Development of Sustainable Waterbased Acrylic Dispersions for use in Floor Coatings- A Biobased Approach

Cornelia Ceraolo

LUND UNIVERSITY

LTH
FACULTY OF ENGINEERING

Bona®

Company Supervisor: Cecilia Hansson
Academic Supervisor: Baozhong Zhang
Examiner: Patric Jannasch

Centre for Analysis and Synthesis
Lund University
June 2024

Abstract

This master thesis investigates the potential of using biobased acrylic monomers to produce more sustainable waterborne floor coatings compared to the petroleum-based monomers currently in use. Dispersions were created through emulsion polymerization and formulated with coalescent and a wetting agent to form films at room temperature. The primary challenge with biobased monomers is their higher hydrophobicity, which can lead to coagulum during polymerization.

To reduce coagulum, various methods were tested, including slower feeding rate, different surfactants, cyclodextrin, and substituting some biobased monomers with hydrophilic monomers (petroleum-based). The monomers investigated were isobornyl methacrylate (IBOMA), 2-octyl acrylate (2OA), and lauryl acrylate (LA), with a side study using itaconic acid (IA). Dispersions from LA resulted in high amounts of coagulum, whereas using the various methods for IBOMA and 2OA achieved lower coagulum levels of 0.5-0.1%, compared to the usual 2-3%.

Using 1% cyclodextrin (based on total weight of monomers added) effectively reduced coagulum, and 5% cyclodextrin reduced it further but negatively impacted coating properties, such as chemical resistance and film formation. A combination of anionic sodium surfactant and non-ionic surfactant minimized coagulum without significantly affecting coating properties, though a completely coagulum-free dispersion was not achieved.

Coatings with IBOMA and 2OA exhibited properties close to petroleum-based coatings, while LA negatively affected chemical resistance and film formation. IA showed similar properties to its substitute methacrylic acid. All coatings with biobased monomers had an oily surface, indicating the need for further improvement.

Sammanfattning

Denna masteruppsats undersökte potentialen i att använda biobaserade akrylatmonomerer för att producera mer hållbara vattenbaserade golvlacker jämfört med de petroleumbaserade monomerer som nuvarande används. Dispersioner skapades genom emulsionspolymerisation och formulerades med koalecenter och vätningsmedel för att bilda lacker vid rumstemperatur. Den främsta utmaningen med biobaserade monomerer är deras högre hydrofobicitet, vilket kan leda till fällning under polymerisationen.

För att minska fällningen testades olika strategier, inklusive långsammare inpumpning av monomerer, olika tensider, cyclodextrin och att ersätta en del av de biobaserade monomerer med hydrofila monomerer (petroleumbaserade). De monomerer som undersöktes var isobornyl metakrylat (IBOMA), 2-oktyl akrylat (2OA) och lauryl akrylat (LA), med en sidostudie som använde itakonsyra (IA). Dispersioner från LA resulterade i stora mängder fällning, medan för IBOMA och 2OA kunde fällningsmädgen sänkas till 0.5-0.1%, jämfört med de vanliga 2-3%.

Användningen av 1% cyclodextrin (baserat på den totala vikten av tillsatta monomerer) minskade effektivt fällning, och 5% cyclodextrin minskade det ytterligare men påverkade lackens egenskaper negativt, såsom kemikalieresistens och filmbildning. En kombination av anjonisk natriumtensid och icke-jonisk tensid minimerade fällningen utan att påverka lackens egenskaper nämnvärt. Däremot uppnåddes ingen helt fällningsfri dispersion med biobaserade monomerer.

Lacker med IBOMA och 2OA visade egenskaper som liknade de fossilbaserade lackerna, medan LA negativt påverkade kemikalieresistens och filmbildning. IA visade liknande egenskaper som dess substitut metakrylsyra. Alla lacker med biobaserade monomerer hade en oljig yta, vilket indikerar behovet av ytterligare förbättring.

Populärvetenskaplig sammanfattning

Utveckling av hållbara golvlacker utifrån biobaserade råvaror.

I detta arbete undersöktes möjligheten för företaget Bona att utveckla en golvlack från biobaserade råvaror eftersom dagens golvlacker är skapade från råvaror med fossilt ursprung. Detta visade sig vara ganska komplicerat och flera problem uppstod, men trots motgångarna visade det sig att möjligheten fortfarande finns, och egenskaperna hos de biobaserade lackerna liknade de nuvarande.
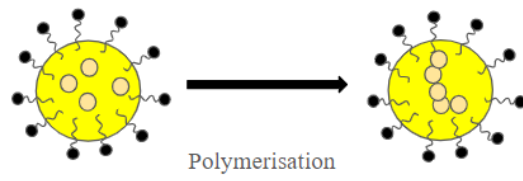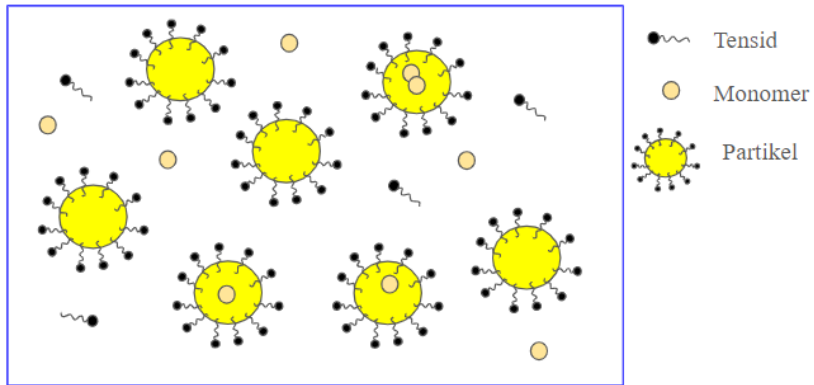
Det största problemet att använda biobaserade råvaror är att dessa har en annan kemisk struktur och därmed besitter andra egenskaper än de fossila råvarorna. Den största skillnaden är polariteten, där de biobaserade är betydligt mer hydrofoba (feta) än de fossilbaserade som är mer polära. Golvlacker består till största del av vatten, och att tillsätta mycket hydrofoba kemikalier kan leda till att dessa separerar ut och bildar fällning. Det finns dock olika metoder för att minska mängden fällning, men för att förstå detta bättre behöver vi gå djupare in på hur en golvlack bildas.

En golvlack tillverkas genom emulsionspolymerisation, där polymerisation innebär att flera molekyler, så kallade monomerer, bildar en lång kedja, en polymer. I emulsionspolymerisation sker polymerisationen i partiklar som är fördelade i vatten, stabiliserade av tensider, molekyler med en hydrofob del och en hydrofil del; den hydrofoba delen vänder sig mot partiklarna och den hydrofila delen mot vattnet (se Figur S1). Fällning bildas när polymerer bildas utanför partikeln och saknar den stabilisering som krävs för att vara jämnt fördelade i vattenfasen.

Fokuset för detta arbete låg på att stabilisera biobaserade monomerer med hjälp av strategier såsom längre reaktionstider, experimentera med olika tensider, tillsats av polära (fossilbaserade) monomer samt användning av cyclodextrin. Dessa metoder lyckades få ner fällningsmängden markant, men aldrig helt. Cyclodextrin är en trattliknande molekyl med en hydrofob insida och hydrofil utsida som underlättar för de hydrofoba monomererna att ta sig in i partiklarna. Även om fällningen minskades, kunde cyclodextrin ha negativa effekter på den färdiga golvlacken.

Generellt kändes alla lacker med biobaserade monomerer feta på ytan och vissa var också klibbiga, vilket är oönskade egenskaper för en golvlack. Därför behövs mer forskning för att undersöka om detta kan förhindras eftersom andra testade egenskaper visade att de biobaserade monomererna fungerade liknande de fossilbaserade.

Det är inte helt omöjligt att en biobaserad golvlack kan finnas på marknaden i framtiden men mer forskning krävs för att minska fällningen ytterligare och optimera den färdiga lackens egenskaper så att de blir konkurrenskraftiga med dagens golvlacker.

Figur S1. Bild av emulsionspolymerisation.

Acknowledgement

Contents

List of Abbreviations

2535 - Abex® 2535

2OA - 2-Octyl Acrylate

AB/20 - Rhodaplex AB/20

ADH - Adipic Acid Dihydrazide

BA - n-Butyl Acrylate

CMC- Critical Micelle Concentration

DAAM - Diacetone Acrylamide

DPM - Dipropylene Glycol Monomethyl Ether

DPnB - Dipropylene Glycol n-Butyl Ether

DS/4 - Rhodacal DS/4-E25

IA - Itaconic Acid

IBOMA - Isobornyl Methacrylate

JKB - Abex® JKB STD

KPS - Potassium Persulfate

LA - Lauryl Acrylate

LMA- Lauryl Methacrylate

MAA - Methacrylic Acid

MFFT - Minimum Film Forming Temperature

MMA - Methyl Methacrylate

SA - Stearyl Acrylate

SMA - Stearyl Methacrylate

T_g - Glass Transition Temperature

XD - Dowfax XD 30599

1. Introduction

In modern society, where our lifestyles have consequences for the environment, it is important for each of us to consider our actions and their impact on the environment. Industries can review their methods and raw materials to become more environmentally friendly, and one approach is to utilize biobased raw materials instead of petroleum-based ones.

Bona, a family-owned company from Malmö, with production facilities in several countries worldwide, manufactures products such as floor coatings and cleaning products for high-quality floors. They are a company that strives to be as sustainable as possible [1], and today their coatings that contain acrylic monomers are derived from fossil fuels, something that Bona is striving to change to be even more sustainable.

Waterborne polyacrylates are essential in the paint and coatings industry. Introduced in the fifties and sixties, they have become a more environmentally friendly alternative to solvent-borne coatings, and at the same time being high-performing. Even though waterbased polyacrylate coatings are more sustainable than solvent-borne coatings, the raw material is still derived from fossil fuels [2] and is therefore in demand to use biobased acrylic monomers to be even more sustainable.

Although various biobased acrylic monomers are available in the market, transitioning from petroleum-based to biobased ones presents challenges due to differences in chemical structure and properties. Biobased acrylics are more hydrophobic, complicating the achievement of a waterbased coating without coagulum or phase separation [3]. Therefore, this thesis focuses on trying to develop a functional system using biobased acrylics for use in floor coatings.

To create a coating, an acrylic dispersion is initially formed through free radical polymerization via emulsion polymerization [2]. This step is crucial as transport through water is necessary for the monomers to polymerize without coagulum. However, various studies have explored techniques, tips, and tricks to achieve successful emulsion polymerization with minimal or no coagulum when dealing with hydrophobic monomers [3]. Subsequently, the dispersion is formulated into a coating by incorporating additives such as coalescent, wetting agent and deformer to produce a coating with desired properties [2].

1.1. Aim

The aim of this project was to develop a waterborne acrylic dispersion for use as a floor coating using emulsion polymerization of biobased monomers. The goal was to achieve the highest possible bio content with as low coagulum as possible during the polymerization process, while also ensuring that the coating properties are competitive with Bonas' current products.

It is important to note that this project scope focused only on the biobased nature of the monomers, with no consideration given to other compounds. Also, this project only focused on commercially available raw materials.

2. Theory

2.1. Emulsion polymerization

Emulsion polymerization is a common free radical method used to produce polymer latex for coatings and paints. An advantage of emulsion polymerization is that it does not require organic solvents, instead, water serves as the main ingredient, making it a more environmentally friendly process compared to, for example, solution polymerization. In addition to water, monomers, surfactants, initiators, and sometimes a chain transfer agent is used [4].

When surfactant is added to water and its concentration exceeds the critical micelle concentration (CMC), micelles form with a diameter of 5-15 nm. Most monomers exist in 'monomer droplets' with a diameter between 1-10 µm, stabilized by surfactants. The remaining monomer molecules are dispersed in the water phase and within the micelles, causing the micelles to swell. The initiator forms oligo radicals with monomer molecules in the water phase and when the oligomer becomes too hydrophobic for the water phase, it seeks a surface. Given the abundance of micelles compared to monomer droplets (approximately 10^8 times more micelles), most radicals transfer to the micelles (particles) where polymerization occurs. Monomer molecules transport via diffusion from the monomer droplets through the water phase to the particles for polymerization. Polymerization terminates when another radical molecule enters the particle and resumes when a new radical enters the particle again. The process is complete once all monomer molecules from the monomer droplets are consumed [4] [2]. *Figure 1* provides an overview of the emulsion polymerization process, though it is not drawn to scale.

The emulsion or dispersion is stabilized by the surfactant, but to improve the stability even more, ionic carrier groups can be introduced as a monomer. These are mostly carboxylic acids, which can be ionized in an alkaline solution, forming negative charges. The anionic charge makes the group highly hydrophilic, thereby further stabilizing the polymer particles in the aqueous phase [5].
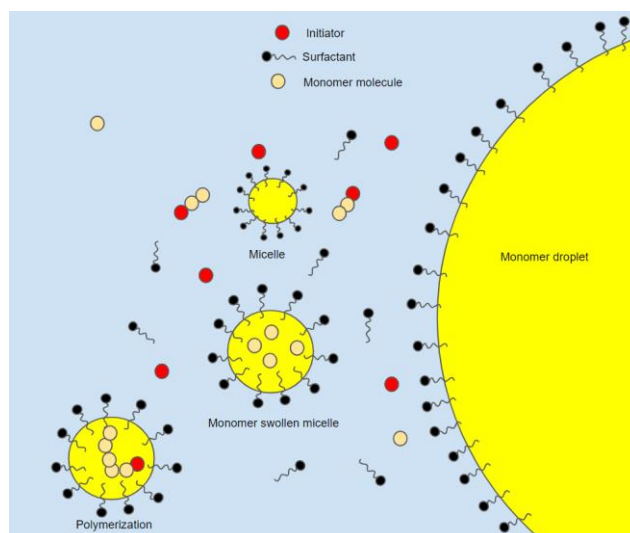
Figure 1. Mechanism of emulsion polymerization.

2.1.1. Seeded semi-batch emulsion polymerization

In semi-batch emulsion polymerization, some of the reactants are initially added, while the remainder is introduced into the reaction at a controlled rate. The most common industrial approach involves starting with a batch of water, surfactant, initiator, and 5-10 wt% of the total monomer, which reacts for a specific time, referred to as a seed stage. Additional quantities of reactants can be added intermittently or continuously using pumps. Often, the remaining monomer is fed as a 'pre-emulsion,' including a mixture of monomer, water, and surfactant. This method facilitates control over particle size, particle quantity, and morphology, and therefore shows good reproducibility [2].

In this study, starved seeded semi-batch emulsion polymerization takes place. Starved conditions occur when the monomer is introduced into the reaction slower than it can polymerize, resulting in high instantaneous conversion and is a common method used in the industry [6].

2.2. Acrylic waterbased dispersions

Acrylic coatings are made from either acrylates or methacrylates, which are esters of acrylic acid or methacrylic acid (see *Figure 2*). These esters polymerize due to the reactivity of their double bonds [5].
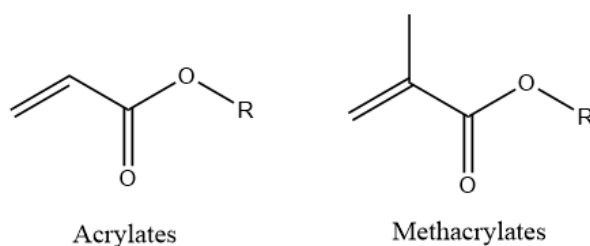
Figure 2. Chemical structures of acrylates and methacrylates.

(Meth)acrylates are widely used in the industry to produce waterbased dispersions for coatings due to their desirable properties, such as UV stability, chemical resistance, and good weathering. Additionally, it is easy to control the variation in flexibility, hardness, and toughness. Properties like polarity, hardness, and flexibility are mainly determined by the choice of main monomers, such as methyl (meth)acrylate, n-butyl (meth)acrylate and ethyl acrylate, which are some of the most used (meth)acrylates for coatings. However, by adding functional monomers like acrylic acids, the colloidal stability of the dispersions is improved. Meanwhile, the addition of crosslinking systems increases the chemical resistance and strength of the final coating [2].

Even though acrylates exhibit desirable properties, a significant disadvantage is that they currently rely on petroleum-based raw materials. Therefore, new production routes need to be investigated. The petroleum-based monomers used in this project were methyl methacrylate (MMA) and n-butyl acrylate (BA), while methacrylic acid (MAA) and diacetone acrylamide (DAAM) were used as functional monomers.

2.2.1. Methyl Methacrylate (MMA)

Industrially, there are different methods to produce MMA, with two of the most common being the use of either acetone or isobutene. Both processes rely on petroleum raw materials and harsh reaction conditions. However, efforts have been made to make the production of MMA more environmentally friendly, including attempts to create fully biobased MMA. Bohre et al. demonstrated in a study that it is possible to create biobased MMA using a single-step process with itaconic acid (IA) and biobased methanol. Although the study showed feasibility, the selectivity was only 38mol%, indicating that further experiments are needed [7]. Itaconic acid is produced from the fungus *Aspergillus terreus* and *Aspergillus itaconicus* [8]. Biobased methanol can be produced in different ways using concentrated carbonaceous materials, such as biomass [9].

Polymer of MMA has a glass transition temperature (T_g) of 105 °C [10], *Figure 3* shows the chemical structure of MMA as well as poly(MMA).

Methyl Methacrylate (MMA)   poly(MMA)
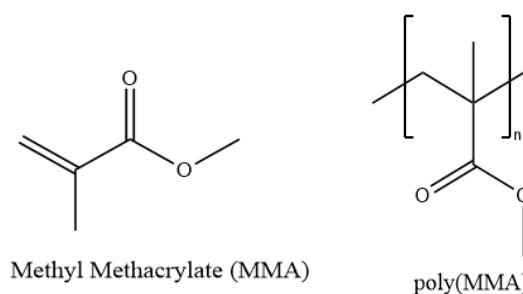
Figure 3. Molecular structure of MMA and poly(MMA).

2.2.2. n-Butyl Acrylate (BA)

BA (see *Figure 4* for molecular structure of BA and poly(BA)), with a T_g of -54 °C [10], is produced from acrylic acid and butanol, both of which have biobased options. However, the

biggest challenge in producing biobased butyl acrylate is achieving the necessary purity of both the biobased raw materials (acrylic acid and butanol) and the final product. Studies by Niesbach et al. have focused on purifying the production process. Although they managed to improve the synthesis purification, the resulting purity is still not sufficient for industrial applications [11] [12]. Biobased butanol can be derived from a fermentation process, known as acetone-biobutanol-ethanol fermentation [13]. Biobased acrylic acid can for example be made from glycerin [14].
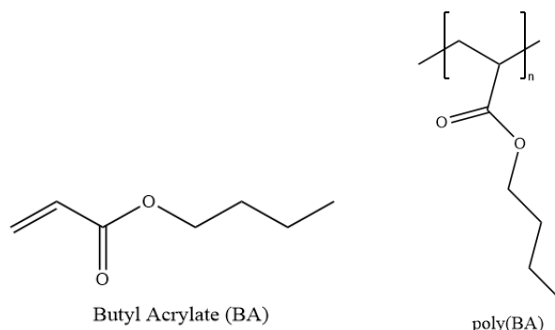
Figure 4. Molecular structure of BA and poly(BA).

2.2.3. Methacrylic Acid (MAA)

The industrial production of MAA is similar to that of MMA, with acetone-based synthesis being one of the most common methods. There have been several studies aimed at producing biobased MAA, with itaconic acid being the most successful precursor. The selectivity of the process varies with different catalysts, achieving a yield of 50% with barium hexaaluminate [15] and over 90% selectivity with ruthenium carbonyl propionate [16]. These promising results indicate that biobased MAA may have commercial potential soon.

Due to the similarity between MAA and IA, see *Figure 5*, there is potential for IA to serve as a direct substitute for MAA [17], with some adjustment since IA contains two carboxylic acid groups and MAA one. MAA has a T_g of 228 °C [10]. However, the T_g of IA was difficult to determine, but a report by Cao indicated that IA has a T_g of 61 °C [18].
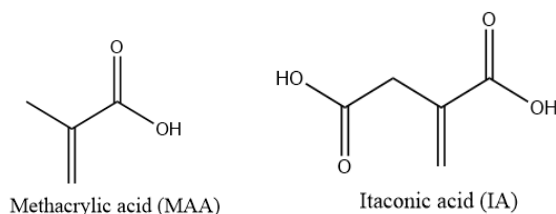
Figure 5. Molecular structure of MAA and IA.

2.2.4. Diacetone acrylamide (DAAM)

DAAM, a monomer that functions as a crosslinker, is essential for improving coating properties such as water and chemical resistance, and increased hardness. The crosslinking mechanism is a self-crosslinking system involving a condensation reaction between DAAM and adipic acid dihydrazide (ADH), see *Figure 6*. While other crosslinking systems can be used, the DAAM

and ADH combination is one of the most common in the floor coating industry. DAAM is manufactured from acrylonitrile and acetone [2]. Even though bio-acetone is available [19], no literature could be found on an attempt to create biobased DAAM.
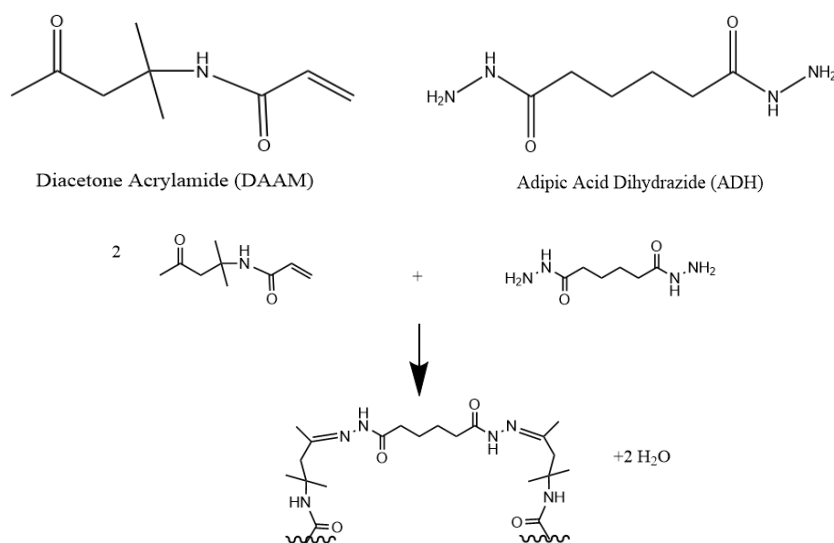
Figure 6. Molecular structure of DAAM and ADH and the crosslinking reaction of DAAM and ADH.

2.3. Biobased acrylates

Since industrial processes for commonly used acrylates rely on petroleum-based sources and face challenges in becoming more environmentally friendly, the focus has shifted to creating entirely new acrylates. Today, several commercially available biobased alternatives are on the market.

2.3.1. Commercially available biobased (meth)acrylates

The most common biobased (meth)acrylic monomers commercially available are 2-octyl acrylate (2OA) and isobornyl methacrylate (IBOMA), often used in copolymerization, as observed in several studies [3] [20] [21]. 2OA is synthesized through the esterification of bio-based 2-octanol with acrylic acid, derived from the cracking of oleic acid from the Ricin plant. Based on carbon, 2OA has a biocontent of 74% [3].

IBOMA, on the other hand, is produced by esterification of MAA with camphene [3], a bio-based raw material derived from pine tree resin, claimed to be harvested without harming the pine trees [22]. IBOMA has a biocontent of 71% based on carbon. 2OA and IBOMA have T_g of -44 °C, respectively 150 °C, making them potential substitutes for BA and MMA, respectively. However, studies have indicated that direct substitution of these biobased monomers for their petroleum-based counterparts is not possible due to differences in hydrophobicity and microstructure [3].

Other commercially available biobased acrylates with even higher biocontent include lauryl (meth)acrylate, L(M)A, as well as stearyl (meth)acrylate, S(M)A, derived from natural oils [22] [23]. However, the high biocontent of these monomers results from longer chains, making them even more hydrophobic than IBOMA and 2OA, thus posing greater challenges in emulsion polymerization.

This project focuses on the monomers 2OA, IBOMA, and LA. See *Figure 7* for the chemical structures of the above mentioned biomonomers, as well as the polymer structures of poly(IBOMA) and poly(2OA). The polymers derived from lauryl acrylate and stearyl acrylate appear similar to poly(2OA).
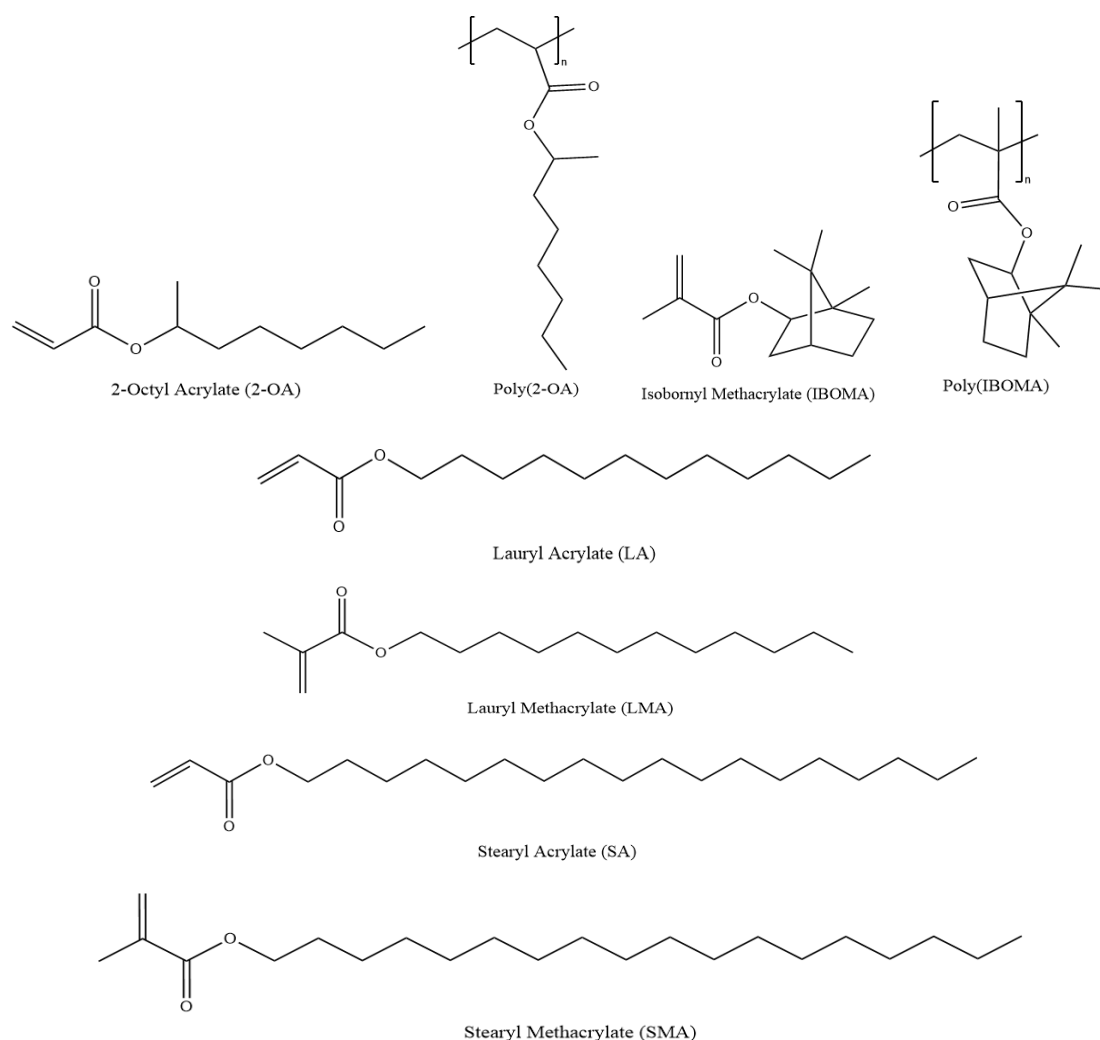
Figure 7. Molecular structure of 2OA, poly(2OA) IBOMA, poly(IBOMA), LA, LMA, SA and SMA.

2.4. Emulsion polymerization of hydrophobic monomers

Since water is the main ingredient in emulsion polymerization some water solubility is needed for the monomers, posing a challenge when using hydrophobic monomers like the current commercially available biobased acrylic monomers. Their hydrophobic nature often leads to coagulum during polymerization. Nonetheless, certain techniques have been developed to overcome the solubility barrier without causing coagulum.

2.4.1. Addition of hydrophilic monomers

One way to facilitate the polymerization of hydrophobic monomers is to add some hydrophilic (petrolum-based) monomers. For example, Badía et al. created different types of latexes with 2OA, IBOMA, and MAA, using different ratios, but with MAA always at 1 wt% of the total amount of monomers without any coagulum [24]. However, Llorente et al. conducted a similar experiment and showed that 1 wt% of MAA did not significantly affect the coagulum percentage. They did show that in the homopolymerization of IBOMA, the addition of 5 wt% MMA reduced the coagulum amount from 15 wt% to 1 wt% [3], indication that a larger amount of hydrophilic monomers is needed in order to lowered the coagulum.

The reason for unstable dispersions of hydrophobic monomers may be the lack of oligo radical formation in the water, as almost all the hydrophobic monomers will be in the monomer droplets and very little in the water phase compared to when using more hydrophilic monomers. By adding a small amount of hydrophilic monomer, more monomers will be present in the water phase, allowing for the formation of oligo radicals and initiating the polymerization process. This eventually facilitates the polymerization of the hydrophobic monomers [3].

2.4.2. Cyclodextrin

Another method to use hydrophobic monomers in emulsion polymerization is to add cyclodextrin. Cyclodextrin is an amphiphilic oligosaccharide molecule shaped like a funnel, with a hydrophobic internal cavity and a hydrophilic external surface. It is commonly used as a phase transfer catalyst, meaning that hydrophobic monomer molecules can fit into the cavity of cyclodextrin and then be transported through the water phase to the particle [25].

Kohut et al. demonstrated that incorporating 5-15 wt% cyclodextrin (based on the total weight of the monomers) reduced the coagulum amount and increased the polymer yield, however total coagulum free latex was not achieved [25]. Similarly, Leyre and Mächtle utilized cyclodextrin to polymerize SA and achieved almost full conversion with 5 wt% cyclodextrin. However, the use of cyclodextrin also resulted in increased particle size. This phenomenon can be attributed to the formation of complexes between cyclodextrin and surfactants, which reduces the number of surfactant molecules able to form particles. This results in the formation of fewer particles and, consequently, an increase in their size [26].

2.4.3. Surfactant

Since the role of surfactants is to stabilize dispersions, the choice of surfactant is an important consideration. Several studies have investigated specific surfactants claimed to work well with hydrophobic monomers for emulsion polymerization. Boscán et al. suggest that a highly hydrophobic surfactant with a low CMC but used at a concentration well above its CMC, is effective because it can stabilize nano-sized monomer droplets in water. This stabilization allows the monomer droplets to collide and polymerize successfully [27]. In contrast, Llorente suggests that less hydrophobic but anionic surfactants work best for the polymerization of IBOMA, while non-ionic and ionic polymerizable surfactants performed poorly [3].

Dong et al. developed a custom anionic surfactant with a 23-carbon alkyl group and a 20-oxyethylene group, leading to improved conversion of SA. They suggest that the interaction between the alkyl group on the monomer and the surfactant facilitates monomer transport. To further improve stability, they also added a non-ionic surfactant [28]. Meanwhile, Tauer et al. emphasize the importance of both surfactant and initiator selection for the polymerization of LMA. They claim that a more hydrophilic polymeric radical works best when combined with an anionic surfactant [29].

From these studies, it can be concluded that anionic surfactants tend to be the most effective, which is also the most common type used in coatings, sometimes in combination with non-ionic types [2]. However, other properties of the surfactant, such as CMC, concentration, and hydrophobicity, may also influence the success of polymerization. The determination of which property is most influential could be affected by various other perspectives as well.

2.4.3.1. Surfactant used in this study

The most used surfactant in this project is called Rhodacal DS/4-E25 (DS/4), an anionic surfactant whose chemical structure can be seen in *Figure 8*. Another anionic surfactant tested was Dowfax XD 30599 (XD), whose chemical structure also is seen in *Figure 8*.
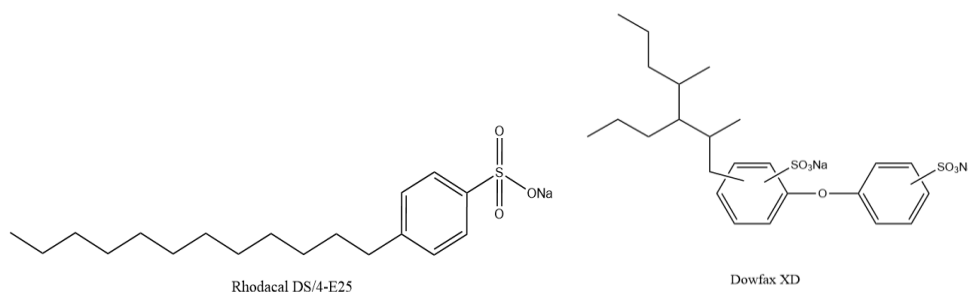
Figure 8. Chemical structure of DS/4 and XD.

When receiving advice from a surfactant supplier, they recommended using ammonium salts surfactants in the water, and a non-ionic surfactant in the pre-emulsion to enhance stability. The ionic surfactants recommended were Rhodaplex AB/20 (AB/20) and Abex® JKB STD (JKB), while the non-ionic surfactant suggested was Abex® 2535 (2535). However, obtaining detailed information regarding their chemical structure proved challenging. 2535 is identified as a blend of ethoxylated fatty alcohols [30]. The only available information about JKB indicates it is an aqueous solution of anionic surfactants [31]. For AB/20, it is known to be an aqueous solution of alkyl ethoxy ammonium sulphate containing the chemical seen in *Figure 9* at a concentration of 25-30% [32].
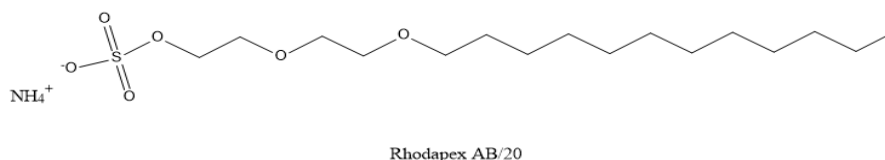
Figure 9. Chemical structure of AB/20.

2.4.4. Other methods

Slower feeding, increased mixing rate [6], lower solid content (monomer, surfactant, initiator) [2], the addition of solvent [33], and the utilization of miniemulsion instead of emulsion polymerization [34] are alternative approaches that also have been observed to facilitate the polymerization process for hydrophobic monomers. However, the addition of solvent and the use of miniemulsion are not attractive in this project, but the other methods are interesting to consider.

2.5. Properties of dispersions for use as floor coating

Some of the main properties to control in a dispersion for floor coating use include residual monomer content, pH, particle size, coagulum, and colloidal stability. The pH is usually neutral or weakly basic due to the stability of the functionalized monomers which lose their protons at higher pH's and thereby leading to better charge stabilization. The residual monomer content should be as low as possible, preferable under 200-100 ppm to avoid labelling of hazardous components due to the toxicity and strong odor of acrylic monomers. Particle size under 100 nm is desired, which is discussed below (2.6.2), and the colloidal stability can be reduced by salts or high/low temperatures. Other important factors are viscosity and the solid content [2].

2.6. Formulation-From dispersion to coating

To transition from a dispersion to a coating, various chemicals must be incorporated to form a proper film with desired properties. These include solvents (coalescent), wetting agents, and defoamers. Additionally, matting agents or pigments may be added during the formulation to achieve specific ascetics [2].

2.6.1. Wood floor coatings

For interior wood coatings, the main considerations are aesthetic and decorative effects, such as enhancing the natural beauty of the wood, and protecting it from mechanical and chemical damage. Therefore, wood coloration, surface hardness, chemical and scratch resistance are some important properties for wood floor coatings. To enhance high surface hardness, a T_g of 30-60 °C is often used, making a need for solvents to get a proper film formation at room temperature, see more information below (2.6.3) [2].

2.6.2. Film formation and MFFT

As the dispersion dries, water evaporates, causing the particles to move closer together until they make contact. Continued evaporation creates pressure, causing the particles to press against each other. If the temperature is above the minimum film formation temperature (MFFT), the particles deform, and polymer chains interdiffuse across particle boundaries, forming a continuous film. If the temperature is under the MFFT, cracks are formed instead of a continuous film. Smaller particle dispersions typically yield better film quality, making industrial acrylate-based dispersions usually have diameters smaller than 100 nm [2].

The MFFT is often close to the T_g of the polymer. For polar dispersions, hydroplasticization occurs, where water plasticizes the polymer, leading to swelling and softening the surface layer, and consequently lowering the MFFT. In contrast, non-polar dispersions tend to have a higher MFFT [2].

2.6.3. Coalescents/solvent

To achieve film formation at room temperature using polymer dispersions with a high T_g, it is a common practice to employ temporary plasticizers known as coalescents, often glycol ethers and their acetates. These solvents evaporate after film formation, ensuring they do not remain in the film for an extended period. However, they can still influence the properties of the final coating, making the choice and amount of coalescents crucial considerations during the formulation [2].

Dipropylene glycol monomethyl ether (DPM) and dipropylene glycol N-butyl ether (DPnB) were used in this project as solvents. See *Figure 10* for chemical structure.

Dipropylene glycol monomethyl ether (DPM)   Dipropylene glycol N-butyl ether (DPnB)
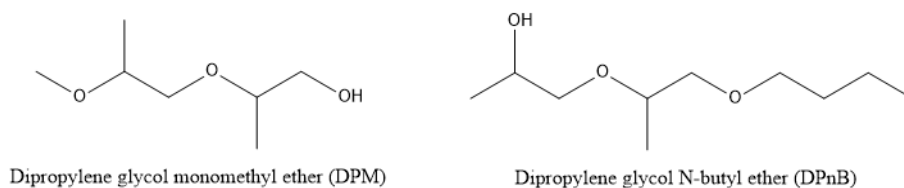
Figure 10. Chemical structure of DPM and DPnB.

2.6.4. Wetting agents

Wetting agents are surface-active molecules (surfactants) that are added to the formulation to decrease the surface tension, allowing the substrate (in this case, the wood) to be wetted. The coating needs to have a surface tension that is lower than the surface energy of the wood to achieve proper wetting [2].

In this project, the wetting agent used was Capstone™ FS-63 Fluorosurfactant, an anionic fluorosurfactant containing a mixture of partially fluorinated alcohol, reaction products with phosphorus oxide, ammonium salts, and propan-2-ol [35].

3. Method

3.1. Emulsion polymerization

For the preparation of the pre-emulsion, DAAM was first dissolved in deionized water, then the surfactant was added to the solution. This solution was added to a glass flask containing the monomer blend, which was set on a magnetic stirrer and connected to a membrane pump. From the pre-emulsion, 7 wt% was taken out to be the seed. The monomer composition for all dispersions has a T_g of 30 °C (if not something else is mentioned), which was calculated using the Flory-Fox equation, see *Equation 1*.

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

1

The initiator potassium persulfate (KPS) was dissolved in water and separated into two: KPS_1 (67 wt%) and KPS_2 (33 wt%). KPS_2 was diluted with water by a factor of 2 and placed in a syringe pump.

In the reactor, surfactant and water were added, with the stirrer set to 100 rpm, nitrogen inlet, and the temperature was set to 75 °C, controlled by a heating mantle. The polymerization took place in a 1 l reactor equipped with a nitrogen inlet, thermometer, condenser, stirrer, and inlets for the pumps. After 30 min, when the temperature had stabilized, KPS_1 was added, and the stirrer speed was increased to 200 rpm. 5 min later, the seed was added. 10 min after that, the KPS_2 pump and the pre-emulsion pump were started.

The feeding time for the pre-emulsion pump was set to 2-6 h depending on the monomer composition (water solubility). 15 min after the pre-emulsion pump finished, the KPS_2 pump was stopped, meanwhile ammonia (19%) was added as neutralization agent. 15 min later, the first sample was taken for GC analysis. 30 min after that, a second sample was taken, making the total post-polymerization time of 1 h. The reactor was then cooled to room temperature using an ice bath. See *Table 1* for the recipe and the quantities of each chemical used.

Table 1. Ground recipe of emulsion polymerization.

	Weight (g)	wt%
Water in reactor from start	381	
Water in pre-emulsion	90	
Water in initiator blend	40.5+27	
Total amount water	**538.5**	**61**
Surfactant in pre-emulsion	6.5	
Surfactant in reactor from start	9.2	
Total amount surfactant	**15.7**	**1.8**
Initiator KPS	**1.7**	**0.2**
Main monomers (MMA/BA/IBOMA/2OA/LA)	284.5	
Functional monomer (MAA)	6.5	
Crosslinking monomer (DAAM)	36	
Total amount monomer	**327**	**37**
Ammonia (19%)	2	

3.2. Analytical methods of dispersion

Different analytical methods were used to characterize the dispersion properties, such as residual monomer content, MFFT, particle size, pH, salt stability, and heat stability.

3.2.1. Residual monomer content

The residual monomer content was analyzed by GC-Headspace. The headspace used was TurboMatrix 16 Headspace Sampler from PerkinElmer and the GC used was Clarus 500 Gas Chromatograph from PerkinElmer. The samples were heated at 100 °C for 15 min in the headspace and then injected to the GC. The temperature ramp for the GC can be seen in *Table A1* in the Appendix. Since new monomers were used that had not been used in the GC before, a calibration curve needed to be created to quantify the residual monomer content. The other monomers (MMA and BA) were already calibrated.

3.2.1.1. Calibration curve

The calibration curve was made using standard addition. 0.2 g of each monomer (2OA and IBOMA) were mixed with 200 g of dispersion (reference with MMA/BA) and stirred for 1 h with a magnetic stirrer, creating a stock solution at 1000 ppm. The stock solution then rested

for 4 h. From the stock solution, 10 g were taken and mixed with 10 g of the reference dispersion, making a solution of 500 ppm. From the stock solution, 1 g was taken and mixed with 19 g of dispersion, making a solution of 50 ppm. 3 samples of each ppm level, as well as 3 references of dispersion without any 2OA and IBOMA, were analyzed in the GC. Curves were plotted of height vs. ppm of 2OA and IBOMA, respectively. The calibration curves can be seen in *Figure A1* and *Figure A2* in the Appendix.

3.2.2. Particle size

Particle size was determined by dynamic light scattering using a Zetasizer Nano ZS from Malvern Instruments. One drop of dispersion was added to a glass cuvette, which then was filled halfway with water and mixed using a plastic pipette.

3.2.3. Coagulum amount

The coagulum amount was measured by filtration. The filter was first weighed, then the dispersion was filtered, and the filter was then washed with water, and placed in an oven at 60 °C to dry for 3-7 days. The filter was weighed again until a constant mass was achieved, and the coagulum amount was determined by the weight difference and the percent of the total amount of monomer used.

3.2.4. Minimum Film Forming Temperature (MFFT)

MFFT was measured with a Minimum Film Forming Temperature Instrument from Rhopoint Instruments. Firstly, a temperature range was set, having the theoretical T_g in the middle. Since the theoretical T_g of the dispersions was 30 °C, the range used was 23-50 °C, where the temperature goes from low to high from left to right. A cube applicator with a film thickness of 75 µm was filled with approximately 1 ml of dispersion. The applicator was then moved on the instrument in a U-shape, starting from high to low temperature (see *Figure 11* below). The film was dried under a flow of nitrogen (4 ml/min) for approximately 30 min. The point where the last crack appeared was determined as the MFFT. 2 U-shapes were made for each dispersion, and the final MFFT was set as the mean value of 4 values. If cracking occurred across the entire temperature range, the temperature was increased, and if a film was formed at all temperatures, the temperature was decreased.

Figure 11. Picture illustrating how the MFFT was determined. Black line represents the temperature where the latest crack could be seen= MFFT. Picture is viewed from the above.

3.2.5. Salt stability

Into a plastic cup, 7.5 ml of NaCl-solution was added, followed by 3 drops of dispersion. The solution was blended with a plastic pipette 3 times. If a clear solution was obtained, a higher salt concentration was tested. If a turbid solution was obtained, a lower concentration was tested to investigate the salt concentrations at which the shift between soluble and insoluble occurs. Solubility over 1 M indicates good salt stability.

3.2.6. Heat stability

Approximately 10 ml of each dispersion was placed into a plastic container and then put in an oven at 50 °C for 5 days. Particle size was measured before and after to observe any potential changes, thereby assessing if the heat had an influence on the stability of the system e.g. changes in particle size, viscosity or coagulum.

3.2.7. pH

pH was determined using a pH meter from Metrohm at 23 °C. The detector was put in the dispersions and allowed to stabilize until a relatively constant value was obtained.

3.3. Formulation of coating

Dispersion and ADH (15 wt% in water) were added to a 500 ml glass beaker and was started stirring at 1000 rpm using a mechanical stirrer. DPM and DPnB, diluted in water, were then added slowly. The solution was stirred for 10 min at 1000 rpm. Next, Capstone™ FS-63 was added, and the solution was stirred for another 10 min at 1000 rpm. After 1-3 days, the coating was applied onto a Leneta card and an oak wooden plank to dry. See *Table 2* for detailed information about the amounts.

Table 2. Recipe for coating formulation.

	g	wt%
Dispersion	200	76
ADH (15 wt% in H_2O)	19.5	7.4
DPM	14.3	5.5
DPnB	7.2	2.7
Water	21.5	8.2
Capstone™ FS-63	0.4	0.2

3.3.1. Coating properties

To analyze the coating properties and characteristics, various techniques were employed. Film formation, chemical resistance, and coloring of the wood were investigated.

3.3.1.1. Film formation

To determine if proper film formation has occurred, similar amounts of coating were applied to wooden pieces and placed in a refrigerator to slow down the drying process and allow for better observation of film formation. The next day, the wooden pieces were removed from the refrigerator, and a methyl blue solution (1%) was applied over the coating, then washed off with water. If any blue color was observed after rinsing, it indicates the presence of cracks in the coating and therefore, improper film formation.

3.3.1.2. Chemical resistance

To investigate the chemical resistance, one week after the coatings were applied on Leneta and wood, 4 drops of each chemical: coffee, red wine, ethanol (48%), water, ammonia (10%), and acetic acid (20%) were placed on separate areas of the coatings. Since ethanol is volatile, a cup was placed over the ethanol drop to prevent rapid evaporation. The chemicals were left on the coatings for 1 h, after which the coating was carefully wiped clean with paper and water. The coatings were inspected the following day to determine if any marks were left where the chemicals had been.

3.3.1.3. Influence of wood color

Circles, approximately 2 cm in diameter, were marked on a wooden piece. Ten drops of coating were added to each circle using a plastic pipette. Then, the wooden piece with the coatings was placed in a cold room at 16 °C with 80% air humidity to slow down the drying process. After drying, the drops were examined to see if any color changes in the different dispersions were visible. Generally, a lighter color is considered more attractive than a darker one, but preferences can vary among different customers.

4. Results and discussion

4.1. Dispersions

Most dispersions were prepared using IBOMA and 2OA. However, from early March to mid-April, IBOMA was unavailable due to supplier issues. Therefore, alternative monomers LA and IA were investigated. As a result, some dispersions are based on an IBOMA/2OA mixture, while others use an LA/MMA mixture. Additionally, a side study was conducted using IA.

The parameters analyzed were residual monomer content, coagulum amount, pH, particle size, MFFT, and stability tests (salt and heat). Heat stability was satisfactory for all dispersions, maintaining consistent particle sizes. Detailed results can be found in *Figure A3* in the Appendix. For experiments with multiple dispersions, the data presented here represents the mean value.

Most of the coagulum adhered to the stirrer and thermometer, occasionally proving difficult to remove. As a result, determining the coagulum amount lacked precision, and minor differences in decimal values may be approximated as equal.

4.1.1. Bio content, IBOMA and 2OA

For IBOMA and 2OA, different proportions were tested, ranging from 20 wt% (10 wt% each) to 87 wt% (43 wt% IBOMA and 44 wt% 2OA), the highest possible ratio when keeping functional monomers MAA and DAAM at a constant level of 2 wt% respectively 11 wt%. An overview of the results can be found in *Table 3*. No significant differences were observed in pH values or particle sizes, with pH around 7 and particle size averaging 70 nm. Similarly, salt stabilization remained consistent across different IBOMA/2OA ratios, measuring between 300-400 mM.

Table 3. Overview of the results for the dispersions containing IBOMA and 2OA.

Entry	Monomer composition* (wt%)				Residual monomer (ppm)				Coagulum	MFFT
	MMA	BA	IBOMA	2OA	MMA	BA	IBOMA	2OA	wt%	°C
A	53	42	-	-	14	17	-	-	0.0	34
B	41	26	10	10	15	5	30	0	0.1	35
C	28	19	20	20	12	1	40	10	0.3	35
D	16	11	30	30	7	0	30	0	0.8	42
E	3	-	40	44	1	-	20	5	2.6	45
F	-	-	43	44	-	-	30	0	2.1	45
G	50	-	-	37	20	-	-	90	0.2	37
H	-	40	47	-	-	0	125	-	2.3	44

*DAAM consistently maintained a concentration of 11 wt%, while MAA remained at 2 wt%.

4.1.1.1. Coagulum

The higher the amount of IBOMA and 2OA, the greater the coagulum, reaching a maximum of 2.6 wt% with 40 wt% IBOMA and 44 wt% 2OA, see entry A-E. However, no significant difference is observed between the utilization of 3 wt% MMA and its absence (compare entries E and F) suggesting that MAA alone might be sufficient as a hydrophilic monomer. To verify this, a dispersion without MAA would also be required for comprehensive assessment. Nonetheless, a notable disparity is observed between entry D and E resulting in 0.8 wt% and 2.6 wt% coagulum, respectively. This suggests the necessity of larger quantities of hydrophilic monomers to facilitate the transport of hydrophobic ones. An examination of the dispersion containing only BA and IBOMA (entry H) reveals that BA is not sufficiently hydrophilic, requiring the addition of large quantities of MMA to avoid precipitation. Also, all dispersions with high content of IBOMA showed larger quantities of coagulum, suggesting that IBOMA is the main problem.

4.1.1.2. Residual monomer

The residual monomer levels were low when mixing IBOMA and 2OA (entry B-F). However, when used alone, the residual monomer levels were higher, particularly for IBOMA at 125 ppm (entry H). This could be due to factors like reduced nitrogen flow, resulting in reduced polymerization. To determine the cause definitively, more experience is required. If it depends on the reaction, possibly due to different reactivity ratios of the monomers, composition drift may occur, with all BA being polymerized first and then IBOMA. In such a scenario, it would

be intriguing to determine the polymer architecture to investigate if block polymerization has occurred.

4.1.1.3. MFFT

The MFFT was higher for larger amounts of IBOMA and 2OA. Specifically, the MFFT increased from 32 °C for the MMA/BA reference to a maximum of 45 °C for the highest ratio of IBOMA/2OA (entry A-F). As described in the theory section, this phenomenon depends on the absence of hydroplasticization in hydrophobic dispersions, resulting in a higher MFFT compared to more polar dispersions. However, the rise in MFFT is not linear, and the influence of hydrophobic monomers becomes apparent at 30 wt% of each IBOMA and 2OA (entry D). This higher MFFT suggests it becomes more challenging to form a film, requiring the incorporation of more coalescents in the formulation to achieve film formation at room temperature.

4.1.2. Lauryl acrylate

For the dispersion with LA and MMA, a 24 wt% coagulum occurred and a low particle size (39 nm), see entry D in *Table 4*. However, due to LA's high boiling point of 296 °C, it was not possible to determine the residual monomers using the GC method. Although alternative methods might work, GC is Bona's preferred method, and implementing a new technique was considered too complicated for this project.

Moreover, the coagulum observed with LA was more gel-like compared to the solid, gravel-like coagulum seen with IBOMA/2OA. This difference made filtration of LA-containing dispersions much more challenging, as the coagulum clogged the filter and adhered to surfaces, making it hard to wash away. This issue could potentially worsen problems on an industrial scale, as the cleaning process would become significantly more difficult. Additionally, all dispersions containing LA phase separated after storing for several weeks where gel-lumps could be seen on the surface.

4.1.3. Feeding time

The standard feeding time was initially set to 3 h, but additional experiments were conducted with 4 and 6 h to assess the impact on coagulum levels. However, variations in feeding times did not significantly affect the overall residual monomer content, MFFT, pH, or salt stabilization. Refer to *Table 4* for an overview of the results with different reaction times.

Table 4. Overview of the results for the dispersions with different feeding times.

Entry	Monomer composition* (wt%)				Feeding time	Coagulum	Particle size
	MMA	LA	IBOMA	2OA	h	wt%	nm
A	3	-	40	44	3	2.6	71
B	3	-	40	44	4	1.3	64
C	3	-	40	44	6	0.5	74
D	42	45	-	-	3	23.7	39
E	42	45	-	-	6	1.1	58

*DAAM consistently maintained a concentration of 11 wt%, while MAA remained at 2 wt%.

4.1.3.1. Coagulum

Expending the feeding time resulted in reduced coagulum, since when adding the monomers more slowly, no large monomer droplets are formed and instead more uniform size, which increases the stability. For instance, with IBOMA/2OA, coagulum decreased from 2.6 wt% with a 3 h feeding time to 0.5 wt% with a 6 h feeding time, compare entry A-C. Similarly, for LA/MMA, the coagulum dropped from 24 wt% to 2 wt% with an additional 3 h of feeding time, see entry D and E.

However, longer feeding times may pose drawbacks, particularly in terms of industrial production capacity. Nonetheless, if demand is not high, this limitation may not be significant. Exploring even longer reaction times would be interesting, but since each dispersion would have taken longer than a workday, it was not possible.

4.1.3.2. Particle size

As shown in entry A-C the particle size of IBOMA/2OA dispersions remains relatively stable across different reaction times, with only a slight reduction observed at 4 h (entry B). This variation could stem from differences in surfactant concentrations, possibly due to human error. Despite efforts to maintain consistent conditions, such slight inconsistencies are not uncommon.

In contrast, the difference in particle size for LA dispersions (entry E-F) are more pronounced and likely linked to variations in coagulum levels. Due to the reduced coagulum in these samples, a greater amount of LA was polymerized within the particles, resulting in larger particle sizes compared to dispersions with higher coagulum.

4.1.4. Cyclodextrin

Cyclodextrin was introduced at the beginning of the process, with water and surfactant. Cyclodextrin at concentrations of 5 wt% and 1 wt% of the total monomer mass was investigated

for the dispersions. Dispersions containing 5 wt% cyclodextrin appeared milky white with subtle green undertones (observation by the eye), whereas regular dispersions maintained a less intense color. Refer to *Figure 12* below for a visual comparison between dispersions containing 5 wt% and 1 wt% cyclodextrin, and without. However, the addition of cyclodextrin had no obvious impact on pH or residual monomer levels. See *Table 5* for an overview of the remaining properties.

Figure 12. Color differences of the dispersion (from left to right): 5wt% cyclodextrin, 1wt% cyclodextrin and no cyclodextrin.

Table 5. Overview of the results for the dispersions containing cyclodextrin.

Entry	Monomer composition* (wt%)				Cyclodextrin	Coagulum	Particle size	Salt stability	MFFT
	MMA	LA	IBOMA	2OA	wt%	wt%	nm	mM	°C
A	3	-	40	44	-	2.6	71	400	45
B	3	-	40	44	1	0.2	79	1000	45
C	3	-	40	44	5	0.1	276	1000	-
D	42	45	-	-	-	23.7	39	300	41
E	42	45	-	-	1	9.5	61	600	40
F	42	45	-	-	5	2.1	148	1000	-
G	50	-	-	37	-	0.2	76	300	37
H	50	-	-	37	1	0.4	72	600	32

*DAAM consistently maintained a concentration of 11 wt%, while MAA remained at 2 wt%.

4.1.4.1. Coagulum

The addition of cyclodextrin was expected to lower the coagulum levels due to its ability as a phase transfer catalyst to facilitate the transportation of hydrophobic monomers to the particles,

which it also did. For IBOMA/2OA, 5 wt% cyclodextrin decreased the coagulum from 2.6 wt% to 0.1 wt% (entry A and C), and 1 wt% cyclodextrin reduced it to 0.2 wt% (entry B). Similarly, with LA, 1 wt% cyclodextrin resulted in a coagulum amount of 10 wt% (compared to 24% without cyclodextrin), decreasing to 2 wt% with 5 wt% cyclodextrin, see entry D-F.

However, for 2OA, 1 wt% cyclodextrin did not affect the coagulum amount, in fact, it appeared to increase it (compare entry G and H). This difference might be due to difficulties in removing the coagulum from the stirrer and thermometer and the observed differences may not be enough to indicate a significant change in coagulum levels. The same trend was observed for IBOMA/2OA, where the difference in coagulum between 1 wt% and 5 wt% cyclodextrin was not significant (see entry B and C), suggesting that 1 wt% cyclodextrin works as effectively as 5 wt% for IBOMA/2OA. However, for LA, 5 wt% cyclodextrin still resulted in considerable coagulum (entry F), suggesting that even higher levels might be necessary.

4.1.4.2. Particle size

The addition of 5 wt% cyclodextrin notably increased the particle size (entry F and C), likely due to its interaction with the surfactant, resulting in the formation of larger particles. However, the use of 1 wt% cyclodextrin (entry B, E and H) had a less pronounced effect on particle size, with a slight increase observed but not significantly. For LA, the larger particle size can be attributed to several factors. Firstly, the interaction between cyclodextrin and the surfactant may have contributed to this increase. Additionally, the reduction in coagulum levels with the use of cyclodextrin resulted in a higher concentration of LA within the particles, consequently leading to larger particle sizes. The more milky-white color of the dispersion with 5 wt% cyclodextrin is likely a consequence of the larger particle sizes.

4.1.4.3. MFFT

Determining MFFT was hindered when using 5 wt% cyclodextrin due to the formation of a white coating on the MFFT apparatus and just at the end where the excess dispersions were collected, a clear coating was achieved. This phenomenon persisted even when increasing the temperature range for MFFT determination. See *Figure 13*. Understanding the reason for this is complex, but one possible explanation could be that the particles are too large, making it harder to form a film or that cyclodextrin stabilize the particles too much, making it difficult for them to come close and form a film.

Figure 13. MFFT of the dispersion containing 5 wt% cyclodextrin, cracks all over.

Conversely, when utilizing 1 wt% cyclodextrin, the MFFT measurement was feasible, and cyclodextrin did not demonstrate any significant effect on the MFFT, see entry A-B, D-E and G-H.

4.1.4.4. Salt stabilization

The salt stabilization increased with the addition of cyclodextrin, particularly at the 5 wt% concentration (entry C and F), which could be attributed to several factors. Firstly, larger particles tend to improve salt stabilization properties, and the increase in particle size observed with cyclodextrin may contribute to this effect. Furthermore, cyclodextrin interacts with the surfactant in the dispersion system and since surfactants play a crucial role in stabilizing colloidal systems, any alteration in their behavior due to interaction with cyclodextrin could influence the overall salt stabilization.

4.1.5. Surfactants

DS/4 served as the reference surfactant in the experiments. XD was also tested as a direct substitution of DS/4. Additionally, the surfactant 2535, was tested in the pre-emulsion along with DS/4, AB/20, and JKB in the water. XD and DS/4 were used in equivalent amounts, approximately 4.7 wt% of the total monomer mass. However, JKB and AB/20 were used in smaller quantities, at 2 wt%, per supplier recommendations, and 2535 at 1 wt%. Using equal amounts of all surfactants could have allowed for a more comprehensive investigation into their differences, but surfactant dosage depends on factors like CMC, active content and surface tension. Staying to supplier recommendations ensures optimal surfactant use. While standardized amounts might offer direct comparability, following supplier guidelines provides a realistic measurement of each surfactant's performance under typical usage conditions.

It is noteworthy that there was no observed effect on residual monomer content or pH across the different surfactants. *Table 6* shows an overview of the resisting properties.

Tabel 6. Overview of the results of the dispersions with different surfactants.

Entry	Monomer composition* (wt%)				Surfactant	Surfactant concentration	Coagulum	Particle size	Salt stability	MFFT
	MMA	LA	IBOMA	2OA		wt%	wt%	nm	mM	°C
A	3	-	40	44	DS/4	4.7	2.6	71	400	45
B	3	-	40	44	XD	4.7	3.2	81	500	42
C	42	45	-	-	DS/4	4.7	23.7	39	300	41
D	42	45	-	-	DS/4 and 2535	2.8+1	4.0	55	400	26
E	42	45	-	-	AB/20 and 2535	2+1	13.5	87	1500	26
F	42	45	-	-	JKB and 2535	2+1	12.0	97	2000	25

*DAAM consistently maintained a concentration of 11 wt%, while MAA remained at 2 wt%.

4.1.5.1. Coagulum

When using IBOMA and 2OA, no significant difference was observed between XD and the reference surfactant DS/4 (entry A and B). However, when LA was utilized, there was a notable decrease in coagulum from 24 wt% to 4 wt% when using 2535 in the pre-emulsion and DS/4 in the water (compare entry C and D). To confirm the effectiveness of 2535 and DS/4, the dispersion was prepared twice, and both batches exhibited similar coagulum levels. For dispersions containing 2535 and AB/20, as well as JKB, the coagulum amounts were similar, ranging from 13-12 wt% (entry E-F), still better than the use of only DS/4.

The choice of surfactants plays a pivotal role in the success of these experiments. The most promising results were obtained when a combination of non-ionic surfactant in the pre-emulsion and a sodium anionic surfactant in the initial water phase was utilized. While the exact composition of 2535 remains unknown, it is challenging to pinpoint precisely why this combination yielded superior outcomes. However, as per theoretical principles, certain surfactants exhibit better compatibility with hydrophobic monomers than others. This highlights the importance of surfactant selection in optimizing dispersion formulations for specific monomer systems.

4.1.5.2. Particle size

Differences in particle size were observed between XD and DS/4, with XD exhibiting slightly larger particle sizes (entry A-B). This disparity was more pronounced in dispersions containing LA, where DS/4 resulted in the smallest particle size (entry C), while dispersions with mixed surfactants yielded larger particles (entry D-F). Variations in particle size among different surfactants are common, as properties such as CMC influence particle size. It is worth noting that this aspect was not specifically considered in this project.

4.1.5.3. MFFT

When using LA, the MFFT was significantly lower when mixing different surfactants (compare entry C-F), suggesting that these surfactants also work as plasticizers which stay in the film after drying and softening it. Another explanation is that these dispersions had higher LA residual monomer content, which softens the film.

4.1.5.4. Salt stabilization

Variations in salt stabilization among different surfactants are expected, as some surfactants are more effective at stabilizing particles than others. Specifically, the ammonium-salt surfactants used showed increased salt stabilization, see entry E-F.

4.1.6. Itaconic acid

IA, which is in solid form, was hard to dissolve both in water and in the monomer blend. Attempts to dissolve it involved pre-neutralization as well as heating in a 60 °C oven for 30 min, where the latest was the most successful. Since IA has 2 carboxylic acid-groups and MAA 1, half of the molar amount of MAA was used for IA to get an equal number of functional groups. The same amount of neutralization agent (ammonia, 19%) was used.

There were no significant effects observed on coagulum, MFFT, salt stabilization, or particle size. However, there was an increase in residual monomer levels when using IA instead of MAA, and the pH was lower. For a detailed comparison, see *Table 7*.

Table 7. Overview of the results of dispersions containing IA in compared to MAA.

Entry	Monomer composition* (wt%)						Residual monomer (ppm)				pH
	MMA	BA	IBOMA	2OA	MAA	IA	MMA	BA	IBOMA	2OA	
A	53	34	-	-	2	-	14	17	-	-	6.5
B	53	34	-	-	-	1.5	40	194	-	-	5.2
C	-	-	43	44	2	-	-	-	30	0	7.1
D	-	-	43	44	-	1.5	-	-	40	50	5.2

*DAAM consistently maintained a concentration of 11 wt%.

The rise in residual monomer levels may stem from IA's partial incompatibility with the monomers and the polymerization process, resulting in less efficient polymerization compared to MAA. Additionally, the lower pH (entry B and D) may be due to IA's higher acidity and to achieve a neutral pH may require further experimentation to balance IA and the neutralization agent. Further investigations and adjustments may be necessary to fully optimize IA's compatibility and performance in polymerization. However, this suggests that substituting IA with MAA is not entirely impossible.

4.1.7. Super-set

To achieve a dispersion with high biocontent (43 wt% IBOMA and 44 wt% 2OA) without any coagulum, everything that reduced coagulum was used together. This included a 6 h feeding time, 1 wt% cyclodextrin, and the surfactant 2535 in the pre-emulsion and DS/4 in the water. However, 0.6 wt% coagulum was observed, indicating that achieving coagulum-free dispersions using biobased monomers was not possible during the time span of this project.

4.2. Coating properties

The formulation process faced unexpected challenges, and achieving a finished floor coating was not possible. These difficulties may arise from the hydrophobic nature of the monomers used, which differ significantly from Bona's current product formulations. Developing a new product typically involves using existing chemicals, and these dispersions may face too many challenges to become financially viable for Bona.

The incorporation of ADH seems a challenge, resulting in hazy coatings. Another crosslinking system might have worked better, but there was not enough time to explore it further. A smaller amount of ADH might also have worked better. One explanation for this could be that the particles are so hydrophobic that ADH, which is more hydrophilic, is poorly compatible with these systems. As a result, it cannot react effectively with DAAM and is instead precipitated upon drying, forming the hazy coating.

Additionally, film formation was challenging, requiring the testing of various coalescents and coalescent mixtures before identifying one that worked satisfactorily, and even then, it was needed in large quantities. Different wetting agents were also tested and Capstone™ FS-63, which is a PFAS substance, is a very efficient wetting agent but is also very hazardous, making it unsuitable for use in floor coatings. Furthermore, no defoamer was added to the formulation because the tested options failed to perform as expected, causing the coatings to foam excessively and form bubbles when drying.

All dispersions containing IBOMA, 2OA, or LA exhibited an oily film on the surface, and even the slightest touch left a mark on the coating, which was difficult to remove. The reason for the oily coatings is not fully understood. It may be due to the use of more hydrophobic (i.e., oilier) monomers, resulting in an oily surface, or it may be that the coatings are exuding some chemical, such as unreacted monomers, surfactant, coalescent etc., that remains on the surface of the coating. For IBOMA and 2OA, the residual monomers are known to be low, but for LA, such measurement was not possible. However, since the same phenomenon occurs for all of them, they might have the same underlying cause and more experiments are needed to fully understand this phenomenon.

Despite the imperfect formulation, it was possible to investigate some properties such as film formation, chemical resistance, and color. However, these properties may differ with an improved formulation.

4.2.1. Bio content, IBOMA and 2OA

4.2.1.1. Film formation

From the film formation test, most of the coatings appeared to form good films. The only ones with some blue spots were the coatings with IBOMA/BA and the one with maximum IBOMA/2OA content. See *Figure 14* for a comparison of these with the reference coating, MMA/BA. For the rest, see *Figure A4* in the Appendix.

Figure 14. From left to right: 1. Reference with MMA/BA. 2. IBOMA/BA. 3. IBOMA/2OA maximum.

4.2.1.2. Chemical resistance

The chemical resistance on both Leneta and wood was similar for the coatings with MMA/BA and those with IBOMA/2OA, with no significant differences observed. The coatings were resistant to all the chemicals tested on both Leneta and wood, indicating that the chemical resistance of these coatings is excellent.

4.2.1.3. Color

When investigating *Figure 15* below, a slightly darker color can be observed with increasing amounts of IBOMA and 2OA. However, the change is not very pronounced and may also be due to natural variations in the color of the wood itself. Importantly, IBOMA and 2OA do not significantly influence the color, indicating that the color of the coating is not a hindrance to its use as a floor coating.

Figure 15. From left to right: 1. Reference with MMA/BA. 2. 10 wt% of each IBOMA/2OA. 3. 20 wt% of each IBOMA/2OA. 4. 40 wt% of each IBOMA/2OA. 5. 40 wt% IBOMA, 44 wt% 2OA. 6. 43 wt% IBOMA, 44 wt% 2OA. 7. IBOMA/BA. 8. 2OA/MMA.

4.2.2. Cyclodextrin

Dispersions for IBOMA/2OA using 1 wt% and 5 wt% cyclodextrin were formulated, as were dispersions with LA. However, due to time limitations, the 1 wt% cyclodextrin dispersion for 2OA was not formulated.

4.2.2.1. Film formation

The incorporation of 5 wt% cyclodextrin with IBOMA/2OA resulted in total lack of film formation, with slight improvement observed with LA. However, at a concentration of 1wt%, film formation was successfully achieved. Interestingly, LA with no cyclodextrin did not exhibit perfect film formation and 1 wt% cyclodextrin made the film formation better. Upon examination of *Figure 16*, it appears that 1 wt% cyclodextrin for IBOMA/2OA also did not display optimal film formation. This observation may be misleading, as some of the coating from the 5 wt% sample overlapped onto the side containing the 1wt% sample.

The poorer film formation of the 5 wt% cyclodextrin dispersion may be attributed to the larger particles, which could hinder the formation of a smooth film. Another possibility is that cyclodextrin stabilizes the particles too effectively, preventing them from coming close and coalescing. Additionally, since it was not possible to determine the MFFT, it is possible that it could be significantly higher, requiring even more coalescent to form a film at room temperature.
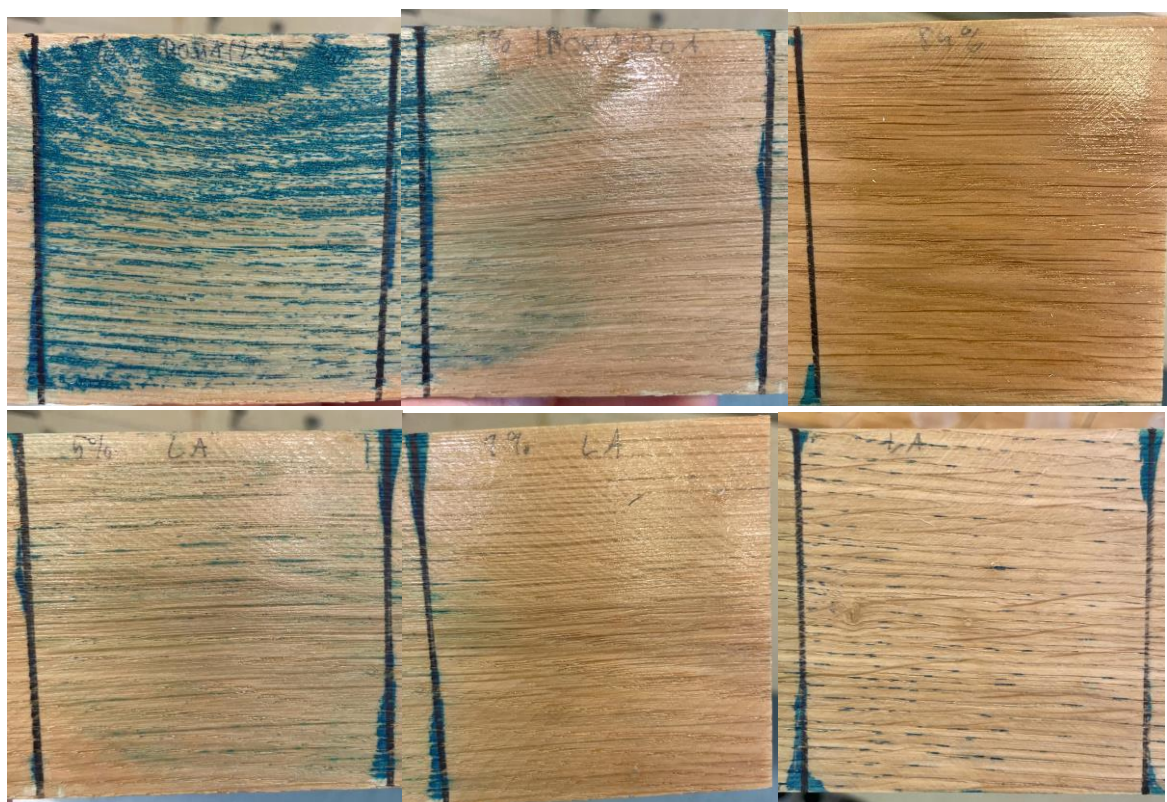

Figure 16. Top left: 5 wt% cyclodextrin IBOMA/2OA. Top middle: 1 wt% cyclodextrin IBOMA/2OA. Top right: IBOMA/2OA no cyclodextrin. Bottom left: 5 wt% cyclodextrin LA/MMA. Bottom middle: 1 wt% cyclodextrin LA/MMA. Bottom right: LA/MMA no cyclodextrin.

4.2.2.2. Chemical resistance

Cyclodextrin did not impact the chemical resistance of the coatings at 1 wt% and was resistant to all the chemicals on both Leneta and wood. However, at 5 wt%, the chemical resistance was worse, with stains from all chemicals visible on these coatings. Furthermore, the chemical drops spread out much more compared to the other coatings, suggesting that they possess a different surface tension. This is probably due to the complex cyclodextrin forms with the surfactants.

4.2.2.3. Color

A clear difference could be seen in the coating with 5 wt% cyclodextrin for IBOMA/2OA, which appears much lighter, likely due to the lack of film formation. In contrast, the color of the dispersion containing 1 wt% cyclodextrin was not significantly affected, see *Figure 17*.

Figure 17. From left to right: 1. IBOMA/2OA. 2. 5 wt% cyclodextrin IBOMA/2OA. 3. 1 wt% cyclodextrin IBOMA/2OA. 4. LA/MMA. 5. 5 wt% cyclodextrin LA/MMA. 6. 1 wt% cyclodextrin LA/MMA.

4.2.3. Surfactants

4.2.3.1. Film formation

For the coatings with IBOMA/2OA, the XD surfactant did not result in good film formation. However, this may be due to variations in the structure of the wood, as some pieces may have a more pronounced texture, requiring a thicker layer of coating to prevent the wood's texture from appearing on the surface above the coating, or that it makes the film formation more difficult.

For the coatings with LA and different surfactants, none resulted in perfect film formation. The best performance was observed with the DS/4 and 2535 mixture, while the others can be considered equally poor. See *Figure 18* below for all the different surfactants.

Figure 18. Top left: DS/4 IBOMA/2OA. Top middle: XD IBOMA/2OA. Top right: 2535+DS/4 LA/MMA. Bottom left: 2535+JKB LA/MMA. Bottom middle: 2535+AB/20 LA/MMA. Bottom right: DS/4 LA/MMA.

4.2.3.2. Chemical resistance

There was no discernible difference in chemical resistance between XD and DS/4 surfactants, showing good chemical resistance. However, the surfactants used for LA non were perfect and stains from ammonium and acetic acid could be seen on all of them. A slightly better resistance for the mixture of DS/4 and 2535, but the rest can be said to be equally bad. This corresponds well with the film formation and is probably the main reason for this.

4.2.3.3. Color

There was no apparent difference observed between XD and DS/4 surfactants. However, with LA, the color appeared lighter (see *Figure 19*), which can be seen as a positive outcome. It is worth noting that this lightening effect may be attributed to the lack of proper film formation. But it can be interesting to investigate more to actually draw a full conclusion.

Figure 19. From left to right: 1. DS/4 IBOMA/2OA. 2. XD IBOMA/2OA. 3. DS/4 LA/MMA. 4. 2535+DS/4 LA/MMA. 5. 2535+AB/20 LA/MMA. 6. 2535+JKB LA/MMA.

4.2.4. Itaconic acid

4.2.4.1. Film formation

For MMA/BA, there was no difference in film formation (see *Figure A5* in Appendix). However, for IBOMA/2OA, IA had a slightly negative effect on film formation, as shown in *Figure 20* below. This may be because not the same amount of coating was applied on each wood piece, resulting in a thinner layer and thereby making the structure of the wood more visible and making more blue stains. Although the same amount of coating was intended to be applied, human error can always play a role, and complete reproducibility is not always possible.
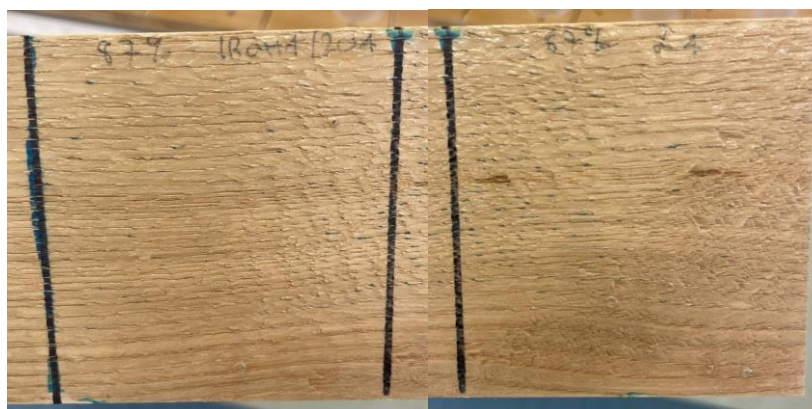
Figure 20. Left is IBOMA/2OA/MAA and right is IBOMA/2OA/IA.

4.2.4.2. Chemical resistance

IA showed slightly less chemical resistance to the acetic acid and ammonium but no difference for other chemicals on both wood and Leneta. This reduction of chemical resistance may be due to imperfect film formation or the lower pH of the dispersions with IA, making it more vulnerable to acidic and alkaline chemicals.

4.2.4.3. Color

For IBOMA/2OA, the IA made the coating slightly darker and more red. However, the difference was not as noticeable for the coating with MMA and BA, suggesting that IA may have a negligible effect on color in these cases. Nonetheless, it may be interesting to investigate further to determine if the color change is consistent and IA could potentially be a component to experiment with when different colors are needed. See *Figure 21* below.
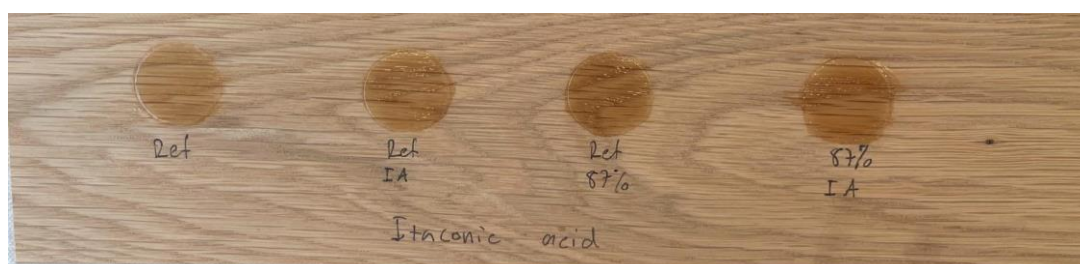
Figure 21. From left to right: 1. MMA/BA/MAA. 2. MMA/BA/IA. 3. IBOMA/2OA/MAA. 4. IBOMA/2OA/IA.

5. Conclusion

The aim of this project was to create a floor coating using biobased monomers with as low coagulum as possible during the polymerization, while still achieving competitive coating properties.

The conclusions of this project are that emulsion polymerization of biobased monomers is possible but comes with the drawback of coagulum during the process. While there are methods to reduce the coagulum to more reasonable levels, a 0.5 wt% of coagulum might sound small, but on an industrial scale using several tons of monomer, it becomes kilograms of coagulum. This not only wastes money but also complicates the filtration of the ready dispersion significantly. Longer reaction times, the use of cyclodextrin, and the choice of surfactants can help reduce coagulum, and more experiments might lower it even further.

For the formulation, improvements are needed, and these dispersions might be too complicated to be suitable for floor coatings, though they might be applicable for other types of coatings. IBOMA/2OA coatings exhibit good properties of chemical resistance, color and film formation, but further experiments are necessary to fully investigate their potential. LA did not show good properties and is probably not suitable as floor coating. However, substituting MAA with IA might be a way to make coatings more biobased. Given that the amount of functional monomer is small, this change may not be worthwhile since it did not improve the properties.

This project has provided valuable insights into how biobased monomers function in both dispersion production and as formulated coatings. This report shows that using biobased raw materials in coatings is possible for the future, but more studies are needed and there are challenges. If it is determined that biobased monomers cannot be used, attention could be shifted to other raw materials to explore whether more environmentally friendly alternatives can be used instead. Alternatively, more research could focus on developing biobased alternatives for the fossil-based monomers currently in use.

6. Future work

- Find a way to measure the residual LA content.
- Investigate further optimization of coagulum, including exploring more with cyclodextrin, surfactants, and reaction time.
- Explore mixing rates and solid contents.
- Try optimizing formulation.
- Try other crosslinking systems or find the optimal ADH content.
- Investigate other biobased raw materials as well.
- Scale up to understand the extent of coagulum issues.
- Investigate other coatings applications for these monomers

References

[1] Bona, "Hållbarhet," Bona, [Online]. Available: https://www.bona.com/sv/om-bona/hallbarhet/. [Accessed 20 May 2024].

[2] R. Baumstark and R. Balk, Water-based Acrylic Dispersions: Applications in Architectural Coatings, 2nd Revised Edition, Hanover: Vincentz Network GmbH & Co, 2022.

[3] O. Llorente, A. Barquero, M. Paulis and J. R. Leiza, "Challenges to incorporate high contents of bio-based isobornyl methacrylate (IBOMA) into waterborne coatings," *Progress in Organic Coatings,* vol. 172, Article 107137, 2022.

[4] J. Cowie and V. Arrighi, Polymers: Chemistry and physics of modern material, Boca Raton: Taylor & Francis Group, 2007.

[5] U. Poth, R. Schwalm, M. Schwartz and R. Baumstark, Acrylic Resins, Hanover: Vincentz Network GmbH & Co, 2011.

[6] P. A. Lovell and F. J. Schork, "Fundamentals of Emulsion Polymerization," *Biomacromolecules,* vol. 21, no. 11, pp. 4396-4441, 2020.

[7] A. Bohre, K. Avasthi, U. Novak and B. Likozar, "Single−Step Production of Bio−Based Methyl Methacrylate from Biomass−Derived Organic Acids Using Solid Catalyst Material for Cascade Decarboxylation−Esterification Reactions," *ACS Sustainable Chemistry & Engineering,* vol. 9, no. 7, pp. 2902-2911, 2021.

[8] N. P. Money, "Chapter 12 - Fungi and Biotechnology," in *The Fungi (Third Edition),* Oxford, Academic Press, 2016, pp. 401-424.

[9] J. Lu, W. Zhang, C. S. K. Lin, Y. Jiang and F. Xin, "Chapter 8 - Biochemical production of bioalcohols," in *Handbook of Biofuels Production: Processes and Technologies, Third Edition*, Woodhead Publishing, 2023, pp. 231-252.

[10] S. Aldrich, "Thermal Transitions of Homopolymers: Glass Transition & Melting Point," Sigma Aldrich, [Online]. Available: https://www.sigmaaldrich.com/SE/en/technical-documents/technical-article/materials-science-and-engineering/polymer-synthesis/thermal-transitions-of-homopolymers. [Accessed 20 May 2024].

[11] A. Niesbach, N. Fink, P. Lutze and A. Górak, "Design of reactive distillation processes for the production of butyl acrylate: Impact of bio-based raw materials," *Chinese Journal of Chemical Engineering,* vol. 23, no. 11, pp. 1840-1850, 2015.

[12] A. Niesbach, T. A. Adams II and P. Lutze, "Semicontinuous distillation of impurities for the production of butyl acrylate from bio-butanol and bio-acrylic acid," *Chemical Engineering and Processing: Process Intensification,* vol. 74, pp. 165-177, 2013.

[13] S. S. Behera and R. C. Ray, "11 - Cell immobilization strategies to enhance yield of liquid biofuels," in *Advances in Lignocellulosic Biofuel Production Systems*, Woodhead Publishing, 2023, pp. 407-416.

[14] T. Dishisha, S.-H. Pyo and R. Hatti-Kaul, "Bio-based 3-hydroxypropionic- and acrylic acid production from biodiesel glycerol via integrated microbial and chemical catalysis," *Microbial Cell Factories,* vol. 14, Artikel 200, 2015.

[15] A. Bohre, U. Novak and M. Grilc, "Synthesis of bio-based methacrylic acid from biomass-derived itaconic acid over barium hexa-aluminate catalyst by selective decarboxylation reaction," *Molecular Catalysis,* vol. 476, Artikel 110520, 2019.

[16] J. C. Lansing, R. E. Murray and B. R. Moser, "Biobased Methacrylic Acid via Selective Catalytic Decarboxylation of Itaconic Acid," *ACS Sustainable Chemistry & Engineering,* vol. 5, pp. 3132-3140, 2017.

[17] C. R. Casas-Soto, A. S. Conejo-Dávila, V. Osuna, D. Chávez-Flores, J. C. Espinoza-Hicks, S. G. Flores-Gallardo and A. Vega-Rios, "Dibutyl Itaconate and Lauryl Methacrylate Copolymers by Emulsion Polymerization for Development of Sustainable Pressure-Sensitive Adhesives," *Polymers,* vol. 14, no. 3, p. 632, 2022.

[18] M. Cao, "Synthesis and properties of poly(itaconic acid)," University of New Hampshire, Durham, 2008.

[19] "BIOFACTURING PARTNER WITH NATURE," Circular Industries Holdning, [Online]. Available: BIOFACTURING. [Accessed 22 may 2024].

[20] A. Badía, M. Kastelijn, J. Scheerder and J. R. Leiza, "Development of biobased waterborne coatings containing Ecomer®: An alkyl polyglucoside maleic acid ester monomer," *Progress in Organic Coatings,* vol. 147, Article 105708, 2020.

[21] A. Badía, M. J. Barandiaran and J. R. Leiza, "Biobased Alkali Soluble Resins promoting supramolecular interactions in sustainable waterborne Pressure-Sensitive Adhesives: High performance and removability," *European Polymer Journal,* vol. 144, Article 110244, 2021.

[22] Evonik Industries, "VISIOMER® The first choice in methacrylate solutions," Evonik Performance Materials GmbH, Darmstadt, 2015.

[23] BASF, "Acrylic & Methacrylic Monomers," September 2021. [Online]. Available: https://chemicals.basf.com/global/en/Petrochemicals/acrylic-monomers.html. [Accessed 20 May 2024].

[24] A. Badía, J. Movellan, M. J. Barandiaran and J. R. Leiza, "High Biobased Content Latexes for Development of Sustainable Pressure Sensitive Adhesives," *Industrial & Engineering Chemistry Ressearch,* vol. 57, pp. 14509-14516, 2018.

[25] A. Kohut, Z. Demchuk, K. Kingsley, S. Voronov and A. Voronov, "Dual role of methyl-β-cyclodextrin in the emulsion polymerization of highly hydrophobic plant oil-based monomers with various unsaturations," *European Polymer Journal,* vol. 108, pp. 322-328, 2018.

[26] R. J. Leyrer and W. Mächtle, "Emulsion polymerization of hydrophobic monomers like stearyl acrylate with cyclodextrin as a phase transfer agent," *Macromol. Chem. Phys.,* vol. 201, pp. 1235-1243, 2000.

[27] F. Boscán, M. Paulis and M. Barandiaran, "Towards the production of high performance lauryl methacrylate based polymers through emulsion polymerization," *European Polymer Journal,* vol. 93, pp. 44-52, 2017.

[28] W. Dong, D. Zhang, Z. Ha, J. Wang, Y. Xia, X. Chen, L. Lei and S. Shi, "Emulsion polymerization of super-hydrophobic acrylate enabled by a novel "ferrying" strategy for developing waterborne coatings with reduced surface tension and glossiness," *Progress in Organic Coatings,* vol. 186, Article 108073, 2024.

[29] K. Tauer, A. I. Ali, U. Yildiz and M. Sedlak, "On the role of hydrophilicity and hydrophobicity in aqueous heterophase polymerization," *Polymer,* vol. 46, no. 4, pp. 1003-1015, 2005.

[30] Solvay, "Abex 2535 Safety Data Sheet," 4 april 2023. [Online]. Available: https://www.syensqo.com/en/product/abex-2535. [Accessed 20 may 2024].

[31] Solvay, "ABEX® JKB STD Safety Data Sheet," 31 october 2023. [Online]. Available: https://www.syensqo.com/en/product/abex-jkb-std. [Accessed 20 may 2024].

[32] Syensqo, "RHODAPEX AB/20 Safety Data Sheet," 2 january 2024. [Online]. Available: https://www.syensqo.com/en/product/rhodapex-ab20. [Accessed 20 may 2024].

[33] H. Ahmad, M. Hasan, M. Miah, A. Ali and K. Tauer, "Solvent effect on the emulsion copolymerization of methyl methacrylate and lauryl methacrylate in aqueous media," *Polymer,* vol. 52, no. 18, pp. 3925-3932, 2011.

[34] T. G. Jansen, J. Meuldijk, P. A. Lovell and A. M. van Herk, "On the Miniemulsion Polymerization of Very Hydrophobic Monomers Initiated by a Completely Water-Insoluble Initiator: Thermodynamics, Kinetics, and Mechanism," *Journal of Polymer Science Part A: Polymer Chemistry,* vol. 54, pp. 2731-2745, 2016.

[35] Chemours, "Capstone™ FS-63 Fluorosurfactant Safety Data Sheet," 7 july 2022. [Online]. Available: https://www.chempoint.com/products/chemours/capstone-fluorosurfactants/capstone-surfactants-and-coating-additives/capstone-fs-63. [Accessed 20 may 2024].

Appendix

Table A1. Temperature ramp for the GC.

Stage	Temperature (°C)	Holding time (min)
1.	50	1
2.	100	2
3.	180	3
4.	270	2.75
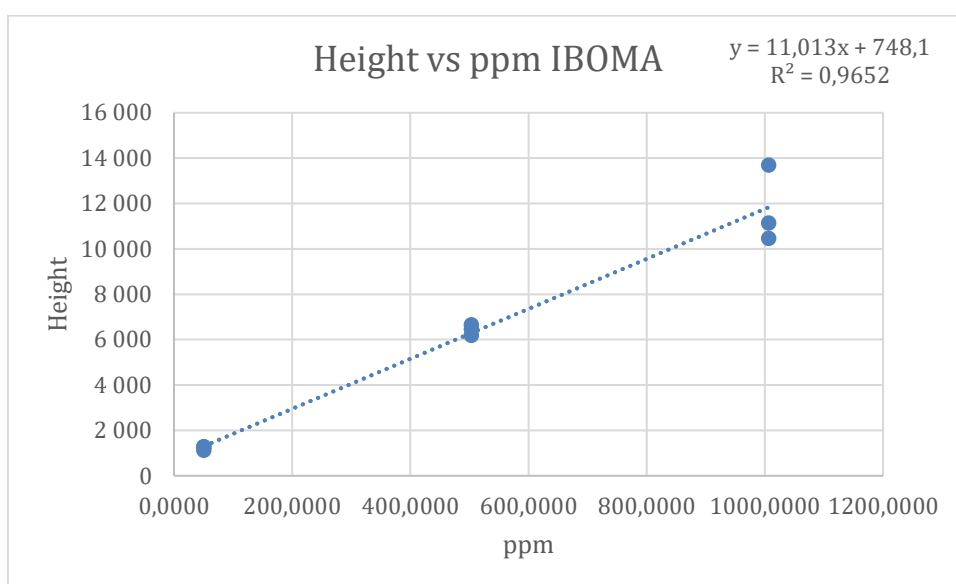
Figure A1. Calibration curve for IBOMA.
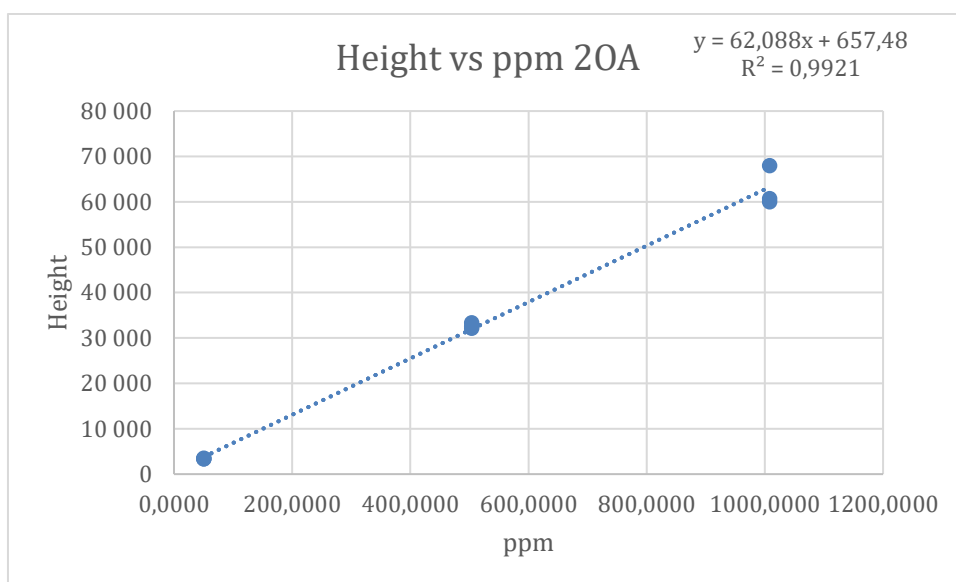
Figure A2. Calibartion curve for 2OA.

Figure A3. All dispersions and their results.

Dispersion Experiment	Description	Monomer composition (w-%)								Residual monomer (ppm)								Coagulation (%)	Particle size dp (nm)	pH	MFFT (°C)	Salt stabilization		Heat stabilization	
		MMA	BA	IBOMA	2OA	LA	MAA	IA	DAAM	MMA+15	BA+15	MMA+45	BA+45	2OA+15	IBOMA+15	2OA+45	IBOMA+45					Ok (mM)	Not OK (mM)	Before dp (nm)	After dp (nm)
1	Ref	53	34				2		11	16	106	9	25	100	120	0	40	not determine	74	5,8	36	300	400	77	73
2	20% IBOMA/2OA	41	26	10	10		2		11	15	12	14	2	585	150	16	90	not determine	74	6,2	36	300	400	73	76
3	40% IBOMA/2OA	28	19	20	20		2		11	9	3	12	1	114	110	10	20	not determine	67	5,9	33	300	400	70	72
4	60% IBOMA/2OA	16	11	30	30		2		11	27	18	8	2	185	200	7	10	not determine	75	5,5	42	300	400	81	77
5	84% IBOMA/2OA	3		40	44		2		11	1		1		84	35	1	10	3,2	70	6,1	42	not determine	not determine	not determine	not determine
6	84% Dowfax XD	3		40	44		2		11	1		1		385	280	6	45	3,2	81	5,6	42	500	600	83	80
7	84% 4h	3		40	44		2		11	1	5	1	0		260		125	1,3	64	6,7	37	not determine	not determine	not determine	not determine
8	IBOMA		40	47			2		11	1								2,3	64	6,2	44	300	400	68	69
9	2OA (Tg0 wrong Tg)	28	3		59		2		11	59		8		745		265		0,5	63	6,7	<0	300	400	66	69
10	84% 6h	3		40	44		2		11	2		2		55	60	7	25	0,5	74	6,5	43	300	400	not determine	not determine
11	84% more surf. F1	3		40	44		2		11	0		1		53	75	2	30	1,4	68	6,2	44	300	400	69	71
12	2OA	50			37		2		11	76		21		300		90		0,2	77	6,6	37	300	400	75	75
13	84% 5% cyclo	3		40	44		2		11	4		1		50	20	13	25	0,1	276	6,2		700	1000	275	276
14	84% 5% cyclo more surf.	3		40	44		2		11	2		2		24	0	9	30	0,2	114	6,7		700	1000	111	109
15	84% 1% cyclo	3		40	44		2		11	2		1		60	20	0	10	0,2	79	6,7	45	700	1000	80	80
16	LA	42				45	2		11	32		14						23,7	39	6,6	41	300	400	46	51
17	Ref with IA	54	33					1,5	11	60	719	14	196					0,1	71	5,1	31	300	400	72	72
18	LA 1% cyclo	42				45	2		11	5		4						9,5	61	6,5	40	300	400	62	66
19	2OA 1% cyclo	50			37		2		11	29		26		137		30		0,4	72	6,9	32	600	700	74	72
20	Ref with IA, pre neut	54	33					1,5	11	320	1344	141	938					0,0	73	4,5	30	200	300	74	75
21	Ref with IA, pre heat	54	33					1,5	11	78	541	40	194					0,0	72	5,2	30	300	400	75	73
22	Ref 2h	53	34				2		11	26	69	14	8					0,0	69	7,1	31	300	400	71	71
23	Ref again	53	34				2		11	14	66	18	9					0,0	67	7,4	32	300	400	73	71
24	Ref Tg10	41	46				2		11	13	145	7	9					0,0	74	7,4	7	300	400	76	73
25	Ref with chain transfer agent	53	34				2		11	19	104	14	33					0,1	68	6,9	28	300	400	68	67
26	LA 5% cyclo	42				45	2		11	10		5						2,1	148	7,1		1000	15000	152	147
27	LA Abex 2535 in F1	42				45	2		11	10		6						3,8	55	7,1	26	400	500	53	54
28	LA AB/20 & Abex 2535	42				45	2		11	20		7						13,5	87	7,4	26	1500	2000	88	86
29	LA JKB STD & Abex 2535	42				45	2		11	16		6						12,0	97	7,4	25	2000	2500	95	94
30	LA 6h	42				45	2		11	14		8						1,1	58	7,4	25	500	600	52	54
31	20% IBOMA/2OA again	41	26	10	10		2		11	14	8	19	8	30	10	0	20	0,1	71	7,4	34	400	500	71	67
32	40% IBOMA/2OA again	28	19	20	20		2		11	14	17	12	1	40	20	0	0	0,3	76	7,3	37	400	500	74	73
33	60% IBOMA/2OA again	16	11	30	30		2		11	8	7	7	0	60	40	0	30	0,8	75	7,3	41	400	500	74	78
34	84% IBOMA/2OA again	3		40	44		2		11	2		1		80	130	0	40	2,0	72	6,6	47	400	500	72	73
35	87% IBOMA/2OA			43	44		2		11					30	35	0	30	2,1	65	7,1	45	400	500	67	68
36	87% IBOMA/2OA with IA			43	44			1,5	11					240	50	50	40	1,9	71	5,2	42	400	500	74	72
37	87% 6h 1% cyclo Abex 2535 in F1			43	44		2		11					60	80	0	20	0,6	72	7,1	44	700	1000	76	76
38	LA Abex 2535 in F1 again	42				45	2		11	9		5						4,2	55	7,1	45	500	600	not determine	not determine

Figure A4. Film formation test, biocontent IBOMA and 2OA. Top left: 10 wt% each IBOMA/2OA. Top middle: 20 wt% each IBOMA/20. Top right: 30 wt% each IBOMA/2OA. Bottom left: 40 wt% IBOMA 44 wt% 2OA. Bottom right: 2OA/MMA.
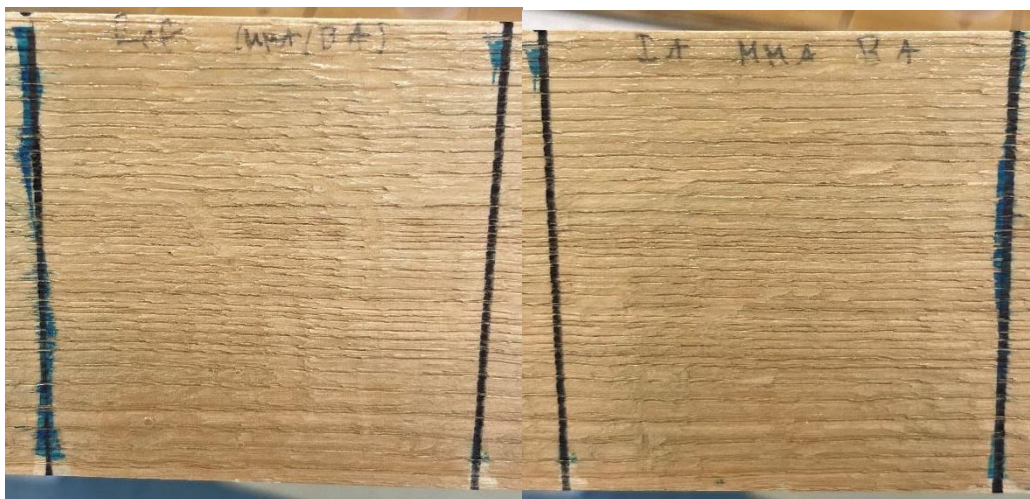

Figure A5. Film formation test for itaconic acid. Left: MMA/BA/MAA. Right: MMA/BA/IA.