

Hydrophobicity Improvement of Cellulose-Based Material

Alina Auyelbekova

DIVISION OF PACKAGING LOGISTICS | DEPARTMENT OF DESIGN SCIENCES
FACULTY OF ENGINEERING LTH | LUND UNIVERSITY
2024

MASTER THESIS



FIPDes

Food Innovation & Product Design

This master's thesis has been done within the Erasmus Mundus Joint Master Degree FIPDes, Food Innovation and Product Design.



**Co-funded by
the European Union**

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Education and Culture Executive Agency (EACEA). Neither the European Union nor EACEA can be held responsible for them.

Hydrophobicity Improvement of Cellulose-based Material

Optimizing the Sizing Agent Emulsion

Alina Auyelbekova



LUND
UNIVERSITY

Hydrophobicity Improvement of Cellulose-based Material

Optimizing the Sizing Agent Emulsion

Copyright © 2024 Alina Auyelbekova

Published by

Department of Design Sciences
Faculty of Engineering LTH, Lund University
P.O. Box 118, SE-221 00 Lund, Sweden

Subject: Food Packaging Design (MTTM01)

Division: Packaging Logistics

Academic Supervisor: Daniel Hellström, Lund University

Company Supervisors: Francesco Prandi, Tetra Pak Packaging Solutions
AB

Examiner: Klas Hjort, Lund University

Abstract

The environmental challenges of plastic pollution and increasingly stringent legislative regulations have directed leading packaging companies to explore more sustainable and eco-friendly packaging materials. As part of these efforts, there has been a significant focus on developing bio-based and biodegradable materials. Among these, cellulose fiber-based materials have emerged as a highly promising alternative due to their renewable nature, biodegradability, and abundant availability. However, the materials are inherently susceptible to water, and to be effectively used as a packaging material they necessitate modifications to enhance their hydrophobic properties.

This degree project investigates the optimization and application of alkenyl succinic anhydride (ASA) emulsion as a sizing treatment to improve the hydrophobicity of cellulose-based material. The study is divided into two phases: the first focuses on characterizing ASA emulsion, and the second assesses the sizing performance of cellulose fiber-based material treated with the ASA emulsion.

In the first phase, nine emulsion samples were prepared using varying shear rates and pH levels. The stability of these emulsions was evaluated through visual assessment, particle size analysis, and zeta potential measurements. Additionally, Nuclear Magnetic Resonance (NMR) spectroscopy was employed to determine the extent of ASA hydrolysis. Results indicated that the most stable emulsion was achieved at a shear rate of 18500 rpm and a pH of 4.

The second phase involved applying the optimized ASA emulsion to cellulose samples and evaluating the sizing performance through the Cobb Test. The experimental trials revealed that the curing step improved water resistance, although the overall Cobb values were higher than those achieved with alkyl ketene dimer (AKD) sizing. Moreover, the infrared spectroscopy method was used to determine chemical variations of ASA after application to the samples. The IR spectra revealed the absence of ester bond formation

between ASA and cellulose, correlating with the observed water resistance performance.

Based on the obtained results, the stable emulsion was not an index of the efficacy of ASA as a sizing agent. A stable emulsion was obtained at the high shear rate and acidic pH level; however, such ASA treatment could not provide sufficient sizing. More parameters must be taken into consideration, such as the formulation of the emulsion, as well as cellulose sample processing that could be addressed in future studies. Nevertheless, the sizing evaluation demonstrated the importance of the curing step in the process. Additionally, the findings contribute valuable insights into optimizing ASA emulsion for industrial application, promoting improved hydrophobicity in cellulose-based material.

Keywords: Alkenyl succinic anhydride, Cationic starch, Hydrophobicity, Emulsion, Acidic sizing

Acknowledgments

I want to express my sincere gratitude to all those who have contributed to the successful completion of this master's thesis. First and foremost, I am deeply thankful to the collaborative parties of the project, Lund University and Tetra Pak Packaging Solutions AB, for providing me with the invaluable opportunity to delve into the realms of innovations in material science.

Throughout this journey, I have been fortunate to receive unwavering support and guidance from my academic supervisor, Daniel Hellström, and industrial supervisor, Francesco Prandi, whose expertise and insightful feedback have shaped this work. I extend my heartfelt thanks to Pernilla Elmhäll, Joachim Bjurenheim, Maria Petersson, Mats Qvardford, and other Tetra Pak employees for their mentorship.

I am immensely grateful to the FIPDes consortium for allowing me to be a part of this incredible journey. Special gratitude goes to Erik Andersson and Jenny Schelin for their support which has been invaluable throughout the whole year. Additionally, I would like to thank the Department of Physical Chemistry, the Department of Microbiology, and the Center of Analysis and Synthesis for their collaboration and assistance.

Lastly, I am grateful to my family and friends for their constant encouragements, which have been the source of motivation throughout the whole project.

Lund, May 2024

Alina Auyelbekova

Table of contents

Table of contents	
List of Figures	
List of Tables	
List of acronyms and abbreviations	
1 Introduction	1
1.1 Background and Motivation	1
1.1.1 Impact of plastics.....	1
1.1.2 Plastic recycling.....	2
1.1.3 Alternative sustainable solutions.....	3
1.1.4 Previous studies.....	4
1.2 Purpose and Objectives	4
1.3 Scope and Delimitations	5
2 Literature Review	7
2.1 Food Packaging Materials	7
2.1.1 Role of plastics as a packaging material.....	7
2.1.2 Bio innovations in packaging materials.....	8
2.2 Cellulose-based Materials and their Properties	9
2.3 Improving Hydrophobicity of Cellulose-based Materials	10
2.3.1 Sizing phenomenon.....	11
2.3.2 Sizing in papermaking.....	12
2.3.3 Migration.....	13
2.4 Alkenyl Succinic Anhydride (ASA)	13
2.4.1 ASA Sizing Mechanism.....	14
2.4.2 Limitations of ASA as a sizing agent.....	15
2.5 Stabilization of ASA emulsion	15
2.5.1 The choice and the dose of emulsifier.....	16
2.5.2 Particle size.....	16

2.5.3 pH	17
2.5.4 Temperature	17
2.6 Comparison of sizing agents (ASA vs AKD).....	17
3 Materials and Methods	19
3.1 Experimental Design	19
3.2 ASA Emulsion Characterization	20
3.2.1 Materials	20
3.2.2 Adjustable parameters	21
3.2.3 Emulsion making procedure	21
3.2.4 Visual assessment	23
3.2.5 Particle size analysis	24
3.2.6 Zeta potential analysis	24
3.2.7 Extracted ASA Characterization	25
3.3 Sizing Performance Characterization.....	25
3.3.1 Cellulose Sample Preparation	26
3.3.2 Cobb Test	27
3.3.3 Infrared spectroscopy	28
3.4 Analysis	29
4 Results and Discussion	31
4.1 ASA Emulsion Evaluation Analysis.....	31
4.1.1 Visual assessment analysis	31
4.1.2 Particle size and zeta potential analysis.....	33
4.2 Extracted ASA Analysis	35
4.3 Sizing Performance Analysis	38
4.3.1 Water absorption analysis based on curing	38
4.3.2 Water absorption analysis based on ASA dose	39
4.3.3 Visual assessment based on ASA dose	40
4.3.4 Sizing treatment distribution analysis	41
4.3.5 Comparison throughout the treatment process	42
5 Conclusion	45
5.1 ASA Emulsion Optimization	45
5.2 ASA Sizing Performance.....	45
5.3 Future research.....	46
References	47
Appendix A	51

List of Figures

Figure 1. Flow diagram of EU recycling system model (Tallentire & Steubing, 2020).....	3
Figure 2. Structure of cellulose (Suopajärvi, 2015).....	9
Figure 3. Schematic illustration of sizing mechanism.....	12
Figure 4. The ene reaction between an isomerized olefin and maleic anhydride in preparation of ASA (Gess & Rende, 2005).....	14
Figure 5. The esterification reaction between ASA and cellulose (Ntifafa et al., 2023).....	14
Figure 6. The hydrolysis reaction between ASA and water (Ntifafa et al., 2023).....	15
Figure 7. Impact of temperature on hydrolysis rate of ASA.	17
Figure 8. Formation of alkyl ketene dimer (AKD).....	18
Figure 9. Experimental design overview.....	19
Figure 10. Emulsion making process.	22
Figure 11. Ystral rotor-stator (Ystral, n.d).....	23
Figure 12. Malvern Zetasizer S (Malvern Instruments Ltd, n.d).....	24
Figure 13. Folded capillary cell (Malvern Instruments Ltd, n.d).	25
Figure 14. Treatment application onto cellulose sample through airbrush application.	26
Figure 15. COLLIN Flat Press (COLLIN, n.d).	27
Figure 16. Specimen holder (TAPPI T441, 2013).....	28
Figure 17. Gelatinization of Sample B12 at 6 hours post-emulsification. ..	32
Figure 18. Phase separation of sample A6 at 24 hours post emulsification.	33
Figure 19. Contour plot of pH vs zeta potential and particle size.	34
Figure 20. Contour plot of shear rate vs zeta potential and particle size.....	35
Figure 21. Labeled ASA structure.	36
Figure 22. Pure ASA (red) and Extracted from the emulsion ASA (blue) spectra.....	37
Figure 23. Pure ASA (red) and Extracted from the emulsion ASA (blue) spectra with unidentified peaks circled.	37
Figure 24. Average Cobb 1800 values for samples with and without curing step in the process.....	39

Figure 25. Water absorbency of cellulose samples based on % ASA dose.	40
Figure 26. Visual appearance of cellulose samples with different ASA dose concentrations: (a) 0.4% ASA dose, (b) 1% ASA dose, (c) 2% ASA dose.	41
Figure 27. FTIR spectra of 2% ASA dose, cured sample.....	42
Figure 28. Scheme of FTIR analysis throughout the treatment process.....	42
Figure 29. FTIR spectra of pure ASA (black), cellulose sample after molding (red), and after curing (blue).	43
Figure 30. FTIR spectra of cellulose sample after spraying (green), after molding (red), and after curing (blue).	44

List of Tables

Table 1. Advantages and disadvantages of cellulose as a packaging material.	10
Table 2. Comparison of ASA and AKD as sizing agents.....	18
Table 3. The raw material used for ASA emulsion.	20
Table 4. Representation of emulsion samples with a unique combination of parameters.....	24
Table 5. Emulsion consistency description based on visual evaluation.	31
Table 6. Expected and observed chemical shift of pure ASA obtained from H NMR spectra.	36

List of acronyms and abbreviations

AGU	anhydroglucose unit
ASA	alkenyl succinic anhydride
AKD	alkyl ketene dimer
CAGR	compound annual growth rate
CDCl ₃	deuterated chloroform (chloroform-d)
DCM	dichloromethane
EU	European Union
FTIR	Fourier Transform Infrared Spectroscopy
GNP	gross national product
NMR	nuclear magnetic resonance

1 Introduction

This section provides information on the background and motivation of the project. Additionally, it delves into purpose and objectives, as well as delimitations that may affect the scope of the thesis.

1.1 Background and Motivation

1.1.1 Impact of plastics

As a ubiquitous material adopted by various industries, plastic has an enormous impact on the world. Its global production, which commenced in the 1950s, has been rapidly increasing each year since and has reached 400.3 million metric tons in 2022 (Statista, 2024). Such a persistent material that is unavoidable in the era of high industrialization and technological advancement, has become a necessity for society. It has seamlessly been integrated into different aspects of daily life, from construction and transportation to healthcare and packaging.

Packaging is one of the leading industries contributing to plastic production. It represents around 2% of developed countries gross national product (GNP), half of which is used in the food industry. Given packaging's main function is to protect its content, plastic has emerged as the material of choice for most producers (Robertson, 2024) It is the most versatile polymer with high functionality and relatively low cost making it ideal for safeguarding food from external factors (Ncube et al., 2021).

Plastics, however, are composed of chains of monomers derived from fossil-based hydrocarbons. Regrettably, most used plastics, which include polypropylene (PP), polystyrene (PS), polyethylene (PE), and polyethylene terephthalate (PET) lack biodegradability, leading to their accumulation in

landfills and the natural environment (Geyer et al., 2017). As the plastic pollution rate is increasing and exceeding the rate of the natural removal process, only 9% of produced plastics is successfully recycled while the rest ends up in landfills, incinerated or leaked into the environment (OECD, 2022). It is negatively affecting the entire globe, from mountains to oceans. The global emission of plastic waste that is found in water bodies is estimated to range from 9 to 23 million metric tons per year which is 80% of marine littering, and similar amounts are emitted into terrestrial environment (Macleod et al., 2021).

1.1.2 Plastic recycling

Recognizing the problem of recourse consumption and the urgency of environmental degradation most of the developed countries in the European Union (EU) had established a recycling system. This infrastructure constantly undergoes a set of reforms and takes sustainable initiatives that are directed by EU legislation (Antonopoulos et al., 2021). Despite set milestones and ambitions of the recently adopted circular economy framework that aims to recycle 70% of plastic packaging by 2025 (Novakovic et al., 2023), the amount of recycled plastics generated from packaging in 2020 was only about 38% (Eurostat, 2022). The EU recycling system experiences significant losses that occur during the stages of material capture, sorting, and recycling, causing littering in the environment (see Figure 1).

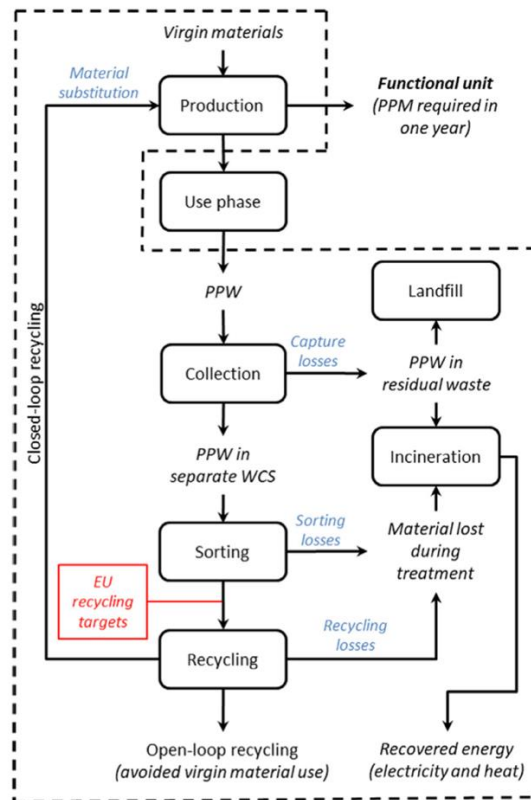


Figure 1. Flow diagram of EU recycling system model (Tallentire & Steubing, 2020).

1.1.3 Alternative sustainable solutions

To combat fossil fuel dependency and reduce negative environmental impact, EU legislation has implemented the Directive (EU) 2019/904 against single-use plastics. The directive action forces companies across diverse industries to explore alternative materials sourced from renewable origins. Advancements in technology, coupled with pressing environmental concerns increased interest and progressed research in biomaterials and biopolymers. Among the new sustainable solutions discovered to replace plastics, cellulose fibers-based material stands out as one of the promising due to its biodegradability and recyclability (Bordón et al., 2022).

However, integrating existing cellulose fibers into food packaging applications presents difficulties related to material performance, given cellulose's inherent hydrophilic characteristics. To tackle the challenge of

water barrier, additives, such as sizing agents, are explored to increase the hydrophobicity of cellulose fibers. Sizing agents, such as alkyl ketene dimer (AKD), alkenyl succinic anhydride (ASA), and rosin have been utilized in packaging (F. Zhang et al., 2020).

1.1.4 Previous studies

Facing escalating environmental degradation and stringent legislation concerning plastic usage in packaging, companies are seeking to diversify their material portfolio and contribute to sustainable solutions. To mitigate the ecological footprint of packaging materials, there is a growing interest in transitioning from conventional plastics to cellulose fiber-based materials treated with sizing agents.

Extensive research has been dedicated to investigating the efficacy of Alkyl Ketene Dimer (AKD) as a sizing agent for cellulose fibers. The studies aimed to understand the potential of AKD in enhancing the hydrophobicity of cellulose fiber-based material. By exploring the properties and applications techniques of treatment solutions, researchers have thought to optimize conditions and parameters for achieving the desired moisture barrier. Moreover, ongoing studies are exploring various formulations and process conditions to maximize the hydrophobic performance of treated cellulose material. This research is crucial for advancing the field of sustainable packaging and addressing environmental concerns associated with traditional plastic use.

1.2 Purpose and Objectives

The overall objective of this project is to explore and understand how the emulsification process and stability of ASA can be optimized to maximize its sizing efficiency and water barrier properties of cellulose fiber-based material. Such an objective can be accomplished through a comprehensive understanding of the chemistry underlying the sizing agent and the sizing reaction with cellulose material. Given that ASA is typically presented in an oily form, the project will be partially devoted to studying the emulsification of the agent and optimizing the process to enhance its efficacy in the treatment of cellulose fibers. Additionally, the project is set to determine if the optimized emulsion would lead to a sufficient sizing degree by assessing

the water barrier properties of molded cellulose fiber samples. Finally, the enhancement of cellulose material's hydrophobicity resulting from ASA treatment is compared to that achieved with AKD treatment, as pursued in previous studies. Pursuing these objectives assists in advancing technological innovations related to ASA sizing phenomena and understanding its feasibility in industrial applications.

1.3 Scope and Delimitations

The scope of the master's thesis is constrained by several factors that necessitate careful consideration and planning. Firstly, the project operates within the predefined timeframe of 20 weeks, which requires efficient time management to accomplish the set research objectives effectively. Alongside timeframe limitations, the availability of resources and scheduling constraints of the laboratory setting have limited the number of parameters for emulsion evaluation down to two, as well as the number of repetitions feasible for data collection and analysis.

Additionally, the prior research analysis conducted on the efficiency of AKD has influenced the methodology employed to characterize ASA sizing efficiency. This approach has been adopted to facilitate a more robust comparison between two sizing agents.

Furthermore, an additional delimitation of the project arises from the set analytical methodology which mandates the execution of one portion of the experimental plan at external laboratory spaces, while the other half is conducted at Tetra Pak facilities. The division introduces logistical challenges and potential discrepancies in experimental conditions. As the emulsion characterization phase is executed at the Lund University facilities, the preparation of identical emulsion at Tetra Pak facilities is challenging due to the difference in external and internal laboratory settings.

2 Literature Review

The segment on theoretical framework introduces the overview of different packaging materials and delves deep into the role of plastics within the food packaging industry and the ways to replace them. The section focuses on cellulose-based alternatives and the ways to improve their properties through sizing methods. It describes and compares ASA and AKD as sizing agents.

2.1 Food Packaging Materials

Packaging plays a crucial role in the food industry with a global value market expected to reach 512 billion U.S. dollars (Statista, 2023). It serves multiple critical functions essential for the successful distribution and consumption of food products. These functions include containment, protection, preservation, communication, utility, and performance. Historically, the primary role of packaging was to act as a guardian of product integrity, ensuring that food remains uncontaminated and safe for consumption. However, nowadays, companies are increasingly focusing on additional aspects such as communication of brand identity and facilitation of consumer convenience (Robertson, 2024).

The performance of the packaging highly depends on the choice of material. Understanding the chemical and physical properties of different materials is extremely important to identifying the most suitable option for each product. Common materials used in food packaging include plastics, metals, glass, cellulose, and ceramics, each offering distinct advantages and disadvantages (Piergiovanni & Limbo, 2016).

2.1.1 Role of plastics as a packaging material

When selecting materials, food companies across various sectors often gravitate towards the use of plastics due to their ability to maintain high

performance across all packaging functions. In 2020, plastics contributed 45% of the global packaging materials market volume, underscoring their dominance in the industry (Statista, 2024). Plastics are particularly favored for their strength, impeccable impermeability, and cost-effectiveness (Zinoviadou et al., 2021). Moreover, plastics are safe and shatterproof, preventing dangerous fragments from forming. Their lightweight nature makes handling and transportation easier offering significant design flexibility. With its unique set of advantages, plastics play an important role in packaging a wide range of food products across the whole food supply chain (Yaris & Sezgin, 2017).

However, around 95% of polymers are predominantly derived from non-renewable sources, specifically from the petroleum industry (Shaikh et al., 2021). This reliance on fossil fuels raises concerns about resource depletion and contributes to the environmental footprints of plastic packaging. The major challenge with synthetic polymers is their persistence in the environment. Due to improper disposal practices and their inability to rapidly degrade, these plastics accumulate as waste, leading to serious environmental challenges (Zhang et al., 2021).

Overall, while plastics remain a dominant material in food packaging, it is imperative for industries to balance performance with sustainability. Efforts must continue to develop and implement more eco-friendly materials and practices, ensuring the long-term well-being of people and the planet.

2.1.2 Bio innovations in packaging materials

Recent innovations in packaging materials are driving towards a shared goal of reducing industries' ecological footprint. With mounting environmental concerns and increasing regulatory pressure, companies increasingly turning towards sustainable packaging solutions. These innovations encompass a wide range of approaches, including the development of biodegradable materials, the use of renewable resources, and the adoption of design for recycling.

Biodegradable materials can be derived both from fossil fuel, such as polylactic acid (PLA), as well as from biomass sources, such as paper or wood (Zinoviadou et al., 2021). Those polymers that come from natural sources such as starch or cellulose are easily degraded by other microorganisms, thus present a lower environmental impact (Cha & Chinnan, 2004). Interestingly,

the greenhouse emissions from the production of biomass-based materials are 20-80% lower compared to fossil-based materials (Steinbuechel Alexander, 2003).

2.2 Cellulose-based Materials and their Properties

Cellulose, sourced from natural origins, is an organic semicrystalline compound characterized by its long, linear carbon chain (Robertson, 2024). This polysaccharide is composed of repeating anhydroglucose units (AGU) linked together by β -(1 \rightarrow 4) glycosidic bonds (Figure 2). Each glucose unit in cellulose has three hydroxyl groups (-OH) that promote the formation of inter- and intramolecular hydrogen bonds and Van der Waals forces. Depending on those interactions, they result in amorphous and crystalline regions (Kadla John & Gilbert R.D., 2000).

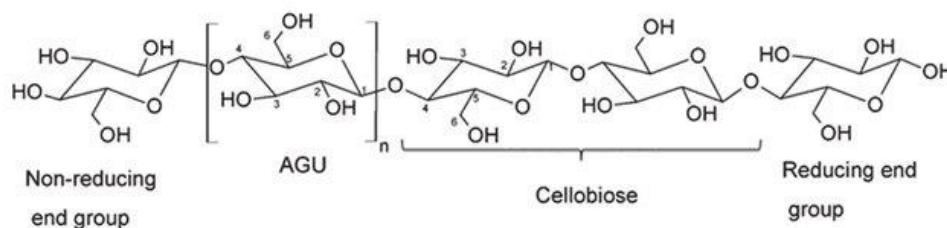


Figure 2. Structure of cellulose (Suopajärvi, 2015).

Abundantly presented in nature, this polymer is found in materials such as wood, sugarcane bagasse, algae, and cotton fibrils reaching one trillion tons of total resources (Klemm et al., 2005). Notably, cellulose is indigestible by humans and unsuitable for nutrient intake, making it an ideal option for packaging materials (Thulasisingh et al., 2022). This inexhaustible natural raw material is widely used in the production of paper, cardboard, textiles, and fibers within the packaging industry.

Cellulose-based packaging material has acclaimed a strong image as an environmentally friendly solution. Its innate biodegradability and biocompatibility make it a valuable contributor to a sustainable economy aligning well with the principles of circularity (Asim et al., 2022). This biopolymer is considered an asset on the path to replacing fossil fuels.

However, as presented in Table 1, While cellulose-based material offers significant advantages, it also has notable disadvantages that should be considered for the food packaging industry. Despite its eco-friendly credentials, cellulose-based packaging materials face certain challenges, particularly in their sensitivity to environmental conditions such as gases and water. Cellulose fibers are characterized by an extremely porous structure that allows the material to absorb water in an instantaneous period (Porkert, 2016). Moreover, due to the presence of the abundant hydrophilic hydroxyl group (-OH), cellulose fibers have a low resistance level toward wetting and water vapor, leading to a possibility of compromising the mechanical integrity of the packaging (Balasubramaniam et al., 2020). The hydrophilic nature of the material can jeopardize the safety and quality of the goods it is supposed to protect. Therefore, improving the hydrophobicity of cellulose fibers has gained more attention among various research groups working on novel innovations in the world of materials.

Table 1. Advantages and disadvantages of cellulose as a packaging material.

<i>Advantages</i>	<i>Disadvantages</i>
High durability	Hydrophilic
Non-toxicity	Sensitive to gases
Biocompatibility	
Biodegradability	

2.3 Improving Hydrophobicity of Cellulose-based Materials

There are various methods for improving the hydrophobicity of cellulose-based materials that are being researched and developed. Many of those studies focus on physical and chemical treatments to modify and reconstruct this natural biopolymer. Physical manipulations include surface treatments using for instance polymeric coating, while chemical modifications study the structural changes and molecule interactions with the use of additives, such as sizing agents (He et al., 2014).

Experimental trials have been conducted to enhance the crystallinity of cellulose through acid hydrolysis. Crystallinity is an important property, as it characterizes the mechanical properties, water absorbency, and reactivity with chemical agents of cellulose (Goldstein, 2004). Given the positive

correlation between the crystallinity of the biopolymer and its hydrophobicity, this physicochemical approach has shown promise in improving both parameters. However, it is worth noting that acid hydrolysis can yield improvements in hydrophobicity, but its efficacy falls short of that achieved through chemical modifications (Ioelovich, 2021).

Conversely, chemical reactions such as esterification play a crucial role in enhancing the hydrophobicity of cellulose and thus broaden its potential applications. This process involves the substitution of free hydroxyl groups with non-polar substituents, resulting in significant improvements in the material's resistance to water (Thakur Vijay K. & Thakur Manju K, 2016). Important to note that such reactions preferentially occur at the primary alcohol group of carbon C-6, which is 10 times more reactive than others (Duceac et al., 2022).

2.3.1 Sizing phenomenon

The sizing process involves introducing hydrophobic components to a hydrophilic surface of a material. It is a complex phenomenon that involves an understanding of colloid and surface interface interactions. The reaction happens with the use of an amphiphilic sizing agent which is typically comprised of a hydrophilic head and a hydrocarbon tail. When introduced to the system, the additive interacts with cellulose fibers shielding their hydroxyl moieties (Figure 3). As liquids interact with cellulose it forms hydrogen bonds with hydroxyl groups with cellulose fibers. This facilitates the penetration and spreading of the liquid through the surface of cellulose (Seppänen, 2007). However, with the addition of a sizing agent into the system, it reacts with cellulose leading to the formation of low-energy regions on the fiber surface that render resistance to aqueous penetration and decreased wettability (Merisalo Jarno-Petteri, 2009).

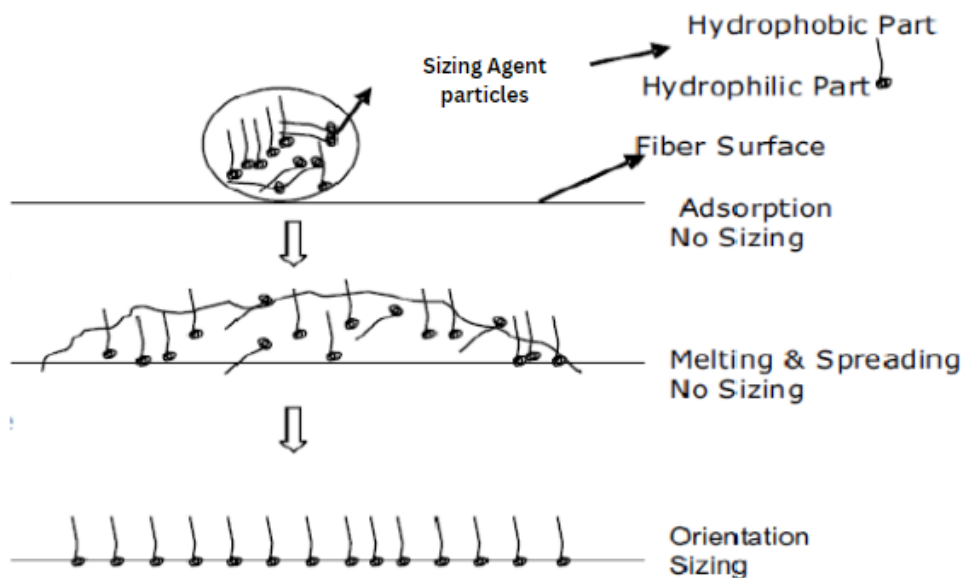


Figure 3. Schematic illustration of sizing mechanism (Kumar et al, 2010).

Alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD) are among the most commonly used sizing agents for the enhancement of the hydrophobicity of cellulose fibers. Different sizing agents have different reactivity within the system, thus achieving different degrees of sizing. Generally, the range of 0.05 – 0.25% is considerably enough for efficient sizing (Hubbe, 2007). When reacting with cellulose, they develop covalent bonds, which are assumed to be a mechanism behind successful sizing (Lindström & Larsson Per Thomas, 2008). However, the validity of such a hypothesis is argued by some scientists and is yet to be proven.

2.3.2 Sizing in papermaking

Cellulose hydrophobicity modification with the use of additives is commonly adopted by various industries such as automotive, textile, and papermaking. The use of chemical additives, in particular, is a very prominent topic in the papermaking industry and contributes to one-third of paper and board production in the world (Porkert, 2016). As vital components in the production process, additives help improve certain properties of paper. The range of additives includes polymer binders, coating additives, process chemicals, sizing, and wet and dry strength agents. Sizing agents are taking second place after polymer coatings and are estimated to be responsible for

12% of the distribution of chemical additives for the world's paper and board manufacture (Suhr et al., 2015).

An internal sizing, as it is recalled in the papermaking industry, involves mixing chemicals with an aqueous slurry of cellulose fibers, leading to reduced fiber absorbency (Hubbe, 2007). The process is usually performed under acidic conditions with a pH ranging from 4.0 to 5.5 using rosin, and under alkaline conditions with the use of AKD. ASA is shown to be efficient at both conditions (Ntifafa et al., 2023).

2.3.3 Migration

The process of internal sizing that involves modification of cellulose properties with the use of ASA or AKD can cause migration of those chemical compounds, meaning they can get absorbed into the packaged food. The research done by Wahyuningsih determined that AKD-coated starch-based biofilm had a higher migration rate than the permitted threshold (Wahyuningsih et al., 2020). However further research is needed to perform more trials on cellulose-based material that is the main focus of this master's thesis.

2.4 Alkenyl Succinic Anhydride (ASA)

Alkenyl succinic anhydride (ASA) was first introduced to the paper industry in the early 1960s as an organic oily compound characterized by its cyclic dicarboxylic anhydride structure (Ntifafa et al., 2023). It is synthesized through an ene reaction between maleic anhydride and isomerized olefins, typically with chain lengths ranging from 15 to 22 carbon atoms (Figure 4). Due to the presence of a highly reactive anhydride ring, ASA is widely regarded as achieving the most effective sizing of cellulose.

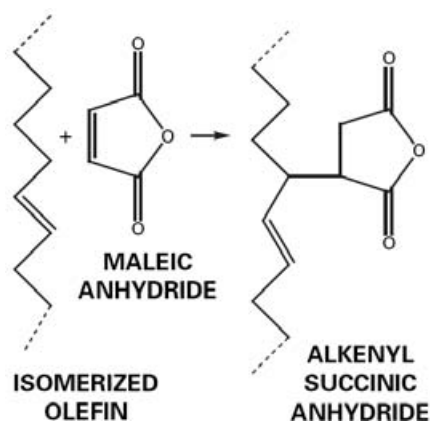


Figure 4. The ene reaction between an isomerized olefin and maleic anhydride in preparation of ASA (Gess & Rende, 2005).

2.4.1 ASA Sizing Mechanism

The sizing mechanism of ASA is known to involve its interaction with cellulose fibers, but not yet fully understood (Martorana et al., n.d.). However, some scientific articles explain the mechanism (Figure 5) of the formation of covalent bonds through an esterification reaction with the hydroxyl groups on the fiber surface (Nishiyama et al., 1995). The process enhances the hydrophobicity of the fibers and creates a coating that is resistant to water penetration through ionic interactions between cellulose and ASA droplets (Hubbe, 2007).

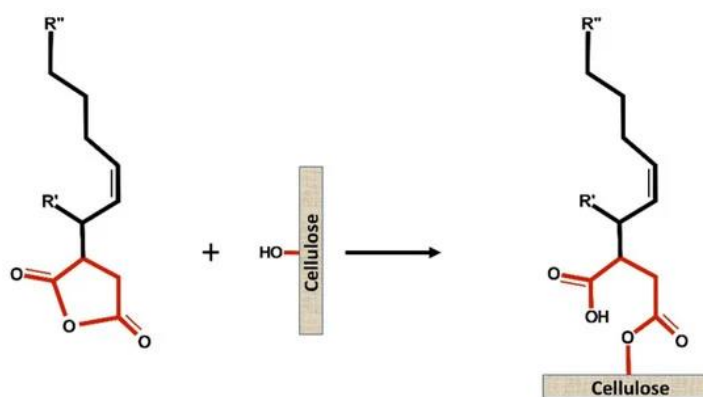


Figure 5. The esterification reaction between ASA and cellulose (Ntifafa et al., 2023).

2.4.2 Limitations of ASA as a sizing agent

ASA is presented as an oily liquid and is water-insoluble, necessitating an emulsification step prior to the desired sizing process. Commonly, the chemical is emulsified with the assistance of additives such as cationic starch or synthetic polymers like polyacrylamide (Gess Jerome & Rende Dominic, 2005). However, ASA's reactivity extends beyond cellulose interaction and includes susceptibility to hydrolysis when emulsified, a process initiated by its reaction with water (Figure 6). The hydrolysis reaction creates amphiphilic ASA acid that is capable of decreasing sizing efficiency by lowering the surface tension of water (Seppänen, 2007).

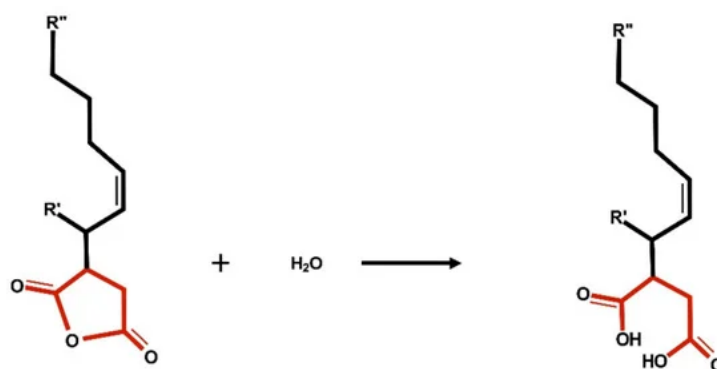


Figure 6. The hydrolysis reaction between ASA and water (Ntifafa et al., 2023).

The presence of water is inevitable, and hydrolysis cannot be fully avoided. This significantly impacts the stability of ASA emulsion, resulting in a relatively short shelf life of approximately 20-30 minutes (Ntifafa et al., 2023). This necessitates meticulous handling of the emulsification step, timely application, and optimization of conditions to ensure successful cellulose treatment.

2.5 Stabilization of ASA emulsion

The rate of hydrolysis often goes in parallel with emulsion stability and sizing efficiency. Consequently, the stability of ASA emulsion is significant and crucial for its effective application. To create an emulsion, oil, and water phases are mixed with the presence of a stabilizer under certain conditions.

2.5.1 The choice and the dose of emulsifier

The stability of an emulsion containing ASA depends on several factors. Firstly, the proper selection and dosage of emulsifiers play a pivotal role, as they facilitate the uniform dispersion of ASA in water and prevent particle agglomeration. Emulsifiers such as synthetic polymers and starches are widely used in the industry to promote sizing performance and increase ASA retention. However, determining the optimal starch-to-ASA ratio is extremely important, as excessive amounts can potentially decrease the yield of the reaction between ASA and cellulose. It has been shown that for low ASA dosages (0.05%), an ASA-to-starch ratio of 1:1 delivers the most prominent sizing (Porkert, 2016).

2.5.2 Particle size

Particle size is another significant parameter that contributes to emulsion stability, as it directly impacts the distribution of sizing agent, surface area, and interaction with cellulose fibers during the sizing process.

In general, smaller particle sizes typically contribute to a more stable emulsion, while larger particles can compromise sizing performance. This relationship is primarily attributed to the larger specific surface area of smaller particles, which facilitates better interaction with cellulose fibers and promotes more efficient sizing. Conversely, larger particles possess reduced surface area that limits their effectiveness in coating cellulose fibers and thereby diminishes the sizing. The stable ASA emulsion has particle size below 1 μm at 50% distribution, and below 2 μm at 90% distribution (Martorana et al., 2008). The acceptable range of particle size lies between 0.5 to 1.5 μm , at which ASA particles are capable of reacting with cellulose but not hydrolyze (Merisalo Jarno-Petteri, 2009).

Additionally, the particle size of an emulsion depends on the shear rate and shear time of the emulsification (Merisalo Jarno-Petteri, 2009). Shear rate refers to the rate at which adjacent layers of fluid move relative to each other, while shear time refers to the duration over which shear forces are applied to the emulsion. Higher shear rates and times of emulsifications result in a smaller particle size (Martorana et al., 2008).

2.5.3 pH

Furthermore, emulsion stability is significantly affected by the pH of a solution. As higher pH affects the ionization state of ASA molecules, it can accelerate particle agglomeration and insufficient distribution throughout the cellulose surface, (Martorana et al., 2008). However, ASA has also been effectively utilized under alkaline conditions and has demonstrated optimal sizing performance within a pH range of 7.5 to 8.4 with the presence of calcium carbonate filler (Hubbe, 2007).

2.5.4 Temperature

Temperature also plays a critical role in particle reactivity. Higher temperatures exponentially increase the rate of chemical reactions, including hydrolysis of ASA. The hydrolysis, as mentioned previously, negatively affects the sizing of cellulose fibers. Figure 7 shows that rapid hydrolysis is achieved at temperatures above 50°C.

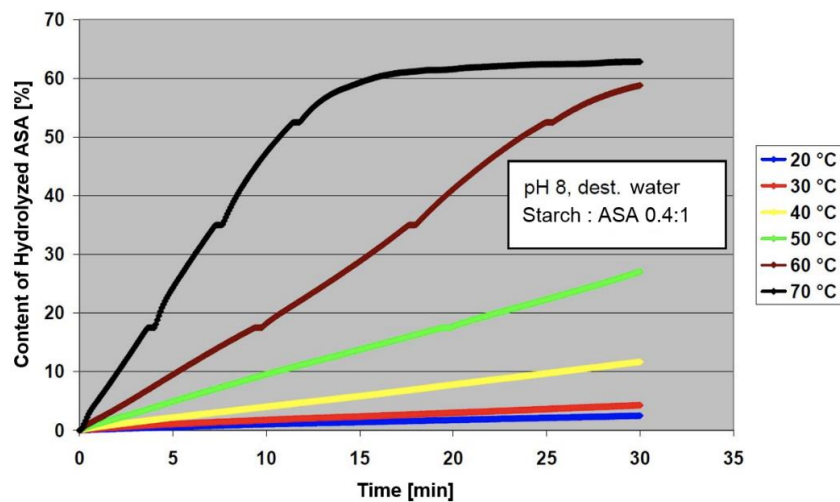


Figure 7. Impact of temperature on hydrolysis rate of ASA.

2.6 Comparison of sizing agents (ASA vs AKD)

In the realm of paper sizing, both ASA and AKD are commonly used as sizing agents to improve the hydrophobicity of the material. Despite their similar purpose of use, they exhibit distinct characteristics and advantages.

Understanding these differences is crucial for selecting the appropriate agent to meet specific production and performance requirements.

Alkyl ketene dimer (AKD), as shown in Figure 8, is synthesized by the reaction of dimerization of fatty acids chloride (Hubbe, 2007). Contrary to ASA, an oily liquid at room temperature, AKD is presented as a waxy substance at ambient temperature. Both agents require an emulsification step with the presence of an emulsifier. Similarly to the anhydride ring of ASA, the lactone ring of AKD exhibits reactivity towards cellulose and water. However, the reactivity of the lactone ring is subtle, rendering AKD more stable under commercial conditions. Its sizing performance is controlled by the formation of covalent bonds between its lactone ring and cellulose, balancing the sizing and hydrolysis reactions. (Lindström & Larsson Per Thomas, 2008).

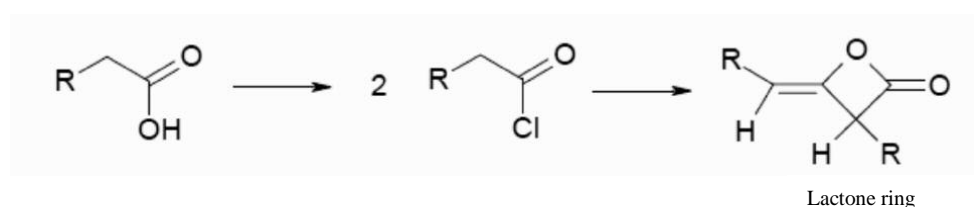


Figure 8. Formation of alkyl ketene dimer (AKD).

To further augment the differences and similarities between these sizing agents, Table 2 provides a comparative overview of ASA and AKD. It highlights key features such as physical state, reactivity, theoretical sizing efficiency, and potential issues.

Table 2. Comparison of ASA and AKD as sizing agents.

Feature	ASA	AKD
<i>Physical state</i>	Liquid oil	Waxy substance
<i>Reactivity</i>	High	Moderate
<i>Reactive element</i>	Anhydride ring	Lactone ring
<i>Potential issues</i>	Sensitivity to hydrolysis	Not efficient sizing

3 Materials and Methods

This section describes an experimental design with a focus on the materials, equipment, and methodologies employed throughout the project.

3.1 Experimental Design

The experimental design consists of two phases aimed at characterizing the emulsion stability and assessing sizing performance (Figure 9). The first phase focused on ASA emulsion characterization, encompassing visual assessment, particle size analysis, and zeta potential determination, which contribute to understanding emulsion stability. Additionally, the hydrolysis of ASA was determined and assessed using a nuclear magnetic resonance (NMR) tool of the extracted compound. The second phase involves evaluating sizing performance using the most stable emulsion identified in the first phase, with measurements such as the Cobb Test. Furthermore, infrared spectroscopy was incorporated to assess the functional band formation of the sizing reaction.

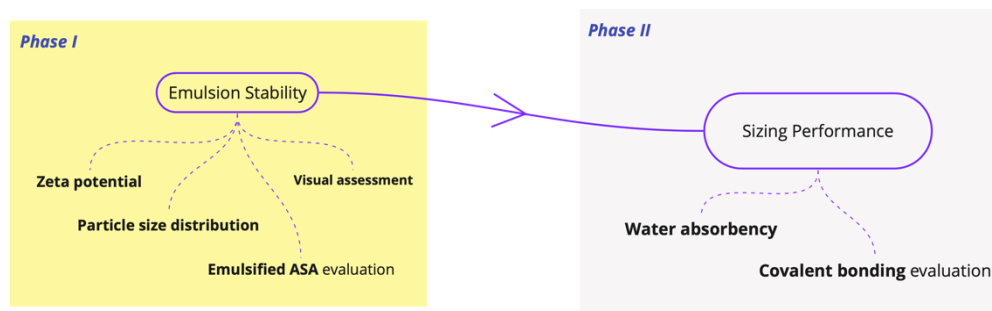


Figure 9. Experimental design overview.

3.2 ASA Emulsion Characterization

Assessing emulsion stability is essential not only for understanding the physical properties of the emulsion but also for optimizing sizing efficiency in the case of sizing agents. Due to the inherent susceptibility of alkenyl succinic anhydride to hydrolysis and the unstable nature of its emulsion, a series of experiments were conducted to thoroughly analyze emulsion stability. As stable emulsion ensures uniform dispersion of ASA particles, trials were carried out to determine the parameters and conditions that will result in the most uniform dispersion of ASA particles at the Kemicentrum of Lund University.

3.2.1 Materials

The primary materials used in the study of ASA emulsion included alkenyl succinic anhydride oil, liquid cationic starch, and deionized (DI) water. Table 3 below provides the specifications of the key raw material. The ASA, a sizing agent, was produced and selected from a reliable chemical supplier and used without further purification. Liquid cationic starch, 25%wt cationic starch solution utilized as an emulsifier, was also sourced from the same specialized supplier.

Table 3. The raw material used for ASA emulsion.

<i>Compound</i>	<i>Specifications</i>
ASA	$C_{18}H_{34}O_3$ 298.5 g/mol b.p > 100°C Liquid oil at RT
Liquid cationic starch	$C_{19}H_{19}N_4O_4S_4Cl$ 531.07 g/mol b.p > 100°C Viscous liquid at RT 25%wt CS concentration

Additionally, various chemicals such as dichloromethane (DCM) for the extraction process, deuterated chloroform ($CDCl_3$) for the NMR procedure, as well as sodium hydroxide (NaCl) for pH adjustments were used.

3.2.2 Adjustable parameters

The choice of parameters for analysis, namely shear rate and pH, was meticulously determined to gain comprehensive insights into the factors that influence emulsion stability and sizing efficiency. Shear rate was selected as it impacts the physical properties of the emulsion, such as droplet size distribution and dispersion uniformity. By varying the shear rate within a specific range, from a minimum of 6000 to 18500 rpm, the effect of agitation intensity on emulsion stability was evaluated. Additionally, pH was considered a critical parameter for the study of ASA emulsion. The pH was adjusted with the use of 0.2M NaOH, across a range from pH 4 to 9 to investigate its impact on emulsion stability. Furthermore, the experimental procedure involved maintaining the temperature at ambient levels to prevent excessive hydrolysis of ASA molecules. Lastly, the ASA to cationic starch ratio (1:1), as well as ASA concentration (5%) were kept constant to isolate the effect of chosen parameters on emulsion stability. The optimal values were chosen based on literature research and recommendations from raw materials suppliers.

3.2.3 Emulsion making procedure

The o/w emulsion making process involves the creation of a stable mixture of alkenyl succinic anhydride, water, and cationic starch. The process (Figure 10) was conducted in a controlled environment under a fume hood to ensure safety and minimize exposure to fumes. The procedure began by accurately weighing the required amounts of liquid cationic starch and water. These components were then slowly mixed using a magnetic stirrer set to a speed of 200 rpm. This gentle mixing allowed for thorough mixing and the formation of a homogeneous mixture was achieved within 5 minutes.

Once cationic starch was fully diluted in water, a specific amount of ASA was added to the mixture. ASA was introduced gradually using a pipette, allowing it to disperse evenly throughout the mixture as it was stirred at the same speed of 200 rpm. This gradual addition and mixing process ensures uniform distribution of ASA within the emulsion.

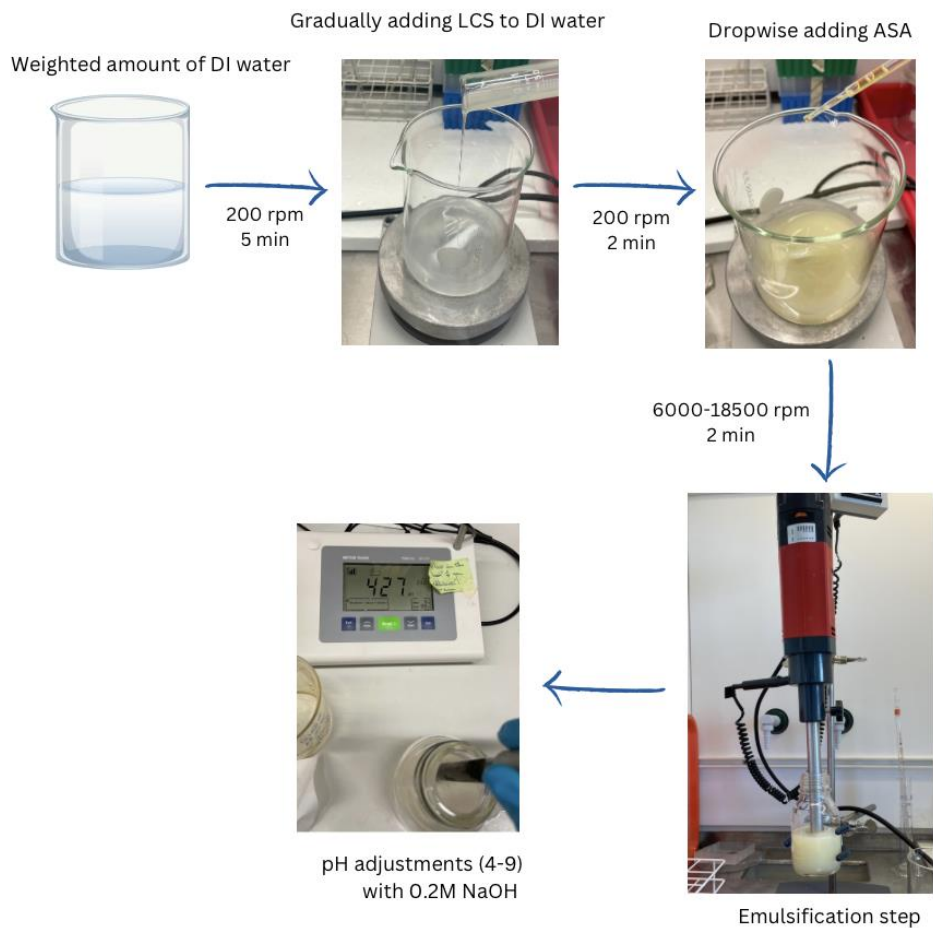


Figure 10. Emulsion making process.

Following the addition of ASA, the mixture undergoes further homogenization using a rotor-stator homogenizer. The operates at a desired range of shear rates, chosen based on the specific requirements. The emulsification process utilized the Ystral X10 rotor-stator (Figure 11), which offers adjustable speed ranging from 3500 to 24000 rpm.



Figure 11. Ystral rotor-stator (Ystral, n.d).

3.2.4 Visual assessment

The stability of the emulsion is visually assessed by observing any signs of separation, sedimentation, or flocculation in comparison to the initial state. Nine emulsion samples, each with a unique combination of shear rate and pH values, were prepared and monitored at specific time intervals: immediately after emulsification (0h), at the 6-hour mark, and 24 hours post-emulsification (Table 4). This qualitative evaluation provides the simplest way to understand emulsion stability under varying conditions of pH and shear rate.

Table 4. Representation of emulsion samples with a unique combination of parameters.

<i>pH</i> \ <i>rpm</i>	6000 rpm	12000 rpm	18500rpm
Acidic pH (4)	Sample A6	Sample A12	Sample A18
Neutral pH (6.6)	Sample N6	Sample N12	Sample N18
Alkaline pH (9)	Sample B6	Sample B12	Sample B18

3.2.5 Particle size analysis

Particle size analysis was conducted to determine the size distribution of ASA particles within the emulsion. The analysis was performed using the dynamic light scattering technique on Zetasizer Nano S (Malvern Instruments Ltd, Worcestershire, UK) with the use of a standard plastic cuvette (Figure 12). To enhance accuracy, each emulsion sample underwent a tenfold dilution to reduce solution opacity and improve data precision regarding particle size.

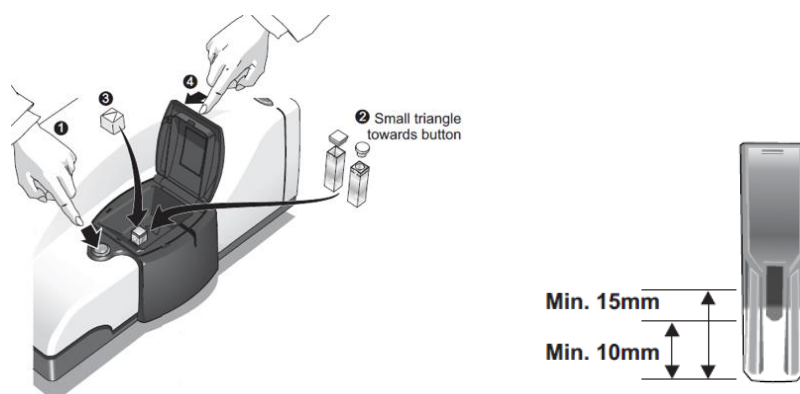


Figure 12. Malvern Zetasizer S (Malvern Instruments Ltd, n.d).

3.2.6 Zeta potential analysis

Zeta potential is another yet important characteristic of emulsion stability, as it provides information on the charge of the particles and their tendency to aggregate or stay discrete. The greater the absolute value of the zeta potential, the more stable the particles, and therefore, the emulsion (Gupta & Trivedi, 2018). The analysis was carried out using the same Malvern Zetasizer Nano S (Malvern Instruments Ltd, Worcestershire, UK), but with a folded capillary

cell, that requires a special filling procedure with the use of a syringe (Figure 13).

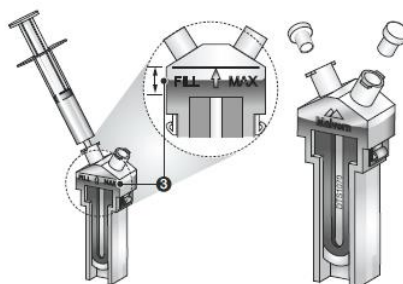


Figure 13. Folded capillary cell (Malvern Instruments Ltd, n.d).

3.2.7 Extracted ASA Characterization

ASA extraction from the emulsion was carried out and characterized to assess the content of hydrolyzed ASA and ASA available for reaction with cellulose, utilizing Nuclear Magnetic Resonance (NMR). Its proton NMR spectra were compared to pure ASA spectra obtained, as well as hydrolyzed the extraction process involved a liquid-liquid extraction technique using DCM as an organic solvent. DCM was chosen after preliminary testing for its ability to dissolve ASA effectively. H NMR spectra were obtained in a Bruker Avance apparatus at 400 MHz. The samples were analyzed in CDCl₃.

3.3 Sizing Performance Characterization

Once the parameters resulting in the most stable emulsion were identified, the emulsion was reproduced at Tetra Pak facilities and subjected to further characterization of its sizing performance. This involved evaluating cellulose water absorption, measuring the change in thickness, and identifying functional groups after sizing treatment.

3.3.1 Cellulose Sample Preparation

The application of emulsion onto the cellulose material was performed through airbrush spraying (Figure 14). The application offers a versatile and efficient method for achieving uniform and precise control over the coating amount. Airbrush spraying involves the atomization of the emulsion into fine droplets, which are then propelled onto the surface of the cellulose sample using compressed air. The technique enables better control and flexibility in tailoring the coating dosage as it provides adjustable spray parameters, such as air pressure and nozzle size.



Figure 14. Treatment application onto cellulose sample through airbrush application.

The samples were presented in a circular shape, with an airlaid layer applied to both sides of the cellulose material. The treatment was only sprayed on one side of the sample, on the top surface of the airlaid. Following the application of the sizing emulsion, the samples underwent post-treatment procedures. Specifically, the samples were molded using a Flat Press (High-Performance Press S&SV, COLLIN Lab & Pilot Solutions GmbH, Maitenbeth, Germany) at a high-temperature range of from 100 – 250°C (Figure 15). Additionally, some samples underwent a curing step at the same temperature range for periods ranging from 5 to 60 minutes to investigate potential variations in sizing degree under different treatment conditions. Subsequently, the samples were stored in airtight containers within a conditioned room maintained at 50% relative humidity (RH) and 25°C.



Figure 15. COLLIN Flat Press (COLLIN, n.d).

3.3.2 Cobb Test

Water absorption of cellulose samples was measured using the Cobb Test following a standardized procedure. The samples were conditioned for 24 hours at 25°C and 50% RH before measuring the Cobb 1800 values. The sizing efficiency of ASA is measured as the Cobb 1800 value to determine water absorption over the period of 30 minutes. The value is calculated according to Eq. (1).

$$Cobb \left[\frac{g}{m^2} \right] = \frac{\text{Weight of the wet sample} - \text{Weight of dry sample}}{\text{Area of the sample}} \quad (1)$$

The specimen holder, presented in Figure 16, served as a platform to hold the cellulose sample during the water absorption process. It consists of a sturdy metal base, ring, mat, and clamping mechanism to secure the specimen firmly in place.

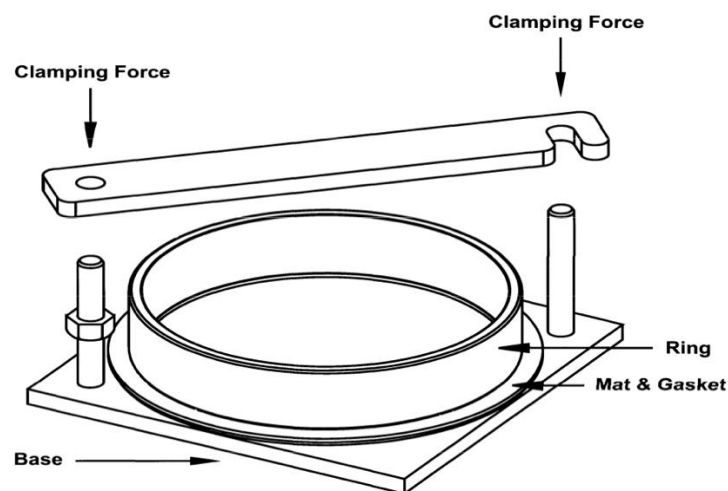


Figure 16. Specimen holder (TAPPI T441, 2013).

3.3.3 Infrared spectroscopy

Fourier-transmission infrared spectroscopy (FTIR) measurements were performed on the sized samples to analyze their chemical composition and identify functional groups representing sizing reactions. FTIR spectroscopy is a powerful analytical technique that provides information on molecular structure based on the absorption of infrared radiation by chemical bonds in the sample (Mohamed et al., 2017). The measurements were performed on ALPHA II (Bruker, Karlsruhe, Germany) with a platinum ATR sampling module.

The samples underwent the sizing distribution evaluation, a meticulous process aimed at ensuring uniform distribution of the ASA treatment across the sample surface. This involved obtaining spectra at five different points on each sized sample to assess the consistency of the chemical composition throughout. Furthermore, the samples were subjected to analysis at various stages of the experimental process to investigate the impact of each step, including sample compression and curing, on the formation of characteristic bands in the spectra.

3.4 Analysis

The quantitative results of the emulsion characterization, focusing on particle size and zeta potential, were thoroughly analyzed using MINITAB Statistical Software. To gain insights into the relationship of the performed measurements and various experimental conditions, a linear regression analysis was employed. The statistical method allowed to identify and quantify the impact of factors such as shear rate, pH and time after emulsification on the particle size and zeta potential of ASA emulsion. Furthermore, contour plots were generated to visually represent these relationships, providing a clear understanding of how changes in experimental conditions influence the emulsion properties. This visual representation helped in identifying optimal conditions for ASA emulsion.

4 Results and Discussion

This section presents the data collected from the experimental model, detailing the analysis of ASA emulsion characterization and its sizing performance. Additionally, it includes a comparative analysis with AKD sizing, which was conducted previously by Tetra Pak.

4.1 ASA Emulsion Evaluation Analysis

4.1.1 Visual assessment analysis

The visual assessment served as the initial screening method for identifying unstable emulsions. Table 5 summarizes and color codes the visual observations obtained in the evaluation of the physical state of emulsion samples, providing a comprehensive overview of the stability issues encountered at various pH and shear rate levels. As shown in Table 5, the results indicate that ASA emulsions with higher pH tended to exhibit particle aggregation and undergo rapid thickening.

Table 5. Emulsion consistency description based on visual evaluation.

Sample	Duration		
	0h	6h	24h
A6	Liquid	Liquid	Phase separation
A12	Liquid	Liquid	Liquid
A18	Liquid	Liquid	Liquid
N6	Liquid	Thickened liquid	Gelatinized
N12	Liquid	Thickened liquid	Gelatinized
N18	Liquid	Thickened liquid	Gelatinized
B6	Liquid	Gelatinized	
B12	Liquid	Gelatinized	
B18	Liquid	Gelatinized	

The emulsion thickening observation was particularly prominent in emulsions with alkaline pH conditions (Figure 17). The finding validates the

literature review emphasizing the critical role of pH in emulsion stability potentially due to changes in electrostatic interaction between the emulsion components. This thickening of the emulsion can be attributed to the increased rate of hydrolysis and subsequent destabilization of the emulsion structure, leading to a more viscous mixture (Gess Jerome & Rende Dominic, 2005).



Figure 17. Gelatinization of Sample B12 at 6 hours post-emulsification.

Moreover, the visual assessment demonstrated that at a lower shear rate of 6000 rpm, the emulsion experienced phase separation, indicating instability (Figure 18). This separation, characterized by the distinct watery layer formed within the emulsion, highlights the necessity of a medium to high shear rate for achieving emulsion stability. As mentioned by Martorana, at lower shear rates, the mixing energy is insufficient to adequately disperse the ASA droplets within the water phase, leading to eventual phase separation.

Based on the visual assessment, it was concluded that higher shear rates and lower pH levels result in a more stable ASA emulsion.

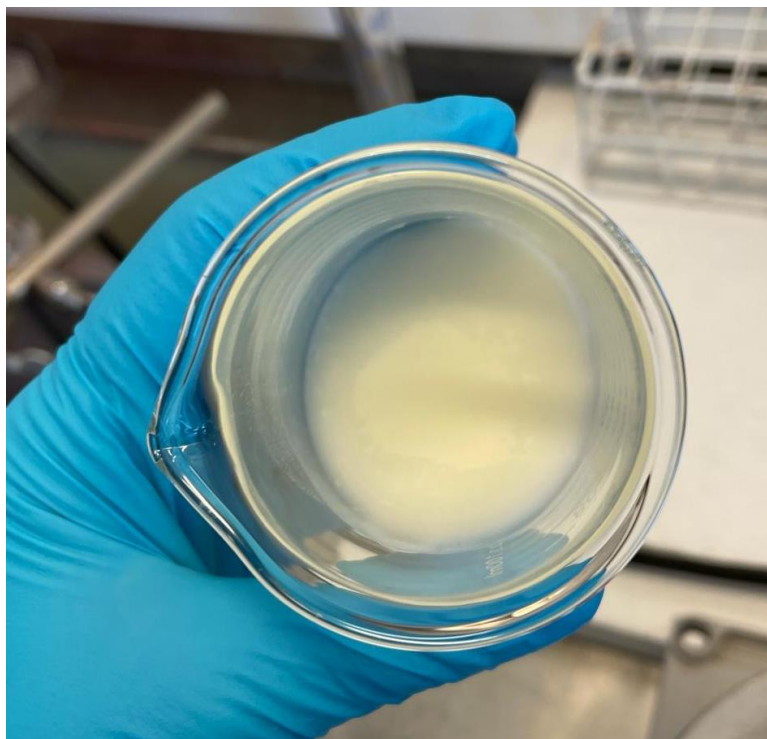


Figure 18. Phase separation of sample A6 at 24 hours post emulsification.

4.1.2 Particle size and zeta potential analysis

Subsequent screening of various parameters in finding emulsion stability was associated with particle size distribution and zeta potential. These measurements were performed to validate the visual assessment, providing a more quantitative approach to understanding emulsion stability. According to the literature review, stable emulsion requires higher zeta potential values and smaller particle sizes.

Contour plots were generated using MINITAB statistical software to illustrate relationships between adjustable parameters – pH and shear rate – and their impact on hydrodynamic radius (particle size) and electrophoretic mobility measurements (zeta potential) of emulsions. These plots provide a

color-coded visual representation of how variations in adjustable variables influence emulsion stability (Figure 19 & Figure 20).

The light green region of pH contour plot (Figure 19) represents area of the optimal emulsion conditions, where smaller values of particle size and high absolute values of zeta potential are observed. The region corresponds to emulsion prepared in acidic conditions. Similarly, the dark green region in Figure 20 represents the same characterized emulsion and corresponds to high shear rate conditions.

Consequently, it was observed that the optimal emulsion parameters emerge at a shear rate of 18500 rpm and acidic pH of 4, as these conditions resulted in the smallest particle sizes and the higher absolute values of zeta potential. This quantitative analysis corroborates the initial visual screening, confirming that higher shear rates and lower pH levels are crucial for achieving stable ASA emulsion.

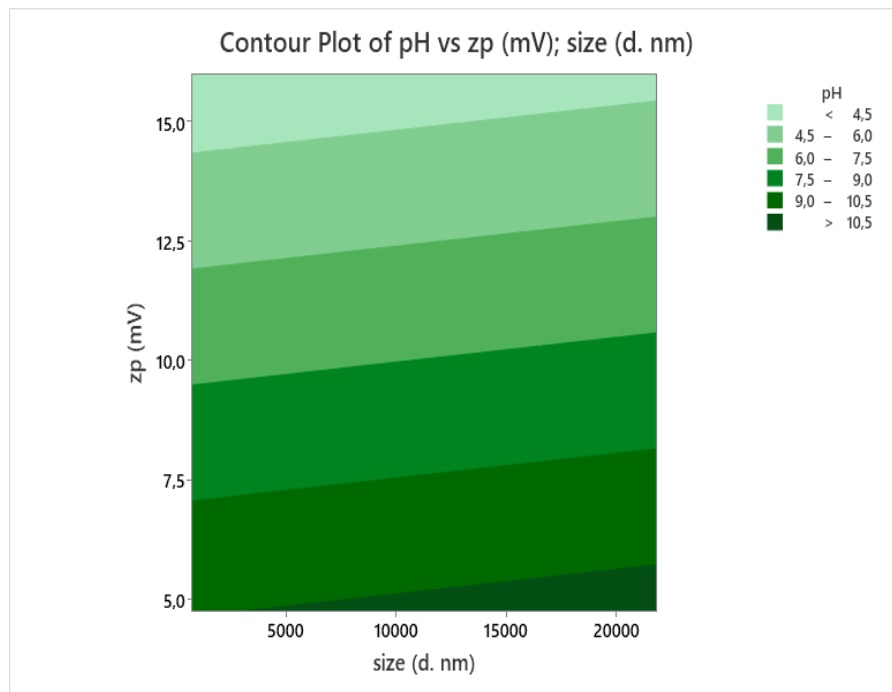


Figure 19. Contour plot of pH vs zeta potential and particle size.

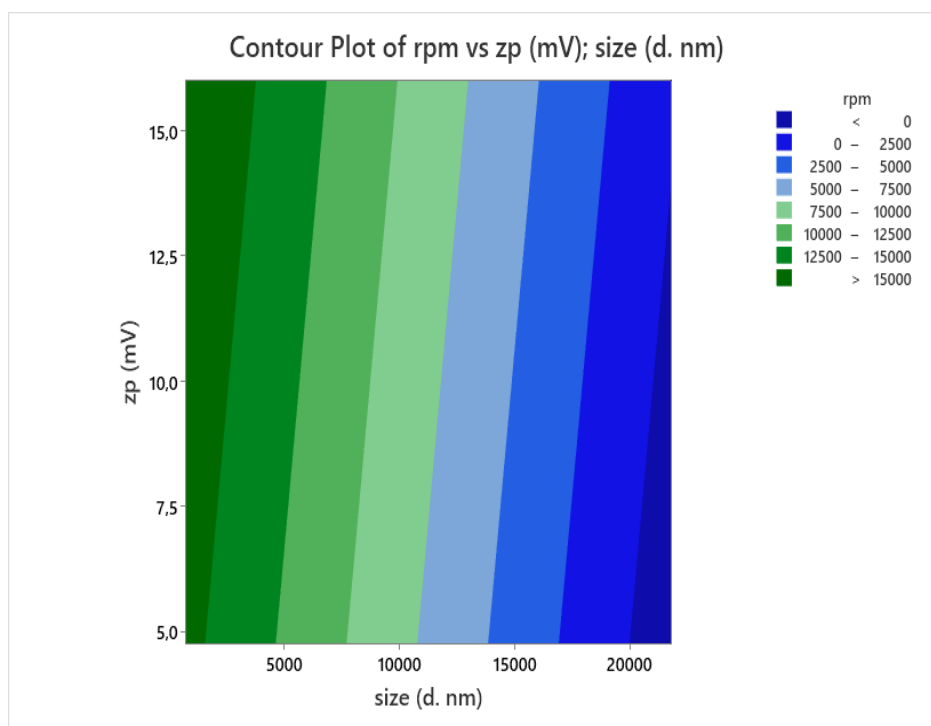


Figure 20. Contour plot of shear rate vs zeta potential and particle size

4.2 Extracted ASA Analysis

It was important to determine whether the ASA emulsion, optimized for its stability, was susceptible to hydrolysis. To address this concern, ASA was extracted from the emulsion, and ^1H NMR spectroscopy was conducted and compared to the spectra of a pure ASA.

The spectra of pure ASA exhibited characteristic peaks corresponding to its functional groups and molecular structure, as summarized in Table 6. This table is a detailed overview of the peak positions and their corresponding assignments, serving as a reference for comparison with theoretical review. To aid in the visualization and understanding of Table 6, Figure 21 represents the molecular structure of pure ASA, with labels indicating the specific atoms and bonds corresponding to each peak. Based on the comparison of observed and expected chemical shifts, the spectra of pure ASA were detected and well-aligned, indicating that the pure ASA was accurately identified.

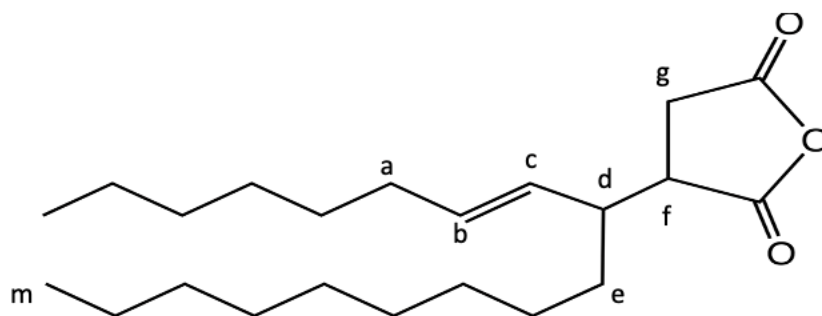


Figure 21. Labeled ASA structure.

Table 6. Expected and observed chemical shift of pure ASA obtained from H NMR spectra.

Label	Specification	Chemical shift (ppm)	
		Expected	Observed
<i>f</i>	-CH (1H, q) succinic anhydride	3.16	3.169
<i>g</i>	-CH ₂ (2H, d) succinic anhydride	2.77 - 2.9	2.7 - 2.9
<i>d</i>	-CH (1H, m)	2.6	2.3
<i>c</i>	-H (1H, t) ethylene	5.4	5.6
<i>b</i>	-H (1H, q) ethylene	5.3	5.1
<i>a</i>	-CH ₂ (2H, q) methylene	2.0	2.0
<i>e</i>	-CH ₂ (22H, q) aliphatic chain	1.4	1.27
<i>m</i>	-CH ₃ (6H, t) methyl	0.88	0.89

Figure 22 illustrates the spectral alignment, demonstrating the integrity of ASA after extraction. It revealed that comparing the spectra of the extracted ASA to the spectra obtained from pure ASA, all major peaks aligned, confirming the successful extraction method of ASA from the emulsion. However, the spectra of extracted ASA also displayed some unidentified extra peaks. Figure 23 highlights these additional peaks, suggesting the presence of potential impurities or byproducts, possibly resulting from interaction with other components in the emulsion, such as cationic starch, which was detected in the range of 3.5 to 4.5 ppm and could partially solubilize along with ASA. Additionally, DCM, used in the extraction process, may also contribute to these interactions. The potential interactions and their implications are further detailed in Appendix A, which provides supplementary spectra of those components.

Nevertheless, the NMR spectra revealed several important observations. Crucially, the absence of the peak corresponding to hydrolyzed ASA (at 10-12 ppm) in the extracted ASA spectra indicates that significant hydrolysis did not occur. This finding is a promising sign, suggesting that the ASA remains largely unhydrolyzed and is thus capable of binding and reacting effectively with cellulose, thereby enhancing the material's hydrophobic properties.

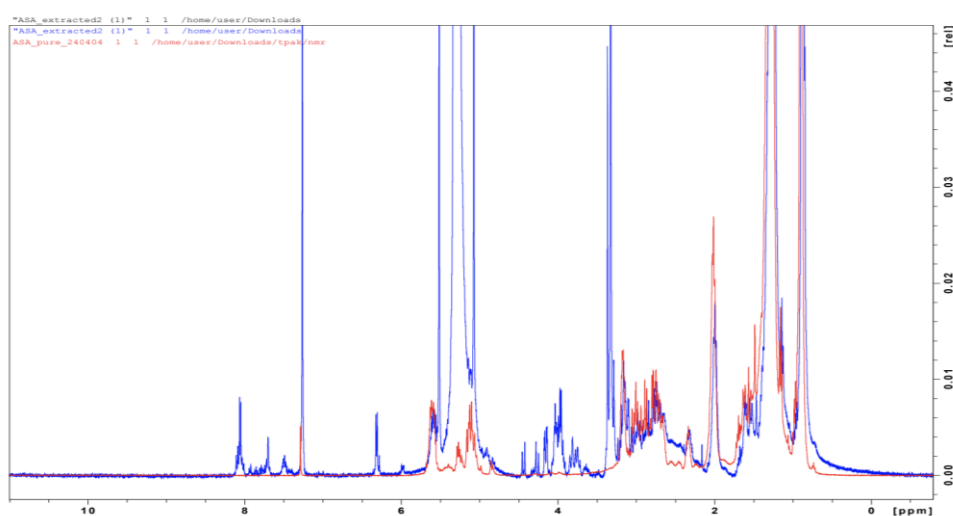


Figure 22. Pure ASA (red) and Extracted from the emulsion ASA (blue) spectra

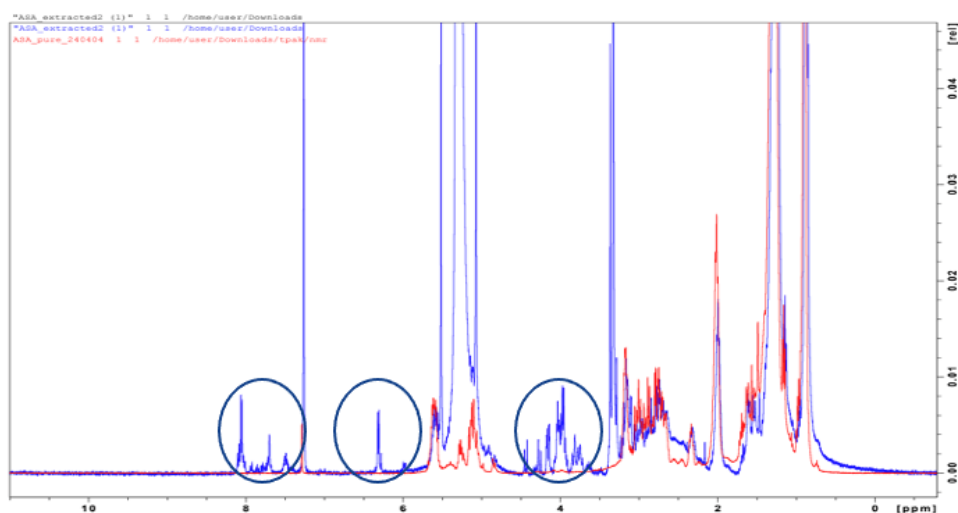


Figure 23. Pure ASA (red) and Extracted from the emulsion ASA (blue) spectra with unidentified peaks circled.

4.3 Sizing Performance Analysis

4.3.1 Water absorption analysis based on curing

Water absorption was measured on treated cellulose samples subjected to different processing conditions to evaluate the curing step on the material's hydrophobicity. Each sample was treated with the same ASA dose (0.4%) to ensure consistency. The experimental setup included two sets of samples: one set underwent a curing procedure, while the other set was processed without the curing step. This comparison aimed to determine whether the curing process significantly impacts water absorption properties, as avoiding the curing step would simplify and streamline the production process.

Figure 24 presents a comparison graph of Cobb Test values for treated cellulose samples, highlighting the difference in water absorbency between samples that underwent a curing step and those that did not. Based on the results presented, it is evident that the curing step significantly impacted the water absorbency of the samples. The data indicate that samples subjected to the curing step exhibited markedly lower Cobb values compared to those that were uncured. This suggests that, at the tested experimental conditions, the curing step enhances the ASA's ability to bond effectively with cellulose fibers, reducing the material's water uptake. Moreover, it is essential to contextualize the water absorbency results considering the baseline Cobb value for untreated cellulose samples, which is around 2500 g/m^2 .

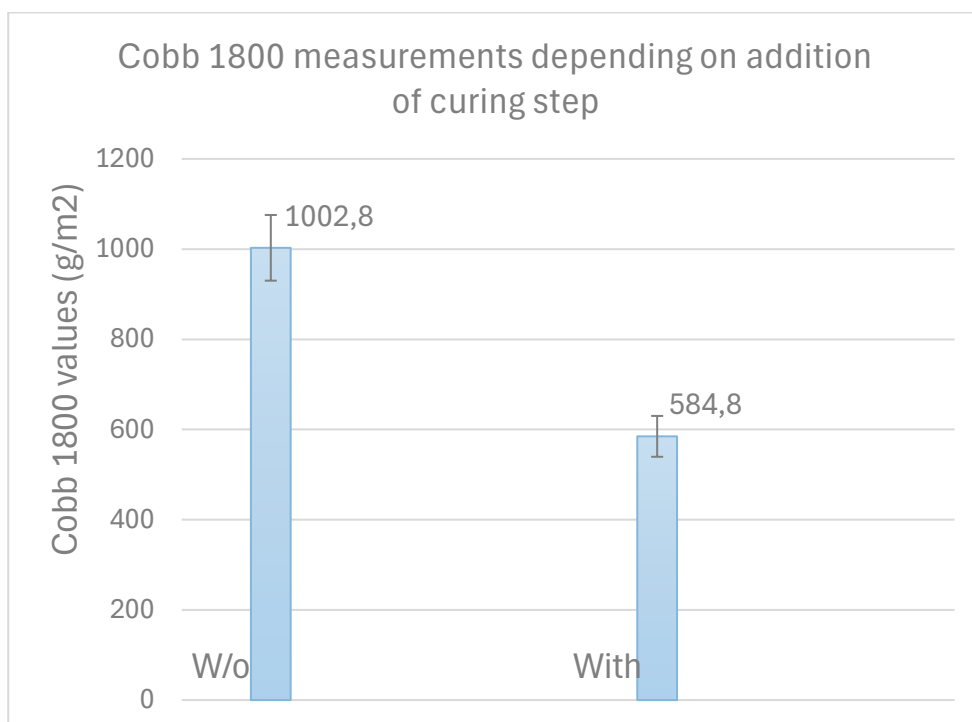


Figure 24. Average Cobb 1800 values for samples with and without curing step in the process.

However, overall values for the Cobb test indicated that the ASA treatment did not improve the hydrophobicity of cellulose fibers. The best-performing cured ASA sample still absorbed $533\text{g}/\text{m}^2$, which is substantially higher than the weakest water absorbency value for AKD sizing under similar conditions, which was under $100\text{g}/\text{m}^2$. This extreme difference highlights that the ASA-treated cellulose material falls short of the water resistance levels achieved with AKD sizing at the particular testing conditions and concentration. Consequently, further optimization and a new approach were considered to improve ASA sizing performance.

4.3.2 Water absorption analysis based on ASA dose

When comparing Cobb Test measurements of samples with different ASA doses, it was observed that higher doses did not significantly improve the water absorbency of the cellulose material. Figure 25 presents a comparison of Cobb Test values for treated samples, illustrating the impact of different ASA doses on water absorbency. The comparison highlights that for cured samples, the best sizing performance was achieved with a 0.4% ASA dose.

In contrast, the sizing performance for non-cured samples showed a slight improvement of approximately 16% at a 2% ASA dose compared to a 0.4% ASA dose.

These results suggest that while a higher ASA dose does not enhance water absorbency in cured samples, it does provide some improvement in non-cured samples. However, the observed improvement is insufficient to justify using higher doses. The results align with the literature, which indicates that excessive ASA dosing may lead to diminishing returns in hydrophobic performance. Nevertheless, more trials and repetitions are needed to confirm and validate these findings to ensure the reliability of the results.

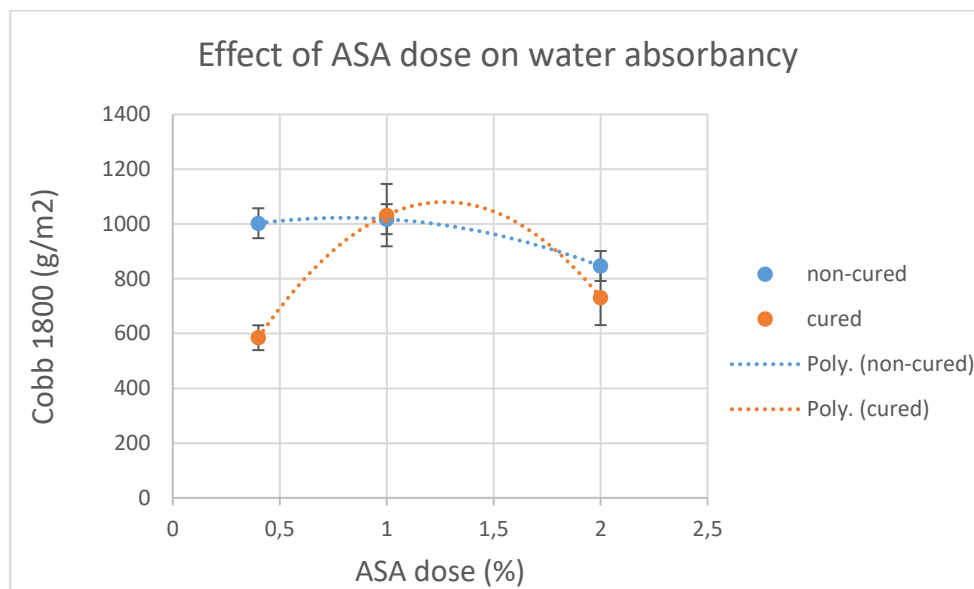


Figure 25. Water absorbency of cellulose samples based on % ASA dose.

4.3.3 Visual assessment based on ASA dose

Visually evaluating samples with varying percentages of ASA doses showed a noticeable trend: the higher the ASA dose, the darker the sample became. Figure 26 presents the trend, illustrating the change in cellulose sample appearance with increasing ASA concentration in a treatment dose. The figure highlights that higher ASA doses result in more pronounced darkening of the cellulose fiber-based material, indicating that the treatment becomes more visible at elevated doses. This darkening effect presents a significant challenge. Maintaining the original visual aspects of the cellulose material is

crucial, as any noticeable change in appearance may not be acceptable for the final product.

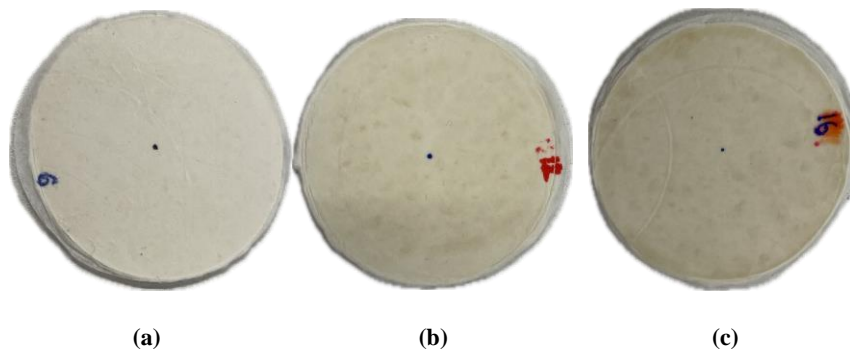


Figure 26. Visual appearance of cellulose samples with different ASA dose concentrations: (a) 0.4% ASA dose, (b) 1% ASA dose, (c) 2% ASA dose.

4.3.4 Sizing treatment distribution analysis

To determine and evaluate the distribution of ASA sizing treatment across the cellulose sample, FTIR spectroscopy was employed. For each sample, five different points on the surface of the treated size were selected and their spectra were compared. As shown in Figure 27, the spectra from all five points for the sample, were closely aligned, indicating that the ASA treatment was evenly distributed across the sample surface. This consistency in the spectra suggests that the sizing agent was uniformly applied, which is critical for ensuring consistent water resistance and overall performance of the treated material. Moreover, the alignment of spectra facilitates further analysis and allows for the comparison of spectra at different stages of the treatment process to be evaluated at a single point.

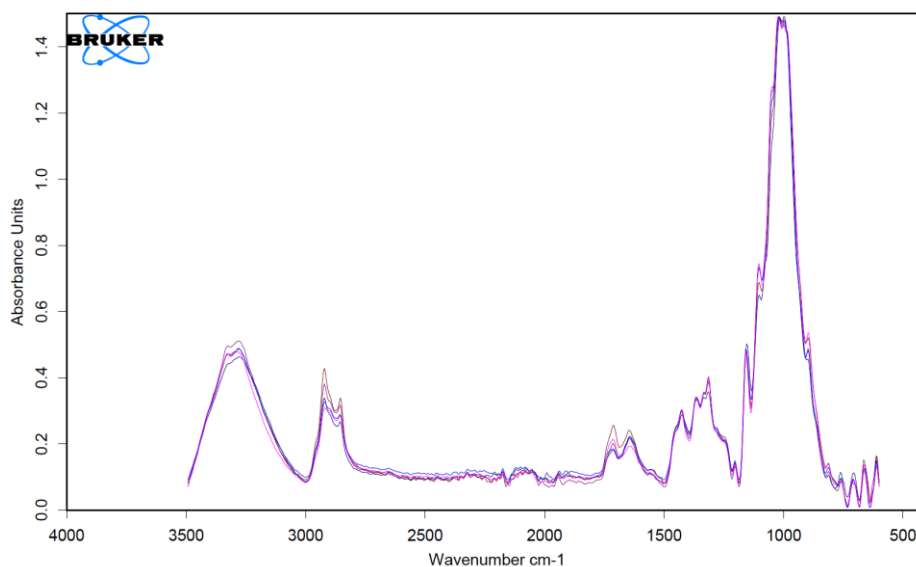


Figure 27. FTIR spectra of 2% ASA dose, cured sample

4.3.5 Comparison throughout the treatment process

To gain a deeper understanding of the chemical interactions and structural changes occurring during the ASA treatment process, the FTIR spectra were conducted at various stages of the treatment process. Subsequently, the scheme for comparison of the effect of different processing stages: spraying, sample compression, and curing is illustrated in Figure 28. Additionally, the spectra of pure ASA were obtained to assist in identifying peaks.

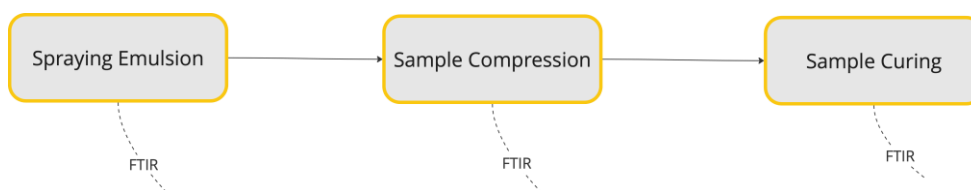


Figure 28. Scheme of FTIR analysis throughout the treatment process.

In Figure 29, FTIR spectra obtained at the stages mentioned above were compared with spectra for pure ASA. Spectra showed the expected strong presence of a peak at 1784 cm⁻¹ in the pure ASA spectrum that corresponds

to the carbonyl stretching vibration of the anhydride group of ASA (Li et al., 2015). Notably, the same peak appeared in the spectra of the molded and cured samples, although with reduced intensity. The reduced intensity suggests that while the carbonyl band remains present, its concentration decreases, likely due to the reaction with cellulose, partial hydrolysis during the treatment process, or thermal degradation.

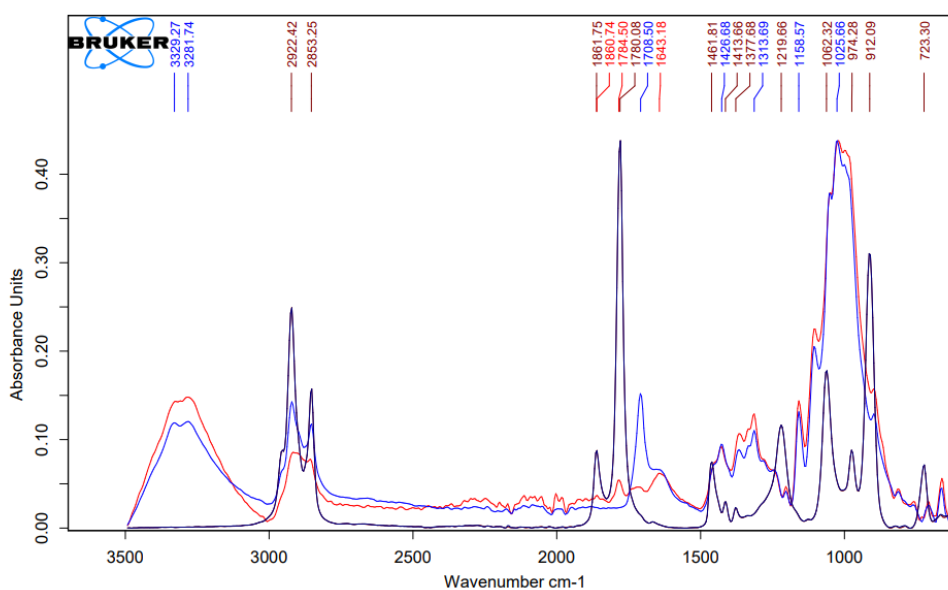


Figure 29. FTIR spectra of pure ASA (black), cellulose sample after compression (red), and after curing (blue).

Figure 30 presents the comparison of spectra corresponding to different stages of the processing procedure. Based on the spectra, the sprayed sample exhibits a peak at 1708 cm⁻¹, which is suspected to correspond to hydrolyzed ASA, as carboxylic acid stretching typically appears in the range of 1700 – 1725 cm⁻¹ (Mohamed et al., 2017). This peak is also present in the spectra of the molded and cured cellulose samples, however at a lower intensity. A similar intensity reduction can be observed for peaks corresponding to an olefinic chain of ASA at 2920 cm⁻¹ and 2853 cm⁻¹. The reduction in peak intensity could be attributed to several factors. As compression and curing stages involve the application of high temperatures, it could facilitate ASA evaporation as ASA with its highly reactive anhydride ring is more volatile compared to other sizing agents. Additionally, higher temperatures could promote ASA to react with other compounds of the system and reduce the presence of free carboxylic acid groups (Wan, 1988)

The covalent bond formation between ASA and cellulose, indicative of the sizing of the material, was not observed in the spectra of the treated samples at any stage. Ester bonds are expected to exhibit stretching in the range of 1730 – 1750 (Mohamed et al., 2017). The absence suggests that the anticipated chemical reaction between ASA and cellulose did not occur or was not sufficiently prominent to be detected by FTIR analysis. This also explains the poor water resistance values obtained in the Cobb Test, as effective esterification is crucial for enhancing hydrophobicity and improving the barrier properties of the treated cellulose material (Li et al., 2015).

However, the possibility that the FTIR tool's sensitivity might not be sufficient to detect the covalent bonding if they are formed in small quantities. This limitation could potentially impact the ability to accurately quantify the extent of covalent bonding within the samples under study.

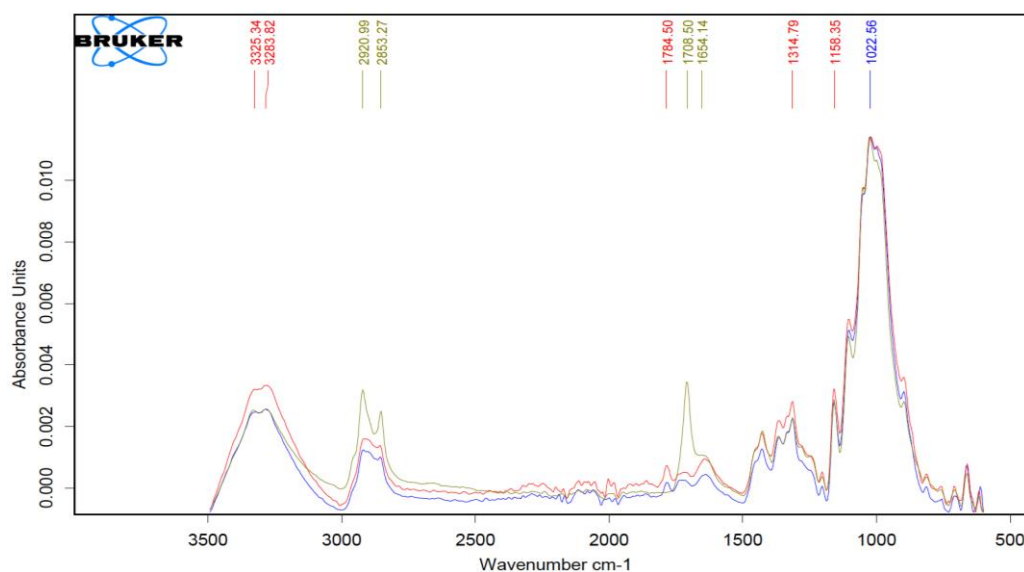


Figure 30. FTIR spectra of cellulose sample after spraying (green), after compression (red), and after curing (blue).

5 Conclusion

This section summarizes and explains important discoveries on ASA emulsion stability and its performance in improving the hydrophobicity of cellulose-based material.

5.1 ASA Emulsion Optimization

Through the initial screening phase, visual assessments were conducted on emulsions prepared under varying parameters of shear rate and pH. This qualitative evaluation allowed for the elimination of visibly unstable emulsions, such as those that exhibited rapid thickening or phase separation.

The second screening phase employed instrumental measurements to further refine the assessment. Particle size distribution and zeta potential measurement provided quantitative data that indicated the stability of the emulsions. The results from these assessments led to the identification of optimal parameters for emulsification: a shear rate of 18500 rpm and an acidic pH of 4. These conditions produced the most stable ASA emulsion, characterized by smaller particle sizes and higher zeta potential values, which correlate with enhanced stability.

5.2 ASA Sizing Performance

Using the optimized emulsion, the sizing performance was evaluated through various tests, including the Cobb Test for evaluation of water absorption and FTIR analysis for functional group identification.

The Cobb Test results indicated that the curing step significantly improved water resistance, as evidenced by lower water absorption values in cured cellulose samples compared to non-cured samples. However, even the best-performing cured ASA-treated sample showed high water absorbency, with

values far exceeding the acceptable range for effective water barriers. In comparison, the AKD sizing agent demonstrated superior performance under similar conditions.

FTIR analysis revealed that anticipated covalent bond formation between ASA and cellulose was not observed. This absence of ester bonds explains the poor water resistance obtained in the Cobb Test. Additionally, the presence of a peak that represents ASA-acid, could also contribute to the suboptimal water resistance.

The study concludes that while the optimization of ASA emulsion achieved a stable formulation under a specific shear rate and pH conditions, the resulting ASA-treated cellulose fiber-based material did not exhibit the desired improvement in hydrophobicity.

5.3 Future research

Based on the findings of the study, several recommendations for future research are proposed to address the limitations and enhance the outcomes of ASA sizing of cellulose-based material. These studies could explore further the influence of ratio deviations of ASA emulsion components on sizing performance. Understanding the balance between those elements could provide insights into optimizing emulsion stability and improve the effectiveness of ASA in binding to cellulose.

Besides ratio, ASA sizing performance could be affected by the low stability of cationic starch, exploring alternative or additional emulsion stabilizers is advised. Beyond cationic starch, other biopolymers or synthetic emulsifiers could be explored in attempts to enhance ASA emulsion stability and sizing behavior (Kumar et al., 2020).

Additionally, exploring other pH levels of ASA emulsion for its sizing behavior could be explored in future trials. Since considerable research has been conducted on alkaline sizing, it would be interesting to investigate whether these conditions, despite their instability in the shelf life, result in sufficient sizing performance.

References

- Antonopoulos, I., Faraca, G., & Tonini, D. (2021). Recycling of post-consumer plastic packaging waste in EU: Process efficiencies, material flows, and barriers. *Waste Management*, *126*, 694–705. <https://doi.org/10.1016/j.wasman.2021.04.002>
- Asim, N., Badiei, M., & Mohammad, M. (2022). Recent advances in cellulose-based hydrophobic food packaging. In *Emergent Materials* (Vol. 5, Issue 3, pp. 703–718). Springer Nature. <https://doi.org/10.1007/s42247-021-00314-2>
- Balasubramaniam, S. L., Patel, A. S., & Nayak, B. (2020). Surface modification of cellulose nanofiber film with fatty acids for developing renewable hydrophobic food packaging. *Food Packaging and Shelf Life*, *26*, 100587. <https://doi.org/10.1016/j.fpsl.2020.100587>
- Bordón, P., Elduque, D., Paz, R., Javierre, C., Kusić, D., & Monzón, M. (2022). Analysis of processing and environmental impact of polymer compounds reinforced with banana fiber in an injection molding process. *Journal of Cleaner Production*, *379*. <https://doi.org/10.1016/j.jclepro.2022.134476>
- Duceac, I. A., Tanasa, F., & Coseri, S. (2022). Selective Oxidation of Cellulose—A Multitask Platform with Significant Environmental Impact. *Materials*, *15*(14). <https://doi.org/10.3390/MA15145076>
- Eurostat. (2022). *Plastic packaging waste*. <https://ec.europa.eu/eurostat/web/products-eurostat-news/-/ddn-20221020-1#:~:text=Plastic%20packaging%20waste%3A%2038%25%20recycled%20in%202020%20%2D%20Products%20Eurostat%20News,-Back%20Plastic%20packaging&text=In%202020%2C%20each%20person%20living,waste%20published%20by%20Eurostat%20today>.
- Gess Jerome, & Rende Dominic. (2005). Sizing background and theory: Alkenyl Succinic Anhydride (ASA). *TAPPI Journal*, *4*(9), 25–30.
- Geyer, R., Jambeck, J. R., & Law, K. L. (2017). Production, use, and fate of all plastics ever made. *Science Advances*. <https://www.science.org>
- Goldstein, I. S. (2004). WOOD FORMATION AND PROPERTIES | Chemical Properties of Wood. In *Encyclopedia of Forest Sciences* (pp.

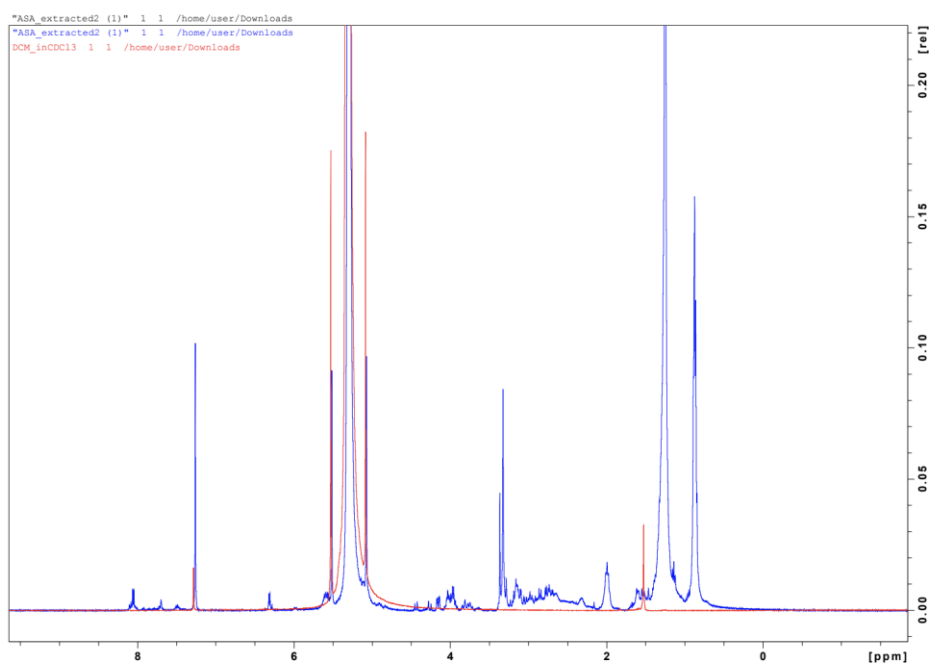
- 1835–1839). Elsevier. <https://doi.org/10.1016/B0-12-145160-7/00042-9>
- Gupta, V., & Trivedi, P. (2018). In vitro and in vivo characterization of pharmaceutical topical nanocarriers containing anticancer drugs for skin cancer treatment. In *Lipid Nanocarriers for Drug Targeting* (pp. 563–627). Elsevier. <https://doi.org/10.1016/B978-0-12-813687-4.00015-3>
- He, M., Lu, A., & Zhang, L. (2014). Advances in cellulose hydrophobicity improvement. *ACS Symposium Series, 1162*, 241–274. <https://doi.org/10.1021/bk-2014-1162.ch018>
- Hubbe, M. A. (2007). *Paper's Resistance to Wetting - a Review of Internal Sizing Chemicals and their Effects*.
- Ioelovich, M. (2021). Adjustment of hydrophobic properties of cellulose materials. *Polymers, 13*(8). <https://doi.org/10.3390/polym13081241>
- Kadla John, & Gilbert R.D. (2000). *Cellulose structure: A review*. Cellulose Chemistry and Technology. https://www.researchgate.net/publication/285045705_Cellulose_structure_A_review
- Klemm, D., Heublein, B., Fink, H., & Bohn, A. (2005). Cellulose: Fascinating Biopolymer and Sustainable Raw Material. *Angewandte Chemie International Edition, 44*(22), 3358–3393. <https://doi.org/10.1002/anie.200460587>
- Kumar, A., Bhardwaj, N. K., & Singh, S. P. (2020). Studies on ASA emulsion stabilized with anionic polyvinylamine and its evaluation for sizing of different types of paper furnishes. *Colloids and Interface Science Communications, 34*. <https://doi.org/10.1016/j.colcom.2019.100229>
- Li, H., Liu, W., Yu, D., & Song, Z. (2015). Anchorage of ASA on cellulose fibers in sizing development. In *PAPER CHEMISTRY Nordic Pulp & Paper Research Journal* (Vol. 30, Issue 4).
- Lindström, & Larsson Per Thomas. (2008). Alkyl Ketene Dimer (AKD) sizing – a review. *Nordic Pulp and Paper Research Journal, 23*(2), 202–209.
- Macleod, M., Peter, H., Arp, H., Tekman, M. B., & Jahnke, A. (2021). The global threat from plastic pollution. *Science Advances*. <https://www.science.org>
- Martorana, E., Belle, & Kleemann, J. (2008). ASA Optimisation-Control of Particle Size, Stability and Hydrolysis. In *Professional Papermaking* (Vol. 5, Issue 2).

- Martorana, E., Porkert, S., & Kleemann, S. (n.d.). *New findings for interactions and mechanisms in paper sizing with ASA and AKD*.
- Merisalo Jarno-Petteri. (2009). *Optimization of ASA Emulsification in Internal Sizing of Paper and Board*.
- Mohamed, M. A., Jaafar, J., Ismail, A. F., Othman, M. H. D., & Rahman, M. A. (2017). Fourier Transform Infrared (FTIR) Spectroscopy. In *Membrane Characterization* (pp. 3–29). Elsevier.
<https://doi.org/10.1016/B978-0-444-63776-5.00001-2>
- Ncube, L. K., Ude, A. U., Ogunmuyiwa, E. N., Zulkifli, R., & Beas, I. N. (2021). An overview of plasticwaste generation and management in food packaging industries. *Recycling*, 6(1), 1–25.
<https://doi.org/10.3390/recycling6010012>
- Nishiyama, M., Isogai, A., & Onabe, F. (1995). *Structures of Alkenyl Succinic Anhydride (ASA) Components in ASA-Sized Papersheet* *.
- Novakovic, K., Thumbarathy, D., Peeters, M., Geoghegan, M., Go Jefferies, J., Hicks, C., Manika, D., & Dai, S. (2023). Zero-waste circular economy of plastic packaging: The bottlenecks and a way forward. *Sustainable Materials and Technologies*, 38.
<https://doi.org/10.1016/j.susmat.2023.e00735>
- Ntifafa, Y., Xu, L., Bollinger, S., Ji, Y., & Hart, P. W. (2023). *Alkenyl Succinic Anhydride: The Question of Covalent Bond-ing and Chemistry Considerations for Better Sizing-Review*.
<https://doi.org/10.20944/preprints202306.0998.v1>
- OECD. (2022). *Plastic pollution is growing relentlessly as waste management and recycling fall short*.
<https://www.oecd.org/environment/plastic-pollution-is-growing-relentlessly-as-waste-management-and-recycling-fall-short.htm>
- Piergiovanni, L., & Limbo, S. (2016). *Introduction to Food Packaging Materials* (pp. 1–3). https://doi.org/10.1007/978-3-319-24732-8_1
- Porkert, S. (2016). *Physico-Chemical Processes during Reactive Paper Sizing with Alkenyl Succinic Anhydride (ASA)*.
<https://doi.org/10.13140/RG.2.2.18268.39045>
- Robertson, G. (2024). *Food Packaging: Principles and Practice* (Third Edition). Taylor & Francis Group.
- Seppänen, Rauni. (2007). *On the internal sizing mechanisms of paper with AKD and ASA related to surface chemistry, wettability and friction*. Kemi, Kungliga Tekniska högskolan.
- Shaikh, S., Yaqoob, M., & Aggarwal, P. (2021). An overview of biodegradable packaging in food industry. In *Current Research in*

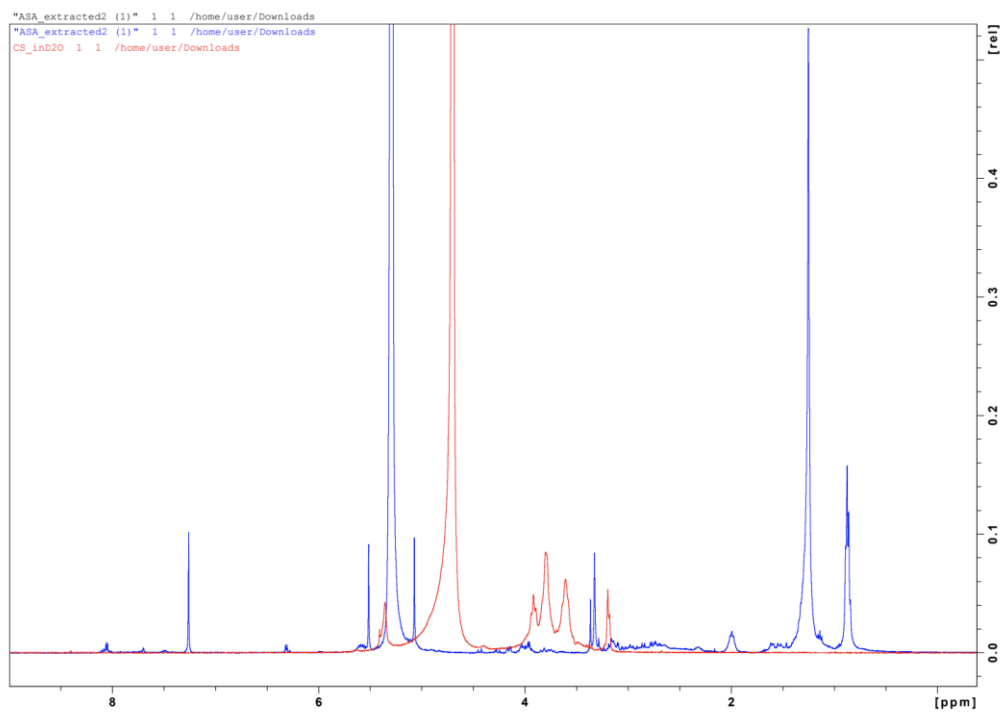
- Food Science* (Vol. 4, pp. 503–520). Elsevier B.V.
<https://doi.org/10.1016/j.crfs.2021.07.005>
- Statista. (2023). *Food packaging industry worldwide - statistics & facts*.
<https://www.statista.com/topics/10806/food-packaging-industry/#topicOverview>
- Statista. (2024). *Global plastic production*.
<https://www.statista.com/statistics/282732/global-production-of-plastics-since-1950/>
- Steinbuechel Alexander. (2003). General Aspects and Special Applications. Biopolymers. *Steinbuechel, Alexander, 10*.
- Suhr, M., Klein, G., Kourti, I., Rodrigo Gonzalo, M., Giner Santonja, G., Roudier, S., & Delgado Sancho, L. (2015). *Best available techniques (BAT) reference document for the production of pulp, paper and board*. <https://doi.org/10.2791/370629>
- Thakur Vijay K., & Thakur Manju K. (2016). *Handbook of Sustainable Polymers* (V. K. Thakur & M. K. Thakur, Eds.). Jenny Stanford Publishing. <https://doi.org/10.1201/b19600>
- Thulasisingh, A., Kumar, K., Yamunadevi, B., Poojitha, N., SuhailMadharHanif, S., & Kannaiyan, S. (2022). Biodegradable packaging materials. In *Polymer Bulletin* (Vol. 79, Issue 7, pp. 4467–4496). Springer Science and Business Media Deutschland GmbH.
<https://doi.org/10.1007/s00289-021-03767-x>
- Wahyuningsih, K., Iriani, E. S., & Yuanita, E. (2020). Characterization of Migration Rate and Biodegradability of Cassava Starch-Based Biofoam Modified with Alkyl Ketene Dimer. *Macromolecular Symposia*, 391(1). <https://doi.org/10.1002/masy.201900131>
- Zhang, F., Wang, L., An, X., Liu, H., Nie, S., Cao, H., Xu, Q., & Lu, B. (2020). Improving sizing performance of middle layer of liquid packaging board containing high-yield pulp. *Cellulose*, 27(8), 4707–4719. <https://doi.org/10.1007/s10570-020-03081-1>
- Zhang, K., Hamidian, A. H., Tubić, A., Zhang, Y., Fang, J. K. H., Wu, C., & Lam, P. K. S. (2021). Understanding plastic degradation and microplastic formation in the environment: A review. In *Environmental Pollution* (Vol. 274). Elsevier Ltd.
<https://doi.org/10.1016/j.envpol.2021.116554>
- Zinoviadou, K. G., Kastanas, P., Gougouli, M., & Biliaderis, C. G. (2021). Innovative bio-based materials for packaging sustainability. In *Innovation Strategies in the Food Industry: Tools for Implementation, Second Edition* (pp. 173–192). Elsevier. <https://doi.org/10.1016/B978-0-323-85203-6.00002-5>

Appendix A

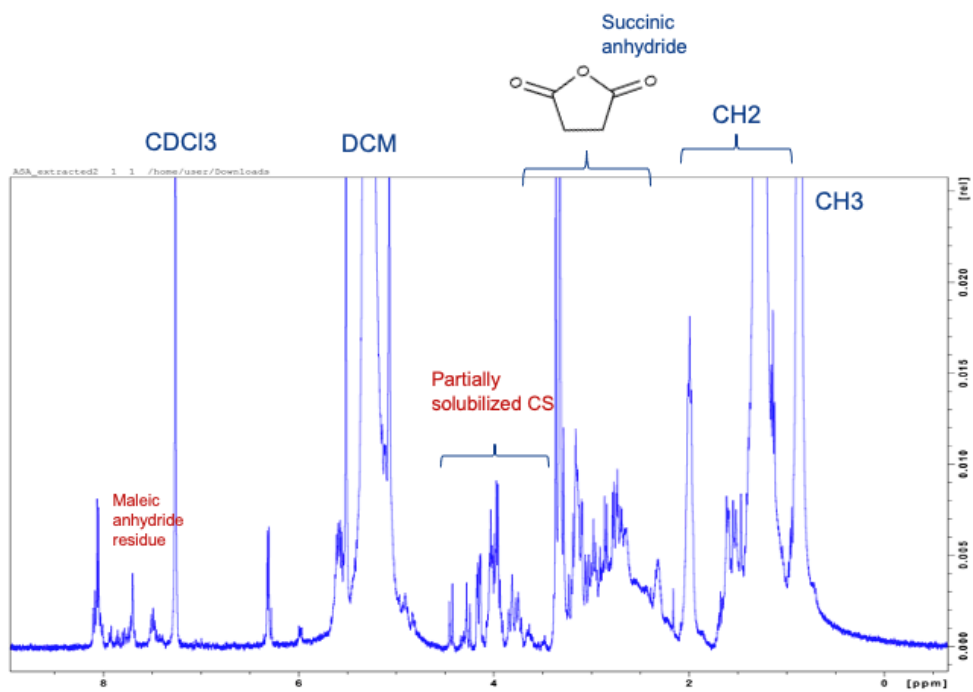
This section provides additional NMR spectra of involved components to better understand the possible outcomes of the extracted ASA spectra.



H NMR spectra of extracted ASA (blue) vs. extraction solvent DCM (red).



H NMR spectra of extracted ASA (blue) vs. Cationic starch in deuterated water (red).



Labeled H NMR spectra of extracted ASA (with assumptions labeled in red).