Chapter 1:

Introduction

1. INTRODUCTION

Polymer is a class of material which is known for its lightweight, strength, flexibility and chemical resistance.[1,2,3] The word “polymer” is derived from the Greek terms '*poly*', which means 'many' and '*mer*', which means ‘*parts*’.[1] First, man-made polymer, Bakelite, which is a phenol-formaldehyde resin was invented by Dr. Leo Hendrick Baekeland in 1907. Being a good insulator, this polymer is used in electric irons, cookware handles, grinding wheels, and electrical plugs.[4] The process by which small molecules are converted into polymer is known as polymerization[1] and the small molecules are known as monomers.[5]

There are several methods by which monomers may be converted into polymers. Based on the mechanism followed during the polymerization, these methods are classified into, free radical polymerization, cationic polymerization, anionic polymerization, Ziglar Natta polymerization etc. (Figure 1.1). Free radical polymerization is a polymerization method which is initiated by free radicals whereas ionic polymerizations are initiated by ions. Ionic polymerization, if it starts through an anionic pathway is called anionic polymerization and if starts through a cationic mechanism is known as cationic polymerization.[6]

In free-radical polymerization (FRP), monomers are added to the growing free-radical chain during the course of polymerization.[6] Due to its simple and robust nature, most commercial polymers are produced by this free radical polymerization method. There are several advantages of this FRP.[7,8] However, it has got some disadvantages too. FRP cannot control the molecular weights and architecture of a polymer. Therefore, a few modified versions of FRP have been introduced later to overcome these challenges. Reversible-deactivation radical polymerization (RDRP) is one such method.[9-12] RDRP methods are again classified into three major categories:

1. Atom transfer radical polymerization (ATRP)
2. Reversible addition-fragmentation transfer polymerization (RAFT) and
3. Nitroxide-mediated polymerization (NMP).

The ATRP is a beneficial method for the synthesis of polymers with predetermined molecular weights and controlled chain end functionality.[13] The ATRP-prepared polymers attain specifically predetermined topologies and compositions.[14,15] All most all the vinyl monomers may be polymerized by ATRP.[14] RAFT polymerization is a versatile and robust polymerization method based on the use of a conventional free radical generator. This method is initiated by azo-based or persulfates initiators in the presence of the chain transfer agent (CTA) such as (thiocarbonyl)sulfanyl compounds (S=C(Z)-SR).[13,16] However, inappropriate choice of CTA may lead to retardation and problems in achieving control over the reaction.[16] The NMP method is one of the most powerful methods established for the reversible dissociation of alkoxyamine initiators.

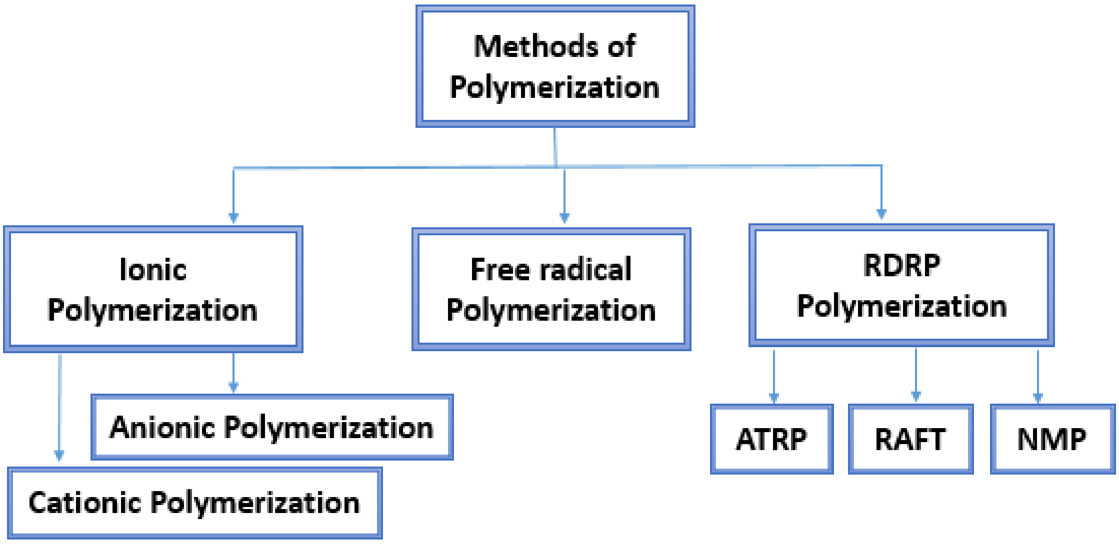


Figure 1.1. Different methods of polymerization.

Polymers are manufactured in industry via different techniques. There are mainly four techniques those are employed to produce polymers in industry: bulk, solution, suspension and emulsion. Among them, emulsion has been used extensively for the production of polymers. Farbenfabriken Bayer was the first to introduce this technique in 1909 to 1912. They investigated the polymerization of diene in an aqueous medium.[17] This manufacturing technique makes it possible to design and synthesize polymers using a greener route for a wide variety of uses.[18,19] The industry remains interested in the development of emulsion polymers due to their simplicity, presence of less volatile organic content (VOC) and their wide range of applications.[20] Free radical mechanism is used in emulsion polymerization technique.[17] The monomers those are water insoluble are mainly polymerized via emulsion technique.[20]

Depending on the number of types of monomers used in a polymer, a polymer may be classified into three categories: homopolymer, copolymer and terpolymer. The polymer produced from one type of monomer is known as homopolymer. If two types of monomers are used for the production of a polymer, it is known as copolymer. If the numbers of types of monomers are three, the produced polymers are known as terpolymers. All these three types of polymers exhibit different properties and characteristics. The terpolymer may have some desirable advantages over other two type of polymers.[21-23] There have been several reports on the preparation of such terpolymers aiming for various applications.[20,24,25]

Furthermore, enhancement of properties of a terpolymer may be achieved via preparation of composite with inorganic filler materials such as clays etc.[26] Natural clays and modified clays may be used for this purpose. Polymer/clay composites prepared by mixing the polymer with a certain amount of clays may possess good flexibility, moldability and better thermal stability.[27] It even may improve properties like barrier properties, mechanical properties, fire retardant properties etc.[28] This versatility of polymer/clay composites makes it more exciting for researchers to produce them.[14]

1.1. Free radical polymerization

Free-radical polymerization (FRP) is a polymerization process in which polymer formation proceeds through the addition of monomers to the progressing free radical chain.[6] FRP is used to produce more than 50 % (approx.) of all the polymers produced worldwide. This makes FRP an ideal commercial method for the preparation of industrial polymer.[7,8] This is primarily because radical polymerization has several notable advantages based on the following features: i) a large number of polymerizable monomers, particularly polar and functional monomers; ii) tolerance to impurity and functionality present in the system; and iii) the ability to forecast and repeat polymerization based on a variety of available data.[29] Three characteristic steps are followed in FRP. These are: initiation, propagation, and termination (Scheme 1.1.).[6,30]

The initiation steps further comprise of two sub steps. In the first step, initiator (I), decomposes to produce two radicals (R·) with a dissociation rate constant of k_{dis}. Subsequently, in the second step, this free radical undergoes rearrangement reactions with a monomer molecule to produce the first radical M· with the rate constant of initiation, k_{in}.[6,9] Continuous linking of monomer units to the chain end and the development of polymer chains with a propagation constant (k_{pro}) are involved in the propagation stage.[6,31] The termination occurs two ways: (i) combination of two growing chains that form a polymer molecule, with the termination rate constant by combination k_{ter} and (ii) developing chains disproportionate to produce a polymer[31] with the rate constant for termination by disproportionation k_{tdis}.[6] The FRP works in this manner:

$$I \xrightarrow{k_{dis}} 2R\cdot \qquad \rightarrow \qquad \text{(Initiation)}$$

$$R\cdot + M\cdot \xrightarrow{k_{in}} RM\cdot \qquad \rightarrow \qquad \text{(Initiation)}$$

$$M_n\cdot + M\cdot \xrightarrow{k_{pro}} M_{n+1}\cdot \qquad \rightarrow \qquad \text{(Propagation)}$$

$$M_n\cdot + M_m\cdot \xrightarrow{k_{ter}} M_{n+m} \qquad \rightarrow \qquad \text{(Termination)}$$

$$M_n\cdot + M_m\cdot \xrightarrow{k_{tdis}} M_n + M_m \qquad \rightarrow \qquad \text{(Termination)}$$

Scheme 1.1. Schematic representation of FRP

1.2. Emulsion polymerization

The word "emulsion" is derived from the root word "emulgeo," which means "to milk." A natural emulsion is a substance like milk. An emulsion liquid is a biphasic mixture of two immiscible liquids that disperses over a limited amount of time.[32] In this polymerization, the basic ingredients are a water-soluble initiator, water insoluble monomers, surfactant and water as a solvent.[33] Sometimes chain transfer agent is also added towards to end of the polymerization. The surfactant is used to form micelles in the water media. The monomers are allowed diffused into the micelles via mechanical stirring.[6] Water soluble initiator dissociates and form radicals in the aqueous phase and gradually diffuses into the micelles where monomers are present. The polymerization is progressed inside the micelles and the polymer chains grows inside the micelles consuming the fresh monomers present.[34,35] Emulsion polymerization is one of the most effective polymerization techniques to prepare homo, co- and terpolymers and schematically it may be depicted as shown in Figure 1.2. Most of the primary constituent monomers of commercial polymers like styrene, butadiene, acrylate, methacrylate vinyl acetate etc. may be polymerized via emulsion technique.[36] Surfactants plays an important role in emulsion polymerization, which regulate the particle size and their distribution, stability and rate of the polymerization.[37]

The advantages of emulsion polymerization are that polymerization rate is very high and polymer of very high molecular can be obtained.[38] The polymerization is possible to carry out even at lower temperature such as 0°C with less possibility of a fire hazard. The whole process is simple and affordable. It uses the most benign solvent, water. This technique yields highly concentrated latexes with relatively low viscosity.[39] The end product of an emulsion polymerization is latex. The latex may be used as such in coatings, paints, adhesives applications and for the production of synthetic leather.[39-42] This technique is used to synthesis polymer nanoparticles.[43] Specialty functional polymers, those are used in electronics and biomedical applications are now a days also prepared by emulsion technique.[44] The main difficulty of this technique is that it requires extra process for purification of the polymer.[39,19,45]

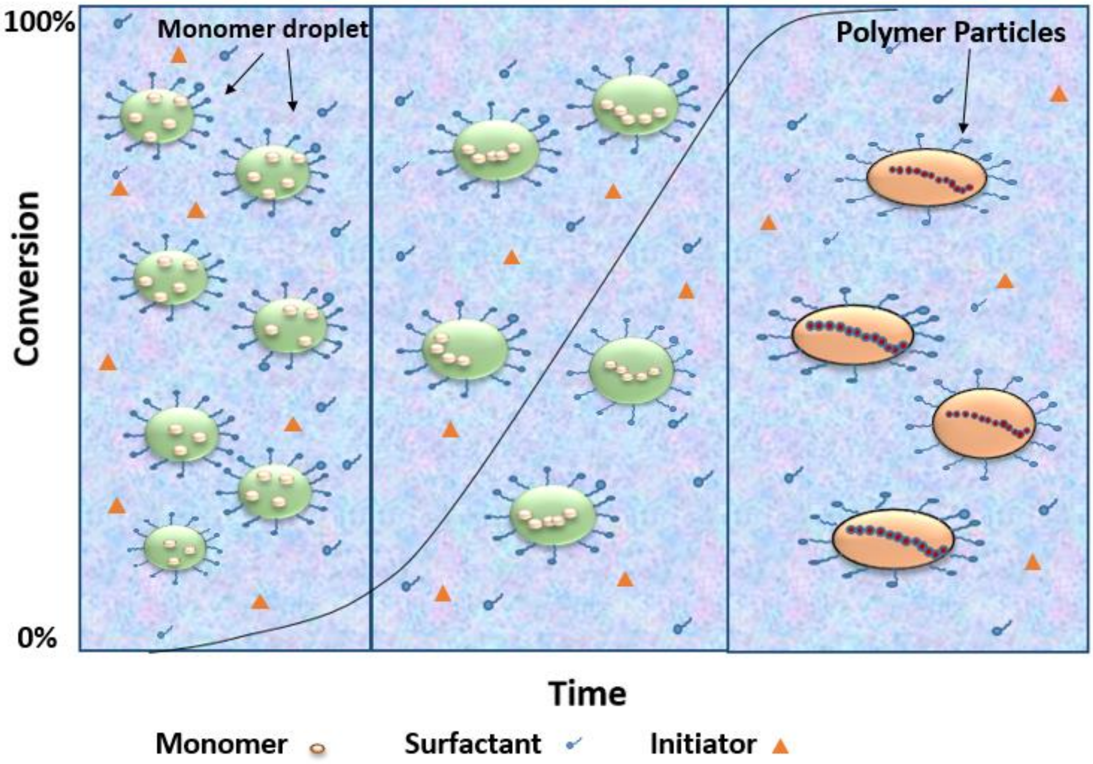


Figure 1.2. Emulsion polymerization mechanism.[46]

1.3. Emulsion polymerization via FRP

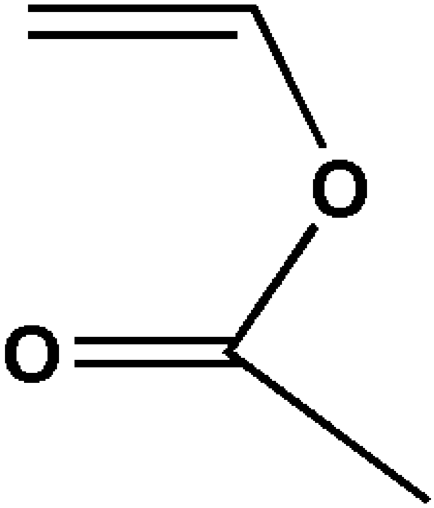
The emulsion polymerization mainly proceeds via a free-radical mechanism.[35] Free-radical polymerization (FRP) is preferred over ionic polymerization due to its advantageous qualities.[32]

This polymerization process consists of three basic steps: initiation, propagation, and termination as explained above.[7,34] In emulsion, a limited quantity of free radicals that exist within a specific, tiny latex volume, as a result, the rate at which the reaction terminates via radical-radical contact or biradical coupling will differ from the rate at which reactions terminate in bulk or solution. Another vital aspect is that during the polymerization process, the monomer strength in the monomer-swollen latex particles is maintained at a consistent level through diffusion. Hence, the rate of propagation of each latex particle will remain constant, and the total rate of the polymerization reaction have an impact on the total number of latex particles.[17] In emulsion free radical polymerization, non-solvated radical growth continues in the particle during chain transfer to the monomer. When the monomer concentration reduction happens in the particle, a reduction in the rate of chain transfer is caused. Thus, the number of longer particle radicals increases almost inversely with monomer strength and the polymerization rate does not change. After the achievement of 90% conversion, the monomer volume in the aqueous phase slowly decreases, radical termination is preferred, and the rate of polymerization reduces.[47]

1.4. Literature review

1.4.1. Vinyl acetate (VAc)

Vinyl acetate is a very important monomer for the paint, coating and adhesive industries. The chemical structure of the VAc is shown in Scheme 1.2. The copolymers of vinyl acetate are eco-friendly and have drawn a lot of interest in the industry due to their widespread applications.[19,48,25] The use of homopolymer latex of polyvinyl acetate was started in Germany around 1935. Since then interest in developing polyvinyl acetate-based material has been growing gradually over the years.[17] VAc (macro) radicals are very reactive toward other vinyl comonomers.[49] Therefore, the negative aspects of the homopolymer of VAc (PVAc) may be eliminated via co-polymerization or terpolymerization with other vinyl co-monomers. The most common methods to prepare such polyvinyl acetate-based copolymers or terpolymers are solution, bulk, suspension polymerization and emulsion polymerization. The emulsion polymerization approach is observed as a more useful method to prepare polyvinyl acetate-based material.[50,39] Typically, PVAc-based polymers are utilized in powder form in the construction and adhesives sectors. This polymer is used to create various tile adhesives, wood adhesives, and other adhesive formulations. In the paper industry and paint technology, it is utilized as a binder for latex paints, which are based on acrylics.[51-56] The emulsion PVAc based copolymer or terpolymer latexes offer superior film-forming qualities, low volatility, and are greener when using water as a solvent.[19]

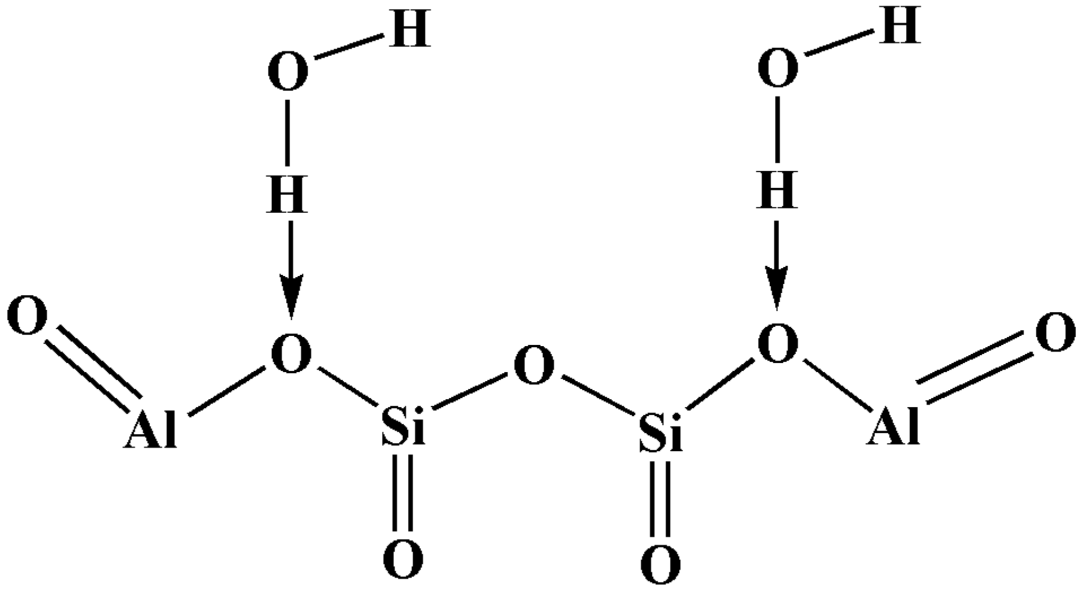


Scheme 1.2. Structure of vinyl acetate (VAc) monomer

The glass transition temperature (T_g) of a polymer defines its applicability. However, T_g can be tuned to make it useable for some specific types of applications. The T_g of PVAc (medium molecular weight) is 28 to 31°C.[19] This can be tuned via copolymerization or terpolymerization with different co monomers to extend its range of applications.

1.4.2. Kaolin clay

The “kaolin” word come from the Chinese word "Kauling" and the theoretical composition 46.54% of SiO_2, 39.5% of Al_2O_3, 13.96% of H_2O. Kaolin is a phyllosilicate clay mineral with the chemical formula $Al_2Si_2O_5(OH)_4$. It is commonly used for filling and paper coating.[57,58] Most nanoclays are found in silicate forms, particularly in certain layered silicates (phyllosilicates), including kaolin, montmorillonite, and talc. The layered arrangement of additive particles in the polymer matrix is often associated with improved barrier characteristics.[59] In the 1:1 di-octahedral structure (Scheme 1.3) of kaolin clay, one octahedral $Al_2(OH)_4$ alumina plate is connected to one tetrahedral SiO_4 silica by means of an oxygen atom.[58] Pseudohexagonal is the shape of a well-ordered kaolinite crystal; nevertheless, arrangements can range from extremely high-degree crystals to poorly-ordered crystals with unknown shapes.[60] Clays are easily accessible silicate minerals that occur naturally. This has led to their widespread use in novel chemical processes, owing to the low cost and eco-friendly nature of the material.[61,62]

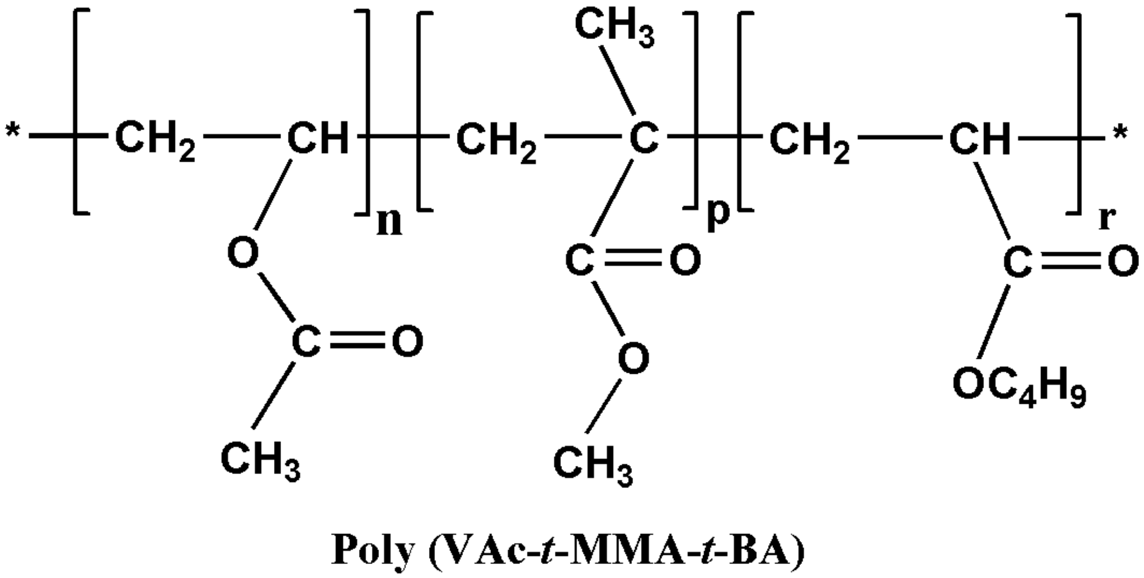


Scheme 1.3. Kaolin clay structure[63]

The addition of kaolin enhances the surface roughness. Kaolin clay has properties mainly eco-friendly, availability, cheapness[59] and good thermo-chemical stability, corrosion resistance, and exceptional radiation shielding capability. This useful character has become more prevalent among scientists.[64] Kaolin also influences some important properties of paper appearance and printability (gloss, smoothness, brightness, and opacity of paper). The modified kaolinite can improve in good filler particle compatibility and dispersibility in a particular polymer matrix.[65] Kaolin is a useful material in industry.[65,60] Kaolin is also characterized as soft and non-abrasive, and has a lower amount of heat conductivity and electricity pass. Some well-known applications of kaolin clay mineral are used in the coating of paper for paints. The plastics involve very rigid specifications containing particle size, colour brightness and viscosity.[60]

1.4.3. Vinyl acetate-based terpolymer

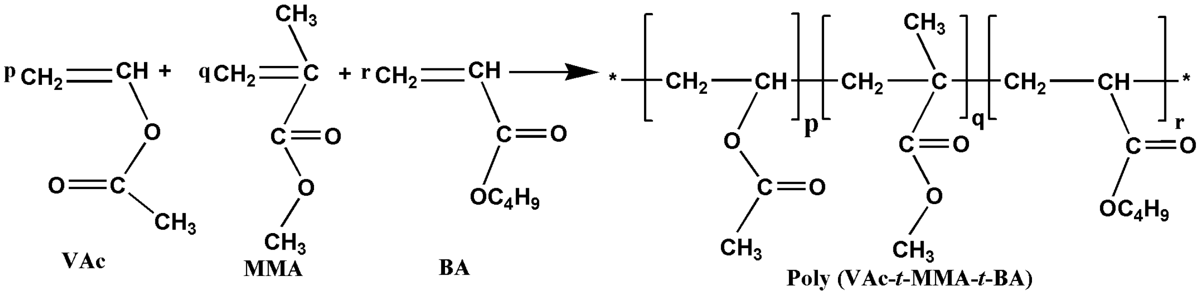
A terpolymer is a polymer which is made up of three different types of monomers. They provide several advantages over homo or co- polymers due to the combination of three different monomers. There are distinct works that describe the production and characterization of different terpolymers. The films made from them have various advantageous qualities for a range of uses. Scheme 1.4 shows the ter-polymerization of vinyl acetate with methyl methacrylate (MMA), and butyl acrylate monomers in emulsion. Urrtabizkaia et al. studied the preparation and kinetics of this terpolymer.[21]



Scheme 1.4. Structure of poly (VAc-*t*-MMA-*t*-BA) terpolymer

The VAc-based terpolymer has numerous potential applications. They exhibit better properties than the homopolymer of VAc. The semi-continuous and batch processes are most useful for the preparation of this vinyl acetate-based terpolymer.

The semi-continuous process is an industrially beneficial process used for the production of several important synthetic polymers.[9,66] The monomer and the other required chemicals are added to the stirred batch reaction vessel fitted with a reflux condenser.[67] This process is useful to have control over molecular weight and its distribution.[68] Preparation of VAc-based terpolymer by semi-continuous emulsion polymerization has been reported by several researchers.[69-72] The use of a semi-continuous process for the PVAc synthesis was initially reported by Elgood et al. in 1964.[17] Urretabizkaia et al. used this process to prepare terpolymer of VAc with MMA and BA using potassium persulfate (KPS) as initiatorand ammonium salt of sulfated nonyl phenoxy poly(ethyleneoxy) ethanol (4 ethylene oxide) (Alipal CO-436), as an emulsifier (Scheme 1.5).[72] In another approach, Unzue et al. used the same set of monomers and polymerization conditions to prepare a terpolymer of VAc. They carried out polymerization using two different emulsifiers, SDS and alipal CO-436. They observed that the quantity of coagulum formed was more when emulsifier SDS was used as a emulsifier.[73] In the same manner, Urretabizkaia et al. prepared the same terpolymer but with high solid content.[20] In another work, Othman et al. reported the preparation of terpolymer of VAc with MMA and BA using the same set of ingredients.[74] In another investigation, Staicu et al. reported the preparation of two kinds of terpolymers using BA, VAc, and acrylic acid (AA) in one combination and 2-ethylhexyl acrylate (2EHA), VAc, and acrylic acid (AA) in the other combination. In the semicontinuous emulsion polymerization technique they used KPS as an initiator and SDS and slovasol 2510 (SVS) as emulsifiers. The prepared terpolymers showed outstanding adhesive qualities.[24]



Scheme 1.5. Synthesis of poly (VAc-*t*-MMA-*t*-BA) via emulsion polymerization

Batch emulsion is a laboratory process used to study reaction mechanisms, new latex products, betterment of kinetic data, and scale up.[75] The batch method is a simple one where all required ingredients are added to the reactor at the beginning. The polymerization is started by adding monomers and application of heat.[67] In the industry, the use of batch processes is limited due to the inherent restrictions in heat transfer and poor control over the copolymer composition.[31] To overcome these disadvantages, semi-batch and continuous processes are used in industries.[67] In a semi-batch process, some ingredients are added to the reactor at the beginning and others are added continuously or in a controlled way.[76] This process is preferred by the industry.[31] Batch is another useful process which has been used by many research groups to prepare VAc-based terpolymer. Huo et al., 1988 reported the first successful preparation of VAc based terpolymer with 2-Ethylhexyl acrylate (2EHA), and AA in batch and semi-batch process.[77] They used KPS as initiator and aerosol A-102 as emulsifier. In another work, Canegallo et al. prepared the terpolymer of VAc with MMA and BA in semi-batch as well as in batch processes. They also used KPS as initiator and SDS as surfactant in this emulsion polymerization.[78] Tang et al. reported the preparation of two types of terpolymers based on VAc in batch process. In one type VAc was polymerized with methyl acrylate (MA) and AA and in the other type, VAc was polymerized with MA and acrylamide (AM) using KPS as initiator and SDS as emulsifier.[79] In a similar manner, Hua et al. synthesized terpolymer of VAc with MMA and BA using APS as initiator and SDS as emulsifier.[80]

Vinyl acetate-based terpolymer exhibits a wide range of applications due to its good mechanical and chemical properties. This type of polymer is used in adhesives and paint applications. Table 1 summarizes the usefulness of VAc-based terpolymers highlighting their preparation process, used co-monomers, and applications.

Table 1.1. Vinyl acetate based terpolymer and some of their characteristics

Polymer Name	Co-monomer, Initiator, Surfactant	Characteristics	Ref.
Poly (Sty-*t*-VAc-*t*-VOH)	Sty, VAc, vinyl alcohol (VOH), APS, tributyl amine (TBA), pluronic F-68	• Copolymerization rate is high for emulsion polymerization than for solution polymerization.	81
Poly (VAc-*t*-MMA-*t*-AM)	VAc, MMA, AM, KPS, sodium 1,2-bis(5-ethylhexyl oxy carbonyl) ethanesulfonate, α-(4-nonyl-phenyl)-ω-hydroxy tetra contakis (oxy ethylene)	• Good Stability polymer formed	82
Poly (VAc-*t*-MMA-*t*-BA)	VAc, MMA, BA, AA, KPS, alipal CO-436	• A good agreement between experimental results and model predictions was achieved.	21
Poly (MMA-*t*-BA-*t*-VAc)	MMA, BA, VAc, KPS, SDS, alipal CO 436	• The homogeneity of the terpolymer improved when the monomer	73

		accumulated in the reactor decreased	
Poly (BA-*t*-MMA-*t*-VAc)	BA, MMA, VAc, APS, SDS	• ATR-FTIR probe used as a polymerization monitoring tool • Homogeneous product formed	80
Poly (MMA-*t*-VAc-*t*-BA)	MMA, BA, VAc, KPS, SDS	• High yield • Improved mathematical modeling efforts	83
Poly (BA-*t*-VAc-*t*-AA)	BA, VAc, AA, KPS, dodecylthiol	• Good adhesive nature	84
Poly (BA-*t*-VAc-*t*-AA)	BA, VAc, AA, KPS, SDS, slovasol 2510	• Better adhesive performance • All the latices have pseudoplastic nature	24
Poly (2EHA-*t*-VAc-*t*-AA)	2-EHA, VAc, AA, KPS, SDS, slovasol 2510	• Better adhesive • All the latices have pseudoplastic nature	24
Poly (ATESPC-*t*-VAc-*t*-2-EHA)	Allyl 3-(triethoxysilyl) propylcarbamate (ATESPC), PU, VAc, 2EHA, KPS, poly propylene glycol 1000, triethyl amine, 3-iso cyanatopropyl	• Improved thermal stability	85

P(VAc-*co*-2EHA)/PU/Si	PU, VAc, 2-EHA, KPS, Polypropylene glycol1000, triethylamine, 3-isocyanatopropyl	• Better thermal stability • Improved the water resistance of PU latex	85
Poly (Sty-*t*-BA-*t*-VAc)	Sty, BA, VAc, APS, abex 26-S, rhodia, disponil AES 13 IS	• Improved flow behavior • Terpolymer solution exhibited non-Newtonian behavior	86
Poly (VAc-*t*-BA-*t*-HEA)	VAc, BA, HEA, KPS, cetyltrimethylammonium bromide (CTAB)	• Used to control the molecular weight • Control the particle size, and viscosity over a wide range by feeding HEA with varying concentrations	87
Poly (VAc-*t*-BA-*t*-AMPS)	VAc, BA, AMPS (2-acrylamido-2-methyl propane sulfonic acid), KPS, hydroquinone	• Improved the thermal stability • Stable and mono disperse polymer latex formed with small particle size. • Low gel content, high conversion	88
PVOH-graft-poly (VAc-*co*-VeoVa10)	VAc, VeoVa10, PVOH, KPS, disponil AFX4060	• Used as coatings	89

Poly (VAc-*t*-acrylic-*t*-epoxy (FVAE))	VAc, acrylic, epoxy (FVAE), KPS, SDS	- Application in stone protection	90
Poly (VAc-*t*-BA-*t*-VEVA)	VAc, vinyl ester of versatic acid (VEVA), BA, AA, AM, KPS, SDS	- Used as polymer modifier - Improved the quality of paving and reduce the cost	91
Poly (VAc-*t*-BA-*t*-VV)	VAc, vinyl versatate(VV), BA, AA, AM, KPS, SDS	- Good adhesion properties - The hydrophobic monomer increased the viscosity.	92

1.5. Vinyl acetate-based polymer/clay composites

Polymer/clay composite (Figure 1.3.) is a well-defined form of the microscopic blend of two or more polymeric, inorganic materials.[26] Clays are naturally occurring silicate minerals. There are a few reports that detailed the beneficial effect of clays in emulsion polymerization.[61,93-95] The polymer/clay composites are an unique materials because of their good strength and thermal stability, flexibility and high-quality moldable properties.[27] Advanced qualities such as gas and liquid barrier, mechanical, thermal, and fire retardant characteristics were also made possible by composite materials developed from polymer latexes.[28] These growths generally found depending on vital role of silicate layers on the degree of dispersion and the dimension of the clay. The movement of the polymer chains is slowed down by the clay mixed into the polymer matrix, which has a strong reinforcing effect.[96] The one of new methodology for synthesis of Polyaniline (PAn)/clay nanocomposite improves the fine electrical conductivity and exceptional physical properties.[97] Polymer/clay nanocomposites also have use in purify process of wastewater and for this purpose polystyrene/TiO_2-NWs nanocomposites material is use. Youssef et al. looked into a novel technique to prepare polystyrene/organoclay (CTA-MMT) nanocomposites via situ emulsion polymerization. This process was a capable and economically decent technique for separating organochlorine pesticides from wastewater.[98] Hydrogels derived from nanocomposite materials are widely used in many different applications, including tissue engineering, medical technology, food packaging, oil development, sensor and actuator arrangements, and separation and bioseparation.[99]

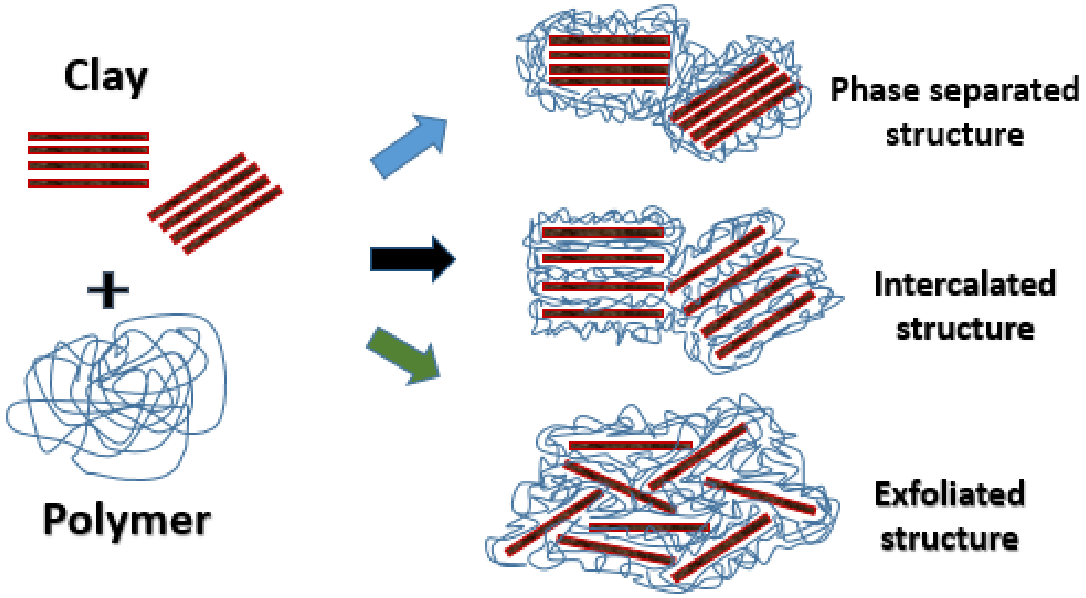


Figure 1.3. The interaction structure between polymer and clay in composites.[100]

Fundamentally, the structure of organic/inorganic hybrid material composites is elucidated as a result of mixture of the clay intercalation with the liquid polymer and the intercalation group is aluminosilicates.[101] These materials offer several fascinating uses in a variety of industries, such as reinforced coatings, surface patterning, electrical applications, and biology. The small hydrophobic RAFT agents attribute less control of the molar mass and to overcome that problem, Ferguson et al. employed water-soluble amphipathic macromolecular RAFT agents. In another approach, Guimaraes et al reported the synthesis of RAFT-mediated polymer/Laponite particle production. The latex particles had an excellent control molar mass.[102] Modified clay offers the major change in its physico-chemical properties that role in a wide series of applications. The physico-chemical properties commonly particle size, surface area, surface charge, porosity, absorptive and cation exchange capacity etc. are changed by the modification of clay. Similarly, biodegradable poly-lactic acid (PLA)-clay based nanocomposites are beneficial in wrapping of cosmetics industry.[103] Although polymer/montmorillonite clay nanocomposites also show exceptional flammability and mechanical properties.[104] In case of PLS nanocomposites physical properties arises from intercalation or exfoliation of the clay layers inside the polymer matrix, diversified potential is applied for the incorporation of superior molecules within the clay to help clay dispersion and reach better properties.[105]

Table 1.2. Vinyl acetate/clay composites their application and properties

Polymer/clay composites	**Polymer matrix**	**Clay**	**Properties and application of composites**	**Ref.**
Polyethylene-*co*-vinyl acetate (EVA)/ magadiite nanocomposite	Polyethylene-*co*-vinyl acetate	Magadiite	▪ Best flammability performance	104
Polyvinyl acetate/ montmorillonite nanocomposite	Polyvinyl acetate	Montmorillonite	▪ High glass transition temperature ▪ Better thermal stability	106
Polyvinyl acetate/ Southern Clay	Polyvinyl acetate	Southern Clay	▪ Improved the thermal stability ▪ Used as wood adhesive	107
Poly (vinyl acetate)/ Eziulo clay	Polyvinyl acetate	Eziulo clay	▪ Used in the surface coatings industry	108
Poly(vinyl acetate)/montmorillonite	Poly(vinyl acetate)	Montmorillonite	▪ Improved physicochemical, mechanical and thermal properties, ▪ Industrial application such as adhesives	110
Poly(ethylene-co-vinyl acetate)/ silver-calcined scallop shell powder	Poly(ethylene-co-vinyl acetate)	Silver-calcined scallop shell powder	▪ Good antibacterial properties ▪ Better tensile strength and thermal properties	111

1.5. Scope and objectives

Vinyl acetate is an interesting monomer for the production of new polymeric materials. VAc-based polymers are eco-friendly and known for their strong adhesive and binding abilities. Therefore, the use of vinyl acetate is on the rise in different areas. The homopolymer of vinyl acetate lacks good properties and therefore it is not suitable for use as such. However, co- and terpolymerization of VAc with other monomers may lead to polymers with improved properties. Thus, they can be made suitable for many applications.

In most cases, vinyl acetate is copolymerized with various types of acrylate and methacrylate monomers. They are widely used in adhesives, carpet backing, and exterior and interior paint applications. These VAc-based co- and terpolymers are manufactured mostly by emulsion polymerization in industry. Moreover, the obtained latexes are also eco-friendly.

Further enhancement of properties of these VAc-based co- and terpolymers may be observed through the preparation of composites with clays. Clays such as Kaolin may be chosen for this purpose. Kaolin is one of the most valuable, environmentally friendly clay minerals that have a wide range of industrial uses. It is readily available in nature, environmentally friendly, it has good thermochemical stability, corrosion resistance, and has remarkable radiation shielding power. Kaolin also act as a filler for a VAc-based polymer matrix. Uniform distribution of clay into VAc-based ter polymer matrix may lead to improvement of properties by many folds.

The objectives of this work are to study the copolymerization and terpolymerization of VAc with other monomers in emulsion using conventional free radical polymerization. One of the objectives of this work is to find out the optimized polymerization conditions for the synthesis of a VAC-based terpolymer with the best properties. This terpolymer would be used as a matrix for the preparation of terpolymer/clay composites. The properties of the terpolymer/clay composites would be evaluated to find their suitable applications.

In general, a polymer/clay composite possesses both organic and inorganic properties, which include flexibility and high-quality moldability, as well as high strength and thermal stability. Literature study prevailed that VAc-based polymer/clay composites offer several advantages such as separating organochlorine pesticides, sensor and actuator arrangements, oil improvement, and food packaging. These composites are also being used in separation, tissue engineering, medicine, electrical applications, biology, and reinforced coatings. The reinforcing effect of clay in these polymer/clay composites may be observed through the enhancement of properties like electrical conductivity, and mechanical properties.