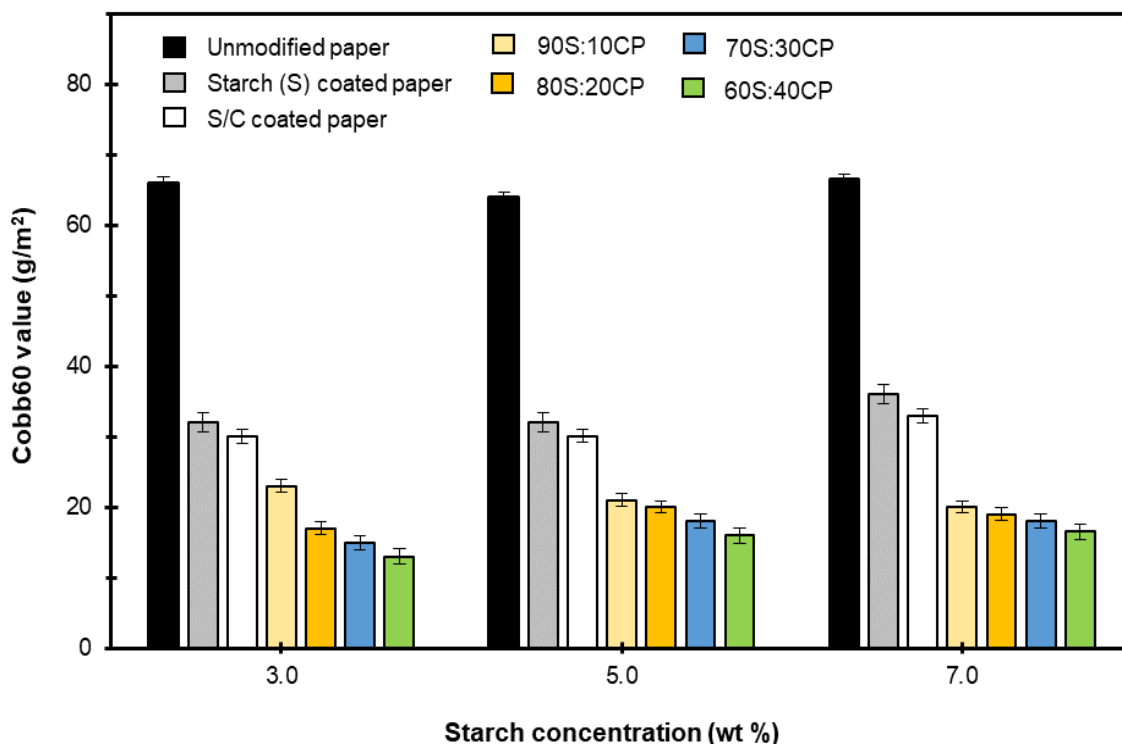
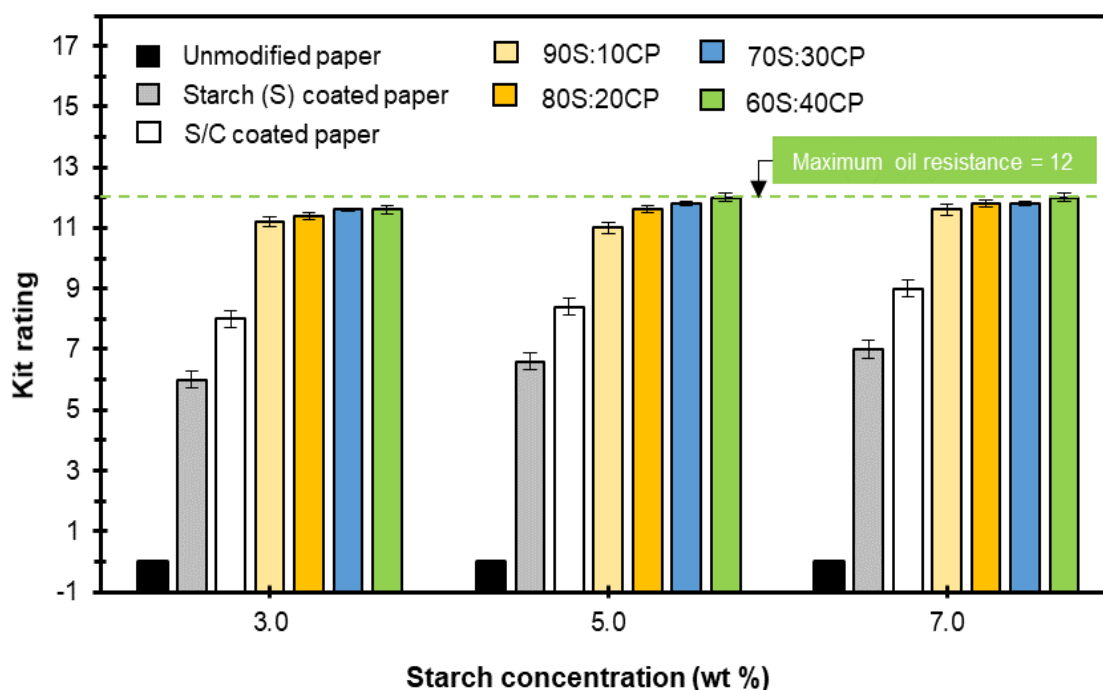


Figure 5.2 Cobb60 values (g/m^2) (A) and kit rating (B) as a function of the starch concentration in different volume ratios of starch (S) to CP for S/CP-coated papers, and different control systems of starch-coated (S), starch/chitosan-coated (S/C, starch blended with 2 wt% chitosan in a volume ratio of 50:50) and unmodified paper samples. For example, 60S:40CP-coated paper consists of starch and CP solutions that were blended together at a volume ratio of 60:40.

Figure 5.2 (cont'd)



5.3 Statistical analysis

The results from the Cobb60 and kit rating tests clearly indicated that the S/CP-coated papers possess excellent water and grease resistant properties, which are a function of the starch concentration and S-to-CP volume ratio. With this in mind, it was necessary to investigate the effects of these independent variables on the Cobb60 values and kit ratings. For this purpose, a two-way Analysis of Variance was conducted for two response variables (Cobb60 value and kit rating) at a level of significance of 5%. The p -values obtained are displayed in **Table 2** whereas the interaction plots for the Cobb60 values and kit ratings are displayed in **Figure 5.3**. As per the obtained p -values, the volume ratios of starch to CP (S:CP ratio) had a significant effect on both the Cobb60 values and the kit ratings with p -values of less than α of 0.05. Out of the various volume ratios tested, the 60S:40CP volume ratio was observed to provide the best results (lowest

Cobb60 value and highest kit rating) for all three concentrations of starch as is evident in **Figure 5.3A** and **5.3B**. In contrast, the starch concentration did not have a significant effect on the Cobb60 values as indicated by the higher p -value displayed in **Table 2** and **Figure 5.3A**, where it is evident that the fitted means of Cobb60 values of 5.0 and 7.0 wt% starch concentration were not significantly different. With regard to the kit rating, the starch concentration showed a p -value of 0.0123, thus indicating that it had a significant effect on the oil resistance. In terms of the combined effect of both the S:CP ratio and the starch concentration, the kit rating was not significantly affected by this combined parameter, whereas the interaction effect was statistically significant in the case of the Cobb60 values with a p -value of 0.0154 thus also indicating that the relationship between S:CP ratio and Cobb60 values was dependent on the concentration of starch. On the basis of the results from the statistical analysis, a 60S:40CP volume ratio for 3.0 and 5.0 wt% concentrations of starch were chosen to be the formulation that provided the optimum Cobb60 and kit rating values for S/CP-coated papers and were thus used for further tests.

Table 5.1. *P*-values obtained for the interaction effect of independent variables on Cobb60 values and kit ratings in a two-way ANOVA test at a level of significance of 5%.

Independent variables	Levels	<i>P</i> -value	
		Cobb60	Kit rating
Starch/chitosan- <i>graft</i> -PDMS (S:CP) Ratio	4	0.0007	0.0012
Starch concentration	3	0.1031	0.0123
S:CP Ratio*Starch concentration	12	0.0154	0.8425

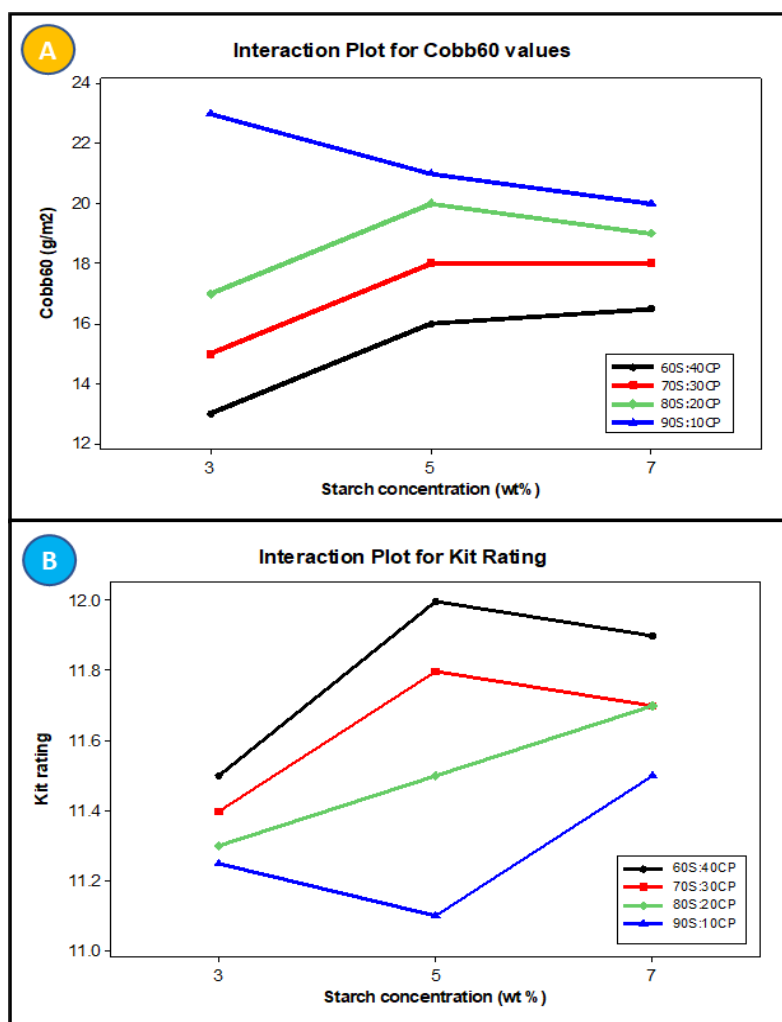


Figure 5.3 Interaction plots for: **A)** Cobb60 values (g/m^2) and **B)** kit rating as a function of the starch concentration.

5.4 Water resistance of coated and uncoated papers

5.4.1 Water contact angles

The water resistance of the paper was further evaluated by studying the wettability of the coated paper using contact angle measurements for the selected samples. Water contact angles were recorded at 30 s and again at 5 min to analyze the de/wettability of the coated paper samples at ambient conditions of 23°C and 50% RH. The difference between the contact angles that were

recorded at 30 s and 5 min indicated the amount of water absorbed into the paper in this time frame. As evident in **Figure 5.4**, the water contact angle for unmodified paper (UM) was observed to be $84.00 \pm 0.80^\circ$ at 30 s and was seen to reduce to 0° after 5 min, thus indicating a strong affinity between the water and paper surface.¹³ The starch-coated papers, namely the S₃- and S₅-coated papers, showed contact angles of $69.57 \pm 1.87^\circ$ and $84.47 \pm 1.70^\circ$ at 30 s, which reduced to $64.40 \pm 3.72^\circ$ and $81.87 \pm 1.61^\circ$ respectively after 5 min. In this case, even though the difference in WCA between 30 s and 5 min was relatively small as compared to that observed with UM paper, the surface was still considered to be hydrophilic because the WCAs were less than 90° . The addition of chitosan to starch did not lead to a significant difference in the contact angles of the S₃/C- and S₅/C-coated papers as compared to the starch-coated papers. However, the difference in WCAs between 30 s and 5 min for S₃/C- and S₅/C-coated papers was observed to be higher as compared to those observed for the starch-coated papers due to the introduction of chitosan which has ionic groups that absorb water, thus leading to a higher wettability.^{14,15} Further, the S/CP-coated paper exhibited WCAs as high as $106.00 \pm 1.20^\circ$ for the 60S₃:40CP-coated paper and $104.00 \pm 1.67^\circ$ for the 60S₅:40CP-coated paper at 30 s. This behavior indicated that there was a low affinity between water and the surface, thus indicative of a hydrophobic surface. The difference between the WCAs measured at 30 s to 5 min for the S/CP-coated papers was also lower than that of the starch- and starch/chitosan-coated papers which altogether denotes a significant improvement in performance on addition of PDMS in the coating system.

5.4.2 Water vapor permeability

The barrier performance of the coated papers were tested against water vapor by determining the water vapor permeability at 23 °C and 50% R.H. As evident in **Figure 5.4**, the UM paper acted as a poor barrier against water vapor due to its porous nature, with values as high

as 9.80×10^{-5} g-m/m²-day-Pa. On the other hand, the permeability values were respectively observed to be 5.90 and 6.72×10^{-5} g-m/m²-day-Pa for S₃- and S₅-coated papers, which showed a considerable improvement in the barrier performance as compared to UM paper. Similar values were observed for S/C-coated papers (with permeabilities of 5.86 and 6.00×10^{-5} g-m/m²-day-Pa for S₃/C and S₅/C coatings, respectively). The permeability values diminished even further in the case of the S/CP-coated paper to 3.50×10^{-5} g-m/m²-day-Pa for 60S₃:40CP-coated paper, which showed an overall improvement of ~64% as compared to the UM paper. This improvement in performance can be attributed to the masked pores in the coated paper samples (evident in the SEM images in **Figure 5.7**) which block the diffusion of water molecules through the paper surface, thus acting as an excellent moisture barrier. Thus, blending the CP coating with starch was observed to compensate for the poor water vapor permeability of starch coating by itself while making the coating system economical at the same time. Overall, we can conclude that WVP analysis confirmed that the S/CP-coated paper samples exhibited a significant improvement in the water barrier properties relative to those of the controls.

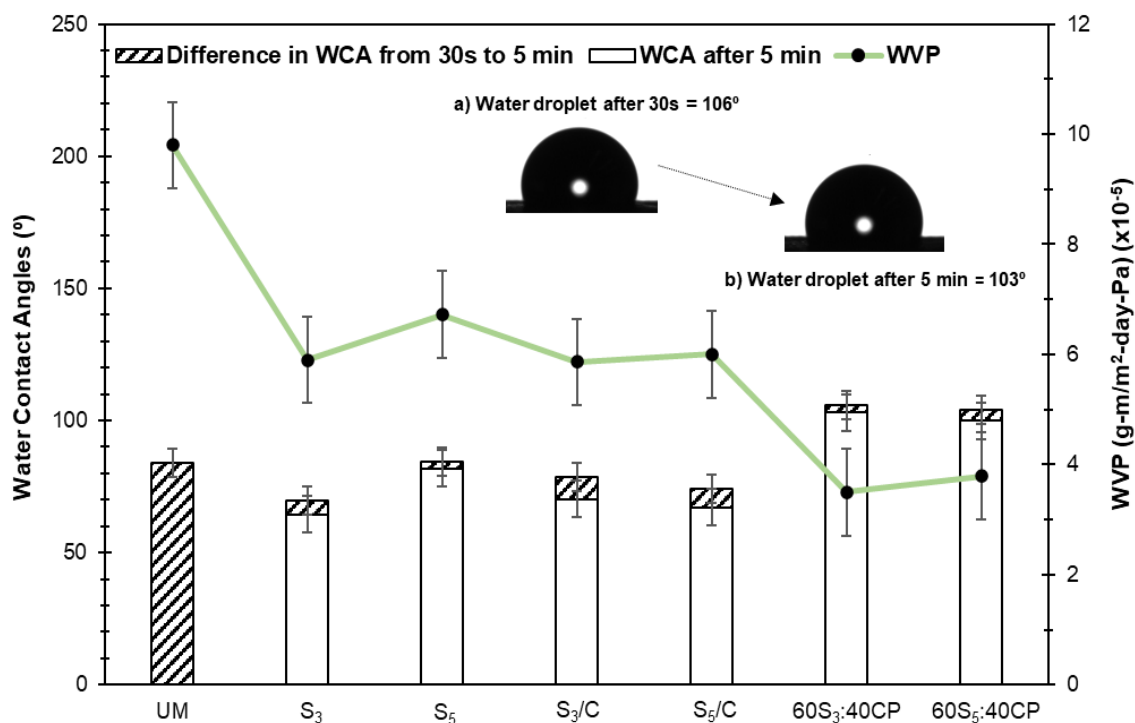


Figure 5.4 WCAs and water vapor permeability of UM paper (unmodified), S₃- and S₅-coated papers (coated with 3.0 and 5.0 wt% starch solutions), as well as S₃/C-, S₅/C- (starch/chitosan), 60S₃:40CP-, and 60S₅:40- (starch/chitosan-*graft*-PDMS) coated paper samples. Water droplet stability after **a)** 30 s and **b)** 5 min on 60S₃:40CP-coated paper.

5.5 Attenuated total reflectance-Fourier transform infrared radiation analysis (ATR-FTIR)

Selected coated paper and their controls were characterized via ATR-FTIR spectroscopy to validate their surface chemistry (**Figure 5.5**). The FTIR spectra of unmodified paper, S₅-coated paper, and 60S₅:40CP-coated paper was observed to exhibit a broad peak at approximately 3300 cm⁻¹ that corresponded to the O-H stretching vibrations in cellulose, starch, and chitosan. This peak was observed to further broaden as the hydroxyl molecules in the system increased with the application of starch into cellulose and further on addition of chitosan to the coating system. The peak at ~2900 cm⁻¹ corresponds to the C-H stretching vibration while that at ~990 cm⁻¹ represents

a C-O stretching vibration. As is evident in **Figure 5.5**, typical peaks corresponding to the Si-CH₃ stretching and Si-O-Si bending vibrations in PDMS are observed at 1257 cm⁻¹ and 790 cm⁻¹ in the FTIR spectrum of the S/CP-coated paper, thus indicating the presence of PDMS on the surface of the coated paper.^{3,5}

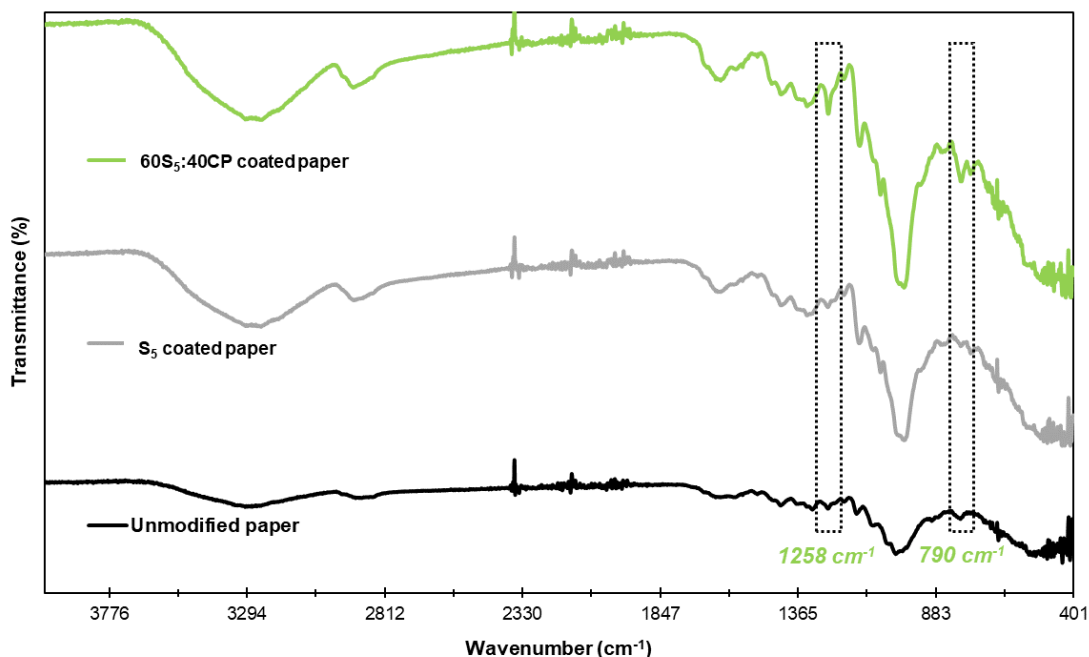


Figure 5.5 ATR-FTIR spectra of UM (unmodified paper), S₅-coated (5 wt% starch-coated paper) and 60S₅:40CP-coated (5 wt% S/CP-coated paper with a 60S:40CP volume ratio) paper samples.

5.6 Thermogravimetric analysis (TGA)

Next, the residual weights of the coating components and thermal degradation of the coated paper samples were analyzed via thermogravimetric analysis (TGA). The coated paper samples were characterized via TGA over a temperatures range from 10 to 600 °C and a loss in mass of the material as a function of temperature was recorded to study the degradation mechanism of the papers.¹⁶ The thermograms of the S/CP coated paper and unmodified paper show the residual

weights in **Figure 5.6 (A)**. These thermograms show a similar decomposition temperature of ~ 300 °C for both of the papers. However, to obtain a precise measurement analysis, first derivatives of the loss in mass were plotted as a function of temperature as shown in **Figure 5.6 (B)**. The derivative weights show a slight improvement in the thermal decomposition temperature for S/CP-coated paper (60S₃:40CP) which indicates that the coated paper had a slightly better thermal stability as compared to the unmodified paper. Further, the coating samples were analyzed separately in order to calculate the decompositions of the individual coating components (i.e., starch, chitosan, and PDMS). The plot showing the derivative weights in **Figure 5.6 (D)** represents the maximum rate of mass loss in which each step of weight loss corresponds to a peak indicating a separate event in a particular temperature range.^{16,17} This especially helps to distinguish mass loss events that overlap with each other, as occurs in the case of starch and chitosan in the S/CP coating which are both known to decompose at a temperature range of 250 to 300 °C.^{16,17} The peak in the range of 450 to 500 °C corresponds to the decomposition of PDMS in the coating system.^{8,4} While TGA successfully validated the thermal resistance of the coated paper, it was difficult to quantify the coating load due to the low coating loads along with the overlap between the decomposition peaks of the coating components and those of the paper substrate.

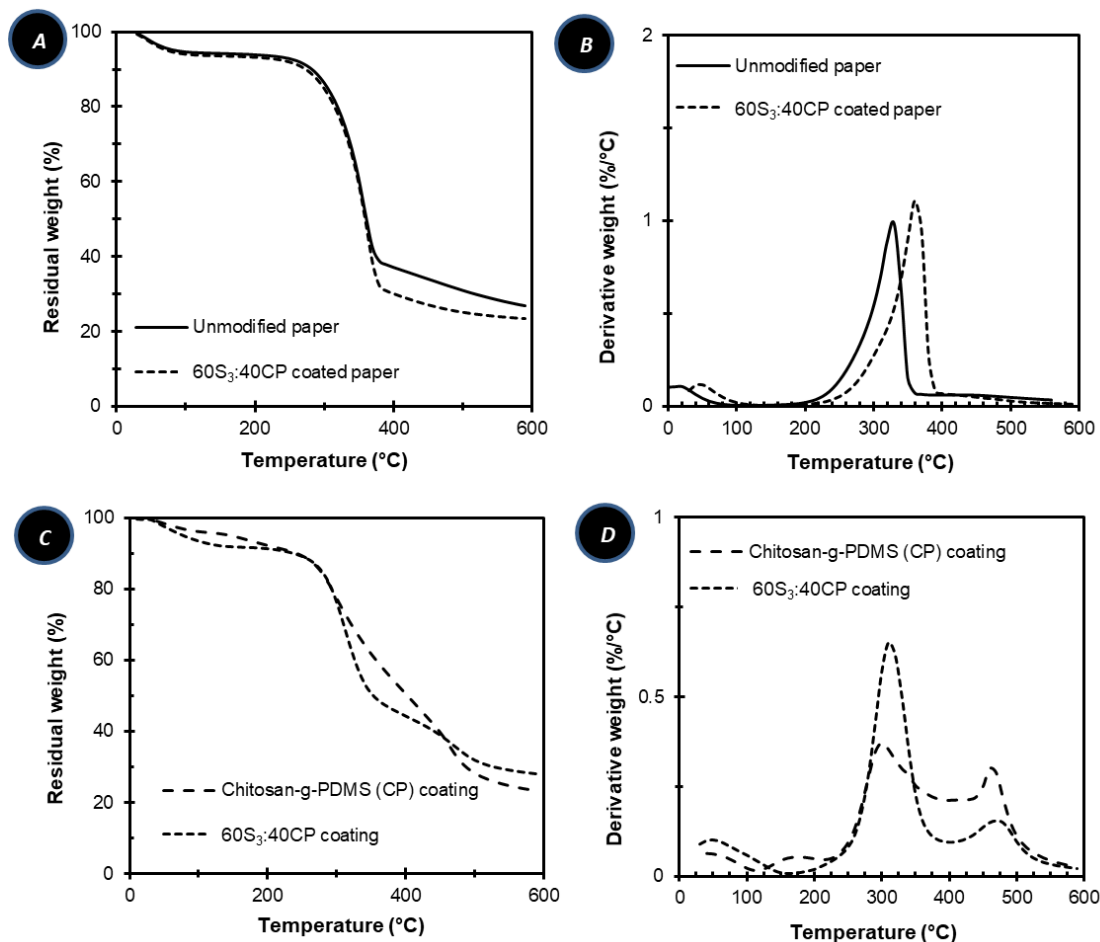


Figure 5.6 A)- Residual weights and **B)-** Derivative TGA analysis of unmodified paper and 3 wt% Starch in 60S:10CP S/CP coated paper **C)-** Residual weights and **D)-** Derivative TGA analysis of coating films (Chitosan-*g*-PDMS film containing 200mg of PDMS-NCO in 100mg chitosan and 3 wt% Starch in 60S:10CP volume ratio of S/CP coating)

5.7 Material thickness, basis weight and coating load

Basis weight technique was used to determine the coating loads via **Equation 1**. The selected samples were subjected to basis weight and thickness analysis as shown in **Table 3**, and subsequently the average coating loads on different coated papers were calculated. The material thickness of unmodified paper was found to be $174.00 \pm 1.73 \mu\text{m}$. Meanwhile, the material

thickness was observed to be $203.67 \pm 0.58 \mu\text{m}$ for S₃-coated paper, which increased to $205.33 \pm 0.58 \mu\text{m}$ for S₅-coated paper. A similar phenomenon was observed for S/C-coated as well as S/CP-coated paper samples, as shown in **Table 3**. Further investigation showed that the thickness, basis weight, and coating load were all observed to increase slightly with an increase in the starch concentration. The thickness of the coatings was observed to reduce with the addition of chitosan in S/C-coated papers and reduced even further with the addition of CP for S/CP-coated papers, possibly due to the excellent miscibility of the blends, which led to a decrease in volume.²² However, the basis weights and coating loads for all of the coatings were observed to be similar as shown in **Table 3**. The optimum 60S₃:40CP- and 60S₅:40CP-coated papers had coating loads of 6.41 ± 1.55 and $8.22 \pm 1.08 \text{ g/m}^2$ respectively. Hence, the coated papers were found to have a uniform thickness and coating load while the S/CP-coated papers exhibited excellent performance despite having lesser overall thickness as compared to the controls.

Table 5.2. Material thickness, basis weight, and coating load of uncoated and coated paper samples.

Type of coated paper	Code	Material thickness (μm)	Basis weight (g/m^2)	Coating load (g/m^2)
Unmodified	UM	174.00 ± 1.73	124.98 ± 0.24	-
Starch (3.0 wt%)	S ₃	203.67 ± 0.58	131.39 ± 3.72	6.41 ± 1.55
Starch (5.0 wt%)	S ₅	205.33 ± 0.58	133.66 ± 0.70	8.68 ± 0.86
3.0 wt% starch/chitosan	S ₃ /C	192.67 ± 1.15	130.36 ± 1.27	5.37 ± 1.05
5.0 wt% starch/chitosan	S ₅ /C	196.00 ± 1.00	133.09 ± 0.76	8.11 ± 0.99
3.0 wt% S/CP	60S ₃ :40CP	190.33 ± 1.53	131.39 ± 2.32	6.41 ± 1.22
5.0 wt% S/CP	60S ₅ :40CP	194.33 ± 0.58	133.20 ± 1.12	8.22 ± 1.08

5.8 Scanning Electron Microscopy

We also analyzed the surfaces of the coated paper and their controls via SEM analysis. **Figure 5.7A** shows that the surface of unmodified paper consists of interlaced cellulose fibers which makes the paper surface porous and thus hydrophilic as well as oleophilic in nature. It is evident that these pores are partially covered with the application of starch onto the paper, as seen in **Figure 5.7B and 5.7C** for the S₃- and S₅-coated paper samples. This also explains the improvement observed in the Cobb60 values and kit ratings of the starch-coated paper in comparison with unmodified paper. However, despite the pores being partially covered, starch-coated papers showed poor hydrophobicity due to the hydrophilic nature that was imparted by the polar hydroxyl groups of starch. Paper coated with 60S₃:40 CP and 60S₅:40CP shown in **Figure**

5.7D and 5.7E, respectively, possessed smoother surfaces that masked the porous structure of the paper even better. This can be attributed to the strong hydrogen bonding between chitosan, starch, and cellulose thus forming a smooth film layer. In addition to the well-masked pores, presence of PDMS in the coating system helped to impart the paper with a high degree of water- and grease-resistance.

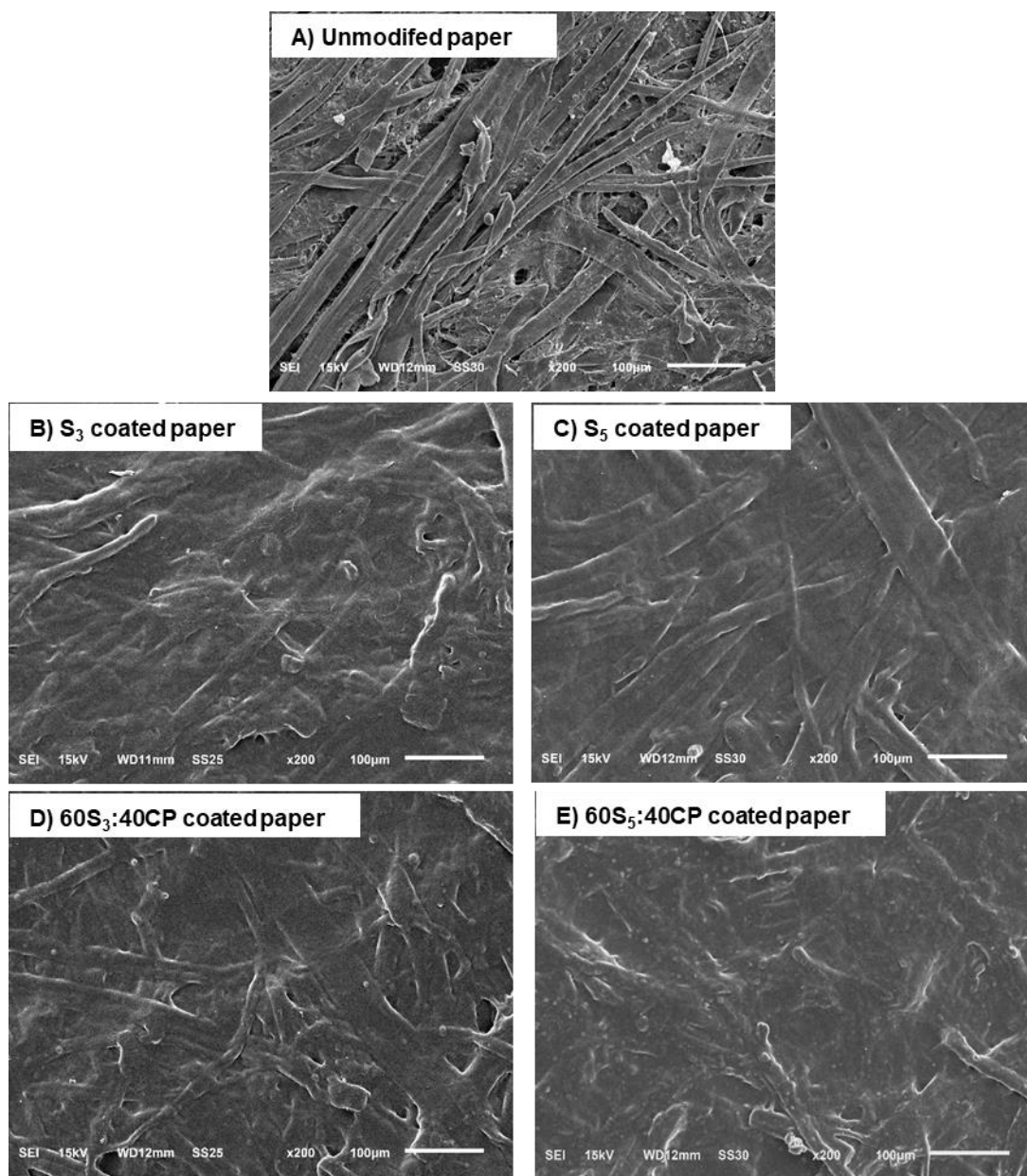


Figure 5.7 SEM analysis of: **A)** Unmodified paper, **B)** S_3 -coated paper (3.0 wt% starch), **C)** S_5 -coated paper (5.0 wt% starch), **D)** $60S_3:40CP$ -coated paper (3.0 wt% starch/CP-coated paper with a volume ratio of 60S:40CP), and **E)** $60S_5:40CP$ -coated paper (5.0 wt% starch/CP coated paper in volume ratio of 60S:40CP). All images were recorded at 200x magnification.

5.9 Mechanical properties

5.9.1 Tensile strength of coated and uncoated paper

Mechanical properties are of great importance for real-world applications; therefore, the mechanical properties of the coated paper and their controls were evaluated.¹⁸ For this purpose, coated paper (60S₃:40CP and 60S₅:40CP) and unmodified paper samples were tested for the tensile strength, ring crush, tearing force and bending resistance in both the machine direction (MD) and cross direction (CD) (**Figure 5.8A-5.8D**). The tensile strength of the UM paper was observed to be 53.41 ± 2.29 lbs/in in the MD and 16.94 ± 3.40 lbs/in in the CD. These values did not change significantly for 60S₃:40CP-coated paper in either the MD and CD. The tensile strength of the 60S₅:40CP-coated paper was observed to increase slightly in comparison to its counterparts in the MD to 55.71 ± 1.50 lbs/in while it remained similar to the other samples in the CD. These results indicate that the tensile strengths of the unmodified and coated papers essentially remained the same.

5.9.2 Ring crush test

The ring crush test determines the compression strength of a paper sample when it stands on its edge and is a useful tool in estimating the edge crush strength of a corrugated box that would be made from this paper. The ring crush test for the unmodified papers was observed to be 34.63 ± 3.34 lbs/in in MD and 28.37 ± 2.00 lbs/in in the CD. The values did not change significantly for 60S₃:40CP-coated papers. Similarly, for 60S₅:40CP coated papers, the crush strength was observed to slightly decrease to 29.13 ± 2.45 lbs/in in the MD and 24.47 ± 0.74 lbs/in in the CD as compared to unmodified paper but were again not significantly different. A similar trend was observed in both the MD and CD.

5.9.3 Tearing and bending resistance

The tearing resistance corresponds to the force required to rupture paper fibers in a perpendicular direction. The tearing force required to rupture 60S₅:40CP-coated paper in the MD decreased by approximately 9% as compared to UM paper whereas it was observed to increase by 9% for both 60S₃:40CP- and 60S₅:40CP-coated paper in the CD. The tearing resistance was observed to exhibit an opposite trend in the MD from that observed in the CD (**Figure 6C**). Bending stiffness is another important physical property that determines the flexural strength of paper. As observed in **Figure 5.8D**, the bending resistance was observed to improve from 96.69 ± 3.57 Nm for UM paper to 122.58 ± 2.91 Nm for 60S₅:40CP-coated paper in the MD and decrease from 85.51 ± 2.77 Nm for UM paper to 64.14 ± 3.73 Nm for 60S₅:40CP-coated paper in the CD, thus again showing an opposite trend in both directions. Overall, the S/CP coatings did not significantly change the mechanical properties of coated papers relative to the unmodified paper, despite offering improved water and oil resistance.

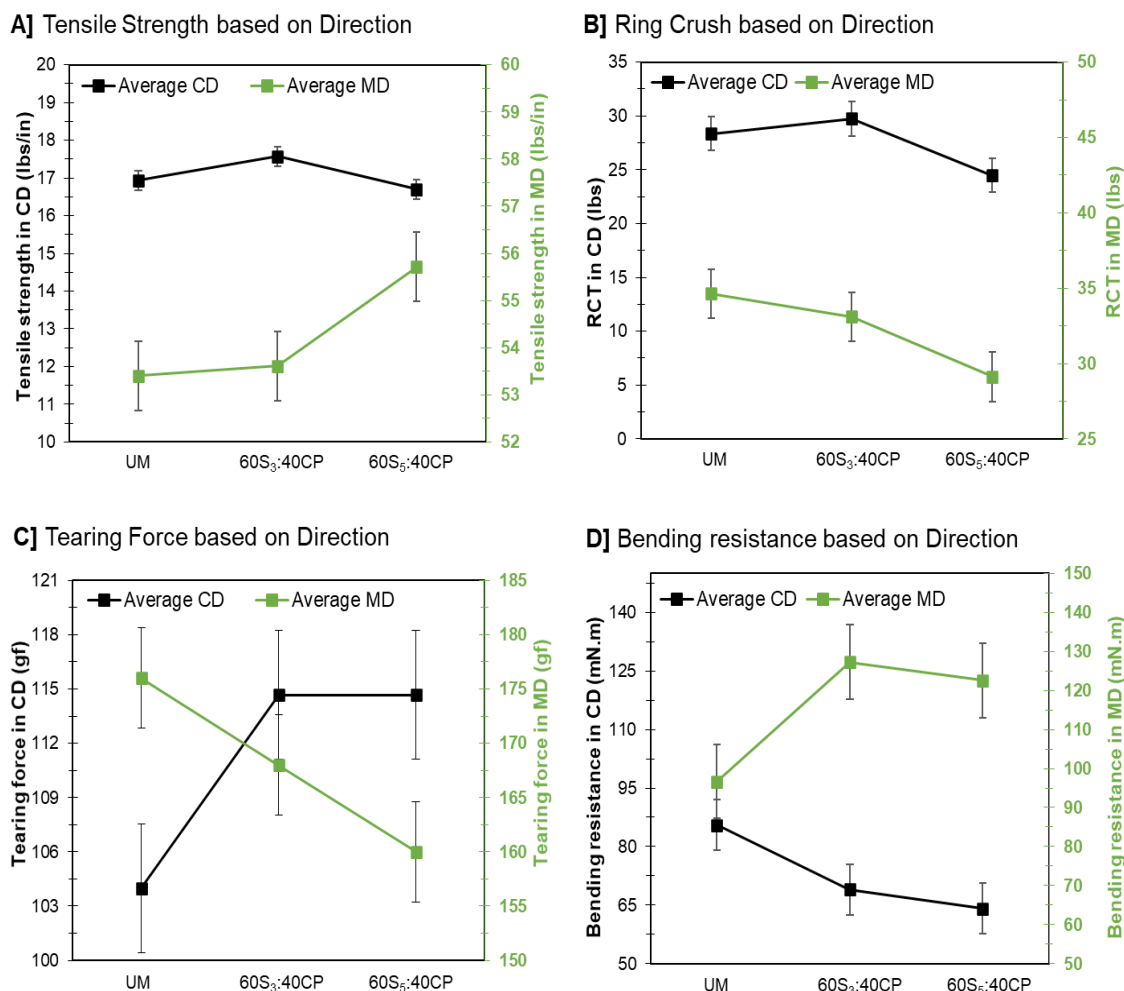


Figure 5.8 A) Tensile strength, B) ring crush test, C) tearing force, and D) bending resistance of UM paper (unmodified), and S/CP (starch/chitosan-*graft*-PDMS)-coated paper samples (with 60S₃:40CP and 60S₅:40 CP formulations)

5.10 Repulpability

Finally, it was important to assess the ease at which the coating could be washed off the paper surface in order to make the approach recyclable. As shown in **Figure 5.9**, the 60S₃:40CP-coated paper was blended into a pulp. The obtained blend was subsequently washed with deionized water and 1 vol% acetic acid to facilitate the removal of CP from the pulp. The recycled paper

made from this pulp was then analyzed via ATR-FTIR (**Figure 5.10**), and the resultant spectrum did not display any characteristic peaks corresponding to PDMS, thus confirming the removal of the coating, and demonstrating that the coated paper was indeed recyclable.^{4,5}

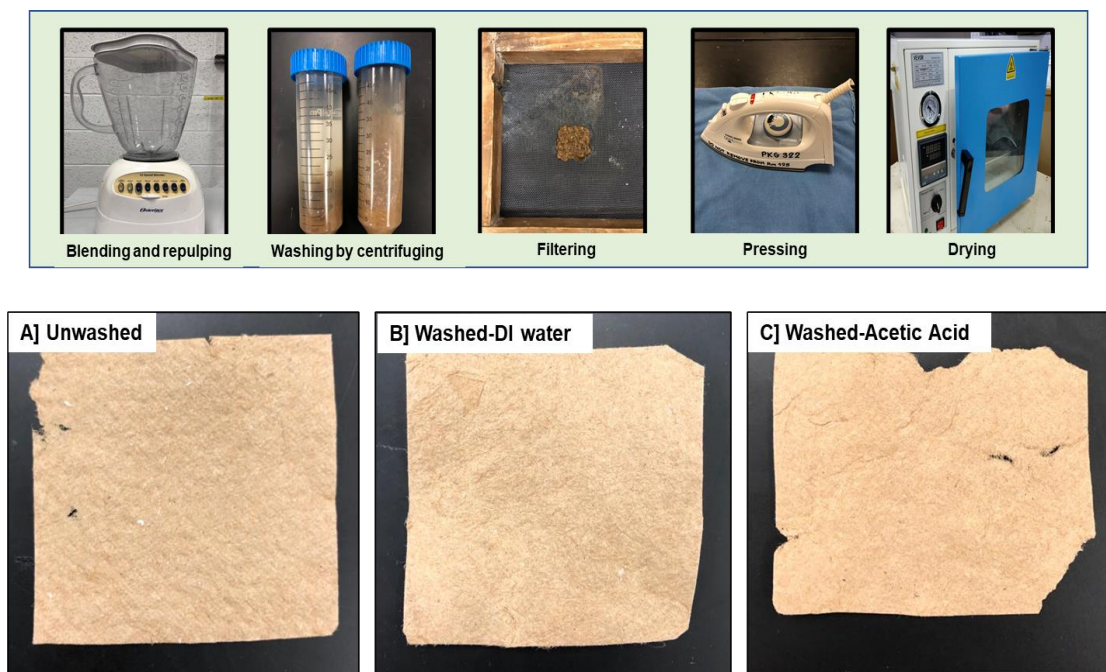


Figure 5.9 Illustration of the repulping process and the paper made from the recycled pulp: **Top)** Illustration of the steps involved in the repulping process; **Bottom)** Paper made from recycled pulp. Photographs of various paper samples obtained from recycled pulp: **A)** unwashed, **B)** washed with deionized water, and **C)** washed with 1.0 vol% acetic acid.

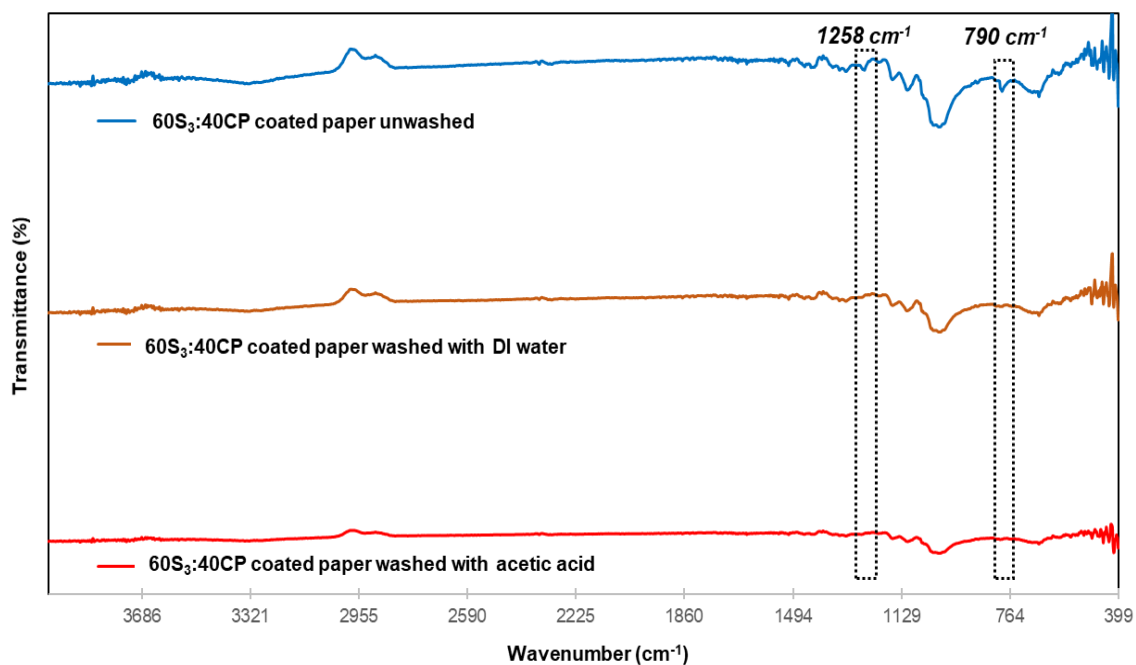


Figure 5.10. ATR-FTIR spectra of the unwashed recycled papers, recycled paper washed with deionized water and 1 vol% acetic acid.

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Chapter 6

CONCLUSION

A version of this section is under review in *Advanced Sustainable Systems* and *The Journal of Applied Polymer Science* by Wiley.

6.1 PVOH as a filler

An economical approach to improve the water and grease resistance of unbleached kraft paper was developed where low-cost PVOH was blended with expensive chitosan-g-PDMS. Good water and oil resistance were obtained even at very high loadings of low-cost PVOH. The paper coated with PVOH/ chitosan-g-PDMS blends has masked the pores and was smoother, as confirmed with SEM analysis. The minimum water absorptivity obtained was 20 ± 2.1 g/m² for 2.0% PVOH concentration, with only 20% of Chitosan-g-PDMS in the overall system, which showed an improvement of almost 70% as compared to the unmodified paper. The highest water and oil contact angles of $119 \pm 6.3^\circ$ and $77 \pm 2.6^\circ$, respectively, and kit rating of 7.6/12, suggested significant improvement in hydrophobicity and oil repellency of the paper. This makes the coating applicable for use in low-cost packaging applications and makes it more commercially viable as PVOH has ~10-fold cheaper than chitosan and PDMS.

6.2 Starch as a filler

The PVOH system was improved by successfully replacing it with starch to achieve coated paper with blends of starch and chitosan-g-PDMS. The coated papers showed superior performance as compared to the PVOH system and an ~82% decrease in water absorptivity, and a kit value of 12/12. This significant improvement in water- and grease-resistant properties was

attributable to the S/CP coating's ability to mask the pores of unmodified paper and thus significantly smoothen the surface of coated papers, as was confirmed via SEM analysis. Surfaces were observed to be much smoother as compared to the P/CP coated papers. The coated papers also possessed a high WCA of $106.0 \pm 1.20^\circ$ and showed a good improvement in water vapor barrier properties as compared to the unmodified paper. The application of this coating did not show any significant effect on the mechanical properties of the paper, thus making it suitable for practical applications. Finally, repulping tests confirmed that the coating could be successfully removed from the paper, thus ensuring that the coated papers were completely recyclable. This novel approach leading to inexpensive, water- and grease-resistant, environmentally friendly coatings is a promising candidate for commercial use in a myriad of applications in the packaging sector and other industries.

The hypothesis was thus proved by successfully maintaining the properties of chitosan-*g*-PDMS coating by adding fillers into the system, thus bringing down the cost of the overall coating system. This study could bring a possible breakthrough by replacing the existing water and oil repellant coatings like PFAS, wax, and synthetic thermo-plastic coatings used in the food containers, cups, and other packaging applications. This novel development could also bring about a shift in the post-consumer recycling process owing to the easily washable coatings and repulpability, thus reducing the ecological risks associated with the existing paper coatings.

6.3 Future work

While this study proved the improvement in water and oil resistance of the coated papers, there are some results that require more in-depth characterization studies; for example- the spheres that are evident in the SEM images of the P/CP coated system (**Fig. 4.8**) must be characterized further to understand the composition of these particles and how it is affecting the system and the

performance of the coating. This can be achieved by employing test methods like E-SEM. On the other hand, the practicality of the coating must also be validated by using the coating with real-life targeted applications. In order to do that, the feasibility of the coating by application techniques like spray coating must be evaluated to support large-scale processing and application of these coatings. Moreover, the migration of the coating can be studied to target food applications. Finally, the performance of the coating as compared to the current market practices must be compared.