



Review Article

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Emulsion Prepared Vinyl Acetate-Based Terpolymer: a Review on Their Preparations, Properties, and Applications

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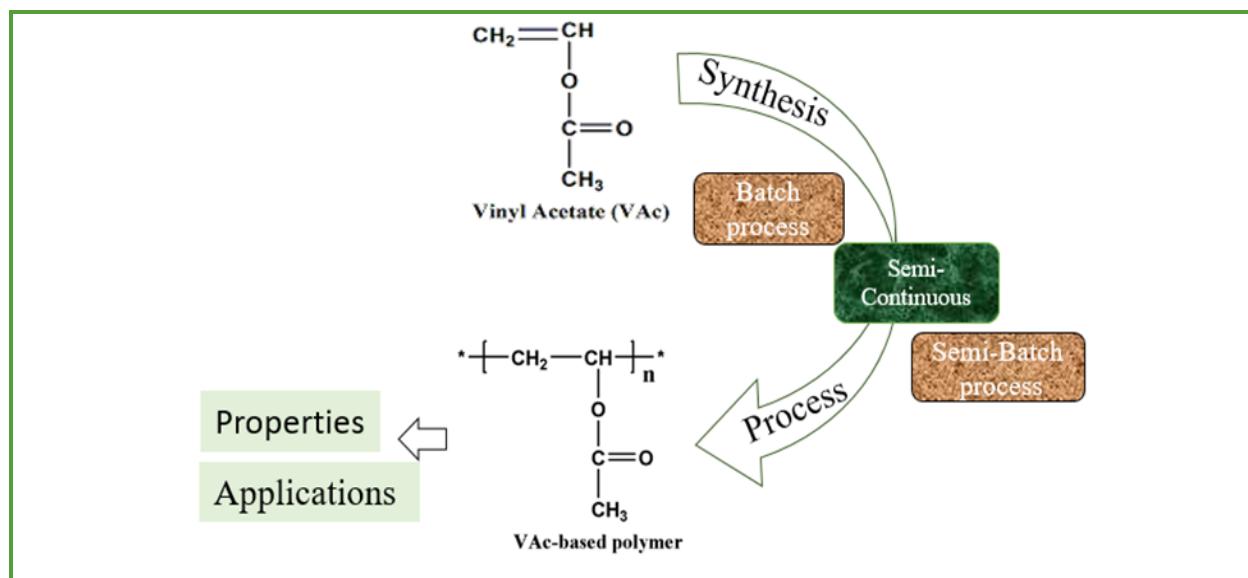
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ABSTRACT

Vinyl acetate (VAc) based terpolymers exhibit some outstanding properties. In this review, we report different types of vinyl acetate (VAc) based terpolymers, their preparation via emulsion polymerization, properties, and applications. Emulsion is an environment-friendly industrial polymerization technique. Latex, the end product of emulsion polymerization can be used directly for certain applications. This draws the interest of the researcher to use it for co- and ter polymerization. Terpolymerization of vinyl acetate with different monomers leads to the preparation of terpolymers with some excellent properties. Various types of processes used for the preparation of such terpolymer were reviewed and discussed in this report. This review also focuses on the morphological and thermal behavior of VAc-based terpolymers for understanding the polymerization chemistry and also the progress in this field.

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Graphical Abstract



Introduction

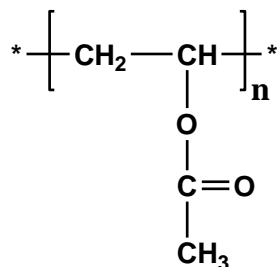
Emulsion polymerization (vinyl acetate)

Emulsion polymerization covers a large part of the global industry for built-up well-designed polymer products [1]. This technique earned great attention to be used in manufacturing from the Second World War [2]. Polymers are popular mostly due to their tunable mechanical and viscoelastic properties [3]. Accordingly, they are being used for the preparation of polymer composites [4-8]. Homo and copolymers of vinyl acetate are mainly prepared by emulsion polymerization and they have widespread use in industry [9-11]. The utility of latexes of vinyl acetate-based copolymer with branched vinyl ester and vinyl acrylic has now been spread [12]. Scheme 1 shows the chemical structure of a PVAc polymer. PVAc-based polymer in powder form is used in the construction and adhesives industry (tile adhesives, wood glues, and other adhesive formulations). They are also used in paper and paints as a binder [13-16]. In recent times, the importance of research optimization has been

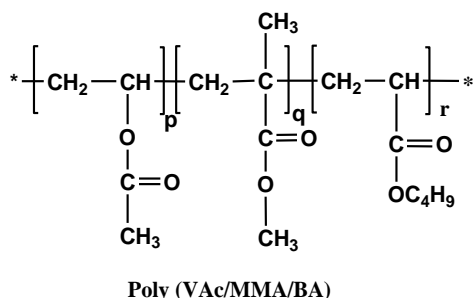
extensively studied, which helps to minimize the cost of production by optimization of parameters like performance, productivity, and efficiency [17].

Emulsion polymerization is a very useful and productive technique for the preparation of low-cost PVAc polymer. The use of water as a solvent and low volatility makes emulsion polymerization a green technique. Green solvent has attracted the attention of researchers due to its benign characteristics [18]. Therefore, the polymers production via emulsion polymerization rises gradually. Moreover, these emulsion-prepared waterborne polymer lattices exhibit very good film-formation properties [2].

Recent literature shows the applicability of PVAc copolymer in the cold filter plugging point where biodiesel blend is used as fuel [19]. It shows synergistic effects on diesel fuel too [20]. PVAc-based terpolymer is also used to replace the volatile liquid electrolyte to improve the efficiency of the dye-sensitized solar cell [21].



Scheme 1. Structure of polyvinyl acetate (PVAc)



Scheme 2. Structure of poly (VAc/MMA/BA) terpolymer

The disadvantages of a homopolymer of VAc may be overcome by preparing its terpolymer with two different monomers. [2]. There have been several such reports, which reported the synthesis and properties of PVAc based terpolymer. Urrtabizkaia *et al.* described the synthesis of PVAc-based terpolymer with methyl methacrylate (MMA) and butyl acrylate (BA) via emulsion polymerization (Scheme 2) [22].

Although there have been other polymerization techniques, those may be used for the polymerization of VAc, but we have chosen the emulsion technique over others because of its eco-friendly nature.

Emulsion polymerization

Emulsion polymerization is one of the outstanding polymerization techniques utilizing a free radical mechanism. It is a heterogeneous system with one aqueous and a non-aqueous phase. In the aqueous phase, surfactant

molecules form micelle and help to grow polymer chains inside it. [23] Non-aqueous phase mainly contains the monomers [24]. The emulsion-prepared polymers have several advantages [25]. They may be prepared by varying variables like different monomers, surfactants, and initiators that leave a particular end group in the polymer chains [26]. Most of the commercial polymers like polystyrene, polybutadiene, etc. are prepared by emulsion polymerization from the nonpolar monomer styrene, butadiene, etc. [27]. Surfactant also plays an important role in emulsion polymerization. It regulates particle size, number, distribution, latex stability, and the rate of polymerization [28]. Sometimes electrolytes are also used to initiate the polymerization. These electrolytes may contain monovalent cations, typically sodium, or potassium, and anions like chloride, sulphate, phosphate, bicarbonate acetate, etc. [29]. F. Bayer invented emulsion polymers using diene monomers in the years 1909 to 1912 [30]. The emulsion technique gained momentum from then. This has been used nowadays to prepare polymers for various industrial applications like automobile, textile, and construction works [31]. The latexes obtained as an end product of emulsion polymerization may be used directly in paints, coatings, and adhesive materials [32-34]. This technique has shown its potential for the synthesis of polymer-coated inorganic nanoparticles, and functional polymers for electronics, and biomedical fields [35, 36]. Emulsion polymerization has several advantages. This polymerization proceeds at a high polymerization rate and offers good conversion. Therefore, high molecular weight polymer may be obtained by this technique [37]. The polymerization may be carried out at relatively lower temperature (0 °C to 80 °C). It is a simple technique which uses benign solvents like water. In this polymerization,

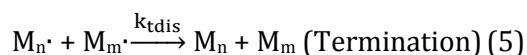
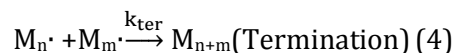
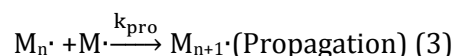
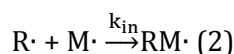
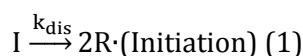
highly concentrated and transparent latexes may be obtained with comparatively low viscosity [32]. However, the polymer purification obtained by this technique requires additional requirements which may be added as a disadvantage of this technique [32]. Moreover, it cannot be used for condensation and ionic polymerization [38].

Emulsion polymerization via FRP

Free-radical polymerization (FRP) is a polymerization method that proceeds via involvement of free radicals for the growth of polymer chains [23]. Emulsion polymerization

is mainly preceded via free-radical mechanism. Therefore, it is important to understand the free radical chemistry in this technique [39].

FRP is an ideal method that plays important role in the production of many commercial polymers in industry. More than 50% of all polymers are manufactured by FRP [40, 41]. Because, it is a simple method and can be used to polymerize almost all vinyl monomers, FRP is tolerant to impurities/functionality present in the system. It is applicable in wide range of polymerization temperatures [42]. FRP follows three steps: initiation, propagation, and termination [43]. Schematically, various steps involve in FRP are shown below.



In the initial step, radicals ($R\cdot$) are generated on decomposition of the initiators. The rate constant for this step is k_{in} . In the second step, the free radicals induce the propagation by attacking fresh monomers. In propagation, the polymer chain grows with the addition of more fresh monomers to the growing chains. The rate constant for this step is k_{pro} . Termination is the third step which leads to the formation of polymer either by termination (rate constant for this step is k_{ter}) or by disproportionation (rate constant for this step is k_{tdis}).

Synthesis of vinyl acetate-based terpolymer via emulsion polymerization

The VAc-based terpolymer has numerous potential applications. They exhibit better properties than the homopolymer of VAc. In this section of this review, the preparation of vinyl acetate-based terpolymer via semi-continuous and batch processes is discussed.

Semi-continuous

The semi-continuous process is an industrially beneficial process and is used for the production of several important synthetic polymers [44, 45]. In this process, particle nucleation is expected to take place mostly in the aqueous phase [46]. The monomer and the other required chemicals are added to the stirred batch reaction vessel fitted with a reflux

condenser [47]. This process is useful for maintaining control over molecular weight and hence distribution [48]. In the semi-continuous emulsion polymerization process, two types of rates are maintained: (a) The rate of polymerization is kept high compared to the feed rate or (b) the feed rate is kept high as compared to the polymerization rate [30]. The use of a semi-continuous process for the PVAc synthesis was initially reported by Elgood *et al.* in 1964 [30].

Batch process

Batch emulsion is a laboratory process used to study reaction mechanisms, new latex products, betterment of kinetic data, and scale-up [49]. 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 [47]. 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 [39]. To overcome these disadvantages, semi-batch and continuous processes are used in industries [47]. The continuous method is applied for large-scale manufacturing, whereas batch and semi-batch are usually used for low-volume but high-value productions [50]. In a batch reactor, all material has the same residence time but in a continuous reactor, they have a broad range of residence times [51, 52]. 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 [53]. This process is preferred by the industry because it offers the mixing of all ingredients well [39]. In semi-batch emulsion polymerization, the main feature of particle nucleation is a secondary nucleation which is caused by the monomer in the emulsion feed [54]. Secondary nucleation affects the particle size distribution and solid

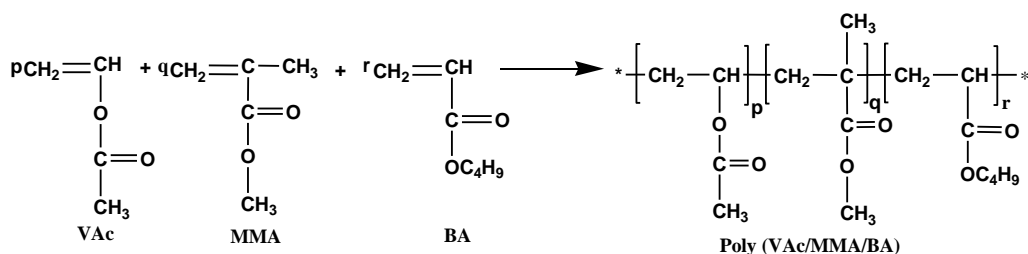
content of polymer latexes [55]. Batch polymerization leads to low-viscosity latex [56]. Semi-batch process is an essential process used for the preparation of polymers for several applications, including coatings, glues, elastomers, etc. [53]. This process offers control of the composition to avoid bulky compositional drifts [57]. However, higher molecular weight polymers may be prepared in the batch process rather than in the semi-continuous process [48].

Vinyl acetate terpolymer via semi-continuous emulsion polymerization

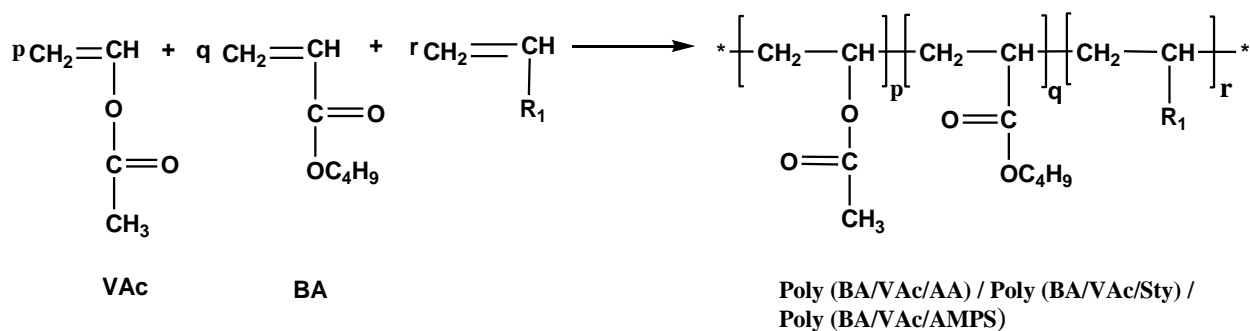
Preparation of VAc-based terpolymer by semi-continuous emulsion polymerization has been reported by several researchers. Urretabizkaia *et al.* used this process to prepare terpolymer of VAc with MMA and BA using potassium persulfate (KPS) as initiator and ammonium salt of sulfated nonyl phenoxy poly(ethyleneoxy) ethanol (4 ethylene oxide) (Alipal CO-436), as an emulsifier (Scheme 3) [55-58]. In another approach, Unzue *et al.* used the same set of monomers and polymerization conditions to prepare a terpolymer of VAc. They tried polymerization with two different emulsifiers, SDS and Alipal CO-436. They reported that more homogeneous terpolymer was formed when the quantity of monomer accumulated was less. The quantity of coagulum formation was found to be more when emulsifier SDS was used [59]. In the same manner, Urretabizkaia *et al.* also prepared the same terpolymer with high solid content [60]. In another work, Othman N *et al.* reported the preparation of terpolymer of VAc with MMA and BA using the same set of ingredients [61]. 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 (Schemes 4 and 5). In the semi-

continuous emulsion polymerization technique, they used KPS as an initiator and SDS and Slovasol 2510 (SVS) as emulsifiers. The prepared terpolymers showed outstanding adhesive qualities [62]. In a similar approach, Naghash *et al.* used semi-continuous emulsion

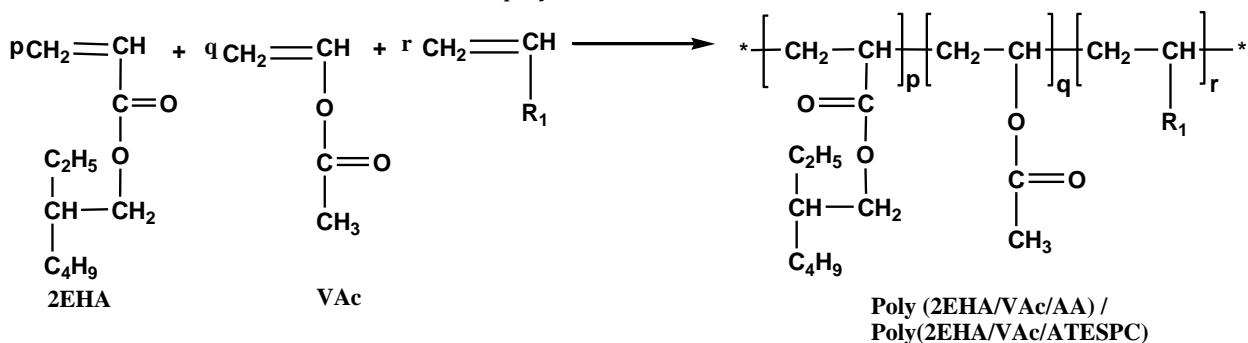
polymerization to prepare a terpolymer of VAc with allyl 3-(triethoxysilyl) propyl carbamate (ATESPC) and 2-EHA (Scheme 5) using ammonium persulfate (APS) as initiator at 65 °C [63].



Scheme 3. Synthesis of poly (VAc/MMA/BA) via emulsion polymerization



Scheme 4. Synthesis of poly (BA/VAc/AA) / poly (BA/VAc/Sty) / poly (BA/VAc/AMPS) via emulsion polymerization



Scheme 5. Synthesis of poly (2EHA/VAc/AA) poly or (2-EHA/VAc/ATESPC) terpolymer via emulsion polymerization

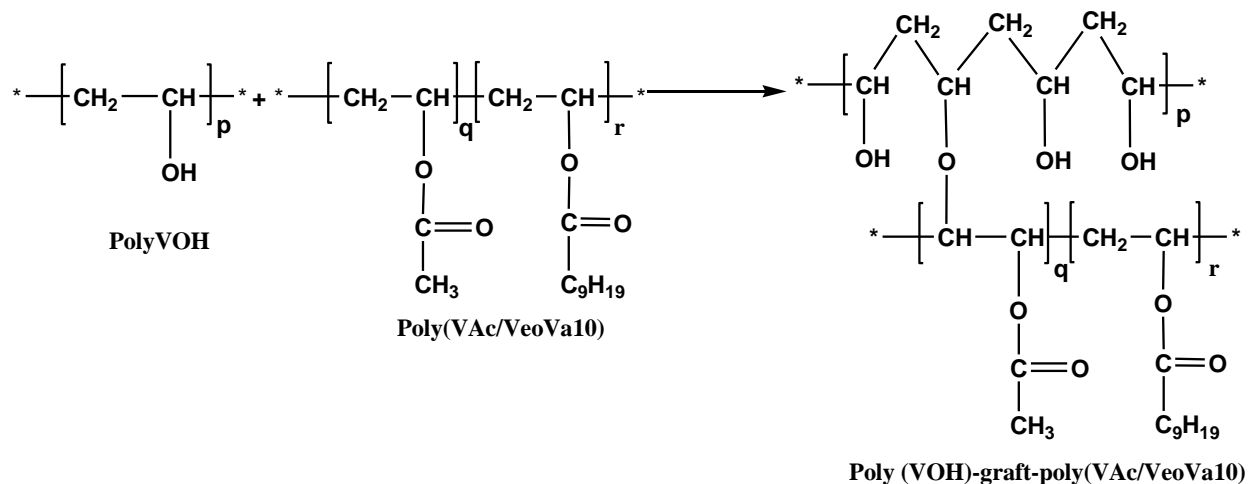
In another work, Castro *et al.* synthesized terpolymer of VAc with styrene (Sty) and BA at 70 °C via a semi-continuous emulsion process using APS (ammonium persulfate) as Initiator and Abex 26-S, Rhodia and Disponil AES 13 IS as emulsifiers (Scheme 4) [64]. In another attempt, Zhang *et al.* reported the preparation of a VAc-based terpolymer with BA and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) by an emulsifier-free emulsion polymerization initiated by KPS at 90 °C through the semi-continuous process (Scheme 4) [65].

In a different approach, Agirre *et al.* studied the emulsion polymerization of VAc with poly (vinyl alcohol) (PVOH) and neodecanoic acid vinyl ester (Veova10) in a semi-continuous

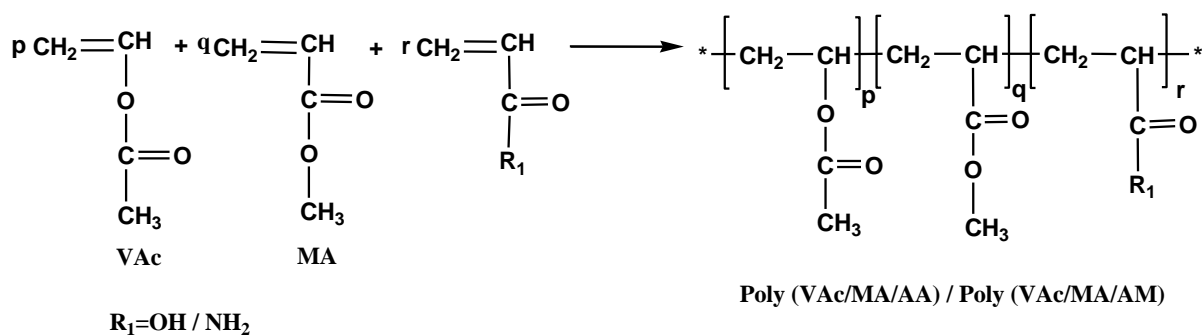
process. They used KPS as initiator and Disponil AFX4060 and SDS as emulsifiers. The polymerization was carried out at 67 °C to synthesize poly (VAc/Veova10) copolymer, and then and this copolymer was grafted to poly (vinyl alcohol) (PVOH) to synthesize PVOH-*g*-poly (VAc/Veova10) polymer (Scheme 6) [66].

Vinyl acetate terpolymer via batch emulsion polymerization

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 2EHA, and AA in batch and semi-batch process (Scheme 5) [67].



Scheme 6. Synthesis of PVOH-graft-poly (VAc/Veova10) terpolymer via emulsion polymerization



Scheme 7. Synthesis of poly (VAc/MA/AA) / poly (VAc/MA/AM) terpolymer via emulsion polymerization

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 (Scheme 3) [68].

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 (Scheme 7) and in the other type, VAc was polymerized with MA and acrylamide (AM) (Scheme 7) using KPS as initiator and SLS as emulsifier [69]. In another attempt, the batch process was used by Marc A. Dube *et al.* to prepare VAc-based terpolymer with MMA and BA using APS as initiator and Aerosol MA-80 (AMA-80) and Aerosol OT-75 (AOT-75) as emulsifiers (Scheme 3) [70]. The same type of terpolymer was also prepared by Araujo *et al.* using a batch process (Scheme 3) [71].

In a similar manner, Hua *et al.* synthesized terpolymer of VAc with MMA and BA using APS as initiator and SDS as emulsifier (Scheme 3) [72]. Following a similar approach, Othman *et al.* reported the synthesis of VAc-based terpolymer using KPS as initiator and SLS as emulsifier SLS (Scheme 3) [61]. In a different work, Jovanovic *et al.* synthesized VAc-based terpolymer with BA and AA via a semi-batch process using APS as an initiator (Scheme 4) [73]. In a different work, Monteiro *et al.* studied the ter-polymerization of VAc with vinylidene fluoride (VDF) and ethylene (EL) in a batch process (Scheme 8) [74]. In that emulsion polymerization, KPS was used as an initiator.

Properties of vinyl acetate based terpolymer

From the above section, the importance of preparation of VAc based terpolymer is seen due to their several useful properties. The

morphological and thermal properties of these ter-polymers are discussed in the following section.

Morphological properties

The morphology and particle size of these VAc based terpolymers depend on the time of polymerization and monomers' conversion [63]. It is also reported that the composite of these type of polymer exhibit various type of morphologies [30]. Naghash *et al.* investigated the morphology of VAc based copolymers using a scanning electron microscope (SEM). They observed that the particle size of the copolymer varies with the type of used comonomer. The size distribution of the particles is also influenced by the used comonomers. In few cases, they observed agglomeration which led to the formation of bigger particles [63]. In a similar manner, Meng *et al.* investigated the morphology of latex particles of VAc terpolymer (with BA and HEA) by transmission electron microscopy (TEM). They found that particle size of the polymer changes with the amount of HEA used in the polymerization [75]. Zhang *et al.* studied the morphology of latex particles of VAc based terpolymer by TEM analysis. They measured the size of the particles and found approximately 150 nm of size with uniform distribution [65]. In another work, they prepared VAc based terpolymer with acrylic and epoxy and also measured the particles size with the help TEM analysis. In few cases, the size of the particle was found to be 100 nm. They also observed core shell morphology in one case correspond to a particular composition [76]. Naser *et al.* reported spherical shape morphology of the terpolymer particles those were distributed uniformly throughout the latex as evident from the TEM micrographs. The dimension of the particles ranges from 214 nm to 1 μm [77]. From the above findings, it is clear

that vinyl acetate terpolymer latex is usually monodispersed in nature and particle size ranges from 100 to 1 μm . The size of the particles depends on amount and type of comonomers used and also on agglomeration.

Thermal properties

Thermal behavior of a polymer is very important to find their applicability. Glass transition temperature (T_g) and melting temperature (T_m), these are the two parameters that illustrate the thermal behavior of a polymer [30].

Among the researchers, Staicu *et al.* reported a single T_g for the terpolymer of VAc with 2EHA and AA. However, T_g of the homopolymers, poly (2-ethylhexyl acrylate) and poly (butyl acrylate) are much higher than the corresponding terpolymer [62]. Meng *et al.* reported the thermal analysis of the VAc based terpolymer, prepared with BA and HEA.

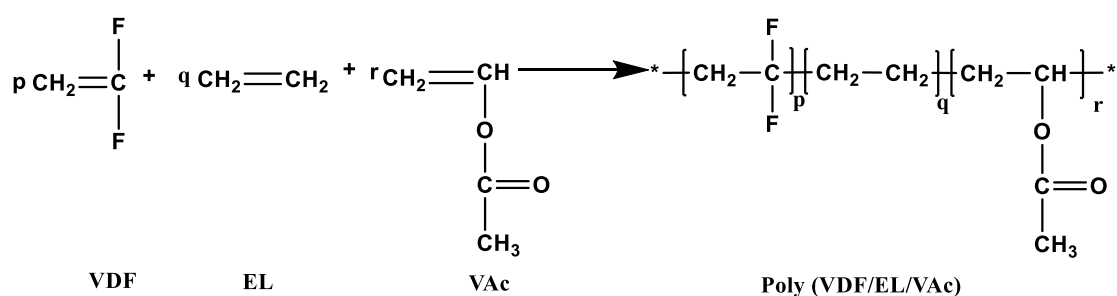
The prepared terpolymers exhibited only one T_g indicates that the monomers were randomly distributed in the terpolymer chain [75]. It was also observed that, the T_g value of the terpolymer is influenced by the amount of HEA units present in the terpolymer. T_g decreases with the increase of HEA amount. Thermal stability of the VAc based terpolymer increases with BA amount in the terpolymer chains. Zhang *et al.* also reported that decreases

the amount of VAc units, increases the thermal stability of the same terpolymer [65]. The decomposition temperature of VAc based terpolymer was 310 $^{\circ}\text{C}$ and 450 $^{\circ}\text{C}$ as reported by Naser *et al.* [77]. TGA analysis also showed that this terpolymer leaves residue 5.4% when heated to 600 $^{\circ}\text{C}$. Abd El-Wahab *et al.* also studied the thermal property of VAc based terpolymer using TGA analysis. The TGA curves of the terpolymer shows initial degradation, which starts at 200 $^{\circ}\text{C}$ and final degradation, which starts at 412 $^{\circ}\text{C}$. The sample was almost degraded at 510 $^{\circ}\text{C}$ leaving a residue 5.4 % of total weight [78].

This has been observed from the above discussion that thermal stability of vinyl acetate based terpolymer varies with the amount and type of comonomers used. It was also seen that stability increases with increasing concentration of acrylate monomer and decreasing VAc monomer.

Application of vinyl acetate terpolymer

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.



Scheme 8. Synthesis of poly (VDF/EL/VAc) via emulsion polymerization

Table 1. The preparation process, co-monomers details, and applications of vinyl acetate-based terpolymer

Sl. No.	Polymer Name	Process	Co-monomer,	Initiator, Surfactant	Application, Properties	Ref.
1	Poly (Sty/VAc/VOH)	Emulsion	Sty, VAc, VOH, and Tributyl Amine (TBA)	APS	Polymer form with higher Rate	[79]
2	Poly (2EHA/VAc/AA)	Semi-batch emulsion	2EHA, VAc, AA	KPS	Use as adhesive	[72]
3	Poly (VAc/MMA/AM)	Emulsion	VAc, AM, MMA,	KPS	High conversions Higher stability	[80]
4	Poly (MMA/BA/VAc)	Semi-continuous emulsion	VAc, BA, and MMA	KPS, Alipal CO436	High solids content	[53]
5	Poly (MMA/BA/VAc)	Semi-continuous emulsion	MMA, BA, VAc	KPS, SDS, Alipal CO 436	High solids content Polymer form with better homogeneity	[59]
6	Poly (MMA/VAc/BA)	Semi-batch and batch emulsion	MMA, VAc, BA	KPS, SDS	Uniform polymer	[68]
7	Poly (VAc/MMA/BA)	Semi-continuous emulsion	MMA, VAc, BA	KPS, Alipal CO-436	High solids content	[60]
8	Poly (VAc/MMA/BA)	Seeded emulsion	VAc, MMA, BA	KPS, Alipal CO-436	High solids content	[81]
9	Poly (VAc/MMA/BA)	Semi-continuous	VAc, MMA, BA, AA	KPS, Alipal CO-436	High solids content	[22]
10	Poly (BA/MMA/VAc)	Emulsion	BA, MMA, VAc	APS, AMA-80, AOT-75	—	[82]
11	Poly (VAc/AA/AM) and Poly (VAc/MA/AA)	Batch emulsion	VAc, MA, AA, and AM	KPS and SDS	Application in textile The polymer particle size of 120 nm	[69]
12	Poly (BA/MMA/VAc)	Batch emulsion	BA, MMA, VAc	APS, AMA-80, and AOT-75	—	[70]
13	Poly (MMA/BA/VAc)	Batch emulsion	MMA, BA, VAc	KPS, SDS	Higher number of particles Homogeneous product	[71]
14	Poly (BA/MMA/VAc)	Batch emulsion	BA, MMA, and VAc	APS and SDS	Used as a polymer monitor Homogeneous product	[72]
15	Poly (MMA/BA/VAc)	Batch and	MMA, BA,	KPS and SDS		

		semi-continuous emulsion	and VAc		—	[61]
16	Poly (BA/VAc/AA)	Semi-batch	BA, VAc, AA, KPS		Used as adhesive	[73]
17	Poly (BA/VAc/AA), Poly (2EHA/VAc/AA)	Semi-continuous emulsion	BA, VAc, AA, and 2-EHA	KPS, SDS	Used as adhesive	[62]
18	Poly (ATESPC/VAc/2-EHA) or P(VAc/2EHA)/PU/Si	Semi-continuous emulsion	ATESPC, PU, VAc, and 2-EHA	KPS	Better heat stability Narrower particle size distributions	[63]
19	Poly (Sty/BA/VAc)	Semi-continuous emulsion	Sty, BA, and VA	APS, Abex 26-S, Rhodia, and Disponil AES 13IS	Viscosity reducers Flow improver	[64]
20	Poly (VAc/BA/HEA)	Cationic emulsion	VAc,BA, and HEA	KPS andCetyltrimethylammonium bromide (CTAB)	Useful to control the molecular weight	[75]
21	Poly (VAc/BA/AMPS)	Semi-continuous emulsion	VAc, BA, AMPS	KPS and hydroquinone	High conversion Improve the thermal stability	[65]
22	PVOH-graft-poly (VAc/Veova10)	Semi-continuous emulsion	VAc, Veova10, and PVOH	KPS and Disponil AFX4060	High solids contents	[66]
23	Poly (VAc /acrylic/epoxy (FVAE)	Seed emulsion	VAc, acrylic, andepoxy (FVAE)	KPS and SDS	Use as coatings Application in stone protection	[83]
24	Poly (VAc/BA/VEVA)	Emulsion	VAc, VV, BA, AA, and AM	KPS and SDS	Use a special polymer modifier	[77]
25	Poly (VAc/BA/VV)	Nano emulsion	VAc, VV, BA, AA, and AM	KPS and SDS	Use as binders for flexographic ink industry	[78]
26	Poly (VDF/EL/VAc)	Batch	VDF, EL, and VAc	KPS	Use as Adhesive Higher values of crystallinity Good piezoelectric properties	[74]
27	Poly (BA/VAc/AA)	Emulsion	BA, VAc, and AA	APS, KPS, and SDS	Transparentlattices	[84]

Conclusion

The emulsion-prepared vinyl acetate-based terpolymers have unique and outstanding properties. They have low costs and are found to be very useful in several industrial applications. Latexes of such terpolymer are used in adhesives, paints, paper coatings, and textile applications. Continuous and batch processes have been found to be the most useful processes for the synthesis of vinyl acetate-based terpolymer. It has also been observed that the polymer prepared by a semi-continuous process results low molecular weight polymer in comparison to the batch process. Therefore, the continuous process has been considered as a beneficial process. It is also observed that the thermal stability of vinyl acetate-based terpolymer increases with increasing the amount of acrylate as a comonomer. The morphological and thermal characteristics make this vinyl acetate-based terpolymer useful for a wide range of applications.

Abbreviation

AA	Acrylic acid
AOT-75	Aerosol OT-75
AMA-80	Aerosol MA-80
AM	Acrylamide
APS	Ammonium persulfate
VDF	Vinylidene fluoride
VOH	Vinyl Alcohol
TGA	Thermogravimetric analysis
BA	Butyl Acrylate
DSC	Differential Scanning
BD	Butadiene
EL	Ethylene
MA	Methyl acrylate
PVAc	Polyvinyl acetate
PVOH	Poly (vinyl alcohol)
MMA	Methyl Methacrylate
PU	Polyurethane
SDS	Sodium dodecyl sulfate

SEM	Scanning electron
VEVA	Vinyl ester of versatic acid
SVS	Slovasol 2510
2EHA	2-Ethylhexyl acrylate
Sty	Styrene
KPS	Potassium Persulfate
FRP	Free radical polymerization
TBA	Tributyl Amine
TEM	Transmission electron microscopy
Tg	Glass transition temperature
VV	Vinyl Versatate
Tm	Crystalline melting
VAc	Vinyl Acetate
Veova10	Vinyl ester of neodecanoic acid
ACO	Ammonium salt of sulfated nonylphenol poly(ethyleneoxy) ethanol (Alipal CO-436)

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Authors' Contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

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