INVESTIGATION OF THE EFFECT OF SPECIAL MONOMERS ON THE SYNTHESIS OF ACRYLIC RESIN BY EMULSION POLYMERIZATION

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

ÜRÜN ÇALIŞKAN

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
POLYMER SCIENCE AND TECHNOLOGY

DECEMBER 2023

Approval of the thesis:

INVESTIGATION OF THE EFFECT OF SPECIAL MONOMERS ON THE SYNTHESIS OF ACRYLIC RESIN BY EMULSION POLYMERIZATION

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ABSTRACT

INVESTIGATION OF THE EFFECT OF SPECIAL MONOMERS ON THE SYNTHESIS OF ACRYLIC RESIN BY EMULSION POLYMERIZATION

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December 2023, 79 pages

The motivation of this study is to investigate the effect of special monomers on purely acrylic resin which affects binder stabilization, surface improvement, corrosion resistance, and mechanical properties of paints.

In this study, acrylic binders were synthesized by emulsion polymerization. After optimization, different types of special monomers sodium-allyloxy-2-hydroxypropane sulfonate; 1-methacylamido,2-imidazolidinone ethane; Polypropylene glycol monomethyl methacrylate phosphate ester; and phosphate ester were used respectively with 3% to overall monomer concentration. According to the results, reaction efficiency was the best when the phosphate ester was used as a special monomer.

Particle size, solid content, MFFT, glass transition temperature, FTIR spectrum, and viscosity were measured. Finally, purely acrylic resin (AcRe-SM_1) and a purely acrylic resin with phosphate ester (AcRe-SM_6) were added to the paint formulation. The adhesion test was applied according to ASTM 3359 and ISO 2409 Standard. Corrosion resistance performance tests were applied according to ASTM B117 and ISO 9227 standards.

It was found that purely acrylic resin with phosphate ester resisted corrosion more than purely acrylic system. Moreover, the adhesion performance of the paint with the resin AcRe-SM_6 was better than the paint formulated with purely acrylic resin.

Keywords: Purely acrylic binders, emulsion polymerization, semi-batch polymerization, phosphate ester, special monomer

ÖZ

EMÜLSİYON POLİMERİZASYONU İLE ELDE EDİLEN AKRİLİK REÇİNELERİN SENTEZİNDE ÖZEL MONOMERLERİN ETKİSİNİN İNCELENMESİ

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Aralık 2023, 79 sayfa

Bu çalışmanın motivasyonu özel monomerlerin emülsiyon polimerizasyon yöntemi ile elde edilen saf akrilik reçinelerde etkisinin incelenmesidir. Özel monomerler, reçine stabilizasyonuna, kaplamanın yüzeye yapışmasına, yüzey özelliğini arttırmaya ve korozyon dayanımı gibi mekanik özelliklerini güçlendirmeye etki eder.

Bu çalışmada akrilik reçineler emülsiyon polimerizasyonu ile sentezlenmiştir. Optimizasyon sonrasında farklı özel monomer olarak sırasıyla sodyum1-alliloksi-2-hidroksipropansülfonat; 1-metakrilamido,2-imidazolidinon etan; polipropilen glikol monometil metakrilat fosfat ester ve fosfat ester kullanılmıştır. Bu özel monomerlerin saf akrilik sisteme reaksiyon verimliliği açısından en uygun olanı fosfat ester olarak belirlenmiştir.

Bu çalışmada, tanecik boyutu, katı madde içeriği, MFFT (Minimum film oluşturma sıcaklığı), camsı geçiş sıcaklığı, FTIR, viskozite incelenmiştir. Sonuçlara göre reaksiyonun kararlılığı açısından en iyi sonucu fosfat ester özel monomeri kullanıldığında bulunmuştur.

Bu çalışmaların en sonunda, özel monomerin boya performansına nasıl katkı sağlayabileceğini kanıtlamak için en uygun özel monomer olan fosfat esterli saf akrilik reçine (AcRe-SM_6) ve kontrol formülü olan saf akrilik reçine (AcRe-SM_1) sistemleri boya formülasyonuna eklenmiştir. ASTM B117 ve ISO 9227'ye standartlarına göre 168 saatlik tuz sisinde bekletilmiştir. Bu sonuçlara göre, fosfat ester içeren saf akrilik reçinenin korozyana karşı direncinin daha yüksek olduğu bulunmuştur. Bununla birlikte yapışma performansı ASTM 3359 ve ISO 2409 Standartlarına göre test edilmiş olup, özel monomer katkılı saf akrilik reçinenin daha iyi olduğu tespit edilmiştir.

Anahtar Kelimeler: Saf akrilik bağlayıcılar(reçineler), emülsiyon polimerizasyonu, yarı kesikli polimerizasyon, fosfat esterler, özel monomer

To my mom,

ACKNOWLEDGMENTS

This research has been carried out at Middle East Technical University and DYO Paint Industry Co.

I would like to thank Prof. Dr. Necati Özkan for his valuable knowledge, experiences, and patience. It was a pleasure to be his student and be part of his research team. His perspective and criticism of the research were a good lesson for building my academic background.

I would like to thank Dr. Beyhan Cansever Erdoğan. I was very indebted for taking her endless support and encouragement in research throughout my studies. Her direction, leadership, and guidance were a great opportunity for my thesis.

I would like to thank DYO Paint and Mr. Ercümend Atakay for allowing me to carry out the experiments at the laboratories in DYO Paint.

The technical assistance and precious experiences of Mr. Mesut Sönmez Mr. Özkan Kozak, Mr Ümit Akıncı in DYO Paint were gratefully acknowledged.

I would like to thank Sibel Feriz Şengül, Dr. İrem Çakar Davaslıoğlu, Dr. Merve Dilaver Ağar, Fidan Bal, and Cangül Gümüş for consultancy about the paint applications.

I would like to thank Dilek Kara for answering all my questions regarding to procedure of the thesis.

I would like to thank their precious friendships Elif Canlı, Ceren Uzun, and Eda Çağlı. They encouraged me to finish my thesis study.

I would like to thank my colleagues at DYO Paint who supports my thesis study.

And I would like to thank my parents for their endless support and their patience.

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LIST OF ABBREVIATIONS

ABBREVIATIONS

BA: Butyl Acrylate

MMA: Methyl Methacrylate

MAA: Methacrylic Acid

AA: Acrylic Acid

HEMA: Hydroxy Ethyl Methacrylate

St: Styrene

2-EHA: 2-Ethyl Hexyl Acrylate

SLS: Sodium Lauryl Sulfate

SDBS: Sodium Dodecyl Benzene Sulfonate

NP: Nonyl Phenol

OP: p-octyl polyethylene glycol phenyl ether

APS: Ammonium persulfate

KPS: Potassium persulfate

Not Applicable: Data were not given

Tg: Glass Transition Temperature

MFFT: Minimum Film Forming Temperature

SM: Special Monomer

Surf: Surfactant

CHAPTER 1

INTRODUCTION

Binders are an important ingredients of paints. Acrylic binders are widely used in the paint, coating, sealant, and adhesive industry. Acrylic binders are both synthesized in water-borne and solvent-borne systems. For over 20 years, water-borne acrylic binders have become popular and commercialized in the paint industry. Water-borne acrylic binders are synthesized by bulk polymerization, suspension polymerization, and emulsion polymerization.

Emulsion polymerization is a cost-effective and relatively new type of emulsion. Emulsion polymerization consists of monomers, initiators, and micelles. In emulsion polymerization, acrylic acid esters and acrylic acids are used as monomers, it can be more effective if various monomers are used. Surfactants are an important component because the reaction initiates inside the micelles. Anionic, nonionic, cationic, and amphoteric surfactants are used. Initiators are used to start the reaction. Peroxy disulfates are reacted as thermal decomposition and sulfate radicals occur.

The mechanism of emulsion polymerization is particle nucleation, particle growth, and Stage III. Three types of emulsion polymerization processes are applied such as; batch, semi-batch, and continuous. In the batch polymerization, all ingredients are added into a vessel and the reaction starts. In semi-batch polymerization, some of the ingredients are added at the beginning of the reaction, and subsequently, the remainder is supplied periodically in a continuous form. In continuous polymerization, all ingredients are joined continuously.

Stabilization is an important goal in achieving emulsion polymerization. Coagulation is the undesired phenomenon during the emulsion polymerization

process. By optimizing the agitation rate and the temperature or controlling the monomer/water ratio, adding surfactant stabilization could be achieved.

In this study, firstly purely acrylic system was designed. The study aims to investigate the effect of special monomers on the emulsion polymerization. The most important property of the special monomers is to develop the final coat of paint film, improve the water resistance, adhesion, and corrosion resistance, and decrease the surfactant leaching.

Phosphate esters which normally occur together as mono and diester mixtures, generally have surface active properties. They are strongly acidic substances that can be neutralized by many types of bases after they are produced. In this way, the products have good or even excellent corrosion resistance.

Recently, it has been shown that the glossiness and color properties of paints are improved by adding phosphate ester into the polymer chain. Furthermore, the addition of phosphate ester prevents rusting (improves longtime corrosion resistance), and increases adhesion performance (especially in concrete and glassy systems) and water resistance ability.

1.1 General Information of Paints

Throughout history, paints have been one of the arts of humanity. It was seen in some cave paintings drawn with red or yellow ochre, hematite, manganese oxide, and charcoal by Homo Sapiens. [1] Paint is a pigmented liquid, which is dispersed mainly in a binder (or resin) and volatile solvents. For the formulation of paints, additives such as driers, stabilizers, plasticizers, flame retardants, etc. are used. Even if paint is used for decorative purposes, the primary use of paint is for protecting materials. Paints can provide resistance to water, organic liquids, chemicals, oils, harsh weather conditions, and UV light.

1.2 Components of Paints

The main ingredients of paint are pigments, solvents, and resins (binders). Moreover, small amounts of additives may be added to the paint formulation for other purposes.

1.2.1 Pigments

The colored surface by a film formation is provided by pigments. Pigments, such as chromium oxide, zinc chrome, and lead also play an important role in resistance to corrosion.

Pigments are categorized into two groups: inorganic and organic pigments. Organic pigments are formed by stable carbon atom bonds and are derived from animal, vegetable, and synthetic organic chemistry. Generally, organic pigments are glossy, light in weight, and rich in tinting strength, but they are not good at light resistance.[2] Inorganic pigments are made up of ground minerals, metals, or metallic salts. Inorganic pigments are opaque and insoluble. Inorganic pigments have excellent fade resistance, and they are cost-effective. However, Inorganic pigments are more toxic to the environment, especially lead-based pigments.

The main role of pigments is decorating and hiding the roughness of the surface. In addition, the pigments may help to prevent the degradation of the resin and improve the strength of the resin. Pigments can improve the corrosion resistance of paints. Extenders, which can be named supplementary pigments, are used for altering the viscosity which affects the rheological properties of paints. calcium carbonate, silica, kaolin, and mica are the typical extenders.

1.2.2 Solvents

Solvents, which are used in paint and coatings formulations, play a vital role in dispersing and/or dissolving various components of the paints. Solvents are volatile liquids, therefore, there are no solvents inside a polymer film. Solvents help to convey the pigment-binder mixture to the surface.

Organic solvents can be toxic and flammable; therefore, water is preferred as a solvent in the paint industry. Paints are divided into two groups according to their solvent structure: the solvent-borne paint and the water-borne paint. For industrial applications, solvent-borne paints are mostly used. However, when the paint is served to the public, water-borne paint is used, especially in decorative paint.

There are some advantages and disadvantages of water-borne paint. Water is not toxic, whereas organic solvents are hazardous to human health and also toxic to the environment. Water is not a flammable liquid, as a result, the possible risks during the transportation and production phase are minimized. It is not easy to clean up the reactor tank in solvent-borne systems after finalizing the production phase of the paints. However, the cleaning stage is cheaper in the water-borne paint rectors. The evaporation process for the water-borne paint is more difficult than that for the solvent-borne paint. The surface tension of water is higher than that of organic solvents. To decrease surface tension surfactants are generally used. Water leads to the corrosion of production equipment such as storage tanks and pipelines etc. [3]

1.2.3 Binders

Resins are an essential component of the paint and coating industry, and many scientific studies are focused on resin properties since resins improve the chemical and physical properties of the paint. The pigment particles are held together, and they are adhered to a surface with the help of the resin.

The role of the resin is essential for the film formation phase. The film formation can be achieved in various ways: physical drying, chemical drying, and oxidative drying. In the physical drying, the solvent is evaporated, as a result, the pigments are held together, and subsequently, the film formation is realized. In chemical drying, the nature of the resin is changed chemically and a new polymerization occurs. In the oxidative air-drying process, the absorption of oxygen from the air takes place.

There are many types of resins; acrylic resin, epoxy resin, polyester resin, polyurethane resin, long oil alkyd resin, and silicone resin etc.

1.3 Acrylic Resins (Binders)

Acrylic resins are widely used in the paint industry. Methacrylic acid and esters of acrylic acids are the main components of acrylic resins. Acrylic resins are also used in adhesive, textile, printing inks, paper coating, and construction industries. Acrylic binders are mainly preferred due to their high block resistance, hardness, gloss, alkali, and oxidation resistance. [4]

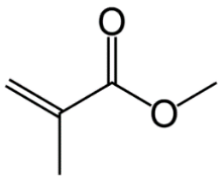


Figure 1.1. Example of acrylate

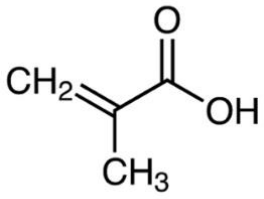


Figure 1.2. Example of methacrylic acid

Esters of acrylic acid and methacrylic acid are differentiated by the reactivity of their double bonds. Following the initiation step, these double bonds connect monomers and polymerization occurs. [5]

Acrylic resins are categorized into two groups: polyacrylates and reactive acrylic resins. Polyacrylates are synthesized by either solution polymerization or emulsion polymerization. In the solution polymerization, an organic solvent is used and the product can be added directly into the paint formulation. In the emulsion polymerization, explained in the next section in detail, water is used as a solvent and an emulsifier is used.

The second group of acrylic resins is named as reactive acrylic resins. Acrylic and methacrylic ester resins have still double bonds. Condensation reactions take place. Acrylic or methacrylic esters are incorporated into a polymer chain or oligomeric molecules during the condensation reaction. Binders, produced during the condensation reaction, especially three-dimensional crosslinked macromolecules are able to form a film.

1.3.1 Acrylic Solution Polymers

Copolymers of acrylate and methacrylate esters are prepared as a reactant and polymerization is carried out in a solvent. The solubility parameter of the solvent should be similar to that of the polymer. Generally, toluene, xylene, or methyl ethyl ketone are used as solvents.

1.3.2 Acrylic Emulsion Polymers

Organic volatile solvents are used in traditional solvent-based resins. These types of solvents may reduce the viscosity of the binders. However, environmentally volatile organic compounds are limited due to the strict environmental laws and policies. [6] Therefore, the water-borne acrylic resins are preferred.

Water-borne acrylic resins are used in especially coating industry. They are also used in ships, containers, bridges, and military industry. Water-borne acrylic

binders are used widely today due to their low cost, weather resistance, pollution resistance, and acid and alkali resistance.

Water-borne acrylic polymers can be synthesized by emulsion polymerization, solution polymerization, or bulk polymerization. Emulsion polymerization is widely used in the coating industry.

The acrylic monomers are emulsified to form an emulsion polymer and then polymerized as small droplets in a continuous water phase. The droplets are typically stabilized by surfactants and without solvents. The emulsion polymerization has both advantages and disadvantages. If a high solid content of polymers is required to produce, the emulsion polymerization is more advantageous than the solution polymerization. Furthermore; due to the low viscosity of the emulsion polymer, it allows fast air drying by the evaporation of water. [7] Polymer microstructure such as; molecular weight distribution, polymer composition, branching and crosslinking, density, particle size, and morphology are important because those properties affect anticorrosive properties. Latex particles also affect film formation and pigment distribution. On the other hand; surfactants affect the stabilization of the reaction thus, sometimes water susceptibility will be observed which means hydrophilic oligomers increase the water permeability of the resultant film. [8,9]

1.4 Emulsion Polymerization

Synthetic rubber is the first emulsion polymer which was synthesized during World War II when America could not access Southeast Asia's natural rubber sources. Vinyl acetate, chloroprene, methacrylate, and acrylates are used as monomers in the commercial stage. The output of the emulsion polymerization is called "latex" which is a colloidal dispersion of polymer particles and ranges from 50 nm to 1µm and has 20-70% solid content. Each particle is composed of up to 10,000 polymer chains and each polymer chain contains 100 to 1 million monomeric units. The

emulsion polymerization is applied in rubber, paint, adhesive, paper coating, and sealant industry. [10,11,12,13]

1.4.1 Components of Emulsion Polymerization

Monomers, surfactants, initiators, and additives such as biocides, redox elements, and crosslinkers are the main ingredients of latex polymers. On an industrial scale, additives could be added to the reactor. Over 20 ingredients may be used in the emulsion polymerization and they could affect the rate, structure, and characteristics of the polymers. (14,15,16,17)

1.4.1.1 Continuous Medium

Water is used in the emulsion polymerization and the reaction proceeds in water medium. Water is selected because of its heat conduction. The quality of the water is an important parameter. Because; the hardness of the water affects the particle size, nucleation, and particle stability. Hence, deionized water should be selected. The oxygen in water should be at a minimum level since oxygen swallows free radicals which quench initiator radicals so the reaction starts later than standard time. Therefore, nitrogen gas purges the oxygen. (14, 15, 16, 17)

1.4.1.2 Surfactants

Surfactants are the short name for surface-active material that can change the surface tension of the fluid. The main duties of the surfactants are stabilizing monomer droplets, making micelles, solubilizing monomers, and latex polymers, and hindering aggregation. The percentage of the surfactants of the latex is around 1-6%. Generally, anionic surfactants are required at minimum concentration whereas nonionic are at maximum concentration. The concentration of the surfactant is important which is called Critical micelle concentration (CMC).

Micelle has polar ends which are located towards to outside and nonpolar chains which are located toward to inside. Because of the polar ends, micelles can repel each other. Micelle size is inversely proportional to the amounts of the surfactants. Generally, the shape of the micelles is spherical however, sometimes rodlike micelle could be observed.

1.4.1.2.1 Classification of the Surfactants

Surfactants are classified into four groups such as, anionic, cationic, amphoteric, and non-ionic. Anionic and nonionic surfactants are compatible with latex particles which are charged negatively.

In anionic surfactants, a negative charge is obtained on the polar head of the molecule. Examples of anionic surfactants are sodium lauryl sulfate (sodium dodecyl sulfate), sodium dodecyl benzene sulphonate, alkyl phenol ether sulfate, and sulfosuccinic acid ester sodium salts.

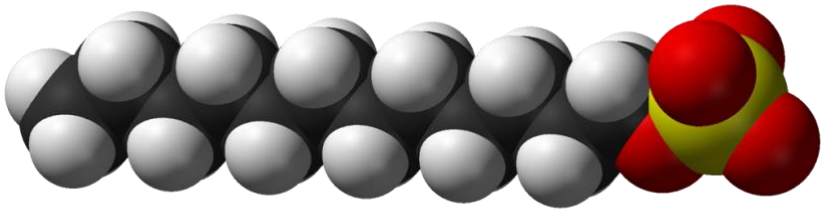


Figure 1.3. Structure of Sodium Lauryl Sulfate (Sodium Dodecyl Sulfate)

Cationic surfactants give a positive charge when the ionization starts in the solution. Cationic surfactants are not capable of easy interaction with anionic surfactants. Thus, cationic surfactants are not preferred to use. Examples of cationic surfactants are polyamines and ammonium salts.

Amphoteric in other words zwitterionic surfactants are different types of surface-active chemicals because it is negatively charged at high pH values and it is

positively charged when the pH is low. Imidazoline carboxylates and amine oxides are examples of amphoteric surfactants.

Non-ionic surfactants have no charge when it is dissolved in water. Non-ionic surfactants have hydrophilic groups that contain covalently bonded oxygen that interact with the hydrophobic part of the other material. Long-chain carboxylic acid esters are a good example of a non-ionic surfactant.

1.4.1.2.2 Selection of Surfactants

Surfactant selection is based on the Hydrophile-Lipophile Balance (HLB) system, which answers the principle of the emulsification power, detergency, foaming, and solubilization. When the HLB value is lower than 6, it can be used as water in oil emulsifiers. On the other hand, if the HLB value is higher than 8, it can be used in oil in water systems. [18]

1.4.1.3 Monomers

Acrylates are the main monomers of latex polymers and acrylic acids are functional monomers that provide stability and adhesion performance, affect polymer solubility, and sometimes add value to the cross-linking performance. More than 95% of monomers are found in monomer droplets so, the absorbed surfactant molecules stabilize them. The solubility is an important parameter. If the solubility of the monomer is too high the solution polymerization will occur, and emulsion polymerization will not successfully proceed.

1.4.1.3.1 Selection of Monomers

Before designing a system, it is necessary to decide what type of monomer will be used. Monomers affect the glass transition temperature (T_g), mechanical properties, and minimum film formation temperature of the latex. One monomer is not an

effective way to synthesize latex particles. The production of copolymer latexes is more desirable because it is possible to design the product so that rubbery properties (influencing flexibility, adhesion, and tackiness) or glassy properties (influencing hardness, strength, and clarity) can be obtained.

Functional monomers such as acrylic acids and methacrylic acids should be added to monomer groups. These acids influence the colloidal stability of the polymer. Crosslinking ability which contributes to application performance, adhesion, and strength will be improved by functional monomers.

1.4.1.4 Initiator

In the emulsion polymerization, water-soluble free-radical initiators are used. Radical reaction in polymerization is promoted by free-radical initiators. [19] Thermal decomposition, redox reactions, and gamma radiation are the types of initiation of the reaction.

Generally, thermal initiators are preferred since the reaction temperature of emulsion polymerization is at 75-90 ºC to maximize the polymerization rate. Peroxydisulfate salts which are ammonium persulfate, and potassium persulfate the examples of thermal initiators. Sulfate radical ions are araised homolytically.

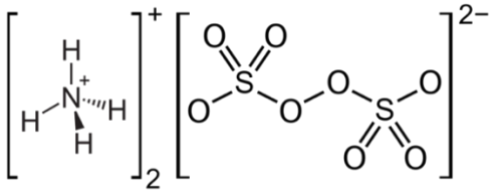


Figure 1.4. Structure of ammonium persulfate

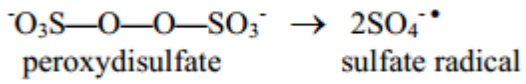


Figure 1.5. Thermal initiation of radicals

1.4.1.5 Other Additives

In emulsion polymerization, various additives are used for specific reasons. Redox initiators are used to achieve unreacted monomers to be added to the reaction. [20] Ammonium hydroxide is also an additive for adjusting pH values. Biocides are used to keep down contamination.

1.4.2 Mechanism of Emulsion Polymerization

Monomers, surfactants, and initiators are the main components of emulsion polymerization. Monomers are not easily soluble in a water medium; this leads to aggregation and then it is stabilized and becomes monomer droplets in the water suspension. The aggregation of the surfactants is named as a micelle. Micelles form with hydrophilic head regions in contact with surrounding water and hydrophobic tail is located in the micelle center. Not all the micelles but, generally monomers are located inside of the micelles and they are getting bigger than their normal size. Initiators command to start the reaction. The difference between emulsion polymerization and suspension polymerization is initiation occurs in monomer droplets. The thermal decomposition polymerization occurs in three stages: particle nucleation, particle growth, and final stage III.

1.4.2.1 Particle Nucleation

Micellular nucleation, in other words, heterogeneous nucleation, is the first type of particle nucleation. It begins when the radical initiator flows into the monomer-

filled micelles. The monomer radical is comprised of the reaction of the monomer and the initiator. The heterogenous nucleation is explained in Figure 1.6.

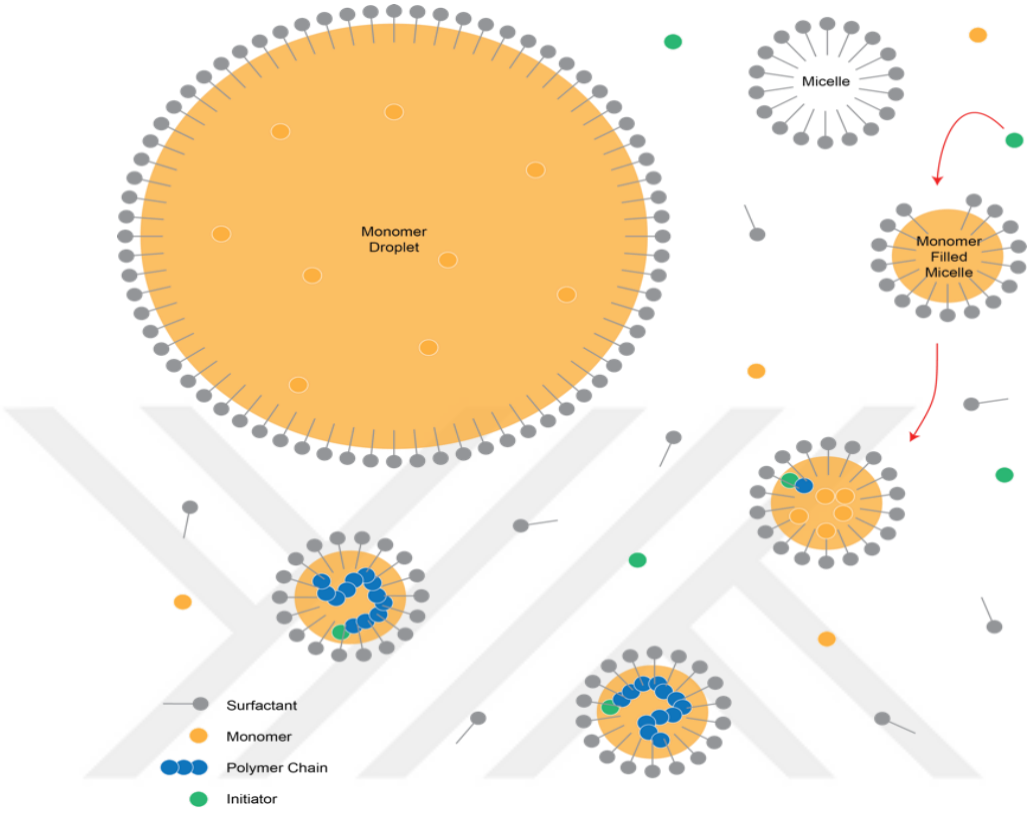


Figure 1.6. Mechanism of micellular Nucleation

Homogenous nucleation is the second type of particle nucleation. The mechanism is seen in Figure 1.7., the radical initiator adds to the monomer and polymerization starts in the aqueous phase. Then, several monomers are added by the initiator until the oligomers are insoluble in water. At this critical point, thermodynamically the chain is not stable and it collapses on itself or onto dead oligomers which are free in the aqueous phase. At the same time, surface active materials absorb on their surface and lower the interfacial energy. Collapsed chains form a coagulum unless surfactant is added. [21]

Monomer droplets' small surface area does not let the nucleation. It could be explained by the initiator molecule cannot enter into the droplets because of their less interaction. This stage could be observed in seed polymerization and it happens rapidly.

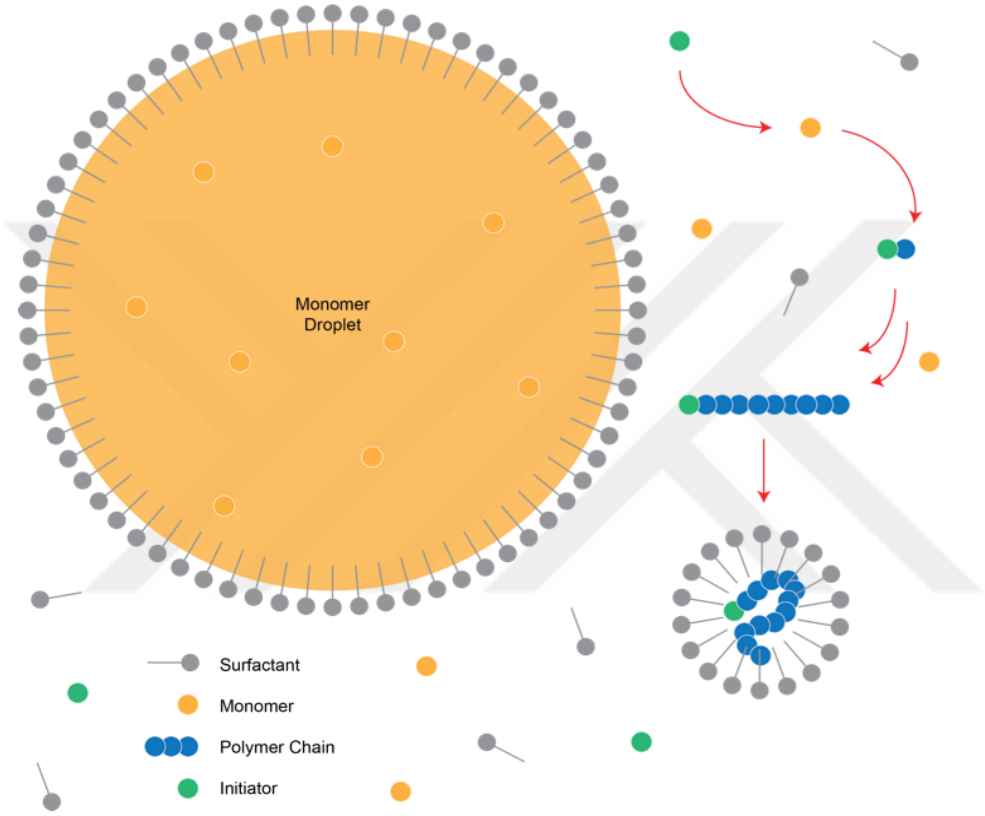


Figure 1.7. Homogenous Nucleation Mechanism

1.4.2.2 Particle Growth

In this step, seeds are grown because monomers which are seen as monomer droplets fed into micellular particles. The solubility of methyl methacrylates or butyl acrylates is limited. Micelles with monomers, water medium, and monomer droplets are in equilibrium concentration with free-floating monomers. Monomers are pulled from monomer reservoirs into the continuous medium by diffusion at

low concentrations of free-floating monomers. Oligomers are formed in water medium and they cannot be dissolved at their critical length. Instead of new being produced new particles, oligomers flow to the surface of the particles, due to the lack of a new stable interface. Monomer diffusion comes into existence from monomer droplets to aqueous phase and particles are grown until the last monomer droplets are consumed.

This stage affects the morphology of polymer latex particles. Hydrophilicity or hydrophobicity, amounts of the monomers, and reaction temperature are the important parameters to control the polymeric latex particles.

According to the morphology, the emulsion polymers are divided into groups such as core-shell, raspberry, and half-moon, etc. Core-shell technology is preferred mostly. In this study, core-shell polymers are synthesized. Spherical core-shell latex particles are formed by the combination of soft which becomes a film at low temperature and in the outer layer, a hard monomer which becomes a film at high temperature. The Core-shell system is desirable for the coating industry because of its low MFFT, high elasticity, tackiness ability, blocking resistance, and coating hardness. [22,23] The polymers are branched and cross-linked in this phase.

1.4.2.3 Stage 3 (Final Stage)

The final stage of the emulsion polymerization is named Stage 3 when the particle growth is stopped since there is no longer a monomer inside the droplets. In this stage, monomer concentration decreases since polymer particles decrease however, particle size does not change

Sometimes, the Tromsdorff effect [24] would be observed. When the conversion of the reaction rises, viscosity increases. The mobility of the polymer chains in viscous medium is very small so the particles cannot find each other to be finalized. This leads to temperature increase and temperature cannot be controlled. [25]

1.4.3 Emulsion Polymerization Process

The emulsion polymerization process can be applied in 3 types of polymerizations. There are; batch polymerization, semi-batch polymerization, and continuous polymerization. Batch polymerization is the simplest polymerization: all the elements are added into the reactor. In semi-batch polymerization, some portions of the reagents are added into the vessel initially, and then the remaining reagents are joined into the reactor periodically over the course of the reaction in predetermined amounts. In continuous polymerization, the elements are fed into the reactor continuously.

1.4.3.1 Batch Polymerization

The system has a constant agitation, and temperature is adjusted to equilibrium when the initiator is added to start the reaction. Particle nucleation occurs in homogenous nucleation. Batch polymerization is applicable in a laboratory setting to start the kinetics of the emulsion polymerization because in industry it is not easy to control particle size and morphology. In addition, the Tromsdorff effect could be seen and it leads to accidents in commercial settings [26]

1.4.3.2 Semi- Batch Polymerization

Semi-batch polymerization is more reproducible and optimizable about their particle size and morphology. The monomer is fed either by pre-emulsion which monomer in water stabilized by surfactants or fed by a monomer periodically. For monomer-flooded condition, particle growth occurs The concentration of monomer is higher than monomer consumption so monomer droplets and particles are saturated with monomer. However, if a lack of monomer concentration occurs particle growth is absent, as a result small particles are occurred.

1.4.4 In Situ Emulsion Polymerization

Seeded emulsion polymerization is a better way to control particle size and distribution. This method evokes making yogurt in daily life. 5-10% of the total monomer is added into the vessel and the reaction is started. Then the remainder is joined as a pre-emulsion over the course of the time periodically. Small seed particles have become optimum size. If the monomers are fed directly particle size of the seed is bigger than adding by the pre-emulsion method. Surfactants shouldn't be so high because secondary nucleation of particles may occur. On the other hand, lack of surfactant results in lowering particle size charge density thus; leading to unstable and coagulation. [27]

1.4.5 Polymer Composition

The distribution of monomers is essential when various monomeric units are introduced into the reaction which is the desired latex copolymer. Copolymers can be blocking copolymers, alternating copolymers, or random copolymers. The structure of polymers would be blocky or cross-linked.

While designing a copolymer; Tg, residual odor, viscosity, and many other properties of the polymeric film are important. Fox Equation is applicable to estimate desired glass transition temperatures and weight fraction is also an important parameter. In addition to these parameters, the reactivity ratio has to be considered in order to describe the tendency of a radical to add to itself as opposed to a comonomer. If reactivity ratios are all large, large homopolymer blocks would be synthesized. If reactivity ratios are the same and close to 1, they will become random copolymers. If reactivity ratios are small, they will be formed as alternating copolymers.

In designing an n-butyl acrylate (BA) and methyl methacrylate (MMA) copolymer, reactivity ratios are explained in Figure 1.8. The Reactivity ratio of BA, $r_{BA,}$ is

small it prefers to react with MMA than BA monomers. The Reactivity ratio of MMA, r_{MMA} is very high, it prefers to add itself. This could be explained by the monomers being stabilized by ester functionality, but the tertiary radical of MMA is more stable than BA radicals. So, BA and MMA would like to add to an MMA monomer.

To design random copolymer further techniques are applicable such as supplying desired monomer fractions under starved conditions by feeding at a slower rate than the rate of propagation of monomer consumption. Thus, the ratio of monomers could be controlled.

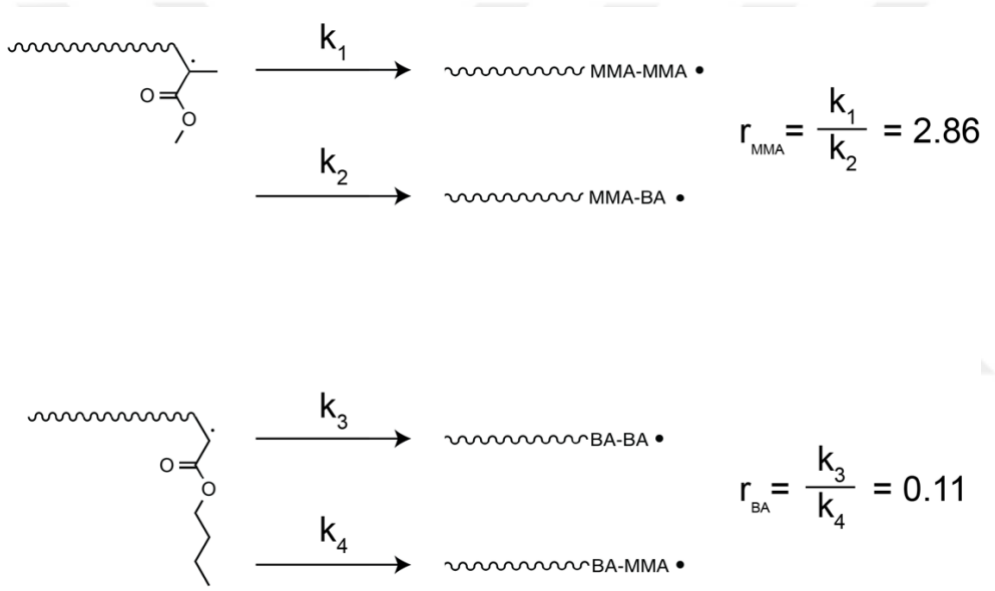


Figure 1.8. Reactivity ratios of nBA and MMA

1.4.6 Stability of the Particles

Generally, it is very difficult to control the stability of the emulsion polymerization because colloidal systems are thermodynamically unstable. To produce colloidally stable latex particles, which are able to remain fully dispersed not only instantaneous but also for a long time is very important. The DLVO Theory [28], describes electrostatic repulsion and Van-der Waals forces. The stability of

colloidal latex particles and coagulation which is not desired in emulsion polymerization is explained.

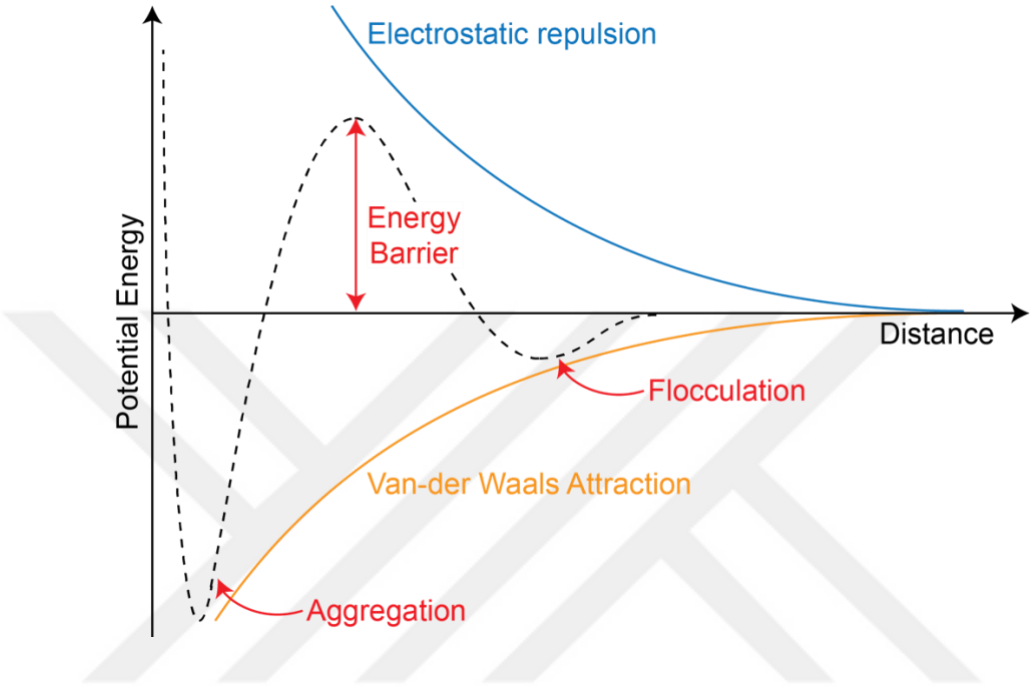


Figure 1.9. DLVO Theory

The dash lines correspond to the energy of both VDW and repulsive forces between the particles. If the distance decreases, flocculation would have occurred which is represented by the secondary minimum in Figure 1.9. If the distance between two particles decreases in an acceptable ratio that overcomes the energy barrier, aggregation would occur, which is the lowest energy minimum described in the plot. On the other hand, interdiffusion of the chains between the particles would be seen. Consequently, particles lose their identity and form a single mass of coagulated polymer. This is explained by coagulation. Coagulation is different from aggregation or flocculation.

Coagulation leads to unstable dispersion at which the temperature is greater than the glass transition temperature. The particles become soft and flexible so they can diffuse each other very easily.

Stability is dependent on reaction conditions, agitation speed, the temperature of the reaction, water-monomer ratio, solubility of the monomer, type of surfactant, type of initiator, and concentration of the total electrolyte.

Functional monomers such as methacrylic acid or acrylic acid could be added to the reaction to stabilize the particles. Functional groups of carboxylic acid are charged and tend to be alkaline state. Repelling of charged surfaces prevents agglomeration. Stabilization is applied by electrostatic and steric repulsion. This could be provided by anionic surfactant. Negative charges of the particles decrease interfacial energy.

To control stability, coagulation is undesired resulting in emulsion polymerization. Coagulation could be observed in 3 forms; coagulum recovered by filtration, coagulum on reaction vessel walls and agitator, and coagulum formed in the latex during storage. Typically, coagulums can be seen as soft and sticky, hard and granular, or hard and friable. Sometimes coagulums can be observed on a microscopic scale which cannot be removed by filtration. This coagulum appears when sliding on glass film.

To prevent coagulation, seeded emulsion polymerization is a better solution. The agitation rate should be at optimum speed because if the agitation rate is higher, the micelles can be disrupted and affect flocculation. In addition, the monomer/water ratio should be small to reduce the collision frequency. [29] Adding a buffer solution is also an alternative way to decrease coagulation.

1.5 Minimum Film Forming Temperature (MFFT) and Glass Transition Temperature (Tg)

Designing a copolymer, monomer selection is important. In the coating industry, the acrylic resin should be flexible.

Before selecting the monomers, the properties of the monomers should be known. MMA has exterior durability, higher stain and water resistance and the hardness of the film is greater than the other monomers. Butyl acrylates are flexible and have a high capacity of water resistance. 2-ethyl hexyl acrylates are also flexible and elastic monomers have good weathering characteristics and have a high UV resistance. Acrylic acids and methacrylic acids films have hardness give functionality and also assist stabilization.

The polymer creep adaptation must be great and viscosity must be low to obtain a continuous pore-free film. According to viscoelasticity theory, film formation will be possible if the glass transition temperature of the polymer latex particle is lower than the ambient temperature. Minimum film forming temperature and glass transition temperature have a relation because of the viscoelastic property of the polymer. [30]

1.6 Special Monomers

The most important property of the special monomers is they improve the quality of the topcoat of the paints. Special monomers increase water resistance, corrosion resistance, and, adhesion. They also decrease surfactant leaching. Phosphate ester monomers are used increasingly.

Adding a small ratio of special monomers, color properties, prevention of rusting, and adhesion property increase. A significant effect would be observed even if it is used in small amounts. [31]

1.7 Aim of the Study

In this study, the acrylic resin was synthesized by semi-batch emulsion polymerization. Firstly, a purely acrylic system was synthesized. Surfactants play an important role as well as the monomer. Therefore, firstly optimization was

applied before the experimental study. After optimization, the effect of special monomers was tested experimentally.

Special monomers affect binder stabilization, coating adhesion, promotion, coating surface improvement, and coating mechanical properties. Phosphate ester and the other special monomers were used and compared according to their stability, Tg, MFFT, and viscosity.

CHAPTER 2

LITERATURE REVIEW

In this study, there are numerous scientific researches regarding emulsion polymerization. Before designing the system, the emulsion polymerization mechanism, emulsion polymerization steps, and stabilization should be investigated. Then, to establish a system appropriate recipe should be decided. In this part, many research papers enlighten this study to select monomers, surfactants, initiators, and other additives. Next analytical characterization techniques should be investigated as well, especially glass transition temperature and minimum film forming temperature should be surveyed in detail.

2.1 Academic Studies of Emulsion Polymerization

Japek, Barton, and Oronilova et al. published a preliminary article for emulsion polymerization. The mechanism of the water-soluble ammonium persulfate-initiated emulsion polymerization of butyl acrylate at 70°C is applied. The effect of initiator type, degree of agitation, and monomer type was observed. This polymerization was a kind of emulsion batch polymerization. They concluded that the viscosity average molecular mass of the polymer was inversely proportional to 0.5 power of initiator concentration. [32]

Chern et al. investigated the semi-batch emulsion polymerization of butyl acrylate and methyl methacrylate. Chern used only methyl methacrylates and butyl acrylates as monomers while, in our study, various monomers were used. [33] This study gave an idea to select the best initiator and surfactant in literature because sodium lauryl sulfate (sodium dodecyl sulfate) was used as a surfactant. Chern's other paper represented the kinetics of the emulsion polymerization in the

propagation step. [34] The propagation of free radicals with monomers was explained briefly. This study focused on the polymerization mechanism of particle nucleation and particle growth and also the kinetics involved in heterogeneous polymerization systems.

Asua et al. studied the fundamental mechanism of emulsion polymerization. [35] Oil soluble initiators, propagation rate constants of acrylic monomers, formation of particle morphology, and reactive surfactants were discussed in the first part of the paper. In the second part, the advances in process development such as optimization, online monitoring, and control were explained. This study was useful for background information regarding emulsion polymerization.

Zhang and Wang et al published a paper regarding the adhesive industry. [36] The study was not related to the paint industry however, some basic knowledge about emulsion polymerization was learned in this paper. Because experiments were carried out in the same manner. This study focused on how the dosage of seed emulsion affects particle size and reaction rate. It was analyzed that particle size was inversely proportional to the amount of seed emulsion and reaction rate was proportional to the dosage of seed emulsion.

2.2 Investigation of the Standard Formulation

Zhang, Wang, Yuan, Chai et al synthesized emulsion acrylic polymer with Butyl acrylate (BA), methyl methacrylate (MMA), acrylic acid (AA), and hydroxyethyl methacrylate. [37] Ammonium persulfate was selected as the initiator. They investigated that when hydroxyl monomer and carboxyl monomer increased, the coagulum increased. This study was useful for designing the recipe for the reaction.

Plesis, Arzamendi, Leize, Schoonbrood, Charmod, and Asua prepared a paper. In this paper seeded emulsion polymerization of n-butyl acrylate was investigated. Potassium persulfate was used as an initiator at 75°C. The effect of initiator

concentration, feed flow rate, molecular weight distribution, and level of branches on the emulsion polymerization system was studied. [38] It was found that gel formation was not affected by initiator concentration or monomer feed flow rate under starved conditions. However, the more branched and the lower molecular weight was dependent on the higher initiator concentration and feed flow rate of monomers. In our study to control the stability seeded emulsion polymerization was used thus, this paper enlightened how to prepare a seeded emulsion polymerization system.

Saijadi and Yiannekis et al prepared a paper that was very close to this study, however, they estimated the reaction rate.[39] Methyl methacrylate, sodium lauryl sulfate, and potassium persulfate were the main ingredients of the reaction. Monomer feed rate, surfactant concentration, and monomer distribution ratio were the parameters to have been studied. When the monomer feed rate decreased, the average molecular weight decreased.

Tigli et al studied purely acrylic systems which had excellent weathering properties, high block resistance, hardness, gloss, and high alkali oxidation resistance. [40] Optimization of emulsifiers, initiators, and water-soluble monomers was applied. This paper was a perfect recipe for a purely acrylic system because our study was based on a purely acrylic system which means no other vinyl group was added to the system. Surface charge density, particle size thermal analysis, and film formation properties were determined. UV resistance, flexibility, hardness, adhesion, and gloss properties of the films were characterized. The rate of methyl methacrylate/ethyl acrylate 1:1.5 copolymer was the best result.

Xiaojie et al studied purely acrylic emulsion polymerization. [41] Methyl methacrylate, butyl acrylate, and acrylic acid were used as a monomer. The effect of the surfactant and the pH value was investigated. When the surfactant concentration was 3%, the initiator concentration was 0.35% and at pH 8-9 water absorbability of the paint reached 7.9%.

Wang et al published a paper regarding nano hyperbranched polymer resin and analyzed its corrosion resistance. [42] SiO2 and TiO_2 mixtures are added and formed as a composite. Purely acrylic emulsion was prepared with these ingredients such as 10 wt % aqueous ammonium persulfate solution as an initiator. The acrylic acid, styrene, methyl methacrylate, butyl acrylate, and hydroxyethyl methacrylate had a fraction of 3:40:20:25:12 to obtain an acrylic binder.

Table 2.1. Literature Surveys of Formulations of Purely Acrylic Systems

	Zhang et. al.	Plesis et.al.	Xiaojie et.al	Saijadi et.al.	Tigli et. al.	Wang et.al
Name of Surfactant	SLS, SDBS, NP, OP	SLS	SLS	SLS	SDS	OP
% of Surfactant	0.9	0.4	0.3	1.5	0.33	Not applicable
Name of Initiator	APS	KPS	APS	KPS	KPS	APS
% of Initiator	0.22 (with %5 of water solution)	0.1	0.35		0.27	Not applicable. (with 10% of water solution)
Name of Monomers	BA, MMA, HEMA, AA	BA	MMA, BA, AA	MMA	MMA, BA	AA, St, MMA, BA, HEMA
Ratio of Monomer Mixture	0.41:0.32:0.23:0.025	-		-	1:1	3:40:20:25:12
% Monomer to Overall	45	19	Not applicable	20	43	Not applicable

SLS: Sodium Lauryl Sulfate, SDBS: Sodium Dodecyl Benzene Sulfonate, NP: Nonyl Phenol, OP: p-octyl polyethylene glycol phenyl ether, APS: Ammonium persulfate, KPS: Potassium per sulfate, BA: Butyl Acrylate, MMA: Methyl Methacrylate, AA: Acrylic Acid, St: Styrene; HEMA: Hydroxy Ethyl Methacrylate, Not Applicable: Data were not given

2.3 Additional Studies

Jiang et al investigated novelty regarding acrylic emulsion polymerization containing phosphorous and silicone components. [43] This study was different from our study because it was the first time adding phosphorous material. The films were characterized by FTIR, DSC, and Contact angle. On the other hand, in our study, phosphate ester was used.

Kohut Svelko et al studied redox initiator which assists unreacted monomers to join into the reaction. [44] Redox initiators were added at the end of the polymerization. It was useful to improve the efficiency of the industry state. Bruggolit and TBHP were the best redox initiator. In our study, these initiators were used. They both discharged each other.

Steward and Wilkinson studied the relationship between Tg and Minimum Film Forming Temperature, MFFT. Toussaint also proposed a model and if a coalescing agent were added, Tg and MFFT were changed and it was calculated with the weight fraction of the coalescing agent. [30].

Hennaux et al published an article about the advantages of specialty monomers with functionality. Although it was used at low levels the effect was very significant. Binder stabilization, coating adhesion promotion, coating surface improvement, and coating mechanical properties were the important properties of the specialty monomers. This article was not experimental however, our study proved the effect of specialty monomers. [31]

CHAPTER 3

EXPERIMENTAL

3.1 Materials

Methyl methacrylate, butyl acrylate, 2 ethylhexyl acrylate, methacrylic acid, and acrylic acid was used as monomers; sodium lauryl sulfate (sodium dodecyl sulfate), sodium dodecyl benzene sulfonate, alkyl phenol ether sulfate, sulfosuccinic acid ester sodium salts were used as different types of surfactants; ammonium persulfate was used as initiator; TBHP and Bruggolite as the chasers or redox initiator; ammonia as a neutralizer. In addition to this, defoamer and biocide were used in this study. Sodium1-allyloxy-2-hydroxypropanesulfonate; 1-methacrylamido,2-imidazolidinone ethane; Polypropylene glycol monomethyl methacrylate phosphate ester, phosphate ester were used as a special monomer. All chemicals supplied by DYO Paint Industry Co.

3.1.1 Special Monomers

3.1.1.1 Sodium 1-allyloxy-2-hydroxypropane sulfonate

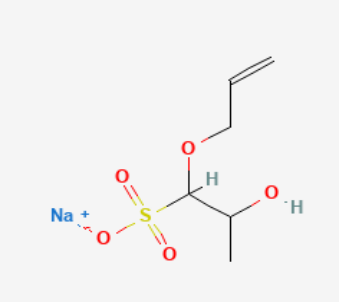


Figure 3.1 Structure of sodium 1-allyloxy-2-hydroxypropane sulfonate

3.1.1.2 1-methacrylamido,2-imidazolidinone ethane 1-methacylamido, 2-imidazolidinone ethane

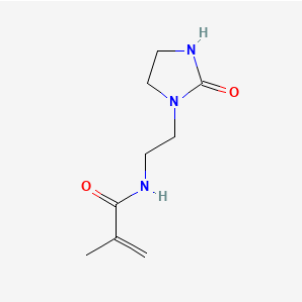


Figure 3.2. Structure of 1-methacrylamido,2-imidazolidinone ethane

3.1.1.3 Polypropylene glycol monomethyl methacrylate phosphate ester

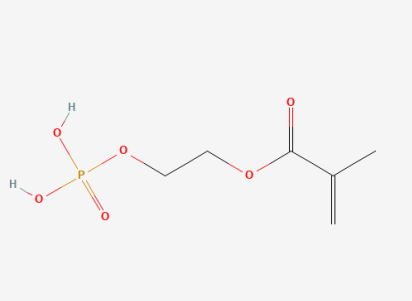


Figure 3.3. Structure of polypropylene glycol monomethyl methacrylate phosphate ester

3.1.1.4 Phosphate ester

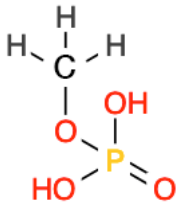


Figure 3.4. Structure of phosphate ester

3.2 Experiment Setup

2L of four-necked glass reactor was placed in a water bath with plastic bubbles. Thermocouple, and agitator with motor 65.DV.00001 were connected into the middle neck. The condenser was connected to another neck; the initiator charge with the valve was connected to the third neck. The monomer charge was connected to the last charge. The picture of the system is in detail as shown in Figure 3.5.

3.3 Mechanism of the Experiment

3% wt. of anionic surfactant with deionized water initially was added into the reactor and heated to 80 °C. On the other hand, monomers, the rest of the surfactants, and deionized water were prepared in a flask and named an emulsion tank. Then, 5% wt. of the emulsion and 5% wt. of initiator in water solution were added into the reactor at 80°C. At 80-85°C, emulsion charge and initiator charge valves were opened and fed to the reactor over the course of 2 hours. When the monomer feed had been finished, the temperature was decreased to room temperature. The chasers, in other words, redox initiators, TBHP, and Bruggolite in water solution were added into the reactor respectively to continue the reaction whether any unreacted monomers have not joined into the polymerization yet. After 1 hour later, ammonia was used as a neutralizer, and defoamer and biocide were added at the end of the reaction.



Figure 3.5. Experiment setup

3.3.1 Optimization of the Reaction

Surfactant ratio and monomer contents were important parameters. Even if, the effect of special monomers was investigated, the optimum recipe should be designed first. After the literature survey, the initiator selected was ammonium per sulfate with 0.1 % wt. of overall the reaction. In addition, all monomer content was 45 % wt. of the reaction. The basic formulation is tabulated in Table 3.1.

Table 3.1. Basic Formulation of Purely Acrylic System

Formulation	
% wt. of Surfactant	Variation
% of Initiator	0.125 (with %5 of water solution)
Name of Monomers	MMA+BA+2EHA+AA+MAA
Ratio of Monomer Mixture	0.59: 0.3: 0.09: 0.008: 0.005
% wt. Monomer to Overall	45

After a purely acrylic system was designed, the surfactant ratio and the type of surfactant were optimized. Firstly, sodium lauryl sulfate (sodium dodecyl sulfate) was used and the ratio of the surfactant was changed from 0.3 to 3% wt. of overall the reaction which is corresponded in Table 3.2. Then, the type of the surfactant was changed and tested such as sodium lauryl sulfate (sodium dodecyl sulfate), sodium dodecyl benzene sulphonates, alkyl phenol ether sulfate, and sulfosuccinyl acid ester sodium salt which is tabulated in Table 3.3.

Table 3.2. Optimization of the Surfactant Ratio

	Name of Surfactant	Amount of Surfactant % wt.
AcRe-Surf_1	Sodium lauryl sulfate	0.3
AcRe-Surf_2	Sodium lauryl sulfate	1
AcRe-Surf_3	Sodium lauryl sulfate	1.5
AcRe-Surf_4	Sodium lauryl sulfate	2
AcRe-Surf_5	Sodium lauryl sulfate	3

Table 3.3. Different Types of Surfactants

Set of The Experiment	Name of the Surfactant
AcRe_Surf_3.1	Sodium lauryl sulfate
AcRe_Surf_3.2	Sodium dodecyl benzene sulfonate
AcRe_Surf_3.3	Alkyl phenol ether sulfate
AcRe_Surf_3.4	Sulfosuccinyl acid ester sodium salt

3.3.2 Investigation of the Effect of Special Monomers

The control sample was selected after the optimization of the experiment. Four different types of special monomers were used. These are; sodium1-allyloxy-2-

hydroxy propane sulfonate; 1-methacrylamido,2-imidazolidinone ethane; polypropylene glycol monomethyl methacrylate phosphate ester, phosphate ester. The set of experiments is explained in Table 3.4.

Table 3.4. Investigation of the effect of special monomers

Set of The Experiment	Name of The Special Monomer	% wt to the overall monomer amount
AcRe-SM_1	-	-
AcRe-SM_2	sodium1-allyloxy-2-hydroxy propane sulfonate	3
AcRe-SM_3	sodium1-allyloxy-2-hydroxy propane Sulfonate	6
AcRe-SM_4	1-methacrylamido,2-imidazolidinone ethane	3
AcRe-SM_5	polypropylene glycol monomethyl methacrylate phosphate ester	3
AcRe-SM_6	phosphate ester	3
AcRe-SM_7	phosphate ester	6
AcRe-SM_8	phosphate ester	9
AcRe-SM_9	sodium1-allyloxy-2-hydroxy propane sulfonate	1.5
AcRe-SM_10	sodium1-allyloxy-2-hydroxy propane Sulfonate	1
AcRe-SM_11	1-methacrylamido,2-imidazolidinone ethane	1.5
AcRe-SM_12	1-methacrylamido,2-imidazolidinone ethane	1
AcRe-SM_13	phosphate ester	1.5

Table 3.4. (continued)

AcRe-SM_14	phosphate ester	1
AcRe-SM_15	polypropylene glycol monomethyl methacrylate phosphate ester	1.5
AcRe-SM_16	polypropylene glycol monomethyl methacrylate phosphate ester	1

3.4 Characterization of the Experiments

3.4.1 Solid Content Analysis

60 mm aluminum dishes and paper clips were used. 300 mg latex samples were placed into the dishes and the total mass of the samples was weighed. 3 mL of deionized water was added to the dishes and then place in the oven. They are dried in the oven and then allowed to equilibrate to room temperature. The solid content was calculated according to Equation 3.1m $aluminum$ solid fraction $= \frac{\text{mass after oven} - \text{mass of aluminum dishes}}{\text{mass of sample}}$ Equation 3.1.

3.4.2 Particle Size Analyze

The particle size of the latex particles was measured by a dynamic light scatter device, Mastersize Hydro 3000 at Izmir Katip Çelebi University Central Laboratory. Mie scattering was applied when particle size was measured. Volume % to particle size was tabulated.



Figure 3.6. Particle Size Analyzer

3.4.3 Glass Transition Temperature

Tg was measured by DSC, Differential Scanning Calorimetry, device Perkin Elmer 6000 at DYO Paint Industry Co. The setup of the DSC was adjusted to first at -10°C. Then heated from -10°C to 100°C at 10°C/min. Then, cooled down from 100°C to -10°C. Finally, the temperature was raised from -10°C to 100°C again.



Figure 3.7. Differential Scanning Calorimetry

3.4.4 Minimum Film Forming Temperature

The minimum film forming temperature was measured by MFFT Device by Rhopoint MFFT-90 at DYO Paint Industry Co. Latex samples were slid with a film applicator and the temperature was recorded.



Figure 3.8. MFFT Device

3.4.5 Viscosity

Viscosity was measured by rheometer TA-ARES at METU Central Laboratory



Figure 3.9. Rheometer

3.4.6 FTIR Analysis

To observe any chemical formation was occurred resin samples were analyzed by FTIR. Each special monomer was analyzed by FTIR. Then, purely acrylic resin sample AcRe-SM_1 was the reference sample to compare with the modified acrylic resin synthesized with a special monomer. Then each special monomer was compared with the amount of variation. FTIR Analysis was done at DYO Paint Factory and the name of the device is Smart ITR as shown in Figure 3.10.



Figure 3.10. FTIR Device

3.5 Paint Application

The motivation of the study is to analyze the effect of special monomers on acrylic binders. Purely acrylic binders consisting of special monomers affect on paint

performance such as corrosion stability in metal coating applications, adhesion performance, color strength, etc. This study, aimed to see the difference between purely acrylic binders and modified purely acrylic binders consisting of special monomers. According to the results, the appropriate special monomer which is the most compatible with this system was selected. Then, purely acrylic resin AcRe-SM_1 and modified acrylic resin consisting of special monomer AcRe-SM_6 were compared after adding them to the paint formula.

3.5.1 Paint Formulation

50-60 % of acrylic binders were added into the paint formula, nearly 20% of water was used as a solvent, and 15-20% of TiO_2 was used as an extender. Smaller than 1 % of ammonia was used as a neutralizer and smaller than 5% of a wetting agent, smaller than 0.5 % of rheology additive, and smaller than 5% of other additives were used. The general paint formula is given in Table 3.5.

Table 3.5. Paint Formulation

Ingredients	Composition (%)
Acrylic binder	50-60
Water	20
Extender	15-20
Neutrilizer	<1
Wetting agent	<5
Rheology additive	<0.5
Other additive	<5

3.5.2 Paint Performance Test

3.5.2.1 Adhesion Test

According to ASTM D3359 and ISO 2409 Standards, adhesion performance was tested. The film was applied on a plate and left to dry at 23°C at 50% humidity for 7 days. The hatch was made with a cutter following the ISO 2409 Standard tabulated Table 3.6. The tests were made with 3m Tape 2525 (7.5 N/cm). Cutter and tape are shown in Figure 3.11.



(a) Cutter



(b) 3m tape 2525

Figure 3.11. Cross-cut adhesion test equipment

Table 3.6. ISO 2409 Standard for cutter

Coating thickness µm	Spacing / cut size mm
1-60 µm	1 mm
61-120 µm	2 mm
121- 250 µm	3 mm
Above 250 µm	X Cut ISO 16276-2

After drying for one week the non-painted zones of the plate were protected with adhesive tape. Next, the plates were submerged in water at 23°C for 24 hours. Then, the excess water was removed with a dry tissue and left to dry for 1 hour at

23°C with 50% humidity. After drying, the hatch was made. The tape is applied on the hatch and removed at 90°C as fast as possible. Evaluation of the cross-cut performance was demonstrated in Figure 3.12.

Table 3.7. Evaluation Criteria of Adhesion Test

Rating	Evaluation Criteria
5B	The edges of the cuts are completely smooth, none of the squares of the lattice is detached.
4B	Small flakes of the coating are detached at intersections; less than 5% of the area is affected.
3B	Small flakes of the coating are detached along edges and at intersections of cuts. The area affected is 5 to 15% of the lattice.
2B	The coating has flaked along the edges and on parts of the squares. The area affected is 15 to 35 % of the lattice
1B	The coating has flaked along the edges of cuts in large ribbons and whole squares have detached. The area is 35 to 65% of the lattice.
0B	Flaking and detachment worse than Grade 1

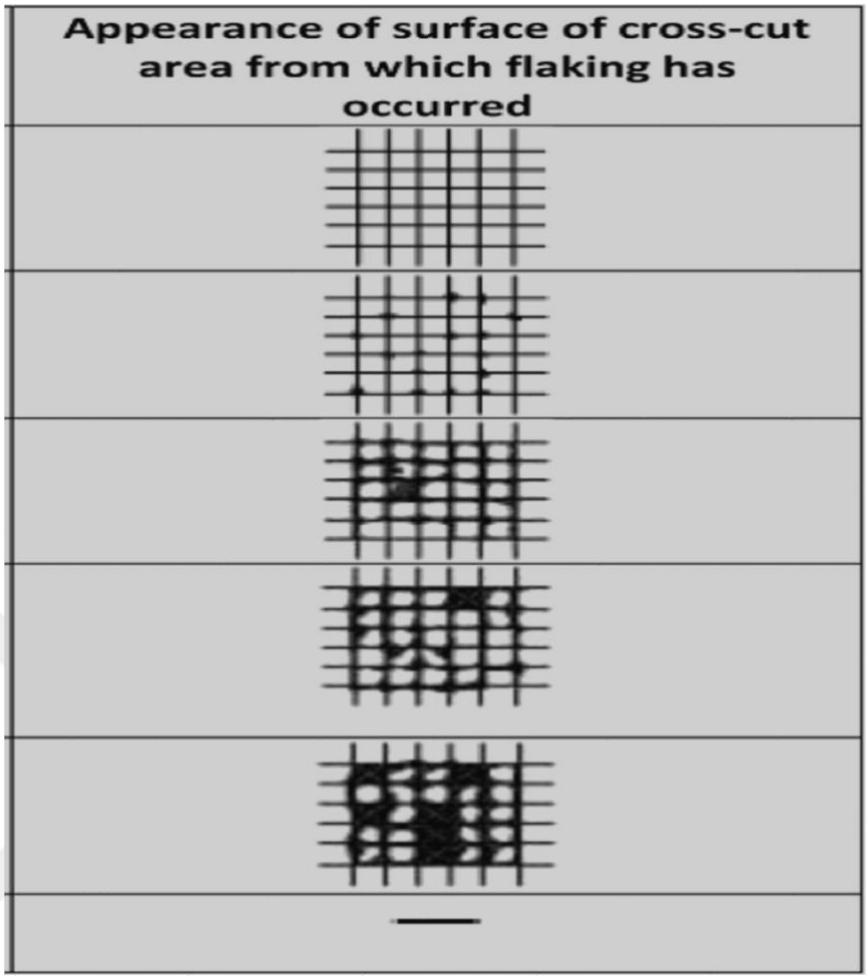


Figure 3.12. Criteria for evaluating adhesion test

3.5.2.2 Corrosion Test

The corrosion test in other words salt spray test was based on ISO 9227 Standard and ASTM B117 Standard. After the application of the film of paint, it was dried for 7 days at 23°C at 50% humidity. Then the non-painted zones of the plate were protected with adhesive tape as shown in Figure 3.13. Then a cross (45°) or a scratch was made with a cutter on the bottom part of the plate. Then the plates were put in a neutral salt spray device Liebisch demonstrated in Figure 3.14. The solution inside of the device should be 5 % NaCl solution with deionized water. The pH of the solution should be 6.5-7.2 and the temperature should be 35°C.



Figure 3.13. Preparation of the sample before salt spray test



(a) (b)

Figure 3.14. Salt Spray device

CHAPTER 4

RESULTS AND DISCUSSION

This study aims to investigate the effect of special monomers on the acrylic resin synthesized by emulsion polymerization. Different types of special monomers; sodium 1-allyloxy-2-hydroxy propane sulfonate, 1-methacrylamido,2-imidazolidinone ethane, polypropylene glycol monomethyl methacrylate phosphate ester, and phosphate ester were used. These monomers were compared according to stability, reaction efficiency by FTIR analysis, viscosity, glass transition temperature (Tg), minimum film forming temperature, and particle size.

Surfactants are also important parameters in acrylic polymer synthesis. Surfactants are composed of hydrophobic branched hydrocarbon chains and hydrophilic ionic polar groups. The head section of surfactants in anionic groups is negative whereas in nonionic groups there is no charge. Surfactants affect the viscosity, water resistance, gloss, and stability of products. Anionic surfactants provide to control the particle size of the polymers.

To control the stability and start with a correct recipe, purely acrylic resin was synthesized first. In this pre-experimental study; optimization of the amount of surfactant was investigated. The amount of sodium lauryl sulfate was used in terms of 0.3%, 1%, 1.5%, 2%, 3%. Maximum stability was obtained when the amount of anionic surfactant was used at 1.5%. It was tabulated in Table 3.2. The stability was not good in AcRe-Surf_1 and AcRe-Surf_2 which is shown in Figure 4.1. (a) and (b). The stability results of AcRe-Surf_3 and AcRe-Surf_4 were better than AcRe-Surf_1 and AcRe-Surf_2. It is shown in Figure 4.2. (a) and (b). The polydispersity of the particles and emulsion stability could be explained by The Ostwald Ripening. When the surfactant ratio is increased particle size decreases because monomer diffusion between the droplets is in the minimum stage. On the

other hand, the stability results of AcRe-Surf_5 correspond that when the amount of surfactant increased greater than the optimum value so much, coagulation occurred as shown in Figure 4.3. At the end of this set of experiments, 1.5% wt. of surfactant usage was decided to be used. In this set of experiments, sodium lauryl sulfate, or in other words, sodium dodecyl sulfate was used.

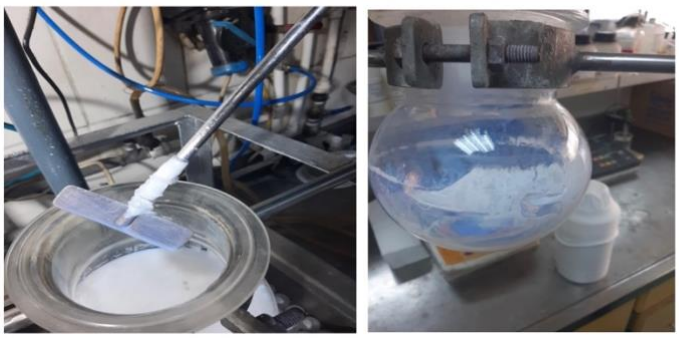


Figure 4.1. Stability result of (a) AcRe-Surf_1 and (b) AcRe-Surf_2



Figure 4.2. Stability result of (a) AcRe-Surf_3 and (b) AcRe-Surf_4



Figure 4.3. Stability result of AcRe-Surf_5

After the optimum amount of surfactant had been decided, different types of anionic surfactants were tested. Anionic surfactants were; sodium lauryl sulfate, sodium dodecyl benzene sulphonate, alkyl phenol ether sulfate, sulfosuccinic acid ester sodium salts. The set of experiments was tabulated in Table 3.3. The stability performance result of sodium lauryl sulfate was the best of all. The effect of sodium dodecyl benzene sulphonate was better than alkyl phenol ether sulfate however; not as good as sodium lauryl sulfate. In AcRe-Surf_3.2 Alkyl phenol ether was shown in Figure 4.4. It is understood that sodium lauryl sulfate was the best one and in literature sodium lauryl sulfate was mostly used.



Figure 4.4. Stability result of AcRe-Surf_3.3

To observe the effect of special monomers firstly, purely acrylic resin, without any special monomers, was synthesized in AcRe-SM_1 Next; sodium 1-allyloxy-2-hydroxy propane sulfonate was used in AcRe-SM_2 and AcRe-SM_3, the amount of sodium allyloxy-2-hydroxypropane sulfonate was increased 2-folds to observe the efficiency on experiment if special monomers were used more than the standard value. In AcRe-SM_4, 1-methacrylamido, and 2-imidazolidinone ethane were used as special monomers. Next, In AcRe-SM_5 polypropylene glycol monomethyl methacrylate phosphate ester was used. The effect of phosphate ester is especially important in acrylic synthesis. Finally, phosphate ester was used in AcRe-SM_6. This special monomer has excellent adhesion to a variety of metals, glass, concrete, and inorganic substrates. It also improves water resistance and anti-corrosion properties of paint. After those sets of experiments, the amount of phosphate ester that stability result was good was increased firstly to observe the limit value of the

phosphate ester in reaction. In AcRe-SM_7 and AcRe-SM_8 the amount of phosphate ester was increased to 2 folds and 3 folds respectively. Then to observe the reaction efficiency the amount of special monomers was decreased and compared according to the FTIR Spectrum. In AcRe-SM_9 and AcRe-SM_10 the amount of sodium 1-allyloxy-2-hydroxy propane sulfonate was decreased to 1/3 and 1/2 folds respectively. In AcRe-SM_11 and AcRe-SM_12, ½ and 1/3 folds of 1-methacrylamido, and 2-imidazolidinone ethane were used respectively. In AcRe-SM_13 and AcRe-SM_14 the phosphate ester was used 1/3 and 1/2 folds respectively. Finally, In AcRe-SM_15 and AcRe-SM_16 polypropylene glycol monomethyl methacrylate phosphate ester was used 1/3 and 1/2 folds respectively.

It is noted that according to the regulations of R.E.A.C.H, (Registration, Evaluation, Authorisation and Restriction of Chemicals) the product of that experiment is not classified as hazardous materials. Unreacted monomers were classified as hazardous substances however; after the polymerization reaction these exist as an impurity which are very small amounts in the product.

4.1 Solid Content

The solid content of all samples of AcRe-SM_1 to AcRe-SM_16 was estimated by Equation 3.1. The control sample of AcRe_SM_1 was targeted at 45% and the other samples were estimated at nearly 45%.

4.2 Particle Size

The particle size of the samples was measured by laser scattering device. According to the literature survey, particle size could be around 100 to 150 nm. In pre-experimental studies; to control final particle size, the amount of seed is important. Theoretically, if the amount of seed decreases, less nucleation is observed. If the more amount of seed is used, the smaller particles occur. Thus, the

percentage of seed is considered around 3%. According to the results, the particle sizes of the samples were similar, however, the particle size distribution of AcRe-SM_4 was wider than the other samples. According to the cumulative curve, it could be explained that bigger sizes of particles were observed in AcRe-SM_4 which means that coagulation occurred.

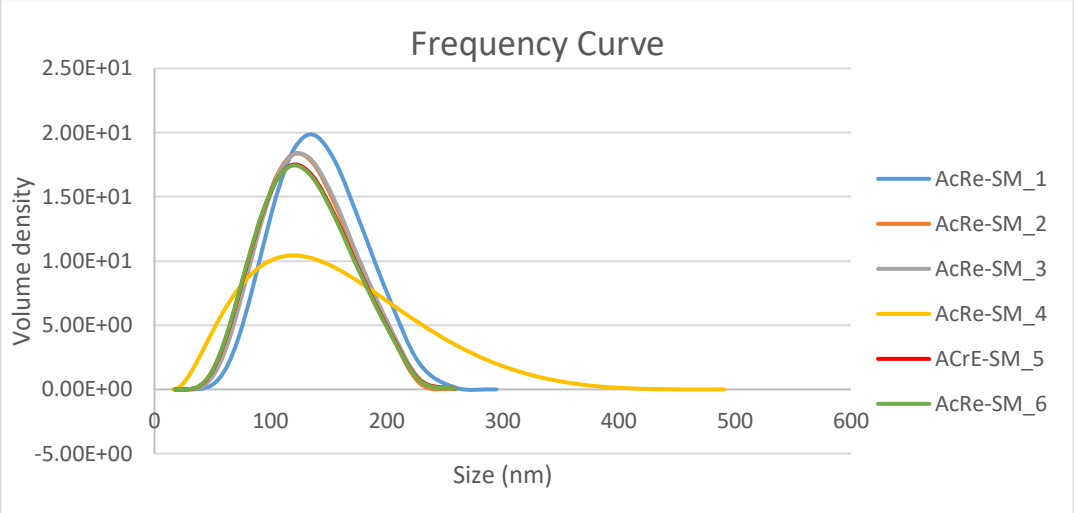


Figure 4.5. Frequency Curve of Particle Size Distribution

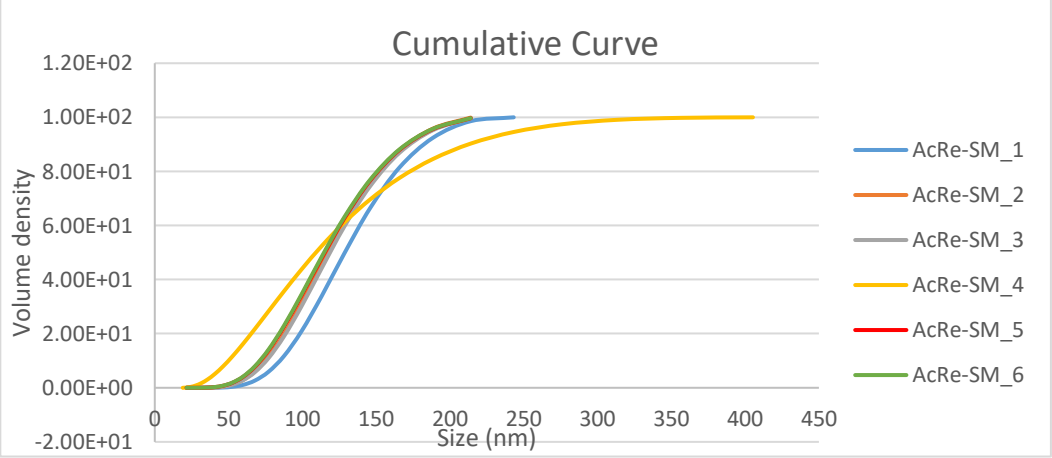


Figure 4.6. Cumulative Curve of Particle Size Distribution

4.3 Glass Transition Temperature

Glass Transition Temperature was measured by Differential Scanning Calorimetry. After the synthesis of acrylic resin, Tg was measured by DSC and it was proven by the Flory- Fox Equation. [44]

The Plot of Tg measured by DSC was illustrated in Appendix A.

Equation 4.1. is used to calculate glass transition temperature Tg. This equation gives accurate results and is commonly used in polymer applications. w_1 and w_2 are weight fractions of polymers.

$$\frac{1}{T_g} = \sum \frac{w_i}{T_{g,i}}$$ Equation 4.1.

The results measured by DSC were tabulated at 4.1 According to the results, Tg values measured by DSC are between 30-35°C. The highest glass transition temperature was 1-methacrylamido,2-imidazolidinone ethane, sodium allyloxy-2-hydroxypropane sulfonate, and purely acrylic resin at 3% to overall monomer concentrations which are 34.71°C, 34.24°C and 34.16°C and respectively. The lowest glass transition temperature was measured at 26.17°C when phosphate ester was used at 9 % to overall monomer concentration. Figure 4.7 shows the plot of Tg versus special monomer concentration, when the amount of phosphate ester and polypropylene glycol monomethyl methacrylate phosphate ester was decreased, the glass transition temperature increased. On the other hand, when the amount of 1-methacrylamido,2-imidazolidinone ethane was decreased glass transition temperature was increased. According to the Flory-Fox equation; the most accurate result between Tg estimated and measured were obtained when phosphate ester with 3 and 1 % to the overall monomer content were used.

Table 4.1 Glass transition temperature measured by DSC

SET	Special Monomer	%wt to overall monomers	Tg 1st Trial (°C)	Tg 2nd Trial (°C)	Tg 3rd Trial (°C)	Tg average (°C)	Error %	Std. Dev.
AcRe-SM_1	-	3	33.93	34.45	34.09	34.16	4.09	1.47
AcRe-SM_2	sodium 1-allyloxy-2-hydroxy propane sulfonate	3	33.88	33.94	34.90	34.24	11.6	3.59
AcRe-SM_3	sodium 1-allyloxy-2-hydroxy propane sulfonate	6	32.46	32.63	32.92	32.67	12.2	3.55
AcRe-SM_4	1-methacrylamido, 2-imidazolidinone ethane	3	34.97	34.58	34.57	34.71	2.69	0.98
AcRe-SM_5	polypropylene glycol monomethyl methacrylate phosphate ester	3	33.02	33.31	33.27	33.20	0.8	0.3

Table 4.1. (continued)

AcRe-SM_6	phosphate ester	3	33.11	32.83	33.05	33.00	0.55	0.22
AcRe-SM_7	phosphate ester	6	30.07	30.55	30.18	30.24	4.89	1.45
AcRe-SM_8	phosphate ester	9	26.01	26.26	26.26	26.17	2.83	0.73
AcRe-SM_9	sodium 1-allyloxy-2-hydroxy propane sulfonate	1	34.27	34.59	34.56	34.47	7.22	2.33
AcRe-SM_10	sodium 1-allyloxy-2-hydroxy propane sulfonate	2	33.48	33.09	33.14	33.24	0.67	0.28
AcRe-SM_11	1-methacrylamido, 2-imidazolidinone ethane	1	34.00	33.75	33.90	33.88	2.94	0.97
AcRe-SM_12	1-methacrylamido, 2-imidazolidinone ethane	2	34.69	34.32	34.66	34.56	5.16	2.25

Table 4.1. (continued)

AcRe-SM_13	phosphate ester	1	33.47	33.22	33.33	33.34	0.67	0.24
AcRe-SM_14	phosphate ester	2	34.22	34.01	34.55	34.26	5.32	1.74
AcRe-SM_15	polypropylene glycol monomethyl methacrylate phosphate ester	1	33.77	33.87	33.90	33.85	2.08	0.7
AcRe-SM_16	polypropylene glycol monomethyl methacrylate phosphate ester	2	33.41	33.48	34.12	33.67	3.19	1.15

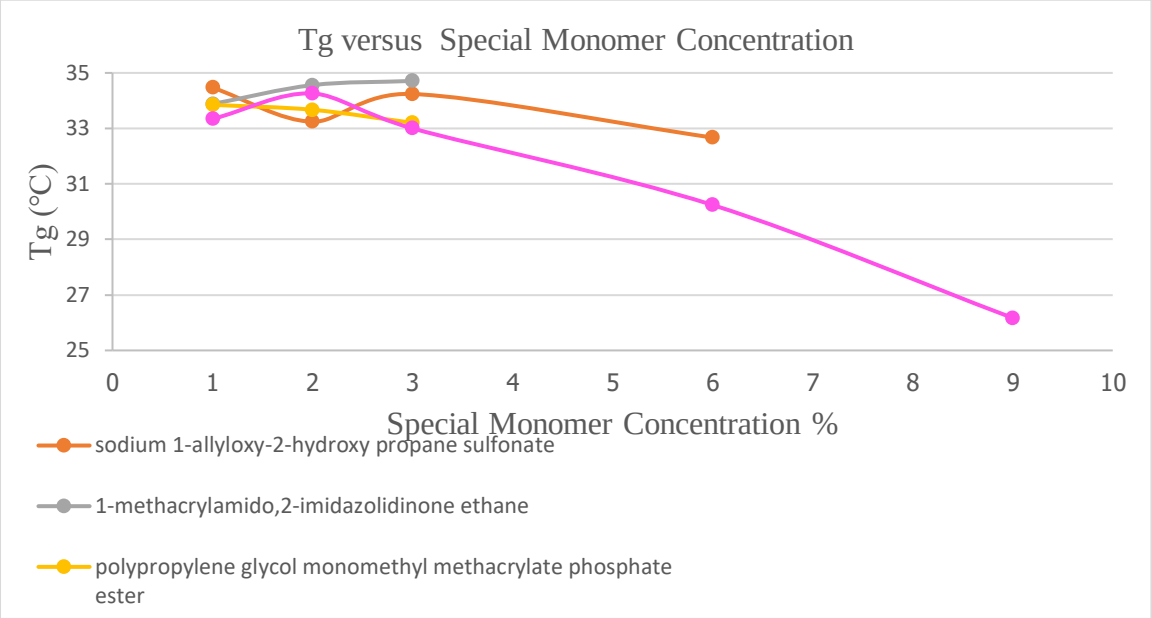


Figure 4.7. Plot of Tg versus special monomer concentration

4.4 Minimum Film Forming Temperature

The minimum film-forming temperature is the lowest temperature that is required to coalesce a polymer and applied to a substrate into a thin film. The minimum film-forming temperature of a polymer is extremely important to understand when applying a coating to avoid a coating failure. Tg is the temperature at which the polymer goes from a hard, glassy state to an amorphous, rubbery state. There is a relationship between minimum film formation temperature and glass transition temperature. If the polymer is soft, in other words, the glass transition temperature is low, film could be formed very easily which means MFFT is low. Comparing the results at 3% of special monomer to the overall monomer concentration used, the minimum film forming temperature was minimum in AcRe-SM_6 when the phosphate ester was used. Minimum film-forming temperature values decreased as the amount of phosphate ester was increased. On the other hand, MFFT values increased when the amount of phosphate ester and polypropylene glycol monomethyl methacrylate phosphate ester was decreased. Glass transition

temperature and MFFT are parallel to each other. The lowest glass transition and minimum film temperature were obtained when phosphate ester was used. The highest glass transition and MFFT were found when the amount of polypropylene glycol monomethyl methacrylate phosphate ester was decreased to 1/3-fold. The structure of phosphate ester is soft and it is able to make film easily.

Table 4.2. Minimum Film Forming Temperatures

Experiment	Special Monomer	MFFT (°C) 1st trial	MFFT (°C) 2 nd trial	MFFT (°C) 3 rd trial	MFFT average (°C)	Tg (°C)
AcRe-SM_1	purely acrylic	28	26	27.2	27.1	34.16
AcRe-SM_2	sodium 1-allyloxy-2-hydroxy propane sulfonate	27.8	26.6	27.4	27.3	34.24
AcRe-SM_3	sodium 1-allyloxy-2-hydroxy propane sulfonate	28.7	26.5	27.3	27.5	32.67
AcRe-SM_4	1-methacrylamido,2-ımidazolidinone ethane	29.7	26.8	28.1	28.2	34.71
AcRe-SM_5	polypropylene glycol monomethyl methacrylate phosphate ester	27.7	26.3	27.6	27.2	33.20
AcRe-SM_6	phosphate ester	26.4	28.3	26	26.9	33.00

Table 4.2. (continued)

AcRe-SM_7	phosphate ester	24.1	22	23.2	23.1	30.24
AcRe-SM_8	phosphate ester	24.1	17.4	26.3	22.6	26.17
AcRe-SM_9	sodium 1-allyloxy-2-hydroxy propane. sulfonate	27.2	22.7	26.7	25.5	34.47
AcRe-SM_10	sodium 1-allyloxy-2-hydroxy propane sulfonate	25.8	27	26.9	26.6	33.24
AcRe-SM_11	1-methacrylamido,2-ımidazolidinone ethane	27	22	24.3	24.4	33.88
AcRe-SM_12	1-methacrylamido,2-ımidazolidinone ethane	26.6	21	27.8	25.1	34.56
AcRe-SM_13	phosphate ester	31.4	31.2	23.5	28.7	33.34
AcRe-SM_14	phosphate ester	30.3	26.1	28.5	28.3	34.26
AcRe-SM_15	polypropylene glycol monomethyl methacrylate phosphate ester	30.1	29.7	28.4	29.4	33.85
AcRe-SM_16	polypropylene glycol monomethyl methacrylate phosphate ester	29.3	28.5	29.2	29	33.64

4.5 Stability

In emulsion polymerization, the significant output of the experiment is the stability of the reaction.

In AcRe-SM_1, purely acrylic resin was synthesized and no special monomer was used. At the end of the experiment, there was no residue in the flask or filter, which means no coagulation occurred.

In AcRe-SM_2, sodium 1-allyloxy-2-hydroxy propane sulfonate was used, and there was a little residue in the flask and the filter. In AcRe-SM_3 which was 2 folds of special monomer used, residue was observed only on the stirrer. As shown in Figure 4.8



(a) (b) (c)

Figure 4.8: Visual results of (a) and (b) AcRe-SM_2, (c) AcRe-SM_3

In AcRe-SM_4, 1-methacrylamido,2-imidazolidinone ethane was used as a special monomer, residue was seen at the stirrer and flask as shown in Figure 4.9

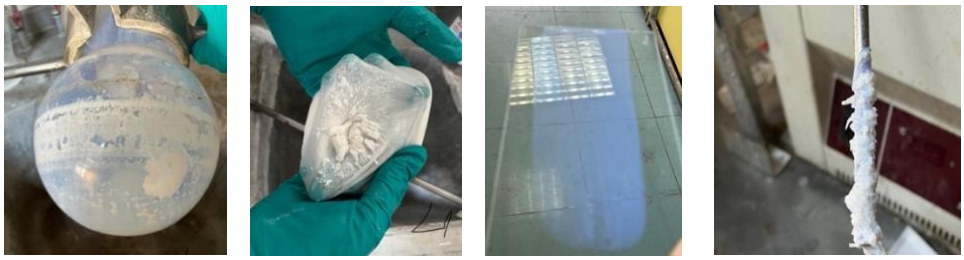


Figure 4.9. Visual Results of AcRe-SM_4

In AcRe-SM_5 polypropylene glycol monomethyl methacrylate phosphate ester was used as a special monomer. There was no coagulation occurring on the stirrer and in the flask. However, a small amount of coagulated particles were observed in the filter.



Figure 4.10. Visual Results of AcRe-SM_5

In AcRe-SM_6, Phosphate Ester was used as a special monomer. There was no residue in the flask, on the stirrer, or in the filter. The stability of the reaction was the best of all that as shown in Figure 4.11. clearly.



Figure 4.11 Visual Results of AcRe-SM_6

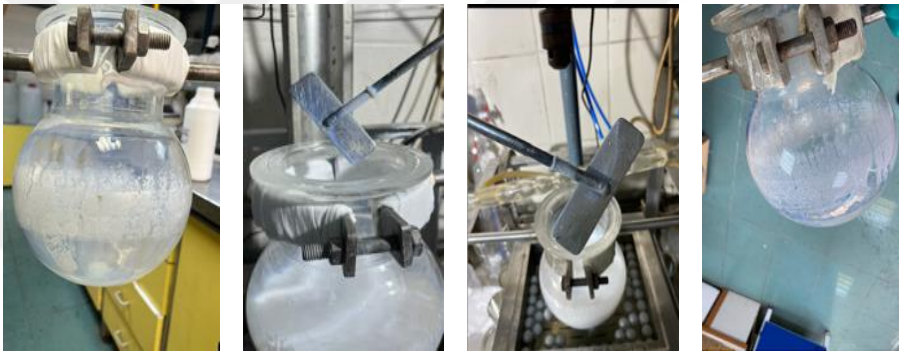
In AcRe-SM_7 and AcRe-SM_8, the amount of phosphate ester was increased by 2 and 3 folds respectively. In AcRe-SM_7 there was some residue on the thermocouple and in the flask. In AcRe-SM_8 residue was seen on the stirrer and in the flask as shown in Figure 4.12. In addition, gel formation occurred.



(a) (b) (c) (d) (e) (f)

Figure 4.12. Visual results of (a), (b), (c) AcRe-SM_7 and (d), (e), (f) AcRe-SM_8

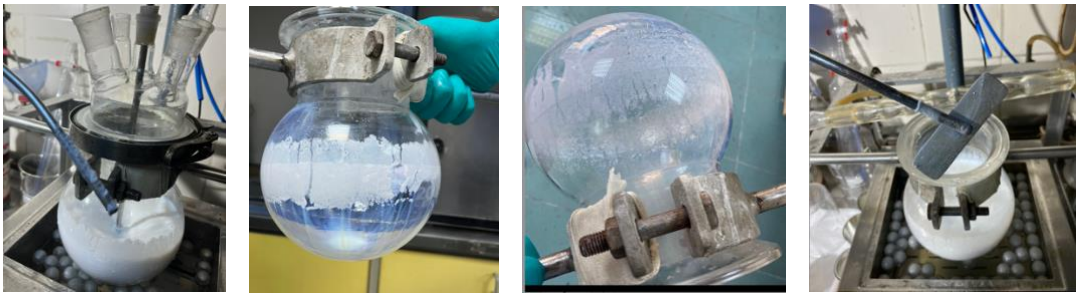
In AcRe-SM_9 and AcRe-SM_10, the amount of sodium 1-allyloxy-2-hydroxypropane sulfonate was decreased to ½ and 1/3 folds of standard value (AcRe-SM_2). Both of in AcRe-SM_9 and AcRe-SM_10 there was significant residue only in the flask as shown in Figure 4.13



(a) (b) (c) (d)

Figure 4.13. Visual results of (a), (b) AcRe-SM_9 and (c), (d) AcRe-SM_10

In AcRe-SM_11 and AcRe-SM_12, the amount of 1-methacrylamido, and 2-imidazolidinone ethane was decreased to ½ and 1/3 folds of the standard value (AcRe-SM_4). In AcRe-SM_11 residue was seen on the thermocouple and in the flask. On the other hand, In AcRe-SM_12 residue was seen only in the flask. However great amount of residues were seen in the flask both in AcRe-SM_11 and AcRe-SM_12 as shown in Figure 4.14.



(a) (b) (c) (d)

(a) Figure 4.14. Visual results of (a), (b) AcRe-SM_11 and (c), (d) AcRe-SM_12

In AcRe-SM_13 and AcRe-SM_14 the amount of phosphate ester was decreased to ½ and 1/3 folds of the standard value (AcRe-SM_6). In AcRe-SM_13, on the thermocouple and the stirrer there was no residue; however, in the flask residue was seen. In AcRe-SM_14, residue was seen in the flask. Visual results are shown in Figure 4.15.



(a) (b) (c) (c) (d) (e)

Figure 4.15. Visual results of (a), (b), (c) AcRe-SM_13 and (d), (e), (f) AcRe-SM_14

In AcRe-SM_15 and AcRe-SM_16 the amount of polypropylene glycol monomethyl methacrylate phosphate ester was decreased to ½ and 1/3 folds. Both in AcRe-SM_15 and AcRe-SM_16, there were no residues on the thermocouple and the stirrer. However, the flasks have both residues inside. It is shown in Figure 4.16 Visual results of AcRe-SM_15 and AcRe-SM_16.



(a) (b) (c) (d)

Figure 4.16. Visual results of (a), (b), (c) AcRe-SM_15 and (d) AcRe-SM_16

4.6 FTIR ANALYSIS

4.6.1 Sodium 1-allyloxy-2-hydroxy propane sulfonate

To begin with, purely acrylic binder without any special monomer was analyzed by FTIR as shown in Figure 4.17 characteristic peaks at 3080 cm^{-1}, 2960 cm^{-1}, 1727 cm^{-1}, 1448 cm^{-1}, and 1250 cm^{-1} were observed. At 3080 cm^{-1} (CH) $C=CH_2$ groups, at 2960 cm^{-1} CH_2-CH_3 groups, at 1727 cm^{-1} COO groups, at 1448 cm^{-1} CH_2 methylene groups, at 1250 cm^{-1} C≡O were observed. Below 1500 cm^{-1} which is finger print area and C-O groups are in this range.

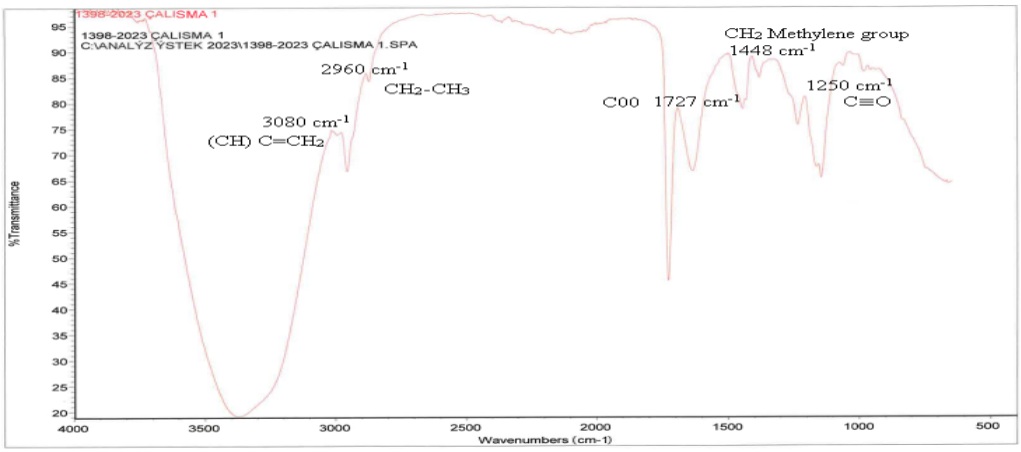


Figure 4.17. FTIR Spectrum of purely acrylic binder AcRe-SM_1

Sodium 1- allyloxy-2-hydroxypropane sulfonate which was used at 3% of the overall monomer concentration corresponded in Figure 4.18. There were different peaks at 2021 cm^{-1} and 1935 cm^{-1} which were the presence of C=C=N stretching groups (2021 cm^{-1}) and C=C=C stretching groups (1935 cm^{-1}) respectively.

When the amount of sodium 1-allyloxy-2-hydroxypropane sulfonate was decreased to 1/3 there was no different peak compared to AcRe-SM_1which was shown in Figure 4.19

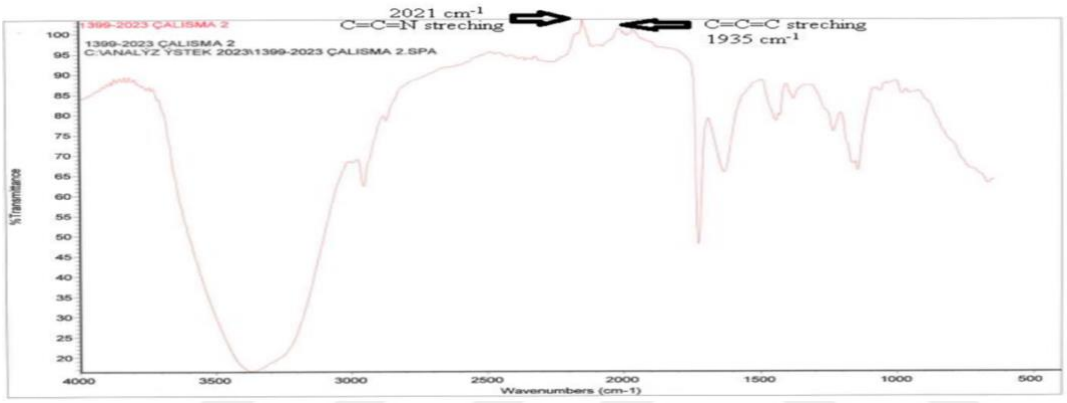


Figure 4.18. FTIR Spectrum of modified acrylic binder AcRe-SM_2

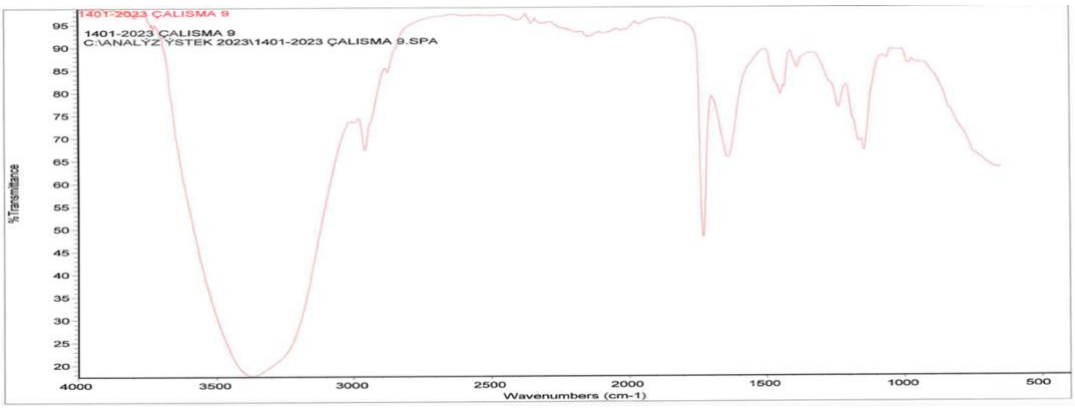


Figure 4.19 FTIR Spectrum of modified acrylic binder AcRe-SM_9

When the amount of sodium 1-allyloxy hydroxypropane sulfonate was decreased to ½ fold of standard value there was no change like the sample AcRe-SM_9 which was demonstrated in Figure 4.20.

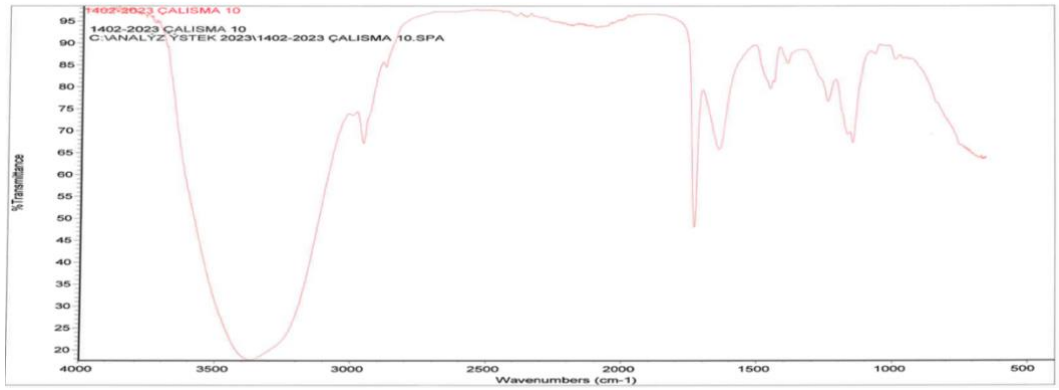


Figure 4.20. FTIR Spectrum of modified acrylic binder AcRe-SM_10

4.6.2 1-methacyrlamido,2-imidazolidinone ethane

Secondly, another special monomer named 1-methacrylamido,2-imidazolidinone ethane was used with 3% overall monomer concentration. The FTIR spectrum is shown in Figure 4.21. It is similar to purely acrylic resin FTIR results.

Next, the amount of special monomer was decreased to 1/3-fold of AcRe-SM_4. Comparing between AcRe-SM_4 and AcRe-SM_11 there was no change and no different peak was observed.

In Figure 4.22. The amount of special monomer was decreased to ½ fold of AcRe-SM_4. According to the figure, there was no chemical formation different from purely acrylic resin.

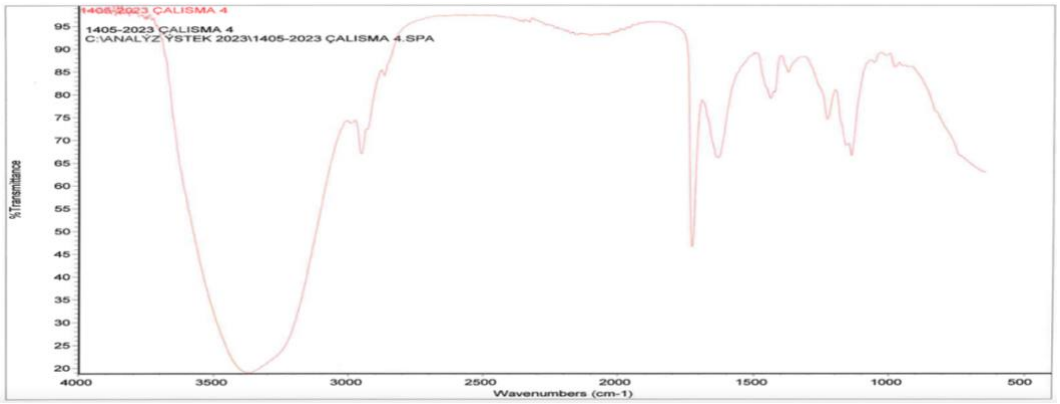


Figure 4.21. FTIR Spectrum of modified acrylic resin AcRe-SM_4

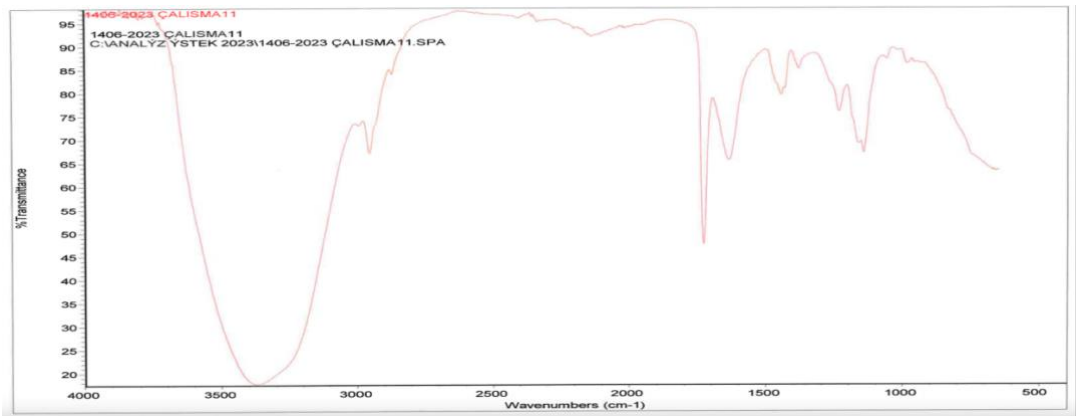


Figure 4.22. FTIR Spectrum of modified acrylic resin AcRe-SM_11

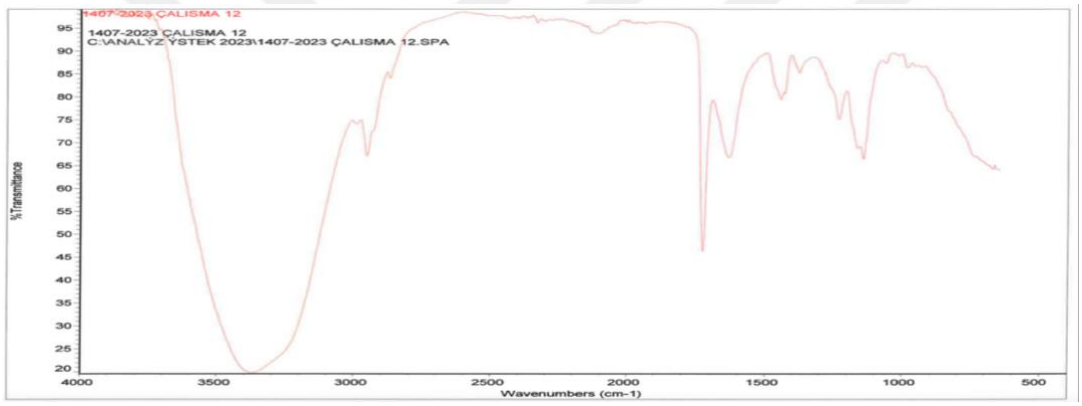


Figure 4.23. FTIR Spectrum of modified acrylic resin AcRe-SM_12.

Finally, comparing between the purely acrylic and acrylic resin consisting of the special monomer of 1-methacrylamido, and 2-imidazolidinone ethane there was no change according to the FTIR spectrum.

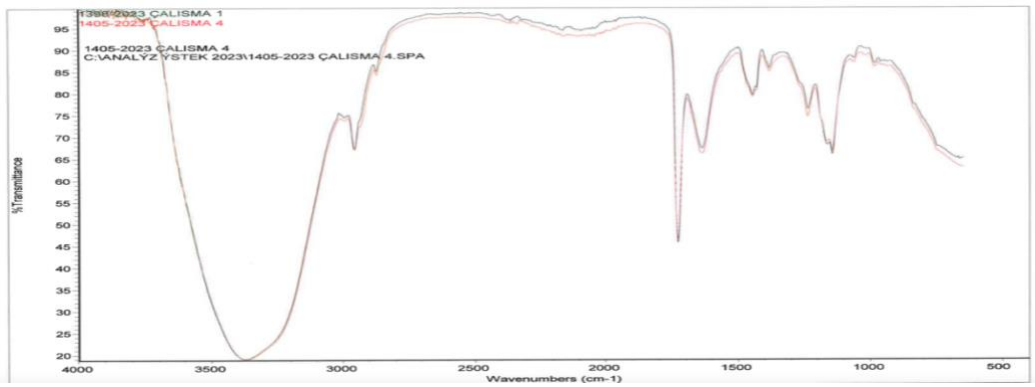


Figure 4.24. FTIR Spectrums of both purely acrylic resin AcRe-SM_1 and modified acrylic resin AcRe-SM_4

4.6.3 Polypropylene Glycol Monomethyl Methacrylate Phosphate Ester

Polypropylene glycol monomethyl methacrylate phosphate ester was used as a special monomer. In Figure 4.25 there was a little change according to the spectrum of the purely acrylic resin. The wavelength at 2479 cm^{-1} and 2300 cm^{-1} different peaks were observed. This could be explained by presence of H bonds of COOH groups and O=C=O stretching groups.

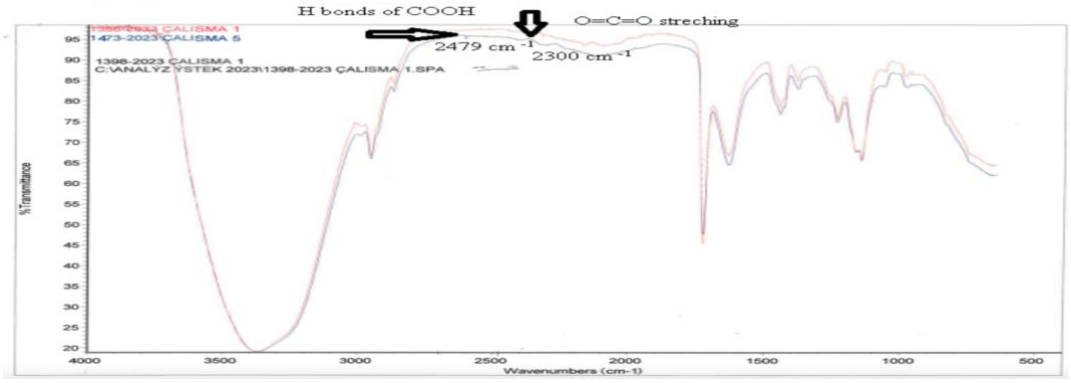


Figure 4.25. FTIR Spectrums of both purely acrylic resin AcRe-SM_1 and modified acrylic resin AcRe-SM_5

The amount of special monomer was decreased to 1/3 fold of AcRe-SM_5. There was not any formation occurred according to the AcRe-SM_5 as shown in Figure 4.26.

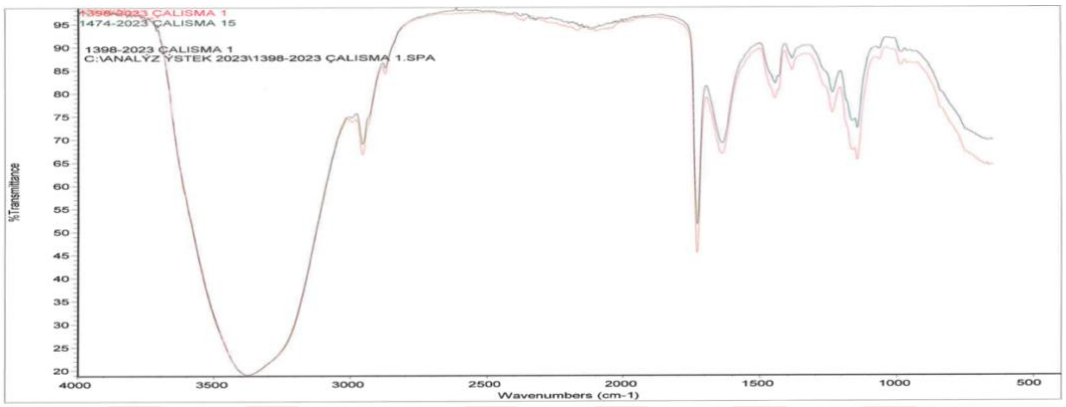


Figure 4.26. FTIR Spectrums of both purely acrylic resin AcRe-SM-1 and modified acrylic resin AcRe-SM_15

When the amount of special monomer was decreased ½ fold of AcRe-SM_5 the FTIR spectrum shows that there were some different peaks at 2378 cm^{-1} and 2250 cm^{-1} as shown in Figure 4.27. These peaks explain that there were some formations of O=C=O stretching groups (2378 cm^{-1}) C≡N stretching groups (2250 cm^{-1})

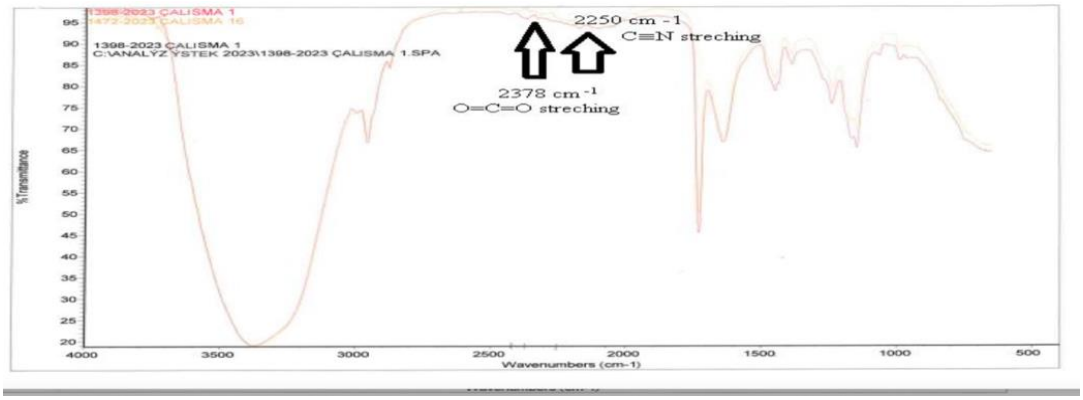


Figure 4.27. FTIR Spectrum of both purely acrylic resin AcRe-SM_1 and modified acrylic resin AcRe-SM_16

4.6.4 Phosphate ester

Phosphate ester was used as a special monomer. 3% of phosphate ester to the overall monomer content was used AcRe-SM_6 and compared with purely acrylic system AcRe-SM_1 in Figure 4.28. It is shown that there were different peaks between AcRe-SM_1 and AcRe-SM_6. These peaks were at 2365 cm^{-1} and 2180 cm^{-1} corresponding to O=C=O stretching groups (2365 cm^{-1}) and S-C≡N stretching groups (2180 cm^{-1}).

The concentration of phosphate ester to the overall monomer content was increased to 6% in AcRe-SM_7 and the FTIR spectrum was compared with the purely acrylic resin system in Figure 4.29. different peaks at 2378 cm^{-1} and 2150 cm^{-1} were determined which refers to O=C=O stretching groups (2365 cm^{-1}) and S-C≡N stretching groups (2150 cm^{-1}).

When the amount of phosphate ester was increased to 3 folds of standard value (AcRe_SM_6) at 2400 cm^{-1}, 2200 cm^{-1}, and 1980 cm^{-1} different peaks were observed. O=C=O stretching groups (2400 cm^{-1}), C≡C stretching groups (2200 cm^{-1}) and C-H bending were found in ır spectrum.

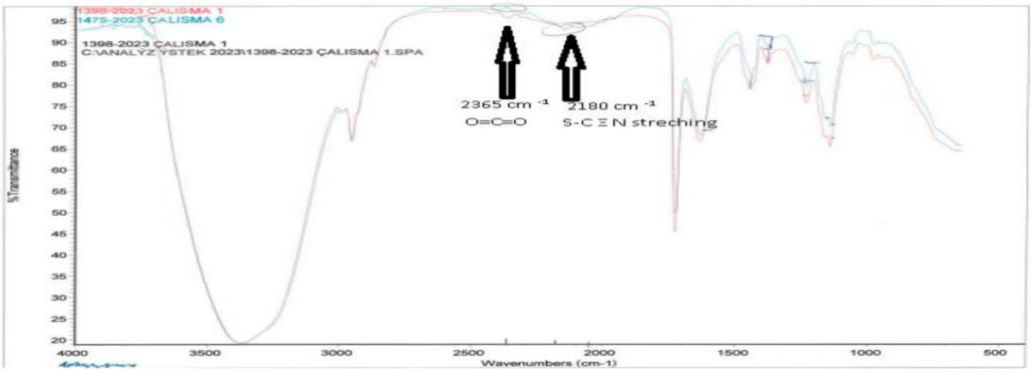


Figure 4.28 FTIR Spectrum of purely acrylic resin AcRe-SM_1 and modified acrylic resin AcRe-SM_6

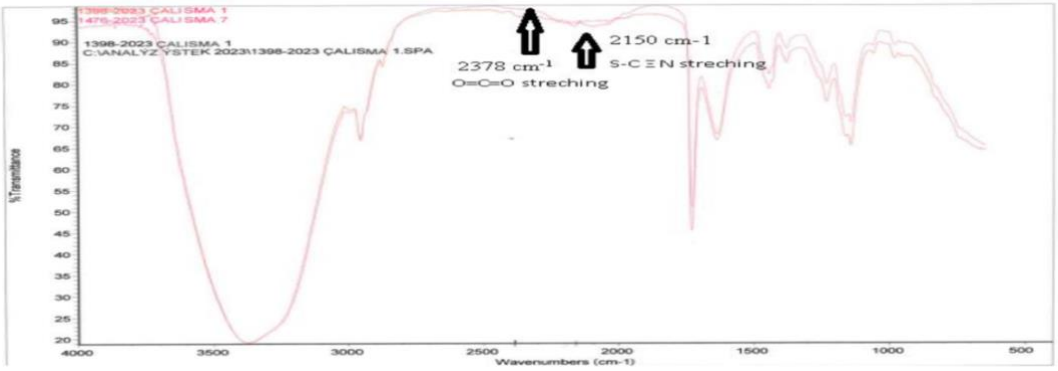


Figure 4.29. FTIR Spectrum of purely acrylic resin AcRe-SM_1 and modified acrylic resin AcRe-SM_7

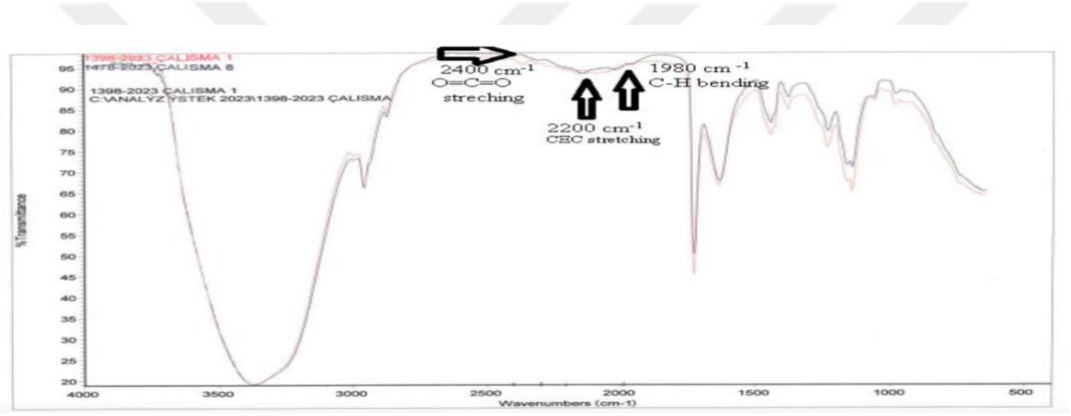


Figure 4.30. FTIR Spectrum of purely acrylic resin AcRe-SM_1 and modified acrylic resin AcRe-SM_8

In Figure 4.31 different peaks at 2690 cm^{-1}, 2193 $cm^{-1,}$ and 2000 cm^{-1}. These peaks refer to C-H stretching groups (2690 cm^{-1}), C≡C stretching groups (2193 cm^{-1}), and C=C=C stretching groups (2000 cm^{-1}). In Figure 4.32 FTIR spectrums show that there were different peaks at 2690 cm^{-1}, 2240 cm^{-1}, and 2000 cm^{-1}. These peaks explain the presence of C-H stretching groups (2690 cm^{-1}), C≡C stretching groups (2240 cm^{-1}), and C=C=C stretching groups (2000 cm^{-1})

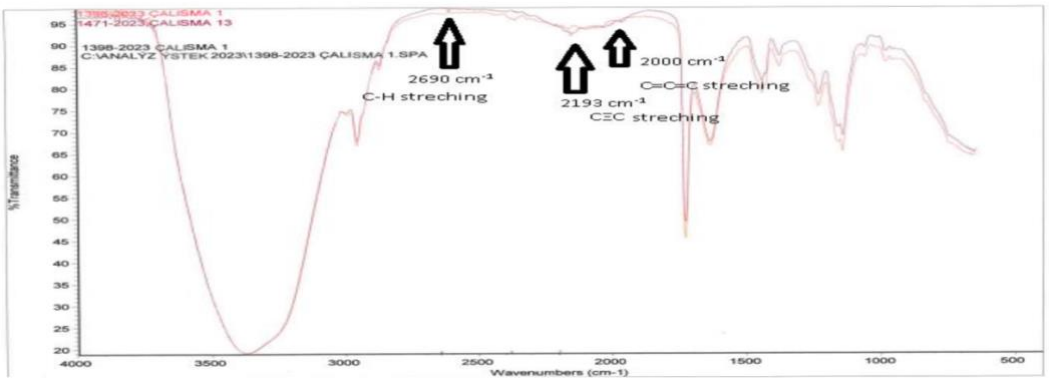


Figure 4.31. FTIR Spectrum of purely acrylic resin AcRe-SM_1 and modified acrylic resin AcRe-SM_13

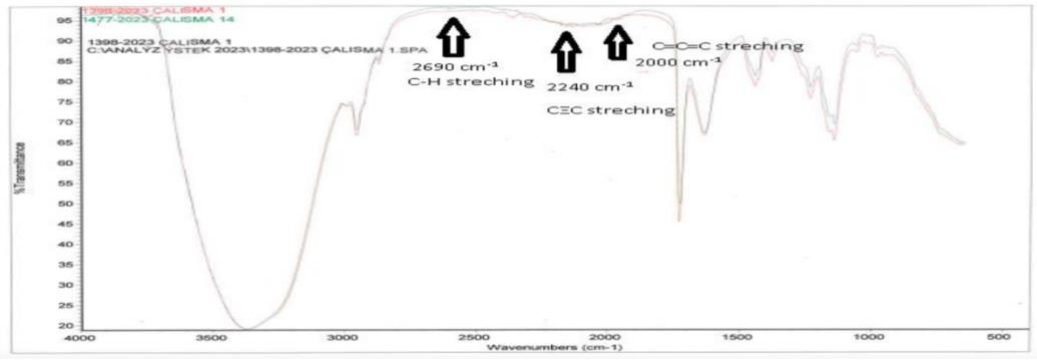


Figure 4.32. FTIR Spectrum of purely acrylic resin AcRe-SM_1 and modified acrylic resin AcRe-SM_14

4.7 Viscosity

The viscosity of the samples which are AcRe-SM_1, purely acrylic resin, AcRe-SM_2, AcRe-SM_4, AcRe-SM_5, and AcRe-SM_6, acrylic resin consisting of special monomer 3% to the overall monomer concentration and 6% of special monomer to overall special monomer concentration AcRe-SM_3 and AcRe-SM_7 and 9% of special monomer concentration to the overall monomer concentration, AcRe-SM_8 was measured by rheometer. The value of apparent viscosity Pa.s was measured over the course of the shear rate (1/s) variation. The graph of apparent viscosity versus shear rate is shown in Figure 4.33.

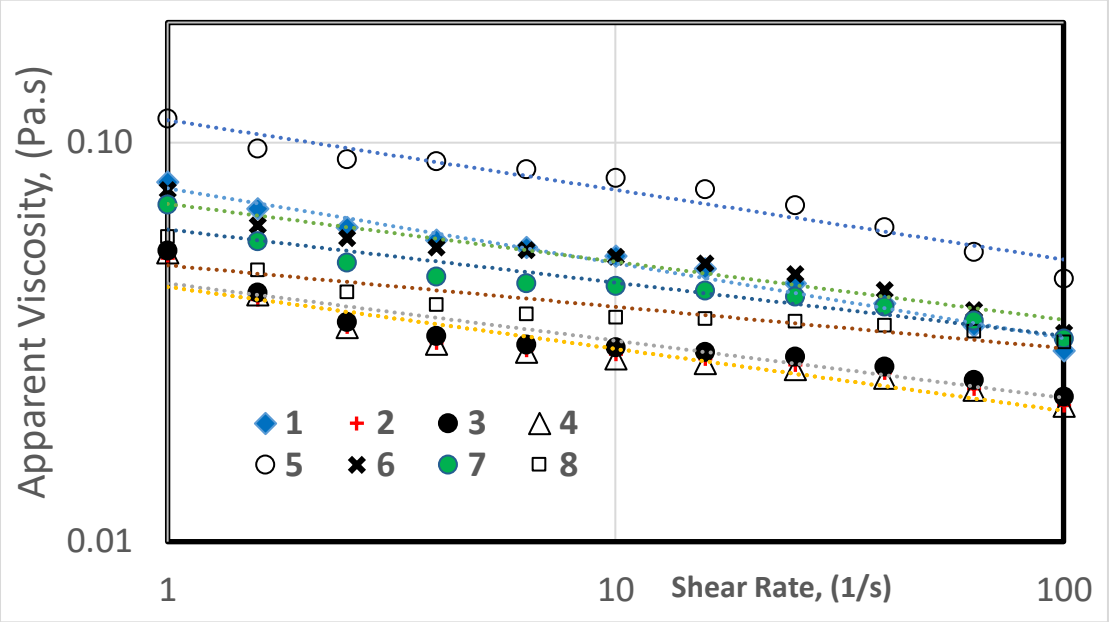


Figure 4.33. Apparent viscosity versus shear rate plot

According to Figure 4.33, regression was estimated and tabulated in Table 4.3. n is the power law and k is the consistency. It was clear that in AcRe-SM_5 and AcRe-SM_6 the results were more accurate than the others. The viscosity of the AcRe-SM_5 was the highest of all and the viscosity of the AcRe-SM_6 was similar to the purely acrylic resin. Molecular weights of all samples were measured by GPC to observe the effect on viscosity that is tabulated in Table 4.4. According to Table 4.4 although the lowest molecular weight of polymer was in AcRe-SM_5 the highest viscosity was seen in AcRe-SM_5 as well. This could be explained by molecular interactions of polypropylene glycol monomethyl methacrylate phosphate ester. However, molecular weight of the AcReSM_5 is close to pure acrylic resin which is reference sample AcRe-SM_1

Table 4.3 Regression Analysis

Sample	n	k	r^2
1	0,812	0,077	0,976
2	0,957	0,044	0,845
3	0,956	0,044	0,839
4	0,845	0,044	0,845

5	0,886	0,114	0,945
6	0,930	0,070	0,931
7	0,867	0,061	0,879
8	0,896	0,049	0,800

Table 4.4. Molecular weight of samples

Sample	M_w ($x10^3$) g/mol	M_n ($x10^3$) g/mol	M_w/M_n
AcRe-SM_1	311	115.3	2.699
AcRe-SM_2	561.9	132.2	4.25
AcRe-SM_3	901.8	293.6	3.072
AcRe-SM_4	349.2	136.2	2.564
AcRe-SM_5	294.6	160.14	1.84
AcRe-SM_6	370.06	213.3	1.7
AcRe-SM_7	295.062	174.76	1.688
AcRe-SM_8	306.8	176.8	1.736

4.8 Paint Application

Special monomers affect on paint performance such as corrosion resistance, adhesion performance, and water resistance. In this study, paint performance tests which are adhesion test according to ASTM 3359 and ISO 2409 Standards and corrosion test according to ASTM B117 and ISO 9227 Standards was done.

Two 1 kg paints were formulated with 2 types of binders which are purely acrylic AcRe-SM_1 and AcRe-SM_6. The reason why AcRe-SM_6 was selected is

because of its stability performance, reaction efficiency, and viscosity similarity with AcRe-SM_1.

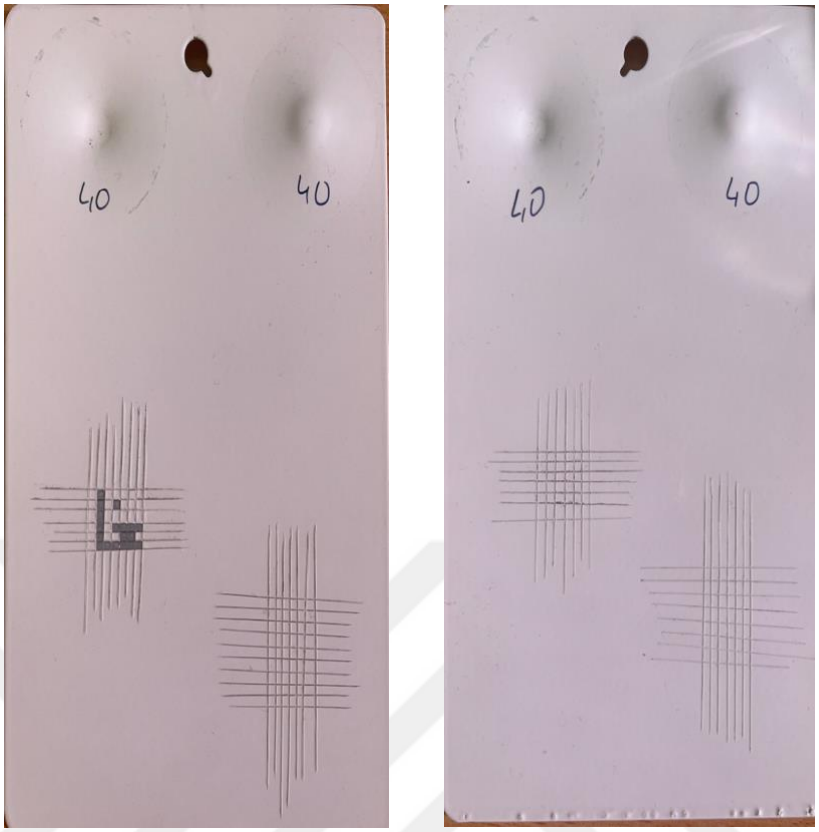
4.8.1 Adhesion Performance Test

2 types of paints with binder AcRe-SM_1 and AcRe-SM_6 were tested and the results were seen in Figure 4.34. According to ASTM 3359 Standard, the score of the paint consisting of binder AcRe-SM_1 was 2B. This score was evaluated by the explanation when the coating has flaked along the edges and on parts of the squares and the area affected is 15 to 35% of the lattice.

Another paint which consists of binder AcRe-SM_6 scored 4B according to ASTM 3359 Standard. This score could be thought of because when the small flakes of the coating are detached at intersections; less than 5% of the area is affected.

4.8.2 Corrosion Resistance Test

Painted panels which were left salt spray tested for 168 hours are demonstrated in Figure 4.35. The score of the paint consisting of binder AcRe_1 was 5 and the paint consisting of binder AcRe-SM_6 was 10. The score is explained by ASTM D610



(a) (b)

Figure 4.34. The adhesion test result of (a) binder AcRe-SM_1 and (b) binder AcRe-SM_6

Table 4.5. Rust assessment test degrees

Score	Explanation
10	No rust or ≤ 0.01%
9	Few rust or > 0.01% and ≤ 0.03%
8	Spot rust or > 0.03% and ≤ 0.1%
7	> 0.1% and ≤ 0.3%
6	> 0.3% and ≤ 1.0%

Table 4.4. (continued)

5	> 1.0% and ≤ 3.0%
4	> 3.0% and ≤ 10.0%
3	> 10.0% and ≤ 16.0%
2	> 16.0% and ≤ 33.0%
1	> 33.0% and ≤ 50.0%
0	> 50%



Figure 4.35. Corrosion test result (a) AcRe-SM_1 and (b) AcRe-SM_6

CHAPTER 5

CONCLUSION

This study was based on semi-batch emulsion polymerization and according to the initiator type, it was a kind of radical polymerization. A purely acrylic system was designed in this study. After the literature review; monomer concentration was 45% and methyl methacrylate, butyl acrylate, 2-ethylhexyl acrylate, acrylic acid, and methacrylic acid were used. Ammonium persulfate was selected as the initiator. The reaction was carried out at around 80ºC.

Before investigating the effect of special monomers, the surfactant ratio was adjusted from 0.3 to 3 % of weight. According to stability, the best result was observed at 1.5% surfactant was used. Then, different types of anionic surfactants were used in terms of, sodium lauryl sulfate, sodium dodecyl benzene sulphonate, alkyl phenol ether sulfate, sulfosuccinic acid ester sodium salts were used. The result was more stable when sodium lauryl sulfate was used.

Special monomers affect binder stabilization, coating adhesion promotion, coating surface improvement, and coating mechanical properties. Sodium1-Allyloxy-2-Hydroxypropanesulfonate;1-methacylamido,2-imidazolidinone ethane; Polypropylene glycol monomethyl methacrylate phosphate ester; and phosphate ester were described as special monomers. Those special monomers were used, and they affected the glass transition temperature and also the minimum film-forming temperature.

According to the stability, the best result was observed when phosphate ester was used at 3% to the overall monomer concentration, AcRe-SM_6. The particle size of the samples was the same and was measured around 110 nm. However, at AcRe-SM_4 the particle size was bigger than the other. This would be explained by

coagulation of the reaction. Glass transition temperature was calculated by Flory-Fox Equation. Then, measured by Differential Scanning Calorimetry. The data from DSC were similar to the values estimated by the Flory- Fox Equation. Comparing the special monomers at 3% to the overall monomer concentration glass transition temperature and minimum film forming temperature of AcRe-SM-6, in other words, the phosphate ester used, was less than the other binders with special monomer. Comparing the acrylic resins consisting of phosphate ester, the binder with the smallest amount of special monomer has the highest glass transition temperature and minimum film forming temperature.

According to the FTIR results; the reaction efficiency was the best in AcRe-SM_6 and as the concentration increases or decreases both the reaction efficiency decreases as well. So, the optimum concentration of phosphate ester was 3% of the overall monomer concentration.

Comparing the viscosities of acrylic binders with special monomers, AcRe-SM_6 has the most similar viscosity. According to the regression analysis, the most accurate results were seen in AcRe-SM_5 and AcRe-SM_6.

At the end of the acrylic synthesis and characterization; the binders' performance was tested in paint formulation. One of the paints was formulated with the purely acrylic binder and another paint was formulated with the binder AcRe-SM_6. According to the adhesion test and corrosion resistance test, paint formulated with acrylic binder AcRe-SM_6 has better results than the paint consisting of purely acrylic binder.

To sum up, the special monomer of phosphate ester is compatible with the acrylic system. This phosphate ester improves corrosion resistance in metal applications and has a good adhesion performance when it is used as an acrylic binder.

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APPENDICES

A. DSC RESULT

DSC Result of AcRe-SM_1-1st trial

