Bio Based Coatings for Packaging Paper Applications - A Brief Technology Review

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ABSTRACT

Hemp has been a longstanding material choice for textile creations. As far back as early Chinese civilizations humans have been using hemp for items including paper, clothing, rope, and various other household items. As trading moved westward, more civilizations began to pick up on cultivating hemp for textile uses. This was easily done due to the simplistic growing conditions necessary for hemp. Items made from processed hemp have since been found and collected from all over the globe and are now preserved in history and art museums. These items began getting recognition by art communities in more recent years. After World War II fiber art became a recognized art medium instead of its previous classification of utilitarian craftwork. Since then, fiber art has flourished, and it is celebrated in art museums and similar works worldwide. Now, old and new items and textiles utilizing hemp are preserved through art museums and collections.

Keywords: Alga, Bacteria, Bees wax, Cellulose, Coating, Chitosan, Diamond like carbon coatings, Nano-fibrillated cellulose, Packaging paper, Paper, Paperboard, Protein, Polylactic acid, Starch

1. INTRODUCTION

The paper industry has been around for hundreds of years as and drive to continuously improve their manufacturing processes, products and the materials used to produce paper.

It all started with Cai Lun who invented the paper in ancient China in 105 BC during the Eastern Han Dynasty. From that point on humans could communicate in written form allowing inextricably the development of culture society and science [1-5], and allowed humans to communicate in written form, preserve knowledge for long periods of time. Paper is light wight, durable and replaced animal Skin based parchment and papyrus, a paper product produced by weaving leaves into a cross pattern, due to its easier manufacturing process, which allowed large quantities to be produced [1]. However, the process how paper is made was kept a secret for over 500 years and made its way over Japan and then through the silk road to the Middle East, Mediterranean till it entered European continent over a millennium later [2,6]. It took almost another 500 years to spread to Mexico and the US and Canada [6].

In 1446 the invention of the printing press by Gutenberg (*1400-†1468) led to a higher demand for paper, replacing the transcription of documents. This led to a much larger demand of paper and resulted in the invention of continuous machine-made paper in 1799 by Nicolas Louis Robert, a mechanic at the Didot paper mill in the French town of Esous. In 1808 the invention of the fourdrinier paper machine by the brothers Henry and Sealy Fourdrinier improved the process significantly.

During this time paper was made from materials such as rags, straw, hemp, and jute. These materials could not be supplied in large enough quantities to produce paper any more using the new machine-based manufacturing process, requiring the search for a new suitable material for paper production. In 1840 wood was introduced into papermaking with the invention of the wood grinding process [1,2], followed by the introduction of chemical pulp in 1890 [2].

Today paper is produced on large machines individually designed for the paper product it produces and can be considered marvels of technology. Large machines can have a length over 600, and a production width of approximately 12.0 m, capable of running at a speed of over 2000 m/min producing over 4,500 metric tons of paper product daily [5,7-9].

According to Statista, the 2022 global production of paper and paperboard was approximately 414.09 million metric tons [10], with a global consumption of paper and paperboard totaling 415 million tons. Paper and Paperboard consumption is projected to continue rising over the coming decade to reach approximately 476 million tons by 2032 [11].

It is known that various fabrics and cloth is one of the oldest packaging materials beside ceramic containers prior to the invention of paper. First, paper was used as writing material, because it was to valuable to be used packaging material. Once it was produced on larger scale on machines during the 1800's paper was used to protect and preserve goods, as well las ship items. For example, in the US colonial time cotton-based materials was used to bag flour and sugar in the 1850s. These materials became scare during the civil war, because cotton was needed to produce uniform an sails, with the result that paper sheets and glued paper bags replaced cotton as packaging material [12-14].

For example, Albert L. Jones was granted the first U.S. Patent No. 122,023 for corrugated paper as packaging material in 1871 [15], which then started to replace wooden boxes [12]. Paper based packaging with its introduction in the late 1800's has come a long way and can be found in almost every item that is shipped and or packaged in the food, beverage, pharmaceutical, and industry sector today.

At present time the packaging and retail industry faces increasing production by raising energy costs, stringent environmental laws, globalization and high competitiveness and pressure on profit margins [1-3,16-18]**.** The use of plastic- based packaging materials due to rising environmental concerns such as microplastic pollution. In addition, consumers require more sustainable packaging solutions, and the industry is required to shift to more sustainable and plastic free packaging solutions [3], because of the paper-based packaging materials recyclability and feasibility of replacing plastic packaging material [20,21]. Therefore, in the packaging industry paper has been rediscovered as a valuable replacement for plastic based packaging material due to its favorable environmental footprint.

Therefore, the demand for pulp and paper product is still growing, especially in the packaging industry due to its more favorable environmental footprint paper has been rediscovered as a valuable packaging material, and our society is far away from becoming paperless [19,20].

However, for food packaging a major requirement for the preservation and shelf life of the packed food product is that the packaging material serves as a moisture barrier [22]. This is achieved with a coating applied to the paper base material, adding for instance an extra layer of protection and strength to a paper base material, and or at the same time increase its functionality either as a moisture barrier or increase the wear life of the piece of paper. These coatings are mostly fossil fuel based and the industry is looking out for more bio-based coating solutions that can serve as a moisture barrier.

The following review paper gives an over few of current and future coatings that are or can be applied to paper products and can serve as an basis of the current state of the art in the packaging industry sector.

2. ALGAE COATINGS

Algae is often overlooked yet abundant in aquatic ecosystems, can offer a rich source of lipids for a variety of applications in the agricultural, industrial, food and pharmaceutical field. Among these diverse organisms, microalgae stand out for their ability to accumulate lipids, particularly triacylglycerols (TAGs), making them promising candidates for biofuel production and nutritional supplements [23,24]. Harnessing the photosynthetic prowess of algae, researchers explore avenues to enhance lipid productivity and optimize cultivation strategies for sustainable resource utilization such as application in biofuels. While microalgae have garnered attention for their lipid content and biofuel applications, macroalgae, or seaweeds, represent another valuable resource with diverse industrial applications. Rich in polysaccharides, proteins, and minerals, seaweed serves as sustainable sources of food, feed, and biochemicals. Additionally, their cultivation contributes to carbon sequestration and ecosystem restoration, aligning with efforts to mitigate climate change and promote marine biodiversity. Furthermore, algae biotechnology extends beyond lipid extraction, encompassing bioremediation, wastewater treatment, and carbon capture. Engineered algae strains capable of producing high-value compounds, such as pharmaceuticals and bioplastics, hold promise for a bio-based economy with a reduced environmental footprint. Today’s collaborative research initiatives, involving academia, industry, and policymakers, drive innovation in algae biotechnology, addressing global challenges related to food security, renewable energy, and environmental sustainability [23,24,25,26].

The marriage of lipids with nano silicate composites represents a convergence of biological and materials science, yielding materials with tailored properties and diverse applications. By incorporating lipids into nanostructured silicate frameworks such as silicate glasses [27]. Researchers work on modulating mechanical, thermal, and barrier properties, paving the way for advancements in packaging materials, drug delivery systems, nanostructures, and biomedical devices [28,29,30,31]. The self-assembly capabilities of lipids further contribute to the versatility and functionality of these composites, offering customizable solutions to meet specific industry needs [32]. The application spectrum of lipid-based nano silicate composites may span a myriad of industries, each benefiting from the unique properties imparted by these innovative materials. In food packaging, these composites offer enhanced barrier properties, prolonging shelf life and preserving freshness [33]. In biomedicine, lipid-based composites facilitate controlled drug delivery, ensuring targeted release and improved therapeutic efficacy. Moreover, their biocompatibility and sustainability render them ideal candidates for various biomedical applications, ranging from tissue engineering scaffolds to diagnostic imaging agents [34,35,36,37,38].

3. ALGINATES

Alginate is a polysaccharide that originates from algae. Alginate-based microencapsulation particles were first discovered in 1980 and have since been extensively researched in order to develop nanomaterials and other functional materials [39,40]. Alginate is a component of the cell walls of specifically brown algae. There are various methods that are used to extract alginate from the algae, and there are different methods used to purify the product depending on its use. Alginate itself has many functional benefits due to its hydrogel forming property and chemical structure. It is also biodegradable and soluble in water which allows alginate to have a vast potential for use in industrial and biomedical industries. However, its hydro gelling capabilities, to create a biphasic material mixture containing porous and permeable solids, are its most attractive feature for industries. The hydro gelling ability of alginates has expanded its uses and research perspectives in biomedicine and multiple disciplines, including the food industry, wastewater treatment, and as an adsorptive material for heavy metal removal from contaminated water” [39]. The greatest potential for commercial use of alginates lies within the food and biomedical industries. However, there has been very minimal research done regarding the use of alginates in the paper industry. Alginates may be used in the coatings of paper-based food packaging products. A study by Kopacic et. al.[41], used alginate as coating on two different types of paper board produced from primary and secondary cellulosic fibers using a draw-down coater. The applied coating showed no air permeability of the alginate coating [41]. The use of alginates in the coating solution had positive impacts such as improved grease resistance, decreased water absorptivity as well. Although there has not been much research into the use of alginates in the paper industry there are still uses for them in the industry. In the future alginates may find usage as retention aid, as strength enhancer, and as a coating additive. However, further studies need to be conducted to show the effectiveness and economic benefit of using alginates in the paper industry.

4. BACTERIAL CELLULOSE

Bacterial cellulose is cellulose that is produced by natural bacteria and was first discovered in 1988 by Brown [42]. On the whole cellulose is one of the most plentiful and easily accessible carbohydrate polymers. The most common source of cellulose is extracting it from plants and trees in the environment. This process involves deforestation. However, bacterial cellulose can be an alternative method to obtaining cellulose for paper making: “Although plant is the major contributor of cellulose, various bacteria are able to produce cellulose as an alternative source [42]. With the ongoing push towards sustainability in the world, bacterial cellulose can be a contributor towards the paper industry in aiding it in being more environmentally conscious. Bacterial cellulose is manufactured in two ways. The first is through static fermentation. Static fermentation occurs under regulated air conditions from a medium surface and the yield is determined by a carbon source concentration. Also, the yield can be varied depending on fermentation time [42]. This form of fermentation takes an abundance of time and has a relatively low yield. On the contrary, agitated fermentation is used commercially: “due to low yield of the static production, most of cellulose used in commercial purpose is generated through agitated fermentation” [42]. The only downside to agitated fermentation is that cellulose has lower crystallinity, mechanical strength, and degree of polymerization. Bacterial cellulose is currently mainly used in the biomedical and food industries. The paper industry is another area in which bacterial cellulose may be applied too. The Pulp and Paper industry is one of the sectors where sustainable and environmentally friendly approach becomes the prime need. Potential application of bacterial cellulose in the paper industry may include strengthening of paper, increase water holding capacity of paper, formation of electronic papers and in making of flame-resistant paper” [43,44]. There are many positives to take away from the use of bacterial cellulose in the paper industry. The physical properties are improved with the use of bacterial cellulose, and the fact that bacterial cellulose is an alternative form of cellulose rather than plant cellulose. However, production on large laboratory and pilot scale first needs to be undertaken to evaluate its application potential and economic benefit.

5. BEES WAX COATINGS

Packaging paper included corrugated board can be coated with a wax layer to make it more durable and moisture resistant. The thin wax coating prevents the paper from disintegrating when it comes into contact with water and or grease which is prevented soaking through the product by the waxy layer. This is for example one of the reasons why customers can enjoy a greasy burger without it soaking through the paper or unwrap a chewing gum without it sticking to its wrapper. The wax coating is applied by immersing the paper product into wax bath and or by rolling (coating) wax onto the paper. Wax is used to laminate (bind) two bond two substrates together, such as foil to paper or paper to paper [45].

Paper can also be printed with a different pattern of wax, which does not fully cover the paper itself. The pattern, for instance a honeycomb pattern, can also be applied by using a patterned coating roll. After the wax is applied to the paper it is cooled by running it over one or more cooling drums so it can be rewound onto a ream [45].

Various wax layers are applied to the paper product depending on the paper products use. For instance, butcher paper contains a heavier coating of wax than candy wrappers.

The amount of wax added to the paper depends on what the paper will be used for. For example, butcher paper has a thicker wax coating on it compared to a candy wrapper [45].

The wax product applied today are low-mid melting point waxes. Mid-meld waxes are usually used for cooking or baking paper. Deli papers, interleaf sheets and patty papers usually use a low melt coating wax. For low melt coat waxes, paraffin wax is used for grease and moisture resistance. Sandwich and butcher paper wraps might be coated in a modified wax blend to give it heat, moisture and grease resistance with slip properties. In addition, additives like EVA polymers, polyethylene and other surface modification materials are applied together with the wax product [45].

The use of bees wax and algae (Lipids) within the applications of bio-coting substances has become of interest in the recent past.

Lipids, the essential molecules that underpin biological systems, exhibit remarkable diversity and functionality. From the intricate architecture of beeswax to the abundant energy stores in algae, lipids play pivotal roles across various domains of life. Moreover, the fusion of lipids with nano silicate composites opens avenues for novel material design with applications spanning from food packaging to biomedicine. This essay delves into the multifaceted realm of lipids, examining the characteristics of beeswax and algae while exploring their integration into nano-silicate composites [46].

Beeswax, a natural secretion of honeybees, serves as a testament to the ingenuity of nature's engineering also called biomimicry or bioengineering. Comprised primarily of esters of fatty acids and long-chain alcohols, beeswax possesses unique properties crucial for hive construction and protection. Its hydrophobic nature ensures the integrity of honeycomb structures, shielding them from environmental moisture and pathogens, while providing a secure environment for honey storage and larval development. Beyond its role in hive construction, beeswax possesses fascinating properties that have intrigued researchers and artisans alike for centuries. Its intricate molecular structure and ability to form stable crystalline lattice arrangements contribute to its exceptional stability and durability. Beeswax has been utilized in various cultural practices, from ancient Egyptian embalming to medieval manuscript illumination, highlighting its historical significance and versatility [47].

Furthermore, modern scientific investigations have unveiled the therapeutic potential of beeswax in skincare products and pharmaceutical formulations. Its hypoallergenic and emollient properties make it an ideal ingredient in creams, balms, and ointments, offering natural alternatives to synthetic additives. Moreover, ongoing research explores the antimicrobial properties of beeswax and its derivatives and how it benefits the packaging paper product, paving the way for the development of novel antimicrobial agents and wound dressings [48,49].

6. CELLULOSE COATINGS

Cellulose is a widely available natural polymer produced by plants and some bacteria. The abundance of cellulose as well as its physical and chemical properties have brought the polymer to the spotlight as a sustainable and biodegradable material. The structure of cellulose is of particular interest because by bundling cellulose chains together, highly ordered regions are generated, which can then be isolated and used in many different applications [50]. These isolated nanoparticles are called nanocellulose and they have unique properties that make them versatile materials. There are several different forms of nanocellulose that differ based on the method of production and the cellulose source, each with its own unique properties and applications. For example, Cellulose nanocrystals (CNCs) are made from cellulose using a process called acid hydrolysis [51]. Acid hydrolysis removes the para-crystalline regions of the cellulose, leaving the cellulose crystals. The process of degrading cellulose fibers using sulfuric acid was reported for the first time by Ränby in the 1950s and later optimized, leading to interest in the biopolymer as a renewable reinforcing agent [51]. Due to their chemical and physical properties, CNCs have been applied in many industries such as biomedical engineering, material sciences, and electronics [52]. In these fields, CNCs have been utilized as carriers for controlled drug delivery and in nanopaper, barrier films, and pH sensors. In the food industry cellulose nanocrystals have been studied for use as food additives and as film for food packaging [53]. As a food additive, CNCs can act as a stabilizer without affecting the food quality and as a film, the nanocrystals can improve the barrier properties of food packaging. Cellulose nanocrystals can be produced from many different sources including lignocellulosic fibers from woody and non-woody plants, as well as bacteria and certain types of algae [50]. The dimensions of the nanocrystals can range depending on the source of the cellulose, with some nanocrystals derived from tunicates being as long as 3000 nm and 30 nm wide to some nanocrystals derived from ramie that were measured to be 50 nm long and 10 nm wide [51]. Recent studies have found many methods to modify the surface of CNCs including grafting molecules to the nanocrystals and the esterification of the nanocrystals using lactic acid [54]. These modifications give the nanocrystals more functionality and expand the possible applications of the biopolymer. However, there are several issues with the surface modification methods that must be resolved to minimize the drawbacks. For example, the studies on chemical surface modifications of cellulose nanocrystals are based on several different sources of CNCs with no standard for surface charge or size distribution, meaning that it would be difficult to create a standard procedure for these modifications. Additionally, chemical modification of CNCs must be performed in a non-aqueous medium, but CNCs are often in an aqueous solution, so they need to be dried or subjected to a solvent replacement process and the current methods for drying or solvent replacement each have their own drawbacks and limitations.

Similar to CNCs, nano fibrillated cellulose (NFC) is derived from cellulose fibers. However, cellulose nanocrystals are produced by removing the non-crystalline regions, NFC is produced by applying a mechanical shearing force to break down the cell wall and release fibrils. Several pre-treatment methods such as TEMPO-mediated oxidation and enzymatic treatment have been studied to reduce the processing energy required for the defibrillation of the cellulose fibers [55,56]. These treatments have varying effects on the properties of the NFC produced and each has its own drawbacks. TEMPO-mediated oxidation can produce NFC with high colloidal stability and uniform diameters of less than 4 nm. The downside of TEMPO-mediated oxidation is that the TEMPO catalyst is toxic. Enzymatic pre-treatment produces NFC with non-uniform size distribution and can result in agglomeration, which reduces the strength and optical transmittance of the produced NFC paper film. NFC with high hemicellulose content was found to have a high mechanical strength compared to NFCs produced from other pre-treatment methods (Yang et al. 2019). NFC has high mechanical strength compared to other nanocelluloses, which makes it a useful additive for cement-based composites and paper [57]. Further applications for NFC have been found in making the biopolymer into a plastic-like film, allowing it to be used in food packaging and OLED displays, and in using nano fibrillated cellulose to make an aerogel for use as a heat insulator [58,59]. Another application of NFC could be in filtering heavy metals from wastewater. A study found that an aerogel made from brushite, and a modified NFC can selectively remove copper (II) from wastewater [60]. This aerogel could be used to filter out copper (II) from wastewater used in the agriculture industries and for drinking water as chronic ingestion of copper (II) can cause diabetes, tremors, and pneumonia. Using chitosan and NFC aerogel resulted in selectivity for removal of chromium (III) and chromium (VI) from wastewater [61]. Both of these aerogels are reusable after being regenerated, providing a high absorption rate and a long lifetime. Bacterial cellulose (BC) is another cellulose-based biopolymer produced by certain bacteria. The reason why these bacteria produce BC is not entirely known, but several theories have been posited ranging from the polymer being used to protect the bacterium from UV rays to promoting cell adhesion [62]. Unlike other plant-derived cellulose composites, BC is not contaminated by lignin or hemicelluloses [63]. BC has found applications in many products including tires, headphone membranes, high performance speaker diaphragms, and many wound dressing materials [64].

While BC has many possible applications in the biomedical industry, occurrences of bacterial adhesion, growth, and infection pose challenges to its use [65]. Another challenge to the use of BC is its low yield, however, genetic modification shows promise as a means to increase the efficiency of BC production [66]. The yield and properties of the BC can also be influenced by the cultivation method. Producing BC using the static culture method takes a long time and has a low yield, but has better properties compared to other methods [67]. The agitated culture method produces BC with unique properties that allow it to be used for bio-separation or as an absorbent. BC can also be produced through fermentation in bioreactors such as airlift bioreactors, biofilm bioreactors, rotating disk bioreactors, or trickling bed reactors. Using a bioreactor greatly increases the yield of BC with a lower production time than other culture methods. Several other methods to optimize the yield of BC production have been researched such as using ethanol to improve the production of adenosine triphosphate (ATP) and suppress mutation into non-cellulose producing mutants. The presence of certain vitamins like vitamin C and ascorbic acid was also found to affect the yield and crystallinity of the BC produced. *G. xylinus* has been used to produce BC at an industrial scale, however, the optimum temperature for fermentation is around 30°C, meaning that outside of tropical regions heat energy must be supplied during cold seasons [68]. The high temperature also induces microbial contamination, which can lead to food safety hazards and other issues. The high-water holding capacity of the BC makes it expensive to transport and store, so it must be dehydrated. Furthermore, BC has been researched as a coating to be used for lubricated surfaces [69]. The coating has a unique architecture that has high mechanical stability and energy dissipation capabilities under compression and shear as well as enhanced lubrication properties.

7. CHITOSAN

Chitosan is a polysaccharide that is used in various industries due to its array of beneficial properties. Chitosan is derived from chitin: “Chitin and its deacetylated derivative, chitosan, are a family of linear polysaccharides composed of varying amounts of (β1→4) linked residues of *N*-acetyl-2 amino-2-deoxy-D-glucose (glucosamine, GlcN) and 2-amino-2-deoxy-D-glucose (*N*-acetyl-glucosamine, GlcNAc) residues” [70,71 Deacetylation is required in order to produce chitosan which adds an extra step to the manufacturing process, and results in increased production costs. Chitin is insoluble in acidic environments, but its derivative, chitosan, is soluble in acidic environments which is a vast benefit. Chitin is a natural biopolymer that has various origins in which it can be sourced: “Chitin is a very abundant biopolymer that can be found in the exoskeleton of crustacea, insect’s cuticles, algae and in the cell wall of fungi. Chitosan is less frequent in nature occurring in some fungi (*Mucoraceae*)” [70]. Although there are many sources of chitin available, chitosan are most commonly produced through deacetylation of crustacean origins. However, sourcing chitin for chitosan production from the cell walls of fungi is becoming more common due to vegan demands. Moreover, the market for chitosan is quite impressive, and with the dawning interest in chitosan the market for it, is set to increase a large amount. The market for chitosan is predicted to increase by about 25%: “In 2019, the global chitosan market size was valued at USD 6.8 billion, and it is expected to expand at a revenue based CAGR of 24.7% between 2020 and 2027” [70]. The increase in market size is mainly the result of the properties of chitosan and its benefits to wastewater treatment, pharmaceutical, and food industries. Some of the benefits that chitosan can provide are, biodegradability, biocompatibility, antimicrobial agent, and it can be used as a flocculating agent. Chitosan can have many possible impacts on the paper industry as well. Chitosan can have a positive impact on the use as an additive in paper coatings, it can be used as a binder, retention aid, and it has positive environmental impacts due to its biodegradability [72]. The interest in using materials based on renewable resources is increasing: The development of polymeric materials, based on renewable resources has become increasingly important in recent years due to the inevitable rising prices of petroleum-based materials and environmental concerns. Nowadays, most materials used in the packaging industry are produced from fossil fuels [73]. The use of materials from renewable resources is critical in these days and age as the push for sustainability is critical. A recent study was done to test the effects of chitosan on paper properties. Chitosan nanoparticles were used in a solution-based form along with nano fibrillated cellulose from rice straw and glycerol in the making of sheets of paper. The addition of chitosan particles had a positive impact on tensile strength, water vapor permeability, grease-proof, and antimicrobial properties. Another study was done using chitosan nanoparticles in a paper coating that comprised nano fibrillated cellulose and chitosan nanoparticles. A thin film of coating was applied to sheets of paper. The results showed that chitosan improved tensile strength, grease proof properties, and decreased water absorptivity and porosity [41,73,74]. The major impact that chitosan can have on the paper industry is environmental, antimicrobial effects, and improved paper properties. However, the manufacturing price of chitosan is greater than materials made from non-renewable resources and still needs to be proven in large scale operations.

8. DIAMOND LIKE CARBON COATINGS

Diamond-like Carbon coating combines the properties of diamonds and graphite's to increase the effectiveness of industrial graded coatings. The highest attribute of diamonds is the hardness coat of the diamond, while the highest attribute of graphite is the lubricity and low coefficient of friction. The graphite and diamonds are combined with a chemical vapor deposition to create the hard coatings of paper [75]. Usually, graphite coating will wear down quickly due to lack of hardness on the coating and the diamond coatings will have high coefficient of friction which results the coating wearing down over time. The hardness and coefficient of friction can vary based on deposition technology, alloying elements and the number of layers of coating. Diamond-like coatings have expanded the use of coatings to automotive to the food industry. The use of diamond and graphite makes the coating have high load, which gives the coating to be used to improve automotive and industrial applications. Since the Diamond-like Carbon coating is bio-compatible, the coating can be used in medical and food applications. The cost of diamond-like coating is allotted higher than traditional coatings due to the process of the diamond-like coating. The cost can range from hundreds to thousands of dollars per square meter, depending on the deposition process and the materials. Diamond-like Carbon coatings will increase hardness, wear resistance, strength and lower coefficient of friction to optimize the coating properties. The Diamond like Carbon coating is made by changing the sp3 and sp2 hybridized atoms, which can alter based on conditions for different types of coatings. There are many different metals that can be used with diamonds for the different applications of diamond-like Carbon coating. Each different provides different max usage chemicals, coating thickness, coefficient of friction and hardness values. In the automotive industry we want to make more fuel-efficient cars/trucks by reducing the friction of the surfaces of the automative components. The automotive industry would switch from traditional coating to diamond-like carbon coating. The automotive industry wants to use diamond-like carbon coating to increase the life of transmissions, brakes and other parts of a vehicle [76]. The friction loss on the parts car engine can make the performance of the engine increase without increasing the power or size of the engine. The lower coefficient of friction will increase the productivity of the automotive industry. The properties of the diamond-like coating are very important to the automotive industry to ensure load carrying capacity, resistance to humidity, and tolerances of the strength of the paper. Each property is important to increase and improve the life span of the automotive parts that need diamond-like coating. If the wear life of carbon coating increases, then it would lower the amount of maintenance needed on a car. Car companies can charge customers more money for their parts with Diamond-like coatings to increase prof it. Diamond-like coatings will reduce friction and increase wear life the increase the durability of engine components like piston rings and valves. This would cause an increase in the lifespan of any engine and would provide less maintenance than other coatings. Diamondlike coatings will increase the lifespan of automotive parts and provide high resistance with low friction coatings.

Thermoplastic coatings are made up by depolymerizing lignin into monomers and polymerizing them into thermoplastics coating with heat. Thermoplastics are heated up into polymers then cooled to solidify each coating. Many times, when adding thermoplastic coating to paper, two rolls are placed in between the piece of paper to help press the thermoplastic to the piece of paper. Many papermills will have coating machines that will take thousand pounds paper rolls and add thermoplastic or other coating to the paper roll. The advantages of thermoplastics are low cost, biodegradable, and lower the use of petrochemicals. Petrochemicals are expensive and will pollute the earth after the use of coated paper due to its qualities. Thermoplastics coatings can be used in packaging, construction, and electronics to add a layer of strength or protection to the grade of paper. In the construction industry, thermoplastic coatings are used to provide waterproof protection for roofs, siding and some wood materials. [77]. Thermoplastic coating is added to packaging to protect the cardboard from grease, oil, water and add strength to the cardboard. Another use of thermoplastics is to provide a layer of protection for everyday items and to increase the lifespan of everyday household items. Over the recent years many companies want to change thermoplastics to be composed of agricultural waste to make thermoplastics coating more environmentally friendly. Thermoplastics provides a better substitute for coatings than petrochemicals and will lower the environmental impact of coatings. Most coatings on paper grades will provide an extra layer of protection and strength to the paper. Thermoplastic coatings are used for construction, packaging and other everyday household items, mostly used for protection and strength for those items. Thermoplastic coatings provide a replacement for petrochemicals coating and are more environmentally friendly than petrochemicals. Diamond-like coatings will provide a hard coating that has low friction and high resistance for each grade of paper.

Diamond-like coatings replace PVC coatings and are mainly used in the medical or automotive industry. The low friction and high resistance of diamond-like coatings will enhance the lifespan of automotive parts. This would allow less maintenance of cars or trucks for the customers, which would save money. The advantages of diamond-like coating technology and thermoplastics provide environmentally friendly and better properties of coatings on paper grades.

9. PROTEIN BASED COATINGS

The proteins in protein-based coatings are extracted from renewable plant sources such as wheat and soy, and/or animal sources such as whey. Typically, the biomass is acquired from waste streams generated from processing in agricultural food industries. Since the biomass is obtained from unwanted waste streams, they are usually a cost-efficient coating material option (Chen, 2019). In addition to this, the ability to acquire biomass from unwanted waste streams makes protein-based coatings environmentally enticing as they maximize the extent to which the biomass can be utilized thus decreasing the waste produced from the process.

9.1 General Properties of Protein Coatings

Protein-based coatings are advantageous to other coatings in that they are biodegradable and, in some instances, may even act as a catalyst to promote the paper product it is adhered to, to biodegrade at a faster rate. In addition to this, the polar nature of protein-based coatings is a significant property regarding the paper industry as it promotes strong adhesion to other polar surfaces such as paper and it provides the coating with a resistance to nonpolar gases such as oxygen and carbon dioxide. The ability of protein coatings to prohibit oxygen from permeating through the surface makes it very appealing for the food packaging industry as it has been found to extend the shelf life of packaged food [78].

Nonetheless, the polar nature of protein coatings is also an unfavorable trait as it causes poor water vapor resistance [79]. Furthermore, protein coatings are often brittle due to the covalent and noncovalent interactions between the free groups on the different types of amino acids that make up the protein. Although this is beneficial in resisting oxygen permeability, it also results in the poor mechanical strength properties associated with protein coatings [78].

Another disadvantage of protein coatings is that proteins are temperature sensitive. When exposed to elevated temperatures, proteins tend to aggregate and form “gel networks” [80]. Within these gel networks there are varying types of intra and intermolecular hydrophobic and electrostatic interactions. These variances provide protein coatings with inconsistent properties and make the process of coating more difficult [80]. In order to prevent the creation of agglomerates, the temperature must be kept relatively low and a pH specific to the protein type may need to be established. If an agglomeration is formed, it is important that it is broken up before the coating process. Agglomerates may be dissociated through “mechanical treatments such as dynamic high pressure, ultrasonic treatment or ionizing radiation” [79].

9.2 Protein from Whey

The whey used to generate protein coatings is obtained from the liquid byproduct produced during the casein coagulation process in cheese factories. Whey is derived from the liquid byproduct for coating purposes in two different methods: either as a whey protein concentrate (WPC) containing 35-80% protein or as a whey protein isolate (WPI) containing a 90% or higher concentration of protein [81]. The coating produced from whey proteins is transparent and colorless. Similarly to other protein coatings, whey is recognized for obtaining a high resistance to oxygen permeation and a low resistance to water moisture, however, it is far superior in terms of its grease and oil properties and flexibility. These properties combined make whey protein coatings highly desirable for food paper packaging.

In a study conducted by Yoo et.al. in 2011 [80] untreated pulpboard, WPC treated pulpboard and fluorinated hydrocarbon (FHC) treated pulpboard were tested to observe their ability to resist oil permeation. Each type of pulpboard was placed on blotter papers soaked with red-dyed oil and allowed to stay there for 24 hours. From this study it was observed that the portion of pulpboard stained by the oil was 19.39% for the untreated pulpboard, 0.13% for the WPC treated pulpboard and 0.64% for the FHC treated pulpboard [80]. This shows that whey protein coatings are highly suitable for products requiring resistant oil and grease barriers such as food packaging.

9.3. Proteins from Soy

Soy proteins are obtained from soy flour, the secondary product produced from the byproduct generated in the soy oil industry [78]. The coating developed from soy proteins is recognized for its ability to provide a simplified production process due to its high solids content and the high solubility of the soy protein powder in coating suspensions. Furthermore, soy protein coatings exhibit an ability to improve the “roughness, sheet gloss, ink gloss, ink absorption and printing surface strength of the paper product, however, they typically lack water, mildew, flexibility and corrosion resistance” [81]. In addition to being utilized as a paper coating material, soy proteins are recognized in the paper industry as a natural binder [81].

9.4 Bio-Polyethylene terephthalate

Bio-Polyethylene terephthalate (Bio-PET) is a biologically derived form of polyethylene terephthalate (PET) created with petroleum. The two coatings have the same chemical structure despite their differing source materials. Due to this they share nearly all the same qualities such as a strong water and oxygen barrier and flexibility [82]. To produce Bio-PET and PET, an ethylene glycol monomer and terephthalic acid (TPA) is required [83]. In regard to Bio-PET, the ethylene glycol is produced by fermenting the selected biological source, such as glucose, and then performing a dehydration reaction followed by oxidation and catalytic conversions, if necessary, to produce a biologically based ethylene glycol monomer [82]. The TPA used to produce Bio-PET is typically petroleum based thus Bio-PET is not entirely produced from renewable sources nor is it biodegradable. A study from Tachibana showed that it is possible to produce TPA from furfural, a renewable resource from inedible cellulosic biomass, through a series of organic procedures. Nonetheless, more research on this topic is required before it is viable to bring the lab scale procedure to an industrial scale [83].

9.5 Addition of Plasticizers

Plasticizers are chemicals added to polymers to improve certain properties such as softness and fluidity [84]. The effect of plasticizers differs between each protein-based coating, nonetheless, one of the most common problems faced with protein-based coatings is that they are quite often very brittle. This problem may be resolved through the addition of plasticizers. Plasticizers effectively decrease the brittleness of the coating by increasing the free volume of the protein network. Although this is advantageous for the brittleness of the coating, it causes a decrease in the coating's ability to resist oxygen permeation [85]. On the other hand, plasticizers have been shown to improve the strength of certain protein coating's ability to resist grease and oil permeation. Moreover, the addition of plasticizers decreases the moisture absorption of certain protein coatings [86].

Conversely, through adding plasticizers, the biodegradability of the protein coating may be interfered with. In some cases, plasticizers may be naturally sourced from animals or plants, however this is not always the case [87]. One of the more common groups of plasticizers are phthalate compounds which negatively affect the environment and humans [84]. Thus, although adding plasticizers may improve many other properties of protein coatings, it comes at a cost to the environment and humans.

10. POLY LACTIC ACID (PLA), POLYHYDROXYALKANOATES (PHA), & OTHER POLYESTERS

Polyesters have found great utility in many industries offering practical advantages and contributing to process efficiencies. Polyester is a synthetic resin in which the polymer units are linked by ester groups. Polyester was first created in 1941 by two British chemists, John Rex Whinfield and James Tennant Dickson and a patent was applied for in Great Britan with

Serial No 618,398. In the United States a patent was filed with the United States Patent and Tradmark Office on in the United States a paten was granted July 29, 1949 with Patent Number 2,465,319 titled Polymeric Linear Terephthalic Esters, which was the first polyester, polyethylene terephthalate Patent [88]. Polyethylene terephthalate is considered the basis of synthetic fiber and inspired other polyesters that would be developed in the coming years.

Polyester is widely used in most industries due to its versatility because of its affordability and ease of care. For example, in the clothing industry polyesters are commonly used because of the previously listed reasons and its durability and because of how easy it is to work with the material. Polyester is also used in the packaging industry due to its strong barrier properties, strength, and clarity, making it a preferred for packaging food, beverages, pharmaceuticals, and personal care products. Polyesters usefulness is also used in industries such as automotive, medical, outdoor gear, and many more.

Even though polyester is a very beneficial resource that many companies use, it has some drawbacks. For example, microplastics can be released from polyesters when in water which can be very unfavourable for the environment. This is because polyester fabrics bring water to the surface which pulls microplastics with the water. This has become a problem due to the large amount of polyester in landfills which can destroy wildlife and aquatic ecosystems nearby. Another negative impact polyester‘s cause is that most polyesters are not biodegradable. This is another variable for how wildlife and aquatic ecosystems get impacted because polyester when left in a landfill can take up to 200 years to degrade without intervention. Another impact that polyesters cause is the pollution produced when working with the fabric. This is because polyester is easiest to manipulate at high temperatures to be able to mold the fibers. Due to this and the large quantity of polyester used by industries, it has created a vast amount of pollution. Even though polyesters have many negative impacts, it has plenty of beneficial factors that are essential in many industries [89,90].

10.1 Biodegradable Polyesters

Many types of polyesters have been developed to suit the field that it is primarily used for. For example, a polyester known as Poly lactic Acid (PLA) has been largely used in the bio and medical fields.

The primary reason for the use of poly lactic acid is largely because of its biodegradable properties, which makes it very beneficial when used in surgeries. By spinning the fibers the fibers can be shaped how is needed and is primarily used for procedures such as implants and sutures. Due to poly lactic acid’s ability to biodegrade, it is primarily used to help the body to be able to close the wound with the fibers while it degrades overtime, so the sutures don’t need to be removed at another time. In addition, smaller PLA fibers are added to help reduce scarring because they help close the wound more efficiently. PLA‘s are considered one of the most sought after biodegradable polymers because it has higher mechanical strength properties due to, “It is the L-lactic acid which provides polymer with high mechanical strength and thus has an edge over the DL-form“ [90,91].

The possibility of strength improvement makes PLA suitable for wet-end applications or coating applications in the paper producing industry [92].

PLA’s are also sought after because it is a cheaper resource considering its benefits. The projected price for Poly lactic acid is at $2.32/Kg in the US and has a similar selling price in every continent [93]. The main environment impact that PLA’s cause is primarily from the chemicals and energy used to produce the poly lactic acid. However, a lifestyle assessment showed low risk to the feedstock-sourcing area to produce the PLA’s which meant that most environment damages could be avoided by optimizing the efficiency of producing the feedstock used for PLA production. This could be beneficial because being able to produce the crops at a more efficient rate can reduce the damages to the environment it produced in and can reduce the amount of chemicals needed for production [94].

Another type of polyester that has seen plenty of use is Polyhydroxyalkanoates (PHA). Polyhydroxyalkanoates are created in nature from bacterial fermentation of sugars or lipids. As a result, when the bacteria creates PHA it uses it as a source of energy and carbon store. Polyhydroxyalkanoates is used commonly as a replacement for plastics because of its biodegradability. Because of PHA's biodegradability and being created naturally, many companies will still use Polyhydroxyalkanoates even though it has a higher cost of about $6.60 per kg. However, the cost can be lowered if the PHA's were made using crop plants instead of using yeast or bacteria to produce the PHA. With more research being put into Polyhydroxyalkanoates, it is believed it could be the solution to producing green plastics. This is because PHA's have a, "high degree of polymerization, are highly crystalline, optically active and isotactic, piezoelectric and insoluble in water" [95]. Because of these properties, researchers believe that PHA's could rival the leading plastics being used now like polypropylene. Polyhydroxyalkanoates have seen use in the medical field as a biofuel using methyl esterfiication. When synthesized into biofuels, PHA's have similar properties similar to biodiesel, however because it can be naturally synthesized it has no environmental damages. The main drawback to using PHA's compared to biodiesel is that PHA's aren't as cost effective so they are overlooked more in other industries that don't synthesize their own PHA's [96,97].

Polyglycolic Acid (PGA) is an additional polyester that has seen use in industries due to its biodegradability. PGA's are an aliphatic polyester that at first was only able to be produced in small quantities, but started to see more use when the company Kureha Corporation [98] developed a commercial processing plant so that they could produce PGA's in higher volumes for much cheaper. It used to be difficult to produce high-molecular-weight PGA's because they were degradable, until Dupont determined a way to synthesize it by using a ring-opening polymerization of glycolide [99]. Different types of PGA's have seen different types of uses in industries. For example, high molecular weight PGA's have seen use primarily in the medical field as an alternative to poly lactic acid for sutures. Due to the high price of high molar weight PGA's, the medical field is the main industry that purchases it. High molar weight PGA's work very well for sutures because of its strong mechanical strength and crystalline structure, which gives it stronger strength properties than other resins used. For normal PGA's, it has seen more use in the drilling industry for shale gas and oil. This is because to reach the shale gas/oil you must be able to drill much lower without increasing losses of oil, which is harder in areas with less permeability. The PGA's help because, "the hydrolyzability of PGA could be effectively used to satisfy the requirements even at relatively low temperatures" [99]. The polyglycolic acid also helps because PGA's can also work as a delayed-release acid due to its degradation, which can help increase the efficiency of the recovery of the gas and oils. PGA's are also very benefial to both these fields due to its high tensile strength and high melting point. These properties are very beneficial to their respected fields because for sutures it is imperative that they are strong so the sutures don't break before a wound is done healing so it doesn't open. The high melting point is also efficient because when using industrial tools they can overheat which would impact the efficiency of recovery if the PGA's were to melt. Besides the high cost to produce polyglycolic acid, another disadvantage of using PGA's is its poor thermal stability. When PGA's reach their melting point they start to undergo rapid degradation which drops the efficiency when it happens too fast. Degradation is both an advantage and disadvantage depending on the industry that it is used in. Many companies can't use PGA's for their products because of the degradation, but also is a reason certain industries such as the medical field, pharmaceutical, packaging, agriculture, and mining industry. Even though Polyglycolic acid is expensive to use, with more research and development in coming years it should be able to be produced in a cheaper method and/or used in new methods of utilizing this polyester.

11. STARCH

Behind biomass fibers and fillers, starch is the third leading component by weight in paper [100, 101]. Starch is considered a low-cost and sustainable product, as it is naturally abundant and biodegradable [102]. In addition, starch provides impressive strength and surface benefits to a variety of different paper grades, including packaging paper and cardboard grades [103].

Starch and its derivatives have garnered considerable interest as barrier coatings due to their renewable, biodegradable, and biocompatible nature. Starch, a polysaccharide composed of polymeric chains of sugar monomers [100] and is a common and crucial bio-additive to papermaking and paper conversion [104]. Application of starch today ranges from dry strength agents, coating binders, retention aids in wet end applications and as adhesives in converting operations [100].

Various starch products find a place in the industrial process of papermaking, because starch can play a variety of different roles, where it can gel, thicken, and form to create optimal sheet construction [105]. Due to starch's substantial use in the paper industry, there are a variety of different products on the market, with major sources ranging from corn and potato to waxy maize, wheat and tapioca [104,106].

Starch applied at the wet-end mixing systems is in most times modified to cationic, anionic or amphoteric cationic or amphoteric. [100, 11,106]

Through modifications and processing techniques, starch receives cationic, anionic or amphoteric cationic or amphoteric properties and is used for wet-end applications [100, 107,108]. In addition, starch modification can be tailored to enhance its barrier performance and compatibility with various substrates. The application range of starch and starch derivatives as barrier coatings is extensive and encompasses industries such as food packaging, pharmaceuticals, textiles, and paper products. In food packaging, starch-based coatings are utilized to provide moisture resistance, oxygen barrier properties, and grease resistance to packaging materials like paperboard, cardboard, and biodegradable films. They find applications in packaging various food products, including snacks, baked goods, and fresh produce. In pharmaceuticals, starch-based coatings are used for tablet coating to offer controlled release, taste masking, and moisture protection. Additionally, starch coatings are employed in coated papers and textiles to enhance printability, surface smoothness, and durability [104,106,108].

Uncharged and unmodified pearl starch is a widely utilized additive to the pulp and paper industry, specifically as a binder and laminate in corrugated board processes [109]. This specific additive is incredibly useful within the industry because it aids in the promotion of inter-fiber bonds, at dosages of up to 20% of the sheet. To influence inter-fiber bonding, the nonionic starch gels cross-link with the fibers within the sheet. Once the gel forms closer contact with the fibers, it can increase and improve formation, influence efficiency in draining on the machine and bind sheets in the corrugation process [9]. This unmodified starch often has limitations, since it is high solids and high viscosity, requiring increased water usage and difficulty in make-down [110]. In addition, this type of starch is often used as a glue between sheets rather than an additive for strength [111]. Therefore, cationic starches are often utilized over unmodified starches in the paper industry.

Since these cationic starches are utilized in abundance over unmodified starches, there are several different types including tapioca, maize, and potato [112]. Studies comparing these types of starches have found that cationic starches perform better than native starches in tensile, tear, and burst [105]. These cationic starches provide several benefits on the wet-end of the machine including increased fiber and ash retention, improved process runnability, better dewatering behavior, and cost-effectiveness [113]. Cationic starch is also preferred on the dry-end because the positive charge that gets introduced on the chain forms an electrostatic bond with the negative cellulosic fibers of the biomass [111]. This bonding is strong, which provides strength and formation benefits in the final sheet [102]. In addition, these modified starches coat the fillers and fiber to create better retention of chemistries within the paper, which promotes better paper performance and cost savings [114].

Ongoing research aims to optimize formulation, processing, and application techniques to further enhance the performance and versatility of starch-based barrier coatings, driving innovation and adoption across various industries.

12. CONCLUSION

Bio-based coatings are advantageous due to their biodegradable nature and renewable sourcing. Overall, bio-based coatings may offer a solution to replacing environmentally harmful coatings and or non-renewable oil-based coating in the future.

However, further research and extensive development is required to modify the today available bio-based coatings for their application beyond the research stage into applications at the pilot stage and further into large-scale applications at the commercial level, including large scale production at an economic level that justifies their application and replacement of currently used coatings in the paper, packaging and converting industry.

13. COMPETING INTERESTS

Author has declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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