The Potential of Paper Pulp Bottles with Inner Protective Coatings: A Review on Sustainable Alternatives to Petroleum Plastic Packaging

Peter Hartman: 20174631

MRes Biomolecular Technology

BIOS4152: Industrial Project and Dissertation

University of Nottingham, School of Biosciences,

Sutton Bonington, LE12 5RD

Email: Styph2@nottingham.ac.uk

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Abstract

The need to replace petroleum-based plastic vessels for containing liquids has prompted the packaging industry to develop novel materials to store and transport different liquids, such as foods, beverages, colloids, detergents and soaps. This has the effect of reducing pollution and waste emitted from the production, consumption and disposal of plastic. The major issue in using sustainable biomaterials is barrier functionality. Innovative inner protective coatings have been used to overcome the shortcomings of these materials. Many containers use sustainable materials with a plastic-based coating. A novel wax-based coating has been developed by Pulpex to remove plastic entirely. Permeability issues regarding barrier functionality to moisture and homogeneity have yet to be fully resolved and are currently under investigation.

1. Introduction

The packaging of food and beverages is important in society. It allows for easier transit of units whilst lowering energy costs (Silva, et al., 2023). As of 2019, the global packaging market was valued at $914.7 billion, an increase of 8.4% from 2015 (Stark & Matuana, 2021). The Covid-19 pandemic has done little to slow the expansion of the sector as the market was forecast to grow at a compound annual growth rate of 2.3% until 2025. This has led to predictions for the packaging industry to be valued at $1.15 trillion by 2030 (Cameron, 2020). This rise is predicted to be caused by the emerging markets in developing countries, in which higher real incomes and populations are increasing as well as the further development of the infrastructure of the representative retail industries. This, paired with the rapid surge of internet culture and the electronic-commerce industry, are the leading factors of the expected growth (Stark & Matuana, 2021).

The difficulties with traditional single use fossil fuel-based plastics are becoming more prevalent. Millions of tonnes of plastic waste are produced by the packaging industry annually. This brings a variety of environmental and pollution concerns, including the growing issue of nano/micro plastics which have the capacity to cause serious environmental and health problems to fauna and people (Silva, et al., 2023, Wang, et al., 2022, Prata, et al., 2020). Due to these concerns, innovations are being developed and presented which aim to launch a system wide shift from the use of plastics and other synthetic based technologies to more

sustainable ones (Wang, et al., 2022). This change will, and in some cases already has, transferred the focus towards the use of more sustainable materials for the manufacturing of packaging products. Consequently, research has increased into bio-based materials which can be supplied in sufficient quantities to be used in an industrial commercial capacity (Nechita & Roman, 2020).

There are many angles to approach the replacement of synthetic petroleum-based plastics. Bioplastics are defined as a type of polymer which can be biodegradable as well as biobased (Sid, et al., 2021, Karan, et al., 2019, Rujinic-Sekele & Pilipovic, 2017). Alternatives to plastics include natural biopolymers such as chitin, lignin and cellulose. These materials are easily accessible and require little modification to be transformed into a useful material (Averous & Halley, 2009, Gadhave, et al., 2018). A commonly used substitute is paper pulp. Its ease of access, renewability and biodegradability complement good mechanical properties which allow it to effectively replace plastics. (Wang, et al., 2021) To increase its effectiveness as a packaging material, specialised coatings can be implemented which overcome many of its shortcomings such as its porous nature which can affect its barrier functionality (Nilofar, et al., 2021, Helanto, et al., 2019). There are several issues associated with each material which must be addressed before any attempt to replacing conventional plastic can be implemented worldwide.

This review article will explore the global issues of unsustainable petroleum-based plastics both in the packaging industry and in the global economy. It will investigate what can be done to reduce pollution and waste from petroleum-based plastics. The focus of this article and its accompanying study will be on the company Pulpex and its use of cellulose paper pulp with an added bio-coating to create a replacement for single use plastic bottles. It will investigate properties of this material and the coating and provide a base for what solutions Pulpex can implement to improve on its technology. This review will examine a variety of characterisation and microscopic techniques and instruments which can be used to characterise the limitations of Pulpex's methodology regarding its coating techniques, and proffer ideas to both examine and remediate the issues raised.

2. The use of Plastics and the Issues Surrounding them.

2.1. Properties and Production of Plastic

The use of plastics in the packaging industry is extensive due to its beneficial properties. One such property is malleability, the ability to be moulded and shaped to whatever is needed. The advantages of this are: (Macarthur, 2017, Schneiderman & Hillmyer, 2017)

- A low financial cost.
- Relatively low weight.
- Ease of processing.

These have allowed plastic to dominate markets globally. Plastics play a vital role in the medical industry by being a main component of much disposable medical equipment. In the food and beverage industry, it can be used to safely contain, maintain and transport various food and liquid based products (Prata, et al., 2020). Estimations have placed the accumulated amount of plastic produced as of 2020 to be at 8300 million tonnes (Almeshal, et al., 2020). Around 33% of the plastics produced are non-recyclable and 50% are single use plastic products such as plastic bottles (Zhang, et al., 2022). The rate of disposable plastic production is accelerating. The global production of primary plastics is forecast to be 1,100 million tonnes by 2050 (UNEP, 2018). As the manufacturing of most of these products are fossil derived and non-biodegradable, pollution linked with this industry has become a major concern (Horejs, 2020, Macleod, et al., 2021).

2.2. Issues Related to Plastic

2.2.1. Plastic Pollution

Plastic production has increased, so has its corresponding waste and its role in global pollution. Figure 1 and Table 1 show the global primary plastic waste generation from 1950 and 2015. A study conducted by the United Nations Environment Programme (UNEP) revealed that 400 million tonnes of plastic waste is produced every year (UNEP, 2018). In 2015 the packaging industry amounted to approximately 50% of the total tonnage of plastic waste (Geyer, et al., 2017). Once a plastic has been used, there are three main methods of treatment which plastic can undergo. These include being placed in a landfill (the most common), incineration or being recycled. A fourth unofficial outcome is the release of plastic waste into natural environments. Of the total plastic produced globally, only 9% is recycled. This

contrasts with 12% which is incinerated and the 79% which is placed in landfills or deposited into the environment (Geyer, et al., 2017). In terms of pollution, between 280 and 360 million tonnes of fossil-based carbon is processed for conversion to plastic. These are then degraded naturally or converted industrially, releasing a large amount of greenhouse gases including carbon dioxide, methane and many others. Even if all plastic production was to halt, pollution stemming from this area would continue for centuries into the future (Dees, et al., 2021). If plastic production were to halt immediately the legacy of plastic waste would continue to pollute for centuries to come.

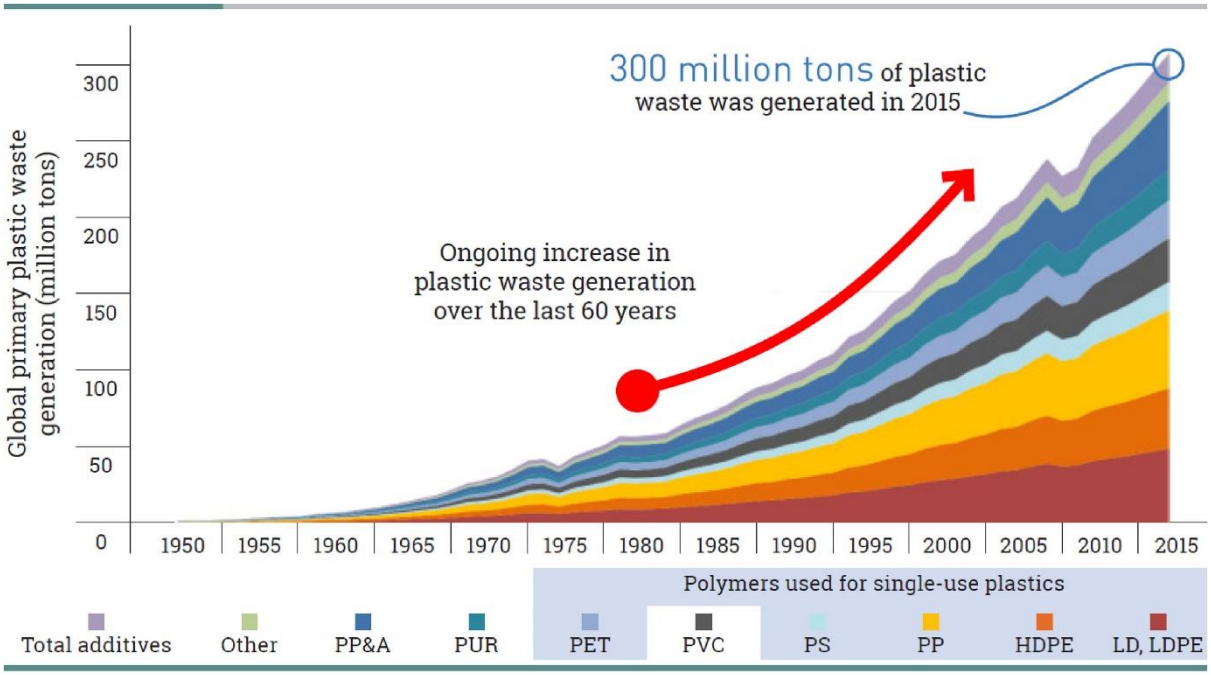

Figure 1: Global plastic waste generation 1950-2015. Source; (Almeshal, et al., 2020).

Table 1: Average global Plastic waste generation by an individual in 2015 both annually and weekly.

Global annual waste per capita (kg)	**37.5**
Global weekly waste per capita (kg)	**0.72**

2.2.2. Plastic waste in the environment

Plastic waste has been identified in almost all environments on the planet. From the Artic, to the deepest parts of the ocean, reports have shown an accumulation of plastic which have only increased with time. Some of the earliest plastic debris found in these marine environments date back 50 years (Carpenter, et al., 1972, Carpenter & Smith Jr, 1972). As the

production of plastics is increasing, the emissions caused by them also rise. Data collected conducted in 2016 estimated that potentially up to 50 million tonnes of plastic are released into the environment annually. (Borrelle, et al., 2020, Lau, et al., 2020). Predictions were made stating that if the status quo remains, emissions will have doubled by 2025. The findings of other studies show that around 5000 million tonnes of plastic waste will reside in the environment. This figure is rising despite the best efforts of many (Almeshal, et al., 2020).

Plastic waste can occur directly through forms of littering. There are five main environments in which plastic is present and difficult to remove. These are coastlines, the water column, the deep sea, soils and the body. Aquatic environments generate the most concern when it comes to plastic waste. Studies estimate that between 10 and 14 million tonnes of waste ends there and consists of 80% of floating debris in the ocean (International Union For Conservation of Nature, 2021). The reason the water-based environments are highlighted is due to the weathering and degradation of plastic particles and the difficulty of recovering plastic which is not present on the surface. Only a small fraction of the total tonnage of plastic is present on the surface of the ocean, around 0.3 million tonnes. (van Sebille, et al., 2020) Most plastic is expected to reach the sea floor. However, a large percentage exists between the floor and the surface in the water column. Many pieces are neutrally buoyant and can remain for a long time depending on their shape and size. Fibres, below ten microns, due to their cylindrical shape and small size have extremely long residence times compared to spherical shaped particles (Khatmullina & Isachenko, 2017). The depth at which the water columns are located can affect degradation times, influencing the amount of ultraviolet light, temperatures and quiescent conditions (Macleod, et al., 2021). Once a plastic particle or product has reached the sea floor, little can be done to remove it. It has been reported that the seafloor has the highest concentration of microplastics (Tekman, et al., 2020). The more extreme conditions present at these locations results in highly reduced degradation of plastic (Tekman, et al., 2017).

2.3. Micro and Nano Plastic Pollution

Plastics present in the environment are broken down to the micro and nano scale. Multiple processes occur which lead to the fragmentation and weathering of plastics. The leading cause is ultraviolet degradation, which produces radicals. This can result in bond scission and other degradations (Shah, et al., 2008, Doğan, 2021). The unpredictability of the compounds

produced and what they could potentially come into contact with are a cause of concern. It can end with the release of soluble and potentially volatile chemicals (Macleod, et al., 2021). Indications that biological weathering taking place can be first detected by observing physiochemical alterations on the surface properties of the chosen sample. Surface charge alterations and cracking may be observed due to the changes in polymer crystallinity, the degree to which the polymers are aligned with each other (Crawford & Quinn, 2017). These processes allow for fragmentation to occur more easily as the surface is more susceptible to mechanical stresses due to increased surface areas and depth (Arp, et al., 2021). These fragments and chemicals are more accessible for uptake by biota in these locations.

2.4. Effects of Plastic Pollution and Waste

Chemicals, micro, nano and macro plastic particles are taken up into the food chain as they are consumed by marine species. There have been many reports of micro plastic particles and films discovered in the guts of marine species. Recent analysis, from around the globe has provided data stating that 914 marine species have been affected by plastic waste and pollution either through ingestion or entanglements (Kuhn & van Franeker, 2020). One of the most highly studied phenomena regards plastic ingestion by turtles and birds (Figure 2). Many independent reports provide evidence of turtles mistaking plastic bags and other particles as the gelatinous prey they live on such as jellyfish. Autopsies have discovered worrying levels of plastic in the gut linings of many animals. These have caused blockages of vital pathways leading to fatalities in many cases. (Mrosovsky, et al., 2009, Duncan, et al., 2021). The ingestion of plastic by marine fauna can lead to harmful substances entering the human body, as we consume many of these species (Engler, 2012). Microplastics present in humans is a major health concern. Cases have already occurred in which these particles have been found in humans. A recent study was conducted on several women who had had unsuccessful pregnancies. Detected for the first-time using

*Figure 2: Contents of a washed-up Albatrosses stomach. Source (*Turn*, 2018) Photograph by Chris Jordan. Assessed 18/05/2023.*

Raman microscopy, fragments of microplastics were found in the placenta (Ragusa, et al., 2021). This needs to be investigated further to ascertain whether it may have transgenerational effects and what factors of development may be affected (Lee, 2018).

Overall, plastic has many benefits to society. It can be used in life saving equipment or can keep food safe to consume for a long time. If correctly managed, it can be a perfectly acceptable material. However, mismanagement of its use and waste has led to it being one of the largest pollutants ever. Without an increase in methodologies to combat this or alternatives to replace its use, the issues of micro and nano plastic particles will only grow.

3. Plastic Alternatives and Replacements for Food and Beverage Packaging

In 2021 it was claimed that 583.1 billion units of plastic bottles and containers were produced, (a unit typically contains 100 bottles) (Statista , 2023). With the advent of extreme plastic pollution, associated waste and increased public concern over climate change and sustainability, opportunities to develop alternatives to plastics have arisen. Many chemicals associated with petroleum based plastic packaging have been studied and findings have discovered 148 compounds which are classed as hazardous, some being found to be carcinogenic, endocrine disruptive and mutagenic (Muncke, 2021). This revelation has allowed for more research into sustainable materials, utilising the planets natural resources which are more biodegradable and renewable (Sid, et al., 2021). Published literature has been increasing exponentially. Each of the alternatives have various advantages and disadvantages. The vast majority can be created using bio-sourced feedstocks.

3.1. Bioplastics

A bioplastic is a polymer that is bio-based, biodegradable or both. These materials are created using a source of biomass and biomass derived chemicals which undergo various treatments allowing for the conversion into a plastic which is considered safe to use in packaging (Sid, et al., 2021, Karan, et al., 2019, Rujinic-Sekele & Pilipovic, 2017). They are mainly categorised as fully bio-based, partially bio-based and non-biodegradable. These differences are due to whether the material is manufactured entirely using fully renewable biomass resources such as microorganisms or plants. Examples include biobased polypropylene (bio-PP) and polyethylene (bio-PE). Biodegradable bio-sourced plastics include polyhydroxyalkanoates

(PHA) and polylactic acids (PLA). Additionally, there a fossil-based plastics such as polycaprolactone (PLC) which are biodegradable and therefore are classed as a bioplastic (Sid, et al., 2021).

There are several sources of raw materials which can be used to produce bioplastics. These materials are split into two categories. The first generation are naturally occurring sources such as plant biomass feedstocks such as corn and other plant species. Second generation raw materials centre around the use of agricultural and food industry waste to refine and synthesise bioplastics (FitzPatrick, et al., 2010).

The issues regarding bioplastics are related to shelf life (Sid, et al., 2021). As of 2020, only 1% of the total plastic produced is manufactured using this material (Zhao, et al., 2020). Predictions have forecasted growth by 2025, to just under 5 million tonnes annually (European Bioiplastics, 2022). If production is not increased dramatically the issues it is attempting to mitigate may not come about swiftly enough.

3.2. Natural Polymers

Natural biopolymers are commonly used due to the abundance of the raw material and the ease of production. Little modification and alterations are needed to manufacture products. The most used materials are starch and cellulose due to their mechanical properties. With further modification these properties can be enhanced and strengthened to become a viable material (Khan, et al., 2017, Mu, et al., 2019).

3.2.1. Starch Based Polymers

Starch is a polysaccharide molecule in plants which is used in storage. It consists of two interlinked glucose molecules and can be represented in two categories (Figure 3). The first is the linear amylose composed of α-1,4-glycosidic bonds at each end. The second is amylopectin, comprising of both α-1,4-glycosidic and α-1,6-glycosidic bonds which form highly complex branched polymers (Sid, et al., 2021, Liu, et al., 2022).

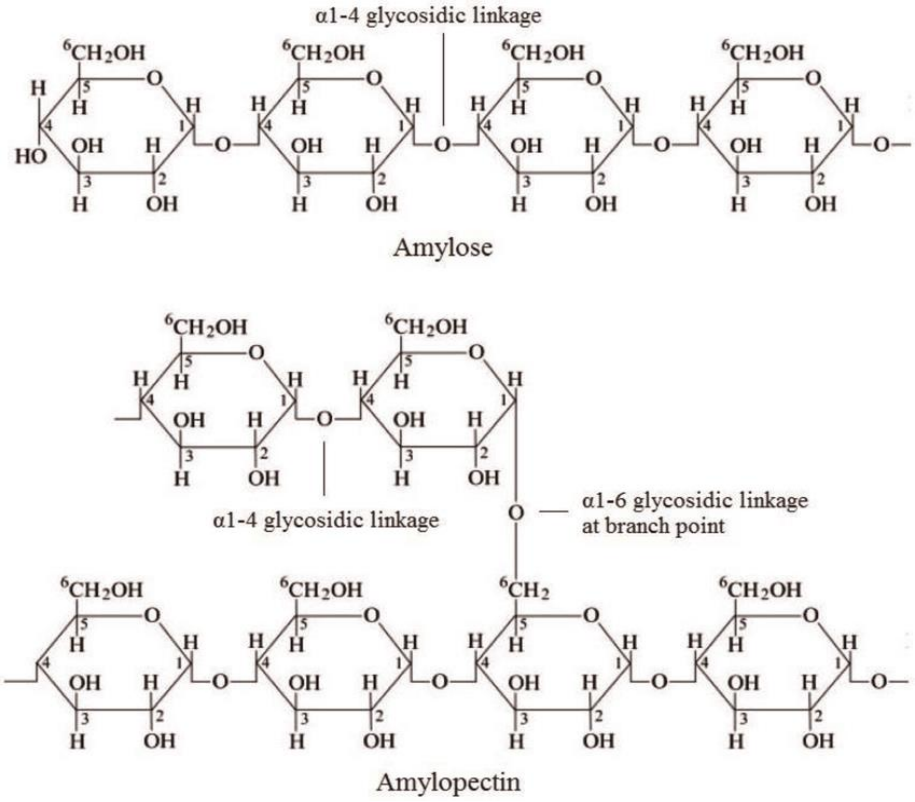

Figure 3: Labelled schematic diagram of amylose and amylopectin. Source (Nawaz, et al., 2020). Accessed 25/05/2023.

As it is easily renewable and widely available, starch is focused on by researchers as a bio-sourced plastic (Nagar, et al., 2020) As of 2020, starch and starch-based polymers comprised 19% of the global bio-sourced plastic production (European Bioiplastics, 2022). The sought after feedstocks for starch-based packaging products are the more highly concentrated starchy crops such as potatoes, rice and maize. Other sources are under investigation and some have shown promise. However, amylose and amylopectin variation have caused some concern regarding crystallinity (Jiménez, et al., 2019, Gadhave, et al., 2018).

Even though starch has many beneficial properties, some mechanical issues such as strength and moisture sensitivity. It must be further processed both mechanically and thermally with the addition of plasticisers to convert the native starch to a material which can be used (Ribba, et al., 2017). The result of this process is a gel-like structure. Further processing and potential purification steps are conducted on the material before a functioning thermoplastic starch is obtained (Avérous & Halley, 2009). Thermoplastics starches can be a successful replacement for food packaging. However due to the presence of functional

hydroxyl groups, which bind to water molecules, the transportation of liquids is not possible without further processing (Cui, et al., 2021).

3.2.2. Cellulose based Polymers

The use of cellulose in the packaging industry is an encouraging prospect. It can be processed into fibres and films and can be moulded using advanced technologies. Around 40-50% of wood is comprised of cellulose, due to this the primary source is collected from wood pulp (Dhall & Alam, 2020). Cellulosic substrates have good mechanical properties whilst being, inexpensive and biodegradable (Marzbani, et al., 2016).

The molecular structure of cellulose, (Figure 4) is the reason for its high mechanical strength. It is comprised of β-glucose units which are covalently bonded to the next via a 1,4 glycosidic bond between carbon and oxygen (C-O-C) (Altaner, et al., 2015). These chains form partial crystalline fibres which can be 3 nm in size and are often referred to as nanofibrils (Fernandes, et al., 2011). Within these fibres hydroxyl groups present can form hydrogen bonds between monomers on the same chain and between chains. (Nishiyama, 2009) The result of the hydrogen bonds between fibres is a high tensile strength. Paper is a matrix of cellulose fibres (Figure 5) bonded together and flattened into a plane. This creates the great mechanical strength which allows it to be a viable material.

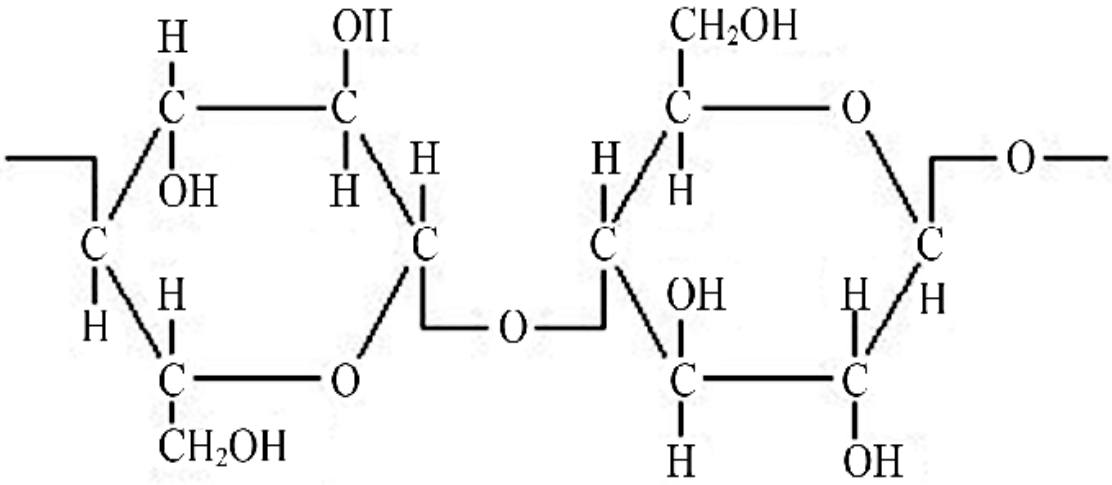

Figure 4: Schematic Diagram of Cellulose molecule. Source (Richards, et al., 2012). Accessed 25/05.2023.

Although cellulose has many properties which makes it an ideal candidate for packaging solids and liquids, there are problems which prevent pure cellulosic polymers from being adopted. Pure cellulose has poor moisture barrier properties and associated mechanical problems (Ferreira, et al., 2016, Rastogi & Samyn, 2015). As the structure is many fibres networked together, paper is a porous material (Figure 5). Pure cellulose derived from the wood pulp can be modified and processed which can improve the mechanical properties many times over.

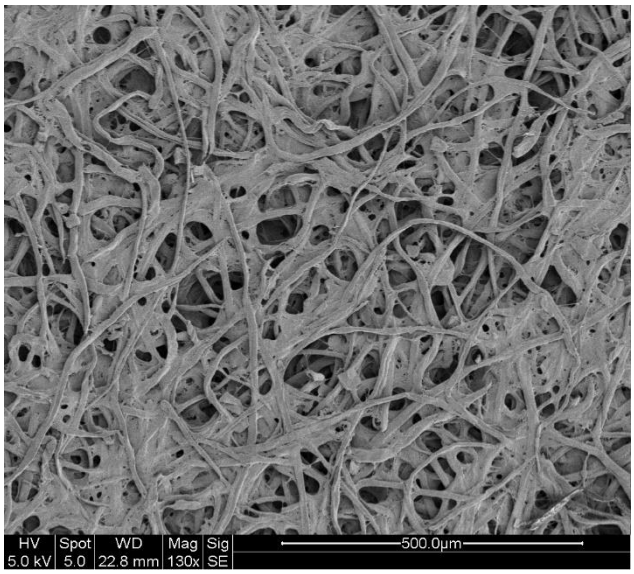

Figure 5: Scanning Electron Microscope image of Whatman filter paper. Magnification 130x. Accessed 25/05/2023.

There are many examples of cellulose derivatives. One such example is cellulose acetate which is manufactured by conducting a reaction between pure cellulose, acetic anhydride and acetic acid. The mixture is dissolved in acetone before being extruded through spinnerets creating the fibres (Kershaw, 2018, Liu, et al., 2021). Cellulose acetate nanofibers combined with zinc oxide have shown to possess antimicrobial properties. This could potentially be a hugely important factor with regards to the packaging of products which are ingested (Khalil, et al., 2016). Another derivative is cellophane. To create cellophane, the wood pulp is dissolved in carbon disulphide and aqueous sodium hydroxide to form a viscous solution. Glycerine is then added to improve flexibility (Helanto, et al., 2019). Usually, a polymer coating is applied to improve barrier functions increasing the shelf life. These can be comprised of a nitrocellulose waxy based coating or polyvinylidene based one (Dhall & Alam, 2020). Other than a barrier against moisture, which is a vital property for a cellulose based container, the coatings also provide thermal protection and a range of other applications which are beneficial to the packaging industry (Piergiovanni & Limbo, 2016).

3.3. The Circular Economy

The culmination of alternative sources to petroleum-based plastics and sustainability goals is the idea of a complete circular economy. This is an economic model which aims to have high waste minimisation, value retention and a reduction in primary resource use. Its goal is

sustainable development (Murray, et al., 2017, Babbitt, et al., 2018, Hofmann, 2019). There are ten main strategies (Figure 6). These form the framework on which it is based. It aims to improve the use of existing resources and production techniques, reduce waste and extend the lifespan of current products (Morseletto, 2020). Multiple organisations and companies have pledged to move towards this singular vision (Stark & Matuana, 2021, Schyns & Shaver, 2021). With more large companies setting deadlines for the removal of plastic from their packaging or hitting sustainability goals within the next five to ten years, the use of bio-sourced materials such as cellulose polymers will be more important. The development and widescale production of these products such as paper bottles will have to be increased to meet the new anticipated demand. Meeting the ten strategies would allow for large gains on the road to becoming a completely sustainable society.

Smarter product use and manufacture	**R0**	**Refuse**	Make product redundant by abandoning its function or by offering the same function with a radically different product
	R1	**Rethink**	Make product use more intensive (e.g. through sharing products or by putting multi-functional products on market).
	R2	**Reduce**	Increase efficiency in product manufacture or use by consuming fewer natural resources
Extend lifespan of product and its parts	**R3**	**Reuse**	Re-use by another consumer of discarded product which is still in good condition and fulfils its original function
	R4	**Repair**	Repair and maintenance of defective product so it can be used with its original function
	R5	**Refurbish**	Restore an old product and bring it up to date
	R6	**Remanufacture**	Use parts of discarded product in a new product with the same function
	R7	**Repurpose**	Use discarded products or its part in a new product with a different function
Useful application of materials	**R8**	**Recycle**	Process materials to obtain the same (high grade) or lower (low grade) quality
	R9	**Recovery**	Incineration of material with energy recovery

Figure 6: Ten strategies employed in the circular economy model, source (Morseletto, 2020), accessed 02/05/2023.

4. Production and Challenges of Manufacturing Paper Bottles: A case study of Pulpex Ltd

4.1. Pulpex' Products and Manufacturing processes

This study's focus is on one innovation in the field of sustainable packaging. The introduction of this technology is a large step towards the reduction of non-sustainable plastic and the associated pollutions and hazards. A product is being developed by Pulpex, a bottling company which produces cellulose paper pulp-based bottles with a propriety inner coating (Pulpex, 2020).

The manufacturing of the bottles involves moulding the slurry of paper pulp in a pressurised system. The material used in creating paper-based containers is comprised mostly of lignocellulosic material obtained from wood and other sources. This material is prepared and undergoes a standard pulping process which removes the lignin from the lignocellulose material. The culmination of this is a paper which can be used to create the containers (Ahuja, et al., 2022). The containers are cured in microwave ovens which is followed by the application of a coating. The coating will be compatible with the various solutions the bottle will contain (Pulpex, 2020).

The company has begun with producing alcohol bottles. However, Pulpex has partnered with several major brands such as Pepsico, Diageo, GSK and Unilever (Pepsico, 2020, Vishu, 2021, Unilever, 2021). All these partnerships are allowing further development and the expansion of the technology to provide a functional barrier to more types of liquid.

4.2. Challenges to making Paper Bottles

4.2.1. Issues with production

Multiple challenges facing paper as a material for packaging liquids have been reported. One is the rate of production. Pulpex is aiming to replace single use plastics. These products which are considered fast moving consumer goods (FMCGs) have a high demand (Ahuja, et al., 2022). This can only be fulfilled with a high production rate. The numerous steps required to create a bottle from pulp such as moulding, curing and coating, may be a limiting factor in the speed in which a unit can be produced.

4.2.2. Properties of Paper: Wettability and Gas Permeability

The main issue is barrier functionality against oxygen and water. The wettability or wetting function is the ability of a liquid to be in contact with a solid medium and its propensity to maintain it. This occurs from intermolecular interactions when the two meet in the presence of a fluid phase such as gas or air (Carroll, et al., 2017). Water can be transported along and within paper by different means: (Eklund & Lindstrom, 1991, Marzbani, et al., 2016)

1. Capillary forces.
2. Diffusion at the cellulose fibre surface.
3. Vapour transport through the pores of the fibre mesh.

Due to the properties of paper, it cannot meet water or another liquid, as it will lose its function as a container. Physical properties of paper include hydrophilicity and porosity which cause high absorption of water. The fibres absorb water and become swollen. The functional hydroxyl groups which bind to other cellulose fibres also form hydrogen bonds with water molecules. Water causes a large change in the strength and range of forces holding the paper together. The Van der Waal forces diminish and Hamaker forces decrease. This results in the material being susceptible to only a small stress for the paper to break (Liukkonen, 1997, Khwaldia, et al., 2010, Garrett & Grisham, 2016).

The porous nature of paper is linked to its rough surface which is defined as the spatial variability in a surface. The interaction of liquids with rough surfaces can be explained using two models (Figure 7).

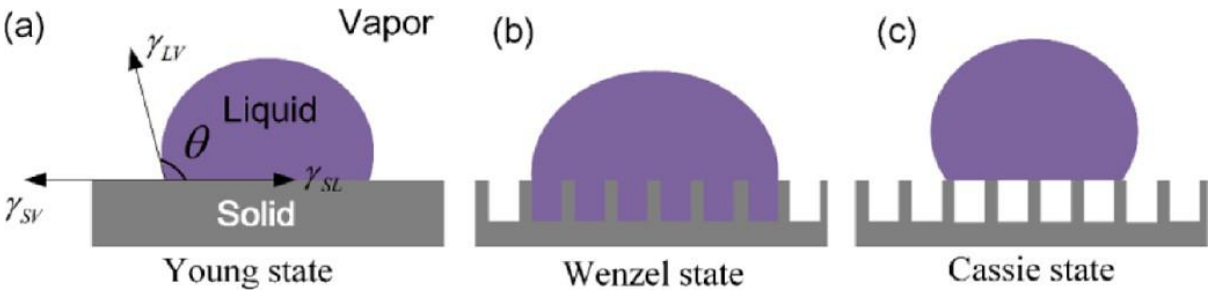

Figure 7: Schematic diagram of: (a) a droplet on a smooth surface, a rough surface in the (b) Wenzel model (c) Cassie-Baxter model. Source: (Chen, et al., 2019)

The Wenzel model (Figure 7b) states that liquid molecules enter groves on a rough surface increasing the solid-liquid interface. In the Cassie-Baxter model (Figure 7c), air pockets form

between the liquid and material surface due to roughness and low surface energy (Ahuja & Rastogi, 2023, Frota, et al., 2022). Studies into the wettability of porous materials has shown that during water saturation, water accumulates in the crevices (Ratrout, et al., 2018).

When a droplet is placed on a smooth surface (Figure 7a) the intrinsic contact angle (ICA) can be calculated using Young's model (Figure 8a). The surface tension can be split into dispersive and nondispersive components resulting in the interfacial energy at the solid-liquid interface being written as Figure 8b.

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \qquad \gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\sqrt{\gamma_{SV}^{d}\gamma_{LV}^{d}} - 2\sqrt{\gamma_{SV}^{h}\gamma_{LV}^{h}}$$

Figure 8: Left (a), Youngs model equation where ϑ is the ICA of the solid surface with a liquid droplet, γ_{LV} is the surface tension of the liquid and γ_{SV} is the surface tension of the solid. Right (b), total interfacial energy equation where γ^{d} represents the surface tension due to London force interaction and γ^{h} denotes the component of surface tension due to dipole-dipole interaction and hydrogen bonds. Source (Chen, et al., 2019)

Additionally, the nature of a rough surface means that substrate curvature changes from area to area resulting in non-homogeneous wettability. Studies of porous materials found that the changes were dependent on pore size. Local variations of pore size over 100µm led to different levels of wettability (Ratrout, et al., 2018). The wetting of the paper leads to the capillary forces holding the fibres together to become too weak to hold them together (Tejado & van de Ven, 2010). These factors cause it to absorb water which will result in the stated loss of functionality.

A similar challenge is oxygen permeability. The introduction of oxygen to the contents of a package may lead to complications such as flavour loss, rancidity and potential microbial infections (Khwaldia, et al., 2010). This is important in a commercial context. The units produced will most likely be in storage for a significant amount of time before being consumed so barrier functionality against gas migration is a serious concern. Solutions to these problems must be developed as barrier properties are essential to ensure shelf life and quality of the contents (Zhang, et al., 2022). Barrier functions are fundamental in separating the external environment from the internal, reducing the rates of chemical, microbial and physical changes (Azeredo, et al., 2017, Khan, et al., 2018).

4.3. Coating solutions and processes

To meet the challenges created by using a cellulose based polymer for a packaging solution, an inner coating of paper bottles has been used. A coating can be used as a protective layer to improve barrier functionality, resistances and shelf life. A coating can cause a material to become hydrophobic by preventing the interaction of water molecules with the cellulose fibres. Depending on the method of manufacturing, the purpose of the container or the manufacturers preference, different methods and types of coatings can be used (Ahuja, et al., 2022, Wang & Lu, 2010)

4.3.1. Coating Materials

Currently, most materials and polymers used in paper alternative packaging products which provide the required barrier properties are synthetic polymers which are supplied via non-renewable sources. These include but are not exclusive to polyolefins and poly(alcohol-co-ethylene), (Rastogi & Samyn, 2015, Vaithanomsat, et al., 2021). Although these materials are effective, they reduce the sustainability of the product. For this reason, other biological-based alternatives are available. The renewable sustainable polymers used in paper packaging products are usually made up of proteins, lipids and polysaccharides either used together or singularly (Khwaldia, et al., 2010).

Proteins cover a large variety of polymeric compounds and have been regularly synthesised into films with advantageous properties (Krotcha, 2002). The options of protein-derived coating materials include milk proteins, whey, soy and zein (corn prolamin), each with advantages and disadvantages. Generally, protein coatings have good oxygen barrier and mechanical properties, however, issues with water barrier functions due to their hydrophilic nature prevent uses in liquid storage. (Avena-Bustillos & Krochta, 1993)

Polysaccharide based coatings are widely available from a variety of easily accessed sources such as algae and chitin. They can form strong films and have good barrier properties. Additionally, polysaccharide coatings are non-toxic and biodegradable. However, similarly to protein-based coatings, unmodified polysaccharides have issues regarding moisture barrier functionality and crystallinity (Nechita & Roman, 2020).

Aside from proteins and polysaccharides, lipid compounds are a third option such as the wax-based coatings (this option is also employed within Pulpex). These are particularly useful in

the coating process due to wax's hydrophobicity. This material is commonly used for food and beverage packaging to increase shelf life and protect from moisture. A waxy coating can prevent the water molecules from binding to the cellulose fibres by physically blocking them. It shields the cellulose by creating a non-polar interface (Wang, et al., 2012). This prevents the water molecules from binding with the exposed hydroxyl groups. A waxy coating can also reduce the surface tension of water when in contact with it. As it is reduced the water forms droplets rather than spreading out along the surface (Li, et al., 2021). Despite this apparent advantage over the other materials, lipids can be brittle and lack homogeneity, leading to cracks and microfractures (Khwaldia, et al., 2010).

4.3.2. Combinations and Modifications

In most cases the individual materials do not possess all the required properties, therefore they are often subjected to modification or combined with other materials. The advantages of both can be used whilst one biopolymer removes the weaknesses of others. Studies conducted with a coating of soy protein with the addition of polyethylene waxes led to improved barrier characteristics (Marzbani, et al., 2021). Other studies have found proteins from tobacco plants can potentially be an effective co-binder to other coating substrates such as a lipid wax (Gutierrez, et al., 2021). Research into chitosan is developing due to natural abundance and antimicrobial properties (Tanpichai, et al., 2022). Additionally, many possibilities of combining them with nanomaterials or other polymers to form bio-composites have been discovered (Nechita & Roman, 2020), (Majid, et al., 2018). The advent of nanotechnology has allowed new ideas on paper coating to be explored. Novel nanofillers allow for additional functionalities to be introduced such as antimicrobial properties (Cha & Chinnan, 2004). The application of nanotechnologies and nanomaterials has revolutionised the coating process. It has reduced the overall cost due to increased efficiency and utilisation of the resources needed (Rastogi & Samyn, 2015).

4.3.3. Methods of coating Application

No uniform coating strategy exists; thus, one must be developed. In the meantime, the coating technique used can vary depending on the chosen method of production. For flexible packages, dip coating can be used. Solvent dispersion is applied. The coating material is dissolved into a solvent. After the coating has been applied the solvent evaporates leaving the desired coating material on the substrate. For rigid paper packages such as paper bottles,

spray coating is used. As a producer of paper bottles, Pulpex employs a spray coating technique. Volatile solvents are used as a dispersing agent to cover the surface of the bottle. A pressure-assisted nozzle is inserted into the bottle (Figure 9) and used to spray the coating from distance. The weight of the coating can be increased with time and pressure (Ahuja, et al., 2022).

Figure 9: Image of spray coating technique used by Pulpex to produce an inner protective coating of the bottle. Source: (Pulpex, 2022)

5. Coating Issues and Characterisation Techniques

5.1. Issues with barrier function and Homogeneity

Although the process of coating is designed to improve the properties of paper pulp, there are multiple complications associated with it. Issues with properties and functionalities have been identified in different types of products from various manufacturers and companies. Pulpex, and similar manufacturers who create moulded paper pulp bottles with an inner coating have had problems with homogeneity and barrier functions to moisture. Due to the porosity of paper, the coating impregnates the surface creating thicker and thinner layers. This causes problems during the drying process regarding mechanical stresses upon the surface, resulting in a loss of barrier functionality due to microfractures along the coating material.

5.2. Imaging and Characterisation techniques

To identify and characterise these surface and coating defects, microscopy and spectroscopy techniques can be employed. Each one can provide a different length scale and this information can then be compiled into a full characterisation profile.

5.2.1. Optical light microscopy

An optical or light microscope is an instrument that commonly uses visible light (Mollring, 1981). A sample is placed on a stage and viewed usually through two eyepieces. A camera can be added to capture images and create micrographs. Optical microscopes can be split into two main classes, simple and compound. A simple microscope comprises of a simple lens which enlarges an image of a chosen object. A compound Microscope incorporates a series of lenses, objectives and eyepieces. This allows for a greater magnification and higher resolution (Blueford, 2016). In this characterisation study, optical microscopy can be used to examine the surface of the coated paper pulp for surface defects and potential damage to the wax coating. It can also be used to provide information on homogeneity, coating thickness, distribution and smoothness.

5.2.2. Confocal Fluorescence Microscopy

Confocal laser scanning microscopy (CLSM) is a technique used in optical imaging to enable taking high resolution micrographs in complex or dense samples. This is achieved by implementing a spatial pinhole to remove out of focus light and improve the image (Pawley, 2006). A sample is inserted with the addition of fluorescent tags, proteins or dyes which can be coupled with antibodies. This allows for micrographs which allow for specific structures to be clearly identifiable (Faklaris, et al., 2022). In a traditional fluorescent microscope, the entire sample is excited resulting in a micrograph with a blurry background. A confocal microscope improves on this design by removing the out of focus signal detected by the photodetector of the system using pinhole and point illumination techniques.

A confocal microscope can provide information on the thickness and homogeneity of the surface of the coated samples. A digital volumetric spectral image can be created via optical tomography. This can allow for three-dimensional visualisation and depth profiling (Lindell & Wetzstein, 2020). It can also examine the penetration of the coating to the pores of the paper

pulps surface, as it can be paired with fluorescent dyes. This can be used to characterise the barrier functions to moisture and gasses.

5.2.3. Scanning Electron Microscopy (SEM)

Scanning electron microscopy is used to acquire images of samples at the micro and nano scale. It is used to create high resolution images of very small samples or specific regions (Eberle, et al., 2015). The process involves scanning the surface of a sample with a focused beam of electrons which interact with its atoms. The electron beam is scanned and the position linked with the intensity of the signal. This produces the image. In conventional SEM, samples are observed through a vacuum. In a variable or environmental SEM, the samples are placed in partial vacuum or wet conditions (Stokes, 2008).

Most samples must be prepared before being placed in a SEM. A Non-conductive sample must be coated with a conductive layer to make them electrically conductive otherwise the sample will accumulate charge. This can cause imaging artefacts and disrupt the imaging process. Conductivity is also important as it stabilises the sample allowing it to withstand the beam of electrons. The most common conductive material added is gold or a gold base alloy, however, other materials such as platinum, tungsten and graphite can be used (Suzuki, 2002).

In a study of paper pulp as a viable alternative for single use bottles and containers, SEM can be used to provide highly detailed images of the surface which can indicate the presence of microfractures or voids in the coating layer. It can show the adhesion of the coating to the paper pulp surface and identify potential contaminants which could hinder the barrier functionality of the waxy coating.

5.2.4. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy is a technique employed to characterise various biomaterials. The infra-red spectrum of a sample is gathered using this technique. High-resolution spectral data can be collected over a large range (Rehman & Bonfield, 1997, Griffiths & de Hasseth, 2007). FTIR aims to discover how much of the light is absorbed by the sample at various wavelengths. A sample is bathed in a beam of light containing various frequencies. After the absorption is measured it is repeated with slightly different frequencies. This process is repeated until the absorption at all the wavelengths can be calculated.

As the light passes through the sample it comes into resonance with different vibrations of the various bonds present. The vibrations can be symmetric, antisymmetric or deformative. The energy detected by the detector is the difference between the energy of incoming and reflected beam (or transmitted beam for the transmission configuration), which is equal to the energy absorbed by the sample. This process can help characterise material properties of a sample.

FTIR can provide chemical information of the waxy coating of the pulp paper. This in turn can provide insight on the chemical bonds present in the coating. The data gathered in the FTIR experiment of the coating can be compared to reference data which allows for comparison and checking of uniformity of the waxy layer.

5.2.5. Contact Angle Measurements

Information on the wettability and surface energy of the coated surface can be ascertained by a contact angle. This angle is usually measured where the liquid-gas interface meets a solid. At the interface the angle results from forces which include, the strength of the interaction of molecules of a similar state (cohesion) and molecules of a different state (adhesion). The contact angle of a substance can be defined as the balance of these forces (Korpela, 2018). It is dependent on the free surface of the liquid and the characteristics of the solid materials with which it is in contact (Shi, et al., 2018). The higher the contact angle the lower the wettability and surface energy. A lower angle indicates hydrophilicity. Multiple studies have corroborated this theory as contact angles ranges of coated paper provided higher ones than uncoated paper. (Tanpichai, et al., 2022), (Ahuja & Rastogi, 2023).

Contact angles in the context of this paper bottle study can provide information on the homogeneity and barrier functions. Multiple measurements can be taken at various locations which can provide information the homogeneity. The differences in angles detected can show the roughness of the surface. The sample can be subjected to a liquid, followed by a measurement. This result can be compared to a dry measurement and checked for similarities in the angles measured. This can indicate the barrier functionality.

6. Conclusion

To summarise, plastic, especially single use plastic products used in packaging is extremely detrimental to the planet and society. The waste and pollution produced poses a serious

threat to ecosystems and the wildlife present in them. Micro and nano plastic are a serious threat as they invade the environment and enter food chains. As cases of micro plastic found in humans are becoming more frequent, the potential risk of human is increasing.

Alternatives to plastics, at this stage of development have issues with barrier functions to moisture and gases. The issues with hydrophilicity and barrier functionality can be solved with the application of inner protective coatings of varied natures. Although the application of a coating vastly improves upon the paper material, there are still technical difficulties o overcome. To find solutions to these issues, the coating must be characterised and analysed using various imaging and characterisation techniques. With these issues resolved, the application of these technologies and products can help in the reduction of plastic pollution. It can be paired with various plastic remediation techniques to remove current plastic waste to resolve the problem at both ends and can assist many companies to reach their sustainability goals.

Acknowledgements

I would like to thank Dr Gleb Yakubov, Professor Steven Harding, the staff of the National Centre for Macromolecular Hydrodynamics and the department of Food Science at Sutton Bonington University of Nottingham for their assistance and guidance during the period of this work.

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Investigating Barrier Functionality of Wax Coatings for Applications in Sustainable Packaging.

Peter Hartman: 20174631

MRes Biomolecular Technology

BIOS4152: Industrial Project and Dissertation

University of Nottingham, School of Biosciences,

Sutton Bonington, LE12 5RD.

Email: Styph2@nottingham.ac.uk

Contents

Abstract

The mechanical strength found in cellulose fibres is highly suitable for packaging. When water makes contact, the strength is lost, due to weakening of van-der-Waals forces resulting in reduced structural integrity. Wax coatings are being considered as a protective layer due to their natural water repellence and biodegradability. There are, however, issues with stress fractures which impact barrier functionality. In this study a rice bran wax based emulsion was formulated and applied via a spray gun to paper samples to investigate the impacts of coating homogeneity on barrier functionality. Initial findings via fluorescence microscopy showed that inhomogeneous surface coatings correlate with a weak barrier function as evident from high water permeability throughout the paper. To perform a systematic investigation of the wax deposition process, the effect spraying temperature on. the surface morphology and permeability was conducted. Scanning electron microscopy and Raman confocal spectroscopy were used to visualise the wax layers. Analysis showed the number of fractures, pores and cracks present decreased with the increase of curing temperature. The hydrophobicity of the samples were tested, and again the curing temperature had a positive correlation with barrier functionality against moisture. The results of this study and the methodologies developed provide a powerful platform for investigation of surface coatings used in direct-contact packaging applications.

1. Introduction

There is an urgent need to shift from petroleum-based plastics to sustainable materials for single-use plastic products. The packaging industry heavily relies on plastics due to its numerous advantages, such as malleability, reduced weight, and cost-effectiveness (Macarthur, 2017, Schneiderman & Hillmyer, 2017). However, the mismanagement of plastics, particularly petroleum-based ones, has resulted in high levels of pollution and waste.

In 2021, the global plastic production reached 390.7 million tonnes, with an estimated annual waste generation of 368.7 million tonnes (Tiseo, 2023, Alves, 2023). The packaging industry alone accounts for almost 50% of the world's plastic waste (Geyer, et al., 2017). Despite efforts to increase plastic recycling, approximately 9%-15% of plastics are recycled, while a significant

portion 12-14% is incinerated, and 72-79% ends up in landfills or leaks into the environment (Geyer, et al., 2017, United Nations Environment Program, 2018). The impact of plastic debris on various animal species, as well as the rising concern about micro and nano plastic particles affecting human health, further highlight the urgency of addressing this issue (Kuhn & van Franeker, 2020, Ragusa, et al., 2021).

Additionally, the production of petroleum-based plastics contributes to greenhouse gas emissions and exhausts the global crude oil supply. Approximately 280-360 metric million tonnes of emissions result from converting petroleum carbons into plastics (Dees, et al., 2021). Growing concerns have resulted in an increased demand for biodegradable materials from sustainable sources (Jakubowska, et al., 2023, Rojas-Lema, et al., 2023).

Cellulose, an abundant naturally occurring polymer derived from wood pulp (comprising 40-50% of wood), presents a promising alternative to single-use plastic products. Pulpex Ltd. is a paper bottle company which aims to take advantage of this material to replace plastic. Cellulosic substrates exhibit favourable mechanical properties, cost-effectiveness, lightweight nature, and biodegradability (Dhall & Alam, 2020, Marzbani, et al., 2016). Biodegradability is particularly crucial for an alternative material, as plastic particles can take centuries to break down in the environment. However, using cellulose for packaging liquids poses some challenges due to its hydrophilicity and poor barrier functions against gases (Derluyn, et al., 2007, Jabeen, et al., 2015, Derluyn, et al., 2008).

One solution used by Pulpex Ltd and others to address the limitations of cellulose is to apply a wax based coating to alter the surface topography (Litvinov & Farnood, 2006). This coating aids in controlling the topography and chemistry of the surface, impacting the wettability by improving barrier function against water and gas (Li, et al., 2007). It prevents water molecules from binding with the cellulose's hydroxyl groups, creating a non-polar interface (Wang, et al., 2012, Dunn, 2015). The low surface energy of the wax surface also enhances hydrophobicity, causing water droplets to form on the surface rather than spreading (Li, et al., 2021). Studies on coating paper with wax use a variety of waxes including, shellac wax, beeswax, candelilla or rice bran wax (Ahuja & Rastogi, 2023, Liu, et al., 2019).

This study aims to explore the use of cellulose paper pulp with a wax based coating as a replacement for single-use plastic bottles, focusing on the case study of Pulpex Ltd. An

emulsion based on rice bran wax was selected. The effect of a wax coating applied via aerosol to a simulated pulp paper bottle was studied. The effect of spraying time was evaluated to find appropriate variables for further analysis. Once this was established, the investigation of the effect of curing temperature on the wax emulsion coating before application to the paper substrate was conducted. The wax emulsion was applied to Whatman filter paper, as it is similar structurally to Pulpex's paper bottles, using a spray gun, and a comprehensive characterisation experiment of the coated paper was conducted using various imaging and characterisation techniques.

2. Methods

2.1. Formulation and Coating

A 4% wax and 10% emulsion were formulated and emulsified, comprised of rice bran wax and rapeseed oil, using a Silverson L5M heated to 90°C. The resulting emulsion was applied to Whatman 4 filter paper using a Gocheer Upgraded Airbrush, maintaining a fixed pressure of 30PSI and a working distance of 15cm. The spraying time were set at 10, 20, and 30 seconds. Following initial analysis, all further investigations were conducted exclusively using a spraying time of 30 seconds.

Subsequently, the formulation was cured at three different temperatures prior to application: room temperature, 62°C, and 80°C. Curing was performed in a convection oven for a minimum of 24 hours before application. The needle size for spraying was fixed at 0.5mm. Following the spraying process, the samples were dried in an at 30^{o}C for 40 minutes.

2.2. Fluorescence Microscopy

To examine the permeability of the paper coating, fluorescence microscopy was selected. The samples were treated with a double-stained emulsion containing two dyes: Nile Red, which binds to oil droplets, and Calcofluor White, which binds to cellulose. This combination of dyes allowed for the visualisation of the interactions between the coating and the paper.

Using an EVOS fluorescent microscope, flat surface and transverse images of the samples were captured. These microscopic imaging methods provided valuable insights into the distribution

and penetration of the coating within the paper structure, shedding light on the effectiveness and permeability of the applied wax emulsion.

2.3. Scanning Electron Microscopy (SEM)

The surface and penetration of the coatings were observed on a Quantas 600 MLA electron microscope operating at a voltage of 5 kV. The samples were coated with 10-15 nm of gold using a sputter coater for better conductivity resulting in an enhanced image. Images were quantified using ImageJ analysis software, analysing mean pore and microfracture size, area and frequency.

2.4. Cryostat Microtome sectioning

To obtain more information about the impregnation of the wax coating on the paper samples, cryostat microtome sectioning was performed. Samples sprayed for 10, 20, and 30 seconds were subjected to this sectioning process for analysis and to determine the optimal spraying time for further testing. The sectioned samples were imaged and analysed using SEM.

2.5. Raman Confocal Spectroscopy

Chemical analysis was conducted via the use of Raman spectroscopy to analyse the heterogenous nature of the coatings within the bulk of the cellulose fibre matrix as well as the homogeneity of the coating itself. A Horiba Raman microscope with a 50x objective was used, calibrated to the 785nm laser with a grating of 300. A 5s time was chosen as well as 5 accumulations with a spectral array of 100-3100.

2.6. Mass Measurements

To assess the absorption of the wax coating by the paper, mass measurements were conducted. Prior to applying the coating, the sample masses were measured using a Sartorius universal scale. After coating, the wet mass was immediately re-measured. Subsequently, the samples were dried in an incubator, and the dry mass (DM) was measured. The absorbance was then calculated as the percentage of mass gain determined by equation 1.

$$X = \frac{DM - PreM}{PreM} \, x \, 100$$

Equation 1: PreM – Pre coating mass, DryM – Post drying mass

2.7. Contact Angle Measurements

To evaluate the hydrophobicity of the samples, a sessile drop test was performed using a pendent drop instrument (Sinterface PAT1). The samples were positioned flat on the sample holder, and a 5µl water droplet was carefully placed at the centre of each disc using a pipette. Images of the water droplets were captured and subsequently analysed using open-source software (opendrop 3.3.1) to determine the contact angle.

2.8. Water Absorbance Test

To determine the water absorbance of the temperature dependent samples, water droplets were placed on the surface of the samples using a Gilson pipette (P1000). The masses of the samples were measured using a Sartorius universal scale before and after 15 minutes. A dry paper towel was used to blot any remaining droplets off the surface before the mass was re-measured.

2.9. Data Analysis

Statistical analysis was performed to test normality, identify and remove outliers (Shapiro-Wilks) and variance of data with the aid of PRYZM graph pad software. Significant differences were tested using T-tests and one-way ANOVA tests.

3. Results and Discussion

3.1. Microscopical Characterisation

3.1.1. Fluorescent Microscopy

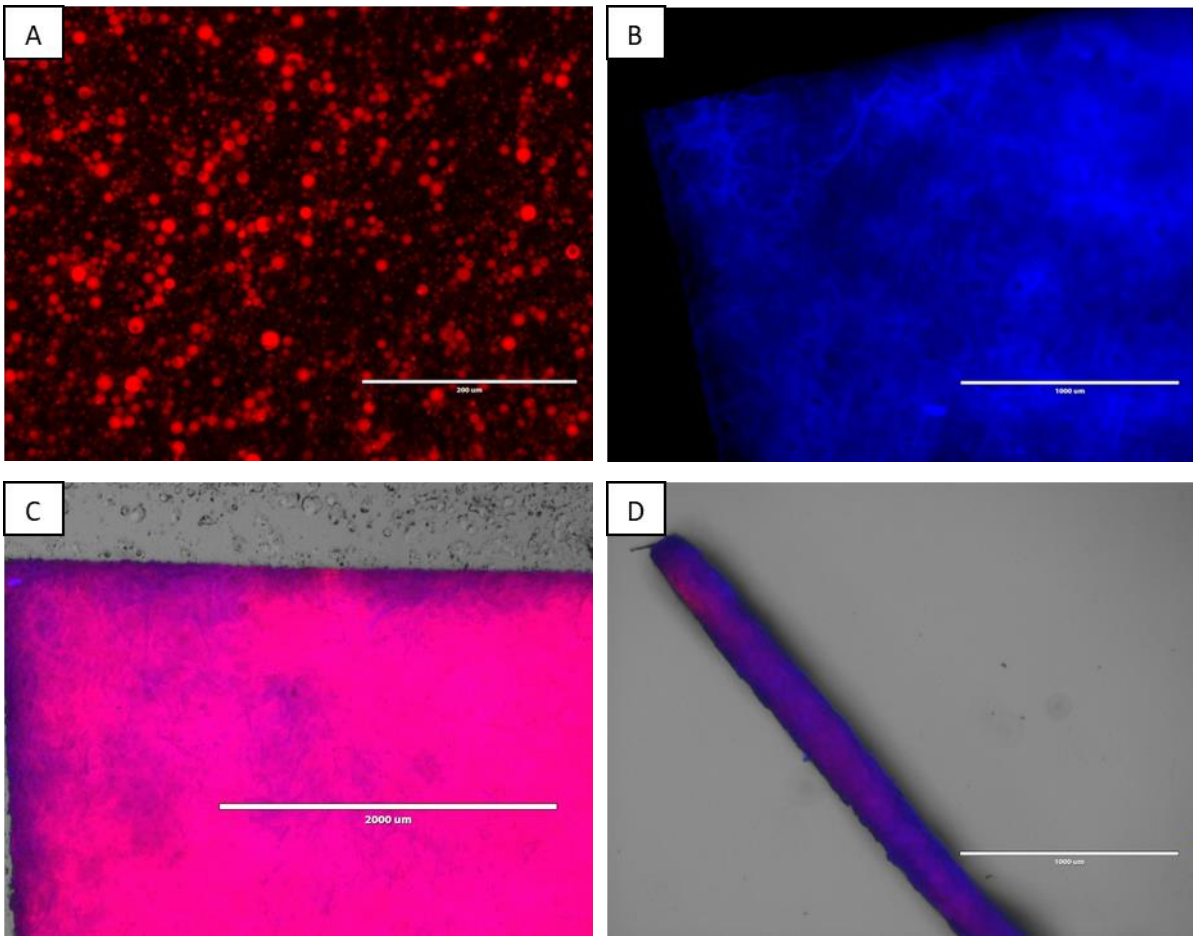


Figure 1: Fluorescent Micrographs of coated paper. A – stained oil micro-droplets in emulsion stained with Nile Red, B – Paper with stained cellulose fibres, C – overlayed surface image of double stained paper, D – Transverse image of double stained paper.

To gain further insight into the homogeneity and permeability of the coating, fluorescent microscopy paired with two dyes, Nile red and Calcofluor white, was conducted. Figure 1 shows the effect of the stains on the emulsion, cellulose fibres and the coating when it was applied. Figure 1A and B highlight the effect of the dyes on the emulsion and cellulose respectively. The images clearly show the oil droplets in the emulsion highlighted in red where the dye has stained. This demonstrates how Nile red will fluoresce in a lipid rich environment (Greenspan, et al., 1985). The addition of Calcofluor white results in the blue fluorescence observed in figure 1B, showing that the dye binds to the 1-3 beta and 1-4 beta polysaccharides

present in cellulose resulting in the shown fluorescence (Bidhendi, et al., 2020, van de Meene, et al., 2021).

Figure 1C illustrates the uneven distribution of the coating across the paper surface. This phenomenon supports the hypothesis suggesting that the paper's rough texture contributes to an irregular coating layer. Regions with thicker coatings are identifiable by their heightened fluorescence, while areas with thinner coatings exhibit less intense fluorescence and reveal blue-stained cellulose fibres on the surface. As discussed in the literature, this lack of homogeneity is a credible reason for the poorer barrier functionality against water (Debeaufort, et al., 1998). The presence of protruding cellulose fibres can act as potential moisture absorption points, compromising structural integrity. Furthermore, variations in coating thickness result in differing hydrophobic properties among these different areas.

The permeability characteristics of the coating are visually depicted in Figure 1D. The image shows a discernible spread of the red-stained emulsion, across the entirety of the paper. This visual representation underscores the successful integration of the coating into the cellulose fibre matrix, illustrating the pathways through which the wax emulsion permeates the paper. Moreover, this observation provides insight into the variance in coating thickness, as indicated by the varying fluorescence in the double-stained samples. The progression of the emulsion throughout the paper not only reinforces the concept of permeability but also sheds light on the distinct levels of thickness within the coating. It also reinforces the idea that the coating thickness is an important variable in the barrier functionality of a surface.

3.1.2. SEM as a function of Spraying Time

To investigate the most suitable spray time, the surface morphology at three different spraying times was studied. A preliminary study was conducted. The three spraying times were selected and the results analysed to determine the most suitable. Additionally, sections were cut using a cryostat microtome to investigate the penetration of the coating under the three different spraying time conditions.

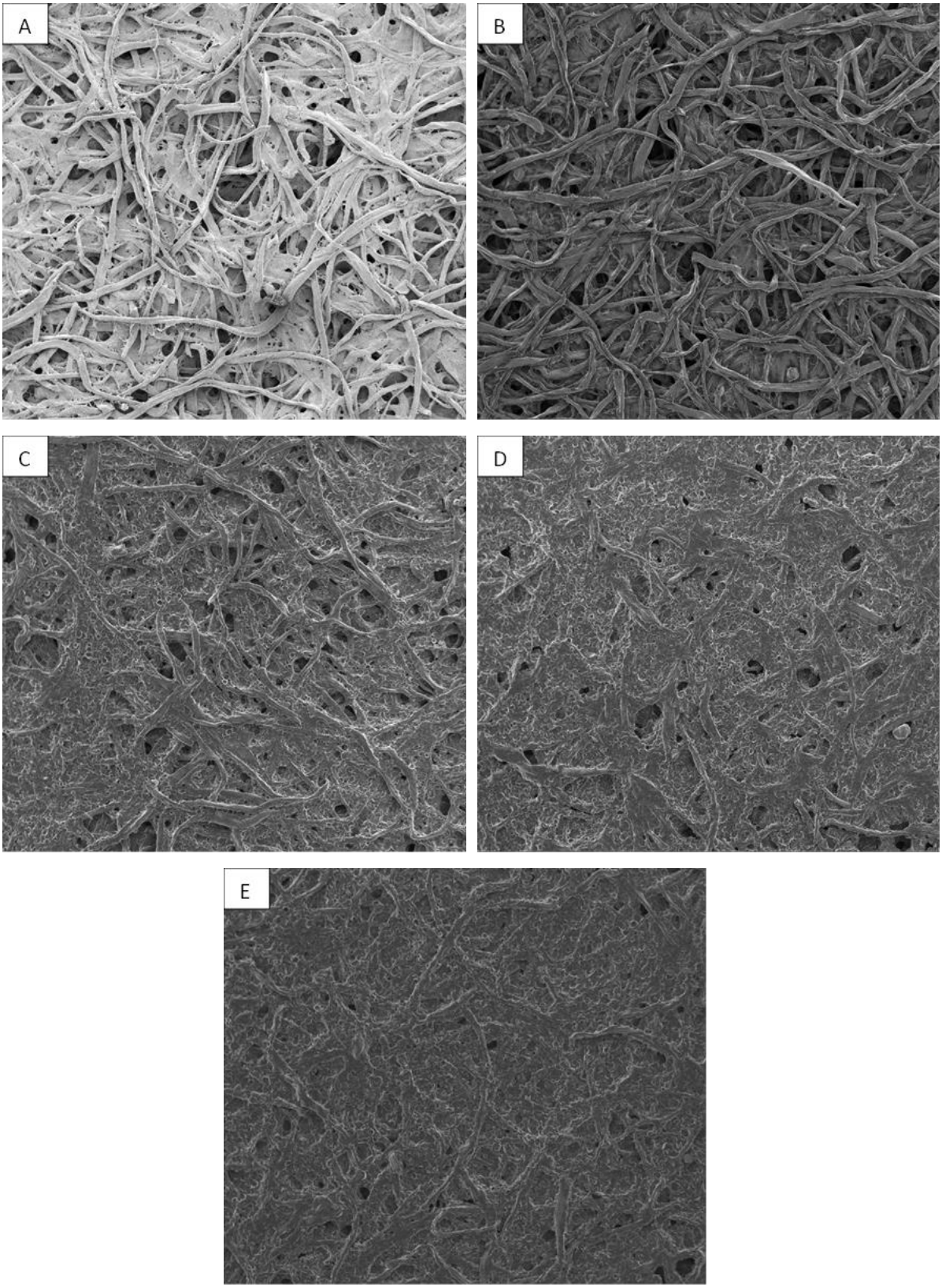


Figure 2: Scanning Electron Micrographs showing surface morphology at a magnification of 100x with a voltage of 5kV and spot size of 5.0. A – Water control (30 second spray time), B – Serum (no wax) control (30 second spraying time), C – Wax emulsion samples with a 10 second spraying time, D – Wax emulsion samples with a 20 second spraying time and E – Wax emulsion samples with a 30 second spraying time.

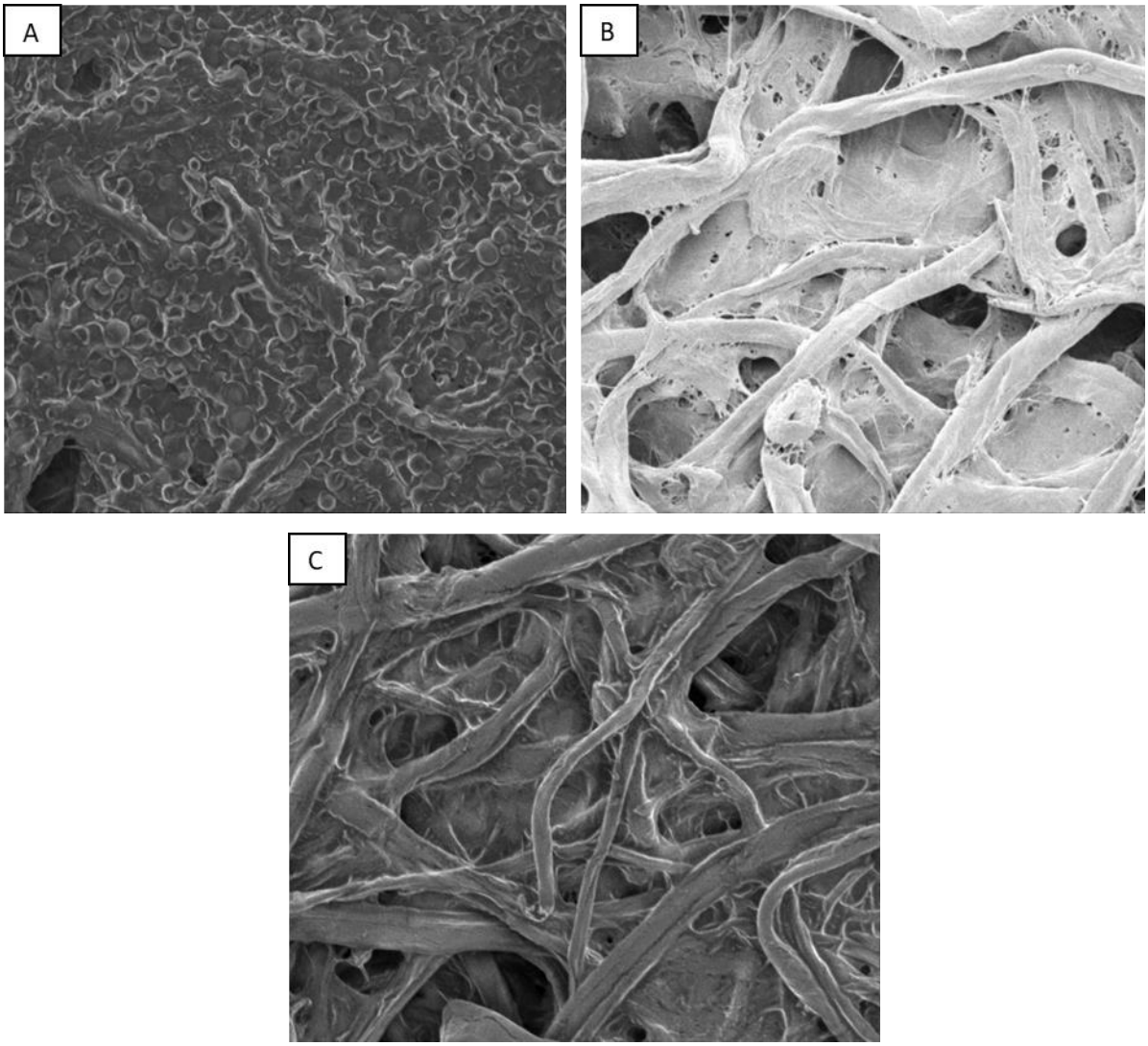


Figure 3: Scanning Electron Micrographs showing surface morphology at a magnification of 425x with a voltage of 5kV and a spot size of 5.0. A - Wax emulsion samples with a 30 second spraying time, B - Water control (30 second spray time), C - Serum (no wax) control (30 second spraying time). Micrographs show the contrast of the individual wax particles on paper against wax free cellulose fibres on controls.

The wax emulsion and two controls, water and serum (no wax) were sprayed onto filter paper. As they made contact with the surface of the paper, the droplets adhered to the surface forming wax particles, creating a layer over the surface. This phenomenon can be observed in the scanning electron microscopy micrographs, as shown in Figure 2. Additionally, the individual wax particles can be clearly seen in Figure 3. This aligns with other wax coated paper studies, (Ahuja & Rastogi, 2023). For the two controls, (Figure 2A and 3B) and (figure 2B and 3C), the cellulosic fibres are visible without the presence of the wax particles. The structures presented on the micrographs are consistent with the literature regarding the fibrous composition of paper and the lack of uniformity. Multiple studies have documented the fibrous network of paper and the porous structure (Alava & Niskanen, 2006, Banerjee, et al., 2009). The serum control shows a clear contrast which can be observed when compared to

the water control. The potential reason for the differences in images could be due to the oil adhering to the fibres.

From Figure 2, a clear positive correlation can be observed between spraying time and coverage of the coating. A ten second spraying time (figure 2C) shows multiple cellulose fibres still present as insufficient coating has been applied for complete coverage. This makes it difficult to identify whether the cracks and pores have been created by stress related reasons due to the roughness of the surface or the lack of coating. Figures 2D and E show that the increased spraying times results in an improved coating.

3.1.3. Transverse Images

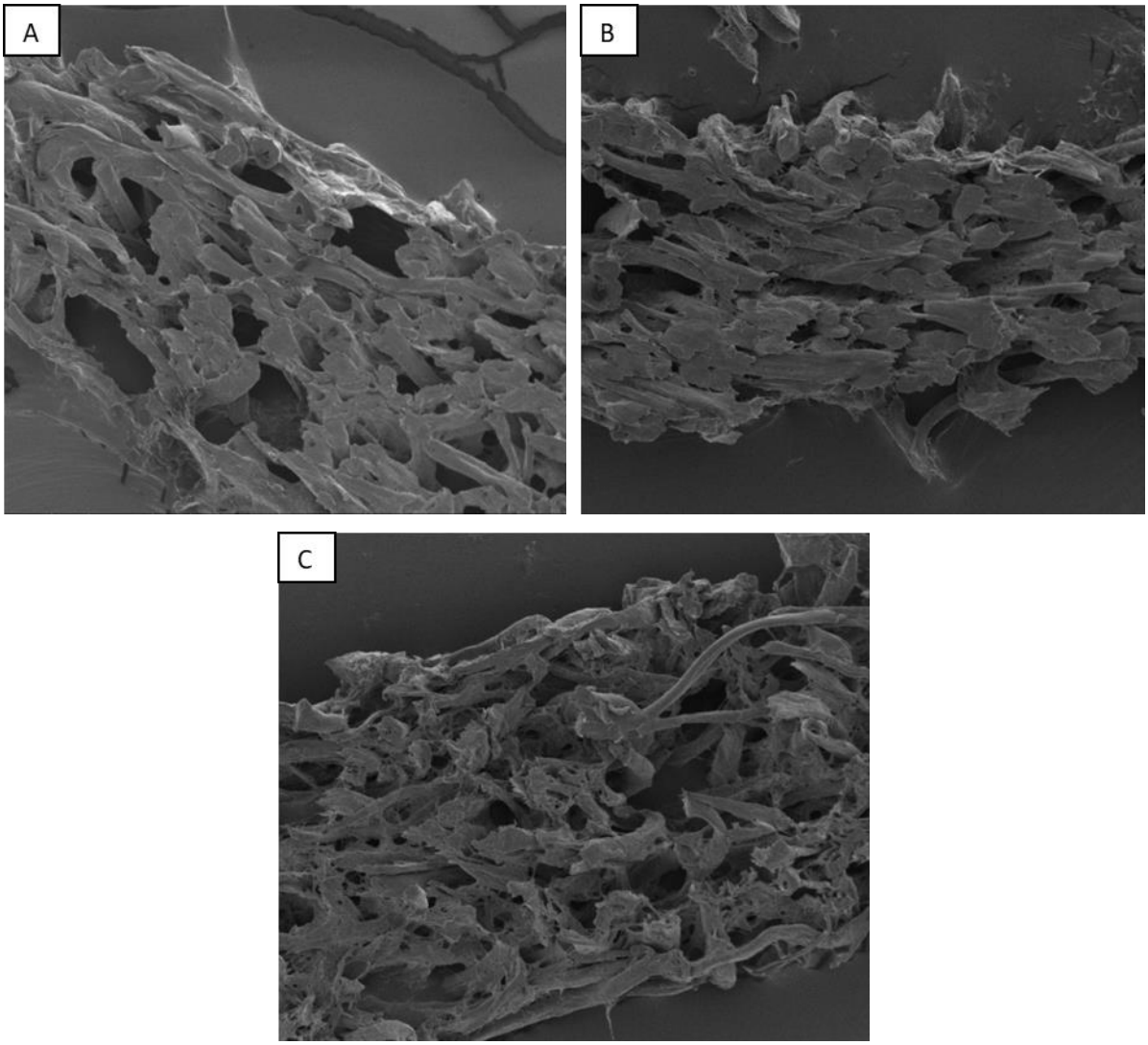


Figure 4: SEM Micrographs showing transverse images at a magnification of 300x with a voltage of 5kV and a spot size of 5.0 of wax emulsions: A – 10s spraying time, B – 20s spraying time, C – 30s second spraying time.

An attempt to visualise the permeability of the coating by the paper was conducted via a cryostat microtome and SEM. Overall the results shown in Figure 5 were inconclusive as a clear penetration by the coating was unobservable with these combined techniques. A layer of coating can be seen on the surface of the micrographs, however, evidence of penetration was inconclusive from observation.

The sectioning techniques themselves may be the reasoning behind the poor quality of results as the processes may lead to the swelling of the cellulose fibres to a point where the coating is removed or blocked. SEM does not provide a good enough contrast between the cellulose and coating for this particular experiment. Further studies and development of this method should be explored. Potentially a thicker layer of wax on the surface may show a clearer distinction and can be combined with other forms of analysis, particularly Raman or FTIR.

Overall, the study of spraying time and its effects on the surface of paper provided insightful conclusions. The increase in time has positive effects. Further increased spraying times were not selected due to the significant amount of coating waste. The threshold of efficiency was located at a 30 second spray time. Therefore, this time was selected for further study.

3.1.4. SEM Characterisation as a function of Temperature

Subsequently, an investigation into the impact of curing temperature on the wax emulsion prior to spraying was carried out. This exploration aimed to assess its effect on both the adhesive properties of the coating to the paper and its effectiveness in providing a barrier against moisture. This included a comprehensive evaluation of adhesion, moisture resistance and uniformity.

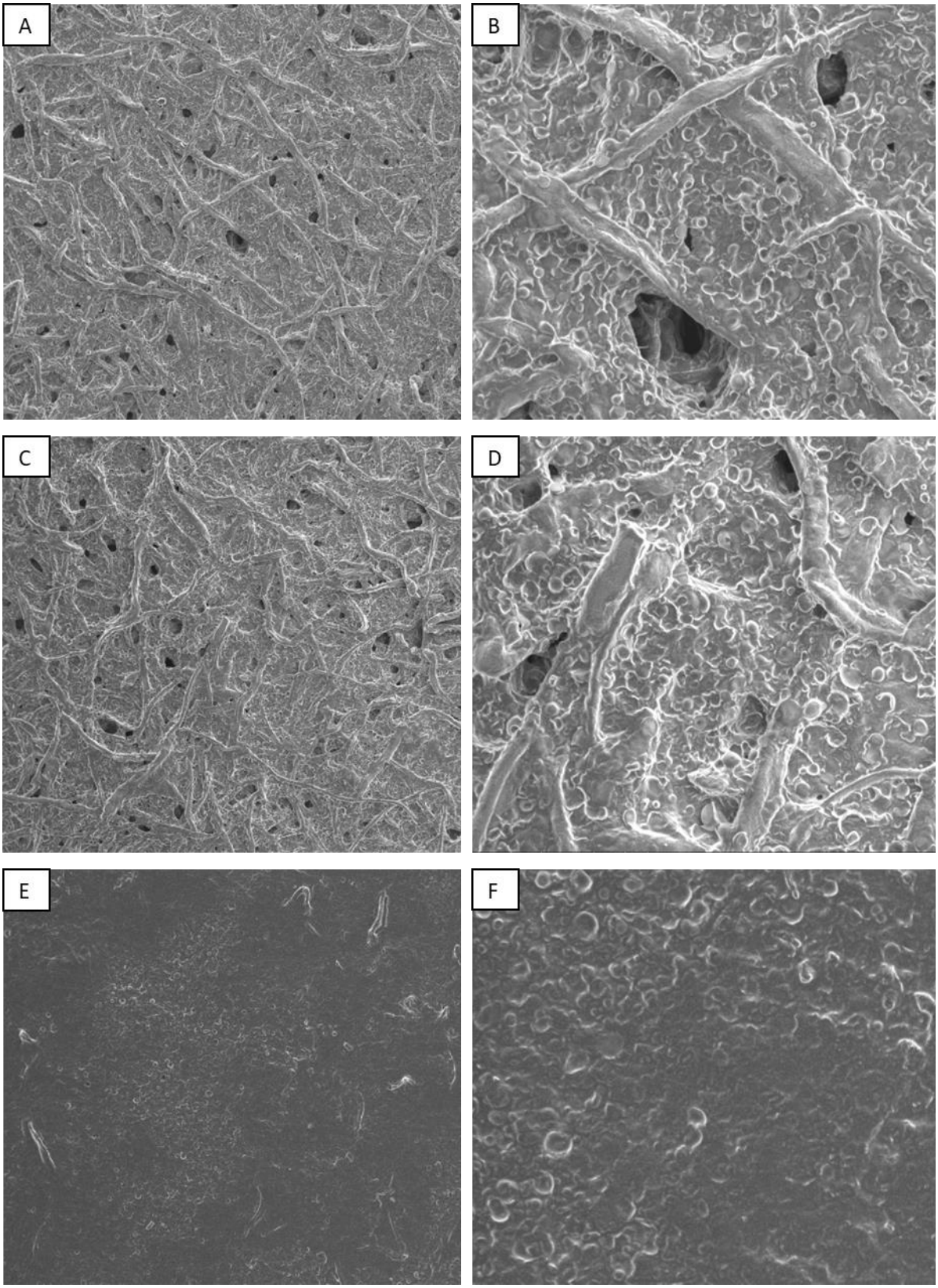


Figure 5: SEM micrographs of wax coated surface of paper at magnifications of 100x (A, C and E) and 425x (B, D, F), with a voltage of 5kV and spot size of 5.0. A and B – emulsion applied at room temperature, C and D – emulsion applied after curing at 62^{o}c, E and F – emulsion applied after curing at 80^{o}C.

The wax was cured at room temperature (RT), 62^{o}C and 80^{o}C before being applied to the paper. At room temperature and at 62^{o}C, the wax particles can be clearly seen (Figure 5A, B, C and D). In addition, the surface morphology of the two temperatures did not appear different, although the total number of pores was reduced. A significant number of them can still be seen at 62^{o}C indicating that this temperature does not result in any significant changes in the morphology of the wax layer on the cellulose matrix.

Heating the wax to a temperature of 80^{o}C yielded notable alterations in surface morphology. Figure 5E and 5F distinctly illustrate a more consistent and substantial coating layer and a significant reduction in the presence of cellulose fibres was observed. The elevated temperature induced the melting of the surface wax, prompting a more uniform distribution across the substrate's surface and resulting in a more continuous and cohesive layer. This outcome effectively concealed the fibrous structure of the paper, evident in Figure 7F. Additionally, the individual wax particles were considerably less pronounced.

This outcome aligns with findings from similar temperature-related investigations, which corroborate the observed effects at 80^{o}C, accompanied by a notable decline in the occurrence of pores and cracks (Rastogi, et al., 2014). Rice bran wax has a melting point of 78-81^{o}C, highlighting why less uniform coatings at lower temperatures and heightened distinctness of individual wax particles were observed (Dassanayake, et al., 2009).

3.1.5. ImageJ Analysis

The number of micro-fractures and general porosity of the samples was quantified using ImageJ analysis software. 10 locations on the samples were selected at random and analysed. To limit technical errors by the software a threshold of 0:50 was selected and the particle analysis settings were set to 50µm^{2} due to individual wax particles being mistaken for fractures. Table 1 and Figure provides quantitative data based on the images collected using SEM.

Table 1: ImageJ data of SEM images with wax coatings as a function of spraying time with two controls. WC and SC stand for water and serum (no wax) controls respectively. 10s, 20s and 30s signify time of application of the wax coating. RT, 62 and 80 signify curing temperature of emulsion.

	WC - RT	SC- RT	10s - RT	20s - RT	30s - RT	30s - 62oC	30s – 80oC
Pore Frequency	**490.4**	**290.4**	**185.7**	**142.9**	**114.4**	**44.7**	**9**
SD	54.6	30.4	20.7	29.1	46.6	8.6	7.4
Total Area of pores/ µm²	**127134.2**	**74941.2**	**38077.7**	**30665.9**	**20708.2**	**6751.7**	**1510.3**
SD	20347.4	10734.8	5529.4	8369.8	20708.2	1859.07	1267.9

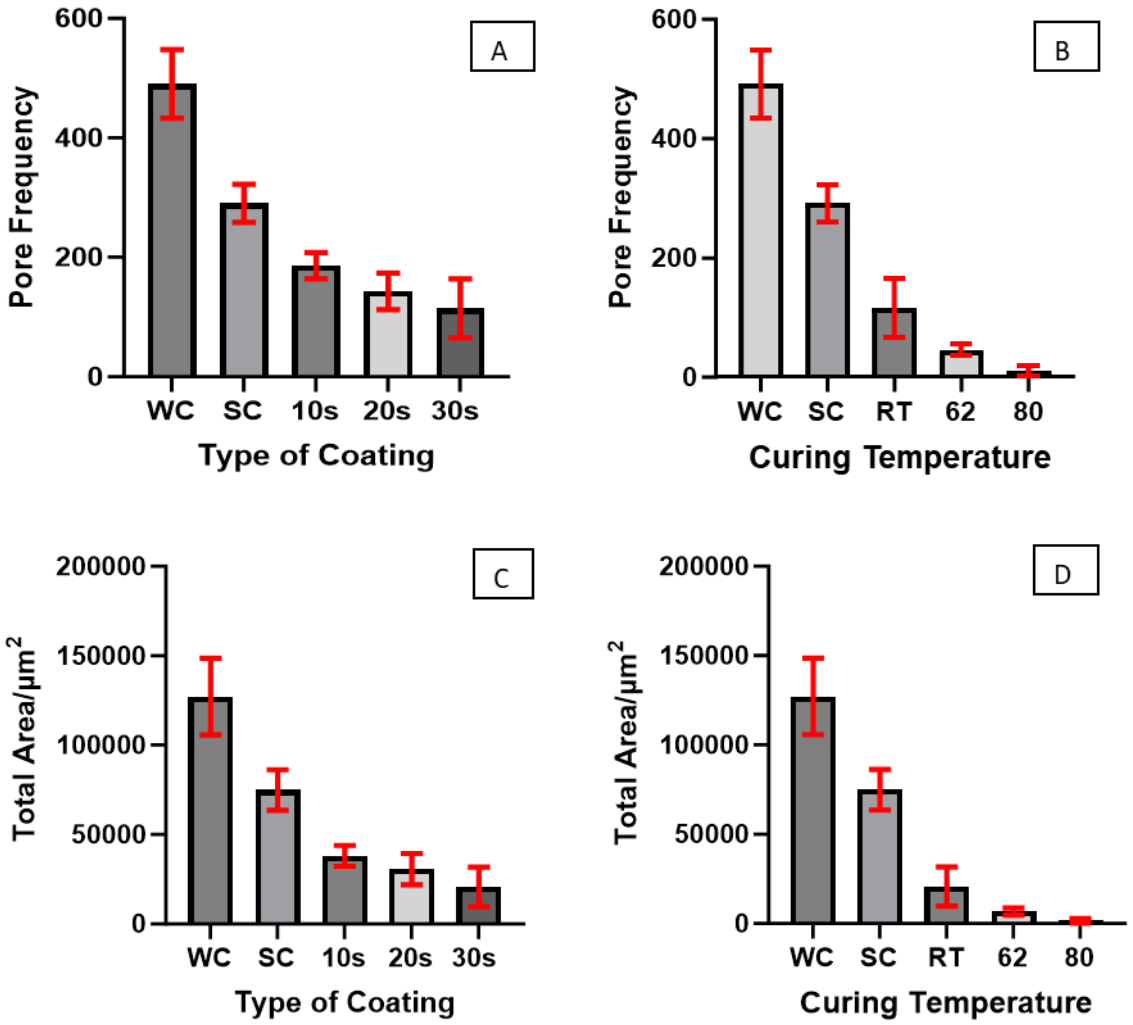


Figure 6: Quantification of SEM images. Histogram with standards error bars highlighting the effect the wax coating on: A - the frequency of pores/ cracks, B – the total area of pores/ cracks on the surface of the paper samples as a function of spraying time. WC and SC stand for water control and serum (no wax) controls respectively. C - the frequency of pores/ cracks and D – the total area of pores/ cracks on the surface of the paper samples as a function of curing temperature. 10s, 20s and 30s are relevant to the time allocated to spraying. RT, 62 and 80 indicate curing temperatures of the coating.

The data (Figures 6A and C) are presented in the format of mean pore frequency and (Figure 6B and D) mean total area. Figures 6A and C show that the application of the wax emulsion coating results in a dramatic decrease in the frequency of pores, cracks and fractures, as well as the total area of pores. Additionally, the increase in time of application has a negative correlation with regards to frequency and therefore area of pores and micro-fractures in the surface of the paper. As stated earlier the decrease is due to the increased amount of coating applied therefore more wax nanoparticles are able to adhere to the fibres providing the better coating.

Similarly, a negative correlation can be observed between an increase in curing temperature of the wax coating and both the frequency and total area of the samples. This can be seen with the decrease in both area and frequency (Figures 6B and D) when compared to the controls as well as the between the temperature samples. The effect of viscosity can be credited. The increase in temperature results in a reduced absolute viscosity of rapeseed oil and water. These are major components of the emulsion used in the formulation of the coating selected for this study (Diamante & Lan, 2014, Korson, et al., 1969). The melting of the rice bran wax is likely the factor for the changes observed and resulted in a far more uniform layer of coating.

The standard deviation for the controls was relatively large. The larger variance of the controls is due to the inhomogeneous structure of the net of cellulose fibres. The randomness of the organisation resulted in a percentage of the images collected for analysis being more porous than others. At 30s, at room temperature, again the SD bars, noted in Figures 3A, B, C and D, are larger. The data set possessed higher variation. This may be due to mechanical and technical errors in the coating process, or in the structure of the particular paper samples. However, the randomness of the locations selected for analysis may be the cause. These may have been areas of poorer coating adherence or possess a rougher surface resulting in the presence of more cracks or pores. At a temperature of 80^{o}C (Figures 6B and D), the SD bars are also large in comparison to the range collected. The cause is likely due to the effect of sectioning of the paper sample in preparation for the SEM analysis. The cutting of the sample to size is likely to cause large fracturing in the areas of contact. This fracturing could result in the increase in pores and cracks detected by the analysis software. Other possible reasons could be technical issues with the spraying, or the rough surface of the paper leading to areas

of poorer coating adhesion. Due to the higher quality of coating applied, the contrast is more extreme resulting in the variation of data shown.

Statistical analysis in the form of a one-way ANOVA has shown that there is a significant difference ($P<0.0001$) between the types of coating applied, the frequency and total area of the pores. Individual T-Tests were conducted to gain further insight between each individual spraying time variable and the controls for both. Again, they all showed significant differences between each individual coating when compared against the controls.

3.2. Raman Microscopy and Spectroscopy

A feasibility experiment using Raman spectroscopy paired with an optical microscope was used to gather surface and chemical information. Raman spectroscopy enables chemical bonds to be analysed via light scattering due to changes in the polarizability of the chemical bonds and functional groups present in the material. Additionally, the use of the optical microscope, allows for further analysis into the effect of the wax coating on the surface of the paper.

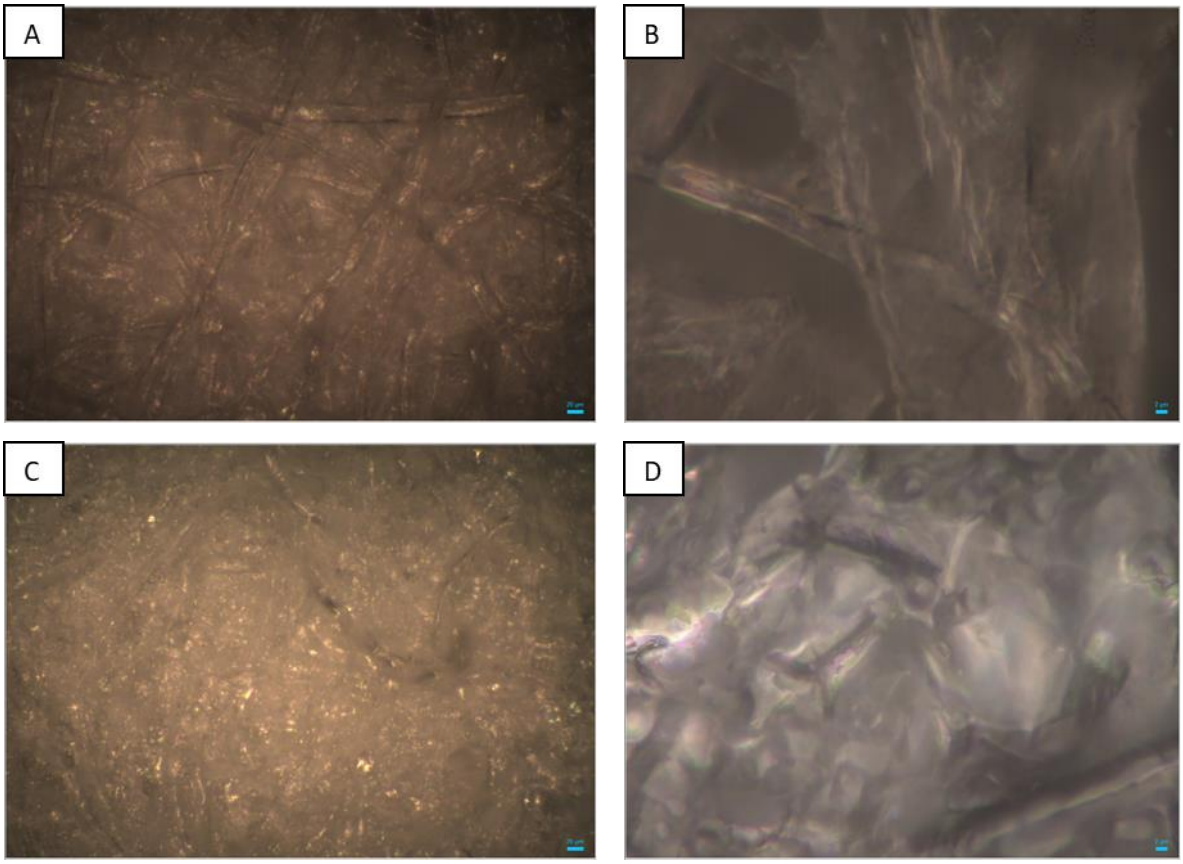
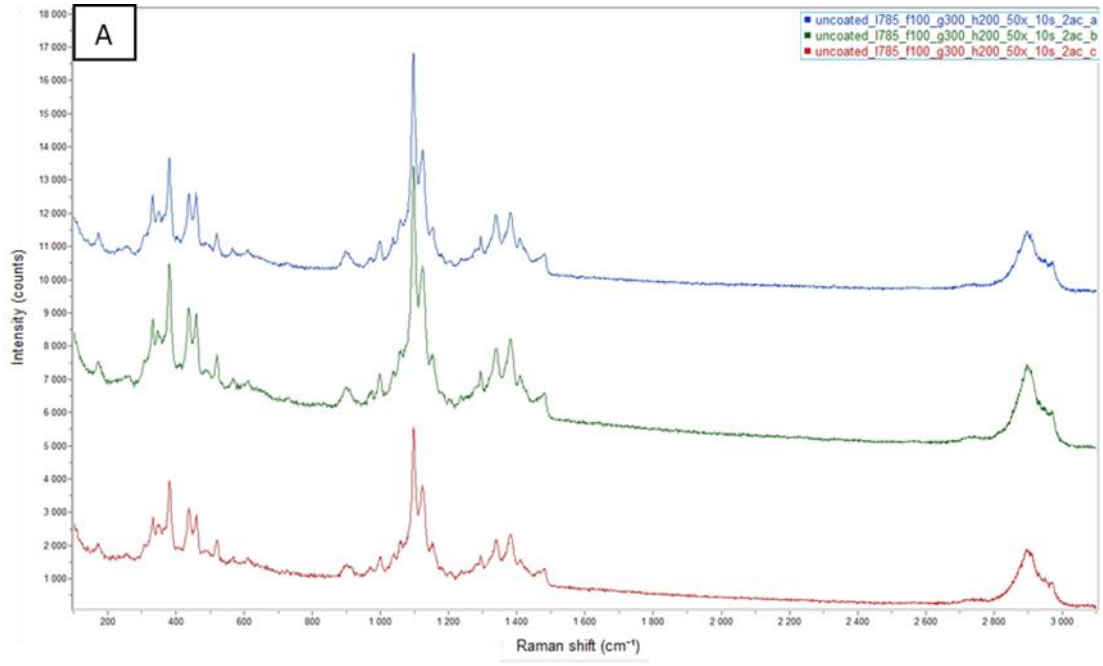


Figure 7: Optical Micrographs from Raman Microscope. A – Uncoated paper at 10x magnification, B – uncoated paper at 100x magnification, C – 80^{o}C cured wax coated paper at 10x magnification and D – 80^{o}C cured wax coated paper at 100x magnification.

The cellulose network (Figures 7A and B) is observable without the coating and highlights the lack of uniformity on the surface of the paper sample. The application of the wax coating cured at 80^{o}C has a clear effect on the surface. At both 10x and 100x magnification the fibres are covered by the wax crystals. Although the shape of cellulose fibres can still be seen they are obscured by the coating.

Although it has positive attributes, the use of optical microscopy makes it difficult to determine the exact location of the pores and microfractures. The cellulose fibres can be visualised but it can be difficult to observe whether it is underneath the coating layer or seen through a gap created by the associated stresses with drying and inhomogeneity. A further investigation was conducted to gain chemical information on the two samples. The use of the spectrometer resulted in the spectra shown in Figure 8.



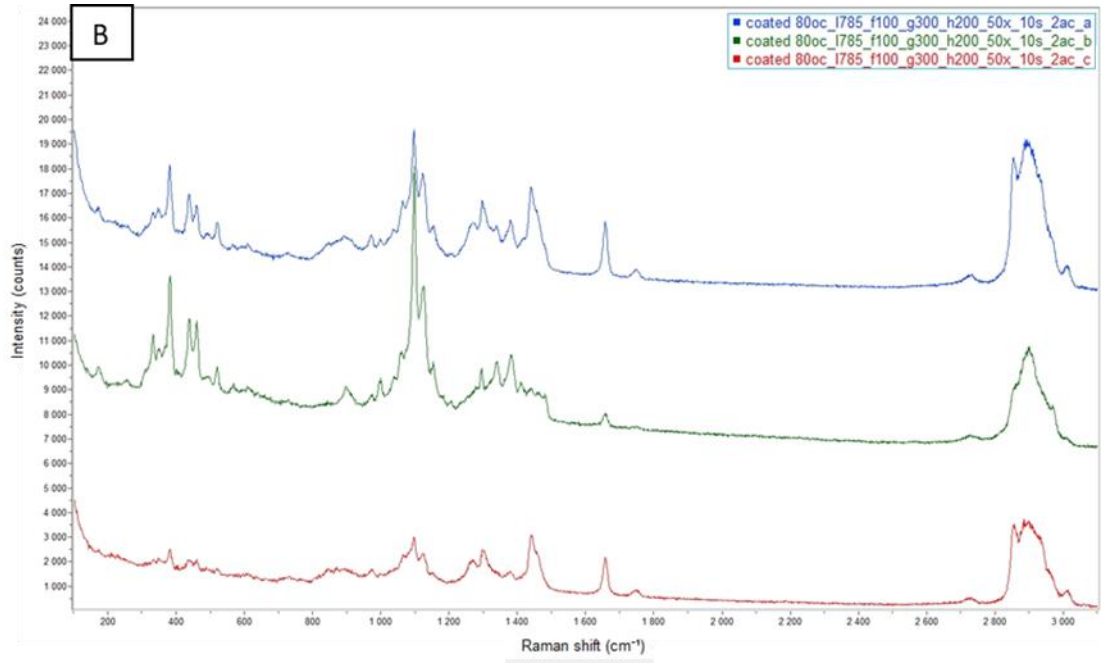


Figure 8: Raman spectra of the: A – Pure cellulose, B – 80°C cured wax emulsion coated samples.

Figure 8A displays the spectra of pure cellulose. An observation is that there is very little variation between spectra. This suggests that there is high homogeneity (as expected). The structure of the paper is purely cellulose with no contaminants present. A strong peak is detected at 1100 cm^{-1}, which correlates to a C-C stretching vibration. It also indicates the presence C-O bonds as these range on a spectra of between 1000-1300cm^{-1}. Both of these peaks are clear indicators that the sample is cellulose. At around 2900cm^{-1} another peak was detected. This is consistent with the literature in signalling the detection of C-H stretching vibrations. In addition, the specific nature of the peak to 2850 to 2960cm^{-1} is clear evidence that the C-H bonds present are Aliphatic. The spectra collected in this experiment are consistent with the literature (Public Spectra, 2019, Adar, 2016).

After the introduction of the wax emulsion, new peaks were detected. The spectra (Figure 8B) are similar to the pure cellulose spectra indicating that the coating is not homogenous, and thin. This is consistent with other techniques employed in this study. The composition is mostly cellulose however, several new bands have emerged. These include C=C and C=O stretches at 1657 and 1748 cm^{-1}. These are clear indicators of unsaturated fatty acids i.e the rice bran wax (Laser Spectroscopy Labs, 2023). Another observation is that the three spectra in Figure 8B are not identical, therefore mapping, univariate (UVA) and multivariate curve resolution (MCR) analysis were required to gain further understanding.

The results of the UVA concluded that the wax coating sits predominantly within the cellulose fibres and confirms that the coverage of the coating is inhomogeneous. This supports the hypothesis stated for this study. MCR has shown that although the coverage of the coating is inhomogeneous the coating itself is homogenous. This is conformation that the emulsion has no phase separation between the wax crystals and liquid oil which comprise it.

3.3. Coating Absorption (Mass Measurements)

To assess the effect of curing temperature on the adhesion of the wax emulsion to the paper, the masses were recorded both before treatment and after drying. The increase in mass as a form of a percentage was calculated to represent the quantity of coating which had been absorbed by the filter paper samples. These can be seen in Table 2 and Figure 9.

Table 2: Masses recorded, PreM – Pre coating treatment, WetM – Immediately after coating and DryM – Post drying mass. WC and SC represent the water and serum control, RT, 62 and 80 indicate curing temperature of wax emulsion before application.

	WC	**SC**	**RT**	**62°C**	**80°C**
PreM/g	**0.134**	**0.132**	**0.137**	**0.138**	**0.137**
SD	0.006	0.004	0.007	0.007	0.009
WetM/g	**0.433**	**0.458**	**0.499**	**0.496**	**0.477**
SD	0.011	0.013	0.026	0.023	0.016
DryM/g	**0.135**	**0.174**	**0.177**	**0.190**	**0.195**
SD	0.005	0.010	0.012	0.012	0.012

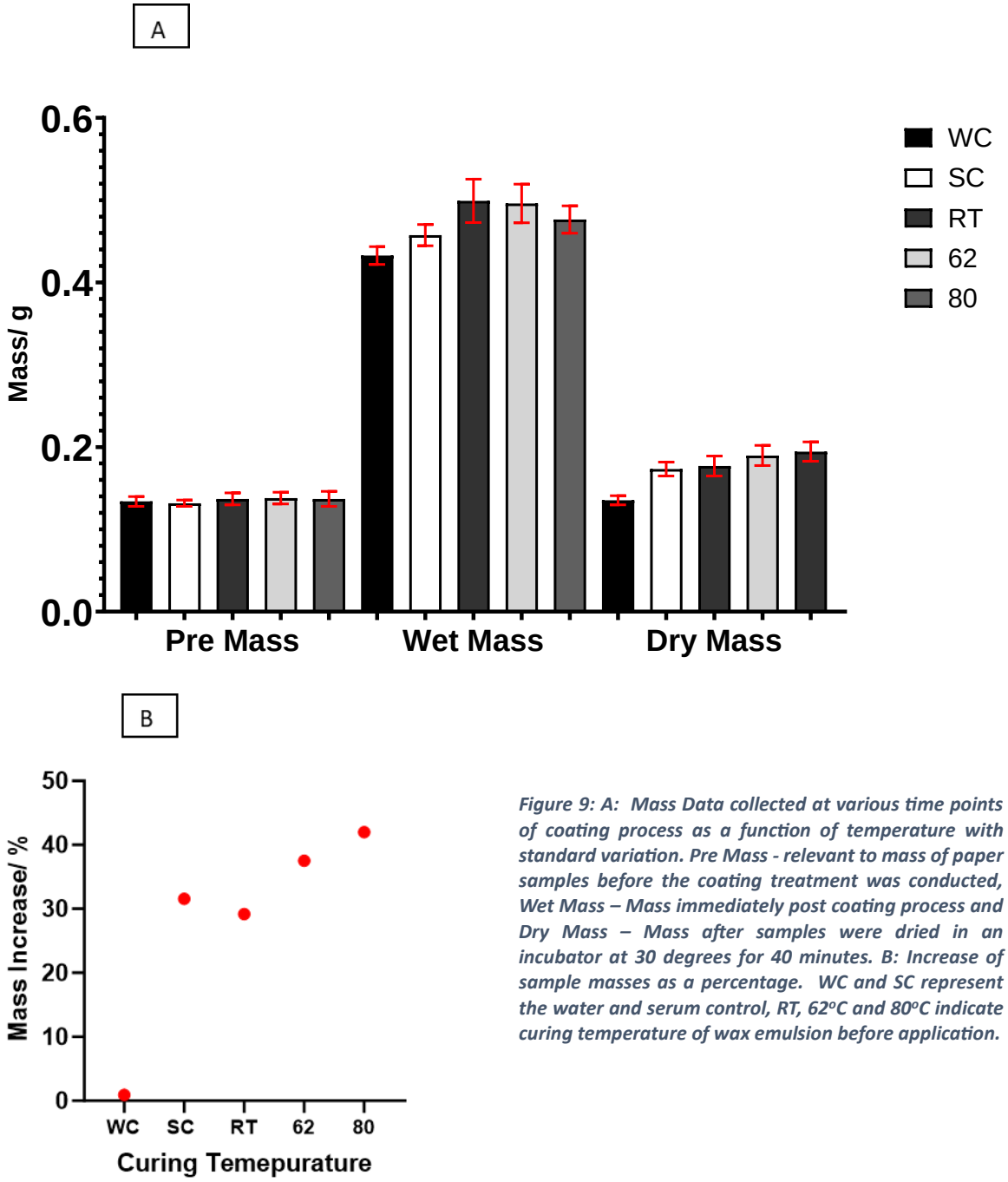


Figure 9: A: Mass Data collected at various time points of coating process as a function of temperature with standard variation. Pre Mass - relevant to mass of paper samples before the coating treatment was conducted, Wet Mass – Mass immediately post coating process and Dry Mass – Mass after samples were dried in an incubator at 30 degrees for 40 minutes. B: Increase of sample masses as a percentage. WC and SC represent the water and serum control, RT, 62°C and 80°C indicate curing temperature of wax emulsion before application.

Figure 9A illustrates the various masses recorded at different time points of the coating process. Figure 9B describes the percentage increase of the samples post coating. It is indicative of the quantity of wax coating adhering to the paper as a function of temperature.

The mass data shows a large increase once the coating is applied. After the drying process is completed a significant decrease in the weight of the samples occurs. The water control, as expected, has a close to 0% increase in mass post spraying. As only water was applied, a reasonable explanation would be that almost all of the applied water evaporated during the

drying process. The slight increase detected may be due to issues with the scale calibration or not all of the water molecules evaporating. The serum control has a larger increase in mass than the room temperature wax emulsion. Although the increase is not significant, it may be due to a slight increase in the concentration of oil, as no wax is present.

The effect of temperature has a positive correlation with the extent of coating detected on the paper. This can be seen clearly in Figure 9B. This data correlates with the data obtained via the image analysis (Figures 5 and 6) of the SEM micrographs. The heavier coatings afforded by the increase in curing temperatures significantly affect the number of pores identified on the surface of the paper.

Statistical analysis shows that the temperature has an effect on the masses of the samples. For all variables, the P value was calculated to be less than 0.05. This is expected for the wet and dry masses. However for the pre-treated mass this was unexpected. As all filter paper was provided by the same supplier a significant difference between uncoated samples was not expected. However, the two controls and the three temperature variables were studied using different packs of Whatman filter paper. This may account for the observed results.

A separate one-way ANOVA was conducted on the three temperature variables. This showed the results to not be significantly different as expected. A T-test conducted on the two controls showed that only a small significant difference was present (P = 0.048). This proves that the packs of sample paper differs from pack to pack. This may be due to batches being produced at different locations or have slight differences in the manufacturing processes which have caused the slight but still significant changes in masses.

3.4. Wettability

3.4.1. Contact Angles Against Water

Water contact angles are used to differentiate the hydrophobicity or hydrophilicity of a given material. An angle below 90^{o} is considered hydrophilic, an angle 90^{o} and above is classed as hydrophobic. A surface or material which produces a contact angle of 150^{o} is considered superhydrophobic (Bacovska, et al., 2016, Lokanathan, et al., 2019). These angles are

determined by the materials surface structure, chemistry and porosity of the material (dos Santos, et al., 2023).

Table 3: Mean contact angles gathered as a function of curing temperature of the wax emulsions. WC and SC represent the water and serum control, RT, 62°C and 80°C indicate curing temperature of wax emulsion before application.

	WC	SC	RT	60°C	80°C
CA/°	**N/A**	**32.64**	**97.43**	**101.29**	**106.25**
SD	N/A	21.27	8.00	8.42	7.46

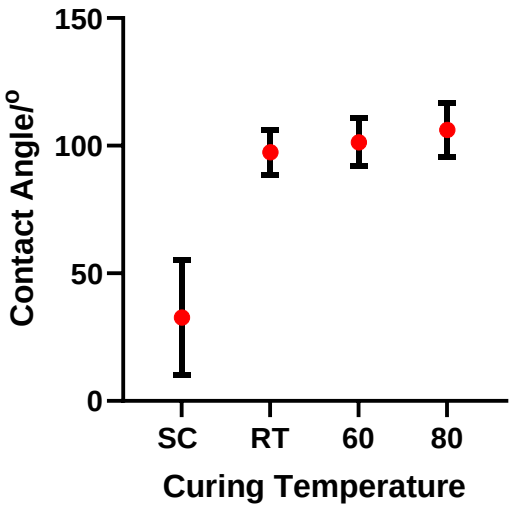


Figure 10: Mean contact angles with standard deviation as a function of curing temperature of the wax emulsions. WC and SC represent the water and serum control, RT, 60°C and 80°C indicate curing temperature of wax emulsion before application.

Table 3 and Figure 10 shows the effect of an increasing temperature on the contact angles of the samples. With regards to the controls, water control data was not gathered due to the extreme speed of absorption of the water droplet by the paper. It was not possible to capture an image of the droplet due to limitations of the instrumentation and methodology adopted in this study. For the serum control, similar issues took place with fast absorption of the droplet, however data was still able to be gathered showing an average of 32.64 ± 21.27°. This low overall angle paired with the high variance is due to large differences in sample angles collected. Similarly, to the water control samples, the speed of absorption paired with the methodology used may have been a cause of this. Overall, this indicated that without the presence of a waterproofing material such as the rice bran wax, the paper has no barrier functionality at all and is extremely hydrophilic. The samples which produced the highest

mean contact angle was found on the samples coated with the emulsion cured at 80°C. A mean angle of 106.25 ± 7.46° was measured and 62°C had a mean angle of 101.29 ± 8.42°.

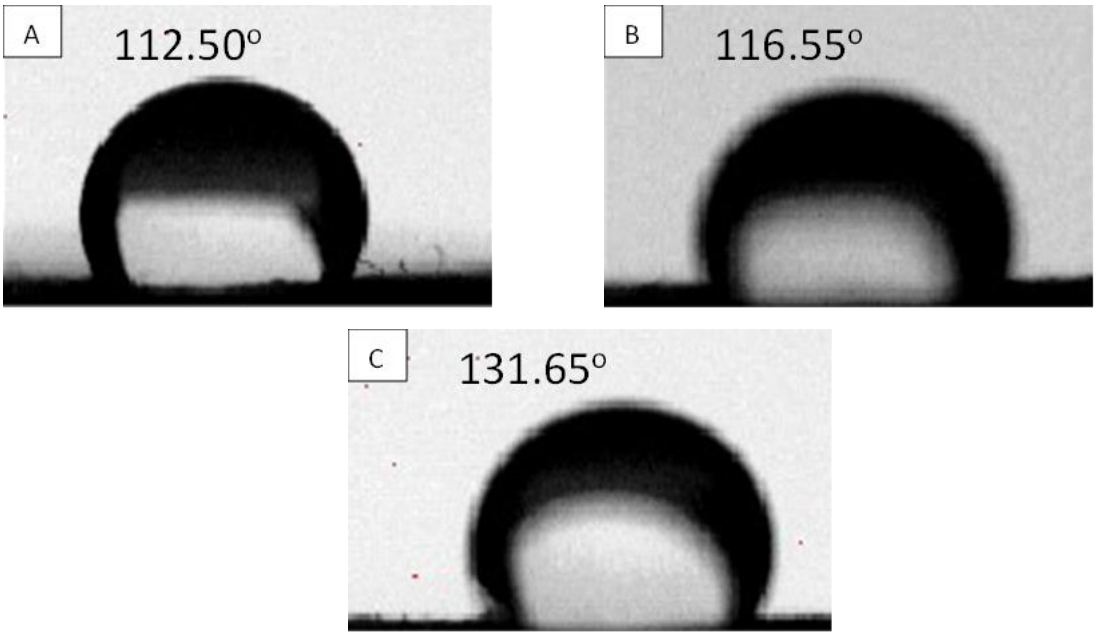


Figure 11: Highest contact angles of spray coated paper of which coating is cured at different temperatures. A – Room Temperature cured emulsion, B – 62°C cured emulsion, C – 80°C cured emulsion.

Figure 11 shows the highest recorded angles of each temperature variable. Although the mean angle ranges gathered for both 62°C and 80°C are similar, at 80 degrees, areas of increased hydrophobicity were present. The highest angle (131.65°) measured was higher than the highest recorded angle (116.55°) at 62°C and (112.50°) at toom temperature. Both figures 10 and 11 show contact angle ranges which coincide with other coated paper studies although methodologies were slightly different (Boonmahitthisud, et al., 2023, dos Santos, et al., 2023, Ahuja & Rastogi, 2023).

On the contrary to the results gathered in this study, previous work has found that wax coated paper, which was annealed to 80°C post coating, the wax migrated into the paper, leading to a reduction in hydrophobicity (Ahuja & Rastogi, 2023). More cellulose fibres were visible on the surface as the wax migrated from the surface into the matrix. This highlights the difference between the two techniques used, thermal curing and annealing.

This positive correlation with barrier functionality to curing temperatures supports the data from other experiments in this study. The reduction in porosity discovered from the SEM characterisation and increased coating adhesion calculated from the mass measurements resulted in the hypothesis that improved barrier functionality would occur. However, the

ranges of angle collected could be indicative of the spraying and sectioning methodologies. The paper samples were sectioned to allow them to fit in the instrument to record the angles. Although the upmost care was taken to produce clean cuts, this may have affected the structural integrity of the paper. Extra cracks or stress fractures may have still occurred which could have resulted in samples having a less functional coating.

Only samples from 62^{o}C and 80^{o}C lasted the holding time of 120s. Within these two ranges the amount of samples which lasted was small, 10% of the 62^{o}C samples and 40% of the 80^{o}C samples. The thickness and adhesion of the wax coating may be the reason. The lack of a complete coating with sufficient weight may enable water to diffuse through the cracks and fractures and come into contact with exposed cellulose fibres. For the other variables the presence of many pores and cracks may have caused rapid absorption of the water.

Amalgamating the findings from literature and empirical studies draws a conclusive link between the presence of wax and the hydrophobic attributes exhibited by surfaces (Liu, et al., 2021). Another perspective concerns the possible presence of air pockets on the papers surface, a notion aligned with the Cassie-Baxter model (Samyn, 2013, Huh & Mason, 1997). In scenarios where the coatings of the samples sustained functional barrier properties until the designated holding time, it is plausible that the wax layer prolonged the prevention of cellulose-water interaction. This effect is likely a result of a more efficacious coating, which actively hindered such contact for an extended duration (Boonmahitthisud, et al., 2023).

Statistical analysis proved that the results are significantly different. An ANOVA test provided a p value (<0.0001) lower than the critical value. This rejects the null hypothesis that there is no significant difference between the effect of curing temperature and the contact angle of the coated samples.

3.4.2. Water Absorption

Water absorption is a crucial parameter when investigating barrier functionality. The ability of the coating to prevent water absorption is important with regards to creating a paper based packaging product as water can considerably impact the structural integrity of the packaging (paper bottles in Pulpex's case).

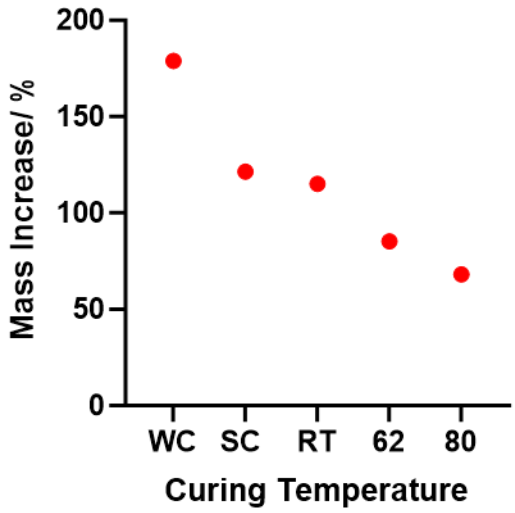


Figure 12: Water Absorbance of samples as a function of curing temperature of the wax emulsion, data given in the format of the mass increase as a percentage. WC and SC represent the water and serum control, RT, 60°C and 80°C indicate curing temperature of wax emulsion before application.

Figure 12 shows the increase in mass of the coated samples after being subjected to water. A clear trend can be observed, as curation temperature of the wax increases, the water absorption reduces. The water control had a mass increase of 178.84%. This is due to an absence of coating therefore no barrier is available to prevent water coming into contact with the cellulose network. Water molecules easily bind to the hydroxyl groups present on the cellulose fibres. This number is comparable to other studies which also gave high water absorbance reaching ranges of around 150% (Boonmahitthisud, et al., 2023, Muryeti, et al., 2019).

The application of the wax coating decreased the absorption with room temperature, 62°C and 80°C, samples having absorptions of 115.16%, 85.20% and 68.06% respectively. This improvement correlates with the literature, however the absorbance is higher indicating the coatings applied in this study were not as effective as others. The most effective was the 80°C cured emulsion, it provided a 61.94% increase in effectiveness. This is very similar to an investigation using chitosan and plant based waxes by (Boonmahitthisud, et al., 2023). The 80°C samples still had multiple droplets present after the time period finished, further indicating that at this curing temperature the coating provides the most effective barrier. This supports the idea stated in section 3.4.1. that the sectioning of the paper to fit in the instrumentation may have resulted in the fast absorption of the droplets, accounting for the low number of samples reaching the holding time.

A thin coating may be responsible for the poor barrier functionality. As the coating is not thick enough, the passage and penetration of the water molecules will be easier and the cellulose fibres will be more easily accessible. This idea coincides with the evidence gathered in both sections 3.1.3 and 3.3. respectively as both experiments have produced data highlighting a thin coating being observed.

A one-way ANOVA statistical test has shown that the variation of curing temperatures results in a significant difference as the P value (0.0001) was less 0.05. Overall, the application of these coatings had an effect on the water absorption as presented by Figure 12. Although a successful and significant reduction in the absorption has occurred, it is not enough to provide an effective barrier. The cracks and microfractures present due to mechanical stress or the lack of coating applied in areas of the paper may result in the cellulose fibres being present on the surface.

4. Conclusion

This study shows how spraying time and temperature affects the efficiency of wax coating paper packaging for liquid storage. The impact of temperature curing of the coating before application was investigated focussing on barrier functionality and homogeneity. The data shows that increasing the curing temperature of the wax emulsion before spraying leads to an improvement in the barrier functionality. Using SEM shows that increasing the temperature to 80^{o}C melts the wax particles allowing it to spread throughout the surface of the paper more uniformly. It appears, however, that the coating remains quite inhomogeneous as revealed by Raman spectroscopy and fluorescence microscopy. The effect of temperature also caused an increase in mass post coating, implying that a heavier application of the coating took place. Linking to this, the 80^{o}C samples showed the highest levels of hydrophobicity, both in the contact angle measurements and the water absorption tests.

To improve the data, the following modifications have been identified and proposed for future study. Developments to sectioning using a microtome should be conducted, combined with methods to create a thicker layer of coating. This would increase clarity when observed under SEM showing permeability and thickness of the coating on the paper samples. With regards to the contact angle measurements, the use of a dedicated instrument such as a Dynamic

Contact Angle Measuring System will remove technical errors. A possible proposal would be to investigate the impact of multiple coatings, a priming and secondary layer. As a temperature of 80^{o}C produced the most positive impact, more detailed investigations should be conducted. This should include using a smaller temperature range (75-95^{o}C) as well as further techniques including particle size and rheology.

Finally, investigations should take place comparing the effect of thermal curing of the wax emulsion and the thermal annealing post-application to categorise the difference between both methods. The formulation step of the process should also be considered e.g. adding polysaccharide based filming agents. These may have similar effects without the increased energy consumption of thermal incubation.

In an industrial setting, other factors must be considered. Pulpex Ltd. and similar companies already have a manufacturing process in place so energy and manufacturing variables must be balanced and a cost/benefit analysis needs to determine if this is commercially viable.

Overall, this study has provided useful insights into coating solutions to sustainable packaging applications and is one of the first steps in applying this technology to a commercial setting allowing for sustainability goals to be pursued.

Acknowledgements

I would like to give thanks to all in food science and the Nano and Microscale Research Centre who aided me in this investigation. I would like to give special thanks to Gleb Yakubov, Lorelei Robertson, Graham Rance and Denice Mclean for their support and help in training and advice in this assignment.

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Appendix

Appendix A: ImageJ Data

Image	**Pore Frequency**						
	WC	SC	10s	20s	30s - RT	62°C	80°C
1	444	269	200	102	109	41	8
2	492	325	197	122	127	45	22
3	496	335	168	163	161	50	17
4	487	253	221	118	207	59	5
5	452	274	197	99	158	36	5
6	385	251	200	159	51	54	0
7	490	296	171	149	65	41	2
8	588	335	188	154	82	48	3
9	563	294	146	184	78	46	20
10	507	272	169	179	106	27	8

Image	**Mean Total Pore Area/ µm²**						
	WC	SC	10s	20s	30s - RT	62°C	80°C
1	125937.2	67639.11	39054.22	24031.35	23632.27	5788.737	1850.432
2	137498.6	81684.6	37656.57	31411.71	29234.1	6536.316	3739.047
3	143514	74880.67	31134.22	46791.48	36591.22	5943.371	2972.444
4	105098.2	73392.83	48990.71	23425.63	133379.2	8029.241	671.967
5	109200.5	74516.74	44005.05	15333.39	36049.26	4312.967	835.509
6	87063.51	60819.75	42485.33	29005.26	10187.79	6919.949	0
7	122935.1	79832.24	31203.56	27742.38	11276.42	7020.031	191.727
8	157556.8	100921	38484.26	35742.29	11076.15	8981.278	950.071
9	139345.2	72985.78	33646.22	37365.38	11367.59	10167.92	3167.086
10	143192.6	62739.71	34117.33	35810.42	16959.17	3816.955	724.364

Appendix B: Coating Mass Data

Sample	Pre M/g					Wet M/g					Dry M/g				
	WC	SC	RT	62°C	80°C	WC	SC	RT	62°C	80°C	WC	SC	RT	62°C	80°C
1	0.13	0.14	0.14	0.13	0.14	0.44	0.44	0.44	0.49	0.47	0.14	0.17	0.18	0.21	0.19
2	0.13	0.13	0.13	0.14	0.15	0.46	0.47	0.51	0.51	0.48	0.13	0.17	0.19	0.21	0.21
3	0.15	0.13	0.14	0.15	0.14	0.44	0.47	0.51	0.53	0.45	0.15	0.18	0.19	0.21	0.18
4	0.14	0.14	0.13	0.14	0.14	0.43	0.45	0.46	0.52	0.47	0.14	0.17	0.16	0.21	0.2
5	0.13	0.14	0.15	0.14	0.15	0.43	0.44	0.51	0.47	0.48	0.13	0.17	0.19	0.2	0.2
6	0.14	0.13	0.13	0.13	0.13	0.46	0.44	0.49	0.51	0.46	0.14	0.16	0.17	0.18	0.18
7	0.13	0.13	0.14	0.13	0.14	0.43	0.44	0.48	0.5	0.46	0.13	0.16	0.19	0.18	0.21
8	0.13	0.13	0.13	0.14	0.13	0.43	0.44	0.53	0.51	0.45	0.13	0.17	0.17	0.19	0.18
9	0.13	0.14	0.14	0.13	0.13	0.42	0.45	0.51	0.51	0.49	0.13	0.17	0.18	0.18	0.19
10	0.13	0.13	0.13	0.15	0.14	0.42	0.45	0.47	0.53	0.46	0.13	0.17	0.17	0.2	0.18
11	0.13	0.14	0.13	0.15	0.15	0.43	0.46	0.49	0.49	0.48	0.13	0.18	0.16	0.18	0.19
12	0.14	0.13	0.13	0.14	0.13	0.43	0.46	0.45	0.49	0.49	0.14	0.17	0.16	0.19	0.19
13	0.13	0.13	0.13	0.14	0.13	0.44	0.46	0.48	0.47	0.47	0.13	0.18	0.17	0.17	0.18
14	0.13	0.13	0.13	0.14	0.15	0.44	0.45	0.47	0.52	0.49	0.14	0.18	0.17	0.19	0.18
15	0.13	0.13	0.14	0.12	0.13	0.43	0.47	0.52	0.44	0.47	0.13	0.18	0.18	0.16	0.2
16	0.13	0.13	0.14	0.14	0.13	0.42	0.48	0.52	0.48	0.48	0.14		0.18	0.18	0.2
17	0.13	0.13	0.14	0.14	0.12	0.42	0.45	0.54	0.51	0.47	0.13	0.18	0.19	0.19	0.2
18	0.13	0.13	0.13	0.13	0.13	0.43	0.44	0.49	0.5	0.48	0.13	0.17	0.16	0.21	0.18
19	0.13	0.13	0.13	0.14	0.14	0.42	0.48	0.52	0.51	0.48	0.14	0.17	0.18	0.19	0.2
20	0.14	0.13	0.13	0.14	0.13	0.42	0.47	0.53	0.48	0.5	0.14	0.18	0.18	0.2	0.2
21	0.13	0.13	0.14	0.14	0.13	0.42	0.44	0.54	0.51	0.49	0.13	0.16	0.18	0.19	0.19
22	0.14	0.13	0.13	0.15	0.13	0.42	0.46	0.54	0.52	0.46	0.14	0.16	0.18	0.21	0.18
23	0.12	0.13	0.15	0.14	0.13	0.43	0.47	0.54	0.51	0.47	0.13	0.17	0.22	0.19	0.18
24	0.14	0.13	0.14	0.14	0.15	0.43	0.46	0.49	0.5	0.51	0.14	0.17	0.18	0.18	0.2
25	0.13	0.13	0.14	0.14	0.15	0.42	0.46	0.51	0.51	0.47	0.13	0.17	0.17	0.19	0.18
26	0.14	0.13	0.13	0.14	0.14	0.43	0.45	0.47	0.5	0.5	0.14	0.17	0.16	0.2	0.19
27	0.14	0.13	0.14	0.13	0.15	0.45	0.47	0.5	0.52	0.49	0.14	0.18	0.17	0.18	0.19
28	0.13	0.13	0.14	0.13	0.13	0.43	0.43	0.51	0.5	0.52	0.13	0.16	0.19	0.19	0.22
29	0.13	0.13	0.14	0.14	0.13	0.43	0.46	0.46	0.49	0.46	0.13	0.17	0.16	0.19	0.2
30	0.14	0.13	0.13	0.14	0.13	0.43	0.44	0.49	0.52	0.49	0.14	0.18	0.16	0.19	0.19
31	0.14	0.13	0.13	0.13	0.14	0.42	0.46	0.47	0.49	0.48	0.13	0.18	0.17	0.19	0.22
32	0.14	0.13	0.13	0.13	0.15	0.44	0.46	0.49	0.45	0.46	0.14	0.17	0.17	0.17	0.21
33	0.14	0.14	0.14	0.13	0.15	0.44	0.47	0.51	0.51	0.48	0.14	0.17	0.17	0.19	0.2
34	0.14	0.13	0.15	0.15	0.15	0.43	0.46	0.49	0.47	0.5	0.14	0.17	0.18	0.19	0.21
35	0.14	0.14	0.15	0.13	0.13	0.43	0.46	0.52	0.49	0.45	0.14	0.18	0.19	0.2	0.19
36	0.13	0.13	0.15	0.14	0.12	0.44	0.46	0.52	0.45	0.47	0.13	0.2	0.18	0.17	0.21
37	0.13	0.13	0.15	0.13	0.13	0.44	0.46	0.53	0.51	0.48	0.14	0.19	0.18	0.19	0.2
38	0.14	0.13	0.13	0.14	0.13	0.45	0.47	0.47	0.47	0.48	0.14	0.18	0.18	0.18	0.2
39	0.13	0.13	0.14	0.15	0.14	0.45	0.48	0.5	0.51	0.45	0.13	0.18	0.19	0.19	0.18
40	0.13	0.13	0.14	0.14	0.14	0.44	0.47	0.5	0.44	0.47	0.13	0.17	0.18	0.18	0.2

Appendix C: Wettability

Sample	Contact Angle/ °			
	SC	**RT**	**62°C**	**80°C**
1	57.1	98.45	93.4	90.25
2	72.3	100.80	96.1	94.4
3	6.2	76.35	89	107.9
4	16.8	97.20	106.8	100.5
5	32.8	106.75	117.8	99.15
6	43.1	97	96.9	100.55
7	3.85	99.8	98.3	105.25
8	32.2	100.55	105.25	96.35
9	29.4	101.6	97.5	116.85
10		92.95	102.65	104.20
11		75.70	97.5	98.15
12		93.70	109.5	121.75
13		104.4	104.1	105.35
14		97.75	107.6	101.70
15		99.5	105.85	131.65
16		92.8	111.5	111.90
17		97.4	38.05	101.15
18		96.35	116.55	109
19		107.1	87.3	102.8
20		112.5	86	126.05

Water Absorbance										
Sample	**Pre Mass/ g**					**Post Mass/ g**				
	WC	**SC**	**RT**	**62°C**	**80°C**	**WC**	**SC**	**RT**	**62°C**	**80°C**
1	0.14	0.16	0.18	0.2	0.19	0.38	0.39	0.4	0.37	0.33
2	0.13	0.17	0.17	0.19	0.2	0.39	0.37	0.37	0.39	0.34
3	0.13	0.17	0.2	0.19	0.2	0.37	0.4	0.42	0.37	0.33
4	0.14	0.17	0.17	0.18	0.19	0.36	0.36	0.39	0.34	0.32
5	0.13	0.17	0.18	0.19	0.2	0.37	0.37	0.39	0.38	0.33
6	0.13	0.17	0.17	0.2	0.2	0.36	0.37	0.37	0.37	0.34
7	0.13	0.18	0.17	0.19	0.19	0.36	0.36	0.39	0.33	0.35
8	0.13	0.17	0.19	0.18	0.19	0.37	0.36	0.4	0.34	0.33
9	0.13	0.17	0.18	0.19	0.19	0.36	0.4	0.37	0.36	0.33
10	0.13	0.17	0.17	0.19	0.2	0.39	0.4	0.39	0.34	0.33
11	0.13	0.16	0.17	0.18	0.2	0.36	0.37	0.36	0.31	0.35
12	0.13	0.17	0.17	0.19	0.19	0.36	0.4	0.37	0.33	0.32
13	0.13	0.17	0.18	0.18	0.2	0.36	0.39	0.38	0.38	0.34
14	0.13	0.17	0.17	0.19		0.35	0.36	0.38	0.34	
15	0.14	0.18	0.18	0.18	0.2	0.36	0.39	0.38	0.35	0.32
16	0.13	0.18	0.18	0.19	0.2	0.37	0.38	0.37	0.3	0.34
17	0.13	0.17	0.18	0.19	0.19	0.34	0.37	0.36	0.36	0.32
18	0.13	0.17	0.17	0.19	0.2	0.36	0.37	0.36	0.33	0.31
19	0.14	0.17	0.18	0.19	0.2	0.34	0.36	0.38	0.34	0.32
20	0.13	0.16	0.18	0.18	0.2	0.34	0.36	0.38	0.31	0.33

Additional Data including ImageJ and Raman Spectra Available if requested.