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A study on effect of ionic and non-ionic surfactants on end-product properties of acrylic Latices

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Abstract
This research work involves the study focused on end-product properties of acrylic latices controlled by using ionic and non-ionic surfactants in emulsion polymerization process. Both the surfactants play different roles vital for proper emulsification and colloidal stability of the latex. Continuous emulsion polymerization process is employed to produce methyl methacrylate and butyl acrylate copolymer latices by incorporation of ionic emulsifier (OPS-25) and non-ionic emulsifier (OP-25) in combination. Both the emulsifiers were experimented at various concentrations to observe their effect on different end-product properties, i.e., rheological, thermal and structural properties. To observe the effect of the emulsifiers on end properties, it was intended to produce a stable and durable commercial grade product and for this purpose, conventional water-borne emulsion polymerization technique was followed. In the product formulation, initially, the concentration of OP-25 is kept constant while the concentration of OPS-25 is varied, and then, the concentration of OP-25 is varied keeping the concentration of OPS-25 constant. Both the emulsifiers showed different effects on the final latex properties i.e. viscosity, abrasion scrub cycles, drying time and glass transition temperature. OPS-25 exhibited stronger effect in increasing the overall viscosity of the latex samples while OP-25 played a significant role in improving abrasion scrub cycles and drying time of the latex samples. OP-25 reinforced OPS-25 in maintaining glass transition temperature of the latex samples. On increasing the concentration of the emulsifiers beyond certain limits, they resulted in poor film properties of the latices. Both ionic and non-ionic emulsifiers strongly affected the end properties of the latices, however, the optimal properties were obtained when both the emulsifiers were employed within certain limits of their concentrations.

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1. Introduction

Emulsion polymerization, a type of addition polymerization usually undergoes generation of free radicals reacting with monomeric molecules to produce large number of polymer particles in a continuous aqueous phase. It is a process predominantly used to produce a number of versatile polymers on industrial scale. They have covered a large area of applications in multiple sectors i.e., paints, coatings, adhesives, varnishes, binders, and rubbers etc. Emulsion is a unique polymerization technique to produce latex with various colloidal and physicochemical properties of esteemed importance appreciated academically and industrially. Copolymer latices of methyl methacrylate and butyl acrylate produced by continuous emulsion polymerization technique are widely used in paint and coating sectors [1]. Emulsion polymerization generally takes place in three stages; initiation, propagation and termination and the process is usually formulated by a hydrophobic monomer, water, oil-in-water (O/W) surfactant and a water soluble initiator. Monomer is dispersed in a continuous aqueous phase in the form of droplets by incorporation of a suitable (O/W) surfactant.

Typically free radical polymerization is followed in emulsion polymerization process which is initiated by using a suitable water soluble initiator. Concentration of the surfactant is always kept above critical micelles concentration (CMC) to initiate proper emulsification process. The process of free radical generation and emulsification leads to form latex particles (submicron) much smaller in size as compared to actual monomer droplets further leading to colloidally stable dispersion. The emulsified monomer droplets (ca. 1-10 µm in diameter, 10^{12}-10^{14} dm^{-3} in number) are dispersed in the presence of swollen micelles (ca. 5-10 nm in diameter, 10^{19}-10^{21} dm^{-3} in number) in the system. The most significant feature of this technique is the segregation of free radicals among monomer swollen particles. This greatly reduces the chances of bimolecular termination of the radicals resulting in faster polymerization rate with high molecular weight polymer [2-4].

Water is used as sole solvent in water-based emulsions. In a controlled reaction, high molecular weight polymers with narrow molecular weight distributions are produced by free radical polymerization. Molecular weight is very high from 100,000 to 1 million. Viscosity of the latex is normally low and independent of the molecular weight of the polymer. The emulsion polymers can either be precipitated to use in solutions such as alcohol soluble printing inks or neutralize to form water dispersible resin such as water based printing inks. Rheologically emulsion polymers exhibit pseudo-plastic behavior. Good reproducibility, fast and rapid reaction, high conversion rate, greater flexibility to produce copolymers and low cost are the significant features of emulsion polymerization [5]. Along with outstanding properties and versatile area of applications, emulsion polymers also has some flaws, e.g., they have relatively poor mechanical properties due to the presence of surfactants, colloids and salts which lead to poor film integrity and performance. The films are also sensitive to strong electrolytes [6, 7].

Emulsion polymerization is rather a complicated process as free radical polymerization mechanism controls various colloidal phenomena along with nucleation, growth and stabilization of the latex particles. Protective colloids are also employed in the system with a good combination of surfactants to improve stability and prevent coagulation of the final latex. The mechanism of particle nucleation, particle size distribution and other physicochemical outcomes are still debatable and understudies so for, however, the preparation of acrylic latices and their stability are more understood and well documented [8].

A surfactant is a vital ingredient of emulsion polymerization process that makes a friendly connection between two non-loving phases i.e. oil (monomer) and water. It plays a major role in establishing colloidal stability of the growing latices and its concentration in the system does not affect particle size very much, however, in certain cases, surfactant’s concentration may cause secondary nucleation leading to smaller particle size in the system [9]. Two types of surfactant are generally used as emulsifiers for emulsion polymerization i.e. ionic (anionic) emulsifiers and non-ionic emulsifiers. Cationic emulsifiers are generally not employed in water born emulsions. When either type of the emulsifier is used in the process, we cannot achieve the required colloidal stability and end-product properties. Therefore a well-balanced combination of ionic and non-ionic emulsifiers is used to enhance colloidal stability and other physicochemical properties. An ionic emulsifier stabilizes particles creating an electrostatic repulsion among them. It imparts repulsive forces when similarly charged electric double bond layers are created between latex particles. These repulsive forces are responsible for stability of the latices against aggregation. On the other hand, a non-ionic emulsifier stabilizes particles by imparting thermodynamically favored steric stabilization mechanism. It enhances chemical and freeze thaw stability of the latex [10]. Particle size goes to decrease on increasing the concentration of an ionic emulsifier but an increase in ionic strength plays a major role in increasing the particle size in polymerization system. Actually ionic strength hinders the decrease in particle size limiting the coagulation process over small increase in the concentration of the emulsifier. During the process, micellar concentration of the system is a noticeable factor, therefore ionic strength can be dominated by using higher concentrations of the emulsifier with growing micelles [11].

There are so many issues that arise as polymerization process proceeds. Initially, colloidal stability of polymer particles during nucleation process is the main issue to be tackled by employing well calculated amount of surfactant. Controlling rheological properties and viscosity along with uneven heat transfer is a big issue in the latter stages. If colloidal stability is disturbed, coagulation will take place leading to problematic process with off-spec product. Inappropriate particle size distribution, conversion rate and molecular weight are the results of inadequate emulsification. Good emulsification in an emulsion process can be achieved by using adequate amount of surfactants along with other additives in a right proportion [12].

For emulsion polymerization, the polymerization plants are similar to those typically used for suspension polymerization. Efficient stirring is required to avoid coagulation. Normally, large reactors having bulk storage capacity are used in industry. Pressure reactors with thick walls are used for gaseous monomers to withstand high pressure. Preparation of pre-emulsion requires a separate tank with agitation and heating systems. The pre-emulsified monomer is continuously agitated during its continuous feeding into the aqueous phase. In emulsion polymerization, unlike solution polymerization, the initiator (aqueous) is not added simultaneously in the aqueous phase but is added periodically at a carefully controlled rate. Correct alignment and proper design of the reactor is indispensable to eliminate the problems during polymerization process. The reaction inside the reactor is exothermic and foaming is recurrent issue that can only be controlled by taking the precautionary measures into account. Reactor is always kept air tight because the presence of oxygen in the system retards the rate of polymerization [13, 14].

Pre-emulsion is a frequently employed technique to produce acrylic copolymers in the industry and is rarely used for vinyl acetate systems. In pre-emulsion, the monomer is pre-emulsified with surfactant (ionic) in a separate vessel. Generally, the surfactant is added as one part of the total emulsifier system to the monomer. This pre-emulsion is then continuously added to the water phase that already contains emulsifier (ionic and non-ionic). So, surfactants are not only added into the water phase but also to the monomer phase. Pre-emulsion is continuously agitated to avoid coagulation during the process of monomer (pre-emulsified) transfer into the aqueous phase [15]. Usually, for emulsion polymerization, the temperature is maintained at 70ºC to 80ºC for thermal initiation but the typical processing temperatures are adjusted between 60ºC and 85ºC depending on the requirements of the process. Water phase also act as a heat sink to dissipate heat of the reaction [16].

The main objective of the present work was to produce emulsion latices of methyl methacrylate and butyl acrylate copolymer using both types of surfactant as emulsifiers (ionic and non-ionic) to analyze the end-product properties. An effort is put to obtain the best practicable results while optimizing the concentrations of both the emulsifiers. The work was carried out to produce stable acrylic latices in a quality conscious way. For this purpose different existing techniques have been used to characterize the acrylic copolymer samples.

2. Literature Review

Harkins Model and Smith-Ewart Theory have always been considered as classical foundations for upcoming theories in developing emulsion polymerization mechanism. Harkins proposed, "Generation of latex particles (submicron) is done when free radicals are captured by micelles in the aqueous phase. Monomer gets solublized in the form of swollen polymer particles and this mechanism of particle nuclei and nucleation is a single step process". Monomer droplets act as particle nucleation loci when their size is reduce to submicron level. This mechanism is termed mini emulsion polymerization [17]. Subsequently, Smith-Ewart proposed a semi-quantitative theory of particle growth on Harkins mechanism. They worked on particles containing radicals and created population balance equation. For derivation of mass balance equation, the theory considers three limiting factors. The first one applies if the rate of transfer of free radicals is pretty high out of the particles. The second case is applicable when the radical transfer becomes unimportant out of particles. And the third one applies if the rate constant for termination becomes too small within the particles. The theory also postulates that number of particles generated in the aqueous phase would be in direct proportion to concentration of the initiator raised to the power of 0.4 [18].

Sutterlin and coworkers worked on homogeneous nucleation and effect of surfactant on particles during polymerization of various acrylate polymers. They proposed that when the homogeneous nucleation becomes more significant below or above the critical micelles concentration (CMC) of surfactant [19]. The theory reveals that exponent value (detailed in Smith-Ewart Theory) varies with surfactant's concentration. Below CMC, exponent value increased with increasing water solubility of the monomer. Roe stepped forward and made critical but important point on Smith-Ewart theory. He derived similar equations avoiding micellar nucleation and proposed that Smith-Ewart Theory could not explain the difference between micellar mechanism and homogeneous nucleation. The exponents used in that theory merely showed a uniform rate of production of free radicals. Roe suggested, "When total surface area occupied by packed monolayer of surfactant is fully covered and exceeded by the surface area of the latex produced, coagulative events do not take place but nucleation mechanism ends up" [20].

Napper and coworkers proposed coagulative mechanism in detail. They pointed out that the primary (precursor) particles which were polymerized at slower rate instead of normal may be formed either by micellar entry or homogeneous nucleation. Priest, Ottewill and coworkers suggested ideas on coagulation among precursor particles depending on concentration of the surfactant and particles formation in surfactant free systems. Napper and Gilbert raised some doubts on Harkins Model and Smith-Ewart Theory regarding initial nucleation sites. They argued that anticipated formation of number of particles by Smith-Ewart was in direct proportion to the surfactants concentration raised to the power 0.6 that is in fact not achieved in many experimental works. The main argument was on the primary free radicals which enter thermodynamically to the non-polar interior portion of a micelle proposed by Smith-Ewart Theory. They suggested "a free radical needs amphipathic properties and surface activity to enter a micelle on adding at least one monomer molecule" [21]. Later on Chern and Hsu investigated the identical systems. They used sodium lauryl sulphate as surfactant for methyl methacrylate and butyl acrylate emulsion copolymers both below and above CMC. They reported the number of particles nucleated was directly proportional to the surfactant concentration raised to the power 0.5-1.2 [22].

El-Assar and coworkers worked on copolymerization of butyl acrylate and studied the rates of reaction for concentration of the surfactant below and above CMC as a function of time. They used sodium dodecyl sulphate as surfactant and potassium per sulphate as initiator and found that near CMC, dependency of particles on surfactant concentration in the final latex varied significantly from the Smith-Ewart Theory of 0.6. Previously, many publications reported emulsion polymerization homogeneous-coagulative mechanism and particle formation below CMC but still there is a big debate on free radicals micellar entry mechanism above CMC of the surfactant [17]. Giannetti used zero-one system approach used by Gilbert and coworkers and modeled particle size distribution theoretically. He raised doubts on particles nucleation and questioned the origin for positive skewness of early-volume particle distribution. He stated that model proposed by Gilbert and coworkers did not fit the particle size distribution data for increasing rate of nucleation, however fitted the results when decreased particle formation was assumed [23].

Recently Coen *et al*. worked out almost all the parameters necessarily required to model. They found, "even above CMC of a surfactant, precursor particles and coagulative phenomenon have huge effect on polymerization rate and considered that adjustment of significant parameters was not definitive [24]. Subsequently, it has been established that surfactants have a massive effect on particle nucleation, number of particles nucleated, particle size and stability of the final latex. However, the characteristics not only depend on type and concentration of the surfactant used but also on ionic strength within the aqueous phase, concentration of the monomer, concentration of the initiator, and polymerization temperature. Regarding polymer particle nucleation, huge controversies surround the mechanism of emulsion polymerization. On one hand, it is claimed that micelles are not required for particle formation while on the other hand, there is a claim that particles nucleation ceases once the micelles are exhausted [25].

For the growth of polymer particles, there is a need of continual adsorption of surfactant molecules to maintain stability. The unstable particles (growing radicals) continue to absorb on to the other polymer particles and rate of adsorption of new particles increases as more polymer particles are nucleated. The number of micelles originally present is substantially greater than the number of particles formed. The rate of adsorption increases until it becomes equal to the rate of formation of polymer particles and the stage before this period is regarded as "seed stage". After the seed stage, the number of polymer particles becomes constant. During the whole process of polymerization, addition polymerization kinetics are obeyed [26].

The initiated species enters micelles instead of monomer droplets as micelles are large in number. Polymerization of droplets is considered responsible for the formation of hard lumps of unstable polymer termed as bits or nibs. Generally for emulsion systems, the rate of polymerization is proportional to the concentration of monomer, propagation rate constant and number of particles nucleated. The number of particles nucleated is proportional to the concentration of the initiator and the surfactant. The number of particles nucleated is inversely proportional to the particle size and increasing the concentration of the surfactant decreases the particle size exponentially. Surfactant and initiator both play substantial role in stabilizing the monomer droplets during polymerization. The surfactant stabilizes the droplets by double layer charge effect & steric stabilization while the initiator stabilizes the growing species by forming acidic fragments [27].

The classical Smith-Ewart theory is more inclined to academic notions but industrial practices are somehow different. According to the theory, the process is accomplished in two stages. The stage-I of the polymer system represents the nucleation of particles only by free radicals entry in the micelles and no formation of the new polymer particles takes place. Surfactant concentration is responsible for controlling the number of particles overcoming the entire surface of the particles. The number of particles is proportional to 0.6 power of the concentration of the surfactant. The stage-II of polymerization describes the number of particles formed is proportional to the rate of polymerization. It was assumed that co-existence of two free radicals is not possible on a polymer particle and the average number of radicals is 0.5 in a particle [28]. Practically, these assumptions are deemed basic and unfitting. Firstly, in stage-I, emulsions can be produced without surfactants by using terminal sulphate groups to stabilize the particles and micelles' formation is not essential. Secondly, the number of particles reaches a constant value mostly during the seed-stages while micelles still exist. There is also a flaw in the theory that it did not describe the difference in rate of reaction and number of polymer particles nucleated using different surfactants. The stage-II has some validity but leads to error considering the Tromsdorf Effect. A polymer particle may contain more than one free radical and as a result grafting may occur. Initiation and termination can take place when free radicals are absorbed on to the polymer particle. When a free radical enters the particle, it may cause to initiate the chain propagation that consequently leads to a stop/start polymerization and formation of a high molecular weight polymer [29].

There are several complex theories proposed on mechanism of emulsion polymerization which differ widely from the mechanisms adapted for the preparation of emulsion polymers on industrial scale. In this research work, the end-product properties of emulsion copolymers are focused regardless the contentious mechanism of emulsion polymerization, and the effect of ionic and non-ionic surfactants on certain properties such as viscosity, wet abrasion resistance, drying time, MFFT (minimum film forming temperature), Tg (glass transition temperature), and polymer structure, is examined.

Maintaining the required viscosity of emulsion product is one of the most important parameters of emulsion process. Usually, on increasing the concentration of the emulsifier, viscosity goes to increase as a result of nucleation process. Stability of a product highly depends on the type and structure of monomers, emulsifiers and colloids used and also the rate of conversion as well but is independent of the viscosity of the latex. Therefore a product with high viscosity may lead to poor quality and some another product with low viscosity can be excellent in its properties and applications. Emulsion latices are stored neither at high nor at low temperatures. Room temperature ranging from 20ºC to 25ºC is a favorable storage temperature for emulsion polymers. At higher temperatures, latex tends to phase separation weakening the interactions of emulsifiers with monomer and water which decreases the overall viscosity of the polymer. At lower temperatures, latex may completely crystallize and loses its required flexibility. Surfactant molecules are the integral ingredients of polymer film formation and they exhibit weak spots in the film. These weak spots are pretty sensitive to aqueous solutions. These can be reduced by inducing the cross-linking in the latex using copolymerizable surfactants, e.g., sodium vinyl sulphonate. The molecular weight does not influence viscosity of the polymer formed, while surfactant system, particle size, and introduction of colloids have significant effect on viscosity [30, 31].

Drying time of the latex film depends on the type of emulsifier used which may exhibit slow or fast drying. Chemically the surfactants with strong packing of hydrocarbon bonds always exhibit slow drying and less water loss (i.e., cationic emulsifiers) as compared to the emulsifiers with weak packing of hydrocarbon bonds (i.e., anionic emulsifiers). On increasing the concentration of surfactant, the evaporation rate of water goes to decrease reducing overall water loss of the latex. Actually at higher concentrations of surfactant, monomer molecules cover more interface area which prevents the evaporation of water molecules. But, extra use of emulsifiers leaves weak spots at interface area causing to reduce the overall drying time of the product. Generally drying of the latices with smaller particle size is slower than latices having larger particle size [32]. Drying time of a product is always maintained according to the weather conditions as it is highly influenced by ambient temperature. For example in winter season, a product takes more time to dry as compared to summer season. So, we have to change the product formulation according to the weather. In winter, those emulsifiers are incorporate which assist fast drying without deteriorating the quality of the product. Conversely, in summer, we introduce those emulsifiers in the same formulation which retard quick drying to enhance drying time maintaining the same quality for better compatibility of the product with the substrate [33, 34].

A latex film is always formed above MFFT through coalescence phenomenon because below this temperature, the film is non-continuous, hazy and chalky. The value of MFFT is somewhat lower than the value of Tg of the polymers due to plasticizing effect of the surfactant and presence of other additives, or the plasticizing effect of water on the polymer film. Mostly emulsion latices are produced for ambient temperature applications with Tg in the range of 0-30 ºC. Glass transition temperature is an important second order transition that represents the changes from glass to rubber. A polymer is flexible above its Tg and has high elongation at break but is brittle below its Tg. A smaller difference between the values of MFFT and Tg describes the ease of film formation and stability of the product. If this difference is large, the film may degrade before reaching the Tg value which indicates the discontinuity and poor coalescence of the film. In fact, the excessive amounts of emulsifiers leave weak areas that cause poor coalescence film formation. A film crystallizes and loses the required flexibility or may degrade completely after cracks development. Therefore, an optimal amount the emulsifier is always suggested to use to achieve the ultimate quality of the product. No doubt, concentration of surfactants strongly affects the values of MFFT and Tg, but monomers involved play vital role in achieving required MFFT and Tg while synthesizing of a copolymer [35, 36].

Surfactants generally do not affect the chemical structure of the monomers. In acrylics, ester C=O stretch usually occurs at 1725-1750 cm^{-1}(s) and it also exhibits a strong band for C-O at higher frequency than ethers and alcohols at 1150-1250 cm^{-1}(s). The IR spectra indicates the presence of functional groups involved in the chemical composition of the latex [37].

3. Materials and Methodology

3.1 Materials

All the materials used in the emulsion process were of chemical grade and used as received without any pretreatment. For the current research work, Syntchem Co. (Pvt) Ltd., Lahore, offered voluntary help and guidance as a part of raw material sourcing.

3.1.1 Water

The quality of water plays a vital role in water borne emulsion polymerization processes [12]. In the present research work, about 48% de-ionized water of the total recipe weight has been used to synthesis of acrylic copolymer latices [38].

3.1.2 Monomers

In acrylic emulsions, normally a mixture of co-monomers is employed and most of the emulsion polymers are copolymers [37]. A balanced combination of hard monomer (methyl methacrylate, Mitsubishi Rayan, Japan.) and soft monomer (butyl acrylate, GL Chem. Ltd., Korea) was employed to synthesize acrylic latices. There is a huge difference between glass transition temperatures of methyl methacrylate (378K or 105°C) and butyl acrylate (219K/-54°C). Methyl methacrylate is known to be a hard monomer as its Tg is higher than the normal ambient temperatures and butyl acrylate is considered a soft monomer as it attains a very low value of Tg (<<0°C). Solubility of methyl methacrylate in water is 150mM and that of butyl acrylate 11mM in the aqueous solution. Reactivity ratio of methyl methacrylate is 2.46 more than butyl acrylate that is 0.33. Boiling point of MMA is 101°C and that of Butyl Acrylate is 147°C (both the monomers have higher boiling points than the normal processing temperature, i.e., 80°C and therefore no vapor formation takes place during acrylic emulsion copolymerization) [18, 39, 40]. Acid monomers (acrylic and methacrylic acid) are used to improve the freeze thaw stability of the final product. Acid monomers sometimes also behave as thickening agent [41]. Acrylic acid (BASF Petronas Chemical Sdn. Bhd., Malaysia) was used as an acid monomer in the current research work

3.1.3 Surfactants (Emulsifiers)

The selection of surfactants is generally understood considering their CMC values and HLB (Hydrophilic Lipophilic Balance) numbers. Generally, ionic surfactants have higher CMC values compared to non-ionic surfactants.

HLB numbers for O/W emulsion : ca.8-16
HLB numbers for W/O emulsion : ca.3.5-8
HLB numbers for antifoams : ca.1-3.5

HLB Number is a semi empirical method to predict surfactant type and structural properties [42, 43]. In the present research work, OPS-25 (octyl phenol polyglycol ether sulphate, BASF The Chemical Company, Germany) and OP-25 (Ethyl Phenol Ethoxylate, BASF The Chemical Company, Germany) were used as ionic and non-ionic emulsifiers respectively.

3.1.4 Initiator

An initiator is a species that causes to produce free radicals in emulsion polymerization. Initiator must be of free radical type and water soluble. Free radicals can be generated thermally or by using Redox-couples. The main initiators used commercially are persulphates e.g. sodium persulfate, potassium persulfate and ammonium per sulphate [44]. In the current research work potassium per sulphate (ADEKA Corporation, Japan) was used as an initiator and no Redox-couples or post polymerization initiator were used.

3.1.5 Colloids

Protective colloid is a term named to high molecular weight water soluble materials e.g. polyvinyl alcohol and cellulose derivatives i.e. cellulose ether. On increasing colloidal contents, viscosity of the latex goes to increase. Considering the protection of the polymer against aggregation, colloids are more effective as compared to surfactants [45]. A carefully calculated aqueous mixture of stearyl alcohol and sodium lauryl sulphate (Lanolin AS-97, was used as a protective colloid in the current research work.

3.1.6 Thickening Agents / Viscosity Modifiers

These are normally highly water-absorbent polymers forming a soft gel with in water phase during emulsion polymerization. These are also known as suspending agents [46]. Acrylamide (Dia-Nitrix Co. Limited, Japan) was used as a viscosity modifier in this work.

3.1.7 Buffers

During polymerization, buffers are incorporated to maintain acidic pH. pH is usually controlled during polymerization but in some cases buffers are added to maintain pH at the completion of the process. Borax, sodium hydrogen phosphate and sodium bicarbonate salts are typical buffers. The pH of the latex depends on the chemical nature of the polymer. Mostly, the latices are produced at a pH above 7.5. From application point of view, a little basic nature of acrylic emulsions does not cause irritation to human hands and other body parts [47]. In the present work, sodium bicarbonate (ICI Pakistan, Pakistan) was used as a buffer and ammonia (local) as a final pH controller.

3.1.8 Antimicrobial Agent

These are the chemicals used to prevent the growth of fungus and bacteria on the final latex and act as product preservatives [48]. Margal (IPEL Biocidas, Brazil) was used as antifungal/

antibacterial in the current work.

3.2 Polymerization Technique and Method

3.2.1 Laboratory Equipment

For the preparation of latices on laboratory scale, a round bottom glass flask (reaction vessel, 1000ml) with a thermostatic water bath was used. A stirrer with a three blade paddle is mounted inside the flask which is connected to a motor. A condenser is attached with the reaction vessel one side to compensate vapors as a result of temperature fluctuations (normally not required for acrylics at a constant temperature) and a monomer reservoir is attached on the other side. A thermocouple is adjusted inside the flask to measure temperature. Other related apparatus including glass beakers, glass rods, pre-emulsion flask, spatula and digital weighing scale was used for experimentation.

3.2.2 Polymerization Method

The process of emulsion polymerization is extremely complex but the knowledge of mechanism is somehow empirical. The conventional emulsion polymerization method was followed in the present research work.

3.2.3 Product Formulation

For laboratory scale preparation of latices, the recipe for continuous emulsion polymerization of methyl methacrylate and butyl acrylate is given as follows.

Table 1: Product formulation for the synthesis of latex samples

Components	Weight (g)
Reactor Charge	
Water	117.11
Buffer (Sodium bicarbonate)	0.65/2 H20
Anionic emulsifier (OPS-25)	1.22 (0.5% of the total Monomer)
Non-ionic emulsifier (OP-25)	0.98 (0.4% of the total Monomer)
Initiator (Potassium per sulphate)	0.73/18.33H20
Pre-Emulsion	
Water	71.28
Monomer-I (Methyl methacrylate)	122.20
Monomer-II (Butyl acrylate)	122.20
Anionic emulsifier (OPS-25)	4.89
Latex Stabilizer (Acrylic acid)	1.83
Viscosity modifier / Suspending agent (Acrylamide)	2.44
Colloid (Water 92% + Stearyl alcohol 4% + Sodium lauryl sulphate 4%)	36.66
Post-Polymerization	
pH Controller (Ammonia)	1.63
Antifungal (Margal)	0.5/0.5H20
	Total: 505.23
	Total Water Contents: ca. 50%
	Total Solid Contents: ca. 50%

3.2.4 Polymerization Process

Following the formulation given in Table 1, the reaction vessel was initially charged with water, sodium bicarbonate, OPS-25 and OP-25. Pre-emulsion of the monomer phase was prepared in a separate pre-emulsion flask. All the ingredients in the pre-emulsion flask were kept on continuous agitation at ambient temperature to obtain a properly mixed, viscous milky pre-emulsified liquid as pre-emulsion. OPS-25 was used in the preparation of pre-emulsion. Heating temperature of the flask was set at 82ºC to maintain an average temperature around 80ºC. Heater and stirrer were turned on simultaneously for homogeneous mixing of the components in the form of aqueous solution within the reaction vessel. The agitation of the stirrer was maintained at a range of 25 to 30 RPM. The initiator was mixed with water in a glass beaker and prepared to be used in the form of aqueous solution. When the temperature reached at 75ºC, the initial dose of the initiator was fed into the reaction vessel. Continuous feeding of the monomer phase into the reaction vessel was started at ±80ºC. Feed time of the monomer phase was noted for 3 hours to obtain a well-defined structure and molecular weight distribution of the resulting polymer. Equal doses of the initiator solution were given periodically dividing in equal intervals of feed hours (after each 20 minutes) but the amount of initial dose was taken a bit higher to initiate the generation of free radicals. The final dose of the initiator was given after completion of the feed time for the purpose of complete polymerization of the unreacted monomer phase. Post polymerization process was noted for 45 minutes. During this time, heater was turned off but stirring was continued. The latex formed began to cool down. At 65^{0}C, ammonia was incorporated to control the pH of the latex. Lastly, Margal was added at about 50ºC and stirring was stopped afterwards. Ultimately, the copolymer in the form of latex was obtained and filtered at ambient temperature (±30ºC).

Total nine lab batches of acrylic latices were synthesized by varying the concentrations of both the surfactants in the process to determine their effect on the properties of the resulting product. Sample A was synthesized as a reference sample for rest of the 8 samples according to the recipe as described in Table 1 where a smooth and uninterrupted emulsion polymerization process took place. In the first four samples (1-4), the concentration of ionic emulsifier (OPS-25) was varied for each sample keeping the concentration of non-ionic emulsifier (OP-25) constant, and in the same way, for the last four samples (5-8), concentration of ionic emulsifier (OPS-25) was kept constant while varying the concentrations of non-ionic emulsifier (OP-25). A difference of 0.24g (ca. 0.1% of the total monomer weight %) was maintained for each sample preparation while varying the concentrations of both the surfactants in either increasing or decreasing manner as given in Table 2. The latices were synthesized at low viscosity to be used especially in paint and coating sector.

Table 2: Weightage of ionic and non-ionic emulsifiers used in the product formulation

Sample	OPS-25 (g)	OP-25 (g)
A	1.22	0.98
1	0.98	0.98
2	1.46	0.98
3	1.70	0.98
4	1.94	0.98
5	1.22	0.74
6	1.22	1.22
7	1.22	1.46
8	1.22	1.70

3.3 Characterization Methodology

The whole experimentation and all the tests were carried out at the laboratory, University of The Punjab, Lahore, Pakistan, except the results for one test (MFFT and TG measurement) which were collected from PCSIR Laboratories Complex, Pakistan. The following tests were performed on the acrylic latices produced during experimentation.

3.3.1 Determination of Non-Volatile Contents

In the current recipe, non-volatile contents (solid contents) were maintained at 50%. Solid Contents of the samples were determined by putting each of the samples in aluminium pans in the oven at 120ºC for one hour. Water was evaporated and the remaining solid contents for each sample were weighed and calculated.

3.3.2 Viscosity Measurement

Viscosity for each sample was measured using Spindle Rotating Viscometer (Sheen Instruments Limited, Model: VM2-R, Sr. No. VSCR310349) at 27ºC.

3.3.3 Porosity Test

A simple but pretty important test was performed on each sample for pores, cavities and pinhole detection. Testing of each sample for cavity / pinhole identification was done using D.C Pinhole Detector (TYPE PHD 1-20, Sheen Instruments Limited UK).

3.3.4 Abrasion Scrub Testing

Wet scrub abrasion test was performed on the samples as abrasion scrub cycles. All the samples were dried first on test sheets. Abrasion scrub cycles for each sample were calculated using Abrasion Scrubber Tester (Sheen Instruments Limited, Model 903/3, ASTM D3450-94) at 25ºC.

3.3.5 Drying Time Calculation

The drying time for each sample was calculated at room temperature (18ºC-20ºC) using BK Drying Time Recorder (Sr. No. 1099805, Sheen Instruments Limited).

3.3.6 Minimum Film Forming Temperature (MFFT) and Glass Transition Temperature (Tg) Measurement

MFFT and Tg were determined using TA Instrument USA SDT, (TGA/SDTA method, Model Q600).

3.3.7 Fourier Transform Infra-Red Spectroscopy (FTIR)

Spectroscopic analysis for functional group determination was done by FTIR Shimadzu Corporation IR Prestige-21, Resolution 4.0 cm^{-1}, Transmittance mode, ATR accessory.

4. Results & Discussions

4.1 Non-Volatile Contents

Table 3: Results of non-volatile contents of the latex samples

Sample	Solid Contents (%)
A	50.02
1	49.97
2	50.21
3	50.14
4	49.98
5	49.43
6	49.86
7	49.94
8	50.19

Quality of an emulsion product highly depends on the solid contents upheld in the product recipe. Higher the solid contents, better is the quality of the product. The solid contents were maintained at 50% and the results of all the samples were obtained around 50% solid contents.

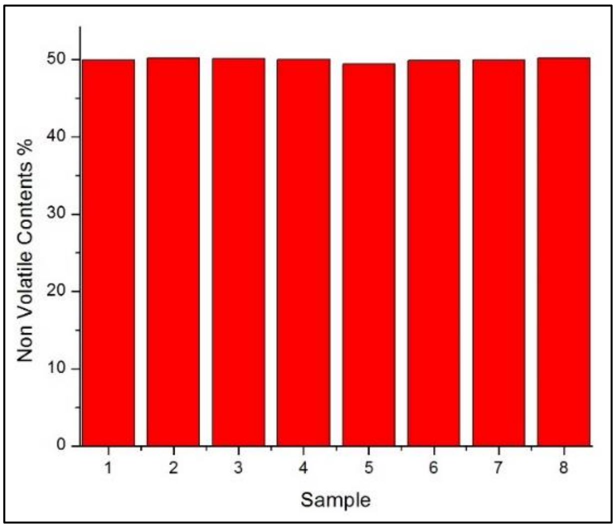

Fig 1: Effect of emulsifiers on solid contents of the latex samples

Change in concentration of the emulsifiers showed minor effect on non-volatile contents because they are used in very low percentage as shown in Table 3. It was found that the solid contents depended on the quantities of the main ingredients used, i.e., the monomers and other additives used in higher proportions.

4.2 Viscosity

Table 4: Results of viscosity measurements of the latex samples

Sample	Viscosity (Centipoise)
A	1256.3
1	985.9
2	1577.7
3	709.1
4	487.2
5	504.8
6	562.5
7	1045.9
8	498.4

Table 4 shows that the viscosity of sample 2 increased on increasing the concentration of OPS-25 as compared to sample A, but further decreased on using excessive quantity of OPS-25 in samples 3 and 4. On the other hand, the increase in concentration of OP-25, did not take part in increasing the viscosity of the latices. However, the variations in the values of viscosity in samples 5, 6, 7 and 8 might be the result of other processing parameters, i.e., temperature, RPM, etc.

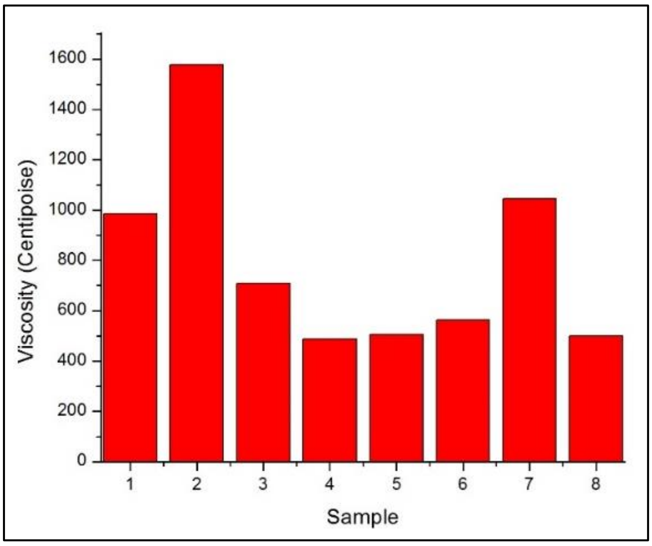

Fig 2: Effect of emulsifiers on viscosity of the latex samples

It was found that an ionic emulsifier exhibited a stronger effect on micelles formation, particles nucleation increasing the overall viscosity of the latex while the non-ionic emulsifier does not affect the viscosity very much as shown in Figure 2.

4.3 Porosity Test

Presence of pores / cavities in the film represents poor integrity and quality of the latex samples. The pin-hole detector produced no beep and voltage did not drop at any point which indicated presence of no pores, holes or cavities across the thickness of the dried films (100 µm). Sample 4 was already degraded on drying due to excessive use of OPS-25 and could not be tested. Hence, both the emulsifier did not cause to produce any pores, holes or cavities in the dried films of the latex samples.

4.4 Wet Abrasion Test

Table 5: Results of wet abrasion testing of the latex samples

Sample	Abrasion Scrub Cycles
A	547
1	600
2	532
3	313
4	Degraded
5	689
6	501
7	438
8	337

Wet scrub testing is associated with the properties of water repellency of a latex film. The scrub abrasion results are shown in Table 5. In sample 1, the concentration of OPS-25 was reduced but its number of abrasion cycles were found greater than samples A, 2, and 3 in which concentration of the OPS-25 was kept higher. As a result, samples A, 2, and 3 destabilize earlier than sample 1. Likewise in sample 5, concentration of OP-25 was reduced but it took the maximum number of abrasion cycles. In samples 6, 7, 8, number of abrasion cycles decreased respectively on increasing the concentration of the OP-25. Sample 4 could not sustain due to the use of excessive amount of OPS-25, so, it could not be tested.

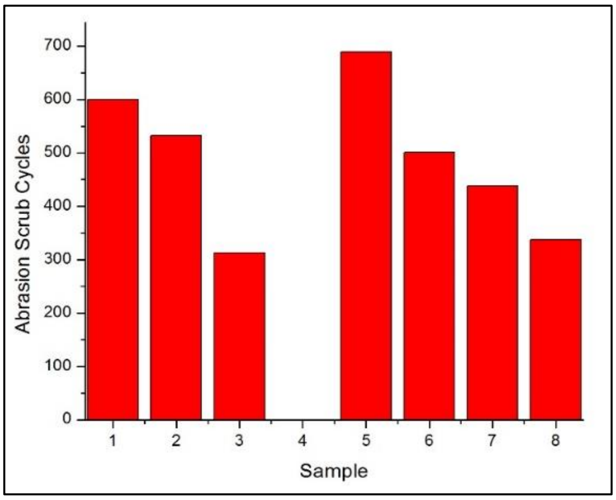

Fig 3: Effect of emulsifiers on wet abrasion properties of the latex samples

Figure 3 shows that on increasing the concentration of the either type of the emulsifiers led to poor water resistance properties of the samples and at a very high concentration of the emulsifiers, the samples degraded. Therefore, it was found that the excessive use of the emulsifiers beyond certain limits destabilized the product. However, on the whole, OP-25 showed comparatively stronger effect in improving the number of scrub cycles that led to improved quality of the product.

4.5 Drying Time

Table 6: Results of drying-time of the latex samples

Sample	Drying Time (HR: min)	Room Temperature (ºC)
A	1 : 30	22ºC
1	1 : 21	22ºC
2	2 : 32	22ºC
3	1 : 46	20ºC
4	1 : 50	20ºC
5	1 : 40	18ºC
6	2 : 10	20ºC
7	4 : 25	18ºC
8	3 : 03	18ºC

Table 6 shows that the concentration of OPS-25 was reduced in sample 1 as compared to sample A and it was found with decreased drying time. In samples 2, 3 and 4, the concentration of OPS-25 was maintained in the increasing order and the drying time of samples 3 and 4 were found lower than samples 2. This happened due to excessive use of OPS-25 beyond certain limit which led to poor bond stability and more water loss. Similarly, in sample 5, the concentration of OP-25 was reduced that led to a decreased drying time. In the last three samples (6, 7, and 8), the amount of the OP-25 was set in the increasing order and as a result, the samples were found with increased drying time. However the drying time of sample 8 was less than that of sample 7 that was due to excessive use of OP-25 beyond certain limit leading to poor stability and easy water loss.

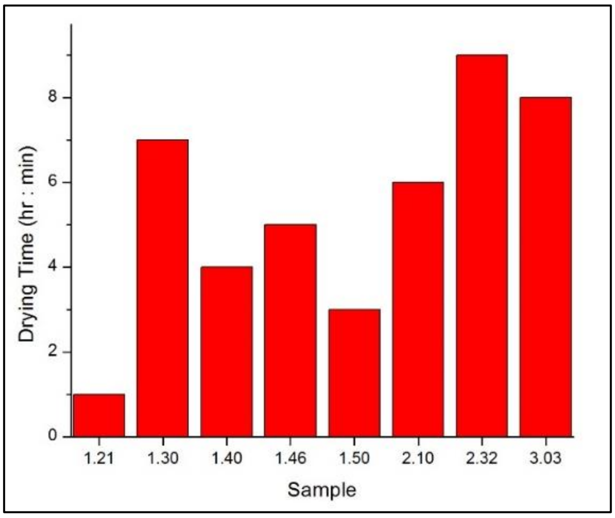

Fig 4: Effect of emulsifiers on drying time of the latex samples

It was found from the above trends shown in Figure 4 that the drying time increased on increasing the concentration of the surfactants up to certain level. Overall, OP-25 indicated improved drying time as compared to OPS-25.

4.6 Minimum Film Forming Temperature (MFFT) & Glass Transition Temperature (Tg)

Table 7: Results of MFFT and Tg measurements of the latex samples

Sample	MFFT (ºC)	Tg (ºC)
A	5	6
1	4.5	5
2	6	7. 5
3	12	17
4	22	Degraded
5	5.5	6.5
6	6	7.3
7	6	8
8	13	15. 5

In Table 7, all the samples except sample 4, got well expected values of MFFT and Tg. The values of Tg and MFFT for sample A is lower than all other samples in which the concentration of the emulsifiers is increased. Sample 1 with decreased concentration of the surfactant attained lower value for both MFFT and Tg which shows its ability to sustain even at lower temperatures. By increasing the concentration of ionic surfactant in the following samples, both the values of MFFT and Tg went to increase with a consistent increase in gap between their values of MFFT and Tg, and it leads to poor film properties. Sample 3 exhibited hazy film but, the film of sample 4 degraded right after drying. Similarly, by decreasing the concentration of the emulsifier in sample 5, the lower values of MFFT & Tg were obtained with a small difference that shows good film properties at this concentration and stability of the product at lower temperatures. When the concentration of the non-ionic surfactant was increased in samples 6, 7 and 8, both the values of MFFT and Tg went to increase in the increasing order respectively with an increase in gap between both the values. No cloudiness and cracks were observed in sample 5, 6, 7 and 8 because non-ionic concentration supports freeze thaw stability of the latex. But at higher concentrations, brittle films of samples 6, 7 and 8 were obtained with poor properties.

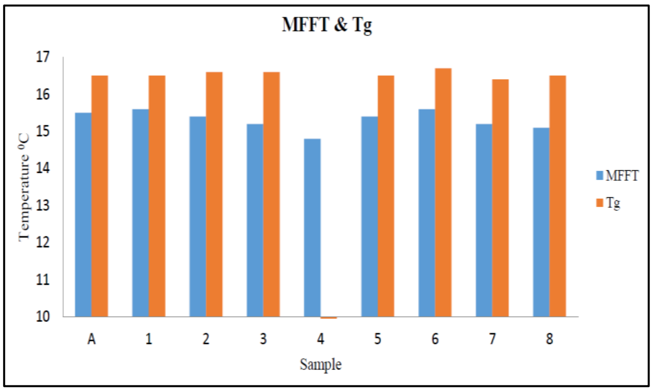

Fig 5: Effect of emulsifiers on MFFT and Tg of the latex samples

Figure 5 shows that both types of the emulsifiers influenced MFFT and Tg, however, the concentration of the ionic emulsifier (OPS-25) showed stronger effect as compared to the non-ionic emulsifier (OP-25). At higher concentrations, the ionic emulsifier strongly retards coalescence phenomenon and the same phenomenon has been observed in samples 3 and 4. Non-ionic emulsifiers do not prevent coalescence but excessive quantity leads to poor interactions among the particles as observed in Samples 5, 6, 7, and 8.

4.7 FTIR (Fourier Transform Infra-Red Spectroscopy)

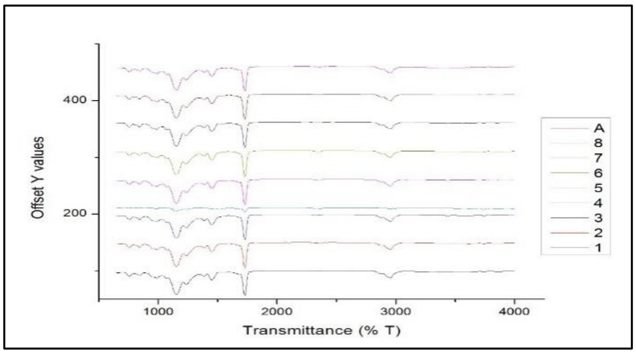

Fig 6: Effect of emulsifiers on FTIR spectra of the particles of the latex samples

In all the spectra of the samples, the same ester and alkane groups were found with prominent peaks and this indicates the presence of acrylic monomers in chemical composition of the samples. In sample 4, only the minor peaks were observed because spectrum of sample 4 was obtained in its degraded form as its film could not sustain. However, the peaks of all the samples were found almost similar representing the similar chemical composition of all the samples as shown in Figure 4-6. Hence, both the emulsifiers showed no or minor effect on the spectra of all the samples which revealed that the peaks of major functional groups were not disturbed on increasing or decreasing the concentration of the surfactants.

5. Conclusion and Recommendation

The effect of ionic and non-ionic emulsifiers on certain important end-product properties of methyl methacrylate and butyl acrylate copolymer latices has been studied systematically. An emulsifier is an additive which is mainly responsible for colloidal stability of the latex and both ionic and non-ionic emulsifiers play different roles in achieving the required properties of the latex. Concentration of both types of the emulsifier is considered acceptable up to a certain limits to achieve maximum colloidal stability of the latex and beyond those limits, the properties lead to destabilize the final product. An ionic emulsifier has stronger effect on micelles formation, particle nucleation and overall viscosity of the latex. A non-ionic emulsifier weakens the surface activity of the particles resulting in formation of aggregates. It has been observed that non-ionic surfactant does not affect viscosity very much while ionic surfactant plays a significant role in improving the viscosity of the emulsion products. Using surfactants at very high concentrations results in poor film properties. The best possible results of wet abrasion resistance of the latex films can be obtained when both ionic and non-ionic surfactant are used at a certain concentration level in product formulation. Non-ionic surfactant assists in improving the number of scrub cycles as compared to ionic surfactant resulting in good stability of the product. Drying time goes to increase on increasing the concentration of either type of surfactant up to a certain level but non-ionic surfactant impart much stronger effect in improving the drying time of the product as compared to ionic surfactant. Similarly, both types of surfactants increase MFFT and Tg as their concentration is increased in the product formulation, however, non-ionic surfactant offers comparatively better results in maintaining good values of MFFT and Tg. It happens due to the fact that at higher concentrations, ionic surfactant strongly retards coalescence phenomenon while non-ionic surfactant supports freeze thaw stability of the latex. As the gap between the values of MFFT and Tg increases, the thermal stability of the emulsion products decreases, and the latices produced at very high concentrations of the surfactants degrade at lower temperatures due to poor thermal properties. It has also been observed that the structures imparted by major functional groups in emulsion latices remain unaffected on increasing or decreasing the concentration of the surfactants. Hence, the peaks of the major functional groups in IR-spectra show similarity in the overall chemical composition of acrylic copolymers. Finally, it has been established that both ionic and non-ionic surfactants strongly affect the end-product properties in emulsion polymerization within their certain limits. Industrially, the preparation and the properties of acrylic latices are better understood and well documented, but the mechanism of emulsion polymerization along with particle nucleation, growth, stabilization and particle size distribution is rather less understood and still debatable. The research on different mechanisms of emulsion polymerization can be the topics of future research work.

6. Conflict of Interest

The author declares no conflict of interest

7. References

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