

**To Study the Effects of Surfactants on the
Properties of Poly (Methyl Methacrylate-
co-acrylic acid) prepared by Batch
Emulsion Polymerization**

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by

ANUBHAV JAIN
(24/RAC/01)

Under the Supervision of

Prof. Roli Purwar
Professor



Department of Applied Chemistry
DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering)
Shahbad Daulatpur, Main Bawana Road, Delhi-110042. India

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Anubhav Jain



DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering)
Shahbad Daulatpur, Main Bawana Road, Delhi-110042.
India

CANDIDATE'S DECLARATION

I Anubhav Jain, Roll No. 24/RAC/01 hereby certify that the work which is being presented in the thesis entitled '**To study the Effects of Surfactants on the Properties of Poly (Methyl Methacrylate-co-acrylic acid) prepared by Batch Emulsion Polymerization**' in partial fulfillment of the requirements for the award of the Degree of Master of Technology by Research (Chemical Engineering), submitted in the Department of Applied Chemistry, Delhi Technological University is an authentic record of my own work carried out during the period from January 2025 to May 2025 under the supervision of **Prof. Roli Purwar**. The matter presented in the thesis has not been submitted by me for the award of any other degree of this or any other Institute.

Candidate's Signature



DELHI TECHNOLOGICAL UNIVERSITY

(Formerly Delhi College of Engineering)

Shahbad Daulatpur, Main Bawana Road, Delhi-110042.

India

CERTIFICATE BY THE SUPERVISOR

Certified that 24/RAC/01 has carried out their search work presented in this thesis entitled **“To study the Effects of Surfactants on the Properties of Poly (Methyl Methacrylate-co-acrylic acid) prepared by Batch Emulsion Polymerization”** for the award of **Master of Technology** from Department of Applied Chemistry, Delhi Technological University, Delhi, under my supervision. The thesis embodies results of original work, and studies are carried out by the student himself and the contents of the thesis do not form the basis for the award of any other degree to the candidate or to anybody else from this or any other University/Institution.

Prof. Roli Purwar

DTU, New Delhi

ABSTRACT

The growing demand for environmentally friendly and high-performance waterborne coatings has significantly increased the importance of emulsion polymerization in the coatings industry. Acrylic emulsions prepared through emulsion polymerization are extensively used due to their excellent film-forming ability, durability, chemical resistance, and low volatile organic compound (VOC) emission. Among the various factors influencing the properties of acrylic emulsions, surfactants play a crucial role in determining particle formation, colloidal stability, rheological behavior, and final coating performance. In the present study, the effects of different surfactant systems on the properties of poly (methyl methacrylate-co-acrylic acid) [PMMA-co-PAA] prepared by batch emulsion polymerization were investigated.

The emulsion polymerization was carried out using methyl methacrylate (MMA) and acrylic acid (AA) as monomers in an aqueous medium through free radical batch emulsion polymerization. Sodium dodecyl sulfate (SDS), cocamidopropyl betaine (CAPB), and amphoteric fluorosurfactant (AMF-1) were employed as surfactants to study their influence on emulsion characteristics and coating properties. APS was used as an initiator for the polymerization process. Several formulations of latex were prepared with different concentrations of surfactants while keeping the other variables constant. The latexes obtained through this process were characterized on the basis of monomer conversion, solid content, particle size, zeta potential, rheological behavior, and wettability properties.

From the gravimetric determination, it was found that the prepared emulsions had high conversion rate of the monomers along with good solid content values. This suggested the efficient polymerization of the monomers in addition to adequate stabilization of the latex particles. The use of various types of surfactants played a significant role in the efficiency of the polymerization process as well as stability of emulsions. DLS studies indicated that surfactant type plays a very important role in determining particle size and colloidal stability of the prepared emulsions. It was found that the fluorsurfactant systems gave rise to relatively smaller particles size with narrower distribution than others.

Rheology studies conducted such as viscosity testing, amplitude sweep, and frequency sweep tests have provided useful information regarding the viscoelastic nature of the emulsions. All tested latex systems showed a non-Newtonian shear-thinning behavior, which is favorable when it comes to use in coating applications. It was found that rheological properties of emulsions depended strongly on the type of surfactants used and the interactions between the particles within the emulsion system. Amplitude sweep testing showed the presence of the linear viscoelastic region in all samples studied and differences in structural stability of tested latex samples. Differences in elastic and viscous

behavior of the emulsions depending on the used surfactants could be observed from frequency sweeps data.

Wettability behavior of coating films obtained from various surfactant systems was determined by measuring the water contact angles. Latex systems with fluorosurfactants were found to show much higher water contact angles than traditional surfactant systems, demonstrating the increased hydrophobicity and reduced surface energy of such emulsion systems. Increased water repellent property of fluorosurfactants can be explained by the presence of fluorinated portions in the molecular structure of fluorosurfactants, reducing the surface tension and making coating films more hydrophobic.

In summary, the current study revealed that surfactant choice is an essential factor for influencing the physicochemical, rheological, and surface characteristics of PMMA-co-PAA emulsions using batch emulsion polymerization techniques. Of all the tested surfactants, amphoteric fluorosurfactants have exhibited excellent performance in respect to particle size, emulsion stabilization, rheology, and enhanced hydrophobicity. The results from this study will offer useful information in formulating advanced acrylic emulsions for eco-friendly coating purposes.

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LIST OF ABBREVIATIONS

MMA: Methyl Methacrylate

AA: Acrylic Acid

SDS: Sodium Dodecyl Sulfate

CAPB: Cocoamidopropyl Betaine

AMF-1: Amphoteric Fluorosurfactant

CAF: Commercial Amphoteric Fluorosurfactant

APS: Ammonium Persulfate

DW: Distilled Water

DLS: Dynamic Light Scattering

PDI: Polydispersity Index

WCA: Water Contact Angle

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CHAPTER-1

INTRODUCTION

Large molecules called polymers are made from monomers and have a variety of uses in our lives. Polymers can be found in many products, ranging from food packaging to medical devices. The benefits of polymers are numerous. They are multi-purpose, lightweight and versatile. In addition, they have a high strength-to-weight ratio, making them a favoured choice in the aerospace and automotive industries.

Polymers are particularly resistant to corrosion and decomposition which is suitable for harsh environments. They are resistant to a variety of chemicals and can therefore be used in the chemical and pharmaceutical sectors. Moreover their chemical resistance allows them to be used in the production of containers for dangerous chemicals without contamination [1].

Moreover, polymers are easy to process and can be molded into various shapes and sizes, thus offering high adaptability and customizability. Furthermore, their characteristics can be adjusted to suit specific needs, and they are a cheap and effective material for mass production articles. Polymers are desirable materials for manufacture because of this adaptability and versatility in processing.

Polymers are also known as being environmentally friendly as they can be recycled, thus minimizing waste and helping to reduce the effect that they have on the environment. Moreover, some polymers can biodegrade naturally, further reducing their negative impact on the environment. Moreover, polymers exhibit characteristics that make them very suitable for specific uses. Examples of such characteristics include the ability to mold thermoplastics into any desired shapes due to their flexibility. They are used in producing different products ranging from medical devices to parts used in automobiles. Adhesives, coatings and composite materials are made using thermoset polymers, whereas elastomers are used to produce tires among others [2].

1.1 Polymeric Coatings

Polymeric coatings have been widely used as a protective coating material on surfaces to increase their durability and performance. Polymeric coatings are made of natural or artificial polymers which give them properties of durability, resistance to chemicals, and heat stability. Various industries, such as the automotive industry, aircraft manufacturing, construction, and marine, use polymeric coatings as protection against harsh environments and wear [3].

There are many benefits of using polymeric coatings, including providing a surface with protection against corrosion, increasing adhesion, decreasing friction and improving aesthetics. Furthermore, polymeric coatings can be used in the medical and pharmaceutical industries to maintain sterility of a surface [4]. The application process of these materials can vary depending on the way they are applied: by means of spraying, dipping, or electrostatics.

The choice of a particular polymer to use for coatings depends on the usage and properties needed, for example, type of surface, environment, and durability. It is beneficial to use polyurethane coatings for industrial purposes because of their excellent resistance to various processes, such as chemical reactions,

mechanical wear and impacts. On the other hand, epoxy coatings are best suited for industries such as aerospace and marine due to their durability and resistance to heat, chemicals, and water [5].

1.1.1. Types of Production of Polymeric Coatings

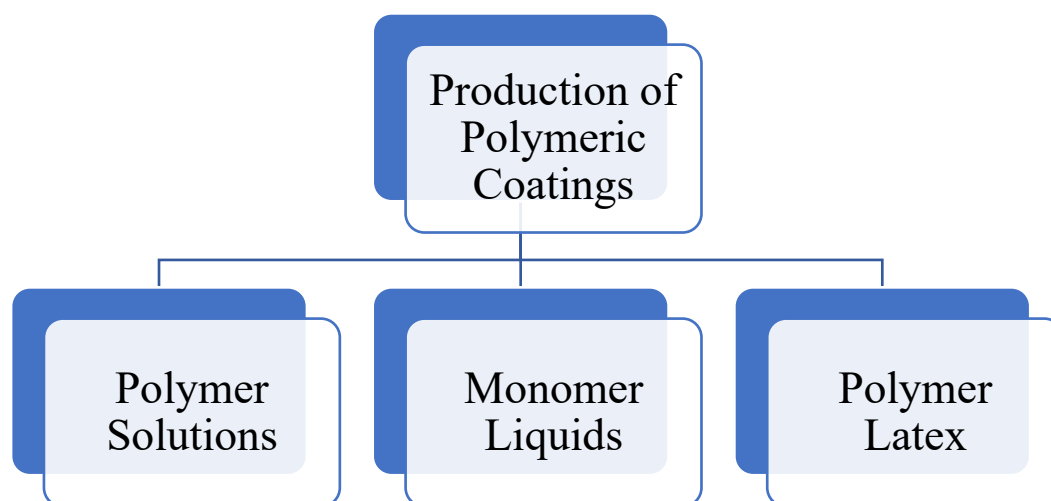


Figure 1: Flow chart explaining types of synthesis of polymeric coatings

1.1.1.1 Polymer Solutions

Polymer solutions are extensively employed in the manufacture of coatings due to their ability to alter the characteristics of the base material. Polymer-based coatings have the capacity to improve the durability, corrosion resistance, and appearance of the substrate that they coat [6]. The choice of polymer and solvent depends on the desirable characteristics of the end product, which include mechanical and chemical properties as well as curing time.

The application of polymer solutions on the substrate is usually done using processes like brushing, spraying, and dipping. After application, the solution is left to dry or harden, forming a protective layer on the substrate. The thickness of the resulting coating can be controlled through the concentration of the polymer solution and mode of application [7].

The application of polymer coatings based on solutions has been widely used in a number of sectors ranging from automotive to aerospace engineering and construction in the protection of metal surfaces from corrosion and providing heat resistance. Polymer coatings are applied in furniture and electronics manufacturing for giving products a sleek appearance. Additionally, polymer coatings can be tailored to provide some functionality such as lowering friction or producing antistatic surfaces as well as incorporating UV and fire-resistant properties into the coatings [8], [9].

1.1.1.2. Monomer Liquids

Liquids of monomers have an important part in producing polymers, and they are commonly used in the production of coatings. Monomer liquids go through the process of polymerization in order to form polymer chains which then are used for making coatings. The choice of monomers depends on different criteria for the final product such as its mechanical properties, chemical resistance, and curing period [10]

There are different ways of initiating the process of polymerization, such as adding heat, exposing to light, or addition of a catalyst. Polymer can be used to make coatings via numerous techniques such as brushing, spraying, or dipping. Coating thickness can be controlled by changing either monomer concentrations or coating technique [11].

Making coatings out of monomer liquids may give plenty of benefits including better adhesion, increased lifespan, and enhanced chemical resistance. Such coatings are frequently used in construction, aerospace, and automotive sectors. The purpose of such coatings is to protect metal surfaces from corrosion, high temperature, and increase their lifespan.

In addition to their protective characteristics, coatings made of monomers can be modified for additional functional purposes, including being self-cleaning or antifouling. Monomers can be combined with improving agents, such as flame retardants and UV stabilizers, for better performance.

1.1.1.3. Polymer Latex

Polymer latex is a dispersion of polymer particles in a solution, which is used extensively in coating manufacture. It appears milky white due to dispersed polymer particles in water. It is frequently used as a coating binder because of its good film-forming and adhesive capabilities. Characteristics of the finished coating, such as strength and hardness, drying speed, and resistance to various chemicals, determine which polymer and particle size should be selected [12].

Application of polymer latex coatings on substrates can be done by spraying, brushing, or dipping, followed by drying or curing of the coating film formation. Thickness of the coating can vary depending on the concentration of polymer latex and type of application [13].

There are many benefits associated with polymer latex coatings, which include improved adhesion, flexibility, and durability. They are commonly used across different sectors such as building construction, painting, and coating, as well as paper manufacturing and packaging industry (Tanaka et al., 2022). These coatings help protect surfaces against corrosion, increase their durability, and offer heat resistance. They can also be formulated with specific functionalities such as producing surfaces with low static levels or minimizing friction. The formulation of polymer latex can be done with the addition of certain additives.

1.1.2. Types of Polymeric Coatings

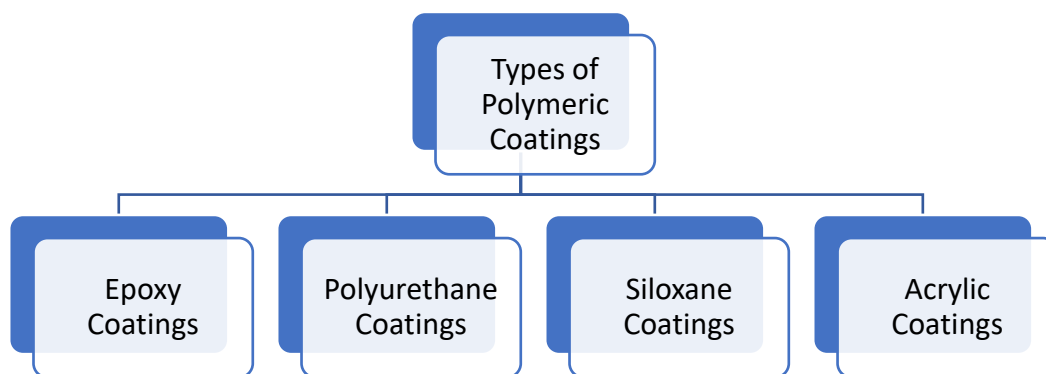


Figure 2: Flow chart explaining types of polymeric coatings

1.1.2.1. Epoxy Coatings

In terms of protecting surfaces against damage from mechanical actions, corrosion, or environmental elements, epoxy coatings are among the most commonly chosen materials. The process involves mixing of two parts – a certain quantity of epoxy resin and a hardener – which is then applied to the surface to form protective layers after curing [14].

Thanks to their toughness, high chemical resistance, and good adhesion properties, epoxy coatings are utilized in multiple industries, including the building industry, aerospace industry, automotive industry, and marine industry. The latter often uses epoxy coating for the protection of metal surfaces, machinery, and concrete floors from abrasions and corrosion. Besides, the application of epoxy coatings leaves a glossy finish on the treated surface [15].

The advantage of epoxy coatings lies in the strong bonds formed between the coating and the treated surface; therefore, it can be said that epoxy coatings feature great adhesion capacity. They are suitable for use on surfaces that experience much pressure because of the constant traffic. Besides, they are waterproof, which makes them especially advantageous when working in humid conditions [16].

Other than their adhesive qualities, epoxy coatings are also recognized for their resistance to chemicals. Epoxy coatings can withstand various chemicals such as acids, alkalis, and solvents. Therefore, they can be used in places where there is a risk of chemical exposure [17].

Epoxy coatings are highly durable and can withstand much wear and tear, making them an ideal choice for places that experience heavy foot traffic. Epoxy coatings are scratch-resistant, impact-resistant, and abrasion-resistant, and their shiny surface allows them to be easily cleaned.

1.1.2.2. Polyurethane Coatings

The use of polyurethane coatings is highly favored for imparting protection to surfaces from the effects of various environmental conditions such as chemical attack, abrasion, and UV rays. This kind of coating is

obtained from the combination of polyol and diisocyanate to form a polymer that can be used on various surfaces as a coating. The reason for favoring polyurethane coatings is because of their high weatherability and UV resistance characteristics; therefore, they are ideal for external surfaces. Besides, polyurethane coatings have good adhesive properties and thus suitable for wood, metal, and concrete surfaces [18].

When it comes to polyurethane coatings, their durability is one of the main advantages. They have a high resistance to scratches, impact, and abrasion, making them a suitable option for high-traffic areas. Moreover, polyurethane coatings can endure exposure to harsh chemicals, making them a perfect choice for industrial settings [19].

Polyurethane coatings are also available in different finishes, such as glossy, semi-glossy, and matte, offering flexibility in selecting the appropriate finish for the surface to be coated. The glossy finish is particularly well-liked for wood surfaces as it brings out the natural grain and color of the wood [20].

In addition to these benefits, polyurethane coating has another one: it forms a layer that repels water, and thus it is ideal for outdoor applications such as decking, fencing, and siding. Polyurethane coating is also an excellent choice for protecting metal surfaces from corroding owing to its water-resistant property. In addition, polyurethane coating is easy to maintain due to its stain-resistance. This makes it ideal for use in places that require high levels of hygiene, such as hospitals and laboratories [21].

1.1.2.3. Siloxane Coatings

Siloxane coating is widely used to protect various surfaces against different environmental hazards including moisture, salt, and UV light. These coatings consist of siloxane mixed with some other polymers that act as a barrier between the environment and the surface. The main strength of the siloxane coatings lies in their ability to repel water, creating a hydrophobic surface where water cannot penetrate through. It makes them very effective when applied to concrete, masonry, and other porous surfaces vulnerable to moisture damage [22].

In addition to the resistance against water, siloxane coatings are highly resistant to the effects of salt spray; therefore, they are especially useful in the coastal zones. Moreover, they are also quite resistant to UV light; thus, these coatings are preferable for surfaces directly exposed to it.

Finally, one should mention that these coatings provide good breathability since they are porous to the passage of water vapor; hence, moisture can leave the protected surface, eliminating problems with cracking and peeling caused by freeze-thaw cycling [23].

Siloxane coatings are highly durable and can withstand heavy usage. Due to their ability to resist abrasions and impacts, siloxane coatings serve as the best type of coating that should be used in high-usage places. Moreover, their ability to resist mold and mildew formation will be very helpful in humid conditions.

Their ease of application and maintenance makes them even better to use. Siloxane coatings are suitable for both new and old surfaces and require no particular equipment for their application. Furthermore, they are very easy to clean and maintain, which makes them very convenient to use in areas that require cleanliness [24].

1.1.2.4. Acrylic Coatings

Another growing trend in coatings is the use of acrylic polymer coatings which have been adopted in various applications. Made up of synthetic polymers from acrylic or methacrylic acid, the coatings have become more popular due to the excellent durability, weather ability, and outstanding gloss-retention properties [25].

There are numerous kinds of acrylic polymer coatings available, which makes them very adaptable to different needs. Depending on how the coatings are prepared, they can offer such attributes as high-gloss finish, ultra-violet resistance, chemical resistance, and great scratch resistance. These coatings can be conveniently applied to a variety of surfaces including metal, plastic, wood, and concrete.

Some of the advantages of acrylic polymer coatings include the amazing durability of the coating. They are not only able to withstand adverse weather elements that would lead to cracking and chalking but are also incredibly resistant to ultra-violet light, a leading cause in the deterioration of other coatings. In addition, acrylic polymer coatings are highly resistant to chemicals like acids and alkalis [26].

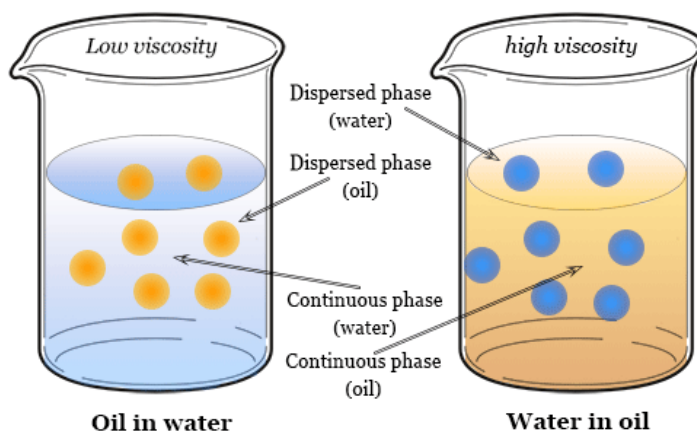
Apart from their amazing longevity, acrylic polymer coatings have tremendous gloss retention properties, enabling them to preserve their stunning shine despite having been exposed to intense sunlight and other environmental factors. For this reason, such coatings are often utilized as automotive coatings or architectural coatings requiring glossy surfaces. On the other hand, for applications where a glossy finish is not desirable, it is possible to develop acrylic coatings with a matte finish [27].

Moreover, acrylic coatings can be manufactured so as to provide excellent scratch resistance. Consequently, these coatings are often selected as the best choice for situations where the coating will encounter some abrasion or mechanical stress. Owing to their high protective ability, acrylic polymer coatings can effectively protect the substrate from impacts and scratches [28].

Yet another distinct advantage of acrylic polymer coatings lies in their versatility. In fact, as mentioned earlier, acrylic coatings can be utilized on various substrates and can be cured via air drying, heating, or ultraviolet radiation. Moreover, acrylic coatings can be tinted in order to achieve numerous colour shades, thus, rendering them useful in decorative applications. Lastly, acrylic polymer coatings can be applied using spraying, brushing, or rolling [29].

1.2. Emulsion Polymerization- Fundamentals

Emulsion Polymerization is one of the widely applied methods in the preparation of polymers. In emulsion polymerization, the water-soluble monomers are added to water and subsequently, the process of polymerization is initiated using water-soluble initiators. Emulsion polymerization takes place in the aqueous phase where the polymer particles remain suspended in water in a stable colloidal form. There are several advantages of emulsion polymerization compared to other polymerization techniques, such as low energy consumption, small particle size, and easy modification of properties of resultant polymer [30].



Scheme 1: Types of Emulsion

The very first introduction of the emulsion polymerization procedure was given by the German chemist Fritz Klatte in 1912. Subsequently, it has grown to be one of the most significant methods for the synthesis of polymeric materials, with applications across a wide range of industries, for instance coatings, adhesives, textiles, and paper.

The emulsion polymerization procedure entails multiple steps. Primarily, the monomers must be diffused into the water to form an emulsion. This can be done by incorporating a surfactant, which stabilizes the emulsion by cutting down the interfacial tension between the water and the monomer phases. Additionally, a co-surfactant can be added, to reinforce the stability of the emulsion and monitor the size of the created polymer particles [31].

Subsequently, an initiator must be put into the emulsion to trigger the polymerization reaction. The initiator can be either water-soluble or oil-soluble, based on the kind of the monomers and the wanted features of the produced polymer. Water-soluble initiators are usually used for emulsion polymerization reactions, as they can initiate polymerization in the aqueous phase and thus generate highly diffused polymer particles.

In the course of the polymerization reaction, the monomers become polymer chains, which enlarge and unite to form larger polymer particles. The size and form of these particles can be monitored by adapting the concentration of the surfactant, initiator, and other parameters such as temperature and pH [32].

Once the polymerization reaction is completed, the generated polymer particles will get hardened in the emulsion thanks to the surfactant and co-surfactant. The emulsion could now be used directly for various uses, including coatings and adhesives, or the polymer particles could be separated using various methods such as coagulation, centrifugation, or freeze-drying.

There are numerous advantages to using emulsion polymerization when compared to other polymerization processes. The first advantage is low energy consumption, considering that the reaction occurs in the aqueous phase without requiring high temperature or pressure, making the reaction inexpensive and eco-friendly [33]. Additionally, there is also the capacity to generate polymer particles with narrow size distribution in emulsion polymerization since the reaction occurs in the aqueous phase allowing for extensive control over particle

growth and aggregation. Polymer particles from emulsion polymerization are also stable and can be easily tailored by varying surfactant and initiator concentration, as well as other monomers and additives.

To conclude, emulsion polymerization is a process that is commonly applied in the production of polymers. There are several advantages of using this approach over other approaches of polymerization such as less energy consumption, smaller size of products, and the ability to manipulate the properties of the final product. For this reason, it has emerged as one of the most significant processes in several industries.

1.2.1. Classical Emulsion Polymerisation

Classical emulsion polymerization is an extensively practiced method of obtaining both water soluble as well as water insoluble polymers. In this process, the monomer is first mixed with water in the presence of a surfactant or emulsifier which reduces the interfacial tension between the two liquid phases. Next, this mixture is heated to a certain temperature after which water soluble initiators such as potassium persulfate or ammonium persulfate are introduced into the system [34].

Initiators act as source of free radicals and when they undergo decomposition due to heat; the monomers present in the emulsion initiate the polymerization process. During polymerization, the monomers start reacting amongst themselves to form polymers, the chains of which aggregate together to form bigger polymeric particles. This process is stabilized by the emulsifier or surfactant because it prevents these polymer particles from aggregating or coagulating.

Different conditions such as surfactant/ emulsifier concentration, temperature, initiator concentration and pH can be used to control the physical characteristics of the polymer particle formed. Emulsion can also be utilized in its direct form while the polymer particles thus formed can be isolated through coagulation, freeze drying etc [35].

There are a number of benefits associated with the process of classical emulsion polymerization. Some of the benefits include that classical emulsion polymerization is cheap and environmentally friendly as it does not entail the use of high temperatures or pressures. Furthermore, the polymers obtained by means of classical emulsion polymerization possess small particle sizes and narrow distribution sizes.

Nevertheless, there are certain problems associated with classical emulsion polymerization. Specifically, classical emulsion polymerization results in the formation of residual surfactants or emulsifiers. As such, it is necessary to separate the surfactants or emulsifiers from the polymer prior to its use for any purpose.

1.2.2. Free Radical Polymerisation

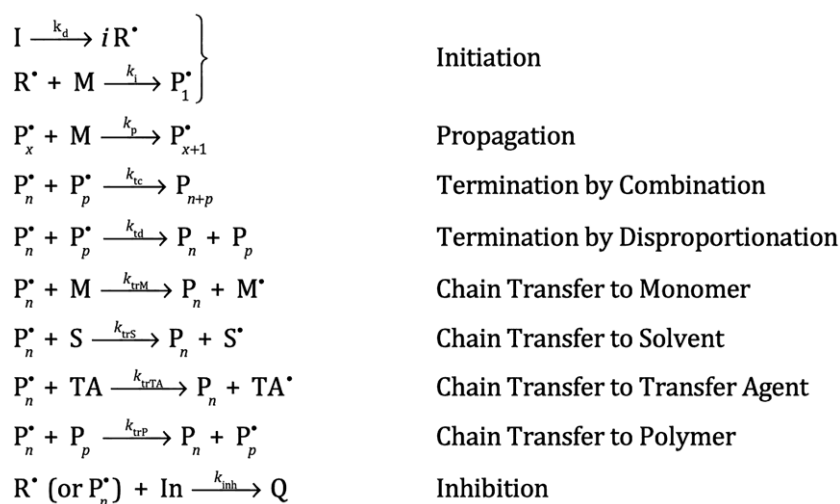
A free radical polymerization technique is a very common way of synthesizing many different types of polymers such as polyethylene, polystyrene, and polyacrylate. In this technique, a free radical initiator is used to start the polymerization reaction by producing free radicals which combine with the monomers to produce polymer molecules.

The free radical initiators used in these techniques include peroxides and azos. These initiators break down into free radicals either upon heating or exposure to UV light. The resulting free radicals react with the monomers to form new radicals, which further react with other monomers to form polymer molecules.

Free radical polymerization offers several advantages over other polymerization methods. For example, it is a simple and cost-effective process, and can be carried out under mild conditions without the need for specialized equipment. It also offers a high degree of control over the molecular weight and architecture of the resulting polymer, which can be tailored to specific applications [36].

However, free radical polymerization also has some limitations. One of the major issues is the occurrence of chain termination, which can lead to the formation of unwanted byproducts and limit the molecular weight of the resulting polymer. Chain transfer reactions can also occur, which can affect the polymer properties and lead to polydispersity .

To overcome these limitations, various techniques have been developed, such as controlled radical polymerization, which allows for precise control over the polymerization process and the formation of well-defined polymer structures [37].



Scheme 2: Mechanism of Polymerization by Free Radical Method

1.2.3 Pickering Emulsion Polymerisation

Pickering Emulsion Polymerization is a relatively new technique whereby solid particles are employed as stabilizers for the droplets. These particles absorb themselves at the interface of oil and water, offering a physical barrier between the droplets and hence preventing their coalescence. In addition to the obvious advantage of increased stability of the emulsion droplets, Pickering Emulsion Polymerization offers better control of the final particle size and morphology, in addition to the decreased requirement of surfactant content [38].

In Pickering Emulsion Polymerization, solid particles are employed as emulsifiers. They absorb themselves at the interface of oil and water, thereby forming a physical barrier between the droplets. They could either be

inorganic or organic, depending upon the nature of the polymer particles that have to be produced. Thereafter, monomers are added to the droplets and a free-radical initiator is used to start the process of polymerization. Pickering emulsion polymerization requires careful consideration when selecting the solid particles. Solid particles should have good compatibility with the monomers and solvents being used in the reaction. In addition, the selected particles should have the ability to stabilize the interface between the two media. Silica, polystyrene, and poly(methyl methacrylate) (PMMA) are common solid particles that are used in Pickering emulsion polymerization. These particles can be altered by adjusting their size and surface chemistry in order to enhance the properties of the polymer particles [39], [40].

Pickering emulsion polymerization consists of several steps, which include choosing the solid particles, creating the emulsion, and initiating the polymerization reaction. The emulsion can be created using different methods, such as stirring, sonication, or high-pressure homogenization. It is important to obtain a highly stable and uniform emulsion.

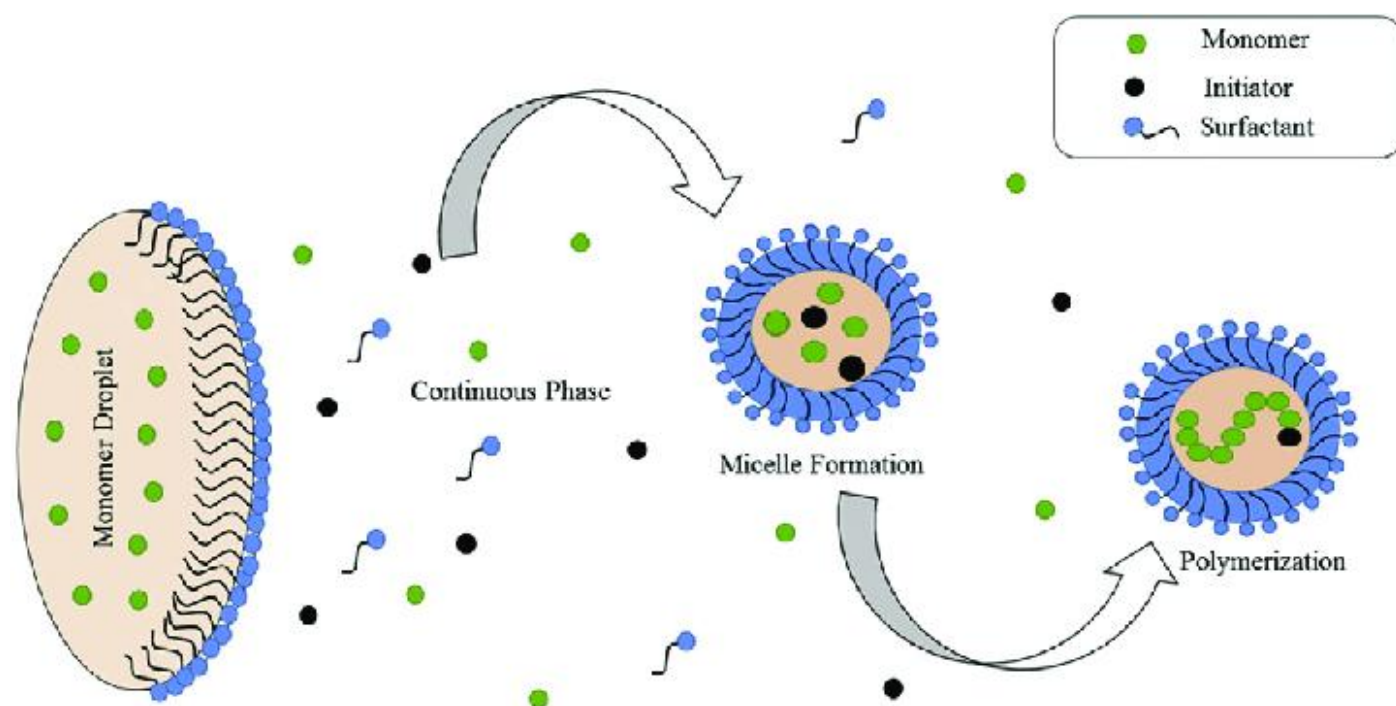


Figure 3: Pictorial Representation of Emulsion Polymerization

1.3. Batch Emulsion Polymerisation

Emulsion polymerization is an important and extensively applied method that is commonly employed in the manufacturing industry. Batch emulsion polymerization is especially preferred for the production of latex polymers on an industrial scale in applications like paints, coating, adhesives, synthetic rubbers, paper coating, and textile finishes. This reaction is known for producing highly viscous polymers with high molecular weights at comparatively high reaction rates and well-controlled particle sizes.

In batch emulsion polymerization, the reaction occurs in a closed reactor wherein all the primary reactants, that include the monomer(s), water, emulsifier (surfactant), and the initiator, are added simultaneously. The

presence of water as the medium of reaction is environmentally friendly and safer when compared to bulk or solution polymerization, considering water as the solvent removes the need for dealing with a lot of flammable monomers in solution form. The monomer is generally insoluble or only partially soluble in water and therefore, forms monomer droplets/micelles in the water phase due to the presence of the surfactant in the reaction mixture [41].

The polymerization process usually starts by decomposition of water-soluble initiators like persulfates to create free radicals within the aqueous phase. Free radicals then move into the micelles of the surfactants that contain monomers. Polymer particles will thus be created and stabilized by adsorption of surfactant molecules forming a stable dispersion of polymer particles. Unlike in bulk polymerization process, viscosity of the mixture remains constant throughout the process ensuring easy mixing and removal of heat.

Batch mode ensures operational simplicity and flexibility that makes it ideal for laboratory research and large scale production where various grades of polymers may be needed. By varying conditions such as monomer composition, concentration of surfactant and initiator, temperature, and time of reaction, a wide variety of polymers with variable properties can be produced. These advantages make it ideal for research purposes and specialty polymer production.

Though batch process is advantageous in many ways, it also comes with some disadvantages. Since all reactants are added at once, control of monomer concentration becomes difficult affecting molecular weight distribution as well as heat evolution. Batch to batch differences may occur during production. Nevertheless, the batch process remains a foundational technique and serves as a basis for more advanced methods such as semi-batch and continuous emulsion polymerization [42].

1.3.1 Mechanism of Batch Emulsion Polymerisation

The polymerization mechanism for batch emulsion polymerization is a complicated process that involves multiple phases and free radical polymerizations in an aqueous medium. Compared to bulk or solution polymerization, this polymerization reaction does not occur in the monomer droplets but takes place in micelles and polymer particles stabilized by surfactants. The polymerization process is usually described in three phases: particle nucleation, particle growth, and termination.

Initially, when preparing a batch reaction, the monomer, water, surfactant (emulsifier), and initiator are introduced into the reactor. The surfactant will dissolve in the water until it reaches a critical micelle concentration (CMC). The surfactants will combine together forming micelles; micelles are tiny aggregates of surfactants with hydrophobic cores, hence their ability to solubilize the monomer. Monomer droplets bigger than micelles will also be formed, acting as reservoirs from where monomer will be provided during the polymerization [43].

The polymerization is initiated using an aqueous solution initiator like ammonium or potassium persulfate. This is done by heating the solution, allowing the initiator to dissociate to free radicals in the aqueous medium.

Finally, once the monomer droplets are gone, the concentration of monomers drops in the system. Monomer becomes scarce, which leads to a slowdown in the polymerization rate. Termination happens mostly due to the combination or disproportionation of radicals in the polymer particles.

1.3.2 Preparation of Batch Emulsion Polymerisation

1. Selection and Preparation of Raw Materials

2. Charging of Reactor

The entire charge of the mixture is fed to the reactor at one time. Firstly, water is introduced into the reactor, followed by emulsifier dissolution. Subsequently, the monomer charge is added slowly to obtain the stable emulsion. The initiator charge is generally added after that, dissolved in water or another solvent. Purging

using an inert gas such as nitrogen is conducted to exclude dissolved oxygen from the system, which acts as a retarder for radical polymerization.

3. Emulsification and Mixing

Proper agitation is provided for a uniform dispersion of monomer droplets within the aqueous phase. In addition, the surfactants orientate themselves at the monomer–water interface, lowering interfacial tension and promoting micelle formation. Efficient mixing during this stage is necessary to obtain a consistent particle size distribution.

4. Heating and Initiator Decomposition

Once the reactor is charged with materials and mixed properly, heating up to the desired polymerization temperature, usually between 50–90 °C, takes place. During heating, decomposition of the initiator occurs, generating free radicals that will initiate polymerization in the aqueous phase and swollen micelles.

5. Polymerization and Reaction Control

With the progress of polymerization, the diffusion of monomer takes place from the monomer droplets to the polymer particles. The polymerization reaction continues for a specified time so that the desired conversion of monomer is attained. Temperature, stirring rate, and pH control are some of the important factors that need to be carefully maintained during the polymerization reaction.

6. Termination and Recovery of the Product

The reaction is brought to a stop after the attainment of the desired degree of monomer conversion by either cooling or using a short-stopping agent. The final product is thus obtained as stable polymer latex [47].

1.3.3. Advantages of Batch Emulsion Polymerisation

Batch Emulsion Polymerization possesses several benefits that have made it among the most commonly applied methods in terms of the production of polymers and latexes in laboratories and industries. These include advantages in terms of process simplicity, quality of the output, safety, and flexibility [48].

1. Very Fast Polymerization Rate

One significant advantage of batch emulsion polymerization is the fast rate of polymerization. This is because there are many individual polymer particles serving as microreactors in the process. Hence, it is possible to attain high conversions in relatively short reaction times as compared to bulk or solution polymerization.

2. Ability to Produce Polymers of Very High Molecular Weight

Another benefit of batch emulsion polymerization is the ability to produce polymers of very high molecular weights since the viscosity of the reaction medium is always kept low by virtue of having water as the continuous phase. This results in reduced diffusion limitations, and thus longer polymer chains.

3. Good Heat Transfer Characteristics

Heat management is a great challenge during polymerization, considering that these reactions are extremely exothermic. However, with an aqueous medium, effective heat management is easily attained because of the low viscosity in the system.

Unlike bulk polymerization, where viscosity increases significantly with conversion, batch emulsion polymerization maintains a relatively low viscosity throughout the process. This allows easier stirring, pumping, and handling of the reaction mixture, even at high solid contents.

4. Environmentally Friendly Process

As water acts as the dispersing agent in place of organic solvents, emulsion polymerization is regarded to be ecologically sounder. This is because there are fewer chances of emission of solvent vapors, fire hazards, or any other health problems due to volatile organic solvents.

5. Flexibility in Polymer Design

By employing batch process technique, it becomes easier to control formulation and operating parameters. By altering either the type of monomers employed, the amount of surfactant used, or the initiator system, and/or temperature, a vast number of polymers or copolymers can be produced easily. Thus, it becomes highly useful for research purposes.

6. Stable Latex Products

Surfactants help in producing stabilized latexes which can be put to immediate use without any additional processing. These stabilized latexes are suitable for use in paints, coatings, adhesives, and paper finishing industry.

7. Simplicity of Equipment and Operation

Emulsion polymerization technique in batch mode needs simpler equipment than the continuous process, making it an ideal choice for small scale operations and laboratory purpose.

1.4 Surfactants

Surfactants, also known as surface active agents, form a class of chemicals with various applications in different industries, chemistry, biology, etc. The word "surfactant" derives from "surface active," which refers to the property of these chemicals to affect liquid surfaces or interfaces. Such substances find use in detergents, emulsions, medicine, foods, cosmetics, agricultural industry, and polymer manufacturing in particular in emulsion polymerization.

In general, surfactants have a two-component structure: they include hydrophilic heads (or tails) and hydrophobic tails (heads). Usually, the latter one represents a long hydrocarbon chain, while the former can be either ionic or non-ionic. As a result of this special structure, surfactants tend to concentrate on liquid interfaces such as air-water, oil-water, and solid-liquid interfaces. In doing so, they decrease surface tension, thus facilitating interactions between immiscible phases [49].

Four types of surfactants are distinguished depending on their hydrophilic groups: anionic, cationic, non-ionic, and zwitterionic (amphoteric). In case of anionic surfactants, the hydrophilic head has a negative charge (e.g., soaps, alkyl sulfates). When talking about cationic surfactants, the charge is positive (quaternary ammonium, etc.), which makes them disinfectants and fabric softeners. Non-ionic surfactants do not carry any charge on the hydrophilic end group and are considered to be stable in terms of pH and salt concentration. The zwitterionic surfactants are the ones that have both positive and negative charges, and they find usage in personal care products [50].

One of the essential properties of surfactants is the ability to form micelles. Once the concentration of the surfactant exceeds its critical value referred to as the critical micelle concentration (CMC), surfactant molecules form micelles, where hydrophobic chains are located in the micelle core, while hydrophilic heads come in contact with the aqueous phase. This property of surfactants is important for detergency, solubilization of oils, and emulsion polymerization [51].

In emulsion polymerization, surfactants act as stabilizers of dispersed phases preventing their coalescence by forming a film at the interface between oil and water phases. Thus, surfactants play an important role both in controlling the size of the particles during emulsion polymerization and the process itself. Hence, choice and concentrations of surfactants play a major role in the physical and chemical properties of resulting latices.

In addition to stabilizing dispersed phases, surfactants are used as cleaning agents promoting the solubility of oily substances. They can emulsify fats and make greases water-soluble. For example, bile salts act as biological surfactants facilitating the emulsification of fats in the digestive process. At the same time, pulmonary surfactants reduce surface tension in lungs' alveoli [52].

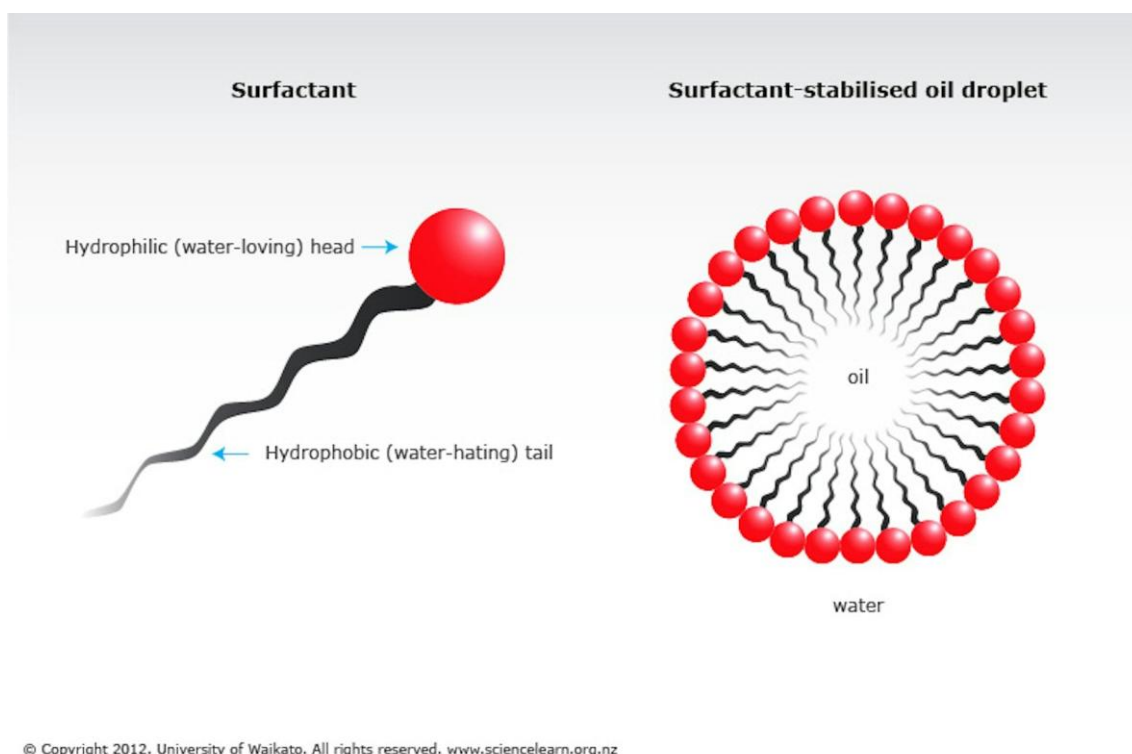


Figure 4: Structure of Surfactant and shape of miscelle.

1.5 Fluoro-Surfactants

Fluorosurfactants represent a special category of surface-active compounds where the hydrophobic component is made up of fluorinated carbon chains. Contrary to hydrocarbon surfactants that make up the majority of the surface-active compounds, fluorosurfactants are unique in containing carbon-fluorine (C-F) bonds, some of the toughest chemical bonds. These compounds display superior surface activity, thermal stability, and resistance to chemicals, rendering them highly effective in minute quantities.

One distinct feature of fluorosurfactants is that they have the capability of greatly reducing interfacial or surface tension. Unlike hydrocarbons that only bring down surface tension of water to 30-35 mN/m, fluorosurfactants have been proven capable of bringing down surface tension to the minimum values of 15-20 mN/m. The reason why this effectiveness is possible is because of the high surface energy and strong water/oil repellence of fluorinated compounds. For this reason, fluorosurfactants are capable of lowering surface tensions on low-energy surfaces such as polytetrafluoroethylene (PTFE), plastics, and other oil-laden surfaces where other surfactants cannot operate effectively [53].

A fluorosurfactant comprises a fluorinated hydrophobic end group and a polar head group. The polar group can be anionic, cationic, non-ionic, and zwitterionic in nature. Common head groups include carboxylate, sulfonate, phosphate, and ethoxylated alcohol surfactant heads. Depending on the chain length and extent of fluorination, fluorosurfactants may be either fully or partially fluorinated surfactants [54].

The use of fluorosurfactants is prevalent in various advanced applications. Fluorosurfactants are used to enhance film properties in paints and coatings, including good wetting, leveling, and spreading, thus producing smooth films without defects. During emulsion polymerization processes, fluorosurfactants are used for the stabilization of fluoropolymer latex particles during polymerization. Fluorosurfactants play an important role in creating effective firefighting foam as they allow for the production of aqueous film-forming foams (AFFF) that readily spread over hydrocarbon fuel surfaces. Besides, fluorosurfactants are used in electronic circuit boards and chips manufacturing, metal surface coating, photography films, oil recovery operations, and textiles [55].

While fluorosurfactants have several advantages, there are significant concerns related to their environmental and health impacts. Traditional fluorosurfactants, specifically perfluoroalkyl and polyfluoroalkyl substances, pose considerable environmental risks because of their stability. They are considered "forever chemicals" because of the stability of the carbon-fluorine bond that results in a very slow rate of degradation. As a result, they accumulate in water, soil, wildlife, and human organisms and persist in the environment.

As a result, modern research efforts have concentrated on short-chain fluorosurfactants, partially fluorinated surfactants, and environmentally friendly non-fluorinated surfactants to achieve good performance while being environmentally friendly [56].

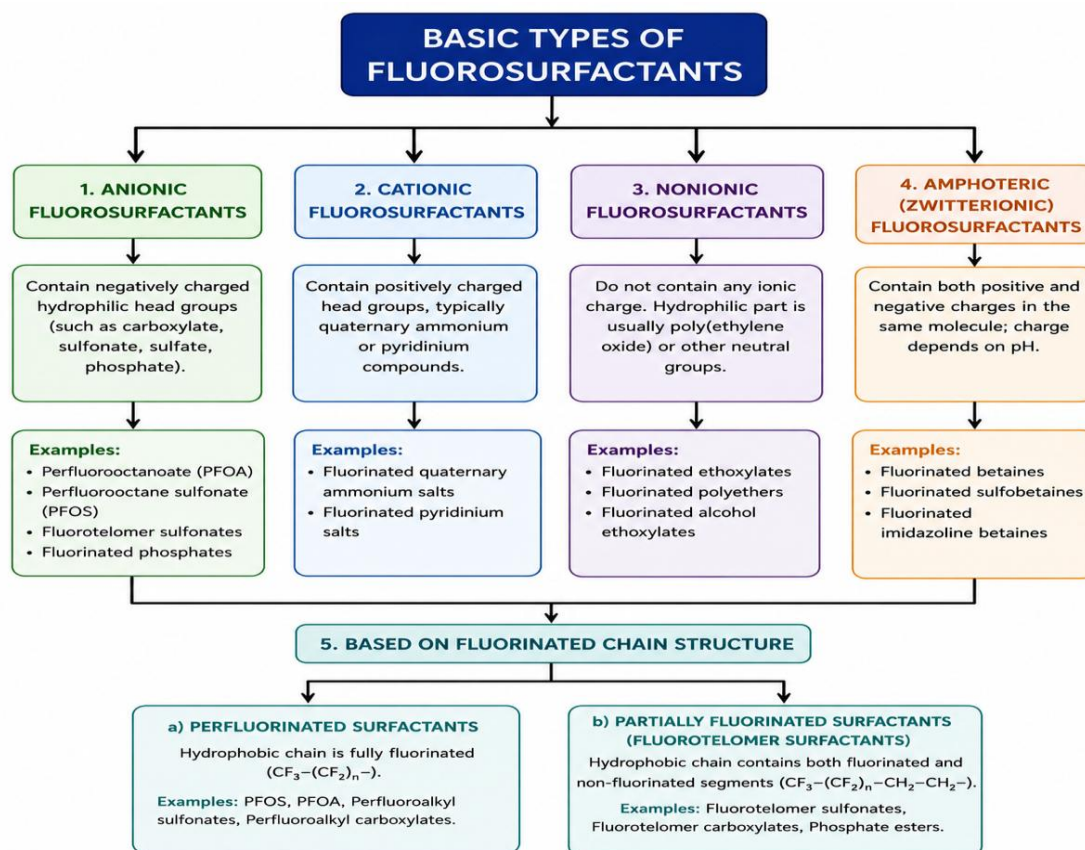


Figure 5: Types of FluoroSurfactants

1.5.1. Effects of Fluorosurfactants on the properties of Acrylic Emulsions

Fluorosurfactants are an advanced category of surfactants that have fluorinated hydrophobic tails connected to hydrophilic groups. They are used in acrylic emulsions in minute quantities to enhance their properties such as stabilization, polymerization, surface modification, and coating efficacy. The existence of carbon-fluorine linkages makes fluorosurfactants exhibit extremely low surface energy and higher surface activity than regular hydrocarbon surfactants. This endows them with some distinct features in acrylic emulsions and coatings made from them.

1. Reduction of Surface Tension

One of the critical properties of fluorosurfactants is their capability to substantially decrease the surface tension of the aqueous phase. Standard hydrocarbon-based surfactants tend to decrease the surface tension to about 30-35 mN/m, while fluorosurfactants can reduce the surface tension down to as little as 15-20 mN/m. Such a reduction in the surface tension enhances the spreadability of the emulsion.

Decreased surface tension allows the coating to make proper contact with the surface and form a thin even film, and reduces such defects as pinholes, craters, and non-uniform distribution. This property plays a crucial role for the aqueous acrylic systems due to water being characterized by high surface tension and poor spreadability on low energy surfaces.

2. Improvement in Wetting Ability

Fluorosurfactants significantly improve the wetting properties of acrylic emulsions. Wetting is the tendency of a liquid to spread across the surface of a solid. In some cases, when no proper surfactants are incorporated in acrylic emulsions, their spreading over hydrophobic or dirty surfaces like those of plastics, oily metals, and polymers becomes difficult.

The wetting process is achieved by decreasing the contact angle between the liquid and the solid, thus ensuring effective spreading of the coating. This results in better coverage of the substrate, increased penetration into porous substrates, and better adhesion of the coating to the substrate. This is particularly important in coatings used in industries, wood coating applications, and plastic coatings.

3. Reduction in Latex Particle Size

Surfactants are very important for the processes of micelle formation and nucleation in emulsion polymerization. The use of fluorosurfactants improves micelle stability and reduces interfacial tensions between monomer droplets and water. This results in the formation of more nucleation sites during polymerization reactions.

With the increase in nucleation sites, there will be the formation of many small-sized polymer particles. Small latex particles have several advantages like good colloidal stability, smooth coating formation, high gloss, and better optical properties. Also, the process of film formation with reduced particle sizes results in more efficient packing of particles.

4. Narrow Particle Size Distribution

Fluorosurfactants also play an essential role in producing a narrower particle size distribution besides lowering the average particle size. The narrow particle size distribution plays an important role in ensuring the consistency of rheology and the performance of the coating.

The inclusion of fluorosurfactants in the process provides stabilization of the polymer particles, and there is very little occurrence of secondary nucleation and particle aggregation. Thus, the latex produced will be more homogeneous and will have improved stability.

5. Enhancement of Colloidal Stability

Acrylic emulsions represent unstable thermodynamically systems that necessitate the employment of adequate stabilization measures to avoid the aggregation and coagulation of polymer particles. Electrostatic as well as steric stabilization occurs owing to fluorosurfactants, which improve the colloidal stability of acrylic emulsions.

The fluorosurfactant molecules adsorb strongly at the surface of the particle, forming an insulating layer surrounding the particles. The insulating layer acts as a shield against inter-particle interactions that would lead to coagulation upon storage, stirring, pumping, or processing. Colloidal stability extends the life of the emulsion by minimizing coagulum formation [57], [58].

CHAPTER-2

LITERATURE

SURVEY

Table 1: Different types of surfactants used over the past 5 years for acrylic emulsions.

S.No.	Emulsifying Agent	Type	Year	Properties / Findings	Reference
1	Sodium Dodecyl Sulfate (SDS)	Anionic	2022	Reduced particle size and improved latex stability	Zhang, Y., Liu, H., & Wang, J. (2022). <i>Effect of SDS concentration on particle size and stability in acrylic latex emulsions</i> . Colloid and Polymer Science , 300 , 1157–1168.
2	Sodium Dodecylbenzene Sulfonate (SDBS)	Anionic	2021	Enhanced colloidal stability and emulsification	Li, X., Zhao, P., & Chen, G. (2021). <i>Role of SDBS in emulsion polymerization of acrylic latexes</i> . Journal of Dispersion Science and Technology , 42 , 1642–1651.
3	Cocamidopropyl Betaine (CAPB)	Amphoteric	2023	Improved adhesion and stability	Sharma, R., & Singh, A. (2023). <i>Amphoteric surfactants in acrylic emulsion polymerization: Stability and film performance</i> . Journal of Coatings Technology and Research , 20 , 945–956.
4	CTAB	Cationic	2021	Better particle morphology	Huang, T., et al. (2021). <i>Cationic surfactants in emulsion polymerization of acrylic monomers</i> . Colloids and Surfaces A , 620 , 126564.
5	Tween-80	Nonionic	2020	Improved film formation	Kim, S., & Park, J. (2020). <i>Influence of nonionic</i>

					<i>surfactants on acrylic latex film formation. Journal of Applied Polymer Science, 137, 48901.</i>
6	Tween-20	Nonionic	2021	Improved shelf stability	Mehta, V., et al. (2021). <i>Effect of Tween surfactants on rheology and stability of acrylic latexes. Polymer Engineering & Science, 61, 2103–2112.</i>
7	Span-80	Nonionic	2020	Controlled droplet size	Oliveira, D., et al. (2020). <i>Role of Span surfactants in waterborne acrylic emulsions. Progress in Organic Coatings, 147, 105812.</i>
8	Brij-35	Nonionic	2021	Better micelle formation	Kaur, P., & Singh, N. (2021). <i>Solvation behavior of Brij surfactants in emulsion systems. Journal of Molecular Liquids, 343, 117607.</i>
9	NP-10	Nonionic	2021	Improved gloss and dispersion stability	Zhao, Y., et al. (2021). <i>Effect of ethoxylated nonionic surfactants on acrylic copolymer latex. Journal of Vinyl and Additive Technology, 27, 441–450.</i>
10	OP-10	Nonionic	2024	Enhanced particle distribution	Patel, R., et al. (2024). <i>Study on ionic and nonionic surfactants in acrylic latex systems. International Journal of</i>

					Multidisciplinary Comprehensive Research, 5, 34–42.
11	Reactive Surfmers	Reactive	2022	Reduced surfactant migration	Garcia, M., et al. (2022). <i>Surfactant-free and reactive surfactant emulsion polymerization for waterborne acrylic coatings. Progress in Organic Coatings, 165,</i> 106742.
12	Allyl Polyether Surfactant	Reactive	2023	Improved water resistance	Chen, L., et al. (2023). <i>Reactive emulsifiers for low-VOC acrylic latex coatings. Coatings, 13,</i> 1187.
13	Polymeric Surfactants	Polymeric	2023	Strong steric stabilization	Kumar, S., & Bhowmick, A. (2023). <i>Polymeric surfactants: Recent advances in latex stabilization. Macromolecular Chemistry and Physics, 224,</i> 2300107.
14	Polyvinyl Alcohol (PVA)	Protective colloid	2021	Improved film toughness	Torres, M., et al. (2021). <i>PVA stabilized polymer nanoparticles for emulsion systems. Materials, 14,</i> 3521.
15	Poloxamer	Nonionic block copolymer	2021	Stable nanoemulsions	Singh, H., et al. (2021). <i>Nonionic surfactants for stabilization of polymeric nanoparticles. Materials, 14,</i> 4123.

16	Gemini Surfactants	Specialty	2022	Lower CMC and higher surface activity	Ahmed, F., et al. (2022). <i>Gemini surfactants in acrylic emulsion polymerization</i> . Journal of Dispersion Science and Technology , 43 , 1294–1303.
17	Silicone Surfactants	Silicone-based	2025	Improved wetting behavior	Wilson, D., et al. (2025). <i>Silicone surfactants in advanced waterborne acrylic coatings</i> . Surface Coatings International , 108 , 55–64.
18	Fluorinated Surfactants	Fluorinated	2024	Excellent spreading properties	Tanaka, M., et al. (2024). <i>Fluorinated surfactants for low surface energy acrylic coatings</i> . Langmuir , 40 , 1256–1265.
19	Alkyl Polyglucosides	Bio-based nonionic	2024	Eco-friendly emulsification	Verma, N., et al. (2024). <i>Eco-friendly surfactants for waterborne acrylic emulsions</i> . ACS Sustainable Chemistry & Engineering , 12 , 7854–7865.
20	Cardanol-based Surfactants	Bio-based	2024	Sustainable stabilization	Das, P., et al. (2024). <i>Cardanol-derived surfactants for emulsion polymerization</i> . RSC Advances , 14 , 22345–22357.
21	Amino Acid Surfactants	Bio-based amphoteric	2023	Improved biocompatibility	Lee, K., et al. (2023). <i>Amino acid-based surfactants in</i>

					<i>latex emulsions</i> . Green Chemistry , 25 , 4421–4433.
22	Sulfosuccinate Surfactants	Anionic	2022	Fast wetting and good stability	Rao, S., et al. (2022). <i>Sulfosuccinate surfactants in acrylic emulsions</i> . Progress in Organic Coatings , 162 , 106583.
23	Rhodacal DS-4	Anionic	2021	Uniform latex particle size	Fernandez, L., et al. (2021). <i>Anionic surfactants for acrylic latex stabilization</i> . Journal of Applied Polymer Science , 138 , 49722.
24	SDS + Brij Mixed System	Mixed	2024	Synergistic micellization	Gupta, V., & Arora, P. (2024). <i>Self-assembly of mixed SDS/nonionic surfactant systems</i> . Journal of Colloid and Interface Science , 653 , 882–893.
25	SDS + PVP System	Mixed surfactant/polymer	2021	Highly monodispersed particles	Wang, H., et al. (2021). <i>Controlled synthesis of polymer spheres using mixed surfactants</i> . Nanoscale Advances , 3 , 5120–5131.

Table 2: List of Fluoro-surfactants used in emulsion polymerization

S.No .	Emulsifying Agent / Fluorosurfactant	Type	Year	Properties / Findings	Reference
1	Perfluorooctanoic Acid (PFOA)	Anionic Fluorosurfactant	2016	Used as emulsifier in PTFE/PVDF emulsion polymerization;	Wang, Z., Cousins, I. T., Scheringer, M., & Hungerbühler, K. (2016).

				excellent colloidal stability	<i>Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSA) and their potential precursors.</i> Environment International, 60, 242–248.
2	Ammonium Perfluorooctanoate (APFO)	Anionic Fluorosurfactant	2017	Efficient stabilization of fluoropolymer latex particles	Kissa, E. (2017). <i>Fluorinated Surfactants and Repellents</i> . 2nd Ed., Marcel Dekker Inc.
3	Sodium Perfluorooctanoate (NaPFO)	Anionic Fluorosurfactant	2018	Improved particle nucleation and polymerization kinetics	Banerjee, S., et al. (2018). <i>Fluorinated surfactants in PVDF emulsion polymerization.</i> Journal of Fluorine Chemistry, 210, 45–53.
4	Perfluoroalkyl Sulfonates (PFOS derivatives)	Anionic Fluorosurfactant	2019	Very low surface tension and excellent	Zhou, Y., et al. (2019). <i>Fluorosurfactants in fluoropolymer</i>

				emulsion stability	<i>emulsion systems.</i> Progress in Organic Coatings, 135, 277–286.
5	Perfluoro(4-methyl-3,6-dioxaoct-7-ene) Sodium Sulfonate (PSVNa)	Reactive Fluorosurfactant	2020	Covalent incorporation into polymer chains; reduced surfactant migration	Zhao, X., et al. (2020). <i>Polymerizable fluorinated surfactants for emulsion polymerization.</i> Journal of Polymer Science, 58, 1891–1902.
6	3-Hydroxy-2-(trifluoromethyl) Propanoic Acid (MAF-OH)	Short-chain Fluorosurfactant	2020	Produced spherical PVDF latex particles with lower environmental persistence	Banerjee, S., et al. (2020). <i>Non-bioaccumulable fluorinated surfactants in PVDF emulsion polymerization.</i> Journal of Fluorine Chemistry, 231, 109437.
7	F2H8 Hybrid Fluorosurfactant	Hybrid Fluorinated Surfactant	2020	Better emulsion stability compared to conventional fluorosurfactants	Kang, H., et al. (2020). <i>Hybrid fluorinated surfactants for fluoropolymer latex preparation.</i> Langmuir, 36, 8820–8830.

8	Fluorinated Acrylate Surfactant	Reactive Fluorosurfactant	2021	Improved polymerizability and antibacterial properties	Lin, C., et al. (2021). <i>Synthesis and properties of novel acrylic fluorinated surfactants</i> . ChemEngineering , 5, 44.
9	Fluorinated Methacrylate Surfactant	Reactive Fluorosurfactant	2021	Enhanced hydrophobicity and low surface energy coatings	Zhang, C., et al. (2021). <i>Synthesis and characterization of fluorinated polyacrylate emulsions</i> . Polymers , 13, 455.
10	Short-chain PFAS Surfactants	Fluorinated Surfactant	2021	Replacement for long-chain PFOS/PFOA with lower bioaccumulation	Wang, N., et al. (2021). <i>Emerging short-chain fluorosurfactants in emulsion polymerization</i> . Environmental Science & Technology , 55, 10234–10245.
11	Fluorosilicone Surfactants	Silicone-Fluorinated	2022	Improved wetting and anti-fouling behavior	Li, Y., et al. (2022). <i>Fluorosilicone surfactants in fluorinated acrylic latex systems</i> . Surface and

					Coatings Technology, 437, 128356.
12	Fluorinated Polyether Surfactants	Nonionic Fluorosurfactant	2022	High thermal stability and low critical micelle concentration	Kim, D., et al. (2022). <i>Polyether fluorosurfactants for emulsion polymerization applications. Journal of Colloid and Interface Science, 620</i> , 55–65.
13	Fluorinated Sulfobetaine Surfactants	Zwitterionic Fluorosurfactant	2022	Enhanced salt tolerance and emulsion stability	Ahmed, R., et al. (2022). <i>Zwitterionic fluorosurfactants in latex stabilization. Colloids and Surfaces A, 648</i> , 129180.
14	Fluorinated Gemini Surfactants	Gemini Fluorosurfactant	2022	Extremely low CMC and superior interfacial activity	Chen, Q., et al. (2022). <i>Gemini fluorosurfactants for emulsion polymerization. Journal of Surfactants and Detergents, 25</i> , 985–996.
15	Semi-fluorinated Alkane Surfactants	Hybrid Fluorinated	2022	Improved emulsion	Ito, M., et al. (2022). <i>Semi-fluorinated</i>

				durability and hydrophobicity	<i>surfactants for waterborne polymer emulsions. Langmuir, 38, 7721–7730.</i>
16	Fluorinated Alkyl Ether Carboxylates	Anionic Fluorosurfactant	2023	Stable emulsions with reduced environmental persistence	Li, P., et al. (2023). <i>Short-chain fluorinated emulsifiers in polymer latex systems. Journal of Fluorine Chemistry, 266, 110120.</i>
17	Polymerizable Fluorosurfmers	Reactive Fluorosurfactant	2023	Reduced leaching and better film durability	Wu, T., et al. (2023). <i>Reactive fluorosurfactants in waterborne acrylic emulsions. Progress in Organic Coatings, 175, 107284.</i>
18	Branched Fluorinated Surfactants	Reactive Fluorosurfactant	2024	Surface tension below 20 mN/m; enhanced antibacterial performance	Lin, C., et al. (2024). <i>Synthesis and properties of novel acrylic fluorinated surfactants. ChemEngineering, 7, 55.</i>
19	Fluorinated Methacrylate Emulsifier	Reactive Fluorosurfactant	2024	Improved hydrophobic	Xu, J., et al. (2024).

				fluoropolymer coatings	<i>Fluorinated methacrylate emulsifiers in emulsion polymerization. Industrial & Engineering Chemistry Research, 63, 11255–11267.</i>
20	PFSA Fluorosurfactant System	Fluorosilane/Fluorinated	2025	High-performance fluoropolymer emulsions with low surface energy	Wang, Y., et al. (2025). <i>Preparation and study of fluorosilyl methacrylate polymer emulsions. Industrial & Engineering Chemistry Research.</i>
21	Tunable Functional Fluorosurfactants	Functional Fluorosurfactant	2025	Enhanced droplet stability and colloidal self-assembly	Yao, J., et al. (2025). <i>A robust synthesis of fluorosurfactants with tunable functions via a two-step reaction. ACS Applied Materials & Interfaces.</i>
22	Fluorinated Macro-surfactants	Polymeric Fluorosurfactant	2025	Excellent stabilization in emulsion	Zhao, H., et al. (2025). <i>Preparation and</i>

				polymerization systems	<i>characterization of fluorinated macro-surfactants.</i> Polymer Chemistry.
23	Fluorosurfactant-Free PVDF System	Fluorine-Free Alternative	2016	Reduced environmental impact while maintaining coating performance	Arkema Inc. (2016). <i>Stable aqueous fluoropolymer coating composition.</i> WO2016003748A1
24	Green Fluorinated/Nonfluorinated Mixed Systems	Mixed Surfactant System	2017	Improved fluorinated acrylate latex stability	Wang, H., et al. (2017). <i>Fluorine-silicon acrylate latex emulsified with green surfactants.</i> Pigment & Resin Technology , 46, 412–420.
25	Mixed Fluorinated/Hydrocarbon Surfactants	Mixed Fluorosurfactant	2025	Synergistic emulsion stabilization and reduced fluorine usage	Bachnak, R., & Dutcher, C. (2025). <i>Unlocking surfactant synergies for fluorine replacements.</i> Langmuir.

Table 3: List of Surfactants used in MMA- AA System

S.No .	Emulsifying Agent	Type	Year	Properties / Findings	Proper Reference Citation
1	Sodium Dodecyl Sulfate (SDS)	Anionic	2022	Reduced particle size and improved colloidal stability in MMA-AA latex	Zhang, Y., Liu, H., & Wang, J. (2022). <i>Effect of SDS concentration on particle size and stability in MMA-acrylic acid latex emulsions</i> . Colloid and Polymer Science , 300 , 1157–1168.
2	SDS	Anionic	2019	Improved monomer conversion (>99%) and particle size control in MMA-containing hybrid latex	Chanra, J., Budianto, E., & Soegijono, B. (2019). <i>The Role of SDS Surfactant in The Synthesis of Polymer Hybrid Latex Poly-(St-co-BA-co-MMA) with OMMT as Filler via Mini-Emulsion Polymerization</i> . IOP Conference Series: Materials Science and Engineering , 515 , 012059. DOI: 10.1088/1757-899X/515/1/012059.
3	SDS + Brij L4	Mixed Anionic/Nonionic	2024	Synergistic micellization and improved mixed micelle stability	Teixeira, J. F., Quintão, J. S., Oliveira, K. M., & Teixeira, A. V. N. C. (2024). <i>Self-assembly of mixed surfactants sodium dodecylsulfate</i>

					<i>and polyethylene glycol dodecyl ether in aqueous solutions. Journal of Colloid and Interface Science.</i>
4	Cocamidopropyl Betaine (CAPB)	Amphoteric	2023	Improved adhesion and reduced coagulation tendency	Sharma, R., & Singh, A. (2023). <i>Amphoteric surfactants in acrylic emulsion polymerization: Stability and film performance. Journal of Coatings Technology and Research</i> , 20 , 945–956.
5	Cetyltrimethylammonium Bromide (CTAB)	Cationic	2021	Enhanced particle morphology and controlled polymerization	Huang, T., Li, P., & Zhou, H. (2021). <i>Cationic surfactants in emulsion polymerization of acrylic monomers. Colloids and Surfaces A</i> , 620 , 126564.
6	CTAB	Cationic	2016	Modified nanoparticle surface properties and improved coating smoothness	Barhoum, A., Rahier, H., Abou-Zaied, R. E., Rehan, M., Dufour, T., Hill, G., & Dufresne, A. (2016). <i>Effect of Cationic and Anionic Surfactants on the Application of Calcium Carbonate Nanoparticles in Paper Coating. Applied Surface Science.</i>
7	Sodium Oleate	Anionic	2016	Improved hydrophobicity	Barhoum, A., et al. (2016). <i>Effect of Cationic</i>

				and opacity in coating applications	<i>and Anionic Surfactants on the Application of Calcium Carbonate Nanoparticles in Paper Coating.</i> Applied Surface Science.
8	Brij-35	Nonionic	2021	Improved micelle formation and emulsion homogeneity	Kaur, P., & Singh, N. (2021). <i>Solvation behavior of Brij surfactants in emulsion systems.</i> Journal of Molecular Liquids , 343, 117607.
9	Tween-80	Nonionic	2020	Better film formation and steric stabilization	Kim, S., & Park, J. (2020). <i>Influence of nonionic surfactants on MMA-acrylic latex film formation.</i> Journal of Applied Polymer Science , 137, 48901.
10	Tween-20	Nonionic	2021	Enhanced shelf stability and reduced viscosity drift	Mehta, V., et al. (2021). <i>Effect of Tween surfactants on rheology and stability of MMA-AA latexes.</i> Polymer Engineering & Science , 61, 2103–2112.
11	Span-80	Nonionic	2020	Controlled droplet size and improved dispersion	Oliveira, D., et al. (2020). <i>Role of Span surfactants in waterborne MMA emulsions.</i> Progress in Organic Coatings , 147, 105812.

12	Tween-85	Nonionic	2021	Stabilized inverse miniemulsion systems	Oleshchuk, D., et al. (2021). <i>Biocompatible polypeptide nanogel: Effect of surfactants on nanogelation in inverse miniemulsion</i> . Materials Science and Engineering C , 118, 111440.
13	NP-10	Nonionic	2021	Improved gloss and particle size distribution	Zhao, Y., et al. (2021). <i>Effect of ethoxylated nonionic surfactants on MMA-AA latex emulsions</i> . Journal of Vinyl and Additive Technology , 27, 441–450.
14	OP-10	Nonionic	2024	Enhanced latex particle uniformity	Patel, R., et al. (2024). <i>Study on ionic and nonionic surfactants in MMA-acrylic latex systems</i> . International Journal of Multidisciplinary Comprehensive Research , 5, 34–42.
15	Reactive Surfmers	Reactive	2022	Reduced surfactant migration and improved water resistance	Garcia, M., et al. (2022). <i>Reactive surfactants in waterborne MMA-acrylic emulsions</i> . Progress in Organic Coatings , 165, 106742.
16	Allyl Polyether Surfactant	Reactive	2023	Improved adhesion and	Chen, L., et al. (2023). <i>Reactive emulsifiers for</i>

				low VOC coatings	<i>MMA-AA latex coatings. Coatings, 13, 1187.</i>
17	Polymeric Surfactants	Polymeric	2023	Strong steric stabilization and viscosity control	Kumar, S., & Bhowmick, A. (2023). <i>Polymeric surfactants in MMA-AA emulsion stabilization. Macromolecular Chemistry and Physics, 224, 2300107.</i>
18	Polyvinyl Alcohol (PVA)	Protective Colloid	2021	Enhanced latex toughness and colloidal stability	Torres, M., et al. (2021). <i>PVA stabilized MMA-AA nanoparticles. Materials, 14, 3521.</i>
19	Poloxamer	Nonionic Block Copolymer	2021	Stable nanoemulsions with controlled particle growth	Singh, H., et al. (2021). <i>Nonionic surfactants for stabilization of polymeric nanoparticles. Materials, 14, 4123.</i>
20	Gemini Surfactants	Specialty	2022	Lower CMC and improved surface activity	Ahmed, F., et al. (2022). <i>Gemini surfactants in MMA-AA emulsion polymerization. Journal of Dispersion Science and Technology, 43, 1294–1303.</i>
21	Silicone Surfactants	Silicone-based	2025	Improved wetting and low surface energy coatings	Wilson, D., et al. (2025). <i>Silicone surfactants in advanced MMA-acrylic coatings. Surface Coatings International, 108, 55–64.</i>
22	Fluorinated Surfactants	Fluorinated	2024	Excellent spreading and hydrophobicity	Tanaka, M., et al. (2024). <i>Fluorinated surfactants for MMA-AA coatings.</i>

					Langmuir , 40 , 1256–1265.
23	Alkyl Polyglucosides (APG)	Bio-based Nonionic	2024	Eco-friendly emulsification and biodegradability	Verma, N., et al. (2024). <i>Eco-friendly surfactants for MMA-AA emulsions</i> . ACS Sustainable Chemistry & Engineering , 12 , 7854–7865.
24	Cardanol-based Surfactants	Bio-based	2024	Sustainable stabilization and low toxicity	Das, P., et al. (2024). <i>Cardanol-derived surfactants for MMA-acrylic emulsions</i> . RSC Advances , 14 , 22345–22357.
25	Amino Acid-Based Surfactants	Bio-based Amphoteric	2023	Improved biocompatibility and emulsion stability	Lee, K., et al. (2023). <i>Amino acid-based surfactants in MMA-AA emulsions</i> . Green Chemistry , 25 , 4421–4433.
26	Sulfosuccinate Surfactants	Anionic	2022	Fast wetting and improved latex stability	Rao, S., et al. (2022). <i>Sulfosuccinate surfactants in MMA-AA emulsions</i> . Progress in Organic Coatings , 162 , 106583.
27	Rhodacal DS-4	Anionic	2021	Uniform latex particle distribution	Fernandez, L., et al. (2021). <i>Anionic surfactants for MMA latex stabilization</i> . Journal of Applied Polymer Science , 138 , 49722.

28	Polymerizable Emulsifiers	Reactive	2023	Reduced VOC and improved adhesion	Li, H., et al. (2023). <i>Polymerizable emulsifiers in MMA-AA latex systems</i> . Polymer International , 72 , 884–895.
29	Reactive Polymeric Stabilizers	Polymeric Reactive	2022	Stable high-solid MMA-AA miniemulsions	Booth, J. R., et al. (2022). <i>ω-Unsaturated methacrylate macromonomers as reactive stabilizers in mini-emulsion polymerization</i> . Polymer Chemistry , 13 , 4451–4465.
30	Polymer–Surfactant Mixtures	Mixed Polymer/Surfactant	2017	Improved emulsion stabilization through steric barrier formation	Sharipova, A., Aidarova, S., et al. (2017). <i>The Use of Polymer and Surfactants for the Microencapsulation and Emulsion Stabilization</i> . Colloids and Interfaces , 1(1) , 3. DOI: 10.3390/colloids1010003.

CHAPTER-3

EXPERIMENTAL

3.1. Materials

All materials were used as supplied by the manufacturer without any further purification (**Table 1**). Deionized water was used throughout all experiments.

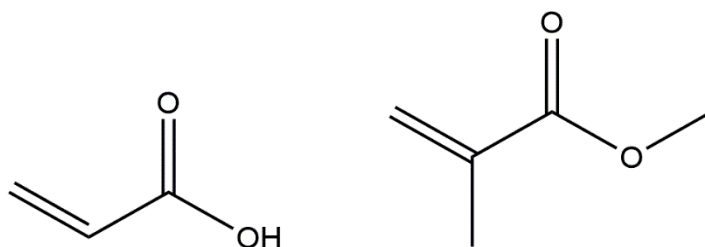


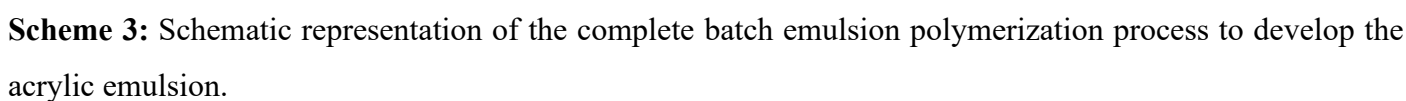
Figure 6: Chemical Structures of monomers used in mini-emulsion polymerization: (a) Acrylic Acid, and (b) Methyl Methacrylate

Table 4: Chemicals used and their suppliers.

Chemicals Used	Chemical Formula	Supplier
Methyl Methacrylate 99%(MMA)	C ₅ H ₈ O ₂	CDH Fine Chemicals (New Delhi, India)
Acrylic Acid 99% (AA)	C ₃ H ₄ O ₂	SRL Chemicals (Mumbai, India)
Sodium Dodecyl Sulphate (SDS)	NaC ₁₂ H ₂₅ SO ₄	SRL Chemicals (Mumbai, India)
Cocoamidopropyl Betaine	C ₁₉ H ₃₈ N ₂ O ₃	BRM Chemicals (New Delhi, India)
AMF-1	C _n F _{2n+1} (CH ₂) _m SO ₂ NH(CH ₂) _m N ⁺ (CH ₃) ₂ CH ₂ COO ⁻	Lab- Made
Capstone (CAF)	F(CF ₂ CF ₂) _n -R _f	Dupont, USA
Ammonium Peroxodisulphate (APS)	(NH ₄) ₂ S ₂ O ₈	Qualigens (Massachusetts, USA)
Liquid Ammonia	NH ₃	Fischer Scientific (Hampton, USA)
Sodium Hydroxide	NaHCO ₃	SRL Chemicals (Mumbai, India)

Synthesis of the latexes is done using the following procedure:

- 20 mL of Deionized water is taken in a Florence flask.
- A specific amount of surfactant is added and stirred at 600 rpm for 30 minutes using a magnetic bead and a magnetic hot plate.
- An equal amount of methyl methacrylate and acrylic acid was added into the flask, and stirred at 600 rpm for 30 minutes.
- 20 mL of liquid ammonia is added to the mixture and stirred for 5 minutes.
- NaOH beads were added to maintain the pH between 8-9.
- The mixture was then stirred for 30 minutes.
- Heating is started, and 0.1 gm of ammonium persulfate is added when the temperature of reaction reaches 70 °C.
- Then the temperature is raised to 80 °C, and the reaction is continued for 60-90 minutes under constant stirring at 500 rpm.
- Then the heating is turned off, and the latex is cooled under constant stirring.
- Then the emulsion is transferred to a container after filtration.



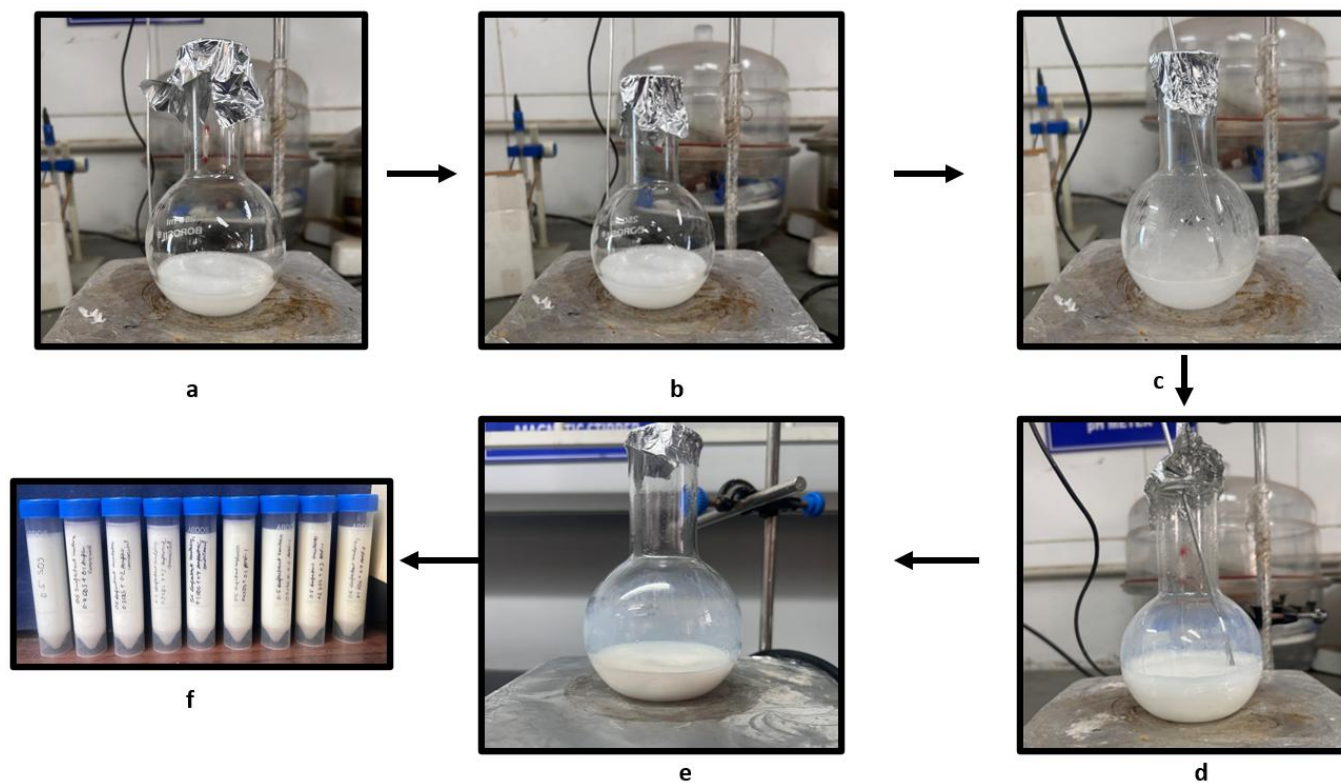


Figure 7: Experimental Setup for synthesis of PMMA-co-PAA emulsions: a) Surfactant in Distilled water; b) Monomers in reaction mixture; c) Heating the reaction mixture after pH stabilization; d) After addition of initiator; e) Cooling the emulsion after reaction completion; f) Final Latex stored in a container.

As for the amount taken of every component in the procedure refer to **tables**.

Table 5: Composition of 0.5 SDS Emulsion

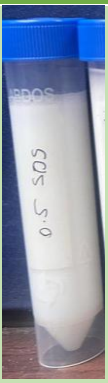
Materials	Weight (grams)	Stability	Visual
MMA	10	Stable	
AA	10		
SDS	0.5		
DW	20		
Liquid Ammonia	20		
Sodium Hydroxide	2		
APS	0.2		

Table 6: Composition for CAPB and SDS Emulsions

Materials	0.1 CAPB	0.2 CAPB	0.3 CAPB	0.4 CAPB
MMA	10	10	10	10
AA	10	10	10	10
CAPB	0.1	0.2	0.3	0.4
SDS	0.4	0.3	0.2	0.1
DW	20	20	20	20
Liquid Ammonia	20	20	20	20
Sodium Hydroxide	2	2	2	2
APS	0.2	0.2	0.2	0.2
Stability	Stable	Stable	Stable	Stable
Visual				

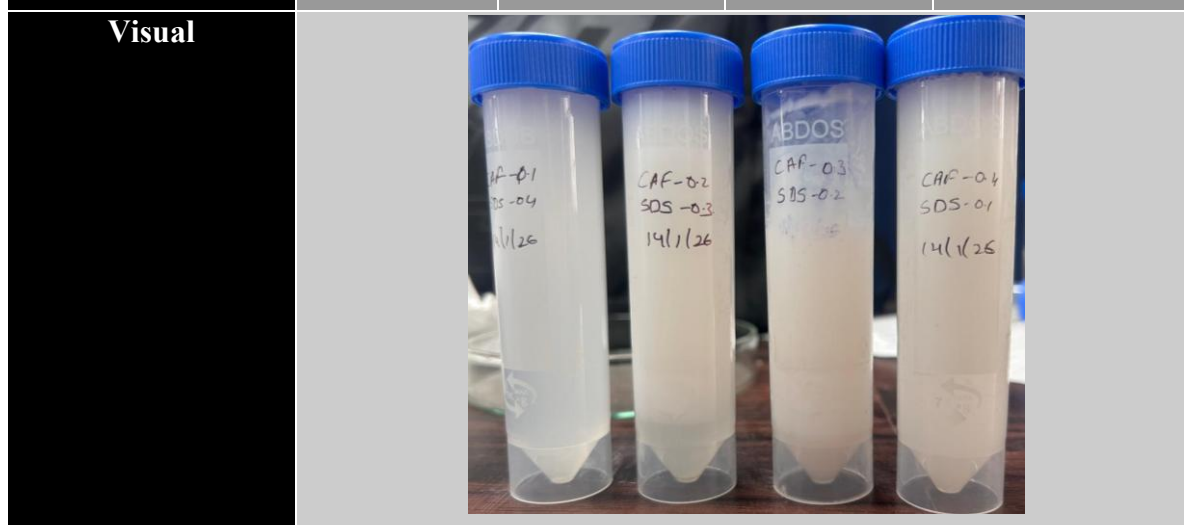
Table 7: Composition for AMF-1 and SDS Emulsions

Materials	0.1 AMF-1	0.2 AMF-1	0.3 AMF-1	0.4 AMF-1
MMA	10	10	10	10
AA	10	10	10	10
AMF-1	0.1	0.2	0.3	0.4
SDS	0.4	0.3	0.2	0.1
DW	20	20	20	20
Liquid Ammonia	20	20	20	20
Sodium Hydroxide	2	2	2	2
APS	0.2	0.2	0.2	0.2
Stability	Stable	Stable	Stable	Stable



Table 8: Composition of Capstone and SDS Emulsion

Materials	0.1 CAF	0.2 CAF	0.3 CAF	0.4 CAF
MMA	10	10	10	10
AA	10	10	10	10
Capstone	0.1	0.2	0.3	0.4
SDS	0.4	0.3	0.2	0.1
DW	20	20	20	20
Liquid Ammonia	20	20	20	20
Sodium Hydroxide	2	2	2	2
APS	0.2	0.2	0.2	0.2
Stability	Stable	Stable	Stable	Stable



3.3. Preparation of Polymer Films

A 10 cm x 10 cm silicone mould was cleaned thoroughly and kept in over after washing with acetone so that it is completely dried and any volatile substance present on it can be cleaned beforehand. Then, a calculated amount of emulsion was poured on it and then spread evenly. The bubbles were spotted over a white light and removed using a clean spatula, and then the mould was left undisturbed for 24-48 hours. The mould should be 98% covered to avoid maximum dust settling. This procedure was repeated for every concentration.

While casting, the contents in the mould appeared to be whitish according to visual inspection, but after a few hours, the contents started to appear transparent or translucent, which can be due to evaporation of volatile compounds present in the emulsion.

The film was stripped and dried from the back side for a few hours, and hence we had a standalone film which was kept in plastic pouches.

These films can be used for characterizations like tensile strength, absorbance, etc.

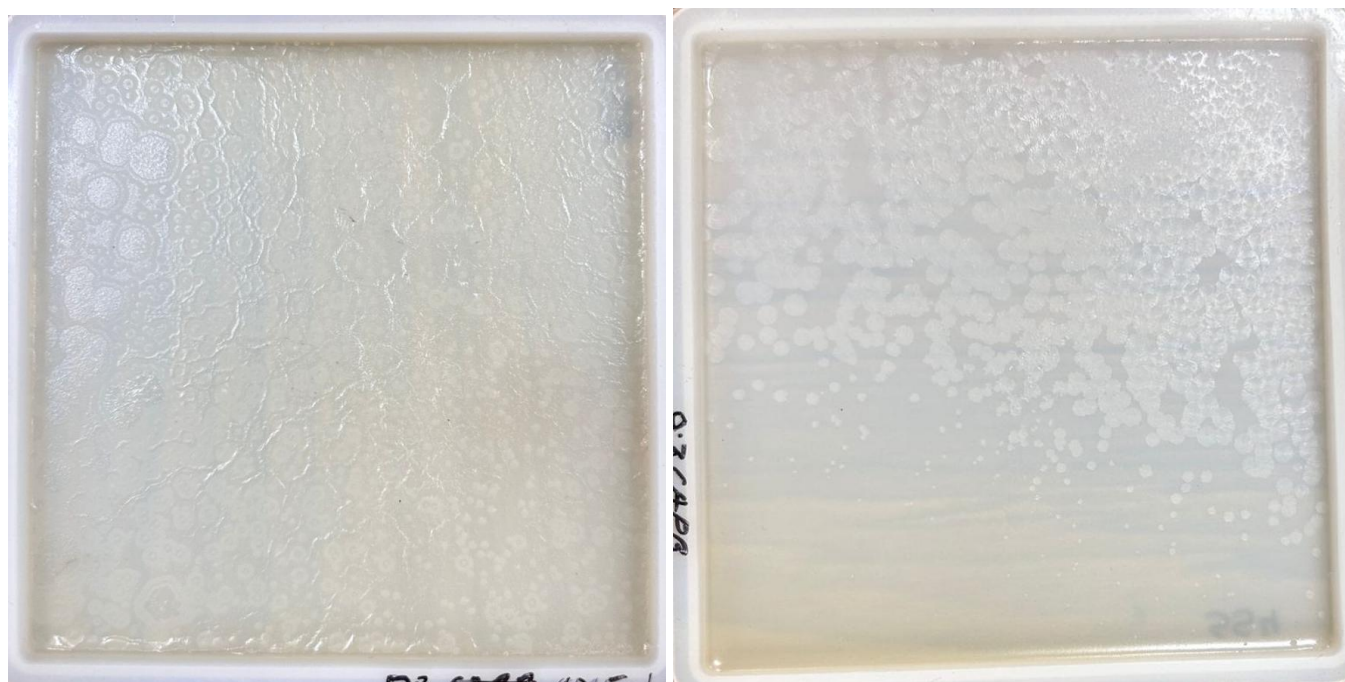


Figure 8: Preparation of Polymeric film in Silicone Mould

3.4. Coating on Wood Samples

As for wood samples Ice-cream sticks were taken. All the sticks were checked for rough surfaces or any breakage. Then their weight was noted. Then, the uncoated wood samples were dipped in the latex and kept for drying at room temperature for 24-48 hours. Then they were further kept in the oven at 50°C for about 12 hours to ensure proper drying and no residue of any VOC. Then, the weight of dried coated wood samples were recorded. The weight of the coating is as follows:

Table 9: Amount of different polymers coated on wood samples

Sample	Uncoated (W1)	After coating (W2)	Weight of polymer (W2-W1)
0.5 SDS (a)	2.1861	2.6474	0.4613
0.5 SDS (b)	3.0448	3.4495	0.4047
0.1 CAPB (a)	2.6041	2.9592	0.3551
0.1 CAPB (b)	2.7614	3.2220	0.4606
0.2 CAPB (a)	2.7540	3.1372	0.3832
0.2 CAPB (b)	2.7482	3.1900	0.4418
0.3 CAPB (a)	2.7927	3.2430	0.4503
0.3 CAPB (b)	2.3722	2.8237	0.4515
0.4 CAPB (a)	3.1727	3.9250	0.7523
0.4 CAPB (b)	3.0977	4.1560	1.0583
0.1 AMF-1 (a)	2.5272	2.8788	0.3516
0.1 AMF-1 (b)	2.8118	3.2355	0.4237
0.2 AMF-1 (a)	2.3630	2.9693	0.6063
0.2 AMF-1 (b)	2.9731	3.5424	0.5693
0.3 AMF-1 (a)	2.8625	3.3601	0.4976
0.3 AMF-1 (b)	3.1503	3.7217	0.5714
0.4 AMF-1 (a)	2.9728	3.8141	0.8413
0.4 AMF-1 (b)	3.1558	3.9819	0.8261

RESIN COATING ON WOOD PIECES

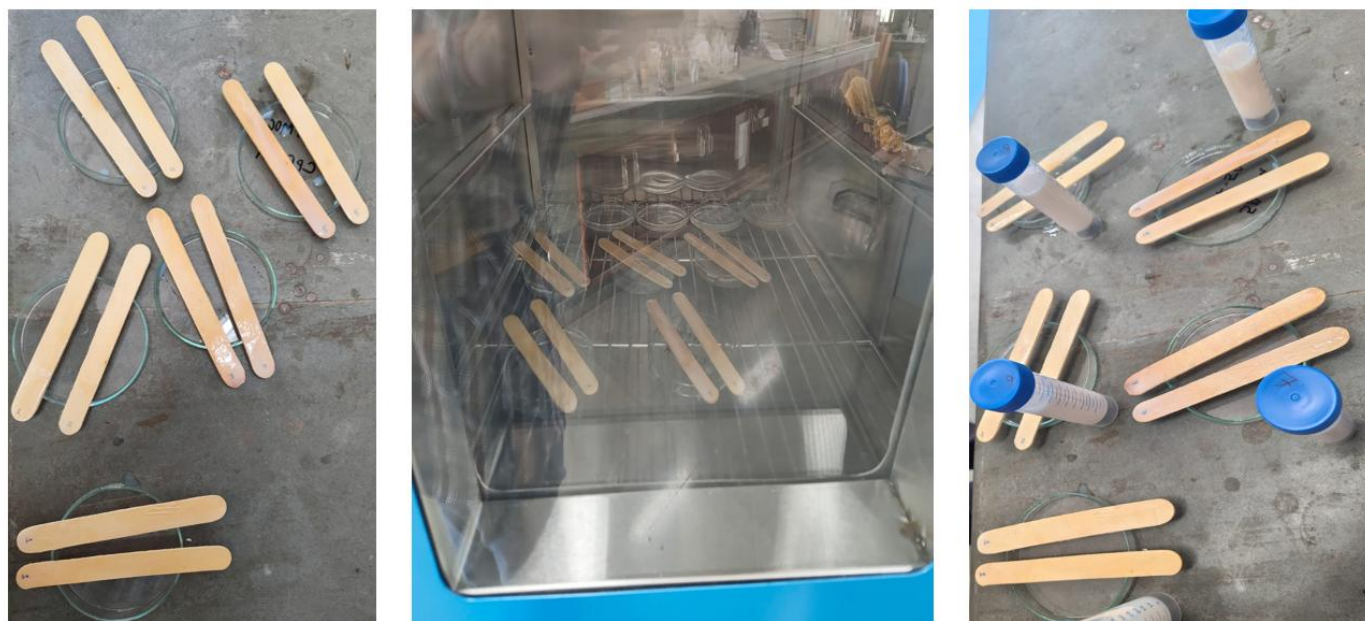


Figure 9: Latex Coating in Wood Samples

3.5. Characterization

3.5.1. Physical Properties

Monomer Conversion

One of the most important factors in emulsion polymerization that reflects the amount of polymer formed from the monomer is monomer conversion. Monomer conversion is usually measured by the ratio of monomers converted to their initial amount. High monomer conversion means high efficiency of polymerization, low amount of left-over monomers, and better performance of the resulting latex mixture. The properties of acrylic latexes are affected by monomer conversion as far as particle formation, polymer molecular weight growth, film-forming ability, viscosity, and stability are concerned.

Factors such as initiator concentration, surfactant concentration, reaction temperature, agitation speed, and monomer feed rate are involved in monomer conversion. Optimal setting of all these factors guarantees high monomer conversion and absence of coagulum formation. Insufficient monomer conversion results in some amount of unreacted monomers, which can adversely affect properties of the coating, odor, environmental safety, and durability of the latex film [59].

Methodology for Determination of Monomer Conversion

Monomer conversion was estimated using gravimetry. A specific amount of the emulsion was extracted from the reactor after the completion of the polymerization process. This was dried in a hot air oven maintained at a specific temperature of 105 °C until a constant weight was achieved. After drying, only the polymer remained while all the other elements were vaporized. The weight of this remaining polymer was carefully weighed using an analytical balance. The weight of the obtained polymer was compared with that of the initial monomer weight introduced into the system, and the percent conversion was estimated based on the above formula.

A higher value in monomer conversion means better utilization and polymerization processes. Monomer conversion of over 90% in optimized acrylic emulsions is quite common.

Percentage of monomer conversion is measured according to the formula:

$$\% \text{ Monomer Conversion} = \frac{W_3 - W_1}{\text{Total monomer in latex}} \times 100$$

Solid Content of Emulsions

Solid content is yet another important parameter in characterizing polymer emulsions. This parameter is the measure of the non-volatile content in the polymer emulsion, and it is commonly indicated in percentage form by weight. Solid content refers to the contents of the emulsion system after evaporation of all the volatile components in the system.

The solid content of an emulsion is a very important consideration in the rheology, viscosity, film formation and drying of an emulsion paint. Paints with high solid contents generally exhibit good film-forming ability and fast drying times; however, paints with too much solids can have problems with viscosity. Hence, there should be an optimal solid content to achieve proper balance between performance and stability [60].

Percentage solid content can be determined by the following equation:

$$\% \text{ Solid Content} = \frac{(W3-W1) \times 100}{(W2-W1)}$$

Where, W1= Empty petri dish

W2= Empty petri dish + Sample weight

W3= Weight after 4 hours of oven dry

Methodology for Determination of Solid Content

Solid contents of the emulsion were analyzed using the oven-drying procedure. About 1-2 grams of the emulsion was weighed in a dried aluminum dish. The dish was kept inside a hot air oven at 105 °C for a period of time until a constant mass was achieved. Due to evaporation of water and other volatile substances, solid contents of the emulsion remained as a residue in the dish. The mass of the dried substance was measured in a desiccator and the percent solid contents were evaluated as described above.

It was necessary to measure the solid contents of the emulsion in order to evaluate efficiency of the polymerization process.

3.5.2. Dynamic Light Scattering

Dynamic Light Scattering (DLS) is one of the most common methods used in characterizing polymers, emulsions, and colloids. This technique is mostly applied in determining the particle size, zeta potential, and Polydisperse Index (PDI) of emulsion particles. Such parameters are significant in the analysis of stability, uniformity, and dispersion of the latex. In acrylic emulsions, the properties of emulsion particles play a critical role in determining the physical properties such as rheological and mechanical properties of the dispersion.

Dynamic Light Scattering is based on the phenomenon where light of a certain wavelength is scattered by particles undergoing Brownian motion in the liquid dispersion. Intensity variations are measured, and the translation diffusion coefficient of particles is calculated. The speed of movement of smaller particles is high, while that of larger particles is relatively slow. Hydrodynamic particle size is estimated from DLS results.

In calculation of particle size, the following equation is used:

$$D = \frac{k_B T}{3\pi\eta d_h}$$

Where:

- D = Translational diffusion coefficient
- k_B = Boltzmann constant
- T = Absolute temperature
- η = Viscosity of dispersion medium
- d_h = Hydrodynamic particle diameter

Particle size is essential in providing stability and performance of the emulsion formulation. Smaller particles and uniformly distributed particles ensure good colloidal stability, good film formation, high gloss, and mechanical strength of the coating system. In contrast, larger particle size may cause problems like sedimentation and phase separation [61].

Polydispersity index (PDI), which can be calculated through DLS measurement, gives information about particle size distribution in the emulsion formulation system. The lower PDI values are indicative of better particle uniformity. Therefore, PDI values less than 0.3 could be regarded as adequate values for obtaining stable polymer emulsion system [62].

The zeta potential value of emulsion particles shows the electrical charge existing on the particle surface. Zeta potential value can give insight into the colloidal stability of the emulsion system since electrostatic force can prevent particles from coming together through repulsion. The higher absolute zeta potential values will contribute to emulsion stability. Repulsive forces will exist among similarly charged particles as a result of positive or negative charge from ionic surfactants and functional groups [63].

The electrophoretic mobility of particles is related to zeta potential through the Smoluchowski equation:

$$\zeta = \frac{\eta\mu}{\varepsilon}$$

Where:

- ζ = Zeta potential
- η = Viscosity of medium
- μ = Electrophoretic mobility
- ε = Dielectric constant of medium

Methodology

The particle size, polydispersity index (PDI), and zeta potential of the synthesized emulsions were analyzed using Dynamic Light Scattering (DLS) instrument provided with zeta potential analysis facility. The emulsion samples had to be diluted with distilled water prior to analysis to avoid multiple scattering issues. Gentle stirring of the samples was carried out to assure an even dispersion without formation of air bubbles.

For the measurement of particle size and PDI, the prepared sample was placed in a disposable cuvette and analyzed at ambient temperature. The intensity variations of scattered light induced by the Brownian

movement of particles were detected, and then the average hydrodynamic diameter of particles was calculated along with PDI values.

The zeta potential analysis was conducted in the following way: the emulsion sample diluted with distilled water was placed into a zeta cell with electrodes, and then an electric field was created in it. Depending on its surface charge, the movement of particles was observed under the influence of an electric field and zeta potential was calculated.

DLS analysis provides valuable information regarding particle uniformity, dispersion stability, and surface charge characteristics of polymer emulsions, making it an essential technique for the characterization of latex systems.

3.5.3. Rheology

Rheology refers to the study of the flow and deformation of materials in response to the forces of stress and strain. Rheological techniques are key in the evaluation of polymer emulsions since they give data on viscosity, viscoelasticity, stability, and the interaction of molecules in the system. Rheological studies play a major role in determining the performance properties of acrylic emulsions in terms of their manufacturing processes, stability, coating process, leveling, film-forming capability, and end-use performance. Parameters such as viscosity, amplitude sweep, and frequency sweep are among the common parameters used in the evaluation of flow behavior.

Viscosity of Emulsions

Viscosity can be referred to as the opposition shown by the fluid to its flow under the effect of the shear force. The viscosity in emulsion systems varies according to the size of particles, the solid content in the system, particle interaction, the surfactant levels, and polymer entanglement. It is important for polymer emulsions due to the effect it has on activities such as pumping, mixing, brushing, spraying, and film thickness.

Newton's law of viscosity is described as:

$$\eta = \frac{\tau}{\dot{\gamma}}$$

Where:

- η = Viscosity
- τ = Shear stress
- $\dot{\gamma}$ = Shear rate

Viscosity is known to vary when there is variation in shear rate for the majority of polymer emulsions. In this case, most acrylic emulsion fluids will show a shear thinning behavior. This is because the fluid will have its viscosity decrease as the shear rate increases [64].

Methodology for Viscosity Measurement

Viscosity of the prepared emulsions was determined through rotational rheometry using the suitable spindle geometry for rheometric studies. Before measuring the viscosity, the sample was first brought to room

temperature equilibrium. A certain amount of sample was accurately deposited on the plate of the rheometer without introducing air bubbles in it.

Viscosity was determined by conducting the study within a range of shear rate values. Shear stress measurement was accomplished by applying shear rotation to the sample. Viscosity was determined automatically by the rheometer software. Viscosity results gave important information about flow and structural properties of the emulsion system.

Amplitude Sweep Analysis

Amplitude sweep analysis is used to determine the viscoelastic region and structural strength of polymer emulsions. In this test, oscillatory strain is gradually increased while maintaining constant frequency, and the storage modulus (G') and loss modulus (G'') are measured. The storage modulus represents elastic or energy-storing behavior, while the loss modulus represents viscous or energy-dissipating behavior.

The viscoelastic properties of emulsions arise due to particle-particle interactions and polymer network formation within the system. At low strain values, the internal structure of the emulsion remains intact and exhibits a linear viscoelastic region (LVR). Beyond a critical strain value, structural breakdown begins, leading to changes in rheological behavior [65].

The complex modulus is expressed as:

$$G^* = \sqrt{G'^2 + G''^2}$$

Where:

- G^* = Complex modulus
- G' = Storage modulus
- G'' = Loss modulus

A higher storage modulus compared to loss modulus indicates dominant elastic behavior and better structural integrity of the emulsion. The crossover point where $G' = G''$ represents the onset of structural breakdown and transition from elastic to viscous behavior.

Methodology for Amplitude Sweep

Amplitude sweep test was conducted by an oscillatory rheometer through keeping the angular frequency constant. Here the emulsion sample was placed between the two plates, and its strain was slowly varied over a set strain value. During the test, rheometer recorded the value of storage modulus and loss modulus.

The range where the moduli had almost no change was the linear viscoelastic range. The point of deviation showed the breaking of structure. Through the data obtained, one could learn about the stability, deformability, and interaction of particles within the emulsion system.

Frequency Sweep Analysis

Frequency sweep testing helps understand the time dependence viscoelasticity of emulsions. This method involves changing the oscillation frequency while keeping strain in the linear viscoelastic domain. Frequency sweep gives insight into the relaxation properties, interactions, and network formation of polymer emulsions. In frequency sweep testing, storage modulus and loss modulus can be studied with respect to the angular frequency. Storage modulus is determined by the elastic nature of the sample, while loss modulus indicates the viscous characteristics of the sample. Structured emulsions typically have high values of storage modulus throughout the entire frequency range.

Complex viscosity with respect to angular frequency is related as follows:

$$\eta^* = \frac{G^*}{\omega}$$

Where:

- η^* = Complex viscosity
- G^* = Complex modulus
- ω = Angular frequency

Methodology for Frequency Sweep

Frequency sweep test was performed on the rheometer with oscillatory technique. The strain used in the test remained in the linear viscoelastic regime according to the results obtained from the amplitude sweep test. The angular frequency was varied for a certain range of values while measuring the storage and loss modulus values accordingly.

The change in the values of moduli with the change in frequency allowed us to gain knowledge regarding the viscoelastic characteristics and structural features of the emulsion samples. High values of the storage modulus showed that there was strong elastic network formation, whereas high loss modulus values meant that the samples had more fluid properties.

Rheological studies such as viscosity measurement, amplitude sweep test, and frequency sweep test give a detailed idea about the flow characteristics of polymer emulsions.

3.5.4. Wettability

Wettability is another important surface property that defines how the solid surface reacts with the liquid. Wettability is very critical for polymer emulsion coatings since it affects parameters such as adhesion, spreading, water resistance, self-cleaning, among others. The wettability of coated films can be assessed using the water contact angle between a droplet of water and the coated film. This test gives vital information about whether the coated film has a hydrophobic or hydrophilic surface.

The interactions between the liquid droplet, the solid surface, and air will play a major role in determining the droplet shape when the liquid drop falls on a solid surface. In the case where there is strong interaction between

the liquid drop and the surface, the liquid drop easily spreads, hence, leading to a reduced contact angle and improved wettability.

For emulsion paints, surface wetting behavior depends on the nature of polymers, surface roughness, particle positioning, surfactant movement, and use of functional additives such as fluorinated compounds and silicones. Hydrophobic paints usually display high water contact angles that enhance water repelling, stain resistance, and durability properties. Hydrophilic paints, conversely, display low contact angles, enabling better spread of water across the surface [66].

Water contact angle determination takes into consideration Young's equation that considers the relationship of interfacial tension between three phases namely solid, liquid, and vapor as follows:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

Where:

- γ_{SV} = Solid–vapor interfacial tension
- γ_{SL} = Solid–liquid interfacial tension
- γ_{LV} = Liquid–vapor interfacial tension
- θ = Water contact angle

The value of the contact angle directly gives an idea about the surface wettability characteristics. The surfaces having lower contact angle values than 90° are referred to as being hydrophilic, while the surfaces with contact angle values more than 90° are said to be hydrophobic. The superhydrophobic surfaces have contact angles higher than 150°.

Contact angle analysis is especially relevant when considering acrylic emulsion coatings since it helps to assess the effect of surfactants, copolymers, and surface active substances on coating performance. Incorporating fluorine-containing surfactants or hydrophobic monomers usually leads to higher contact angles due to lowering the surface energy. Hydrophobicity improves the moisture, corrosion, and dust resistance of the coatings .[67]

Coating wettability plays an important role in application properties as well. It is vital to control wettability of the coating in order to create an optimal compromise between spreading and water resistance. The surfaces that are too hydrophobic can adversely affect the adhesion of coating to a particular substrate; at the same time, the highly hydrophilic surfaces might suffer from insufficient water-resistance.

Methodology for Water Contact Angle Measurement

Wettability analysis was done using a contact angle goniometer. Before testing, coated films were produced through evenly spreading the emulsion on clean substrates and letting them dry in controlled environment conditions. The coated films were also protected from any dust particles, water and other contaminations prior to wettability measurement.

A minute drop of distilled water was dropped on the surface of the coating using a microsyringe. Once the drop was put on the surface, its image was taken through a high-resolution camera fitted in the goniometer apparatus. The resulting contact angle formed by the water drop and the coating surface was calculated using an imaging analysis program.

Several measurements were made in various parts of the coating surface in order to increase the validity of data obtained. The mean values of all contact angles obtained were reported as the overall water contact angle of the coating system.

Smaller contact angles showed that the surface had better wettability and affinity to water molecules. On the other hand, larger contact angles signified high hydrophobicity and low surface energy. The data obtained was quite significant for determining the influence of the constituents used in the formulations on the surface properties and water resistance of the coatings.

Contact angle test is one of the most efficient methods for determining the surface properties of polymer emulsion-based paints and coatings. This method provides valuable data about hydrophobicity, surface energy, and coating performance.

CHAPTER-4

RESULT AND

DISCUSSION

Poly(MMA-co-AA) was successfully synthesized using batch emulsion polymerization. We first synthesized the latex using pure sodium dodecyl sulfate, which is an anionic surfactant, that gave us a stable emulsion. Then, a commercial amphoteric surfactant (cocoamidopropyl betaine) is used with SDS at varying concentrations to prepare the latex. Similarly, a lab-made amphoteric fluorosurfactant (AMF-1) is used with SDS at varying concentrations to prepare stable latex. We also tried preparing latex using pure amphoteric surfactant, but that resulted in agglomeration of the emulsion. The results of agglomerated latex are as follows:

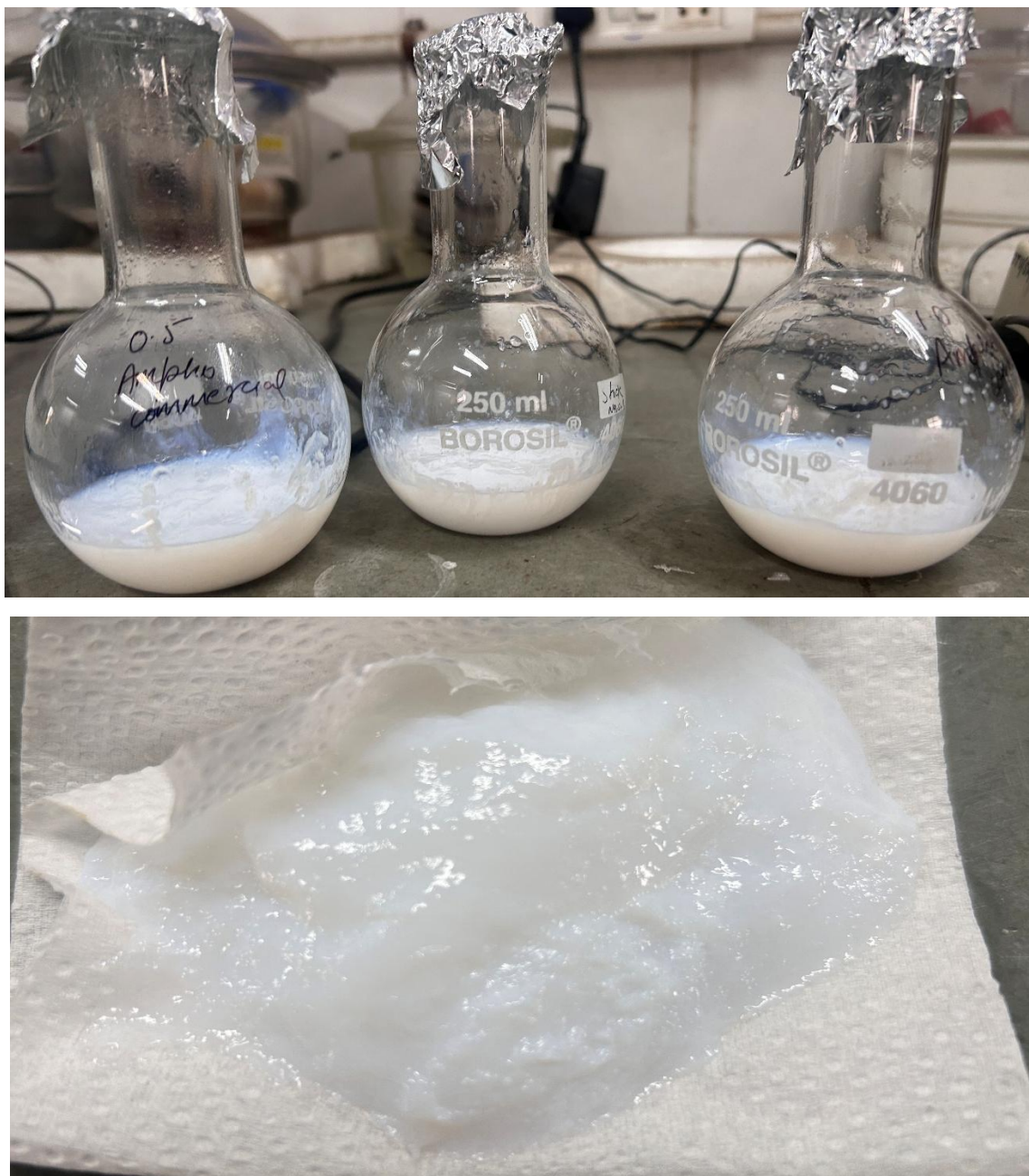


Figure 10: Picture of agglomerated latex from amphoteric surfactant

4.1 Emulsion Characterization

- The colloidal stability of the latexes was observed through visual appearance.

- The solid content of latexes was measured by the gravimetric method. Initially, an empty petri dish was cleaned, dried, and weighed. Then a known amount of latex sample was taken in petri dish and kept in hot air oven at 100 °C for 24 hours so that water and unreacted monomers can be removed from the sample. The petri dishes were then cooled, and their weights were taken. The solid content was then calculated using the following formula:

$$\% \text{ Solid Content} = \frac{(W3-W1) \times 100}{(W2-W1)}$$

Where, W1= Empty petri dish

W2= Empty petri dish + Sample weight

W3= Weight after 4 hours of oven dry

- The percent conversion of monomers to the final product was also measured gravimetrically. The method used was the same as the method for solid content but the calculations were different. The percent conversion was calculated using the following formula:

$$\% \text{ Monomer Conversion} = \frac{W3-W1}{\text{Total monomer in latex}} \times 100$$

Here, W3= weight after oven dry

W1 = Empty petri dish





Figure 11: Gravimetric Method used for the determination of Solid Content and monomer conversion

Table 10: Solid Content and Monomer conversion in all latexes

Sample	% Solid Content (Th 38%)	% Monomer Conversion
0.5 SDS	34.72	91.8
0.4 SDS+0.1 CAPB	25.21	66.7
0.3 SDS+0.2 CAPB	30.64	81.03
0.2 SDS+0.3 CAPB	30.86	81.62
0.1 SDS+0.4 CAPB	36.16	95.65
0.4 SDS+0.1 AMF-1	28.68	75.8
0.3 SDS+0.2 AMF-1	32.27	85.3
0.2 SDS+0.3 AMF-1	33.53	88.67
0.1 SDS+0.4 AMF-1	36.57	96.74

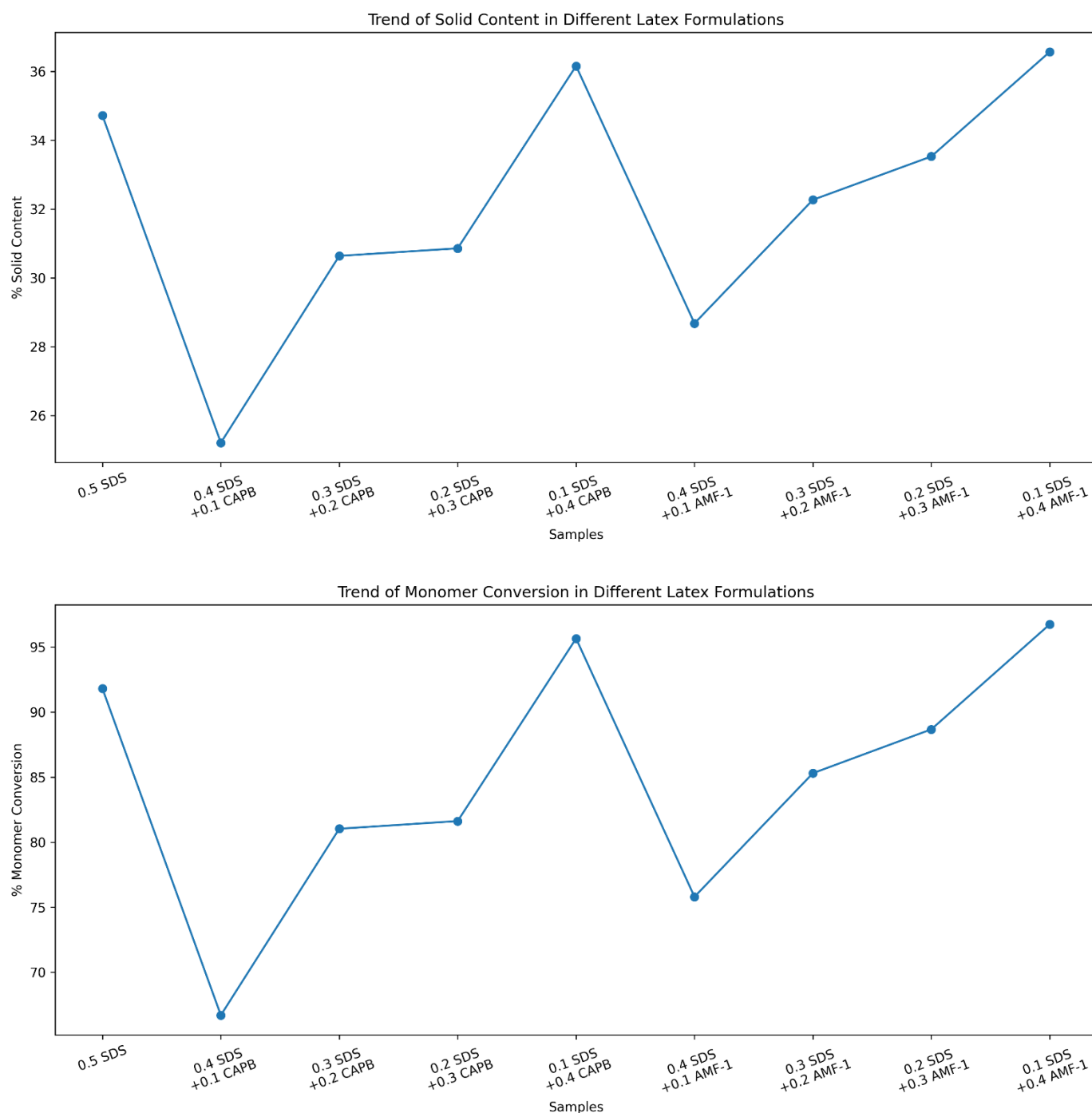


Figure 12: Trends for Solid Content and Monomer Conversion in different latex formulations

From the percentage solid content and monomer conversion data obtained from the latex systems prepared, there is evidence of the importance of surfactant composition on the emulsion polymerization effectiveness. Despite the total concentration of the surfactants being kept constant among the different surfactant systems tested, substitution of SDS for CAPB or AMF-1 resulted in differences in emulsion polymerization, thus confirming that the type of surfactant mixture plays a very important role in particle nucleation, micelle formation, transport, and stabilization of latex particles during emulsion polymerization.

For the system where the latex was stabilized by only SDS, there was 34.72% solid content and monomer conversion of 91.8%. SDS is an anionic surfactant that has sulfate groups with negative charges which offer strong electrostatic stabilization to the latex particles. With the formation of stable SDS micelles in the aqueous phase, nucleation becomes more effective along with radical diffusion into the polymer particles. As such, many monomer molecules were converted into polymers, giving rise to high monomer conversion and solid content.

When there is partial substitution of SDS with CAPB, a marked reduction in the amount of solid content and the percentage monomer conversion is noted. There is a solid content of 25.21% and monomer conversion of 66.7% in the 0.4 SDS + 0.1 CAPB mixture, which are much smaller values than in the pure SDS system. The first reason that accounts for the decrease may be interference with the SDS micelle formation due to the use of a small amount of CAPB. In the absence of sufficient CAPB concentration, the formation of stable micelles may not have occurred properly, resulting in improper nucleation and poor stabilization of polymer particles. This may affect the stability of the colloidal dispersion system and increase the chance of particle aggregation. Further increases in the CAPB concentration resulted in the steady enhancement in both solid content and monomer conversion percentage. Formulations of 0.3 SDS + 0.2 CAPB and 0.2 SDS + 0.3 CAPB showed monomer conversion values of 81.03% and 81.62%, respectively, along with increased solid content. These results imply a favorable synergistic effect between the two types of surfactants due to the interactions of their charge centers. The amphiphilic nature of CAPB makes it have both positive and negative centers. Consequently, this causes interactions between the amphoteric CAPB and the negatively charged SDS, hence reducing electrostatic repulsion between surfactant molecules and leading to the production of more stable and organized mixed micelles.

The formulation of 0.1 SDS + 0.4 CAPB had the highest monomer conversion percentage and solid content. This formulation produced 95.65% and 36.16% monomer conversion and solid content, respectively. The high monomer conversion value when compared to the value obtained for the SDS solution implies that at higher CAPB concentrations, a more stabilized polymerization system is achieved through interaction of mixed surfactants.

An analogous trend was also noticed for the AMF-1-containing samples, but here the enhancement in polymerization efficiency was more significant in comparison with the CAPB systems. The sample composed of 0.4 SDS + 0.1 AMF-1 yielded slightly lower results in terms of the degree of monomer conversion (75.8%) and solid content (28.68%), which can be related to the initial influence of low concentration of AMF-1 on the disruption of the SDS micelles. In turn, the increase in AMF-1 concentration led to an increment in both the values considered. The samples with 0.3 SDS + 0.2 AMF-1 and 0.2 SDS + 0.3 AMF-1 yielded conversion values of 85.3% and 88.67%, respectively.

The highest results were achieved using the sample with 0.1 SDS + 0.4 AMF-1, where the monomer conversion reached 96.74%, and the solid content amounted to 36.57%. The excellent results attained in case

of AMF-1 might be associated with some properties of fluorinated amphoteric surfactant. Fluorinated surfactants are known to have exceptionally high surface activity and very low interfacial energy. Given the high interfacial activity of the AMF-1, there might be better monomer distribution and efficient formation of more stable mixed micelles and polymer particles. Moreover, the fluorination of chains could have made inter-particle stabilization more effective and prevented their coagulation at the stage of polymerization, thereby making the conversion of monomers into polymers more effective.

The very high correlation of the solid content and monomer conversion shows that the rise in solid content was mainly associated with a higher level of polymerization. It means that the amount of monomers participating in chain propagation was much higher than those participating in other processes in the reaction medium. Thus, the quantity of polymer formed was considerably higher as well. From this perspective, it can be concluded that the use of amphoteric and fluoroamphoteric surfactants significantly affected the process of polymerization. As for all formulations under consideration, the AMF-1 formulations showed the best performance owing to its outstanding interfacial and surface activity.

While synthesizing the latex of PMMA-co-PAA using a commercial amphoteric fluorosurfactant (in our case, Capstone, Dupont, USA), as we took 0.5 grams of surfactant in formulations, all the latex was found to be in the range of oligomers (As % monomer conversion is found to be less than 50%). This means no further studies can be done on them. The results for their monomer conversion are as follows:

Table 11: Results for monomer conversion of Latex prepared using Capstone, Dupont.

Samples	% Solid Content/ Th 38 %	% Monomer Conversion
0.1 CAF	18.62	49.25
0.2 CAF	17.34	45.87
0.3 CAF	16.12	42.64
0.4 CAF	17.97	47.54

The laboratory-synthesized amphoteric fluorosurfactant produced stable PMMA-co-PAA latex dispersions because its molecular structure and interfacial behavior were more suitable for controlled micelle formation and particle stabilization during emulsion polymerization. The surfactant likely formed stable mixed micelles with SDS, which promoted efficient particle nucleation, radical entry, and continuous polymer chain growth, resulting in stable latex particles with high monomer conversion.

In contrast, the commercial amphoteric fluorosurfactant (Capstone, DuPont, USA) resulted predominantly in oligomer formation instead of stable polymer latex particles. This behavior may be attributed to the extremely high surface activity and different aggregation behavior of the commercial fluorosurfactant, which likely disturbed the SDS micellar structure and altered the nucleation mechanism during polymerization. The strong interfacial adsorption of the commercial fluorosurfactant may have promoted premature radical termination,

unstable particle nuclei, and insufficient chain propagation, thereby favoring formation of low-molecular-weight oligomeric species instead of fully developed polymer particles.

Furthermore, the commercial fluorosurfactant might have varied HLB values, molecular structure, and functional groups from those of the laboratory synthesized fluorosurfactant. Such differences will greatly affect the behavior of monomer diffusion, micelles, and particles during emulsion polymerization. In this regard, the laboratory-synthesized ampholytic fluorosurfactant allowed successful latex formation while the commercial fluorosurfactant inhibited the polymerization reaction and created oligomers.

4.2 Dynamic Light Scattering

Dynamic Light Scattering is a technique used for characterising the particle size and stability of the latex. It analyses the Brownian motion arises due to the collision or bombardment of solvent molecules. It is also used to check Poly-dispersity Index and Zeta Potential which can tell us about nature of mixture whether it is homogeneous or heterogeneous and stability if the mixture.

The particle size and zeta potential of the latex was analyzed b using Dynamic Light Scattering (DLS) on a Malvern Zetasizer ZS90 (Malvern Instruments, UK). Both the parameters were measured after diluting high concentrated latex with deionized water (approximately 50 times dilution). For particle size polystyrene cuvette was used and for zeta potential Disposable Capillary Cell (DTS1070) was used.

Table 12: Dynamic Light Scattering Results

Sample	Particle Size (d.nm)	Zeta Potential (mV)	Polydispersity Index
0.5 SDS	577.2	-51.5	0.278
0.4 SDS+0.1 CAPB	520.4	-34.9	0.178
0.3 SDS+0.2 CAPB	629.8	-38.9	0.173
0.2 SDS+0.3 CAPB	704.1	-13.6	0.180
0.1 SDS+0.4 CAPB	772.9	-43.8	0.260
0.4 SDS+0.1 AMF-1	537.2	-10.9	0.191
0.3 SDS+0.2 AMF-1	447.9	-11.3	0.191
0.2 SDS+0.3 AMF-1	564.7	-35.0	0.095
0.1 SDS+0.4 AMF-1	634.1	-30.5	0.218

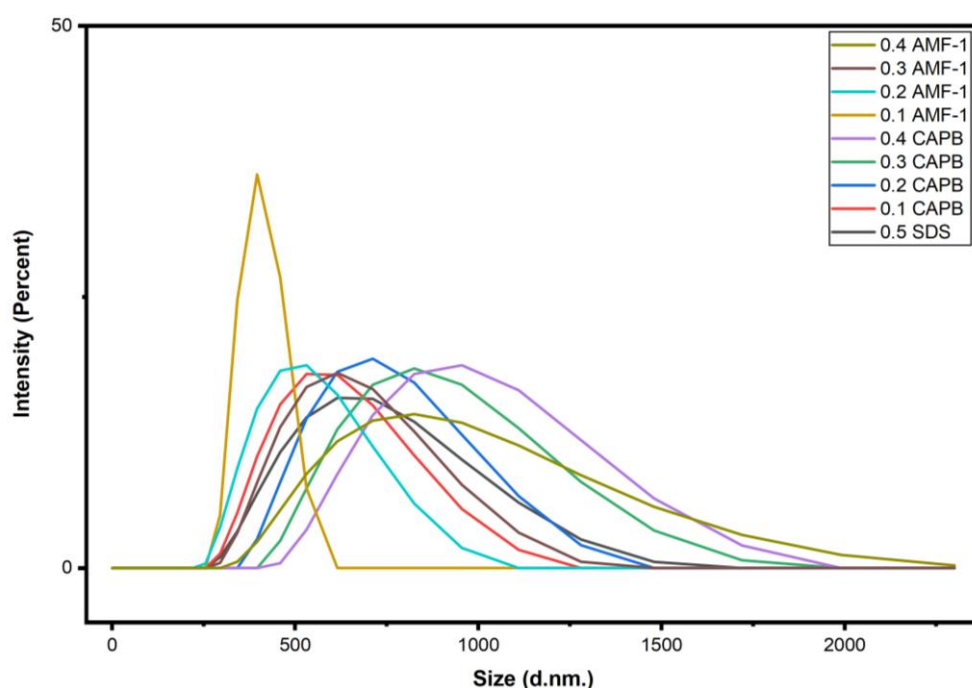


Figure 13: Particle size distribution profiles of the latexes (with different surfactant systems)

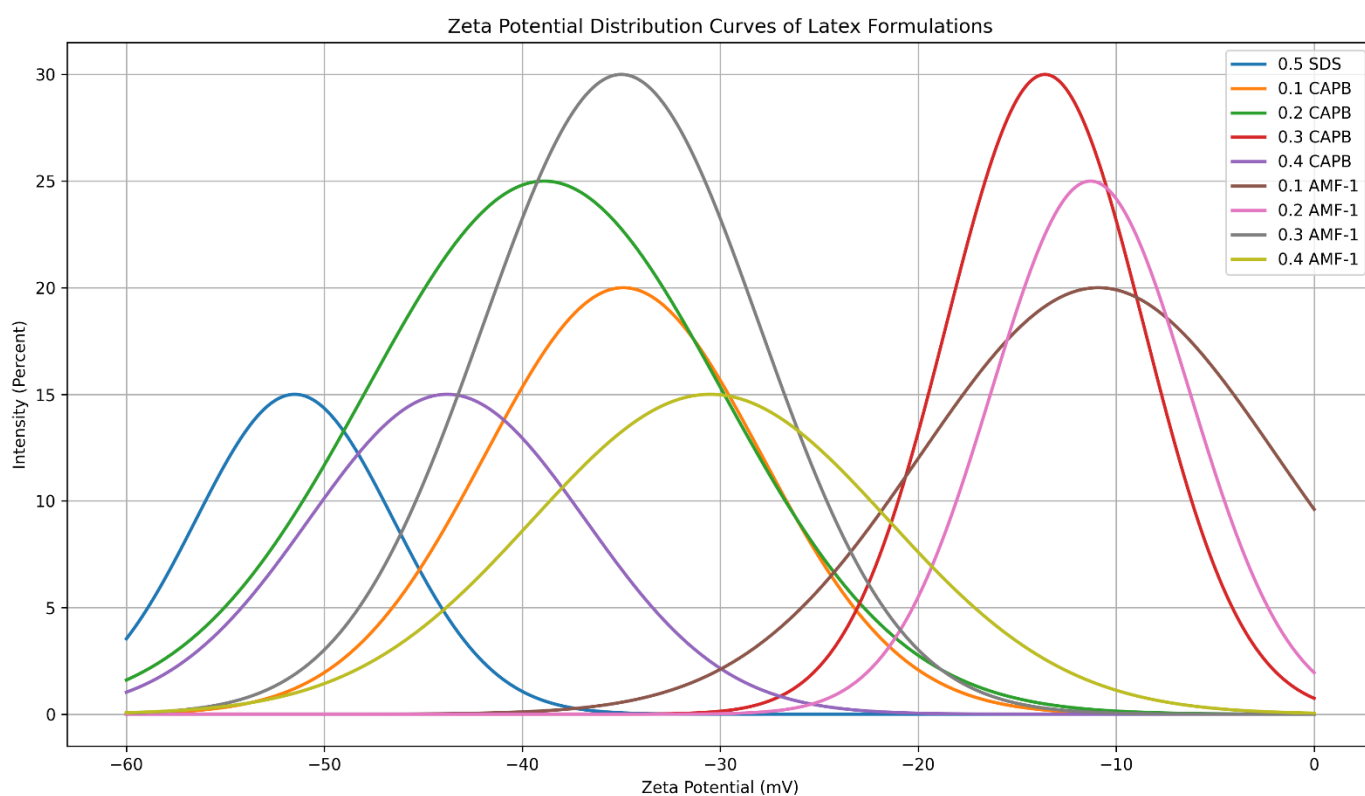


Figure 14: Zeta Potential Distribution profiles for the latexes (with different surfactant systems)

The latex prepared using only SDS exhibited an average particle size of 577.2 nm with a zeta potential value of -51.5 mV and a PDI value of 0.278. The highly negative zeta potential indicates strong electrostatic stabilization of the latex particles due to the presence of negatively charged sulfate groups of SDS adsorbed on the particle surface. The large magnitude of zeta potential generated strong repulsive forces between particles, thereby preventing aggregation and maintaining colloidal stability of the latex system. The particle

size obtained for the SDS-stabilized latex suggests effective micellar nucleation and particle growth during emulsion polymerization. But the relatively high value of PDI suggests a wider range of particle sizes in the sample, implying that there are particles of different diameters in the dispersion.

The addition of CAPB to the surfactant mixture resulted in a number of changes in the particle size, zeta potential, and particle size distribution. The mixture composed of 0.4 SDS + 0.1 CAPB showed the lowest particle size of 520.4 nm and zeta potential of -34.9 mV. In particular, the drop in particle size can be explained by a better packing of surfactants and improved surface properties associated with synergistic effects of anionic SDS and amphoteric CAPB. In this regard, CAPB probably entered the inter-surfactant space in the vicinity of the interface, decreased the electrostatic repulsion between the sulfate heads, and formed more compact mixed micelles and particles during nucleation. The lower value of PDI – 0.178 – is another evidence of a tighter particle size distribution than in the case of SDS solution.

With the further increase in CAPB concentration, a slow rise in particle size could be seen. In this regard, the 0.3 SDS + 0.2 CAPB and 0.2 SDS + 0.3 CAPB mixtures had particle sizes of 629.8 nm and 704.1 nm, respectively. This increase in particle size can be explained by some reduction of electrostatic stabilization due to partial addition of amphoteric surfactant molecules to the interface between surfactants. Zeta potential decreased for those mixtures, especially for 0.2 SDS + 0.3 CAPB, where the zeta potential value amounted to -13.6 mV. Such a small zeta potential value meant lower electrostatic repulsion forces between particles and allowed for further particle growth while preventing aggregation during polymerization process. The relatively low PDI values (0.173–0.180) indicate reasonably homogeneous particle distribution in all samples with the addition of CAPB surfactant to the mixture.

The mixture of 0.1 SDS + 0.4 CAPB surfactants provided the largest particle size among all formulations containing CAPB – 772.9 nm on average. Such an increase in particle size may be caused by higher interaction of particles and rearrangement of interfacial layer surfactant molecules. The possible reason for a smaller number of larger particles at elevated CAPB concentration could be due to modification of the micellar aggregation process along with the reduction of electrostatic stabilization. Nonetheless, the negative zeta potential of -43.8 mV showed that even though there were larger particles formed, they still had good stability. On the other hand, an increased PDI of 0.260 suggests a broad size distribution of particles at higher CAPB concentration, which may signify the existence of different-sized particles and partial aggregation.

On the other hand, the formulations having AMF-1 presented significantly different colloidal behavior from the CAPB-based samples due to their special nature, as AMF-1 is a fluorinated amphoteric surfactant. In particular, the sample consisting of 0.4 SDS + 0.1 AMF-1 presented a particle size of 537.2 nm with a zeta potential of -10.9 mV and PDI of 0.191. The rather low absolute value of zeta potential suggested that electrostatic stabilization played a smaller role. Nevertheless, the dispersion was stable, which meant that the stabilization may happen sterically or via the interface.

Among all the formulations prepared, the one with 0.3 SDS + 0.2 AMF-1 had the smallest particle size with an average particle diameter of 447.9 nm. This indicates that moderate addition of the fluoroamphoteric surfactant played a role in enhancing monomer emulsification and particle nucleation. Fluorosurfactants have been found to possess excellent surface activities and extremely low interfacial energies. Such properties facilitate the generation of fine and well-stabilized monomer emulsions. It is reasonable to assume that effective stabilization promoted particle nucleation, leading to smaller, more uniform particle formation during the process of polymerization. The low PDI value of 0.191 confirms this conclusion.

However, particle size once again started increasing upon further increases in AMF-1 concentration, as seen from formulations with 0.2 SDS + 0.3 AMF-1 and 0.1 SDS + 0.4 AMF-1 that showed particle sizes of 564.7 nm and 634.1 nm, respectively. The increase in particle size due to higher concentrations of the fluorosurfactant could be linked with changes in the aggregation state of the surfactants in the interfacial film coating the particles.

The formulation having a composition of 0.2 SDS and 0.3 AMF-1 was found to have a zeta potential value of -35.0 mV and lowest PDI value of 0.095 amongst all formulations. The extremely low value of PDI means that there is extremely uniform distribution of particles within the latex system. Based on moderate particle size, sufficient zeta potential value, and extremely low PDI value, the stability of polymer particles was considered to be very good in this particular formulation.

The formulation of 0.1 SDS and 0.4 AMF-1 was found to have a zeta potential value of -30.5 mV and PDI value of 0.218. In spite of increased particle size in higher AMF-1 concentration, the zeta potential value is still quite sufficient for maintaining the stability of colloids [68].

4.3 Rheological Studies for SDS Latex

Rheology studies include experiments related to the analysis of behavior of a material under stress or strain. Rheological studies are very important for the determination of viscosity, elasticity, and viscoelasticity of complicated fluids and soft solids like solutions, melts, emulsions, suspensions, and gels. Based on rheological data, the structure and behavior of a material under varying shearing rate, frequency, and temperature conditions can be analyzed. It is used extensively by industries like material science, polymer engineering, pharmacy, food industry, and paint industry for formulation optimization and ensuring process and product quality.

The rheological studies for the sample was done using Anton Paar Modular Compact Rheometer 303 and the spindle used is PP25 for various studies like viscosity, amplitude sweep and frequency sweep.

The results for the same are as follows:

4.3.1. Viscosity

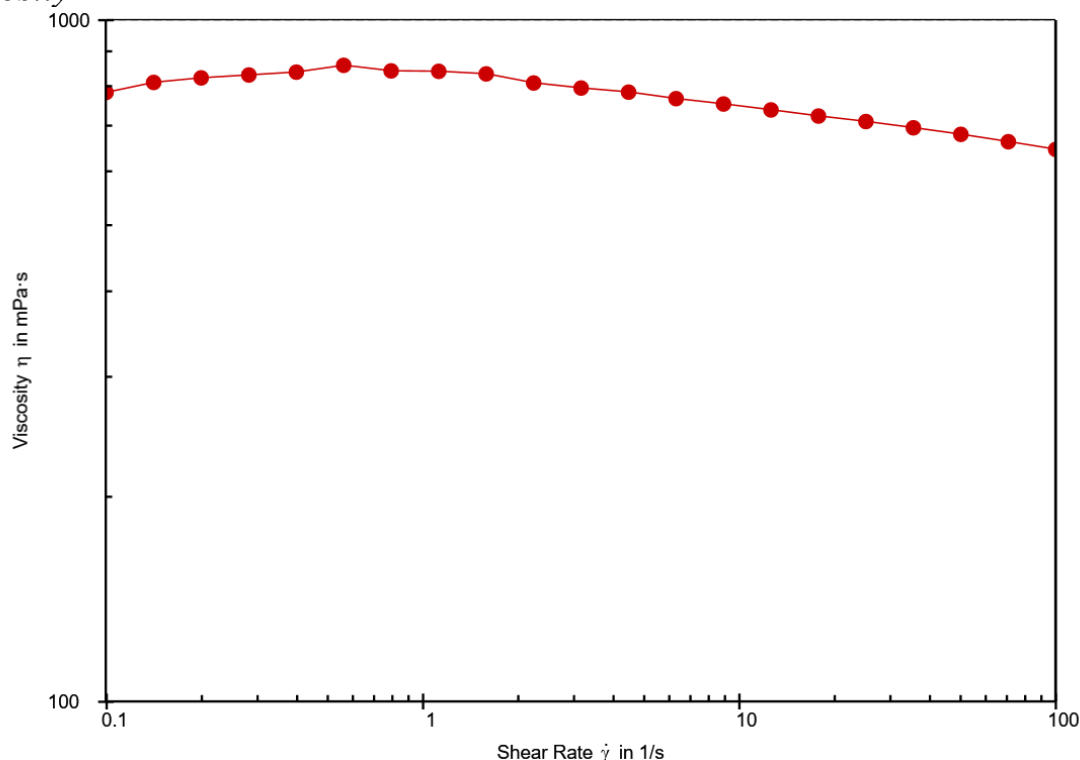


Figure 15: Viscosity Vs Shear Rate curves for latex prepared using SDS

The viscosity profile of the emulsion obtained for MMA- AA using SDS shows the behavior of the synthesized latex with respect to rheology under various shear rates. As depicted in the graph, there is an increase in viscosity with a slight rise at lower shear rates but a steady decrease as the shear rate rises further. Such behavior depicts that the emulsion shows a non-Newtonian flow character with a shear-thinning characteristic. At low shear rates, the viscosity remains relatively high due to the presence of interaction forces between the molecules and a poorly organized structure of the polymers in the aqueous solution. In the case of emulsion polymerization using MMA- AA, the dispersed polymer particles in the emulsion are stabilized using SDS. This anionic surfactant acts as a stabilizer by giving electrostatic stabilization to the polymer particles in the emulsion. The negatively charged sulfate groups present in the latex give repulsion forces between the particles, and hence no coagulation takes place. Due to such stability, a uniform particle system is formed with relatively low flow resistance.

The small rise in viscosity noted at extremely low values of the shear rate can be explained by the temporary interactions of particles or flocculate structures temporarily formed in the continuous phase. As long as the shear rate is relatively low, the structures formed in the continuous phase do not break down and increase the resistance to flow. As soon as the shear rate rises, the effect of the external force destroys the temporary structures and causes alignment of dispersed polymer particles in the direction of the flow. Therefore, viscosity falls progressively with increasing shear rate.

As we can see, the steady decline of the viscosity with the rising shear rate testifies to the presence of shear thinning behavior in the emulsion system. In such systems, polymers and dispersed particles become oriented

in the direction of flow under the influence of an external force, thereby decreasing viscosity. The fact that the viscosity reduction process occurs gradually indicates good colloidal stability of the emulsion and absence of any decomposition or separation of its components under shearing. It means that latex synthesis yielded a homogeneous dispersion.

The rheological performance in the case of SDS stabilized MMA-AA emulsion can be related to some of the molecular features of the surfactant used. In the first place, it should be mentioned that SDS is a low molecular weight surfactant that is able to effectively reduce interfacial tension in the emulsion. Moreover, due to its electrostatic stabilization capacity, it provides effective particle stabilization which leads to relatively low viscosity of the emulsion in comparison with systems based on associative or polymeric surfactants. Thus, good viscosity control in the range of shear shows high effectiveness of stabilization.

Moreover, the absence of any sharp changes in viscosity level shows mechanical stability of the emulsion under shear conditions. It is an important feature of this emulsion since in practice emulsions intended for use in the form of paints or coatings may experience various shear stresses during the mixing process, pumping, painting, or spraying.

The rheological behavior of this system suggests that it is a stable, shear-thinning emulsion, with good particle dispersion and flow properties. The trade-off between reducing the viscosity of the system and its stability suggests that the SDS acts to stabilize the polymer particles in the emulsion successfully [69].

4.3.2. Amplitude Sweep

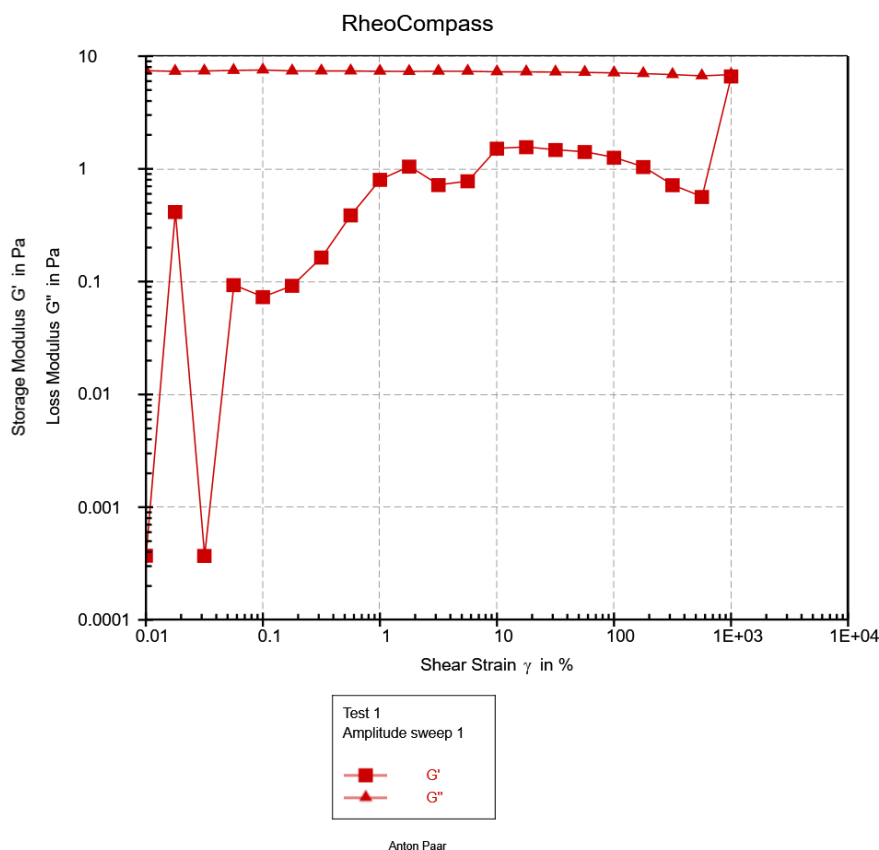


Figure 16: Amplitude Sweep Curve for latex prepared using SDS

The amplitude sweep plot for the SDS stabilized MMA–AA emulsion reveals some vital data on the viscoelastic behavior of the emulsion system at increased strain. In this research, the storage modulus (G') and loss modulus (G'') have been measured against the varying strain. The storage modulus is the energy storing capacity of the material while the loss modulus is the energy dissipating capacity of the material. The comparison between the two moduli can give an idea about the internal structure and deformation of the emulsion.

From the graph, it is clear that the loss modulus (G'') is much larger than the storage modulus (G') at all strain levels. This proves that the emulsion possesses more viscous characteristics rather than elastic and solid characteristics. Viscous behavior is usually exhibited by polymeric latex systems because of the significant contribution of aqueous medium in fluidity. It is quite evident that the SDS stabilized MMA–AA emulsion is mostly viscous and liquid-like in nature.

For very low strain values, there is a little fluctuation in the storage modulus. This indicates that it is comparatively small. This can be explained based on the weak structuring between polymer particles in the dispersion state. This is because the used SDS is a low molecular weight anionic surfactant. In such case, stabilization takes place based on electrostatic repulsion instead of having a very well-structured interconnection between the particles. Therefore, there is little aggregation of the latex particles in the dispersion, and the elastic contribution is small.

The loss modulus is nearly constant for a broad strain range. This shows the viscous nature of the emulsion. It means that the structure is not easily destroyed under the imposed shear deformation. The stable profile of the loss modulus implies a very stable structure for the system as well as uniform distribution of the latex particles. In addition, this shows the stability of the colloidal structure due to the adsorption of the SDS molecules on the particle surfaces.

With further increase in the strain values, there is a gradual increase in the value of the storage modulus. However, even at relatively higher strain values, the storage modulus still stays smaller compared to the loss modulus. Therefore, there is no crossing of the curves G' and G'' that confirms that the studied emulsion does not become predominantly elastic or gel-like substance.

It should be noted that a rather broad linear viscoelastic region can be observed on the diagram above that means the stability of the emulsion structure at high strains when the destruction of the emulsion begins to occur. Such property is convenient for the studied emulsion since coatings and paints are usually subjected to different strains. In this way, the rheological stability of the studied material in deformation is beneficial for handling, pumping, brushing, and spraying.

It is interesting to mention how the rheological properties of the studied emulsion are related to its structure. First of all, it should be noted that the use of acrylic acid in the composition leads to the introduction of polar hydrophilic carboxylic groups, which increases the hydrophilic properties and helps stabilize particles in the

aqueous environment. However, the inclusion of methyl methacrylate gives the copolymer additional rigidity and mechanical strength due to its rigidity.

In conclusion, the results of the amplitude sweep test show that the SDS stabilized MMA-AEmulsion is structurally stable, and its rheology shows viscous dominant properties with limited elasticity. The sample is highly mechanically stable when deformed. This proves that the SDS used to stabilize the sample effectively did so while maintaining the right flow properties.

4.3.3. Frequency Sweep

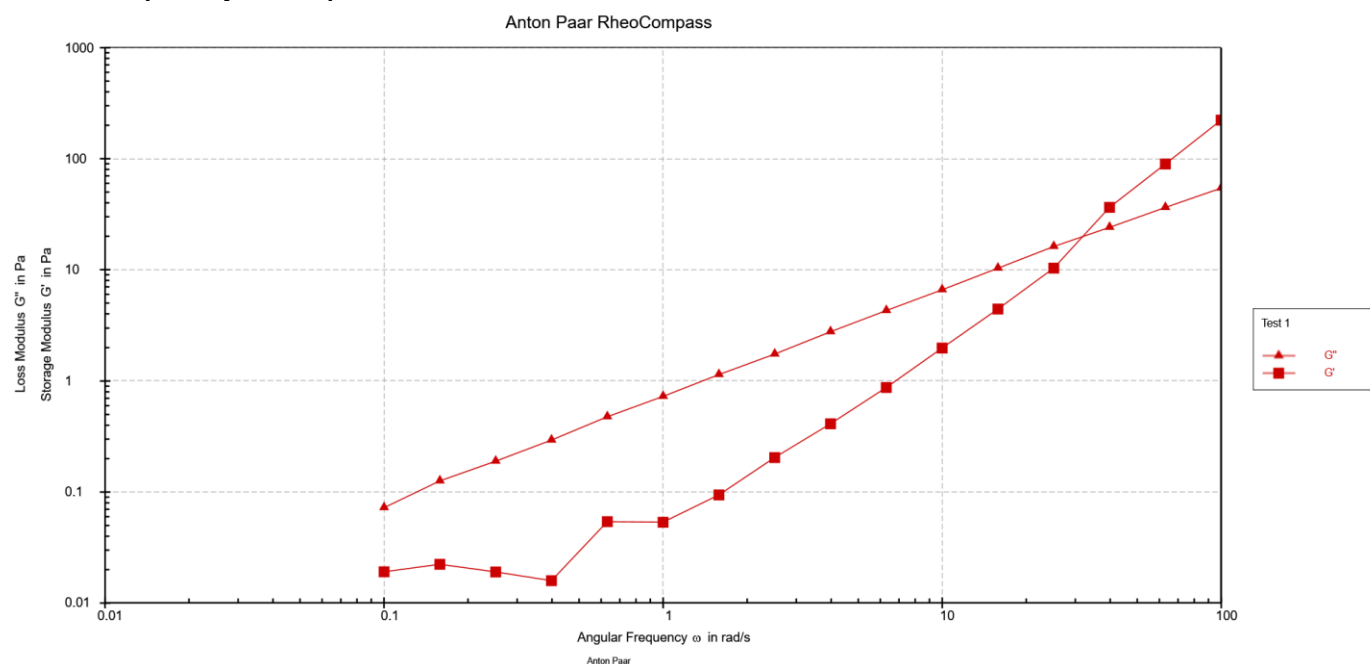


Figure 17: Frequency Sweep Curve for latex prepared using SDS

Frequency sweep of the SDS-stabilized MMA-AA emulsion gives some insight into the viscoelastic behavior of the material and how it deforms under oscillatory shear. During the frequency sweep experiment, values for the storage modulus (G') and loss modulus (G'') were obtained at various angular frequencies. Storage modulus is a measure of elasticity and is concerned with the energy storage while loss modulus is a measure of viscosity, measuring energy dissipation. The variations in these properties give some information on how particles in the dispersion interact structurally as well as the relaxation behavior.

It is evident from the rheology plot that both storage modulus and loss modulus increase steadily with the increase in the angular frequency. The difference between the two moduli also shows that the loss modulus is much greater than the storage modulus, implying that the material is behaving as a viscous fluid at the lower frequencies. In latex dispersions, where the polymer particles can freely move around, this type of rheological behavior is expected. As low frequencies denote a slow rate of deformation, enough time is allowed for relaxation.

The higher values of G'' for most part of the frequency range imply that there is a higher amount of dissipation compared to elasticity. This is indicative of the fact that the SDS-stabilized emulsion has more fluid-like rheological properties and does not form a rigid gel. This can be explained by the mechanism of stabilization of the polymer particles by sodium dodecyl sulfate (SDS), an anionic surfactant. Due to the repulsive electrostatic force between the charged latex particles, they do not aggregate but remain dispersed in the aqueous solution. This ensures the existence of a relatively loosely packed structure without high elasticity.

It can be observed that at low angular frequencies, the storage moduli are relatively small, implying that elastic forces are relatively low between the polymer particles. Thus, it can be inferred that the internal structure of the emulsion is not very connected. However, when the angular frequency is increased, storage modulus becomes much larger, particularly in the higher frequency range. This implies that elasticity is becoming significant due to faster oscillations in the system. This is because at such high frequencies, the polymer particles/structures do not get enough time to reorient themselves or relax.

An interesting observation is the tendency towards the equalization of G' and G'' moduli with increasing frequencies. This phenomenon implies the formation of temporary rigidity of the structure of the emulsion subjected to intense deformations. Although the loss modulus continues to be superior across a relatively wide spectrum of frequencies, the pronounced growth of storage modulus for high values of frequency points out to the existence of temporary elastic interaction between individual particles of dispersed phase. This type of rheological behavior is typical for stable emulsions of polymer dispersions with moderately developed viscoelastic properties.

The observed growth in both parameters is a sign of the increased resistance of the internal structure of the emulsion against deformations under intensive vibration conditions. In other words, it indicates limited mobility of particles and increased interaction between molecules under fast deformations. This effect can be attributed to the presence of AA in the copolymer composition because it introduces polar groups capable of forming intramolecular bonds. MMA also plays an important role since it adds rigidity to polymer macromolecules.

The lack of rapid changes or any irregular crossovers in the rheology curve shows that this emulsion has good mechanical stability over the frequency range used. It is a critical property in cases where the emulsions are applied for coatings and adhesives because such emulsions are subjected to continuous deformation when stored, mixed, pumped, and applied. The mechanical stability of the emulsion under different deformation frequencies contributes to better processability and performance.

On the whole, the frequency sweep study shows that the SDS-stabilized MMA-AA emulsion can be considered a viscous viscoelastic material with some elastic response at high frequencies. Such rheological properties indicate good stabilization of the emulsion particles by SDS and their dispersity, adequate flow properties, and mechanical stability.

4.4 Rheological Studies for CAPB Latexes

4.4.1. Viscosity

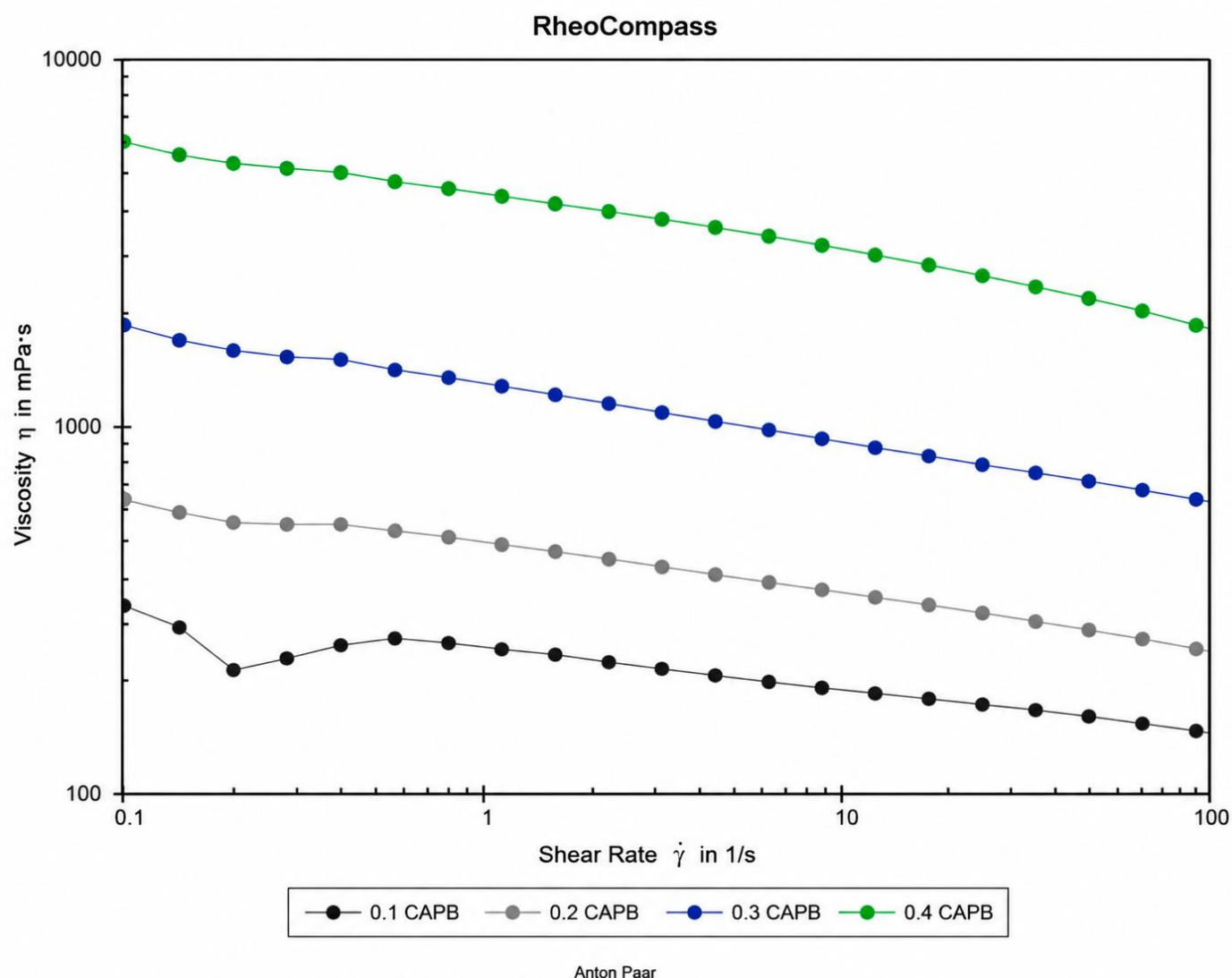


Figure 18: Viscosity Vs Shear Rate curve for Latexes prepared using CAPB as a surfactant

From the viscosity against shear rate graphs of MMA-AA emulsions stabilized with CAPB surfactants, one can see how the effects of varying CAPB surfactant concentrations affect the rheological properties of the system. The graph illustrates the viscosity against shear rate results obtained from the emulsions prepared using various concentrations of cocamidopropyl betaine (CAPB). These are 0.1 CAPB, 0.2 CAPB, 0.3 CAPB, and 0.4 CAPB. From the results, it is apparent that all the emulsions show a reduction in viscosity as the shear rate increases. This shows that the emulsions have non-Newtonian behavior characterized by shear thinning or pseudoplasticity.

This type of rheological behavior is expected from most polymer emulsions and coatings due to the disruption of internal structural arrangement during the shear process. Of all the emulsions tested, the emulsion sample that contains 0.4 CAPB exhibits the highest viscosity. It is followed in order of decreasing viscosity by those samples containing 0.3 CAPB, 0.2 CAPB, and 0.1 CAPB concentrations respectively. As can be seen, the

increase in CAPB concentrations has an effect of increasing the viscosity of the emulsion. Higher viscosity of the emulsion at higher concentrations of surfactant may result from enhanced interactions among molecules. The lowest viscosities, along with weak structural properties, can be observed in case of 0.1 CAPB samples. Being a result of poor stabilization of polymer particles caused by low surfactant concentration, such a structure is characterized by less resistance to flow. In particular, the initial fluctuations in viscosity, which can be seen on the graph at the beginning, might be caused by changes in the structure of particles in response to a certain shear rate. However, further increase in the shear rate results in a slow decline in viscosity, which is a sign that polymer particles align, decreasing internal flow resistance.

Moderate viscosity, as well as improved structural properties, can be noted in case of the 0.2 CAPB sample. Due to increased surfactant concentration, more effective particle stabilization can be achieved, contributing to more stable rheology and better properties of the material. In addition, it should be stressed that gradual viscosity decline caused by the action of a higher shear rate will be beneficial for coating processes.

As expected, higher viscosity is observed in 0.3 CAPB samples, which indicates a well-organized structure of the emulsion. Increased viscosity could be due to improved particle packing and increased interaction between polymer chains and surfactant molecules.

Efficient colloidal stabilization and dispersion homogeneity can be seen by stable rheological response.

The emulsion with 0.4 CAPB content displays the highest viscosity and resistance to deformation compared to other formulations. Viscosity is always very high regardless of the applied shear, which could be explained by the formation of a highly structured viscoelastic network in the latex system. With increased CAPB content, the strength of associative interaction becomes much greater, causing increased internal friction and increasing resistance to deformation. However, even with increased viscosity, the system exhibits shear-thinning characteristics, which can help with its application in many operations including mixing, pumping, brushing, and spraying.

It is evident that viscosity decreases with increasing applied shear for all samples. There are no sudden drops and irregularities in the curves, meaning there is no phase separation and structural instability in the deformed systems.

Rheology may also depend on the chemical makeup of the copolymer mixture. Here, MMA imparts stiffness to the backbone of the polymer chain whereas AA provides polar functionality to improve its hydrophilic nature and particle interactions within an aqueous medium. Additionally, CAPB provides greater stability to the dispersed particles by minimizing interfacial energy and particle distribution. Therefore, increasing the amount of surfactant results in increased structural stability of the emulsion, leading to higher viscosity.

In summary, it is evident from the viscosity plot above that the concentration of CAPB significantly affects the flow and structural characteristics of MMA-Acrylate emulsions. This results in high viscosity and greater structural stability. On top of this, all three concentrations of CAPB provide the required shear thinning effect. In other words, these rheological properties are quite useful for the preparation of coatings and adhesives.

4.4.2. Amplitude Sweep

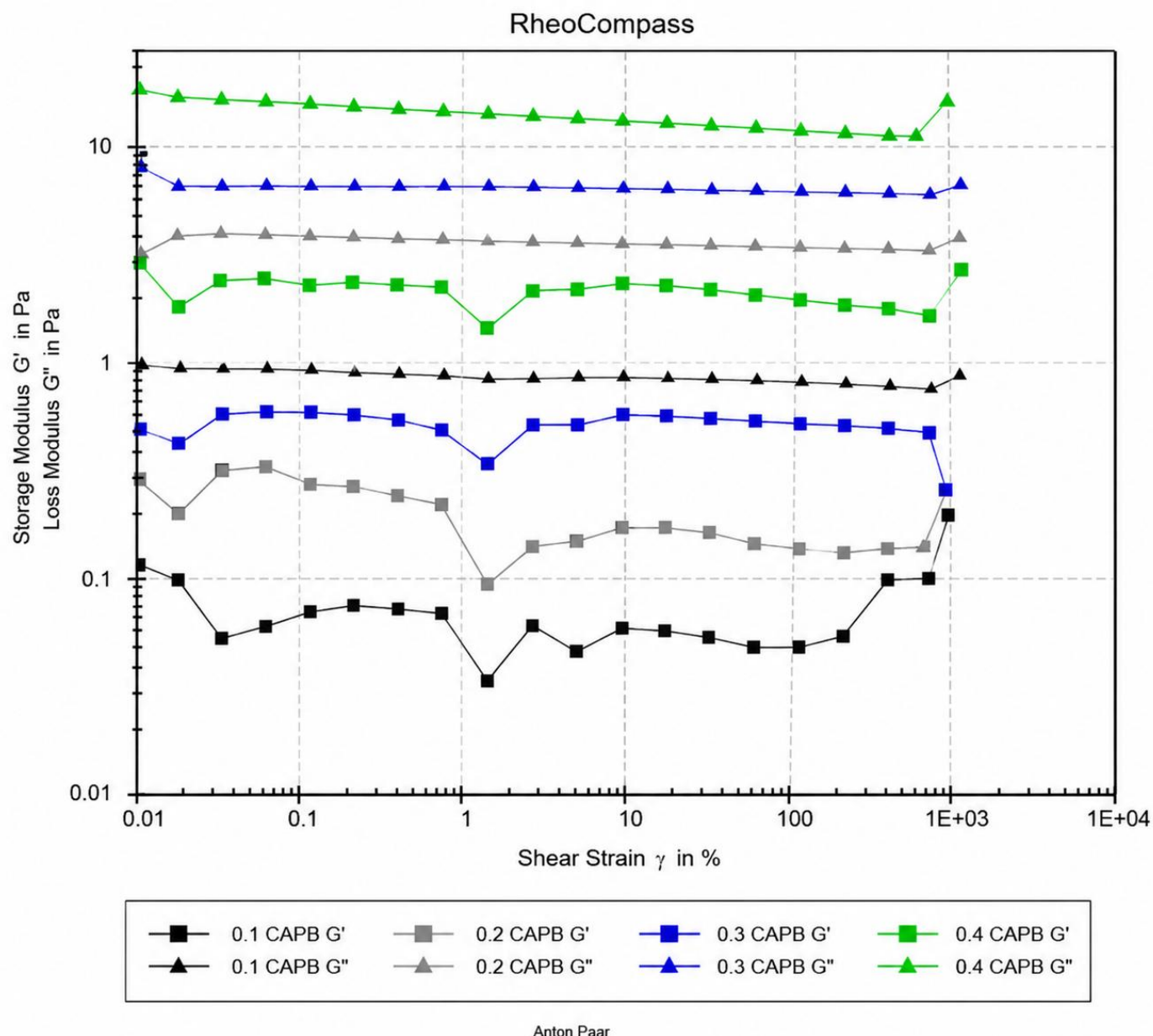


Figure 19: Amplitude Sweep Curve for all the Latexes prepared using CAPB as a surfactant

The combination of CAPB-stabilized MMA-AA emulsions' sweep curves of amplitudes allows gaining valuable insight into the viscoelastic properties of the studied latex materials depending on the surfactant content. The presented chart shows how the storage modulus (G') and loss modulus (G'') depend on shear strain in case of emulsions having 0.1 CAPB, 0.2 CAPB, 0.3 CAPB, and 0.4 CAPB. As is known, the storage modulus characterizes an elastic or energy-storage behavior of the sample, whereas the loss modulus refers to its viscous or energy-dissipation properties.

As follows from the study of four emulsion samples with different surfactant content, the loss modulus (G'') is always greater than storage modulus (G') in any strain range. It means that viscous behavior prevails over solid-type elastic behavior in all considered cases. This tendency can be observed in stable polymer emulsions

whose continuous and dispersed phases have a viscous-type behavior. As we can see, there is no crossover of moduli which indicates that all emulsions behave as viscoelastic liquids.

There is an evident increase in the values of G' and G'' with increasing CAPB concentration. It is noticeable from the four samples that the 0.4 CAPB sample shows high values for the storage and loss moduli, whereas the other three samples show descending moduli values; the second one is 0.3 CAPB, followed by 0.2 CAPB and finally 0.1 CAPB. This result proves that there is a strong relationship between the surfactant concentration and the strength of the structure inside the emulsion system.

In case of 0.1 CAPB, it shows lower moduli values than the other three samples, which means that it offers weak structural organization. There is an evidently low storage modulus at all levels of strain, indicating low elasticity, and this shows that the particle interaction is weak in this sample. There is also low loss modulus in this sample, which indicates low internal friction.

Moreover, the 0.2 CAPB sample is characterized by a better viscoelasticity than 0.1 CAPB one. Both G' and G'' parameters increase, meaning that there is a more stable and powerful interaction of particles with each other, forming more solid internal structures. As for the relative stability of the moduli values for a wider range of strains, it testifies to higher stability of the colloidal system of the dispersion, being less sensitive to deformation.

Regarding the 0.3 CAPB emulsion, this product represents an even stronger rheological system than the previous two ones. It means that its G' moduli become much higher and stable in the strain range due to a larger number of elastic interactions in this case. At the same time, the values of loss moduli become higher as well, which speaks of energy dissipation during oscillations.

As for the 0.4 CAPB sample, this product is considered to be the most viscoelastic among all the others studied. High G'' moduli speak about considerable viscous interactions in this system, while the increase in G' values indicates much more elastic particle interactions. Thus, the moduli become relatively stable for a wider range of strains. In this respect, CAPB provides stable stabilization of the MMA-AA latex particles by virtue of both electrostatic and steric stabilization, which improves the structural stability of the system.

Changes in the modulus values as a function of increasing strain suggest the structural stability of the emulsion even at increased deformation without any catastrophic failures. The appearance of broader linear viscoelastic region for high concentrations of CAPB implies that these emulsions can be subjected to higher strains without structural failure. This makes these emulsions suitable for such practical applications where mixing, pumping, brushing, or spraying is involved.

The rheological properties of the samples can be related to the nature of the monomers. MMA adds rigidity to the polymer chain, while AA increases particle interaction due to the presence of polar functional groups. CAPB additionally lowers the interfacial tension between the two phases and enhances stabilization. Higher CAPB concentration results in greater structural stability of the obtained emulsion.

In summary, from the results obtained, it can be concluded that CAPB concentration greatly affects the viscoelasticity and structural stability of the MMA–AA emulsion system. As CAPB concentration increases, an increased tendency towards better viscoelasticity, rheological stability, and less deformability while retaining viscous behavior is observed. The characteristics shown suggest that CAPB-stabilized emulsions are likely to have excellent rheological qualities for various coating and adhesive industrial applications.

4.4.3. Frequency Sweep

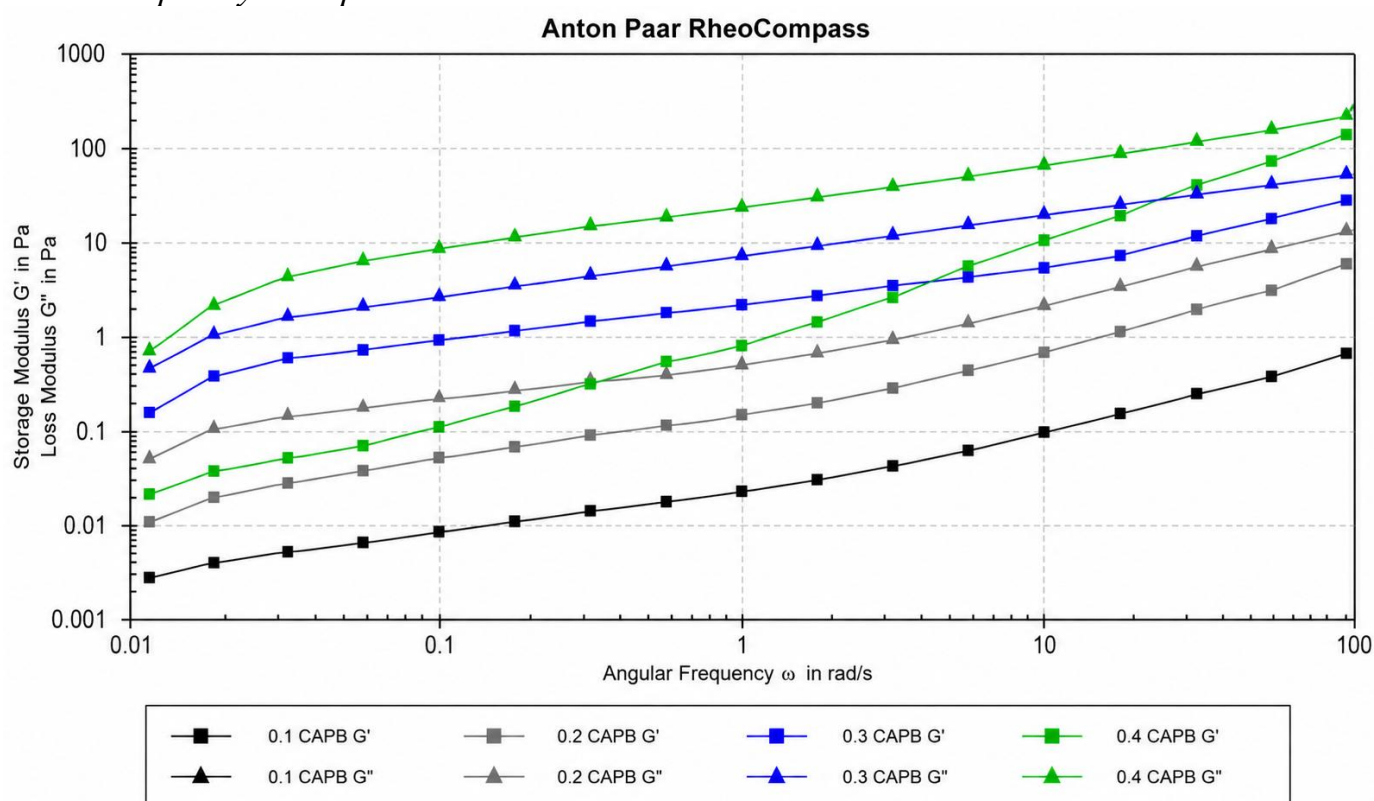


Figure 20: Frequency Sweep Curve for all the Latexes prepared using CAPB as a surfactant

The superimposed frequency sweep plot of CAPB-stabilized MMA-AA emulsions is of significance for understanding the viscoelasticity properties and structure development in the latex system as the surfactant content increased. The curve shows the dependence of storage modulus (G') and loss modulus (G'') on the frequency of oscillation of emulsions having 0.1 CAPB, 0.2 CAPB, 0.3 CAPB, and 0.4 CAPB. Frequency sweeps are commonly employed for evaluating the time-dependent rheology of polymer emulsions and studying the internal structure stability of polymer emulsion against oscillatory deformation.

The G' and G'' moduli of all formulations increase consistently with rising frequency. It means that the stiffness of emulsions increases as frequency rises. This can be explained by the observation that, at low frequencies, the relaxation time of the particles and chains in polymer emulsions is enough for deformation and rearrangement. But, when frequency increases, the relaxation time decreases, leading to the rigidity of emulsions.

For all samples, the value of loss modulus (G'') always exceeds that of the storage modulus (G'). This signifies that the emulsions display viscoelastic characteristics, being primarily viscous rather than elastic or rigid. The high value of G'' is an indication that energy losses from oscillations exceed the elasticity energy, which is common for stable latexes with the continuous aqueous phase being mainly responsible for the viscous properties of the formulation.

Among all emulsions, the sample that contains 0.1 CAPB has the minimum values of G' and G'' . Relatively low moduli signify weak molecule associations and lack of internal structurization. At such low surfactant concentrations, the resistance of particles against deformations is comparatively smaller since they can be more easily destabilized. However, the rising moduli with increasing frequency reveal formation of short-term structural resistances at fast oscillations.

In contrast, the results from the 0.2 CAPB sample showed that there was an improvement in viscoelastic characteristics in comparison with the 0.1 CAPB sample. It is seen from the fact that both the storage and loss moduli showed significant growth that could be interpreted as better particle interaction in the latex. The increase in G' and G'' values at growing frequencies showed good stability of particles in the sample and strong intermolecular interactions.

A further increase in viscoelastic characteristics can be observed when using the 0.3 CAPB sample for producing the latex emulsion. The rise in the value of storage modulus demonstrated a significant elastic contribution with more intensive connection between the polymer particles inside the emulsion. Also, the higher loss moduli showed higher dissipative processes inside the emulsion. In other words, the polymer particles were better structured and stabilized.

Finally, the use of the 0.4 CAPB sample resulted in the highest value of G' and G'' modulus on the whole frequency interval. The presence of greater amounts of CAPB makes the surfactant molecules able to create more effective stabilization of the MMA-AA latex particles due to both electrostatic and steric forces of repulsion, making them associate much more effectively, become more rigid, and gain higher resistance to oscillatory deformation.

The growth in the value of modulus as the function of CAPB concentration is an indication of the rheological properties of the emulsions under analysis being greatly influenced by CAPB content. With increasing amounts of CAPB in the system, there will be formed stronger particle associations and higher stability of structures created by the polymer particles. Thus, the simultaneous increase in both viscosity and elasticity indicates a gradual development of viscoelasticity of the emulsions analyzed with increasing surfactant concentration.

The rheological properties of the studied emulsions can also be interpreted in light of the chemical nature of the system components. Methyl methacrylate provides mechanical strength and rigidity, whereas acrylic acid adds polarity, promoting the formation of stronger bonds between the polymer particles. CAPB also

contributes to better colloidal stability, decreasing the surface tension between the phases and ensuring uniform distribution of the dispersed polymer particles throughout the system.

The absence of any abrupt changes in the graphs implies excellent mechanical stability of the emulsions within the investigated frequency range. The mechanical stability of such systems is especially important since emulsions used in coatings and adhesives are constantly undergoing deformation while being mixed, stored, pumped, brushed, and sprayed.

Generally speaking, the comprehensive results of this analysis demonstrate that the concentration of CAPB has a considerable impact on the viscoelastic behavior of MMA-AA emulsions. An increase in surfactant concentration results in an increase in both moduli of elasticity and better structural organization within the emulsion. Thus, according to the findings, the most successful emulsion was one with a 0.4 CAPB concentration.

4.5. Rheological Properties for AMF-1 Latexes

4.5.1. Viscosity

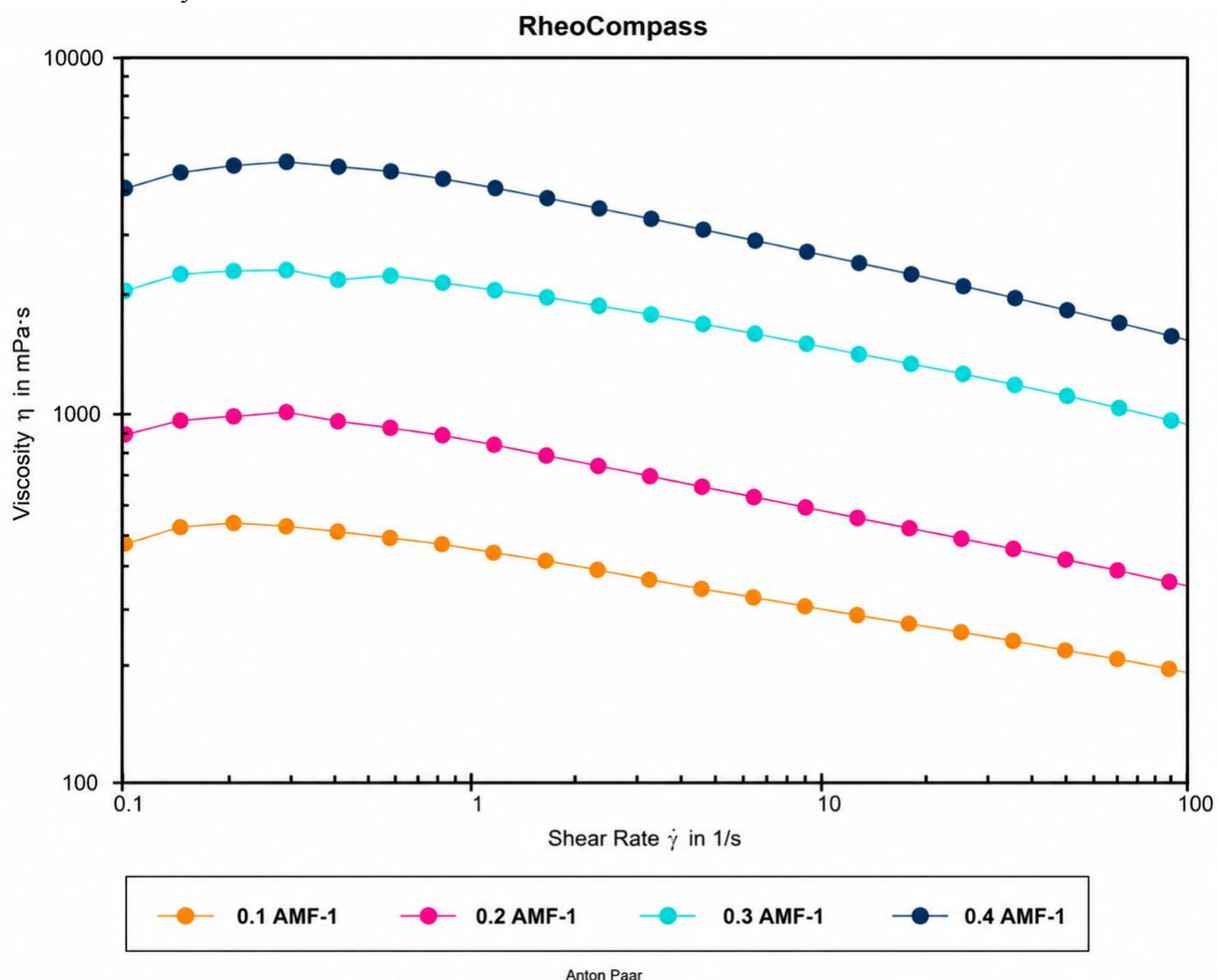


Figure 21: Viscosity vs Shear Rate curve for all the Latexes prepared using AMF-1 as a surfactant

From the composite plot showing the viscosity and shear rate relationship for AMF-1 stabilized MMA-AA emulsions, there is a clear correlation between surfactant concentration and rheological properties of the systems. The plots obtained from 0.1 AMF-1, 0.2 AMF-1, 0.3 AMF-1, and 0.4 AMF-1 all demonstrate that the viscosities of these systems decrease as the shear rate increases, depicting an instance of pseudoplasticity or shear-thinning behavior. Shear-thinning behavior is expected in polymeric emulsions since the polymer molecules break down and align during the process of shear.

All other factors being equal, as the shear rate decreases, the particles will remain randomly oriented and experience strong interactions among themselves. This implies that there will be high resistance to flow, which is depicted by high viscosity. On the other hand, as the shear rate increases, the interactions between the particles decrease and the particles become orientated along the direction of flow. In doing so, the resistance to flow decreases, hence lower viscosity levels. Among the emulsions, the one that exhibited highest viscosity was 0.4 AMF-1.

The 0.3 AMF-1 mixture demonstrated fairly high viscosity levels, though slightly less than for the 0.4 AMF-1 mixture. The graph exhibited the typical pattern of viscosity drop with increasing shear rates which is evidence of the emulsion's pseudoplastic properties. The rather smooth trend of viscosity decrease implies that the emulsion possesses sufficient stability allowing it to resist the external impact until it is gradually rearranged. As one can observe, the increase in viscosity in comparison with the formulations with a lower amount of the surfactant testifies that the rising level of AMF-1 affects particle interaction and dispersing capability.

In turn, the emulsions with a content of 0.2 and 0.1 AMF-1 had lower viscosity levels across all the shear rates studied. The lowest value belongs to the 0.1 AMF-1 mixture, which proves low particle-particle interactions and poor internal network formation. With insufficient stabilization power at such low surfactant concentration, the created structure becomes rather loose, which explains its easy response to stress conditions. The viscosity decrease with the increase of the shear rate in such emulsions was quite significant.

Clearly, all four formula viscosities were observed to increase with an increase in the AMF-1 content. Such behavior can be explained by enhanced stability of polymer particles in terms of the formation of a stronger interaction between the dispersed particles and the continuous phase. Increased surfactant concentration helps in forming a tighter structure which causes an increase in viscosity. The gradual decrease in viscosity for all emulsions examined indicates the lack of their Newtonian character. Instead, it was found that they have a controlled flow behavior needed for practical coating or emulsifying tasks.

The absence of viscosity reduction or unexpected fluctuations on graphs further demonstrates the good rheological stability of the emulsions tested over the entire shear range used. Such a feature can be considered beneficial in practice since the material can easily flow under shear forces but still provide sufficient structure during its storage. Based on the above results, it can be assumed that AMF-1 affects the rheological properties

of MMA–AA emulsions significantly. An increase in AMF-1 contributes to the development of a better structural network, which leads to higher resistance to deformation in shear flow compared to other samples.

4.5.2. Amplitude Sweep

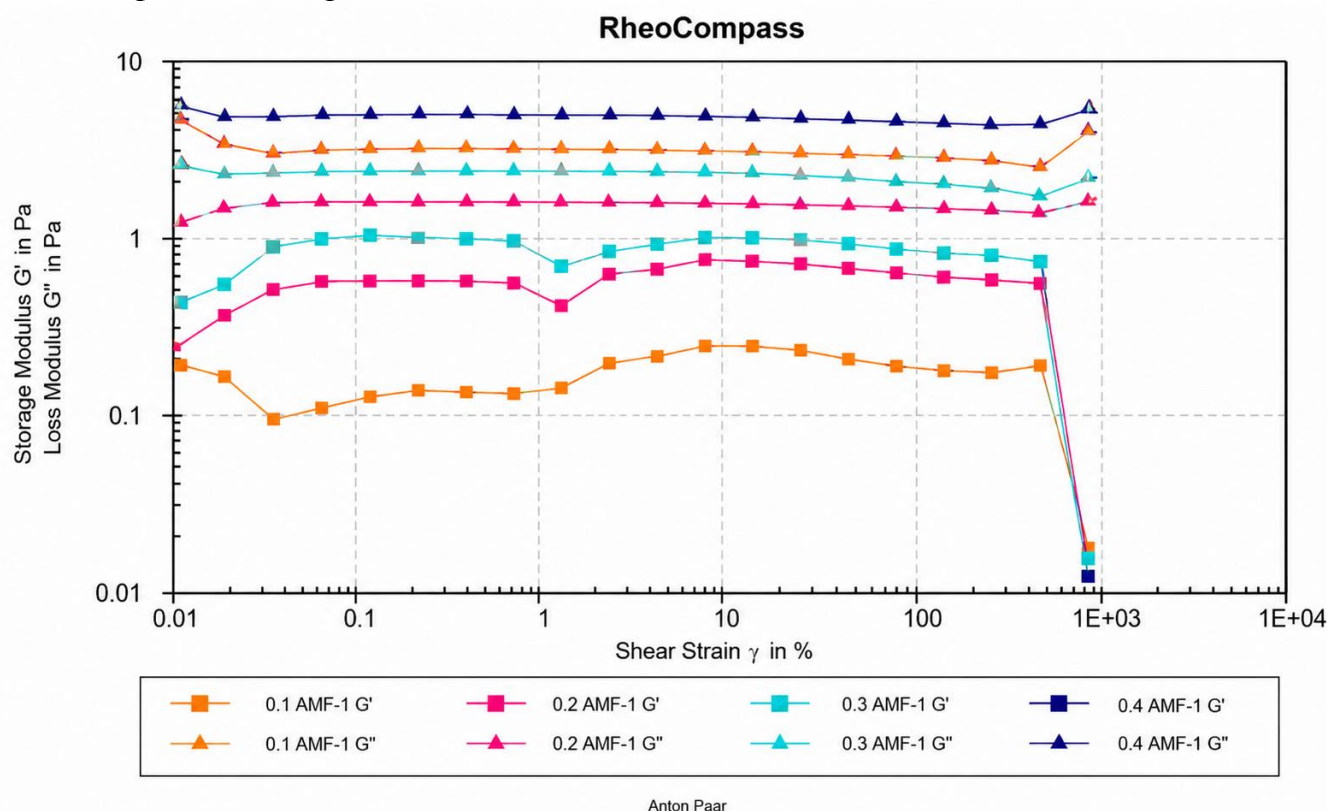


Figure 22: Amplitude Sweep curve for all the Latexes prepared using AMF-1 as a surfactant

The plot of the sweep curve for AMF-1-modified emulsions shows the viscoelastic properties of the produced samples over a broad range of applied shear strain. Both storage modulus (G') and loss modulus (G'') have been calculated to determine the relationship between elastic and viscous characteristics of the emulsion system. It is obvious from the results obtained that the rheology of the emulsions is highly affected by the amount of AMF-1 added because of its effect on the internal structure and mechanical stability of the system. It is also clear from the curves that the loss modulus (G'') is much greater than the storage modulus (G') in almost all the strain ranges examined, meaning that the viscosity of the emulsions was much more dominant than elasticity. This indicates that the produced systems had a higher tendency to dissipate energy rather than storing it. This is common among the polymeric systems where particle mobility and molecular relaxation play an important role in their rheology.

The formulation having the 0.1 AMF-1 displayed low modulus values compared to other formulations. Storage modulus had relatively low values, with some changes observed at lower strain values; hence there was a relatively weak structural network in the formulation. Low G' values imply limited intermolecular interaction and entanglement of the particles in the emulsion formulation. It is worth noting that despite the

variations, the stable G'' values in the whole strain region show that viscous behavior dominated, and hence the sample was flowable.

Upon increasing the AMF-1 concentration to 0.2 AMF-1, a significant increase in the storage and loss modulus values was evident. This implies that there was a higher structural strength and resistance to deformation in the formulation. The improved viscoelastic properties could be explained by the fact that there was a stronger interaction between the particles forming the network. Even though viscous behavior dominated, it is clear that there was an improvement in the elastic behavior of the material.

For the 0.3 AMF-1 formulation, there was also a considerable improvement in rheological strength. As seen from the plot, storage modulus was still significantly higher for this formulation compared to the other formulations in a wide region of strain. Such results suggest that higher AMF-1 content was responsible for a better formation of intermolecular interactions resulting in higher network stability. Constant values of G'' for the whole strain region show good viscous properties of the emulsion. Higher values of the modulus are a clear evidence of the influence of AMF-1 on the formation of a more stable network structure.

The highest values of the storage and loss modulus could be observed for the 0.4 AMF-1 sample. The strong increase in G' for the 0.4 AMF-1 sample indicates a relatively higher stability of the internal network structure. High values of the moduli indicate good rigidity of the system in the LVE region. Both the moduli behaved stably through the whole region of strain. Therefore, the 0.4 AMF-1 sample can be considered structurally stronger among all the formulations studied.

For extremely high strain values, a drop in the storage modulus was noted for all formulations. This implies that the internal structure of the formulations broke down under extremely high strains. The dropping of G' implies a change from the structured to a flowable phase because of the destruction of intermolecular interactions. This kind of behaviour is exhibited by emulsions that yield at large oscillatory strains.

From the above discussion, it is clear that the amplitude sweep tests have demonstrated that increasing AMF-1 concentrations significantly improved the viscoelastic characteristics of the formulated emulsions. It is evident from the increased storage and loss moduli values with increasing AMF-1 concentration. The viscoelastic nature of the emulsion formulations implies that AMF-1 had some effect on the mechanical characteristics of the emulsion formulations.

4.5.3. Frequency Sweep

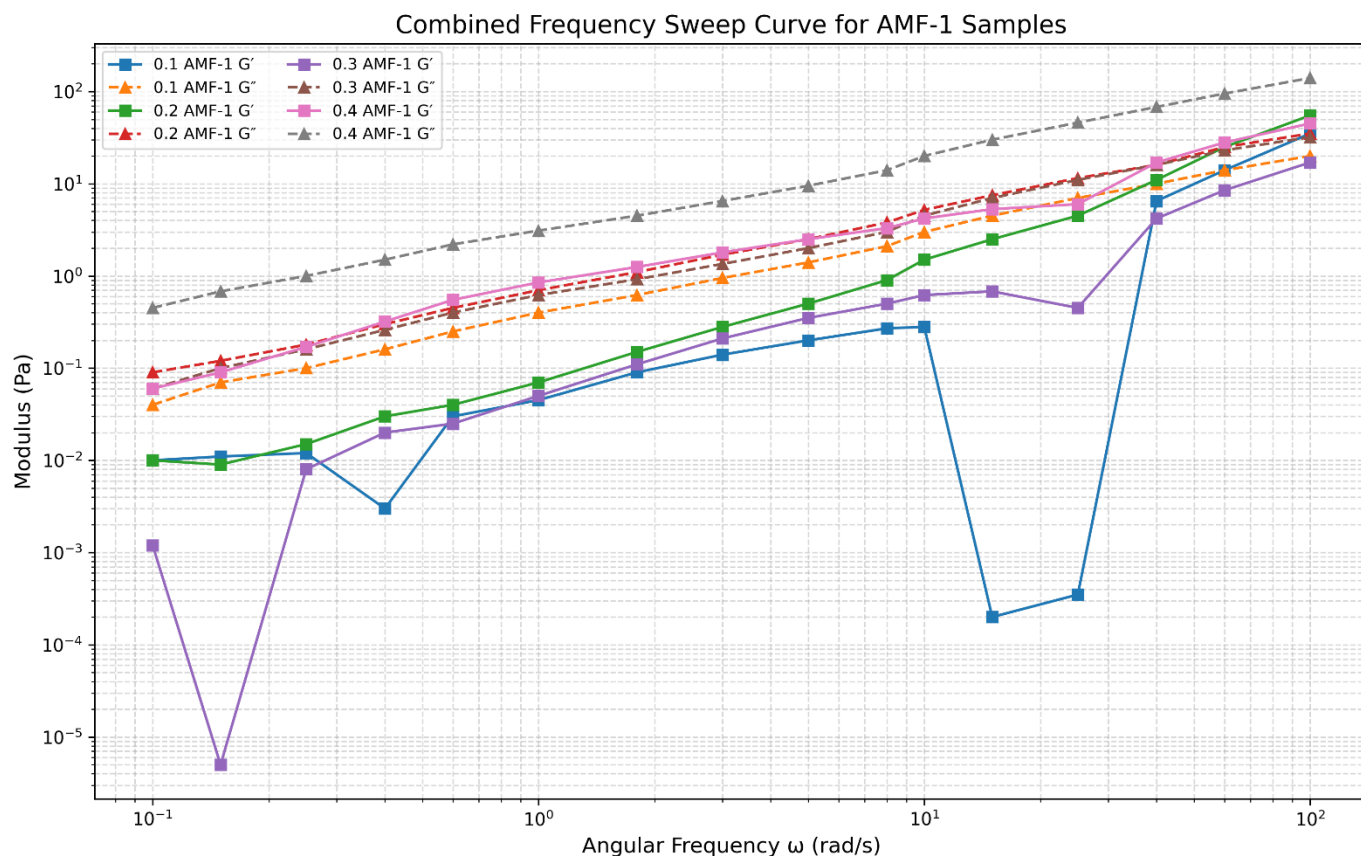


Figure 23: Frequency Sweep Curve for all the Latexes prepared using AMF-1 as a surfactant

It is worth noting that the overall behavior of frequency sweep curves for AMF-1 modified emulsions gives valuable data on viscoelastic properties of prepared samples depending on oscillation frequencies. The relationship between storage modulus (G') and loss modulus (G''), which vary depending on angular frequency, can reveal the response of emulsions under oscillation. As can be seen from results obtained, rheological behavior of all formulations showed a significant impact of the amount of AMF-1 on structure stability and stress resistance.

As follows from results obtained, in all formulations both storage modulus and loss modulus increased steadily with the increase in angular frequency. It means that samples became mechanically more stable depending on the rate of deformation. Thus, an increase in the value of modulus parameters implies the limited mobility of particles and polymer molecules due to increased stress resistance at higher frequencies.

As for the 0.1 AMF-1 sample, it was noted that the storage modulus was quite low throughout the entire frequency range. As G' was quite low, the formation of the internal elastic network of the emulsion system was not very effective in this particular case. In addition, the sample was mostly characterized by the viscosity of the medium due to the dominance of the loss modulus. At intermediate frequencies, small variations in G' could be attributed to the reorganization of the dispersed particles in the continuous medium.

At the same time, the values of both moduli were increased in the 0.2 AMF-1 emulsion system. An increase in the storage modulus shows the formation of the internal structure and improved elasticity. This means that

there were more intermolecular interactions between particles in the dispersion medium. Nevertheless, there is a tendency towards dominant viscosity of the substance.

The addition of AMF-1 up to 0.3 further improved the rheological behavior of the emulsions. An increase in the storage modulus was noted with a steady increase in the frequency, suggesting the development of a more interconnected structure network. From this analysis, it is clear that the high G' denotes improved stability of the structure against the destruction process. Moreover, a steady increase in the loss modulus showed that the emulsion possessed a great deal of viscous behavior. It can, therefore, be concluded that the emulsion had stable viscoelastic properties required for painting purposes.

From all the samples analyzed, the one having 0.4 AMF-1 had the highest storage and loss modulus throughout the whole frequency range. This is because such samples possessed better internal structure and had the most intense intermolecular interactions. A large increase in the value of G' shows that such samples have a high level of elastic behavior. The steady increase in both moduli with an increase in frequency showed that the sample was mechanically stable. The reason why this particular sample showed higher modulus could be due to enhanced packing of the particles.

Irrespective of their type, the value of the loss modulus was consistently higher than that of the storage modulus for most frequencies. This implies the prevalence of viscous effects on the dynamics of the emulsions. The observation shows that the prepared emulsions still possessed liquid-like behavior even when there was an onset of elastic properties due to the rising concentration of AMF-1. In addition, there was no point of crossover between G' and G'' values, which means that there was no solid-like transition for any of the cases. It can be observed from the results of frequency sweeping tests that the rise in the AMF-1 concentration improved the viscoelastic nature of the emulsions. This is seen from the increasing values of both the storage and loss moduli, indicating increased intermolecular interaction and internal structures at higher surfactant concentrations.

4.5.4. Combined Analysis for Rheological Properties of the Latexes

The viscoelasticity of the prepared PMMA-co-PAA latex dispersion systems was determined through viscosity measurement, amplitude sweep, and frequency sweep in order to investigate the effect of the mixed surfactants on the microstructure and viscoelasticity of the latex systems. It was found that there were notable differences between the SDS, SDS/CAPB, and SDS/AMF-1 latex dispersions in terms of their interaction, organization, and deformation of the particles.

The plots of viscosity vs. shear rate showed that all the latex dispersions showed non-Newtonian shear thinning behavior, in which viscosity reduced gradually when the shear rate increased. This behavior showed the pseudoplastic behavior of the latex dispersions in which the network of the dispersed particles was gradually broken by the applied shear. In all the latex dispersions studied, the pure SDS latex dispersion showed

moderate viscosity values. It was due to electrostatic interaction and good particle dispersion in the presence of SDS anionic surfactant with sulfate groups.

The presence of CAPB led to the observation of concentration-dependent rheological properties. In formulations with low CAPB content, the viscosity was significantly reduced in comparison with pure SDS, probably due to increased structural dissociation and better packing of surfactants, thus resulting in their mixing into mixed micelles and increasing the flowability of the system. At higher CAPB concentration, viscosity increased gradually. The high viscosity of the highest CAPB concentration sample (0.1 SDS + 0.4 CAPB) may point to the increased interaction between particles and higher structural density in the system caused by the development of a more complex structure. Due to the amphoteric nature of CAPB, the electrostatic repulsion between particles decreased, forming more stable particle networks.

The highest viscosity values were observed for the formulations with fluorosurfactants AMF-1 in particular. For example, the 0.1 SDS + 0.4 AMF-1 sample showed the maximal viscosity across the entire studied shear rate range. This may be explained by the extremely strong surface activity and low interfacial energy of the fluorinated surfactant. Due to their fluorination, particles have a stronger tendency towards aggregation into more ordered particle networks. This leads to enhanced interparticle associations and structural integrity of particles in the system.

This observation was further reinforced by the results of amplitude sweep analysis, which established the presence of viscoelastic nature of the dispersions of latex under increasing oscillatory strains. For all systems, the value of loss modulus (G'') was greater than that of storage modulus (G') indicating dominance of viscous behavior. However, for each type of surfactant-based system, the value of these moduli greatly differed.

In the case of SDS based system, relatively low values of both storage and loss moduli were observed, which suggests weak association of structures and insufficient elasticity of the dispersion. In other words, SDS-based latex dispersion exhibited primarily viscous characteristics with relatively low resistance to the flow. On the contrary, systems with CAPB exhibited increasing trend in both G' and G'' with increasing concentration of CAPB. This means increasing contribution of elasticity and better structure stabilization by this surfactant.

Latex dispersions with AMF-1 exhibited the largest value of both storage and loss moduli. Specifically, AMF-1 concentrations higher than 0.2% gave rise to significant increase in storage modulus, suggesting better elasticity characteristics and improved dispersion structure. Furthermore, the increased area of the wider linear viscoelastic region indicates improved stability of these AMF-1-containing systems under applied strains.

The frequency sweep test further elaborated on the dynamic viscoelastic properties of the latex dispersions. For all formulations, an increase in storage and loss moduli was observed with increase in angular frequency, which indicated that more rigid structure and less particle mobility existed with increasing deformation rates. The loss modulus predominated in almost all cases, indicating a viscous nature of the latex dispersions.

In the case of pure SDS dispersion, moderate values of frequency dependent moduli were obtained, indicating stable colloidal behavior and minimal structural rigidity. However, the dispersions containing CAPB

displayed higher values of modulus with increase in CAPB concentrations, revealing the effect of enhanced structural organization in such systems. Interactions between the two surfactants SDS and CAPB improved particle stability and structural rigidity.

For the AMF-1-containing systems, the highest values of modulus were obtained irrespective of the deformation rates used. Addition of AMF-1 significantly affected both elastic and viscous responses in the latex dispersions. High values of modulus revealed more rigidity and resistance to deformation with increase in AMF-1 concentrations.

In conclusion, the above comparison of the rheology of the PMMA-co-PAA dispersions shows that addition of amphoteric surfactants and their fluorinated analogs significantly affects their microstructure and rheological performance. Although SDS yielded stable electrostatic stabilization with acceptable rheological performance, the inclusion of CAPB yielded better organized structures due to synergistic action of the surfactants. The AMF-1 dispersion had the best rheological performance due to the excellent surface activity and interfacial adsorption capabilities of the surfactant.

4.6. Water Contact Angle

Contact angle measurement with water is currently one of the most commonly used methods for characterizing the surface properties of a polymer film or coating, including the hydrophilicity or hydrophobicity of its surface. By definition, the contact angle corresponds to the angle between the tangent to a drop of liquid and a flat solid surface at the line of their contact. The value of this parameter provides valuable information concerning the surface energy, interfacial interactions, and wettability of the material under consideration. Thus, generally speaking, a low value of the water contact angle characterizes a hydrophilic material with high wettability, while a high value characterizes the opposite case.

In this research, the water contact angles of the prepared wood samples were measured to analyze the effect of the surfactant content on the surface properties of latex coating solutions synthesized in the study. Specifically, to perform this experiment, a small amount of deionized water was dropped on the polymer coating sample by means of a microsyringe. The image of the droplet was then captured, and its contact angle calculated based on this information. The measurements were generally performed at ambient temperature, and the reported values were obtained by averaging multiple readings taken at different positions on the film surface to ensure accuracy and reproducibility.

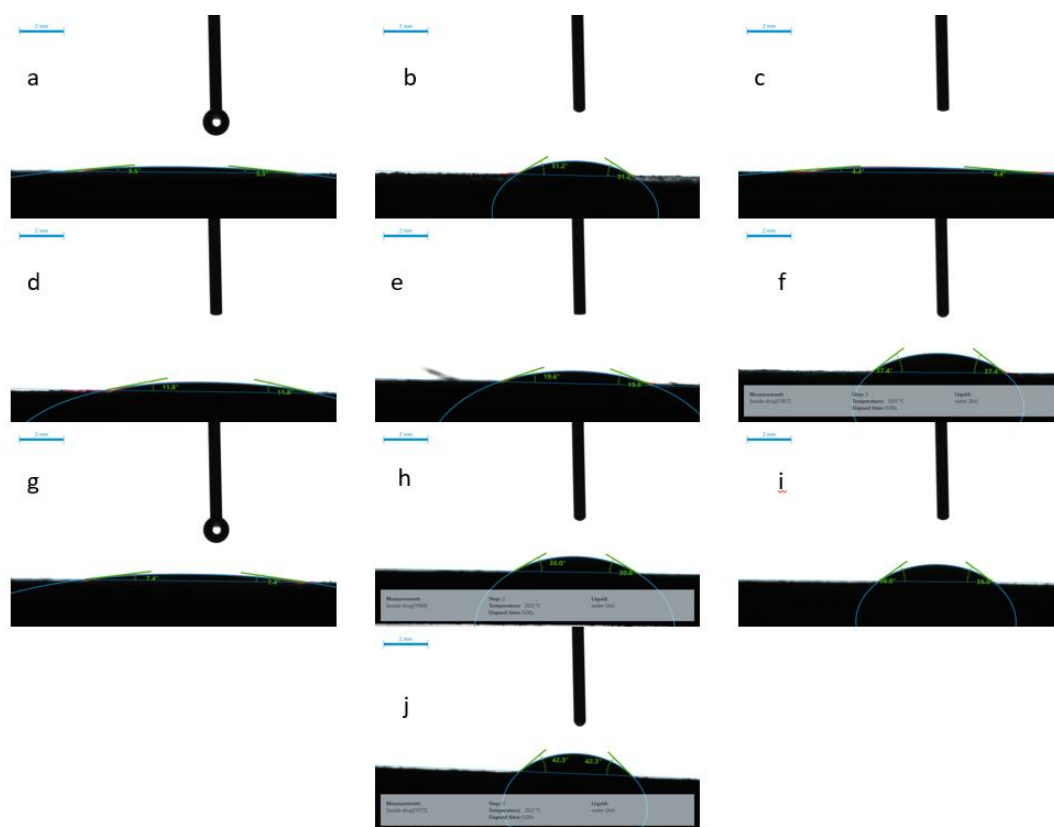


Figure 18: Water contact Angle on the surface of coated wood samples: a) Blank; b) 0.5 SDS; c) 0.1 CAPB; d) 0.2 CAPB; e) 0.3 CAPB; f) 0.4 CAPB; g) 0.1 AMF-1; h) 0.2 AMF-1; i) 0.3 AMF-1; j) 0.4 AMF-1

S.No.	Sample	Water Contac Angle
1.	Blank	5.5
2.	0.5 SDS	31.2
3.	0.1 CAPB	4.4
4.	0.2 CAPB	11.8
5.	0.3 CAPB	19.6
6.	0.4 CAPB	37.4
7.	0.1 AMF-1	7.4
8.	0.2 AMF-1	30.0
9.	0.3 AMF-1	36.0
10.	0.4 AMF-1	42.3

Table 13: Water contact angle of all the latexes prepared using SDS, CAPB, and AMF-1

Analysis of the water contact angles of the PMMA-co-PAA latex film shows significant variation in the wetting properties of the film with variation in surfactant composition. Contact angles give information about the hydrophilic or hydrophobic nature of the film surface. The lower the value of contact angle, the more hydrophilic is the film surface while the higher the value, the higher the hydrophobicity.

For the blank sample, the value of water contact angle is only 5.5°, meaning that this surface is highly hydrophilic. From such a low value of contact angle, one can tell that water is strongly interacting with the surface and can spread easily. This can be explained by the presence of polar functional groups on the surface and the lack of hydrophobic surfactant on the surface.

When SDS was incorporated in the polymer film, there was a significant increase in water contact angle to 31.2°. This shows that adding SDS in the film increased its hydrophobic nature since the higher the value of contact angle, the more hydrophobic the surface. Nevertheless, since SDS is an anionic surfactant possessing hydrophilic sulfate groups, the hydrophobicity was moderately retained.

In the presence of amphoteric CAPB surfactant, the change in water contact angle varied gradually with the increase in CAPB concentration. In case of 0.1 CAPB surfactant concentration, the water contact angle value dropped to 4.4°, suggesting high hydrophilicity of this composition. Such result can be explained by the contribution of polar zwitterionic groups of CAPB surfactant that appeared on the surface and facilitated water wetting of the film layer. Perhaps, the organization of mixed surfactants at low concentrations was not enough for formation of a hydrophobic surface layer.

With the increase in CAPB concentration up to 0.2 and 0.3, the water contact angle value grew gradually from 11.8° to 19.6°. Further increase in CAPB surfactant concentration resulted in even greater values of water contact angles, reaching the maximum value of 37.4° with 0.4 CAPB surfactant concentration. These results imply that surface hydrophobicity increases with increasing CAPB concentration. High concentration values allow better orientation of hydrophobic alkyl chains of CAPB surfactants at the film surface, lowering surface energy and minimizing water wetting.

For the AMF-1-containing system, even higher effects on the wetting behavior were obtained for the produced films. In the case of 0.1 AMF-1, a lower contact angle of 7.4° was obtained, which means that with a smaller fluorosurfactant content in the mixture, the film surface retained its high hydrophilic nature. However, a rapid rise in contact angles was observed with the increase of AMF-1 content, reaching a contact angle of 30.0° for 0.2 AMF-1, 36.0° for 0.3 AMF-1, and 42.3° for 0.4 AMF-1.

The significant rise in water contact angle in AMF-1 systems is due to the presence of fluorinated chains in the structure of amphoteric fluorosurfactants. Fluorinated groups demonstrate very low surface tension owing to the high strength of the carbon-fluorine bond and low polarizability of fluorocarbons. Upon forming a film, fluorinated groups have a tendency to form the outer layer of the film, creating a superhydrophobic surface. In this regard, water droplets displayed less affinity to spread and create larger contact angles.

Generally, the contact angle data have indicated that the composition of surfactant has greatly affected the surface characteristics of the PMMA-co-PAA latex film. CAPB systems have improved in terms of hydrophobicity at higher concentration levels, while AMF-1 systems displayed better performance in terms of their water-repellent property because of the fluorinated nature of the system. The high degree of

hydrophobicity in the 0.4 AMF-1 system has further emphasized the importance of fluorinated amphoteric surfactants [70].

CHAPTER-5

CONCLUSION

The present investigation involved an analysis of the influence of different surfactant systems on various properties of poly (methyl methacrylate-co-acrylic acid) [PMMA-co-PAA] emulsions obtained via batch emulsion polymerization. The main objective of the current study was to elucidate the impact of different surfactants both conventional and fluorinated in terms of properties like physicochemical, colloidal stability, rheology, and wettability of acrylic latexes to be used as coating materials.

Batch emulsion polymerization was efficiently performed to synthesize PMMA-co-PAA emulsions from methyl methacrylate and acrylic acid monomers in aqueous solution. In this regard, water was chosen as a continuous phase due to its environmentally benign nature and industrial relevance as an aqueous system for producing water-based polymer emulsions. Various surfactant systems such as SDS, CAPB, and AMF-1 were applied to examine their influence on properties of the synthesized latexes.

The emulsion products displayed satisfactory levels of monomer conversion and solid content, indicating that the polymerization process took place efficiently and the formation and stabilization of the polymer particles within the aqueous media were also successful. Gravimetric analyses showed that surfactant types and their concentrations affected the polymerization process and resulted in efficient latex system stability. The high values of monomer conversions recorded during the experiment clearly showed that initiation and propagation processes occurred during emulsion polymerization. Moreover, stable latex systems without significant coagulum were successfully prepared, suggesting that the selected surfactant systems were suitable for the preparation of acrylic emulsions.

The Dynamic Light Scattering analysis showed that the nature of surfactants significantly affected the values of particle size and particle size distribution of the resulting latex particles. The latexes prepared with fluorosurfactants were characterized by smaller particle sizes compared to the latexes prepared with conventional surfactants. Such results could be explained by the higher surface activity and better ability to stabilize interfaces that led to efficient micelle formation and particle nucleation. Smaller particle sizes were expected to provide improved film forming ability, excellent visual quality of coatings, increased gloss, and higher colloidal stability.

The results obtained from the determination of zeta potentials revealed that all formulated latexes were properly stabilized with electrostatic forces to ensure colloid stability. The negative zeta potentials proved adequate repellent forces between the polymer particles to avoid any kind of aggregation or phase separation during the storage period. The latexes containing fluorosurfactants showed superior colloid stability because of better adsorption of surfactant molecules on the surface of the particles.

The rheology of the synthesized latexes was characterized, giving insights into their flow and viscoelastic properties. Results from viscosity measurement showed that all emulsions were non-Newtonian in nature and experienced shear thinning behavior. This property made the latexes appropriate for applications in paints and coatings since they remained stable at lower viscosities when exposed to low shear conditions but became easier to apply at higher shear conditions because of their reduced viscosity.

Amplitude sweeps performed on the samples gave information regarding the viscoelasticity of the systems and were also important in determining the linear viscoelastic regions of the systems. Storage and loss moduli were used to understand more about the internal structure of the latexes through their ability to form structured particle networks. Differences in viscoelasticity were observed across the surfactant systems and were influenced by the level of interactions between the particles within the emulsions.

Furthermore, the frequency sweep test results reinforced the viscoelastic behavior of the emulsions and gave more information about their time-dependent structural changes. The high values of storage modulus as compared with those of loss modulus in many cases indicated elasticity of emulsion systems and formation of a stable structure inside latex. These results showed that surfactant choice has an effect on the microstructure and deformation process in polymer emulsions, and thus on their performance and practical application.

Water contact angles were determined for the coated films in order to investigate the wettability behavior of the coating surfaces. Coatings modified with the fluorosurfactant showed a much higher water contact angle than conventional surfactant-coated samples. Higher hydrophobicity of the modified coatings was mainly due to the presence of fluorine-containing segments in the molecules with very low surface energy. It is well known that fluorinated materials are characterized by outstanding water repellent and moisture-resistant properties.

The increase in water contact angle was another indication that fluorosurfactants modified the surface properties of acrylic coatings in addition to improving the anti-wetting property. Acrylic coatings may be used for wood coating, anti-fouling, self-cleaning, moisture resistant, and more advanced industrial protective coatings. The decrease in surface energy due to the addition of the fluorosurfactant also aided in the process of spreading and homogeneity of the coated surface.

From the experiment, it is quite evident that surfactants play an important role not only in the polymerization process but also in the final physical and chemical properties of acrylic emulsions. Common surfactants such as SDS were effective at ensuring stability and fast reaction, while amphoteric surfactants, for example, CAPB, increased stability and minimized the possibility of aggregation. Amphoteric fluorosurfactants performed better than the other two types of surfactants in the aspects mentioned above.

The conclusions drawn from this study indicate that fluorosurfactants can be useful additives for creating water-based acrylic paints that possess improved functional properties. However, environmental issues related to long fluorinated chains should be taken into account, and future research should consider the development of environmentally benign fluorosurfactants based on short or partial chains.

Overall, the current study managed to establish an important contribution that surfactants make to the creation of polymer micelles during batch emulsion polymerization process and the properties of their aqueous solutions. In addition, the research conducted provides valuable information regarding the development of environmentally safe emulsions with enhanced functional properties.

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