# A NOVEL WATERBORNE COATING BASED ON STYRENE-ACRYLIC COPOLYMERS FOR CONSTRUCTION APPLICATION

by

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## DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled 'A Novel Waterborne Coating Based on Styrene-Acrylic Copolymers for Construction Applications'. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

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# LIST OF SYMBOLS

Ao	Initial cross-sectional area
Ср	Heat Capacity
D	Translational diffusion coefficient $[m^2/s]$ – "speed of the particles"
Е	Young modulus
F	Force applied
h	Viscosity [pa.s]
KB	Boltzmann constant [m²kg/ks²]
L	Length
Lo	Initial length
Μ	Molecule of monomer
R•	One molecular of the initiator
RH	Hydrodynamic radius [m]
RM•n	Propagating chain radical with degree of polymerization
RM•n S	Propagating chain radical with degree of polymerization Seed
S	Seed
S SC	Seed Seed-core
S SC T	Seed Seed-core Temperature [K]
S SC T T-a	Seed Seed-core Temperature [K] Chain transfer
S SC T T-a Tg	Seed Seed-core Temperature [K] Chain transfer Glass transition temperature
S SC T T-a Tg Va	Seed Seed-core Temperature [K] Chain transfer Glass transition temperature Potential energy
S SC T T-a Tg Va Vr	Seed Seed-core Temperature [K] Chain transfer Glass transition temperature Potential energy Electrostatic interaction
S SC T T-a Tg V <sub>a</sub> V <sub>r</sub> V <sub>t</sub>	Seed Seed-core Temperature [K] Chain transfer Glass transition temperature Potential energy Electrostatic interaction Attractive interaction

# LIST OF ABBREVIATIONS

ATR	Attenuated Total Reflectance
APAC	Asia-Pacific
BA	Butyl Acrylate
CAGR	Compound annual growth rate
CMC	Critical micelle concentration
DI	Deionized Water
DL	Double Layer
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform infrared Spectroscopy
KPS	Potassium sulfate
MFFT	Minimum film formation temperature
MVTR	Moisture vapor transmission rate
PBA-Sty	Poly- <i>n</i> -Butyl acrylate- <i>co</i> -styrene
Sty	Styrene
RH	Relative Humidity
SDS	Sodium Dodecyl Sulfate
TSC	Total Solid Content
VOC	Volatile Organic Compounds

# SALUTAN BAWAAN AIR NOVEL BERASASKAN KOPOLIMER STYRENE-ACRYLIC UNTUK KEGUNAAN PEMBINAAN

### ABSTRAK

Tesis ini mempunyai tiga peringkat yang merujuk kepada tiga objektif. Pada peringkat pertama, tesis ini mengkaji kesan kelajuan pergolakan, jenis surfaktan, masa yang diambil oleh monomer, kepekatan monomer, kepekatan pemangkin, dan kepekatan penampan untuk mendapatkan zarah emulsi yang bersaiz nano (~70nm). Pada peringkat kedua, tesis ini mengkaji taburan saiz dan kestabilan emulsi terhadap perbezaan kepekatan monomer dengan menggunakan pempolimeran emulsi berbiji. Pada peringkat terakhir, filem PBA-sty dikeringkan diatas pinggan kaca pada suhu bilik selama 24 jam dan tesis ini mengkaji tindak balas glass transition temperature (Tg) pada sifat mekanikal dengan menggunakan kalorimetri pengimbasan perbezaan dan pengukuran tegangan. Kompisisi bahan kimia telah dikaji menggunakan Fourier Transform Infrared (FTIR). ciri-ciri zarah emulsi pada peringkat pertama dan kestabilan seed-core emulsi telah dikaji berdasarkan nilai pH, Total Solid Content (TSC), Dynamic Light Scattering (DLS) dan Zeta potential. S17 menunjukkan bacaan Dynamic Light Scattering (DLS) yang paling kecil dengan nilai (66.53nm) dengan menggunakan surfaktan bukan ionik. SC5 dengan kepekatan styrene yang paling tinggi (36/54) menunjukkan kadar penukaran polimer yang paling tinggi, bacaan glass transition temperature (Tg) yang tinggi dan kekuatan tegangan tinggi dengan bacaan 48.06%, 24°C dan 7.70MPa. sementara itu, SC1 dengan kepekatan (54/36) menunjukkan pemanjangan yang tertinggi dengan bacaan (680.83%) dimana Butyl Acrylate menyediakan fleksibiliti pada filem. Peningkatan kepekatan styrene dalam emulsi dapat meningkatkan bacaan glass transition temperature (Tg) sekaligus kekuatan tegangan kerana sifat styrene yang menyediakan sifat ketegaran pada filem dan sifat hidrofobik yang menyumbang kepada pertukaran polimer yang sangat tinggi.

# A NOVEL WATERBORNE COATING BASED ON STYRENE-ACRYLIC COPOLYMERS FOR CONSTRUCTION APPLICATION

### ABSTRACT

This study consists of 3 stages which reflected by three objectives. At the first stage, this study investigated the effect of agitation speed, types of surfactants, feeding time monomers and concentration of monomers, initiator, and buffer to obtain seed nanoparticles (~70nm). At the second stage, the different compositions of two monomers; n-Butyl Acrylate (BA) and Styrene (Sty) was studied to obtain the high stability of polymer and were synthesized by seeded emulsion polymerization. At the third stage, the PBA-Sty films were casted on glass plate at room temperature for 24hours and the corresponding of glass transition temperature (Tg) on mechanical properties of poly (n-butyl acrylate-co-styrene) (PBA-Sty) films were studied using Differential Scanning Calorimetry (DSC) and tensile measurements. The chemical composition of materials was analyzed using Fourier Transform Infrared (FTIR). The pH, Total Solid Content (TSC), Dynamic Light Scattering (DLS), Zeta potential were studied in determining the characterization of seed nanoparticles and the stability of Seed-core emulsion. The Dynamic Light Scattering (DLS) showed S17 obtain the smallest particles size (66.53nm) by using non-ionic surfactant. The highest concentration of Styrene (Sty) (SC5) showed high polymer conversion, high glass transition temperature contributes to having high tensile strength of films by obtaining (48.06%), 24°C and (7.73Mpa) respectively this is due to the styrene provide the rigidity and high of hydrophobic chain which contribute to high conversion of polymer. while highest concentration of Butyl Acrylate (BA) (SC1) showed high elongation at break (680.83%) which function in supplying the flexibility of film.

#### **CHAPTER 1**

## **INTRODUCTION**

#### 1.1 Background

The term "waterborne coatings" refers to coatings whose primary liquefying ingredient is water. The primary purpose of the water is to distribute the resin that has been introduced to create the coating. While the overall composition of different waterborne coatings may vary, they can have a water content of up to 80% by volume and concentrations of other solvents like glycol and ethers. This coatings' high-water content provides them a unique level of workability and environmental advantages (J.L. Hall, 2022).

Styrene and Butyl Acrylic monomers are combined to create milky-white water-based emulsions known as styrene-acrylate copolymers. Their solid's weight ranges from 40% to 60%. They are produced by combining liquid acrylic and styrene monomers with water. For a stable monomer-in-water suspension, the mixed monomers are emulsified with ionic and/or non-ionic surfactants. A free-radical initiator initiates a polymerization reaction, and the monomers react to generate styrene-acrylic copolymers that remain in a stable emulsion form (M.C. Polymers, 2019).

Waterborne coatings are becoming a desirable alternative to traditional solvent-based coatings since they are VOC-free (Volatile Organic Compounds). As a coating matrix resin, styrene-acrylic emulsion offers several benefits over standard acrylate emulsion products, including good adhesion, strong water resistance, good heat resistance, and good ageing resistance. The styrene-acrylic emulsion offers the advantages of high performance and cheap cost at the same time when compared to acrylic emulsion. Due to its versatility and economic effectiveness, it is widely utilised in adhesives, paper size machines, coatings, and other sectors (Jiao et al, 2021).

The modern society's rising urge to reduce the emission of volatile organic compounds (VOC) sparked the scientific community's attention in creating a new class of coatings: Water is used to distribute a resin in waterborne coatings, which are simple to apply and environmentally friendly. Because American and European rules mandate waterborne coatings to have a VOC concentration of less than 3.5 pounds per gallon of water, these coatings are ecologically beneficial. Furthermore, because aqueous coatings emit less VOCs during application, they minimize the risk of fires, are easier to clean up (producing fewer harmful residues), and result in lower worker exposure to organic toxins (Ulker, 2022).

Most coating producers are attempting to reduce their VOC levels below the restrictions, not only to comply with the legislation, but also to gain a competitive edge as future legislation tightens and to meet consumer expectations. Low VOC content can increase the value of a product by increasing its appeal to consumers. Many countries have implemented special labelling procedures to identify 'environmentally sound' items (Dennington 2007). In this study, five latex particles (SC1, SC2, SC3, SC4, SC5) with different composition of monomer (54/36, 50/40, 44/46, 40/50, 36/54) were created by seeded emulsion polymerization to evaluate the relationship between Tg of Seed core emulsion and mechanical properties. The film formation process for water-borne coatings may be separated into three basic sequential processes. Stage I involved water evaporation, which brought the latex polymer particles into proximity. Stage II was particle deformation, in which the latex particles deformed and created a void-free solid structure; the film was typically mechanically weak during this stage. Stage III was latex coalescence, in which the molecules of the polymer diffused over the borders of the particles and formed entanglements that gave the films their mechanical strength. The particle deformation mechanism in the film formation process of water-borne coatings played a key role in determining the final film properties, such as flexibility and strength (P.A. Steward et al, 2000).

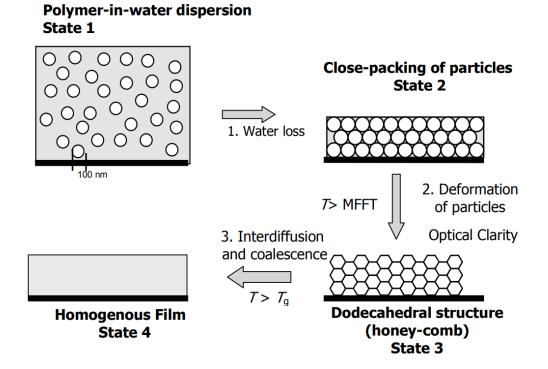


Figure 1.0 Schematic of the film formation process: a colloidal dispersion's transition into a continuous polymer film (P.A Steward et al, 2000).

Waterborne coatings may not always have chemical-based solvents, but they do so in suitably small amounts. Waterborne coatings are a practical solution to fulfil or exceed strict environmental and human health and safety criteria since they employ little to no solvents, if any at all. Waterborne coatings also enable producers of industrial coatings to spend far less on regulatory compliance consultancy while assisting them in avoiding hefty fines for non-compliance (K. Nanan, 2019).

## **1.2 Problem statement**

In the past, polymers have been deposited from solution in organic solvents for coating applications as well as in a variety of industrial operations. Volatile organic compounds, or VOCs, are small organic molecules that vaporise and are released into the atmosphere. Reduced VOC levels in coatings and other goods are being driven by both environmental and health and safety concerns. Organic solvents, which have traditionally been employed in coatings, produce hazardous oxidants that are harmful to the environment. It has been discovered that some VOCs harm the ozone layer, while others may contribute to the 'greenhouse gases' connected to global warming (E. David et al. 2021).

In addition, there is another reason contributing the usage of waterborne coating is the cost of material use such as pure acrylic and polyurethane. Therefore, by copolymerization them with other materials such as styrene, can reduce the cost while improving and maintaining the properties of the latex. It is highly in demand because the styrene was cheap comparing with pure acrylic with good ability usage in coating applications (Overbeek, 2010).

Therefore, in order to accomplish this objective, it is crucial to comprehend how the parameters of polymerization element such as concentration and process parameters such as agitation speed can contribute to the properties of the latex by comparing their copolymerization, thermal and mechanical properties with the theoretical data or the existing product.

# **1.3** Research Objective

- 1. To synthesize and characterize the particle size of Poly-*n*-Butyl acrylate-*co*-styrene (PBA-Sty) seed nanoparticles.
- 2. To synthesize and characterize the particles size and stability (PBA-Sty) emulsion.
- 3. To characterize the tensile properties of the (PBA-Sty) films.

## 1.4 Thesis Outline

This thesis consists of 5 chapters

Chapter 1 refers to the thesis' introduction, which includes the research background, problem statement, goals, and dissertation outline.

Chapter 2 of the thesis includes a literature review, which provides background research on broad knowledge about industry, building and construction in coating, polymer used for construction application, emulsion polymerization, polymerization components, colloidal stability, particle morphology, and comprehensive literature review of polymer and film characterization. Chapter 3 contain thesis' material techniques and research methodology. The chemicals used and their sources are thoroughly covered in this chapter. This chapter covers the full preparation procedure of seed, seed-core emulsion, formation of film and its characterization procedures.

The findings and conclusions from this study are presented in Chapter 4. This chapter offers discussion on the concerns as well as a thorough explanation. The outcome of this investigation is reported in Chapter 5. A conclusion based on the project's goals is presented in this chapter, along with some suggestions for more research.

## **1.5** Research Scope

In this research, there are 3 objectives to achieve. At the first stage, the synthesized of Poly-*n*-Butyl acrylate-*co*-styrene (PBA-Sty) seed nanoparticles (~70nm) by changing several parameters such as concentration of monomer, surfactant, initiator, buffer, monomer feeding time, agitation speed and types of surfactants. Next, by choosing the suitable seed nanoparticle, the research continued by synthesize and characterize the seed-core emulsion by changing composition of monomer BA-Sty 54/36, 50/40, 44/46, 40/50, and 36/54 and was labelled as SC1, SC2, SC3, SC4 and SC5, respectively. At the last stage, the characterization of PBA-Sty films was studied. The characterization of PBA-Sty seed nanoparticles and PBA-Sty seed-core emulsion was determined by using Total solid content (TSC), Dynamic light scattering (DLS) and Zeta potential. While the characterization of films by measuring the copolymerization by Fourier transform infrared (FTIR), thermal properties by Differential scanning calorimetry (DSC) and mechanical properties by Tensile test.

#### CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Industry | Building & Construction

The worldwide waterborne coatings market is expected to increase at a 5.8% Compound annual growth rate (CAGR) between 2019 and 2024, from USD 72.9 billion in 2019 to USD 96.8 billion by 2024. The main factors driving the growth of the worldwide market for waterborne coatings are the expansion of infrastructure and building & construction projects, the quality of industrial production in emerging nations, and the need for coatings protection (K. Suryavanshi, 2022).

Waterborne coatings are surface coatings that employ water as a solvent to distribute the resin applied to make the coating. Waterborne coatings are convenient to apply and eco-friendly due to their high-water content. Rising raw material prices, rising energy costs, and a lack of knowledge in the unorganized sector of construction developers are the key issues limiting the market's growth (K. Suryavanshi, 2022).

Acrylic is expected to account for the highest proportion of the resin market throughout the projected period. Compared to epoxy-, oil-, and alkyd-based coatings, waterborne acrylic coatings are more resistant to oxidation and harsh weather. The polymer structure of waterborne acrylic coatings also has a lesser propensity to absorb UV radiation, which aids in the long-term retention of gloss and color. Southeast Asia is predicted to have a strong demand for acrylic aqueous coatings because of the rising demand for acrylic resins for construction-related end uses. Waterborne acrylic-based coatings are in great demand since construction activity in the Southeast Asia is expanding quickly (K. Suryavanshi, 2022). Architectural coatings are anticipated to hold the biggest market share in terms of application over the forecast period. Due to stricter laws in Europe and North America than in Asia-Pacific (APAC) and other smaller areas, waterborne coatings are mostly employed in architectural applications in these nations. As a low-cost substance that offers strong water resistance, good stain protection, and good water resistance, waterborne coatings are widely employed in architectural applications. Numerous efforts are fostering the market's expansion on a worldwide scale (K. Suryavanshi, 2022).

The waterborne coatings market in APAC is anticipated to grow at the highest CAGR over the forecast period. APAC has a wide spectrum of economies with various economic development levels and numerous sectors. The development is mostly linked to the strong economic growth rate that was followed by significant investment in a variety of industries, including automotive, consumer goods & appliances, building & construction, and furniture. In terms of both supply and demand for waterborne coatings, it is one of the markets with the quickest growth rates. The APAC industry is expected to grow at a rapid pace over the next five years, providing considerable commercial potential for participants in the waterborne coatings market (K. Suryavanshi, 2022).

### 2.2 Polymer used for construction application

#### 2.2.1 Acrylic Polymer

Acrylic polymers have the highest rates of water vapor transfer (breathability) of any polymer. Styrene acrylics operate quite similarly to acrylics, except they are better at withstanding water and less stable under UV light (M.C Polymers, 2022).

Acrylate copolymer emulsions are made by copolymerizing acrylate with other vinyl esters using emulsion polymerization and the acrylic systems based on BA are preferable for outdoor usage, especially for paints and coatings with low pigment contents. In this study, Butyl acrylate is used and utilized in copolymers to increase flexibility, softness, tackiness and block resistance, strength and durability and low temperature characteristics because of its low homopolymer glass transition temperature of -45°C. It has high photostability and is a desirable monomer where weatherability and UV resistance are required. By increasing the BA concentration, the minimum film formation temperature (MFFT) is reduced to below room temperature. Polymeric binders based on styrene monomer and butyl acrylate have great water resistance, excellent hydrolysis resistance, and superior wet scrub resistance. However, it also has certain flaws, including a low water tolerance, brittleness at low temperatures, and viscidity loss at high temperatures (R.-M, et al, 2011).

### 2.2.2 Styrene acrylic

Styrene is described as a hydrophobic monomer and styrene homopolymers have been found to having characteristics that make them appropriate for a wide range of industrial applications. However, due to molecular rigidity, the pure homopolymer is brittle when impacted and cracks under stress. It is also unable to tolerate high rates of mechanical loading. Polystyrene's limitations can be mitigated by copolymerizing it with other monomers such as acrylates (M.C Polymer, 2022).

In comparison to all-acrylic polymers, styrene-acrylic polymers have good hydrophobic properties, which means they have better water resistance and a lower moisture vapors transmission rate (MVTR). Furthermore, because styrene is a hydrophobic monomer, it is feasible to create styrene-acrylic polymers with small particle sizes. This leads to polymers that are perfect for certain purposes, such a coating for the building sector or binders for paper coatings. The high glass transition temperature of styrene-acrylic polymers is another significant characteristic. As a result, they frequently have strong mechanical properties, excellent abrasion resistance, and a long lifespan (M.C Polymer, 2022).

#### **2.3 Emulsion Polymerization**

The lattices were prepared by using emulsion polymerization. The polymerization used water as a dispersant medium, making emulsion less dangerous to the environment than the other process. It is a complicated process since many colloidal phenomena work in conjunction with free radical polymerization processes to govern the nucleation, growth, and stability of polymer particles. In contrast to other polymerization methods, emulsion polymerization allows for increasing molecular weight of the produced latexes by lowering the reaction temperature or the initiator concentration (P.A. Lovell & F.J. Schork, 2020).

Waterborne acrylic resins are typically copolymerized by acrylic acid and its esters, and the ratio of different monomers may be adjusted to customise the characteristics. It is made up of monomers, emulsifiers, water, and initiators. The synthetic macromolecular chain is mostly made up of a carbon chain that is separated into soft and hard segments. Styrene, a hard monomer, makes up most of the hard segment, which can increase the resin's hardness, while acrylate, a soft monomer, makes up most of the soft segment and can provide the resin flexibility. The resin framework's structure and composition have an impact on product performance (C. Jiao, 2021). Figure 2.1 shows the formation of copolymer by emulsion polymerization.

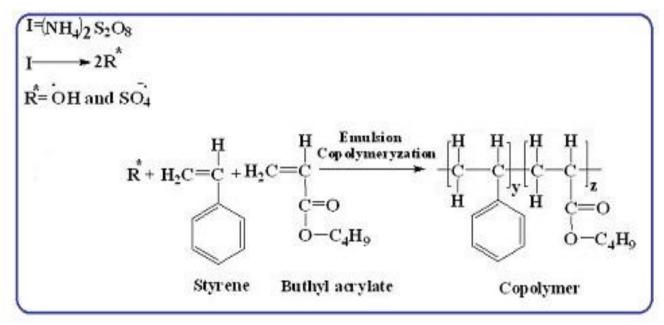


Figure 2.1 Formation of copolymer

In this process, the monomers are emulsified in water as the surface-active agents (surfactant) dispersion medium. Surface tension at the surface decreases due to the surfactant concentration exceeding the critical micelle concentration (CMC), forming spherical micelles. Hydrophobic monomers then enter the area around the micelle, and the reaction continues until all monomer droplets are used up and the micelle containing the monomers grows. Micelles typically have diameters of 2-10 nm and to include 50-150 surfactant molecules. Water-soluble initiators penetrate the micelle, where free radical propagation begins. Because of their relatively limited surface area, monomer droplets often cannot compete with micelles to capture free radicals produced in the aqueous phase, acting as a point of contact between water-soluble initiators and hydrophobic monomers. As polymerization continues inside the micelle, monomer addition from monomer droplets outside causes the micelle to expand and latex to develop (A.N.M.B. El-hoshoudy, 2018). Figure 2.2 shows the schematic representation of emulsion polymerization.

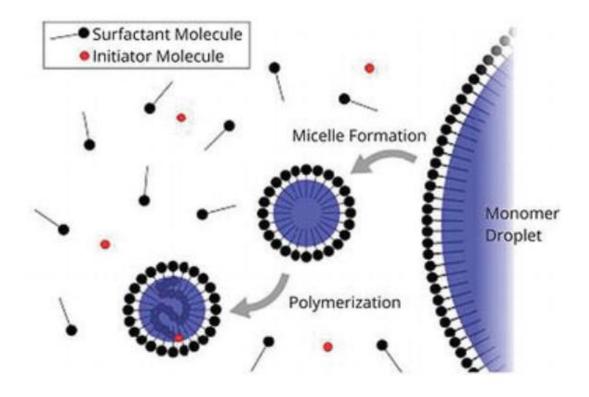


Figure 2.2 Schematic representation of emulsion polymerization (A.N.M.B. Elhoshoudy, 2018).

There're three steps of emulsion polymerization which are known as initiation, propagation, and termination. Initiation referred to as seed stage, usually it will take 10-15 minutes for particle nucleation to be completed (H.B Yamak, 2011).

$$k_i \\ \mathbf{I} \to x \mathbf{R}^{\bullet} \tag{2.1}$$

$$\mathbf{R}^{\bullet} + \mathbf{M} \xrightarrow{k_I} \mathbf{R} \mathbf{M}^{\bullet}_{1} \tag{2.2}$$

where x is the number of primary free radical  $R^{\bullet}$  formed from one molecular of the initiator, M is a molecule of monomer or a monomer unit in a polymer chain. This stage can be referred to the equation 2.1 and 2.2.

The propagation stage is known as the growth stage or Stage II of the emulsion polymerization. In Stage II, the polymer particles grow through a steady diffusion of monomers from the monomer droplets to the particles. The propagating of chain radical can be measured by using equation 2.3.

$$\mathrm{RM}^{\bullet}_{n} + \mathrm{M} \xrightarrow{k_{p}} \mathrm{RM}^{\bullet}_{n+1} \quad (n \ge 1)$$
(2.3)

where RM• n is propagating chain radical with the degree of polymerisation.

Termination consists of two types either combination or disproportionation which shown in equation 2.4 and 2.5, respectively. Combination in which two active radical end groups meet and disproportionation in which the active radical is lost from a growing polymer chain by the abstraction of hydrogen from another growing chain. Final product obtained at the end of Stage III is called latex (H.B Yamak, 2011).

$$RM^{\bullet}_{n} + RM^{\bullet}_{p} \rightarrow RM_{n} - M_{p}R \quad \text{(combination)}$$
(2.4)

$$k_{td}$$
  
RM<sup>•</sup><sub>n</sub> + RM<sup>•</sup><sub>p</sub>  $\rightarrow$  RM<sub>n</sub> + RM<sub>p</sub> (disproportionation) (2.5)

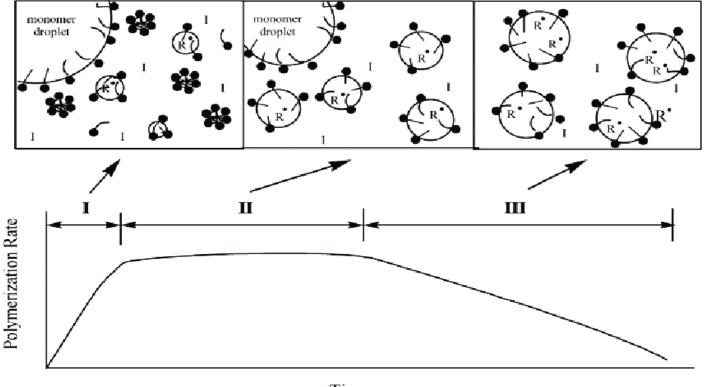
RMn, RMp and RMn–MpR are terminated polymer chains with the degree polymerisation equal to n, p and n + p respectively.

For terminations of the chain growth radical there is a reaction which is known as chain transfer reaction as shown in equation 2.6.

$$\mathrm{RM}^{\bullet}_{n} + \mathrm{T} - \mathrm{A} \to \mathrm{RM}_{n} - \mathrm{T} + \mathrm{A}^{\bullet}$$
(2.6)

T-A is a chain transfer

The formation of emulsion polymerization can be categorized by three intervals as shown in Figure 2.3.



Time

Figure 2.3 Emulsion polymerization intervals (A.N.M.B. El-hoshoudy, 2018).

In intervals I, there is a distinct monomer phase. In interval I, the particle number grows with time, and particle nucleation occurs. The most of surfactants are used up at this point (i.e. micelles are exhausted). It is possible to effectively transform around one out of every 102–103 micelles into latex particles. Surfactant concentration has a significant impact on the particle nucleation process, which in turn influences particle size and particle size distribution in latex. The polymerization process continues at interval II (the particle growth stage), and polymer particles get bigger until the monomer droplets run out. Monomer droplets serve as reservoirs to provide monomer and surfactant species to the developing particles. At interval III, the polymer size increases as the latex particles become monomer-starved, and the amount of monomer at the reaction loci keeps decreasing as the polymerization process continues (A.N.M.B. El-hoshoudy, 2018).

#### 2.3.1 Seeded Emulsion Polymerization

Reaction loci are present in the starting system in this sort of reaction. The initial stage of the emulsion polymerization is a distinct process that creates the loci. By using a pre-formed latex, the particle nucleation step of the process is removed. Then, at the start of the reaction mixture, the pre-formed latex is added. To prevent the future nucleation of new particles, there must be a sufficient number of seed particles. The seed particles effectively catch free-radical species from the aqueous phase and all primary particles that form through homogeneous nucleation if the particle number is high enough (second stage of the emulsion polymerization). It's also feasible that, in the absence of an emulsifier, microscopic primary particles might coagulate onto seed particles (heterocoagulation heavily

influenced by the surface charge on the seed particles). When an emulsifier is included in a formulation, the amount must be just right to keep the seed latex particles' colloidal stability as they expand through polymerization and/or coagulation with primary particles, but not too much to produce new particles. There are three alternative ways to introduce monomer to the reaction system, including the seed particles, during the second stage of emulsion polymerization: dynamic swelling, batching, and semi-continuous (H.B Yamak, 2013).

The second stage of the dynamic swelling process is completed when the second monomer has swelled the seed particles. In a batch technique, a second monomer is introduced to seed latex during the second step of emulsion polymerization. In the semi-continuous technique, the second monomer is continually introduced to the reaction system, including the seed latex, under monomer-starved circumstances. Additionally, both phases of the seeded emulsion polymerization might employ one or more different kinds of monomers. (H.B Yamak, 2013).

Furthermore, this technique offers several benefits in the manufacture of homogeneous latex particles with outstanding monodispersity in size. Additionally, it has great output yields. These characteristics make these latexes more useful in a wide range of applications (H.B Yamak, 2013).

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#### **2.4 Polymerization components**

#### 2.4.1 Monomer

A molecule of any of a class of compounds, mostly organic, that can react with other molecules to form very large molecules, or polymers. It is the most important in the emulsion polymerisation. In this study, Butyl Acrylate and styrene monomer were used in synthesising the latex (Anne.M.H, 2020).

### 2.4.1.1 Butyl Acrylate

Butyl acrylate is an organic compound which is known as butyl ester of acrylic acid. Butyl acrylate appears as a colourless liquid with a sharp characteristic odour. It is slightly soluble and less dense in water. A monomer containing 7 Carbon atoms, 12 Hydrogen and 2 Oxygens (CH<sub>2</sub>=CHCOOC<sub>4</sub>H<sub>9</sub>) atoms including one double bond in molecules. It is a low Tg acrylate monomer that is produced by the esterification of acrylic acid with n-butanol. Butyl acrylate incorporation into a polymer improves tack, flexibility, impact resistance, and overall durability. It is an ideal monomer for generating polymers used in adhesive and sealant formulae due to its flexibility and tack (K.K. Ajekwene, 2020). Figure 2.3 shows the structure of Butyl Acrylate.

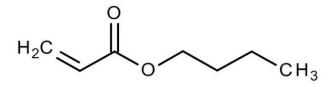


Figure 2.3 Structure of Butyl Acrylate

# 2.4.1.2 Styrene

Styrene is a liquid hydrocarbon that is known for its high tendency for polymerization. It consists of 8 Carbon and 8 Hydrogen atoms ( $C_8H_8$ ) with structural formula  $CH_2$ =CHC<sub>6</sub>H<sub>5</sub>. Styrene is a colourless liquid which easily evaporates and has a sweet smell. Due to the hydrophobic nature of styrene, it is feasible to create low-particle-size styrene-acrylic polymers and it is ideal for coating application. Styrene can improve the resin's impact resistance, wear resistance, and mechanical characteristics. The benzene ring or ring structure can enhance the resin's mechanical characteristics (Encyclopaedia.B, 2022). Figure 2.4 shows the structure of styrene.

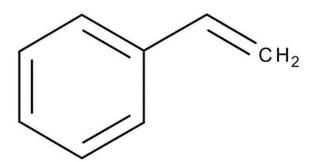


Figure 2.4 Structure of Styrene (Haz-Map, 2022).

## 2.4.2 Initiator

Initiator is a chemical species also known as catalysts which are used to induce the curing process by combining with a monomer (molecular crosslinking) to generate an intermediate product capable of joining many additional monomers to build a polymeric complex. The initiator acts to produce free radicals through thermal breakdown or redox reactions. Watersoluble and partially water-soluble peroxides are two possible choices for the initiators (Encyclopedia.B, 2022).

## 2.4.2.1 Potassium Sulphate

Potassium sulphate is an inorganic crystalline salt with a chemical formula K<sub>2</sub>SO<sub>4</sub>. It is a white crystal or powder and odourless, bitter tastes, and nontoxic. Potassium sulphate is soluble in water because it is an ionic compound. However, it is not soluble in ethanol. Potassium persulfate is used as free-radical initiator for polymerization. Figure 2.5 shows the structure of Potassium Sulfate (A. Emerson, 2021).

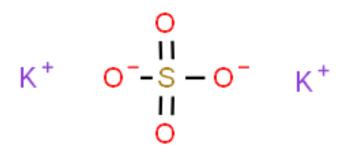


Figure 2.6 Structure of Potassium Sulphate (R.S. of chemistry, 2022).

#### **2.4.2.2 Potassium Persulfate**

Potassium persulfate is an inorganic compound with formula  $K_2S_2O_8$ . Also known as potassium peroxydisulfate. It is a white solid odourless crystal which dissolves in water but insoluble in alcohol and strong oxidising. It almost does not absorb moisture and has high stability at room temperature. It's used to initiate the polymerization. Figure 2.6 shows the structure of Potassium Persulfate (A. Emerson, 2021).

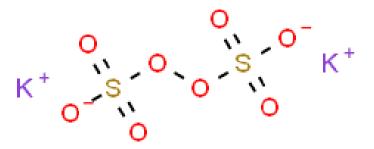


Figure 2.6 Structure of Potassium Persulfate (R.S. of chemistry, 2022).

## 2.4.3 Surfactant

The emulsifying agent helps in reducing the interfacial tension between two immiscible phases by creating an interfacial film with repulsive electrostatic interactions and steric hindrance between continuous and dispersed phase which leads to improved stability of nanodroplets against coalescence (F. Ravera et al, 2021). Surfactant called as surface-active agent, substance such as a detergent when added to a liquid, it lowers the liquid's surface tension and increases the spreading and wetting qualities. Surfactant molecules are typically organic substances with hydrophobic and hydrophilic "heads" and "tails" groups. Because of this, the molecule may interact with polar molecules like water and oils (which are nonpolar). A micelle is made up of many molecules of a surfactant. A micelle is a spherical structure. In a micelle, the hydrophilic heads face outward while the hydrophobic or lipophilic tails face inward. The micelle sphere can hold fats and oils. There are four different kinds of surfactants, which are classified as non-ionic, anionic, cationic, and amphoteric based on the polarity of the head group (M. Hirsch, 2018).

There are no charge groups in the head of a non-ionic surfactant. Surfactant with a negative charge when it is anionic and cationic when it is positive. Zwitterionic surfactants are those that have a head with two oppositely charged groups (M. Hirsch, 2018). The type of surfactant is shown in Figure 2.7.

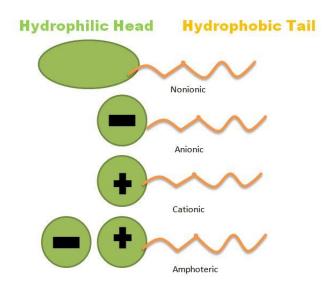


Figure 2.7 Types of Surfactants (J. Shapiro, 2018).

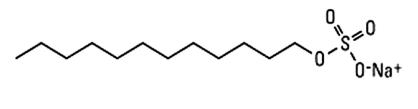
It should be noted that the distribution of surfactants in a latex film is not constant. The surfactant can continue to move after a film has dried, which results in a significant ageing impact (M. Hirsch, 2018). The distribution for a certain latex might change based on the circumstances surrounding film formation.

For instance, it has been observed that films dried at or near the MFFT had an accumulation of surfactant along the film-air interface, but films dried much above the MFFT had surfactant clumps throughout the film. In this case, the variation in surfactant distributions was attributed to differences in surfactant mobility in the polymer phase as a function of temperature (I. Ludwig et al, 2007).

The type of surfactant has an impact on the gloss of a greater gloss results from the use of non-ionic surfactants than from the use of ionic surfactants coating (). Higher surfactant concentration causes both a reduction in particle size and a narrowing of the particle size distribution. Due to this effect, particles may be packed more densely, and a smoother film surface is more likely. A surfactant layer at the coating surface was also suggested to fill in the troughs between particles and lessen roughness (M. Hirsch, 2018).

#### 2.4.3.1 Sodium dodecyl sulphate (SDS)

Sodium dodecyl sulphate (SDS), known as anionic surfactant, contains anionic functional groups at their head. Low SDS concentrations produce unstable microemulsions that break down within a few hours and have poor repeatability. Higher SDS concentrations result in more repeatable, stable systems, but higher operating currents (A. Ashok et al, 2020). The chemical formula of SDS is CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>OSO<sub>3</sub>Na and their structure was shown in Figure 2.8.

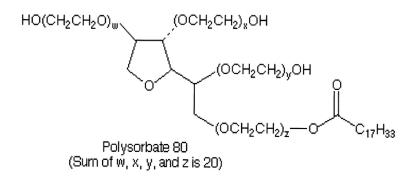


# Sodium dodecyl sulfate (SDS) MW 288

Figure 2.8 Structure of Sodium Dodecyl Sulfate (SDS) (Lebouachera et al, 2018).

### 2.4.3.2 Polysorbate 80 (Tween 80)

Tween 80 is an artificial surfactant having low mass and nonionic nature. (P. Singh, et al, 2021), which helps ingredients mix and prevent separation. This synthetic compound is a viscous, watersoluble yellow liquid and commonly are surfactant micelles. When Tween 80 was dissolved in the aqueous phase, the particle size was found significantly larger than when it was dissolved in the organic phase (F. Ostertag, et al, 2012). Its structure is shown in Figure 2.9.



#### Molecular Mass = 1310

Figure 2.9 Structure of Tween 80 (Nair, et al, 2003).