Eco-friendly Water Repellent Polymers for Superhydrophobic Compositions in Industrial Applications

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This thesis is submitted to the National University of Sciences and Technology, Islamabad, in partial fulfillment of the requirements for the degree of

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Nanoscience and Engineering

Supervisor: Dr. Nasir Mehmood Ahmed

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DEDICATION

To my esteemed parents, Muhammad Yousaf Awan and Tahira Yousaf, whose steadfast support and encouragement have been the cornerstone of my academic journey. To my siblings, whose love and camaraderie have been a constant source of strength. And to my friends, whose unwavering belief in me has inspired perseverance. This thesis is dedicated to you all, with deepest gratitude and heartfelt appreciation.

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LIST OF SYMBOLS, ABBREVIATIONS AND ACRONYMS

KPS	Potassium per-sulphate
DMC	Dimethyl aminoethyl methacrylate methyl chloride
FRP	Free radical polymerization
BA	Butyl acrylate
M	Monomer
CS	Cationic starch
S	Surfactant
µS	Micro-Siemen
SEM	Scanning electron microscope
FTIR	Fourier transform infrared
TGA	Thermal gravimetric analysis
NPEs	Nonylphenol ethoxylate
PDI	Polydispersity index
EP	Emulsion Polymerization

ABSTRACT

Polyurethane emerged as an extraordinary class of polymer having outstanding mechanical strength, toughness and durability etc. PU coatings can be found as a top coat on many different substrates such as metals, wood, leathers, textile, etc. But it has been observed that various polar groups are present in the polyurethane chemical structure. These polar groups provide hydrophilic character to the PU coatings and decrease their hydrophobicity. This study focuses on synthesizing an eco-friendly water repellent polymer emulsion that is mostly made up of base monomers, including n-butyl acrylate, styrene, DMC (dimethyl aminoethyl methacrylate ammonium chloride) and acrylic acid. The semi-batch emulsion polymerization procedure was utilized in an attempt to develop a stable latex for further study of the latex system. The main objective was to generate a latex with high stability and little coagulum content that would be able to impart hydrophobic properties to the Polyurethane polymer. The emulsion stability was investigated by using two different surfactant Disponil FES77 and Nonylphenol ethoxylate and their effect was studied. Then the optimized formulation of emulsions was investigated by different characterization techniques ZETA potential analysis, FTIR, TGA, SEM, pH and Conductivity test to examine particle stability, thermal stability, morphology, and ionic content of emulsions ENS10 (15%) and E2NS10 (20%). After the successful formation of the emulsion, a series of samples prepared by combining different % compositions of the emulsion with polyurethane resin in order to investigate the hydrophobic impact. The compositions were modified by including emulsion at varying percentages of 0%, 1%, 2.5%, 5%, 10%, and 20% by weight. After proper drying of samples these samples were placed under hot press make sheets to examine their water repellence behavior.

Keywords: Hydrophobicity, Eco-friendly water repellent polymer, Polyurethane coatings, Semi batch emulsion polymerization, Acrylate emulsion, Styrene butyl acrylate, Copolymerization

CHAPTER 1: INTRODUCTION

1.1 Historical Background

Polymers, which are a natural gift, have been there since the beginning of life in the universe. However, humans only became aware of them at a later time. Before the early 20th century, chemists were skeptical about the existence of molecules with molecular weights exceeding a few thousand. Hermann Staudinger, a German scientist well-versed in studying natural compounds, challenged this narrow perspective. Natural polymers form the fundamental building blocks of life. Human beings derive pleasure from utilizing natural polymers such as rubber, wool, wood, leather, silk, and others in their daily lives. Polymers are macromolecules consisting of repeating chemical units.

The term "polymer" comes from the Greek words "poly," meaning many, and "meros," meaning component. However, the field of polymer science and the development of synthetic polymers are relatively recent advancements, dating back to the mid-19th century when vulcanization was accidentally discovered. Nevertheless, its growth rate remained slow until the beginning of the 20th century. Currently, the field of science related to synthetic polymers is continuously expanding. In our current era, it is astonishing to imagine a world without these man-made materials. Furthermore, considering the depletion of natural resources, synthetic polymers have emerged as a smart substitute. Synthetic polymers have the ability to imitate and substitute a wide variety of materials such as metals, rubber, cloth, and leather, among others. A diverse selection of synthetic polymers with various unique properties is readily available in the market. Some examples include polystyrene, polyolefins, polyurethanes, and acrylic polymers, among others.

1.2 Advancement in Polymer Coatings

Currently, there have been significant research and improvements in polymer engineering and technology. These developments have increased the adaptability of polymer materials, allowing them to be utilize in variety of applications, from household items to industrial settings. Polymer coatings are manufactured on a huge scale and are utilized in various engineering disciplines. Polymer coatings are seen everywhere in contemporary culture. They serve the purpose of providing adornment, safeguarding, and fulfilling specific tasks [1].

During the last ten years and likely continuing into the next century, the coatings sector will have undergone a transformative era of technological advancements. One significant factor behind this sudden increase is the growing emphasis on health, safety, and environmental issues. The industrial revolution of the 1800s was partially driven by the necessity to enhance production and manufacturing methods to accommodate a growing population. Similarly, the recent advancements in coatings technology have been motivated by the demand for safer and environmentally friendly materials. The mitigation of volatile organic compounds (VOCs) in paints and coatings is particularly significant due to their detrimental impact on the environment. However, the performance characteristics of conventional solvent-based coatings, which were often more than sufficient, are still desired. To address the need for reduced VOCs while maintaining satisfactory performance, there has been a great research and development of low VOC coatings, particularly waterborne, high-solids, and powder coatings [2]. Overall, polymer coatings are classified as superior coating systems due to their widespread availability, affordability, and improved performance. The research community has introduced various advancements in traditional coating systems, such as multifunctional smart coating systems. These include superhydrophobic coatings, self-healing coatings, self-cleaning coatings, and super-hydrophilic coatings. These advancements have gained significant attention from both the scientific community and various industrial sectors [3].

1.3 Superhydrophobic Coatings

Wettability is a significant attribute that is often defined by the hydrophobic and hydrophilic nature of a surface [4]. The hydrophobicity of a surface is commonly quantified using the numerical values of the contact angle (CA) and slide angle (SA) between the surface and water.

Superhydrophobic surfaces have been extensively replicated from natural sources i.e. shark scales, gecko feet, wings of butterfly, and lotus leaves. Superhydrophobicity refers to a unique surface wetting phenomenon characterized by a contact angle exceeding 150° and a sliding angle lower than 10° when in contact with water [5,6]. This type of surface is highly regarded for its extensive potential applications, owing to its water repellent, anti-icing, and oil-water separation properties [6-8].

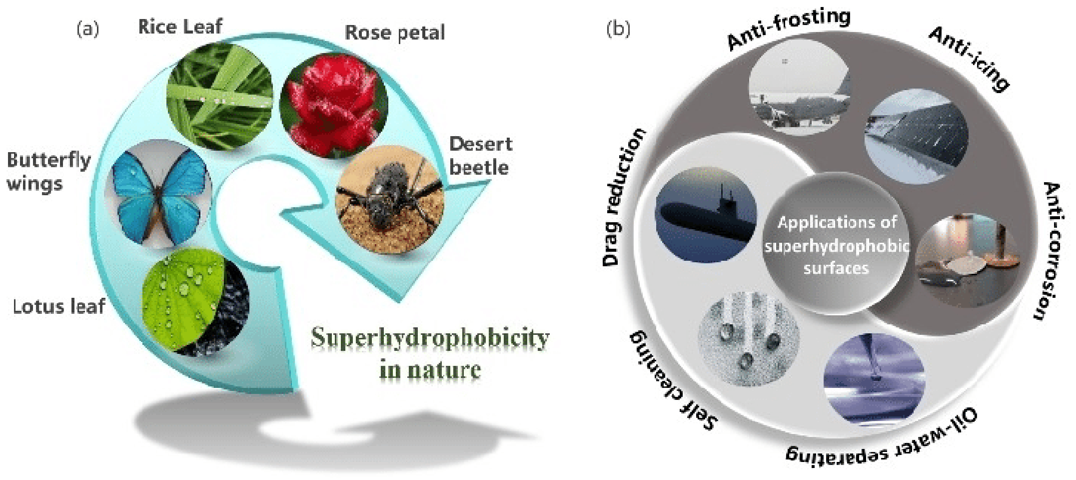


Figure 1. 1Existence-of-superhydrophobic-surfaces-in-nature and their applications

In order to create superhydrophobic surfaces, two conditions must be met: firstly, the free energy of the material surfaces must be minimized, and secondly, a rough microstructure must be constructed on the material surfaces [1,6,7]. This text provides a concise overview of the wettability models for surfaces with superhydrophobicity and discusses the advancement of theories related to superhydrophobicity.

1.3.1 Young's equation - ideal surface

The first model, known as Young's equation, was introduced in 1805. In this model, it is assumed that the solvent surrounding the solid surface in contact is chemically unreactive with each other [8].

$$\cos \theta c = \gamma SV - \gamma SL \ \gamma LV \ (1)$$

This model calculates the static contact angle of a fluid droplet on surface that is smooth, insoluble, homogeneous, and rigid. Wetting is explained through Young's equation, which is derived from equation (1) and pertains to the surface free energy of the solid. Young's equation (1) specifically describes the contact angle that results from the thermodynamic equilibrium of the free energy surfaces at the interface of solid, liquid, and gas.

The variables in question are θ, which represents the contact angle, γSV, which signifies the surface tension of the solid-vapor interface γSL, which refers to the surface tension of the solid-liquid interfaces, and γLV, which the surface tension of the liquid-vapor interfaces [9]. The equation demonstrates a clear correlation between the surface energy and contact angle. Young's equation is limited in its capacity to explain most contact angle states due to the presence of diverse surface conditions and solid roughness on real surfaces, which have an impact on wettability.

1.3.2 Wenzel model

The Wenzel model was developed by updating the premise of Young's equation. Its purpose is to determine whether a uniformly uneven surface can be wetted. The Wenzel model equation, established in 1936, establishes a relationship between surface energy, roughness, and the contact angle, as expressed by equation (2).

$$\cos \theta c = \mathrm{r} \cos \theta c = r\ (\gamma SV - \gamma SL)\ \gamma LV \ (2)$$

The contact angle, θc, is controlled 'r' represents the roughness of surface. The roughness factor, as depicted in equation (3), is the ratio between the actual surface area and the geometric or planar surface area. Consequently, a surface that has undergone roughening will consistently display a value greater than 1.

$$r = Actual\ Surface\ Geometric\ project\ surface \ (3)$$

The Wenzel model asserts that the contact between a solid surface and a liquid is completely close together for homogeneous wetting. The Wenzel model quantifies surface wettability by assessing energy difference between a dry surface and a wetted surface. Surface roughness has the power to modify the wettability and anti-wettability properties of a surface. It has been shown that an increase in surface roughness leads higher contact angle [10]. The surface energy of a substance is assessed by its surface chemistry, specifically the presence of an interface that is generated due to changes in energy at the surface. When a surface is made rough, the contact area between the surface and other substances rises. As a result, the surface energy of a certain unit area also increases, depending on the surface's natural ability to be wetted. It is crucial to mention that the specific surface energy of a solid is unaffected because it is dependent on the surface chemistry of the solid. On a rough surface, however, the alteration in energy resulting from the formation or elimination of a new boundary will be more noticeable. One idea suggests that there is an inverse relationship between surface wettability and roughness. This means that as a surface becomes more hydrophobic, the contact angle also increases accordingly [11]. Conversely, a hydrophilic surface will have the opposite outcome since its contact angle tends to be zero.

1.3.3 Cassie-Baxter model

The Cassie-Baxter model was created in 1944 to provide an alternative framework for studying liquid droplet and a solid surface interaction with each other, whether it is homogeneous or heterogeneous. Their model consists of two components. The first component includes the surface fraction, denoted as f1, and the contact angle, denoted as 1. The second half includes the surface fraction f2 and the contact angle 2. Therefore, in Cassie Baxter's equation, the contact angle is denoted as equation (4):

$$\cos \theta = f1 \cos \theta 1 + f2 \cos \theta 2 \ (4)$$

In the Cassie-Baxter model, θ represents the contact angle, whereas fi represents the surface area fraction with a contact angle of θi. It is important to note that the sum of f1 and f2 is equal to 1. The Cassie-Baxter model assumes that air pockets are restricted below the liquid and that the liquid only touches the solid at the roughness tips [11]. In this scenario, the area on the surface can be considered as a region where air is confined instead of being covered by liquid. If there is simply air between a solid and a liquid, the angle θ2 will be 180°. Therefore, equation (5) can be expressed as the following equation, where the solid surface fraction is denoted as fs and contact angle with θs.

$$\cos \theta CB = fs\ (\cos \theta s + 1) - 1 \ (5)$$

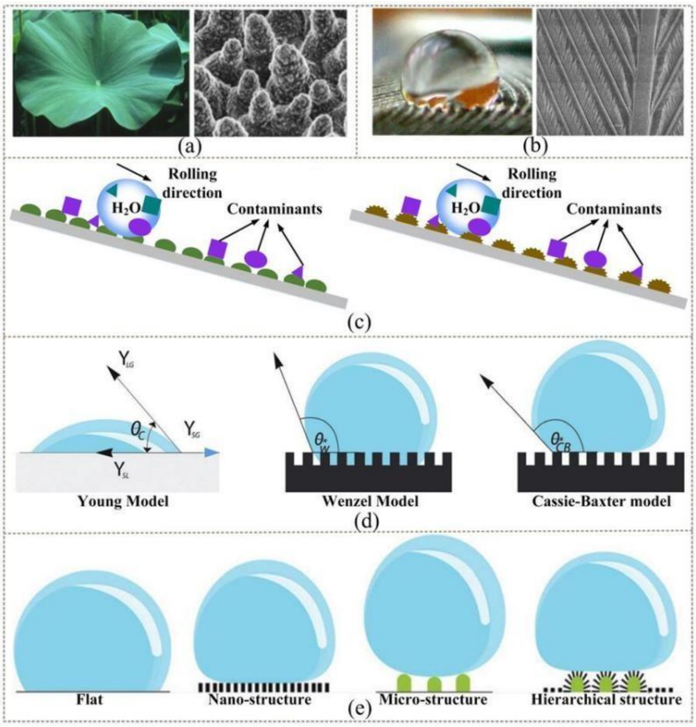
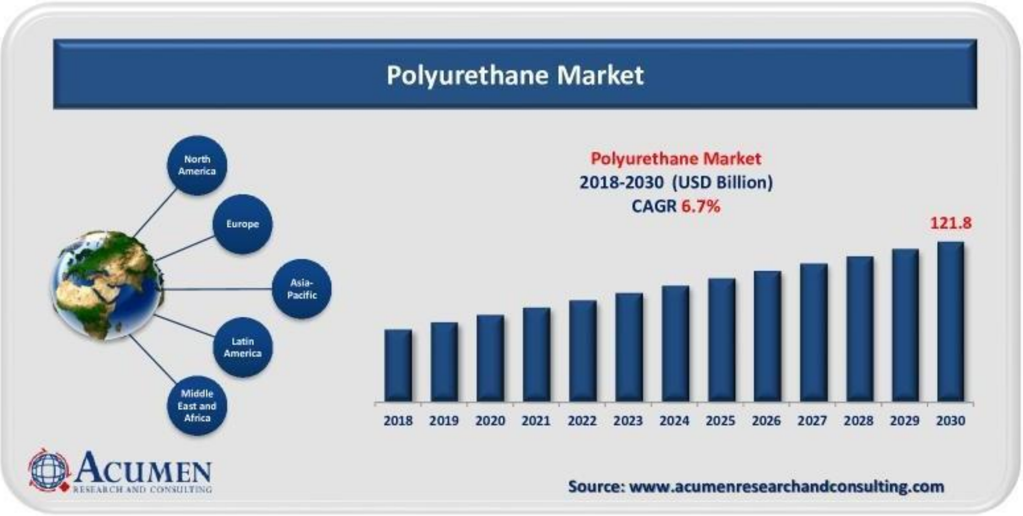


Figure 1. 2: Typical hydrophobic mechanisms of superhydrophobic surfaces in nature: (a) SEM images of lotus leaf surfaces; (b) SEM images of bird feather surfaces; (c) self-cleaning mechanism of superhydrophobic surface]; (d) liquid droplet on solid surfaces

1.4 Polyurethane (PU as a coating material)

In 1849, Wurtz successfully created the initial urethane compound. However, it was not until 1937 that Professor Otto Bayer in Germany made significant advancements by effectively synthesizing polyurethane as a result of the reaction between a polyester diol and a diisocyanate. Since then, PU polymers have been widely utilized in various applications such as coatings, elastomers, foams (both flexible and rigid), adhesives, sealants, paints, varnishes, and more. This is due to their versatility, exceptional mechanical and chemical resistance properties, comfort, cost-effectiveness, and environmentally friendly characteristics [13,14]. Covestro LLC, a German maker of advanced polymers, conducted a survey revealing that the worldwide demand for PU in 2019 was approximately 18.4 million tons. It is projected to rise to 22.5 million tons by 2024. According to another report, the global consumption of PU was valued at 60.5 billion USD in j2017 and is projected to exceed 79 million USD by 2021 [15].



Source: www.acumenresearchandconsulting.com

Figure 1. 3: Polyurethane Trend, Share and Market Size Analysis Report, Forecast 2022-2030

Due to its flexible qualities, it has had an impact on various fields of material engineering, ranging from footwear to coatings used in aeronautics [16,17].The prominent industries that utilize PU include sports, textile, biomedical, leathers, footwear, building and construction, The wide range of applications is a result of the customizable and the flexibility of polymers based on polyurethane, even at lower temperatures.

1.5 Basic Chemistry of Polyurethane

Polyurethanes are produced by the reaction of di/poly isocyanates with diols or polyols, leading to the creation of repeated urethane linkages, as illustrated in Figure 1.4. This reaction occurs in the presence of a chain extender and various additives [18].

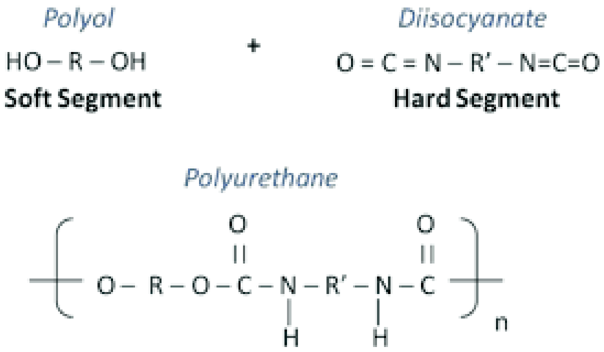


Figure 1. 4: Reaction of di/poly isocyanate and a diol or polyol, forming repeating urethane linkage.

The fundamental constituents of polyurethane can be simplified to two primary components: a polyol and an isocyanate. The characteristics of the product are assessed by both the polyol and the isocyanate. Modifying the polyol or the isocyanate might result in significant alterations in the characteristics of the polyurethane. Therefore, comprehending and creating polyurethane goods relies heavily on understanding the connection between the structure and properties of the polyol and isocyanate [19]. The polyol and the isocyanate create distinct domains or regions inside the resulting polyurethane. These domains have a crucial role in determining the characteristics, such as softness, flexibility, or hardness, of the end product. The soft segments and hard segments are depicted in Figure 1.5 Polyols often possess longer chain lengths, leading to enhanced mobility and hence imparting flexibility to polyurethane. Diols with longer chain lengths offer even greater flexibility. Meanwhile, the isocyanates and chain extender used control the hard portions. Isocyanates are typically composed of short chain molecules, resulting in a higher degree of crystallization. This leads to the formation of compact and tightly packed segments that are rigid and inflexible in nature [20]. The polyurethane's very adaptable and functional nature for variety of applications is attributed to the combination of hard and soft segments it possesses.

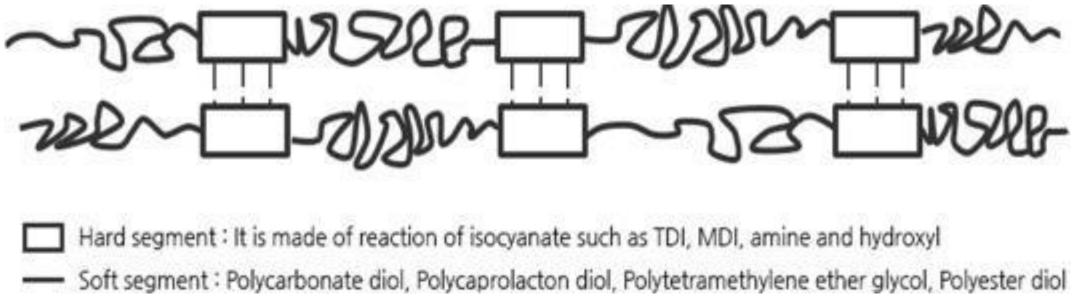


Figure 1. 5: The soft segments and hard segments in polyurethane

1.6 Problem Statement

Polyurethane emerged as an extraordinary class of polymer having excellent mechanical strength, toughness and durability etc. But it has been observed that various polar groups are present in the polyurethane chemical structure. These polar groups provide hydrophilic character to the PU coatings and decrease their hydrophobicity. Furthermore, another distinctive behaviour of PU coating is their ability to form strong interaction by forming a powerful interchain hydrogen bonding among urethane linkages that gives significant mechanical properties and superiority to PU coatings over most other coating systems. This extra hydrophilic character makes PUs a challenging material for inculcating superhydrophobic character [21].

1.7 Aims and Objectives

Acrylic resins have proven to be superior in industry due to their ability to give better stain protection, water resistance, improved adhesion, and resistance to blocking and cracking, surpassing the performance of various latexes. This study focuses on synthesizing an eco-friendly water repellent polymer emulsion that is mostly made up of base monomers, including n-butyl acrylate, styrene, DMC (dimethyl aminoethyl methacrylate ammonium chloride) and acrylic acid. The semi-batch emulsion polymerization procedure was utilized in an attempt to develop a stable latex for further study of the latex system. The main objective was to generate a latex with high stability and little coagulum content that would be able to impart hydrophobic properties to the Polyurethane polymer.

1.8 Research Framework

The work scheme was expanded into following parts;

1.8.1 Part one

This part includes successful synthesis of styrene acrylate emulsion via semi-continuous emulsion polymerization using styrene, butyl acrylate, acrylic acid, cationic starch, dimethyl aminoethyl methacrylate methyl chloride (DMC) as monomers and a surfactant (Disponal FES77 and Nonylphenol Ethoxylate) under inert atmosphere. Potassium per-sulphate (KPS) was used as initiator.

1.8.2 Part two:

The prepared emulsion was then characterize using different techniques such as; zeta potential, zeta sizer, contact angle, FTIR, TGA, SEM, PH and conductivity test were performed.

1.8.3 Part three:

Sheets of polyurethane resin were formed with different %composition of prepared emulsion by using hot press. After that characterization such as contact angle, TGA, and surface energy of prepared samples were calculated.

CHAPTER 2: LITERATURE REVIEW

2.1 Previously used Hydrophobic Agent and their Environmental Concerns

A wide range of low surface energy compounds, both organic and inorganic, have been extensively researched and employed as durable hydrophobic agents. Various techniques, like as impregnation and spraying, have been utilized to achieve significantly reduced hydrodynamic resistance [22]. Nevertheless, the practical use of hydrophobic materials is hindered by the unsuitability of inorganic materials, such as SiO2 and CuO nanoparticles or nanoarrays, due to their weak adhesive force, poor washing resistance, and inadequate abrasion resistance. Hydrophobic organic materials, such as fluorinated compounds and siliceous compounds, have gained significant interest due to their capacity to be designed, low surface energy, strong contact force, and great resistance to washing and abrasion. Fluorine-containing compounds are regarded as highly characteristic hydrophobic organic materials that have exceptional surface hydrophobicity, low surface energy, and chemical durability. The fluorine atom possesses a naturally strong electronegativity and a noticeable shielding effect, leading to a significantly lower critical surface tension of the C-F bond compared to a typical alkyl chain. Furthermore, the fluorinated groups move towards the interface between the solid and air due to thermodynamics. This can be explained by the substantial polarity contrast between the fluorine side chain structure and the hydrocarbon chain found in fluoropolymers. At high temperatures, a significant number of side chains containing fluorine migrate to the surface, leading to a notable enhancement in the hydrophobic properties of the coating. Zhao et al. synthesized a cationic waterborne polyurethane-fluorinated (WFPU) coating using soap-free emulsion polymerization. The resulting coating demonstrated exceptional water repellence and mechanical characteristics. Nevertheless, coatings that contain fluoropolymers possess an inherent carcinogenic nature and are readily released during the processes of manufacture and finishing. Fluoropolymers, like perfluoro caprylic acid (PFOA) and perfluoro octane sulfonate (PFOS), exhibit exceptional chemical stability and are resistant to degradation, resulting in their long-lasting presence in the environment and organisms. Moreover, fluoropolymers provide a significant challenge in terms of metabolic decomposition, rendering them highly detrimental to both human health and the environment [23].

2.2 Emergence of Ecofriendly Emulsion Polymerization

This is a widely recognized technique used to produce homopolymers and different types of copolymer dispersions. Emulsion polymerization was first utilized for industrial purposes during World War II to produce 1,3-butadiene and styrene rubber. This was in response to the threat posed by Japanese troops to the global supply of natural rubber. Subsequently, emulsion polymerization has been utilized in diverse industries for varied purposes. Emulsion polymerization offers numerous distinct benefits. For example, the colloidal system allows for easier manipulation, with fewer difficulties in terms of temperature and viscosity compared to bulk polymerization. This method exhibits favorable viscosities even with high polymer content, allowing for the simultaneous attainment of higher molecular weight and increased polymerization rate [24]. Emulsion polymerization offers the advantages of surface impregnation and control over the micro and mesoscale of the product [25,26].

Water-based emulsion polymers are considered to be a suitable option for coating applications. This approach has gained significant interest due to its advantages, such as decreased volatile chemical emissions, ease of application, and the potential to contain nanoparticles [27].

2.2.1 Water-based Polymers versus Solvent-based Polymers

One significant benefit of water-based polymers compared to solvent-based polymers is that they have lower viscosity at medium solids levels, even with very large molecular weights (above 100,000 g mol-1) [28]. Substituting solvents with water in water-based polymers has several benefits, including a decrease in volatile organic compounds, reduced environmental impact, and decreased hazards during synthesis and application. Consequently, multiple ongoing research efforts are being conducted to diminish and substitute the solvents.

Humans, animals, and plants can absorb solvents, particularly when they are in a gaseous or liquid state. This can lead to various difficulties, especially if the exposure is prolonged. Currently, water-based procedures can be used to make classic solvent-based polymers for many coating applications, while also being environmentally benign. Shoaf and technology (2010) conducted research that demonstrated the use of emulsion polymerization in the production of a wide range of items that were previously only possible to generate using organic solvents. This research will focus on water-based acrylic styrene emulsion polymerization, which is one of the many types of water-based emulsion polymers. Various water-based emulsion polymers exist, including homopolymers and copolymers.

2.3 Introduction to Acrylic Polymer Emulsion

Acrylic polymers are renowned for their exceptional water resistance, durability, customizable mechanical properties, and affordability. However, they exhibit limited resistance to solvents and abrasion. Acrylic polymer emulsions have been widely employed in the leather industry for coating purposes, as well as for finishing on paper and textiles [29]. Polyurethane acrylates are materials with a comb-like structure that have the potential to combine the desirable properties of polyurethanes, such as high abrasion resistance, low temperature characteristics and greater toughness, with the advantageous water resistance properties, wear resistance, and weather ability of the acrylates.

2.4 Significance of Styrene acrylic Polymer Emulsion

Styrene-acrylic polymers provide exceptional hydrophobic properties, resulting in superior water repellence behavior and moisture vapor transmission rate (MVTR) compared to all other acrylic polymers. Furthermore, styrene possesses hydrophobic properties as a monomer, enabling the production of polymers of small particle sizes. As a consequence, these polymers are well-suited for certain uses, such as being used as primers in the construction sector or as binders in paper coatings [30,31].

Styrene-acrylic polymers possess a notable characteristic of having a high glass transition temperature. Consequently, they have a tendency to be long-lasting and demonstrate excellent resistance to wear and tear, as well as strong mechanical characteristics [32]. Additional characteristics of styrene-acrylic emulsion polymers include;

- Excellent resistance to weathering and stains.
- Achieving a broad balance between tensile strength and elongation.
- The capability to establish crosslinks.
- High capacity to bind pigments Optimal gloss, high film strength, and exceptional resistance to removal by detergents.
- Excellent adherence to commonly used materials such as galvanized steel, aluminum, and wood.

2.5 Basics of Polymerization

From decades, the progress of human development has been closely connected to the use of polymeric materials, even predating the scientific investigation of materials with distinct properties from metals and ceramics. Silk and cellulose, which are common natural polymers found in wood goods, fibre, and linen, played a vital role in advancing human activities like commerce and transportation. However, their composition and structural element were not well comprehended or valued until the 1900s. Most of these natural polymers predominantly have existence in forms with modest molecular weights, and chemists were skeptical about the plausibility of molecules with high molecular weights. Hermann Staudinger's proposal of the rubber structure marked the beginning of synthetic polymers replacing natural polymeric materials. During this period, the word polymerization was employed for describing the chemical process of combining tiny monomeric units to form extensive chains or networks known as polymers [33,34]. Synthetic polymers have now become an essential component of our everyday existence. Synthetic polymers can be intentionally crafted and controlled to possess a diverse array of physical, chemical and mechanical characteristics, rendering them very desirable in numerous industrial processes.

2.6 Methods of Polymerization

Polymers are synthesized by two methods:

2.6.1 step-growth polymerization process

2.6.2 chain growth polymerization process

This process entails the reaction of multifunctional monomers to form dimers. Figure 2.1 illustrates this phenomenon, specifically the synthesis of Nylon-6,6 through the condensation reactions of adipoyl acid and hexamethylenediamine monomers. During the beginning of the reaction, the functional groups of the monomers undergo a rapid reaction, results in the quick production of many chains with a relatively small number of repeating units. During the course of the reaction, the small chains gradually merge together to form larger chains, and this process persists until only chains with higher molecular weight are left. Thus, a high molecular weight can only be attained when there is a significant level of conversion [35,36].

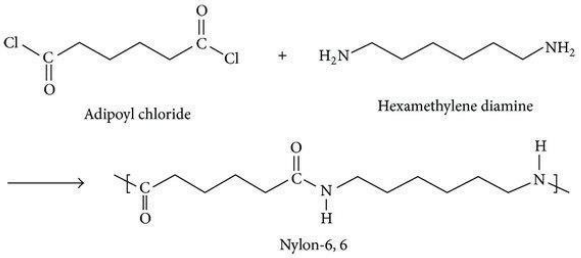


Figure 2. 1: Nylon 6,6 synthesis

This method primarily different because it utilizes an initiator to give rise to an active site, which form a free-radical, cation, or anion. Monomers are sequentially added to polymer's chains active site, and when a monomer is added, the reactive part is transferred to the new monomer, thus renewing the active part and allowing the propagation to continue. This leads to a significant surge in the molecular weight while the conversion of the monomer remains minimal. Commonly for radical chain-growth reactions monomer used are vinyl compounds.

2.7 Free-Radical Polymerization Process (FRP)

(FRP), a subset of chain-growth process, is mainly employed for manufacturing polymers obtained from olefinic monomers. It is distinguished by the rapid incorporation of monomers. Active sites exist in less concentrations, ranging from 10-5 to 10-8 mol/L. However, chains can expand rapidly in a less period of time due to addition of monomer at higher rate, with 103 to 104 monomers being added per second. Therefore, the duration and makeup of a chain are established during a timeframe of 33 to 34 seconds.

FRP can be divided into three distinct stages:

2.7.1 Initiation

Initiation can be categorized into two distinct stages, as depicted in Figure 7. Initially, molecules that initiate the reaction break down (with a breakdown rate coefficient, kd) at a high temperature, typically resulting in the formation of two radicals. Initiator radicals (R●) undergo homolytic reactions with monomers (rate coefficient, ki) to generate a novel and bigger free-radical (RM●). An example of a commonly used initiator which is employed in FRP is ammonium persulfate, which undergoes thermal decomposition to produce two radical anions. Radicals can be generated through thermal decomposition and electrochemical processes.

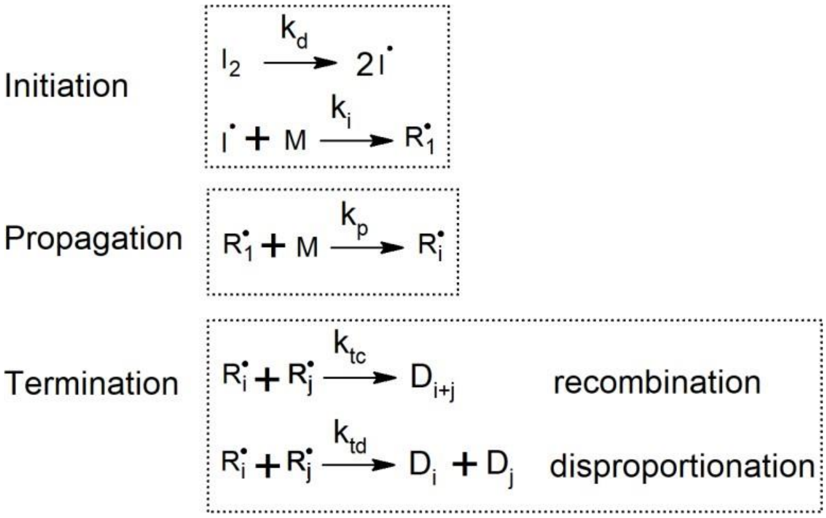


Figure 2. 2: FRP initiation, propagation and termination

2.7.2 Propagation

In propagation, chains undergo growth (rate coefficient, kp) through the repeated incorporation of monomers. A new radical which is bigger in size than the previous one forms, upon each new addition.

2.7.3 Termination

Over time, chains cease to expand and come to an end through either combination or disproportionation. The majority of chains are terminated by a process called combination, in which two radicals together produce a bigger chain. Disproportionation is a chemical reaction in which a radical from one chain removes a hydrogen atom from another chain, leading to the creation of one saturated chain and one unsaturated chain. [35,36,37].

2.8 Techniques of Polymerization

Polymerization techniques have four major types including:

2.8.1 Bulk polymerization

This is the most straightforward method, since it involves the use of very small number of components and is mostly employed for liquid monomers polymerization like styrene. In this method both monomer and initiator in liquid form are added to reactor, where polymerization occurs under continuous stirring and at higher temperatures. This method is uncomplicated and enables the creation of a polymer that is free from impurities. However, this method is not frequently employed due to the fact that free-radical mechanism are extremely exothermic. This may result in auto-acceleration, leading to the production of high viscosity products with wide molecular weight, and the destruction of the product through charring, burning, or other means, or even causing the reaction vessel to explode at greater extent. The drawbacks of this approach are overcome by employing solution polymerization [35,36].

2.8.2 Solution polymerization

Solution polymerization involves dissolving monomers and an initiator in a solvent, results in the production of the polymer. Similar to bulk polymerization, this polymerization process is conducted with continuous stirring and at higher temperatures. After the process of polymerization is finished, the resulting polymer is commonly utilized in the form of a solution or can be separated by evaporating the solvent. In this method the addition of solvent prevents rise in viscosity of the solution because the solvent is diluent, facilitating the reaction process and effortless stirring occur.

2.8.3 Suspension polymerization

In order to mitigate the expensive nature of solvents, this method is frequently employed, where in water both lipophilic monomers and initiators are suspended. Due to the initiator's solubility in monomer, the polymerization process occurs within monomer droplets that are sustained by constant shaking. Every individual droplet particle can be compared to a large-scale reactor, and the resulting polymer, which resembles pearls, which in water soluble. Surfactants can be included to hinder the merging of droplets before polymerization. In contrast to solution polymerization, where the viscosity rise is insignificant and temperature control is easier, the isolation of the result is straightforward in this case since in water polymer is insoluble. Although suspension polymerization has several benefits, it is limited to water insoluble monomers, lacks the ability to regulate particle size, and results in low polymer purity due to the usage of stabilizers. Furthermore, the synthesis of elastomers is not feasible using this process due to the tendency of sticky elastomer particles to form agglomerates. Therefore, in order to overcome these restrictions, the production of commercial plastics and elastomers is predominantly carried out via an alternative method known as emulsion polymerization.

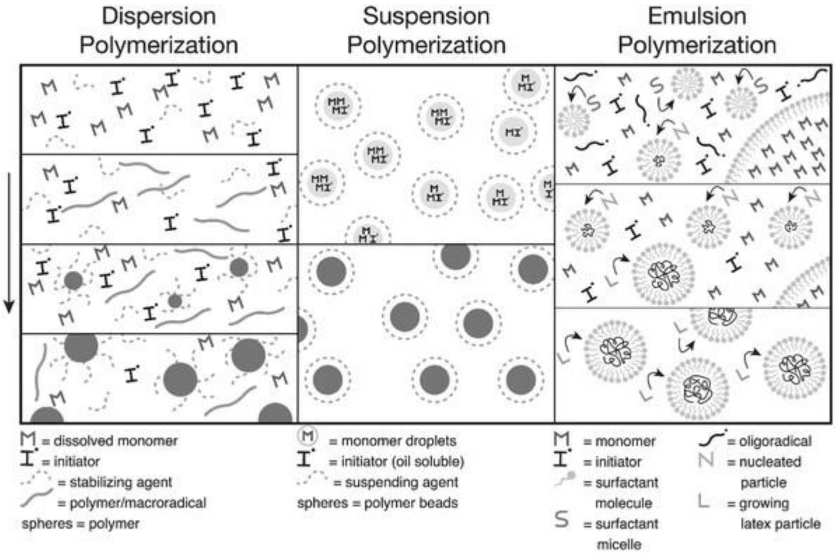


Figure 2. 3: Comparison of dispersion, suspension and emulsion polymerization

2.8.4 Emulsion polymerization

This process differs from suspension process in that it employs a initiator which is soluble in water. Therefore, this process is distinctive because it begins and spreads in water instead of the monomer droplets. This process requires the inclusion of a surfactant which stabilize the monomer droplets and the growing polymer chains. This technique enables a diverse range of monomer species to be used and provides particle size control, resulting in the production of more intricate polymer products [35,36,37].

2.9 Emulsion Polymerization

Emulsion polymerization involves dispersing combinations of monomers in water using appropriate emulsifiers. The polymerization reaction happens in micelles and is triggered by water-soluble initiators at high temperatures. The result is the production of stable aqueous dispersions, which are utilized in different application such as textile treatments, in paints and printing inks.

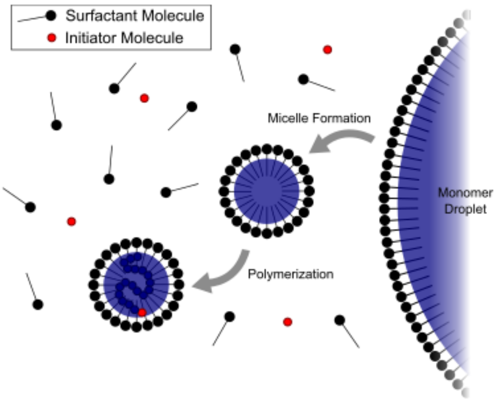


Figure 2. 4: Mechanism of emulsion polymerization

This is a form of free-radical polymerization. It is conducted in an aqueous medium employing monomer, surfactants (in an emulsified form), and a water-soluble initiator. Figure 2.4 illustrates the emulsification of monomers in water, where surfactant molecules are situated at the surface of the emulsion droplets to stabilize the mixture. Additionally, some surfactants dissolve in the water, while an excess of surfactant exists in micelles. This polymerization process is a sequential reaction initiated by the decomposition of an initiator molecule. These initiator radicals kickstart the reaction by attacking the double bond of the monomer, leading to the formation of chain radicals. These radicals undergo a reaction with an additional monomer molecule, resulting in the formation of elongated chain radicals. The chain reaction persists until the expansion of the chains is halted by recombination. Polymers generated by this process are derived from monomers. The monomers used can include styrene, vinyl, and acrylics.

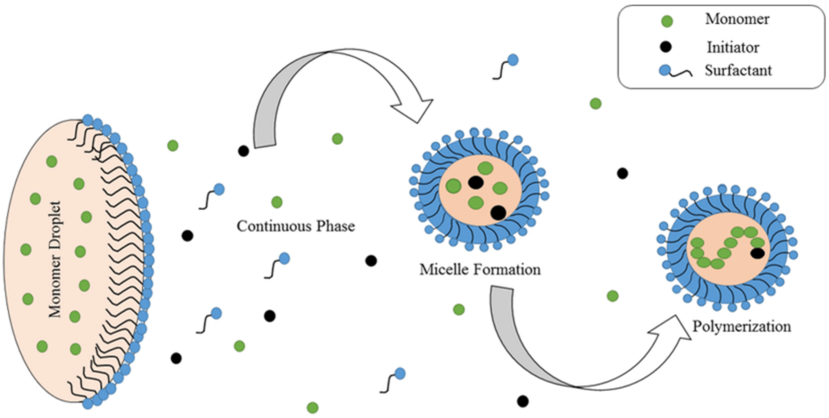


Figure 2. 5: Fundamentals of Emulsion Polymerization

The homopolymer latexes derived from these monomers are extensively utilized in several industries including paint, coating, textile, leather, construction, and paper. These polymers exhibit stability, possess a high capacity for binding pigments, demonstrate durability, show resistance to chemicals, and have a high impact resistance within the range of [34-38].

2.10 Components of Emulsion Polymerization

Formulating latexes involves the use of different components, including synthetic materials like monomers, surfactants, initiators, and post-synthesis additives like biocides, which are added for specific purposes.

2.10.1 Monomers

2.10.1.1 Demand for butyl acrylate and its applications

N-butyl acrylate (BA) is the most often utilized acrylate ester in the manufacturing of all-acrylic, vinyl acrylic, and styrene acrylic copolymers.

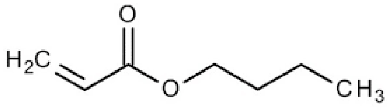


Figure 2. 6: Butyl acrylate chemical structure

(BA) is a leading provider of acrylic ester monomers, accounting for around 60 percent of the global market. BA's consumption volume exceeds 2,000 kilo tons. Butyl acrylate is utilized as a "soft-monomer" to enhance the low temperature characteristics and durability. BA primarily targets the paint and coatings industry, specifically architectural and automotive coatings. It also has a presence in the adhesives and sealants business. BA is a very adaptable component used in copolymers, providing exceptional resistance to weathering and sunshine, great performance at low temperatures, hydrophobic properties, and resistance to water [39,40].

The incorporation of butyl acrylate with various polymerizable monomers, including styrene, acrylic acid, and other acrylate ester monomers, enables the creation of a wide range of copolymer. BA copolymer compositions frequently consist of four or more distinct co-monomers.

Butyl acrylate monomer is utilized in the formation of acrylic resins and emulsion polymers, which are water-based. Waterborne butyl acrylate polymers find use in architectural sectors such as latex paint, as well as in paper coatings, adhesives, sealants, and leather and textile finishes. Butyl acrylate is a valuable raw material for chemical syntheses due to its ability to easily react with a diverse range of organic and inorganic molecules [41].

2.10.1.2 Styrene

Styrene is an organic molecule represented by the chemical formula C8H8. The structure of the compound includes a vinyl group attached to a benzene molecule. Styrene monomer exhibits hydrophobic properties and is utilized in applications that require hydrophobicity [42].

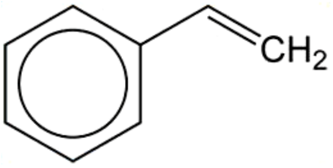


Figure 2. 7: Styrene chemical structure

2.10.1.3 Acrylic acid

Acrylic acid, also known as prop-2-enoic acid, is an organic molecule represented by the chemical formula CH2=CHCOOH. It is the most basic form of unsaturated carboxylic acid, composed of a vinyl group immediately attached to a carboxylic acid end.

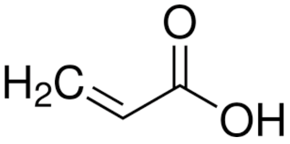


Figure 2. 8: Butyl acrylate chemical structure

Acrylic acid monomer is frequently employed in emulsion polymerization to achieve precise film generation and electrostatic colloidal stability [43].

2.10.1.4 DMC (Dimethyl aminoethyl methacrylate methyl chloride)

It is used as cationic monomer in emulsion polymerization.

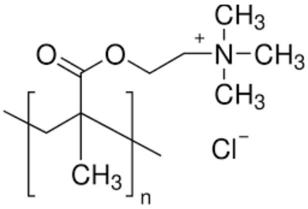


Figure 2. 9: DMC chemical structure

2.10.2 Continuous Medium

As continuous medium water is used in emulsion process because of its high heat conductivity. This allows for higher polymerization rates while limiting auto-acceleration by keeping the reaction viscosity similar to that of water. The hardness of water can vary based on its source and can affect the size of particles, the process of nucleation, and the stability of particles. Consequently, deionized water is commonly employed. Furthermore, it is important for the water used to have a low oxygen concentration. This is because oxygen acts as a scavenger for free radicals, which can hinder the initiation of polymerization and cause delays. In order to circumvent this delay in the start of the process, the water is frequently deprived of oxygen by purging it with nitrogen gas before the polymerization takes place [44-45].

2.10.3 Initiator

Water-soluble free-radical initiators for emulsion polymerization can be generated through thermal breakdown, redox processes, or gamma radiation. The selection of the free-radical generation method is based upon the specific latex type being produced and, consequently, temperature of the reaction. Most emulsion polymerizations are conducted at temperatures ranging from 75 to 90 ºC in order to optimize the rate of polymerization. Consequently, thermal initiators are more frequently employed in these processes. Thermal initiators consist of peroxydisulfate salts, such as ammonium persulfate and potassium persulfate (KPS), which breakdown through homolytic cleavage to produce sulphate radical anions [44-47].

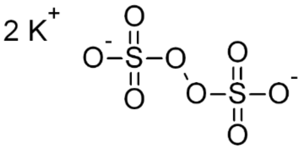


Figure 2. 10: Homolytically decomposition of KPS to yield sulphate radical anions

2.10.4 Surfactants

Surfactants, which are chemicals that modify the surface tension of a liquid, play a crucial role in emulsion polymerization due to various reasons:

(1) Provide stability to monomer droplets.

(2). Create micelles which behaves as nucleation sites.

(3). Dissolve polymers latex and monomer

(4) Enhance the stability of developing particles by inhibiting aggregation, leading to the formation of a durable final product.

Surfactants are commonly added to monomer at a weight percentage ranging from 1% to 6%. Anionic surfactants usually have lower concentrations, whereas non-ionic surfactants tend to have greater concentrations. Surfactants are molecules that have both hydrophobic and hydrophilic parts, making them amphiphilic. They have a tendency to arrange themselves at interfaces, such as the boundary between water and air, because of the existence of these different segments. Surfactant molecules dissolve in a manner consistent with their solubility when present in low concentrations. However, when the concentration reaches a level known as the critical micelle concentration (CMC), the solution becomes saturated, and surfactant molecules (typically between 50 and 150) begin to aggregate to form a micelle. These micelles have a diameter of approximately 2-10 nm and are structured in a way that the polar ends face outward while the nonpolar chains face inward, forming a hydrophobic pocket. Micelles exhibit repulsion in aqueous environments as a result of the existence of polar heads, which possess similar charges and hence experience mutual repulsion inside the solution. The quantity and dimensions of micelles are contingent upon both the quantity and nature of the surfactant; specifically, greater quantities of surfactant result in smaller-sized micelles. Micelles typically exhibit a spherical morphology, although their shape can vary to a rod-like structure it depends on the surfactant concentration being used. [44-47].

2.10.4.1 Surfactant Classification

Surfactants can be divided into four types based on the type of their hydrophilic part: “anionic, cationic, amphoteric, or non-ionic”. In emulsion polymerization, anionic and non-ionic surfactants are predominantly utilized owing to their enhanced affinity with negatively charged particles. Anionic surfactants undergo ionization, resulting in the generation of a negative charge on the polar head of the molecule. Sodium dodecyl sulphate (SDS) is a frequently employed anionic surfactant in emulsion polymerization. SDS undergoes ionization when dissolved in water, as depicted in Figure 2.11.

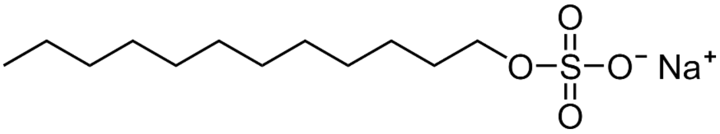


Figure 2. 11: Structure of SDS

Amphoteric or zwitterionic surfactants can undergo ionization to generate an electric charge. At greater pH, they acquire anionic qualities, while at lower pH value, they acquire cationic attributes. Some examples of these compounds are imidazoline carboxylates and amine oxides.

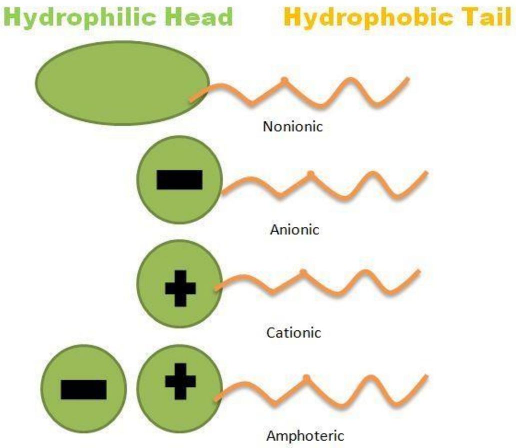


Figure 2. 12: Classification of surfactant

Non-ionic surfactants differ from the other three types in that they do not separate into charged particles when dissolved in a solution. [44-47].

Disponil FES77

Disponil FES 77 behaves as a surfactant and emulsifier in emulsion polymerization processes. The properties of dispersing, emulsifying, formula stability, and solubilizing are present.

Nonylphenol Ethoxylate

NP/NPEs, which are sometimes referred to as nonylphenols and nonylphenol ethoxylates, are a type of non-ionic surfactants. These detergent-like chemicals find application in various industrial processes as well as in consumer products such as laundry detergents, personal hygiene products, automotive products, and latex paints.

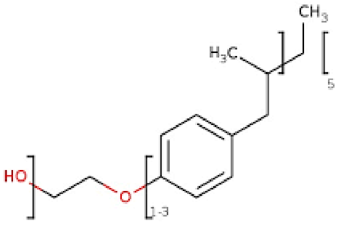


Figure 2. 13: Nonylphenol ethoxylate chemical structure

2.11 Emulsion Polymerization Mechanism

The synthesis of emulsion polymers involves many methods that can vary depending on the specific system. The subsequent text provides a comprehensive summary of theproposed hypotheses. The positioning of the major constituents (initiator, surfactant, and monomer) is determined by the ability to dissolve in the water-based solution. Monomers exhibit low solubility in water, resulting in their aggregation to create monomer droplets. These droplets, which are stabilized by both agitation and surfactants, have a diameter ranging from 5 to 20 microns. Surfactants possess amphiphilic properties and can exist as individualmolecules or form micelles when their concentration surpasses the critical micelle concentration (CMC). These micelles can either be empty or filled with monomer. Molecules of initiator are predominantly present in continuous phase, where the production of initiating radicals takes place.

The process of initiation does not take place within individual droplets of monomers in emulsion polymerization due to the fact that the initiators employed are not soluble in oil. This distinguishes emulsion polymerization from suspension polymerization, as the initiation process takes place within the monomer droplets. Ammonium persulfate (APS) is a frequently used initiator in emulsion polymerization. Thermal decomposition of APS produces two disulfate anionic radicals, as depicted as follows:

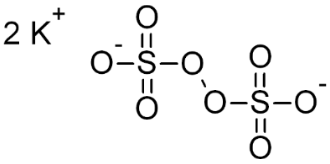


Figure 2. 14: Decomposition of potassium per-sulphate

After the initiator decomposed, this process can be categorized into 3 stages:

- *Stage I (particle nucleation)*
- *Stage II (particle growth)*
- *Stage III.*

2.11.1 Particle Nucleation (Stage I)

This precise process has been extensively discussed in literature, however there is little agreement because of the presence of several types of particles in a reaction vessel.

One of the initial suggested mechanisms is micellular (heterogeneous) nucleation, which involves nucleation happening solely within micelles and polymer particles. Figure 2.15 illustrates the initial step of micellular nucleation, when an oil-insoluble initiator radical enters a micelle packed with monomers. Within the micelle, it undergoes a reaction with a monomer to produce either a monomer radical or a latex particle that is actively developing. Figure 2.15 illustrates the process of micellular nucleation.

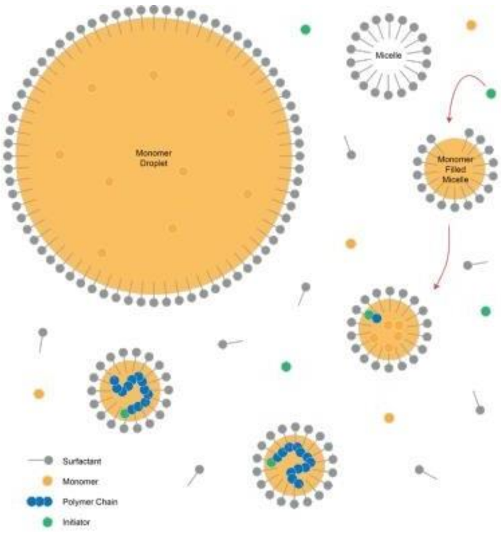


Figure 2. 15: Micellar Nucleation Mechanism

Homogeneous nucleation, the second hypothesis of nucleation, is largely acknowledged by professionals in the industry as the prevailing type of nucleation. In this method, illustrated in Figure 2.16, the initiator does not enter a micelle. Instead, it initiates polymerization within the aqueous medium by adding an initiator radical to a monomer. This radical then incorporates additional monomers until the chain reaches a critical length, at which point the oligomer becomes insoluble in water. Currently, the chain is in a state of thermodynamic instability and undergoes collapse either upon itself or onto inactive oligomers present in the water phase, results in the production of latex particles. At the same time, surfactant molecules attach to their surface to provide stability by reducing the energy at the interface. In the absence of surfactant, the chains collapse and produce coagulum [44-47].

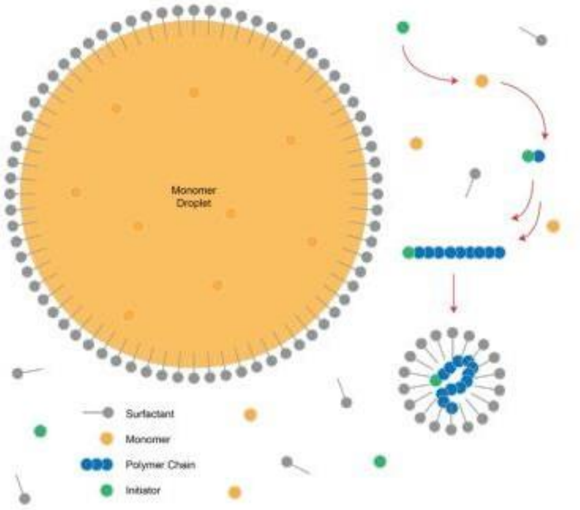


Figure 2. 16: Mechanism of Homogenous Nucleation

Nucleation does not happen in monomer droplets because their surface area is limited compared to micelles. The chances of an initiator molecule entering a droplet are highly unlikely because great chances of its interaction with a monomer that is freely floating before reaching a droplet. In summary, this phase is quite brief and yields stable seed particles with a diameter of approximately 25 nm. These seeds undergo expansion in the subsequent step.

2.11.2 Particle Growth (Stage II)

In this stage, monomers are transferred from droplets to micellular particles to facilitate the growth of the seeds. Solubility of monomers like n-butyl acrylate and methyl methacrylate is low in water. As a result, there is an equilibrium between monomer droplets, monomer-rich micelles, and the continuous phase to maintain a constant concentration of freely available monomers. When the number of unattached monomers falls, monomers are drawn from droplets into the water phase through diffusion. Monomers can undergo a reaction in a watery environment to create oligomers or "z-mers" which shows insolubility when they reach a certain length known as their critical length. Subsequently, they migrate towards particles surface instead of undergoing particle formation, as there is an insufficient amount of soap remaining to facilitate the creation of a new stable boundary. Particles undergo growth by extracting monomers through diffusion from droplets across the watery phase. On complete depletion of monomer this Stage II concluded. Polymer particles microstructure and morphology can be manipulated in this step based on the quantities of individual monomers, the hydrophobic and hydrophilic properties of the monomers employed, and the temperature at which polymerization occurs. More branching and crosslinking arm are introduced during this stage. [44-47].

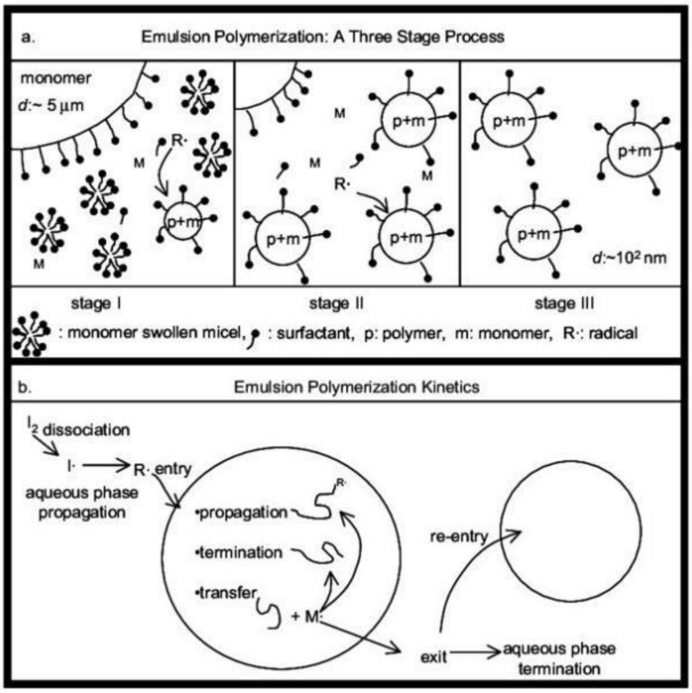


Figure 2. 17: Classical three-stage concept for the emulsion polymerization process (a) and the events controlling the kinetics

2.11.3 Stage III

Growth of particle ceases once the monomers are completely depleted and there is no source to restore the balance of the system. Now during this stage, the presence of polymer particles is exclusive. In stage *III*, the amount of monomer in polymer particles progressively decreases while the conversion rate increases. A polymer colloid consists of many chains of polymer enclosed within the particle, which can be organized in a crystalline, amorphous, rubbery, or glassy form. The monomer can be present in the particle and serves as the solvent for the particles. The size of the particle remains same at this stage. During this stage, the Tromsdorff effect, also known as auto-acceleration, may be detected. This phenomenon arises when the viscosity of the system experiences a significant increase as the conversion level increases. Due to the limited mobility of polymer chain radicals in a viscous media, they are unable to locate each other for termination, leading to a significant increase in temperature and heat generation [44-47].

2.12 Processes of Emulsion Polymerization

The procedure and conditions utilized in this process have a substantial impact on the characteristics of the final product. In batch polymerization, at the beginning of the reaction, all reagents are introduced at once. In semi-batch polymerization, only a small amount of the reactants is added at the beginning, and the rest addition done at specific times during the reaction in predetermined amounts. The third phase, known as continuous polymerization, involves the continuous introduction of monomer and the continuous product removal [44-47].

2.12.1 Batch Polymerization

Batch polymerization refers to a process in which polymerization reactions are carried out in a batch mode, meaning that all the reactants are introduced to a reactor at once and the reaction proceeds until completion.

This is the most basic form of emulsion polymerization. At the start of the reaction, all materials, except for the initiator, are introduced to the reactor. The system, which is continuously stirred, is brought to a certain temperature and then the addition of initiator done, to initiate the polymerization process. The factors like temperature, stirring speed, and design of reactor may be modified due to the straightforwardness of the process and to resolve any issue [39,40]. All three phases mentioned before occur in a batch polymerization process. Particle nucleation can happen through either micellular or homogeneous nucleation processes. Extraction of monomer from droplets via continuous phase until all the droplets consumed, this generates particles. This procedure is not employed in the manufacturing of commercially used latexes due to the drawback of having less particle size control and restricted control over morphology of the particles. Furthermore, the TromsdoSrff effect is quite pervasive in this procedure, leading to expensive disruptions in a business environment. The text refers to pages [44-46].

2.12.2 Semi-Batch Polymerization

The semi-batch approach is extensively employed in emulsion polymerization due to its adaptability and superior benefits compared to a batch process. Semi-batch polymerization, in contrast to batch polymerization, is characterized by its excellent reproducibility, operational flexibility, and ability to adjust the size and shape of particles generated. These processes involve the deliberate and regulated introduction of, surfactant, initiator, and monomer or water into a reactor at specific intervals during the course of the process. The monomer can be added in two forms: as a pre-emulsion, where the monomer is mixed with water and stabilized by surfactants, or as a plain monomer feed, where just the monomer is present. Furthermore, monomer can be introduced to either saturate or deprive the system. Particle growth takes place during Stage II under situations when the monomer is present in abundance, as explained before. The monomer addition rate, exceeds monomer usage, resulting in the accumulation of monomer as droplets and particles and saturation of monomer within particle occur. Under conditions where there is a scarcity of monomers, the rate at which monomers are added is considerably slower than the rate at which they are consumed. As a result, Stage II is not present. A semi-batch operation with limited feed often results in the formation of tiny particles and can be operated at high concentrations [44-46].

CHAPTER 3: MATERIALS AND METHOD

In this chapter an overview of the materials, equipment, and technique utilized to synthesize the styrene butyl acrylate acrylic emulsion polymer has been provided.

3.1 Materials

The materials used in this research was described and mentioned in detail in table 3.1.

Table 3. 1: List of materials for synthesizing styrene butyl acrylate emulsion

Materials	Appearance	Role	Supplier
Butyl acrylate	Clear liquid	Monomer	Sigma USA
Acrylic acid	Colourless clear liquid	Monomer	Sigma Aldrich
Styrene	Colourless oily liquid	Monomer	Sigma Aldrich
DMC	Clear liquid	-	Sigma Aldrich
Cationic starch	Powder	Cationic Monomer	
Potassium persulfate	Powder	Initiator	99% Merk
Disponal FES 77	Surfactant	Emulsifier Anionic	BASF
Polyurethane resin	-	Polymer	Crosby and Baker
Nonylphenol ethoxylate	Surfactant	Surfactant	BASF

3.2 Equipment used

Table 3.2, the equipment used for the synthesis of the water-based acrylic emulsion polymers are described.

Row	Equipment
1	Reactor
2	Condenser
3	Thermometer
4	Syringe pump
5	Oil bath

6	Magnetic stirrer
7	Oven
8	Balance
9	Nitrogen cylinder
10	Hot plate

3.3 Methodology

The emulsion polymerization preparations were conducted in a 500ml round bottom reaction flask placed in an oil bath. The temperature of the oil bath was regulated by a mercury contact thermometer and maintained at a precise temperature of 70 ± 1 degrees Celsius. The flask was furnished with a condenser, stirrer, and two inlets for the purpose of nitrogen purging and monomer supply. The reaction occurred in three distinct stages, as outlined in Table 3.3.

The subsequent sections provide a description of the experimental methodologies employed.

3.3.1 Seed Stage

The surfactant and water were introduced into the reaction flask during the seed stage, and then stirred under a nitrogen atmosphere for 15 minutes to reach the desired reaction temperature. A blend of styrene, butyl acrylate, and acrylic acid (in a ratio of 5:14:1) was combined with varying amounts of DMC in a distinct vessel. The initial amount of the seed monomer was introduced, and after a 5-minute interval, the seed-stage initiator was added, which had been dissolved in deionized water. After a period of 30 minutes, a 2 ml sample of latex was extracted using a 30 ml ground glass syringe equipped with a 6-inch needle measuring 14 gauge in diameter. The sample was then transferred into a pre-weighed vial. The vials containing the material were chilled in an ice bath to rapidly stop the polymerization process, and subsequently examined for solid contents and particle diameter. After an additional 25 minutes, another portion of initiator was dissolved in deionized water and applied. Five minutes later, a second sample of latex was obtained, marking the completion of the seed stage.

Table 3. 3: Formulation used for emulsion polymerizations.

Stage	Time / min	Event and Reagents used	Quantity/g
Seed Stage	15	temperature equilibration water + surfactant	80 + 1.33g (a)
	5	seed monomer added	18.76
	0	water + initiator added	8 + 0.17 (b)
	30	sample removed	2ml
	55	water + initiator added	8 + 0.04 (c)
Growth Stage	60	sample removed monomer + surfactant feed begun	2ml 18.76 + 1.33g (d)
	90	sample removed	2
	115	water + initiator added	8 + 0.017(e)
	120	sample removed	2
	150	sample removed	2
	175	water + initiator added	8 + 0.0171 (e)
	180	sample removed	2
	210	sample removed	2
	235	water + initiator	8 + 0.017 (e)
Final Stage	240	sample removed feed finishes	2
	270	sample removed	2
	300	sample removed latex cooled and filtered	2

(a) 4% by weight surfactant to seed monomer for Butyl acrylate, DMC, Cationic Starch and styrene

b) 0.1 mol% $K_2S_2O_8$ to total monomer;

c) 0.025 mol% $K_2S_2O_8$ to total monomer;

d) 1% by weight surfactant to total growth monomer;

e) 0.01 mol% $K_2S_2O_8$ to total monomer.

3.3.2 Growth stage

Precisely measured quantities of monomer and surfactant for the growth stage were placed in a flask with a flat bottom. Achieving a uniform solution was accomplished by subjecting the monomer/surfactant mixture to magnetic stirring.

The monomer/surfactant mixture in the growth stage was pumped using a peristaltic pump equipped with silicone rubber tubing in a closed circuit. This setup allowed the tubing to reach swelling equilibrium, ensuring a consistent feed rate during the development stages. The output i.e. tube end was then connected to the reaction vessel in preparation for supplying the growth stage.

After the seed stage was finished (with a reaction duration of 60 minutes), the growth stage feed began by injecting the combination of monomer and surfactant into the reaction flask. This process took 3 hours and the injection rate was set at 0.1 grams per minute. Every 30 minutes, 2 ml samples were extracted from the reaction vessel using a syringe and then transferred to pre-weighed sample vials. The quantities of the monomer/surfactant that were introduced into the reaction flask were recorded at each sample period. Precisely measured quantities of initiator were dissolved in deionized water and added 5 minutes before to the conclusion of each hour. Emulsion photopolymerizations of butyl acrylate (BA), acrylic acid (AA), and styrene were conducted following the aforementioned process.

3.3.3 Reaction to High Level of Conversion

After adding the monomer feeds, the polymerization process was extended for a further hour without adding any more reactants. The objective was to maximize the conversion rate of monomer into polymer. After a total reaction time of 5 hours, the latex was cooled to ambient temperature while being stirred and then passed through a sieve before being stored in HDPE bottles.

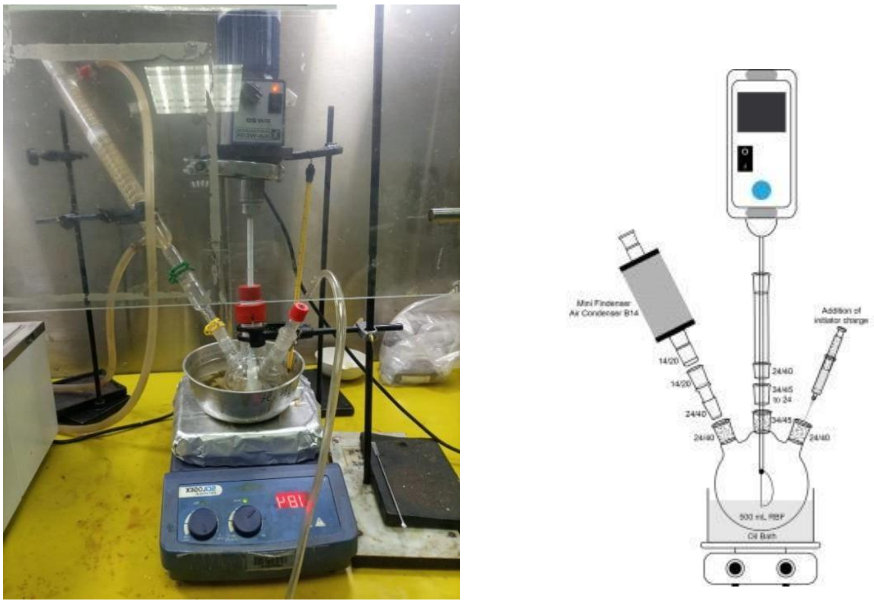


Figure 3. 1: Set-up for emulsion polymerization composed of nitrogen inlet, condenser, thermometer and magnetic stirrer.

Table 3. 4: Concentration used for emulsion polymerization of styrene butyl acrylate using Disponil FES 77 surfactant

Sample	%	BA	AA	Styrene	DMC	CS	S
EP2S3	2.5%	0.1g	1.4g	0.5g	0.002g	0.5g	0.5g/0.025g
EP4S10	20%	0.8g	11.2g	4	0.016g	2g	0.8g/0.2 g
EP5S10	10%	0.4g	5.6g	2g	0.008g	1g	0.4g/0.1g
EP6S10	15%	8.4g	0.6g	3g	0.012	1.5g	0.6g/ 0.15g
NS10	10%	5.6g	0.4g	2g	-	-	0.4g/0.1g
N2S10	10%	5.6g	-	2g	0.008		0.4g/0.1g

(a) 4% by weight surfactant to seed monomer for Butyl acrylate, acrylic acid, DMC, Cationic Starch and styrene

(b) 0.1 mol% $K_2S_2O_8$ to total monomer

(c) 0.025 mol% $K_2S_2O_8$ to total monomer

(d) 1% by weight surfactant to total growth monomer

(e) 0.01 mol% $K_2S_2O_8$ to total monomer.

Table 3. 5: Optimized formulation of emulsion polymerization using Nonyl Phenol Ethoxylate Surfactant

Sample	%Composition	M1(BA)	M2(AA)	M3(S)	M4 DMC	M5(CS)	Surfactant
ENS10	15%	8.4g	0.6g	3g	0.012g	-	1g
E2NS10	20%	11.2g	-	4g	0.016	-	1.33g

(a) 2% by weight surfactant to seed monomer for Butyl acrylate, DMC, Acrylic acid, Cationic Starch and styrene.

(b) 0.1 mol% $K_2S_2O_8$ to total monomer;

(c) 0.025 mol% $K_2S_2O_8$ to total monomer;

(d) 2% by weight surfactant to total growth monomer;

(e) 0.01 mol% $K_2S_2O_8$ to total monomer.

Figure 3. 2: Optimized emulsion samples

3.4 Dip coating

This is a common method used to create a thin layer. It is a cost-effective process that requires less experience. [47] The dip coating process is driven by the disparity in zeta potential or charges between the polymer and membranes [48,49]. A layer of emulsion was applied onto a pristine glass slide in order to determine the contact angle. The glass slide was cleaned using the following way.

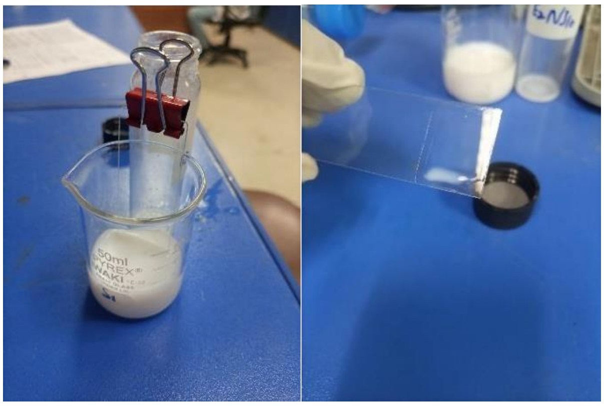


Figure 3. 3: A layer of emulsion on glass slide by dip coating

3.5 Cleaning of Glass Substrate

Overnight soaking of micro-glass slides in chromic-sulfuric acid solution:

- 50% sulphuric acid
- 50% potassium dichromate
- Rinse with water and dried under ambient conditions.

3.6 Blending of Emulsion with Polyurethane Resin

After the successful production of the emulsion, a series of samples prepared by combining different compositions of the emulsion with a total of 5g of polyurethane resin in order to investigate the hydrophobic impact. The compositions were modified by including emulsion at varying percentages of 0%, 1%, 2.5%, 5%, 10%, and 20% by weight. As a result, the polyurethane concentration varied, resulting in final samples containing 100%, 99%, 97.5%, 95%, 90%, and 80% polyurethane respectively. These samples are thereafter stored at room temperature for the purpose of drying.

Table 3. 6: % Composition of polyurethane with varying amount of emulsion

Samples	**Polyurethane w/w %**	**Emulsion w/w%**
1	1oo%	0%
2	99%	1%
3	97.5%	2.5%
4	95%	5%
5	90%	10%
6	80%	20%

Figure 3. 4: Samples with different composition of emulsion(a) and Polyurethane resin (pallet)(b)

3.7 Sheet Formation

After proper drying of samples these samples were placed under hot press at temperature 190˚c and pressure of about 15MPa for 10 min to make sheets for further characterization.

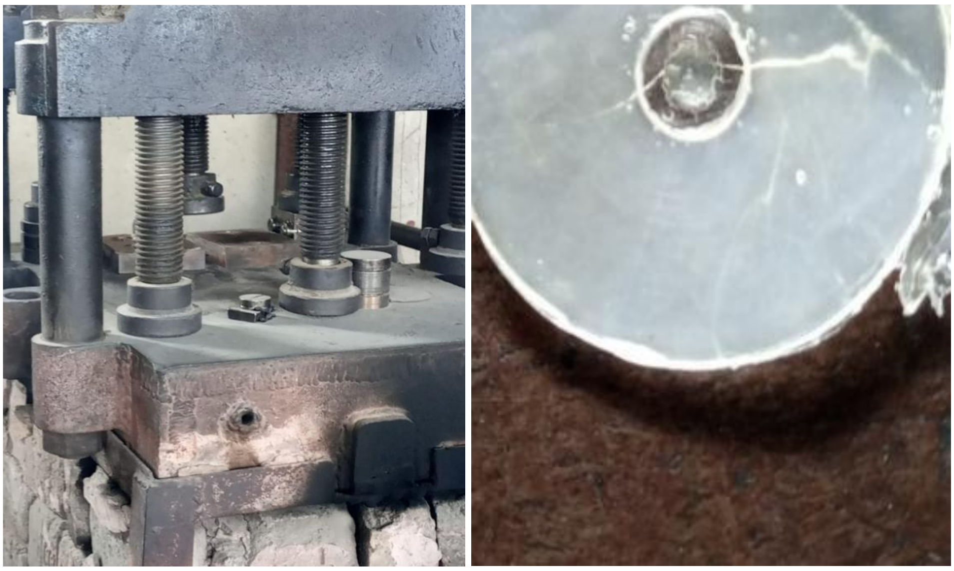


Figure 3. 5 Set up for making Polyurethane sheet

CHAPTER 4: CHARACTERIZATION TECHNIQUES

4.1 Scanning electron microscope (SEM):

This technique entails directing a concentrated electron beam onto the surface of a substance. Electrons engage in interactions with the surface of the sample, resulting in the expulsion of photons or electrons from the surface of the material. Afterwards, the detector focuses on these displaced electrons. The detector's output enhances the luminosity of the cathode ray tube (CRT). The interaction between the electron surfaces facilitates the emission of secondary electrons (SE), back-scattered electrons (BSE), and X-rays. A frequently employed method for detecting scanning electron microscopy (SEM) is by utilizing secondary electrons (SE). The release of these secondary electrons takes place in close proximity to the surface of the sample.

As a result, a clear and unequivocal image of the sample is obtained. It is capable to revealing intricate characteristics of samples that are less than 1 nm in size. Furthermore, the incident electrons experience elastic scattering, leading to the emission of backscattered electrons. They come from deeper locations as opposed to secondary electrons. Consequently, their resolution is quite low.

Figure below shows the scanning electron microscope (SEM) apparatus, namely the JSM 6490LA model, that is present in the SCME department of the School of Chemical and Materials Engineering at NUST in Islamabad.

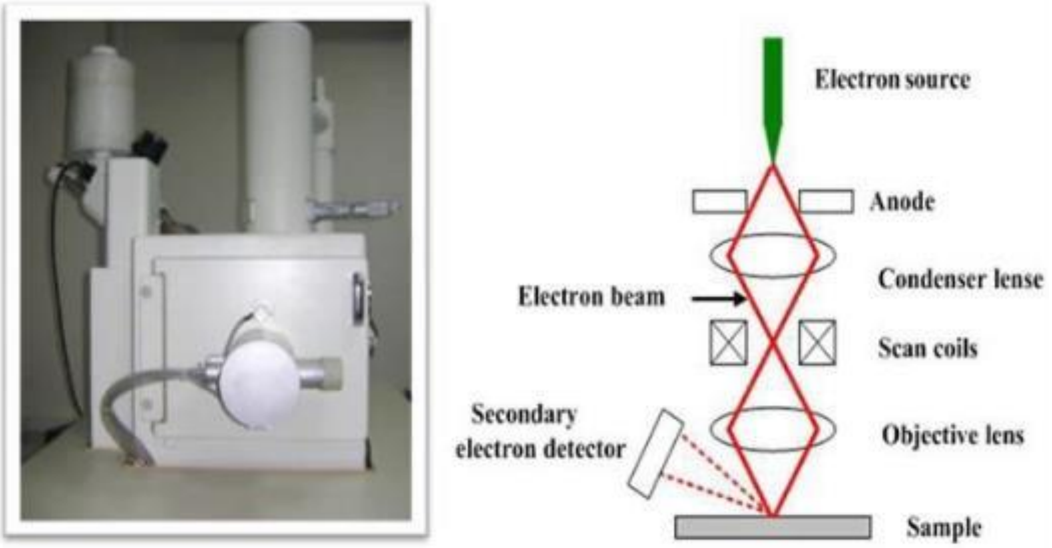


Figure 4. 1: (a) SEM (JOEL JSM-6490LA) present at SCME, NUST (b) Schematic representation of SEM

This method is extremely versatile and robust for testing compounds at the nanoscale. It possesses the capacity to produce a three-dimensional depiction of the surface characteristics and can precisely assess the altitude and dimensions of nano materials. As the cantilever's tip gets closer to the sample's surface, both the surface and the tip cause the cantilever to bend towards the sample. Upon contact between the tip and the sample, repulsive forces arise, resulting in the displacement of the cantilever away from the surface [50].

4.2 TGA (Thermogravimetric Analysis)

Thermo quantitative analysis, also referred to as thermal quantitative analysis (TGA), is a technique used to analyse heat by measuring the mass of a sample at different time intervals in response to temperature changes. This process provides knowledge about the concrete phenomena that take place in the material realm, such as;

- Molecular transitions
- Thermal absorption
- Surface assimilation
- Surface desorption
- Chemisorption
- Thermal decomposition
- Solid-gas reactions

The thermal processes required for this operation can occur in several environments, including ambient air, vacuum, or inert gas [51]. The instrument TGA Q50 V6.2 BUILD 187 was used for conducting this test.

Figure 4. 2: Thermogravimetric Analysis (TGA) Tester

4.3 FTIR Spectroscopy

Infrared spectroscopy refers to the analysis of materials using infrared radiation. The term "Fourier-transform" is derived from the need to use a mathematical process called Fourier transformation to convert raw data into the actual spectrum form [52].

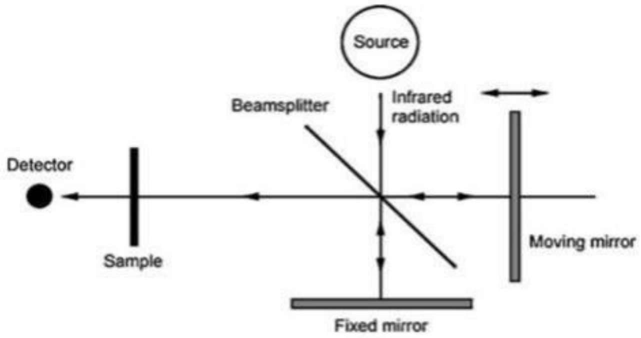


Figure 4. 3: Schematics of an FTIR spectrometer (Perkin Spectrum 100) present at SCME NUST

4.4 Zeta Potential

Zeta potential analysis is a quantitative assessment of electric charge present on a surface. The term refers to the disparity in electrostatic potential between a nanoparticle and the surrounding solution. The zeta potential is determined by subjecting a nanoparticle solution to a varying electric field while passing a laser through it. The change in frequency, known as phase shift, of the light that is dispersed due to the Doppler effect is quantified and linked to electrophoretic mobility. Malvern Panalytical zeta-sizer ver. 8.02 serial number (1168467) used for this analysis.

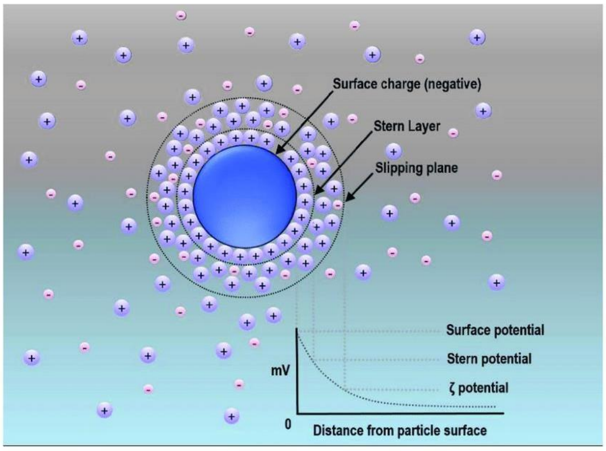


Figure 4. 4: Schematic Representation of the Electric Double Layer (EDL) on a Negatively Charged Particle

The electric double layer (EDL) formed around a negatively charged particle consists of two distinct layers. The inner layer, known as the Stern layer, is made up of ions with charges opposite to those of the particle surface, specifically positive ions in this case. The outer layer, called the diffuse layer, contains a mixture of both negative and positive charges. The Zeta Potential refers to the electro-kinetic potential present at the sliding plane. [53].

CHAPTER 5: RESULTS AND DISCUSSION

The emulsion stability was measured by using two different surfactants i.e. Disponil FES77 and nonylphenol ethoxylate. A series of emulsion polymerization reactions were performed as explained in table 3.4 using a disponil FES77 surfactant. By using Disponil FES77, instability of the emulsions was observed.

- Separation of two phases occur
- Coagulation and flocculation
- Emulsion was not stable for longer period of time when kept for 3-4 days
- Disponil FES77 lacks the ability to generate a strong interfacial film or offer significant steric stability.
- The amount of surfactant used was not enough to stabilize the particles.

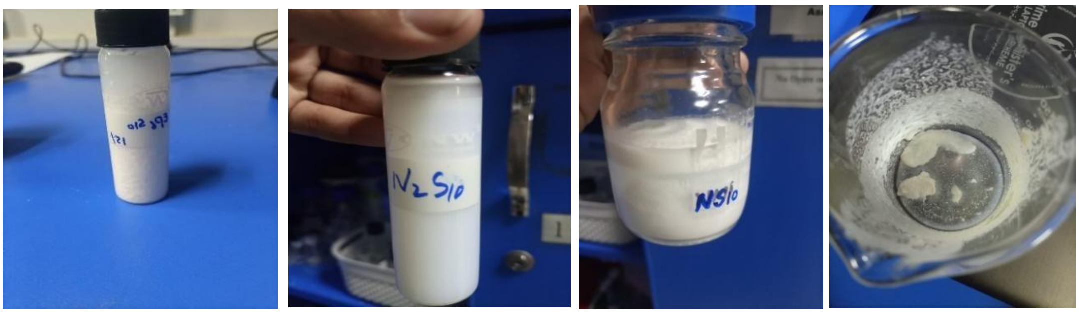


Figure 5. 1: Instable Emulsion using Disponil FES77 surfactant sowing separation of phases and coagulation

The zeta potential values of the emulsions using Disponil FES77 are shown in following table. Lower zeta potential also depicts the instability of emulsion.

Table 5. 1: pH and zeta potential values of samples using disponil FES77 surfactant

Sample	pH	Zeta potential m/v
EP2S3	2.54	8.3
EP4S10	2.60	21.06
EP5S10	2.98	9.71
EP6S10	3.28	14.94
NS10	3.52	13.9
N2S10	3.84	10.3

Figure 5. 2: Samples preparation for pH measurements and zeta potential analysis

Then optimized formulation was performed using Nonyl phenol ethoxylate as explained in table 3.5. The emulsions (ENS10 (15%), E2NS10 (20%)) were stable for longer period of time with no coagulation and separation of phases and can be used for further characterization such as FTIR, TGA and SEM.

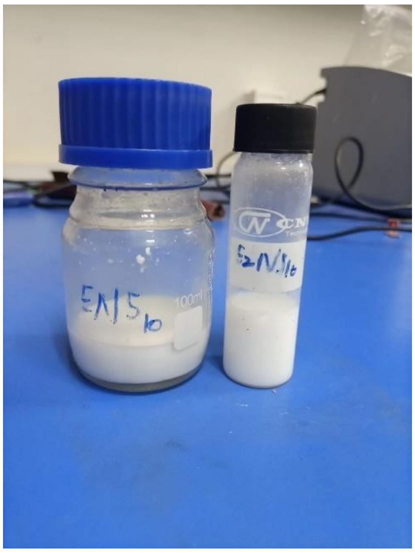


Figure 5. 3: The emulsions (ENS10 (15%), E2NS10 (20%)

5.1 Characterization of Emulsion

5.1.1 FTIR Spectrum of Emulsion

The FTIR spectrum of the polymer emulsion displays results for emulsions ENS10 (15%) and E2NS10 (20%). The absorption peak at 1159 cm−1 corresponds to the asymmetric stretching vibration of C-O-C in the ester group. Peaks in the range of 1700-1732 cm−1 are associated with the asymmetric stretching vibration of C=O. The absorption peaks at 2920 cm−1 and 2505 cm−1 are due to the anti-symmetric stretching vibrations of C-H in methyl and methylene groups. Peaks at 3411 cm−1 and 3425 cm−1, as well as 1433 cm−1 and 1447 cm−1, are attributed to the stretching and bending vibrations of O-H in -COOH for both emulsions. The peak at 764 cm−1 represents the single substitution absorption peak of the benzene ring, while the peaks in the range of 1680–1600 cm−1 refer to the stretching vibrations of C=C. These findings indicate that there are no double bonds present in the polymer and confirm the involvement of both styrene and butyl acrylate in the free-radical emulsion polymerization process.

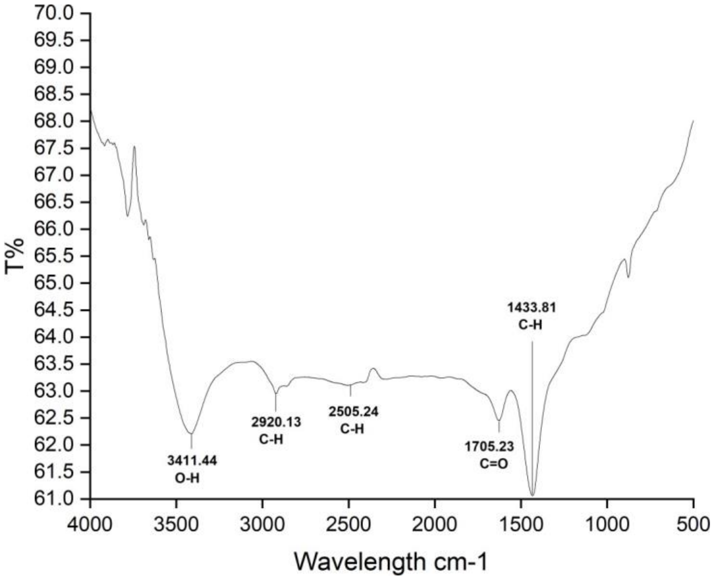


Figure 5. 4: FTIR data for sample ENS10

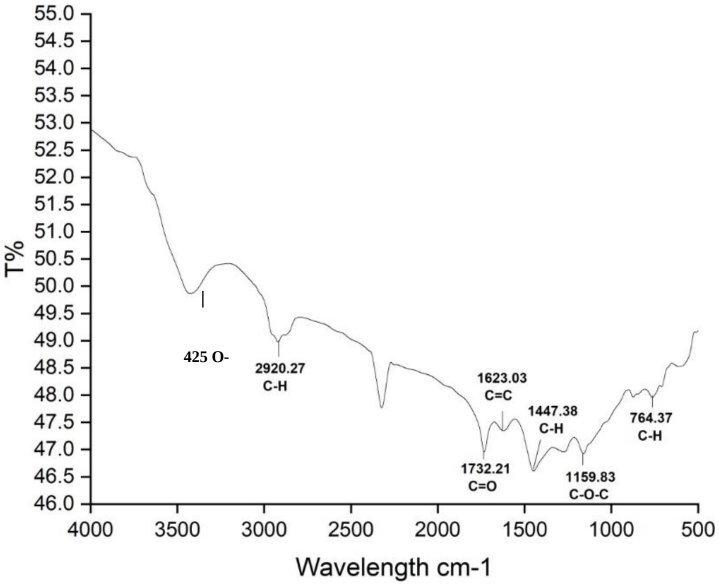


Figure 5. 5: FTIR data for sample E2NS10

5.1.2 Thermal Gravimetric Analysis

The thermal stability of the emulsion was further investigated by the thermogravimetric analysis. It has been observed in the emulsion ENS10 (15%) shows two step degradation process. At temperature 231 ˚C a very small weight loss of about 5% has been observed at this temperature about 95% of the bulk material is intact. At temperature 396 ˚C which is second degradation temperature 20% weight loss has been observed which could be due to the breakdown of small molecular weight polymer chain exceeding this temperature polymer backbone degrades and cleavage of more stable bonds such as C-C and C-H within the aromatic ring of the styrene has been observed. So, it is concluded that the emulsion is stable to higher temperature of 231 ˚C and 396 ˚C.

The emulsion E2NS10 (20%) has greater stability at higher temperature of 384.64˚C is showing single degradation process. At this temperature 80% most of the material is intact and bulk of the material is present. Before this temperature the small weight loss could be due the breakdown of small molecular weight polymer chain and volatilization of water. So, it confirms the stability of emulsion to higher temperature compared to ENS10 (15%).

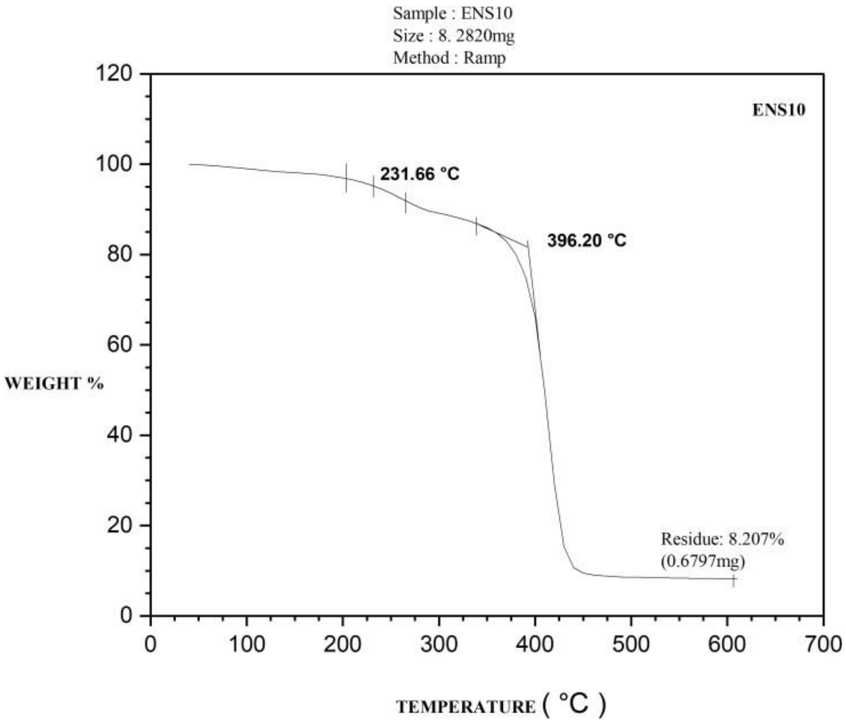


Figure 5. 6: TGA analysis of ENS10 (15%)

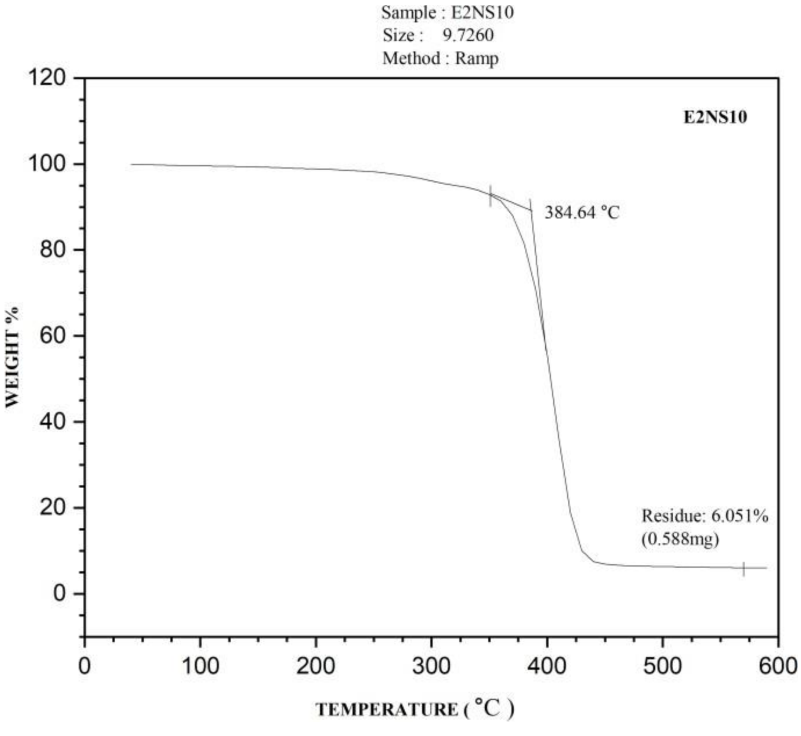


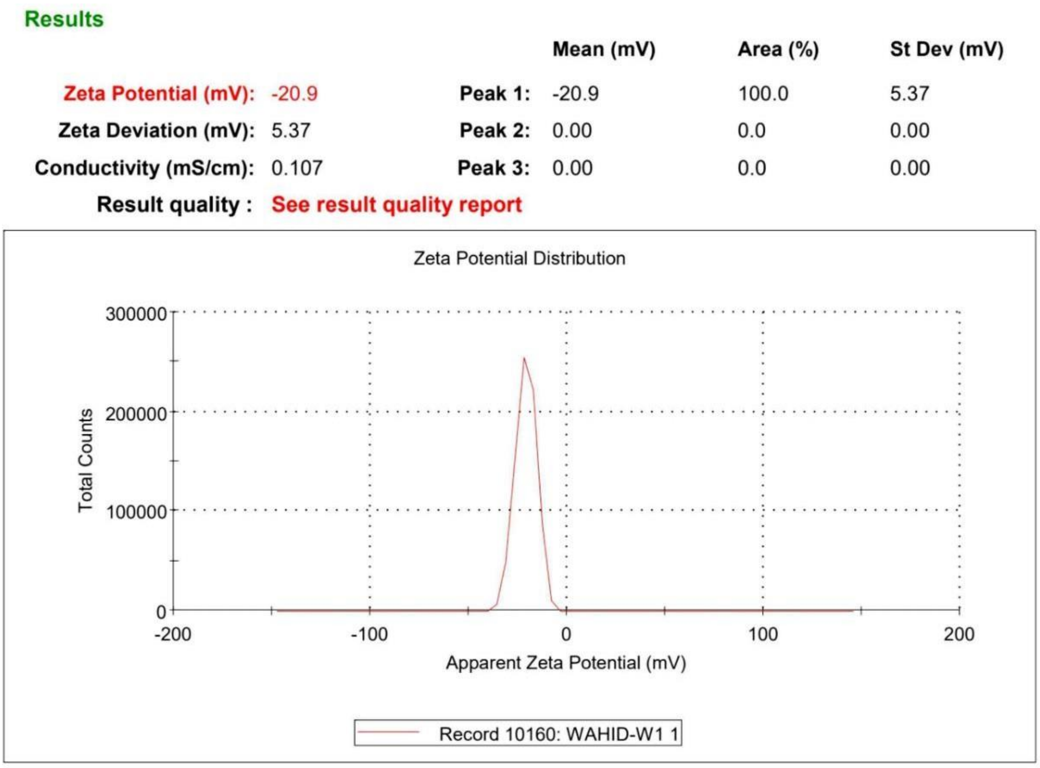
Figure 5. 7 TGA analysis of E2NS10 (20%)

5.1.3 Zeta potential and Zeta Size

Zeta Potential of ENS10 (15%) and E2NS10 (20%)

Zeta potential is simply measure of the electrical charge present on particle’s surface. Additionally, it is used for the prediction of the stability of a colloidal system. The zeta potential value of sample ENS10 is -20.5, refers that the particles in the system carry a negative charge. This is shown in figure 5.5. The zeta potential value of -20.5 indicates a moderate level of stability.

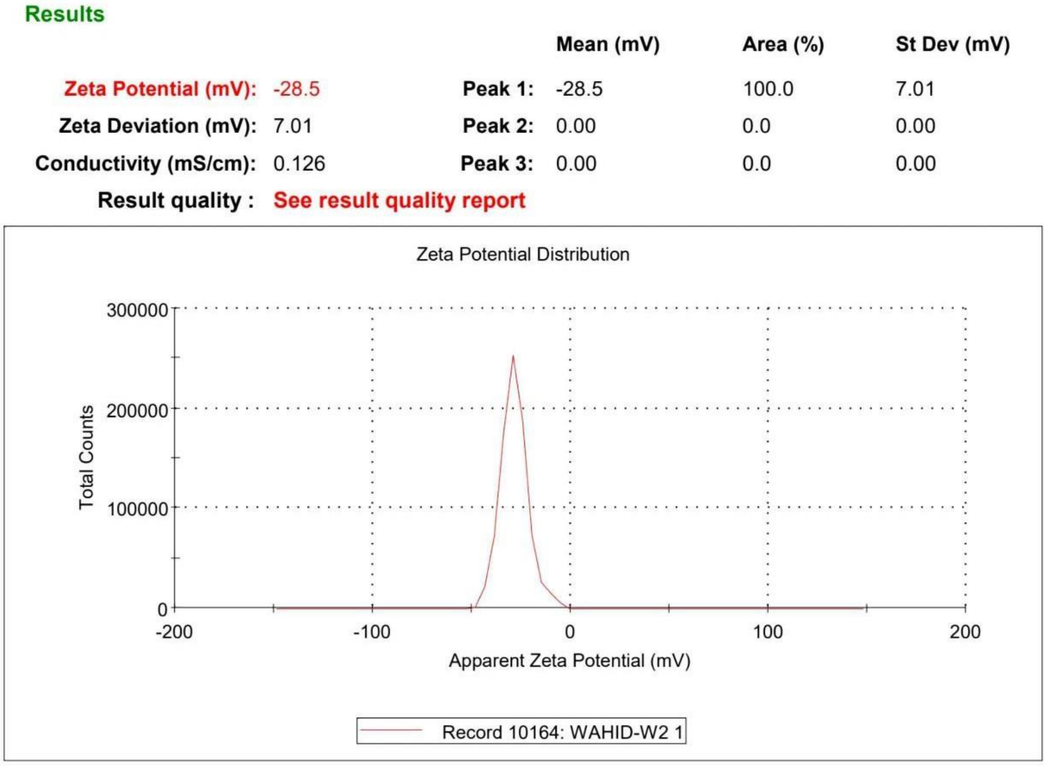
The zeta potential of sample E2NS10 is -28.5, shows that the particles in the system carry a negative charge, as illustrated in figure 5.6. A greater the value of negative zeta potential suggests that the particle within the system are negatively charged and shows greater repulsion between particles which enhances emulsion stability and prevents phase separation and coagulation.



Results

			Mean (mV)	**Area (%)**	**St Dev (mV)**
Zeta Potential (mV):	-20.9	**Peak 1:**	-20.9	100.0	5.37
Zeta Deviation (mV):	5.37	**Peak 2:**	0.00	0.0	0.00
Conductivity (mS/cm):	0.107	**Peak 3:**	0.00	0.0	0.00
Result quality :	**See result quality report**				

Figure 5. 8: Zeta Potential analysis of ENS10 (15%)



Results

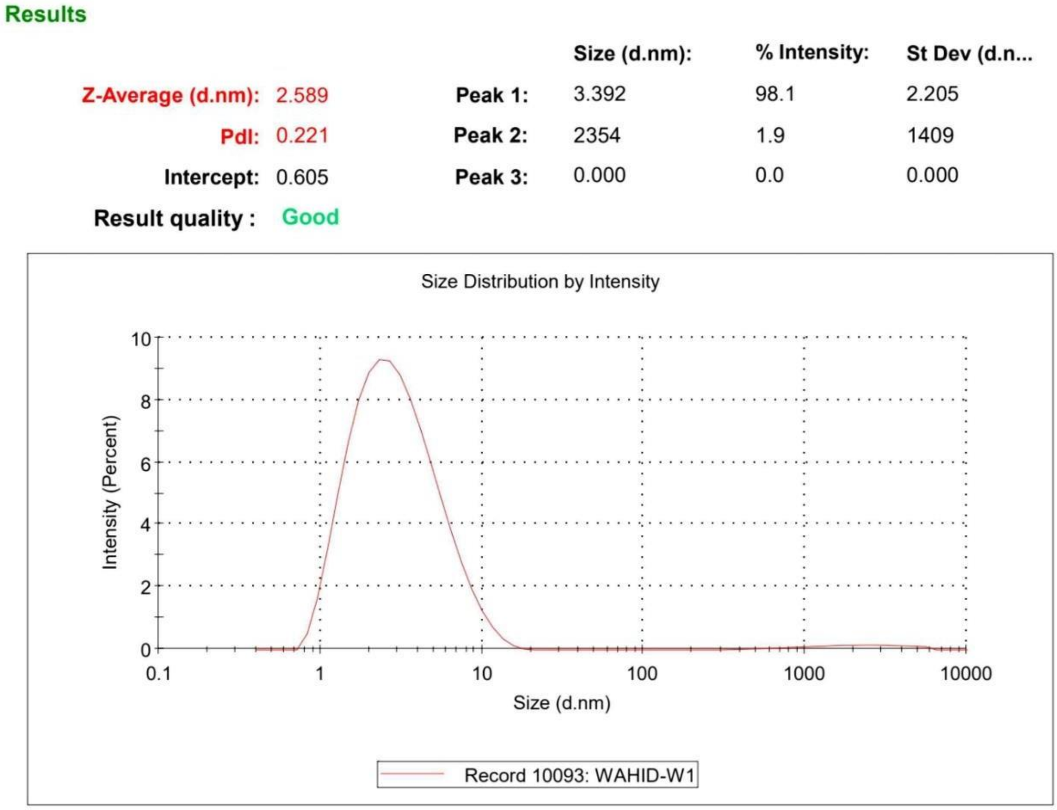
			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-28.5	**Peak 1:**	-28.5	100.0	7.01
Zeta Deviation (mV):	7.01	**Peak 2:**	0.00	0.0	0.00
Conductivity (mS/cm):	0.126	**Peak 3:**	0.00	0.0	0.00
Result quality :	**See result quality report**				

CS

Figure 5. 9: Zeta Potential analysis of E2NS10 (20%)

5.1.4 Size Distribution by Intensity of ENS10 and E2NS10

The Z-average particle size in ENS10 is 2.589 nm, while in E2NS10 it is 2.137 nm. This suggests that most of the particles lies within this size range. The polydispersity index (PDI) quantifies the extent to which the particle size distribution varies. A PDI value of ‘0’ signifies uniformity in particle size, whereas a PDI value of “1" signifies a high degree of polydispersity, indicating a broad distribution of particle sizes. The polydispersity index (PDI) of ENS10 is 0.221, whereas the PDI of E2NS10 is 0.235. These values indicate that the particle size distribution is rather narrow. A narrow particle size distribution is typically advantageous for numerous applications, as it enhances the uniformity and effectiveness of materials and processes.



Results

			Size (d.nm):	% Intensity:	St Dev (d.n...
Z-Average (d.nm):	2.589	**Peak 1:**	3.392	98.1	2.205
PdI:	0.221	**Peak 2:**	2354	1.9	1409
Intercept:	0.605	**Peak 3:**	0.000	0.0	0.000
Result quality :	Good				

Figure 5. 10: Size Distribution by intensity of ENS10 (15%)

Results

			Size (d.nm):	% Intensity:	St Dev (d.n...
Z-Average (d.nm):	2.137	**Peak 1:**	2.896	96.2	1.560
PdI:	0.235	**Peak 2:**	0.6670	2.3	0.04899
Intercept:	0.629	**Peak 3:**	3255	1.5	1294
Result quality :	Good				

Figure 5. 11: Size Distribution by intensity of E2NS10 (20%)

5.1.5 Solvent Content for ENS10 (15%) AND E2NS10 (20%)

The solvent content for sample ENS10 and E2NS10 was calculated by gravimetric analysis (weight loss on drying) by using the following formula.

$$\text{Solvent content \%} = \frac{\text{Weight of wet sample} - \text{Weight of dry sample} \times 100}{\text{Weight of wet sample}}$$

$$\text{Solid content \%} = \text{Weight of dry sample} \div \text{Weight of wet sample} \times 100$$

Table 5. 2: Solvent content% and Solid content % of samples ENS10 and E2NS10

Sample	Emulsion weight before drying (wet)	Weight of foil	Amount of hydroquinone added	Emulsion weight after drying (dry)	Solvent content%	Solid content %
ENS10 15%	2.001g	0.334g	0.003g	0.555g	88.95	11.05
E2NS10 20%	2.001g	0.334g	0.003g	0.714g	81.0	19.0

5.1.6 pH and Conductivity Test

Conductivity is typically measured in units of micro-siemens per centimetre (µS/cm) and is a measure of the concentration of ions or electrolytes present in the emulsion. PH is the measure of acidity and basicity of the solution.

The conductivity value of 249 µS/cm for ENS10 is relatively moderate and confirms the presence of some ions and electrolytes which contribute to the stability of emulsion. Due the presence of acrylic acid the PH value for emulsion is 3.35 which is acidic in nature.

The conductivity value of 264 µS/cm for E2NS10 is greater than ENS10 and confirms the presence of more ions and electrolytes which enhances to the stability of emulsion. Due the absence of acrylic acid the PH value for emulsion is 4.85.

Table 5. 3: pH and Conductivity test of samples ENS10 and E2NS10

SMAPLE	***PH***	***CONDUCTIVITY***
ENS10. (15%)	*3.35*	*249µS/cm*
E2NS10 (20%)	*4.85*	*264 µS*

5.1.7 Contact Angle OF ENS10 AND E2NS10

The emulsion containing acrylic acid, namely ENS10, demonstrates a contact angle of 26°, suggesting a surface that is relatively hydrophilic. The reason for this is most likely the hydrophilic characteristic of acrylic acid, which has the ability to enhance the surface energy of the polymer particles. Consequently, the emulsion droplets have a tendency to disperse further across the substrate, resulting in a reduced contact angle. Acrylic acid's presence can result in the creation of hydrophilic regions on the polymer particles' surface, hence causing a decrease in the contact angle.

On the other hand, the emulsion lacking acrylic acid, specifically E2NS10, demonstrates a greater contact angle of 69.9°, suggesting a surface that is more hydrophobic. The absence of hydrophilic acrylic acid is the probable cause for the dominance of the surface properties of the emulsion by the hydrophobic monomers, namely butyl acrylate and styrene. Consequently, the emulsion droplets have a tendency to form into beads on the substrate, resulting in an increased contact angle. The lack of acrylic acid also decreases the creation of hydrophilic regions on the polymer particles' surface, enabling the hydrophobic regions to prevail and enhance the contact angle.

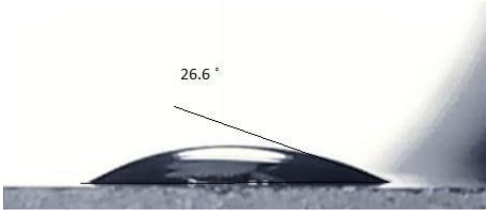


Figure 5. 12: Contact angle: 26.6 °

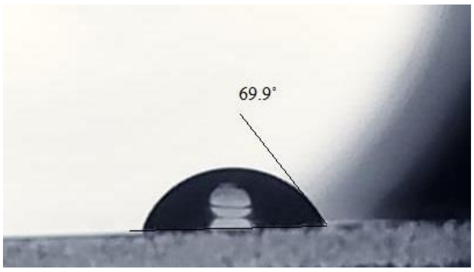
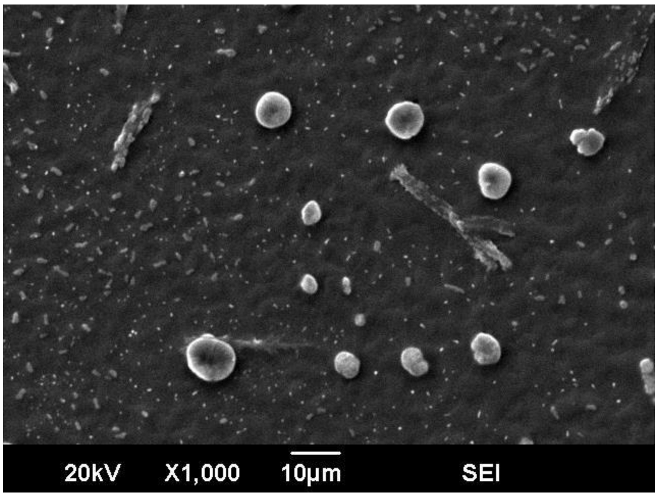


Figure 5. 13: Contact angle: 69.9 °

The presence of acrylic acid in emulsion ENS10 increases the surface energy and hydrophilicity, leading to a lower contact angle, while its absence in emulsion E2NS10 results in a lower surface energy and higher hydrophobicity, leading to a higher contact angle.

5.1.8 Scanning Electron Microscope

The SEM analysis shows that the emulsion E2NS10 has shown narrower size distribution of particles within the emulsion that enhances the emulsion stability.



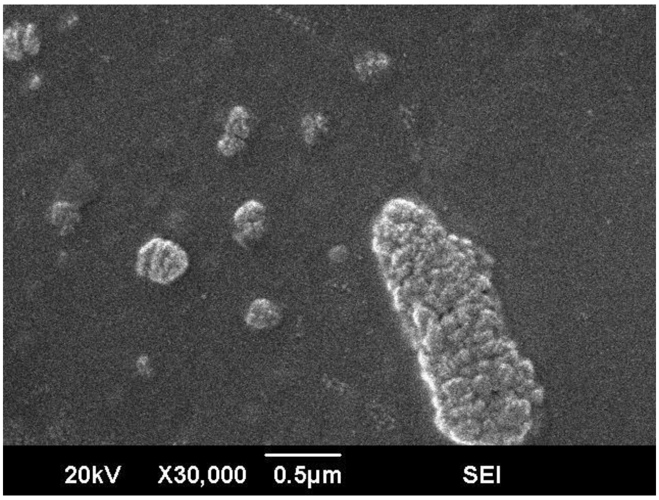


Figure 5. 14: SEM images of ENS10 (15%)

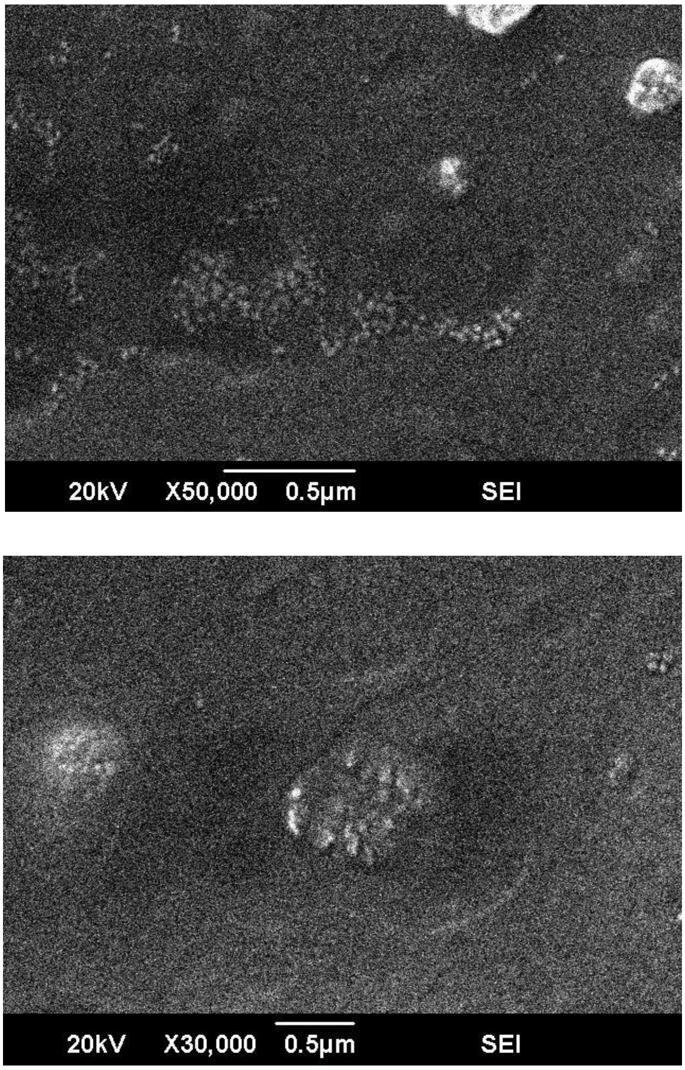


Figure 5. 15: SEM images of ENS10 (20%)

5.2 Characterization of PU sheets

5.2.1 *PU Sheets Contact Angle*

The contact angle of PU Sheets was measured after the successful addition of different % of E2NS10 emulsion. It has been observed that by increasing the % of E2NS10 in polyurethane resin the contact angle increased from 93.1˚ to 104.7˚.

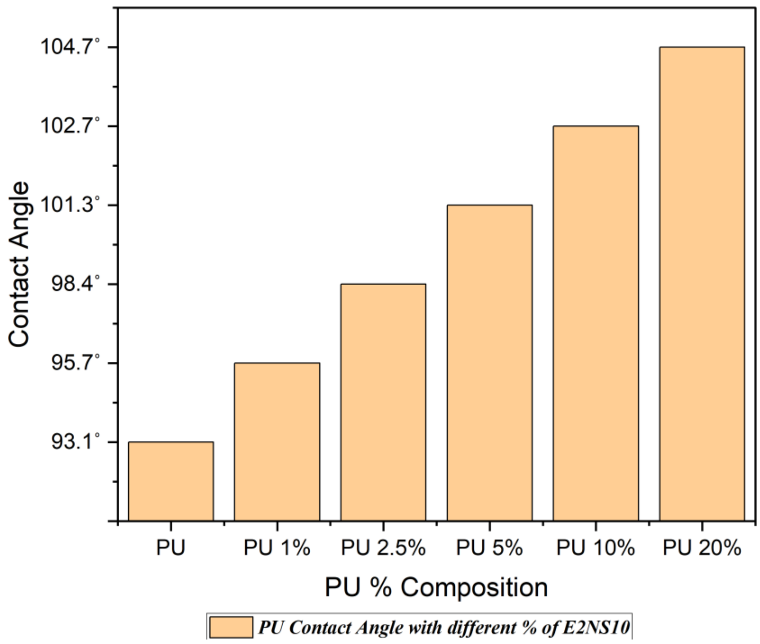
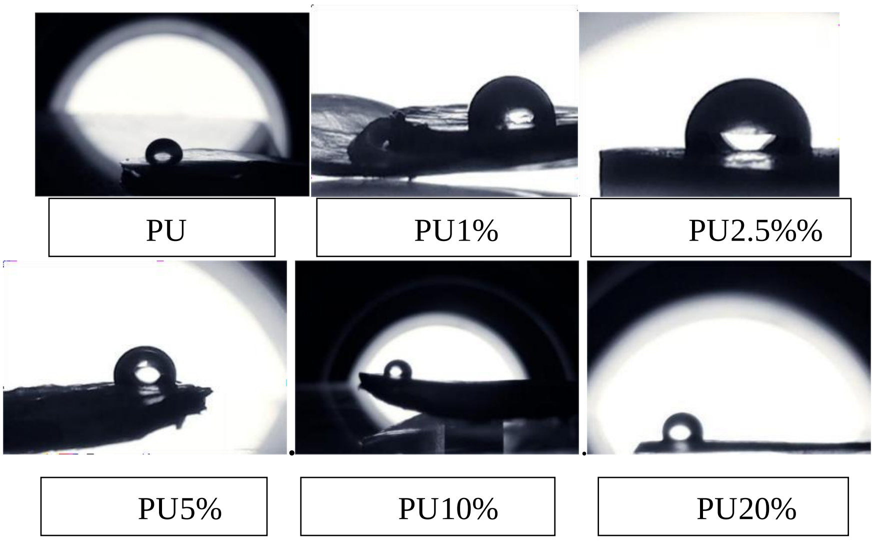


Figure 5. 16: Contact Angle Measurements of different PU samples



PU

PU1%

PU2.5%%

PU5%

PU10%

PU20%

Figure 5. 17: PU Contact Angle with different % of E2NS10

5.2.2 *Thermal Gravimetric Analysis of PU sheets with different %*

compositions of E2NS10

Thermal gravimetric analysis was then performed for the PU sheets which were blended with different % compositions of emulsion E2NS10. It has been observed that due to the emulsion stability at higher temperature the TGA value for the 20% of emulsion was increased. The polyurethane sheet with 0% of emulsion has TGA value of 427.7 ˚C which was then increased to 430.2 7 ˚C for 20% of emulsion composition.

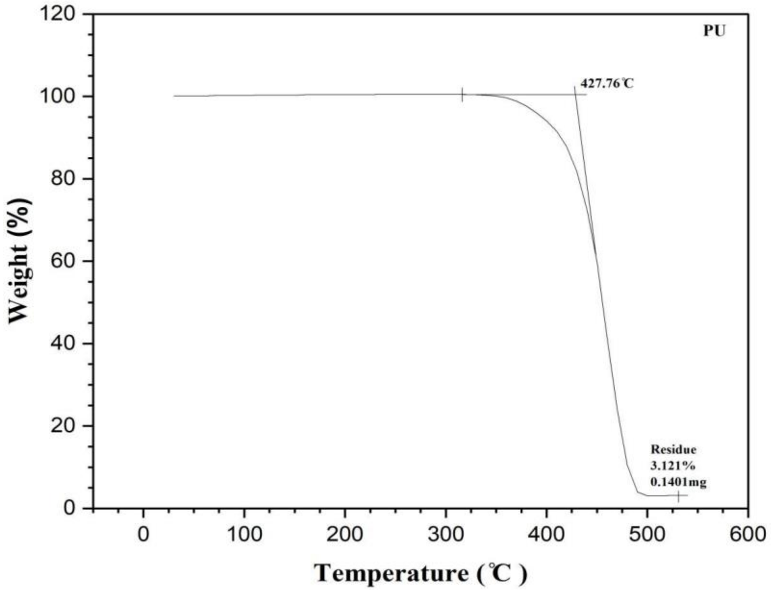


Figure 5. 18: Thermal gravimetric analysis of PU sheet

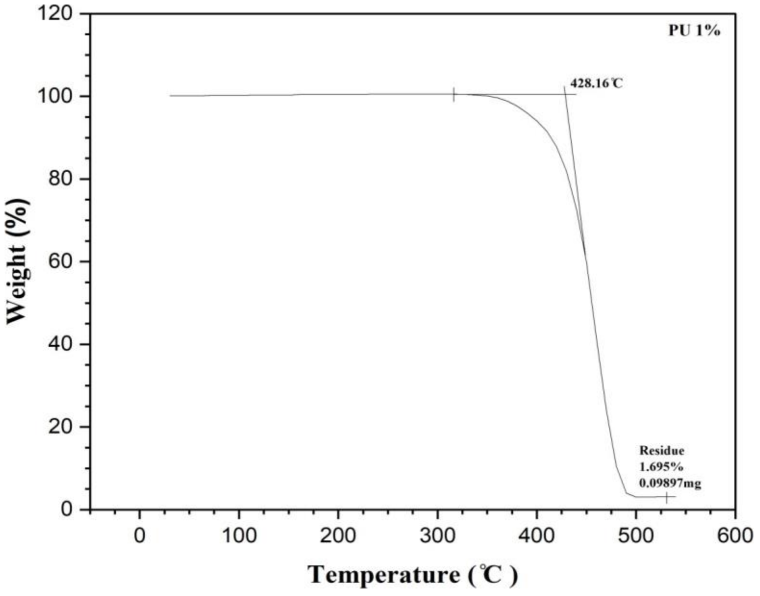


Figure 5. 19: Thermal gravimetric analysis of PU 1%sheet

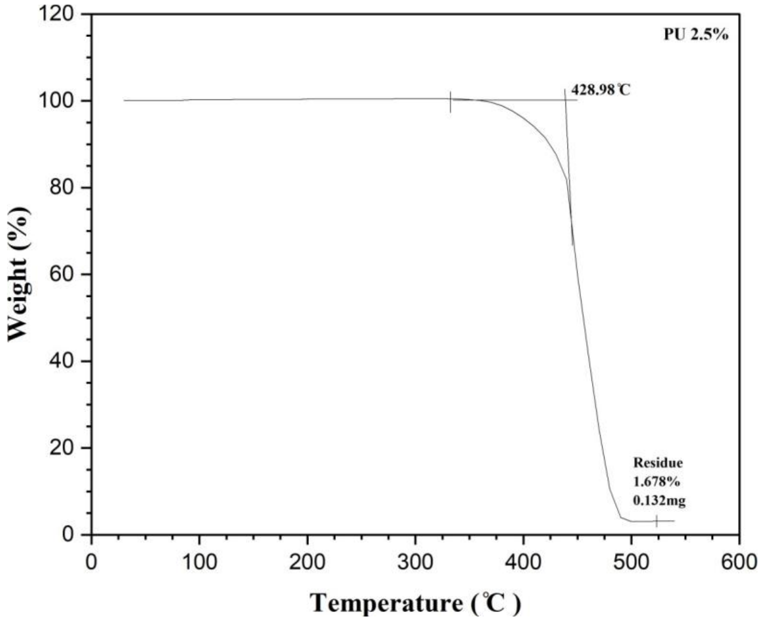


Figure 5. 20: Thermal gravimetric analysis of PU 2.5% sheet

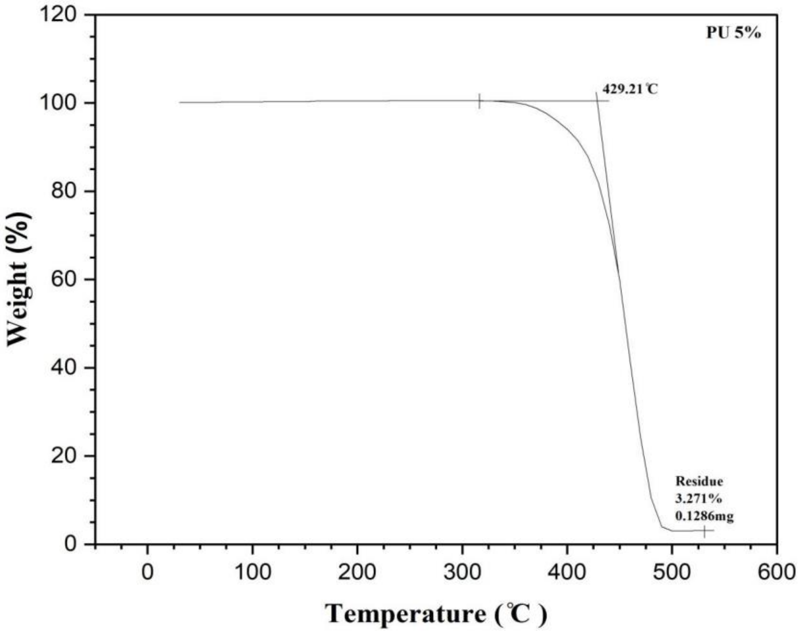


Figure 5. 21: Thermal gravimetric analysis of PU 5% sheet

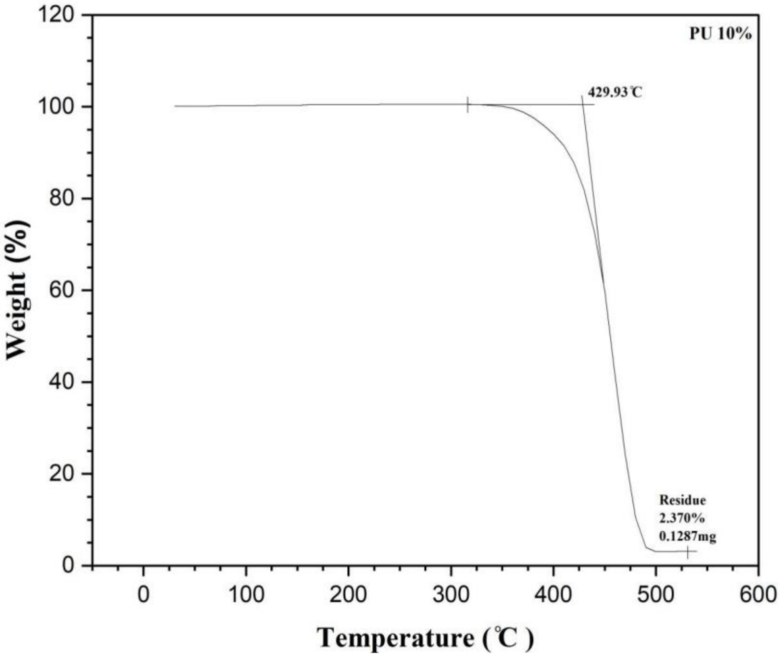


Figure 5. 22: Thermal gravimetric analysis of PU 10% sheet

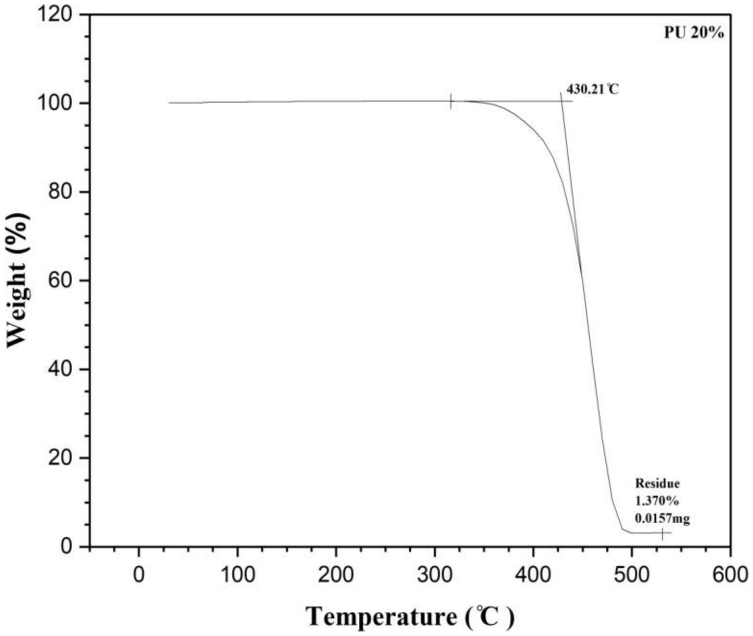


Figure 5. 23: Thermal gravimetric analysis of PU 20% sheet

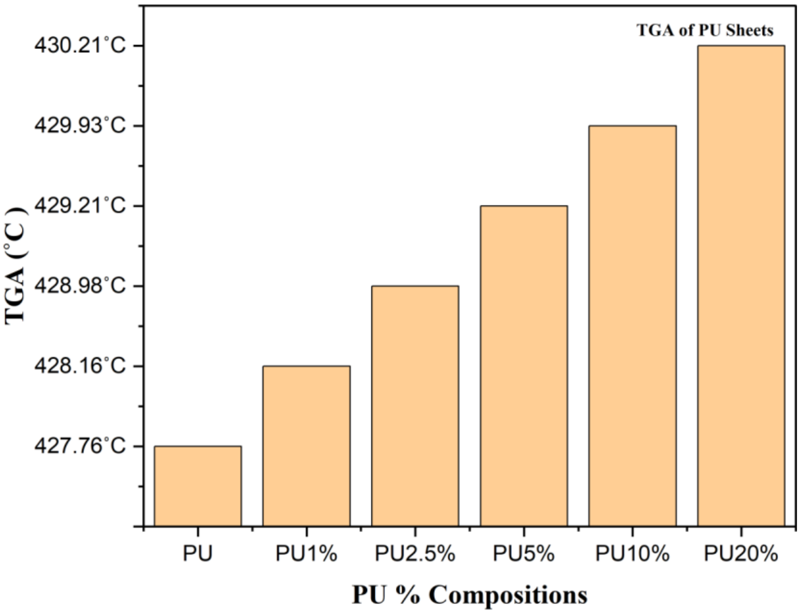


Figure 5. 24: TGA analysis of PU sheets with different % of emulsion

5.2.3 Wettability Model Owns-Wendt-Rebel-Kaelble (OWRK) for calculating surface energy

This model is widely used for calculating the surface energies (SE) of solid (γs) material from the contact angle measurements from two different solvent one is polar (water) and other is non-polar such as toluene, diiodomethane, and benzene etc. Its theories involve the divisions of interfacial energies into two parts: polar components (γsP) and disperisve components (γsD). The surface energy of the material can be computed by using the following equation where (γs) is total surface energy i.e. is equal to the sum of dispersive component and polar component[54].

Total surface energy :(γs) = (γsD) + (γsP)

Table 5. 4 Surface tension components of water and toluene

Solvent	Surface tension	Dispersive component	Polar component
Water	γw 72.8 mJ/m^2	γwd 21.8 mJ/m^2	γwd 51.0 mJ/m^2
Toluene	γt 28.4 mJ/m^2	γtd 28.4 mJ/m^2	γtd 0 mJ/m^2

Dispersive component calculation

For calculating the dispersive components, the contact angle of solvent with known dispersive and polar interaction on surface is required. As we used water and toluene, contact angle is 104.7 ° and 25.2 ° respectively with both liquids.

The following equation will be used to calculate the dispersive component for both liquids water (w) and toluene (t).

$$\gamma sD = \gamma wD * (1 + \cos\theta\ W)/2 + \gamma tD * (1 + \cos\theta\ t)/2$$

Polar component calculation

By using the following equation, the polar components of the surface energy of material can be calculated.

$$\gamma sP = \gamma wP * (1 + \cos\theta\ W)/2$$

The surface energies of PU sheets with different % composition of emulsion has been calculated by contact angle measurements with two different solvents polar and non-polar water and toluene respectively.

Table 5. 5 Representing surface energies of different PU sheets

Samples	**CA with water**	**CA with Toluene**	**Surface energy mN /m**
PU	93.1 °	24.7 °	30.4
PU1%	95.7 °	25.3 °	29.7
PU2.5%	98.4 °	24.5 °	27.6
PU5%	101.3 °	25.9 °	26.4
PU10%	102.7 °	25.6 °	24.5
PU20%	104.7 °	25.2 °	23.7

By calculating the surface energies of the PU sheets with different % of emulsion, it has been observed that as the contact angle increase, the surface energy of material decreases which shows that the material is less susceptible to interaction with polar solvents and have greater hydrophobic character.

CHAPTER 6: CONCLUSIONS AND FUTURE RECOMMENDATIONS

6.1 Conclusion:

The conclusions from the current work are listed below.

- The emulsion prepared by using Nonylphenol ethoxylate as a surfactant has shown greater stability, low coagulation, and stable for longer period of time with no phase separation compared to the emulsion formulated with Disponil FES77.
- The emulsion E2NS10 (20%) that is without acrylic acid has shown zeta potential value of -28 m/v compared to ENS10 (15%) that is with acrylic acid has lower zeta potential value of -20m/v which effect its stability.
- Thermal gravimetric analysis of both emulsions shows that emulsion E2NS10 (20%) has thermal stability at higher temperature of 384˚C and has single step degradation process compared to ENS10 (15%) which has two step degradation process at 231 ˚C and 396 ˚C.
- The contact angle measurement results revealed that E2NS10 (20% without acrylic acid) has greater contact angle of 69˚ compared to ENS10 (15% with acrylic acid) which has hydrophilic character and has contact angle of 26˚.
- The emulsion showing superior performance was then successfully blended with PU resin has shown to cause serge in hydrophobicity of PU sheets. The pure PU sheets without emulsion addition has contact angle of 93˚ which is then increased to 104 ˚ upon addition of 20% of emulsion
- The thermal stability of PU sheets has also increased from 427.7 ˚ to 430.2 ˚upon addition of different % of emulsion to PU resin.
- The surface energy of PU sheets shown to be decrease from 30.4 to 23.7 as contact angle increase indicating the material's hydrophobic character.

6.2 Future Recommendations

- As the formulated emulsion has shown superior performance as a hydrophobic agent it could be used as additive in paints, textiles where water repellency behavior is required to investigate its effectiveness in imparting hydrophobicity.
- As this emulsion was used to examine only for Polyurethane resin, it can also be used for other polymer having hydrophilic group in their structure.

- The mechanical properties of the modified PU resin can also be investigated to examine its suitability in various applications

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