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Curriculum Vitae

Maromi Roy

PhD Scholar
Bodoland University
Kokrajhar, BTAD
783370, Assam
India
E-mail: ***maromimarom@gmail.com***
Mob No. +91-9365522325

Permanent Address:
Vill- Harigaon
P.O. Kalipukhuri, P.S. Salakati
Dist.- Kokrajhar, BTR, Assam,
India (783369)

Correspondence Address:
Vill- Basugaon
P.O. Basugaon, P.S. Basugaon
Dist.- Chirang, BTR, Assam
India (783372)

Educational Qualifications:

- ✓ **Ph.D.** from Bodoland University in Chemistry (***Polymer Science***), Kokrajhar, BTR, Assam (Ongoing from April 2019) **PhD Supervisors: Dr. Dhruba J. Haloi**
- ✓ **M.Sc.** in Chemistry (***spl. in inorganic chemistry***) from **Bodoland University**, Kokrajhar, BTR, Assam, India (2018).
- ✓ **B.Sc.** in Chemistry from Science College, Kokrajhar, BTR, Assam, India (2016).

Project Experience:

- M.Sc. Dissertation entitled "**Synthesis and characterization of co-polymer of vinyl acetate and butyl acryale by emulsion polymerization**" this dissertation work was carried out at Department of Chemistry Bodoland University Kokrajhar, Assam, from January 2018 to June 2018.

Research Publications:

1. Mehdi Al Kausor, Sharmistha Chakraborty, **Maromi Roy** and Sujata Brahma; "Assesment of groundwater quality of Kokrajhar town of Assam in terms of some physic-chemical Parameters" (**International Journal of Current Advanced Research, 6, 11, 7663-7669, 2017**). (Impact Factor: SJIF: 5.995)
2. **Maromi Roy**, Madhabi Bhattacharjee, Anjana Dhar, Bikash Baishya and Dhruba Jyoti Haloi; "Synthesis and compositional analysis of co- and ter-polymers of butyl acrylate with vinyl acetate and acrylic acid prepared via emulsion polymerization" **(Indian Journal of Chemical Technology, 27, 2020, 509-514).** (CSIR-NISCAIR, Impact Factor: 0.475)

3. **Maromi Roy,** Uddhab Kalita, Nabendu B. Pramanik, Madhabi Bhattacharjee, Jayanta Barman and Dhruba J. Haloi; **"**Effect of addition of various amounts of kaolin clay on the properties of a terpolymer of vinyl acetate (VAc), butyl acrylate (BA), and acrylic acid (AA)" (**Biointerface research in applied chemistry,** 14, (5), 113, 2024) (BUCURESTI, Romania) Impact factor 0.247)
4. **Maromi Roy**, Dhruba J. Haloi and Jayanta Barman; "Emulsion Prepared Vinyl Acetate-Based Terpolymer: a Review on Their Preparations, Properties, and Applications" (**Asian Journal of Green Chemistry, 8, 2023, 108-123)**. (Sami Publishing company (mEDRA) Impact Factor: 3.137)
5. Apurba Taye**, Maromi Roy,** Anjana Dhar, Jayanta Barman, Nabendu B. Pramanik and Dhruba J. Haloi; " Synthesis and Characterization of Poly(methyl methacrylate-co-vinyl triethoxysilane) Prepared by Free Radical Polymerization" (French-Ukrainian Journal of Chemistry, 11, 2023 Impact Factor: 0.3)

Book Chapter:

Maromi Roy and Deepjyoti Mazumdar; "**Nutritional status of Small Indigenous food Fishes w.r.t. their proximate composition, amino acid, fatty acid, vitamin and mineral contents**" on book "Small indigenous food fishes and their nutritional significant", Kripa Drishti Publications, Pune, 1st Edition, **2024**, ISBN No. 978-81-19149-98-8

Conference Presentations:

1. Presented a poster on 17th International Conference on **Polymer Science and Technology (SPSI MACRO 202023) held at IITG in Guwahati, India from December 10-13, 2023.**
2. Presented a poster on **Bodoland Knowledge Festival (BIKF2023)** Organized by Government of Bodoland territorial council (BTR) **held at Bodoland University**, **7th February 2nd March 2023.**
3. Presented a paper on National conference on **Science & technology for sustainable development (STSD-2022)** organized by Science College, Kokrajhar, BTR, Assam, India, **June 17th to 18th 2022**
4. Presented a paper on National Conference on **National Conference on Advanced in Sustainable Chemistry and Material Science-2022 (ASCMS-2022)** organized by Department of Chemistry, Bodoland University, Kokrajhar, BTR, Assam, India. April 29-30, 2022.
5. Presented a paper on International e-Conference on **Advances in Science and Technology for Betterment of Health, Environment and Energy** Organized by GITAM Bengaluru, Karnataka, India on Zoom **from December 1-3 2020.**
6. Presented a poster on International e-Poster Conference on **Current Outlook in Material Science and Engineering (COMSE-2k20)** Organized by Bodoland University in Association with Tripura University, ADP College, Nagaon & MIT Aurangabad **On Facebook from May 15-16, 2020.**

7. Presented a poster on International Conference on **Polymer Science and Technology** (**SPSI MACRO 2018) held at IISER- Pune and CSIR- NCL Pune in Maharashtra, India from December 19-22, 2018.**
8. Attend the Conference on National Conference on **Applied Sciences, Sustainable & evolving Technologies (ASSET 2018)** jointly organized by Bodoland University and Central Institute of Technology **held at CIT Kokrajhar, Assam, India from March 9-11, 2018.**

Workshop/Seminar/Science Talk attended:

1. ACS Science Talk, **Chemical toxicology of human gut microbiota** organized by the **American Chemical Society (ACS)** held on **December 3, 2021**.
2. ACS Seminars, **Advances in Polymer Nanocomposites** organized by the **American Chemical Society (ACS)** and Indian Institute of Technology Roorkee (**IIT Roorkee**) on zoom **from October, 18-19 2021**.
3. Online workshop on **Flow Cytometry Techniques and Applications** organized by North East Centre for Biological Sciences and Healthcare Engineering (**NECBH**) Indian Institute of Technology Guwahati, Assam on Webpage: http://www.iitg.ac.in/necbh/events3.php **from December 21- 22, 2020**.
4. International Online Workshop on **Academic Writing and Communication Skills, Research Methodology, Reference Management, and Academic Publishing** organized by National Institute of physical medicine and rehabilitation (**NIPMR**) in association with Mahatma Gandhi University library, Kottayam & Lore & ED Research Associates **from 23 November - 31 December 2021**.

Equipment handland:

1. pH meter,
2. Conductometer,
3. Polarimeter,
4. Gel Permeation chromatography,
5. UV-Vis Spectroscopy

Other qualifications:

Knowledge of Computer (Windows 7, Windows XP, Windows Vista, MS Office, Linux, C++, JAVA, Origin, CS Chem Draw, Bruker Topspin etc.). Computer Science Diploma (1year) PGDCSA from Education & training Division AEDCL.

Languages known: English, Hindi, Assamese.

Declaration:

I, ***Maromi Roy***, *solemnly declare that the particulars given above information by me are correct to the best of my knowledge and belief.*

Maromi Roy

Maromi Roy

Date: 08/11/2024
Place: Kokrajhar

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Review Article

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

Maromi Roy[a], Dhruba J. Haloi[b,*], Jayanta Barman[c]

[a]Department of Chemistry, Bodoland University, Kokrajhar, Assam-783370, India
[b]Department of Applied Sciences, Tezpur University, Assam-784028, India
[c]Department of Physics, ADP College, Nagaon, Assam-782002, India

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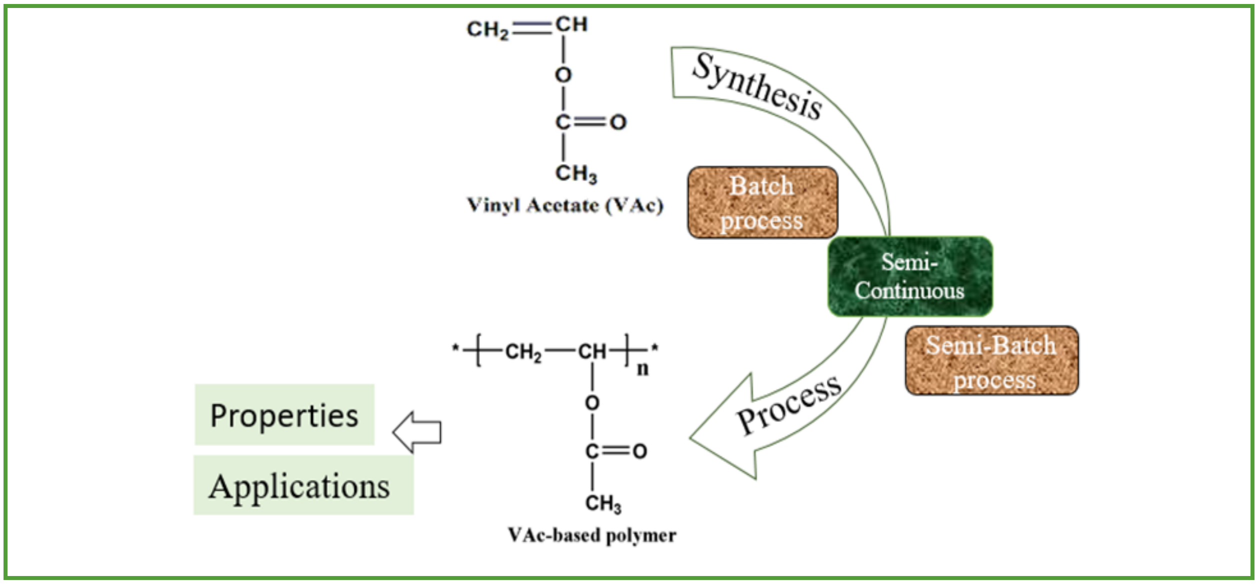
ABSTRACT

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.

Corresponding authors, email: dhruba2k3@gmail.com, djhaloi@tezu.ernet.in(D.J. Haloi).
Tel.: 917896777085.

Graphical Abstract



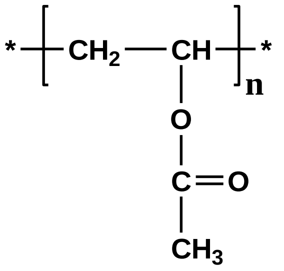
Introduction

Emulsion polymerization (vinyl acetate)

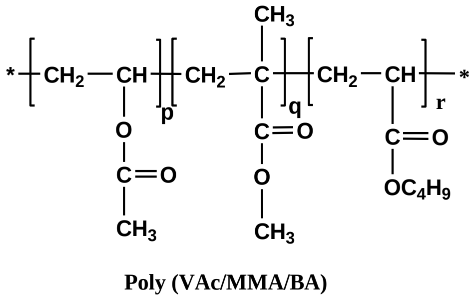
Emulsion polymerization covers a large part of the global industry for built-up well-designed polymer products [1]. This technique earned great attention to be used in manufacturing from the Second World War [2]. Polymers are popular mostly due to their tunable mechanical and viscoelastic properties [3]. Accordingly, they are being used for the preparation of polymer composites [4-8]. Homo and co-polymers 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.

$$\mathrm{I} \xrightarrow{\mathrm{k_{dis}}} 2\mathrm{R}\cdot\text{(Initiation) (1)}$$

$$\mathrm{R}\cdot + \mathrm{M}\cdot \xrightarrow{\mathrm{k_{in}}} \mathrm{RM}\cdot \text{ (2)}$$

$$\mathrm{M_n}\cdot + \mathrm{M}\cdot \xrightarrow{\mathrm{k_{pro}}} \mathrm{M_{n+1}}\cdot\text{(Propagation) (3)}$$

$$\mathrm{M_n}\cdot + \mathrm{M_m}\cdot \xrightarrow{\mathrm{k_{ter}}} \mathrm{M_{n+m}}\text{(Termination) (4)}$$

$$\mathrm{M_n}\cdot + \mathrm{M_m}\cdot \xrightarrow{\mathrm{k_{tdis}}} \mathrm{M_n} + \mathrm{M_m} \text{ (Termination) (5)}$$

In the initial step, radicals (R·) 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

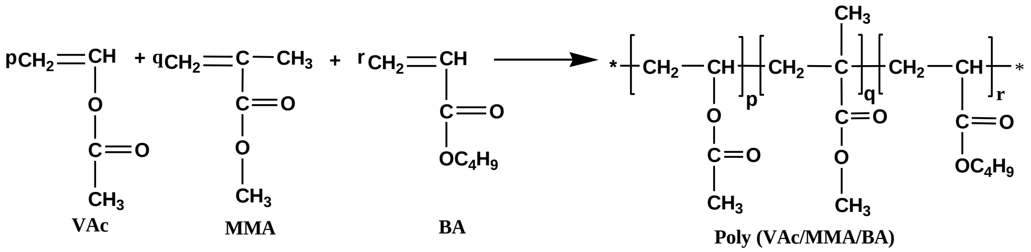
The semi-continuous process is an industrially beneficial process and is used for the production of several important synthetic polymers [44, 45]. In this process, particle nucleation is expected to take place mostly in the aqueous phase [46]. The monomer and the other required chemicals are added to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

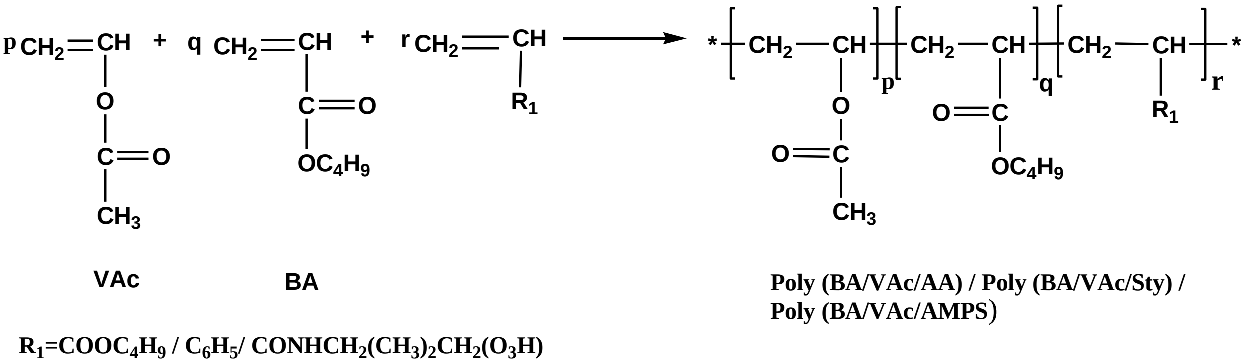
Batch emulsion is a laboratory process used to study reaction mechanisms, new latex products, betterment of kinetic data, and scale-up [49]. The batch method is a simple one where all required ingredients are added to the reactor at the beginning. The polymerization is started by adding monomers and 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

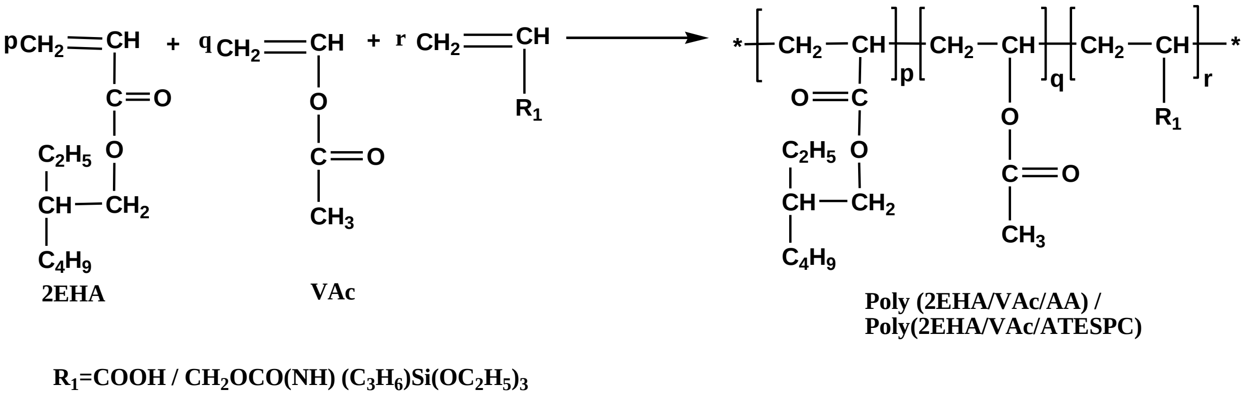
Preparation of VAc-based terpolymer by semi-continuous emulsion polymerization has been reported by several researchers. Urretabizkaia *et al.* used this process to prepare terpolymer of VAc with MMA and BA using potassium persulfate (KPS) as initiator and ammonium salt of sulfated nonyl phenoxy poly(ethyleneoxy) 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



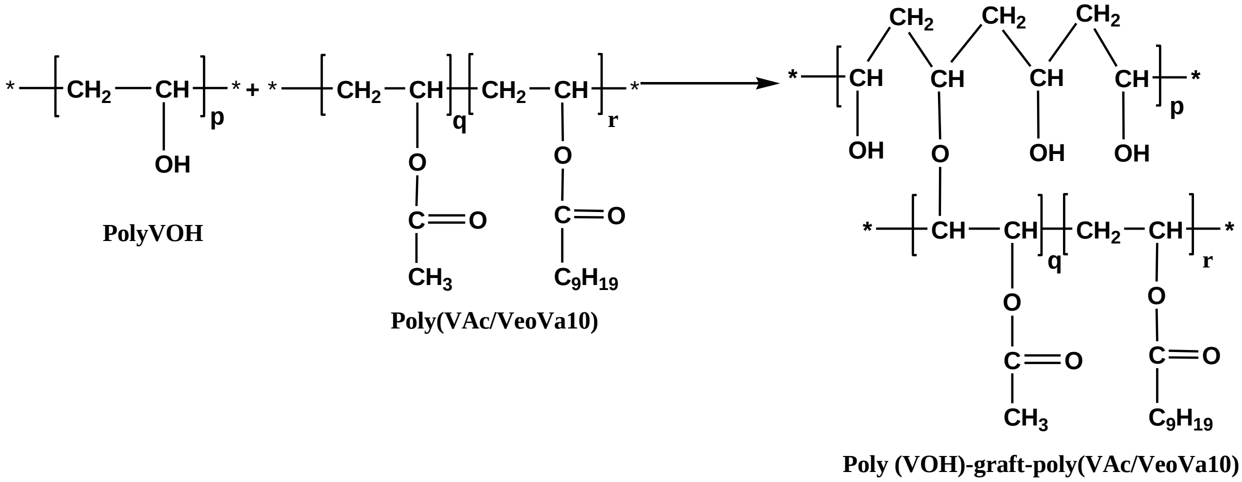
Scheme 5. Synthesis of poly (2EHA/VAc/AA) poly or (2-EHA/VAc/ATESPC) terpolymer via emulsion polymerization

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].

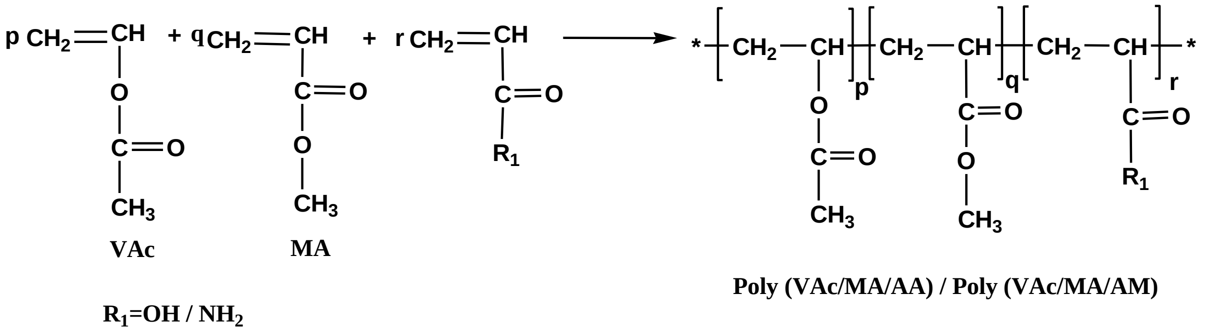
In a different approach, Agirre *et al.* studied the emulsion polymerization of VAc with poly (vinyl alcohol) (PVOH) and neodecanoic acid vinyl ester (VeoVa10) in a semi-continuous process. They used KPS as initiator and Disponil AFX4060 and SDS as emulsifiers. The polymerization was carried out at 67 °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 co-monomers 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].

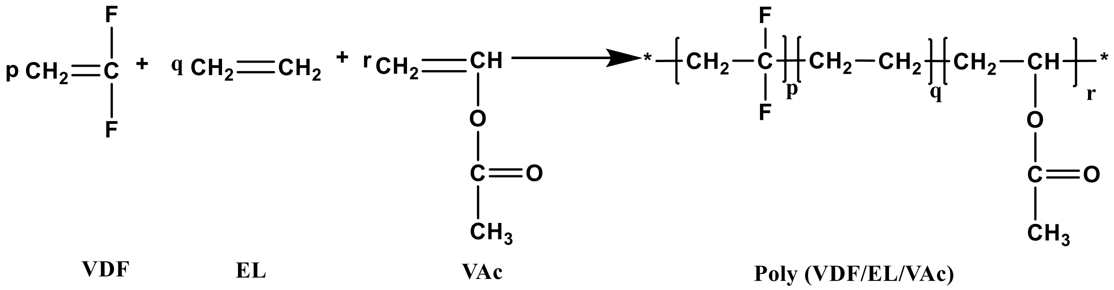
Among the researchers, Staicu *et al.* reported a single Tg for the terpolymer of VAc with 2EHA and AA. However, Tg of the homopolymers, poly (2-ethylhexyl acrylate) and poly (butyl acrylate) are much higher than the corresponding terpolymer [62]. Meng *et al.* reported the thermal analysis of the VAC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

The prepared terpolymers exhibited only one Tg indicates that the monomers were randomly distributed in the terpolymer chain [75]. It was also observed that, the Tg 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 °C and 450 °C as reported by Naser *et al.* [77]. TGA analysis also showed that this terpolymer leaves residue 5.4% when heated to 600 °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 °C and final degradation, which starts at 412 °C. The sample was almost degraded at 510 °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, andAM	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	Usedas 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 Use as coatings	[66]
23	Poly (VAc /acrylic/epoxy (FVAE)	Seed emulsion	VAc, acrylic, andepoxy (FVAE)	KPS and SDS	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 Use as Adhesive	[78]
26	Poly (VDF/EL/VAc)	Batch	VDF, EL, and VAc	KPS	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 co-monomer. 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(ethylenoxy) 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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Synthesis and compositional analysis of co- and ter-polymers of butyl acrylate with vinyl acetate and acrylic acid prepared via emulsion polymerization

Maromi Roy[1], Madhabi Bhattacharjee[1], Anjana Dhar[1], Bikash Baishya[2] & Dhruba J. Haloi*[1]

[1]Bodoland University, Kokrajhar, Assam 783 370, India
[2]Centre of Bio-Medical Research (*CBMR*), Lucknow 226 014, India
E-mail: dhruba2k3@gmail.com

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This investigation reports the synthesis and characterization of copolymers and ter-polymers of butyl acrylate (BA) prepared via emulsion polymerization. Vinyl acetate (VAc) has been used for the synthesis of copolymer and VAc along with acrylic acid (AA) for the synthesis of ter-polymerswith BA. The polymerizations have been carried out at 70°C for 30 minutes at 470 rpm using two different thermal initiators, ammonium persulfate (APS) and potassium persulfate (KPS) and an emulsifier sodium dodecyl sulfate (SDS). Attempts have also been made to prepare co- and ter-polymers of BAwith varying amounts of monomers. The prepared copolymerswere characterized by GPC, FT-IR, NMR and UV-Vis analyses. The percentage of conversion of monomers to polymer has been calculated gravimetrically. UV-Visible analysis has been used to confirm the preparation of transparent lattices. Furthermore, the incorporation of monomers in the co- and ter-polymers are confirmed by FT-IR and ^{1}H NMR analyses. The molar compositions of the prepared polymers are determined by ^{1}H NMR analysis comparing the areas under the characteristics ^{1}H NMR peaks of the repeating units.

Keywords: Copolymer, Emulsion, Terpolymer, Butyl acrylate, Emulsion polymerization

Emulsion is a liquid-liquid colloidal system where the finely divided droplets are dispersed in a liquid[1]. Emulsion polymerization is a complex process in which the radicals are added into the heterogeneous systems formed by water, monomers, emulsifiers, initiator etc. The initiator used in this process is soluble in the aqueous phase.The polymer chain grows inside the micelle formed by the emulsifier used for emulsification[2].

In the last few decades, emulsion polymerization is growing up as one of the important methodologies for the synthesis of polymers for wide varieties of applications[3]. This versatile and flexible polymerization technique offers us a greener and more convenient route to prepare materials for wide range of applications[4]. Moreover, the wide applications are resulted from their waterborne nature e.g., poly vinyl acetate (PVAc) and vinyl acetate/acrylic copolymer latexes are eco-friendly being capable for waterborne[5,6]. Copolymers of VAc have extensive applications such as in adhesives, carpet backing, exterior and interior paints, and adhesives for clay coatings on paper etc[7]. They also have some unique properties such as excellent mechanical and water resistance properties, which allows them to use even in aqueous phase[8]. Even acrylic based pressure-sensitive adhesives are obtained by using water as a solvent, which can adhere strongly to solid surfaces upon implication of light contact pressure in short contact time[9]. Moreover, latex form of the copolymers of VAc and acrylates are found to be eminent components of both interior as well as exterior paints[10-12]. Also, ter-polymers of VAc have broad applications such as re-moisturable, water soluble packaging etc[13]. Ter-polymer films of methyl methacrylate/styrene/acrylonitrile were found to be water permeable[14].

Many works have been put forward on the syntheses and characterization of copolymers and ter-polymers with different properties for various applications. N. Shinde and his co-workers synthesized polymer using isopropenyl acetate (IPA), BA and methyl methacrylate as monomers and studied their behaviour using FT-IR and GPC analysis[15]. H. Berber and his co-workers prepared water-based VAc-co-BA lattices by using semi-continuous emulsion polymerization technique in presence of oligomeric-NMA[16]. C. F. Jasso-Gastinel and his co-workers synthesized copolymer of Styrene with BA by using same polymerization technique.

The formation of copolymer was confirmed by FT-IR, ^{1}H-NMR and other physical techniques[17]. Yilmaz and his co-workers prepared a few acrylic based copolymers via RAFT mini-emulsion polymerization process and characterized their functional behavior with different physical techniques mostly FT-IR, GPC, ^{1}H NMR and ^{13}C NMR[18]. L. Yang and his co-workers prepared three kinds of ter-polymers which contain N-phenylmaleimide via emulsion polymerization and investigated the mechanical and rheological behaviour of poly (vinyl chloride) blended with the terpolymers[19].

In our investigation, the synthesis and characterization of copolymers of BA with VAc and its ter-polymers with VAc and AA are reported. Two different thermal initiators APS and KPS and the surfactant SDS were used. All the reactions were carried out at 70ºC and at an intermediate stirring speed 470 rpm. The purified polymers were further characterized by GPC, FT-IR, NMR, and UV analyses.

Experimental Section

Materials

Vinyl acetate (VAc) (99%, SRL, India), Butyl acylate (BA) (99%, Aldrich, USA) and Acrylic Acid (AA) (99%, Loba, India) were used as monomers. Ammonium persulfate (APS) (98%, Merck, India) and potassium persulfate (KPS) (98%, Avra Synthesis Pvt., India) were used as initiators. Sodium lauryl (dodecyl) sulfate (SDS) (99%, SRL, India) was used as surfactants. Distilled water was used as a solvent. Other chemicals- Acetone (≥ 99%, EMPLURA, India), Tetrahydrofuran (THF) (99.5%, Rankem, India) and Acetic acid glacial (≥ 99%, Emplura, India) were used in different purposes.

Synthesis of (butyl acrylate-*co*-vinyl acetate) and (butyl acrylate-*co*-vinyl acetate-*co*-acrylicacid)

In a typical co-polymerization or ter-polymerization reaction, distilled water (5g, 0.27 mol) and the surfactant SDS (0.1g, 0.35 mmol) were taken in a dry Schlenk tube equipped with a stirrer, a magnetic bar and a rubber septum. The mixture was stirred for 15 min, and then varying composition of BA/VAc or BA/VAc/AA (total 2g) was injected to the Schlenk tube. After 15 min of stirring, APS (0.02g, 0.08 mmol) was then added and allowed to stir for 1 hour. The Schlenk tube was then sealed and nitrogen gas was passed through the mixture for 20 min to expel out the dissolved oxygen in it. The reaction tube was then placed in the preheated oil bath and polymerization was carried out at 70°C for 30 min at 470 rpm. The aliquot was taken out at the end of the polymerization and the conversion was determined gravimetrically. Similar approach was adopted for the second initiator KPS (0.02g, 0.07 mmol) with the same composition.

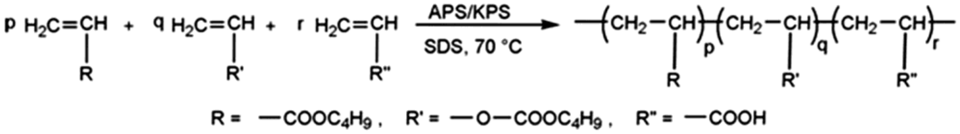
The prepared latex was then coagulated by acetic acid, washed thoroughly with distilled water and was then filtered. The residual polymer was then dissolved in THF, re-precipitated from water, filtered and dried over oven at 60°C to get the pure polymer Thus, the obtained purified polymers were used for GPC, FTIR and NMR analyses. Same procedure was used for the ter-polymerization of BA with VAc and AA.

Characterization

UV-Visible spectra of the purified copolymers and ter-polymers were recorded in the wavelength range of 200-1000 nm on UV-Visible Spectrophotometer. ^{1}H NMR spectra of the synthesized polymer samples were recorded on 400 MHz Bruker NMR spectrometer using $CDCl_3$ as a solvent. FT-IR spectra of purified samples were also obtained as a thin film on KBr plate in the region of 400 to 4000 cm^{-1} and recorded with a Perkin Elmer FT-IR spectrometer. Size Exclusion Chromatography (SEC) was carried out in an Agilent GPC system with configuration comprises of a 50 µL manual sampler, Isocratic pump and 1260 infinity II refractive index (RI) detector. The analysis was performed at room temperature and THF was used as an eluent at a flow rate of 1mL/min in the analysis.

Results and Discussion

In emulsion polymerization, VAc was used for the synthesis of copolymer with BA and VAc along with AA was used for the synthesis of ter-polymers (Scheme 1). The reaction was carried at 70ºC for



Scheme 1 — Emulsion ter-polymerization of butyl acrylate/vinyl acetate/acrylic acid.

30 min with 470 rpm. The initiators APS and KPS with the surfactant SDS was used in emulsion polymerization for the synthesis of copolymer and ter-polymer latices. The copolymerization results are summarized in Table 1 and Table 2. The monomer conversion for the copolymerization was determined gravimetrically. In most cases, the conversion of monomers was found to be more than 90 %. The transparency of the prepared lattices was studied by UV-Visible spectroscopy. Fig. 1 shows the UV-Vis spectra of copolymers of BA/VAc. All the prepared latexes were found to be stable even after few weeks and stable, indicating that there was no macroscopic phase separation and no formation of large amounts of homopolymer. Sparidans *et al.* also reported the same kind of findings in their study of copolymers of styrene with methyl acrylate andBA[20]. In Fig. 1(a), absorbance versus wavelength for BA:VAc (0.0117:0.0056) curve shifts towards higher wavelength in comparison to BA:VAc (0.0078:0.0113) (Fig.1(b)). This shows that with the increase in BA content the particle size increases and curve shows bathochromic shift or red shift.

The incorporation of the monomers was also confirmed by the ^{1}H NMR spectrum. Fig. 2(a) and 2(b) showed the ^{1}H NMR spectra of poly(BA-*co*-VAc) and poly(BA-*co*-VAc-*co*-AA) respectively. The ^{1}H NMR spectroscopy shown in Fig. 2(a) and 2(b) indicate the presence of monomers in the final copolymers and ter-polymers respectively which allows the quantitative determination of the amount of incorporated second monomer unit (Table 3 and Table 4). In Fig. 2 (a), the signals at δ =0.95 ppm and δ =1.99 ppm were attributed to the protons of –CH_3 (a) and –CH_3 (g) of BA and VAc respectively. Signals at δ =1.39 and 1.61 ppm was assigned to the protons of –CH_2– (b) and –CH_2– (c) respectively which corresponds to main chain backbone of BA. In case of VAc, signals at δ =1.50 and 1.58ppm was assigned to the protons of –CH_2– (f) and –CH_2– (i) respectively which corresponds to main chain backbone of VAc. Signals at δ =4.0 ppm attributed to the –O–CH_2– (d) protons of pendant BA group. Signal at δ =1.92 ppm and 5.03 ppm to the backbone proton of –CH– (e) and –CH– (h) of BA and VAc respectively. In Fig. 2(b), the signal at δ =0.94 and 1.97 ppm was attributed to the protons of–CH_3 (a) and–CH_3 (f) of BA and VAc respectively. Signals at δ

Table 1 — Co-polymerization of BA and VAc in emulsion at 70°C using initiators APS and KPS, copolymerization time = 30 min, speed = 470 rpm

Run and Sample No.	Composition of BA (mol)	Composition of VAc (mol)	Conversion %
A-1	0.0117	0.0056	87
A-2	0.0078	0.0113	97
A-3	0.0039	0.0170	98
K-1	0.0117	0.0056	88
K-2	0.0078	0.0113	94
K-3	0.0039	0.0170	86

*A refers to APS and K refers to KPS

Table 2 — ter-polymerization of BA, VAc and AA in emulsion at 70°C using APS and KPS as initiators copolymerization time = 30 min, speed = 470 rpm

Run and Sample No.	Composition of BA (mol)	Composition of VAc (mol)	Composition of AA (mol)	Conversion (%)
A-4	0.0117	0.0048	0.0015	93
A-5	0.0117	0.0035	0.0028	97
A-6	0.0117	0.0022	0.0041	99
K-4	0.0117	0.0046	0.0014	94
K-5	0.0117	0.0035	0.0028	97
K-6	0.0117	0.0023	0.0042	99

*A refers to APS and K refers to KPS

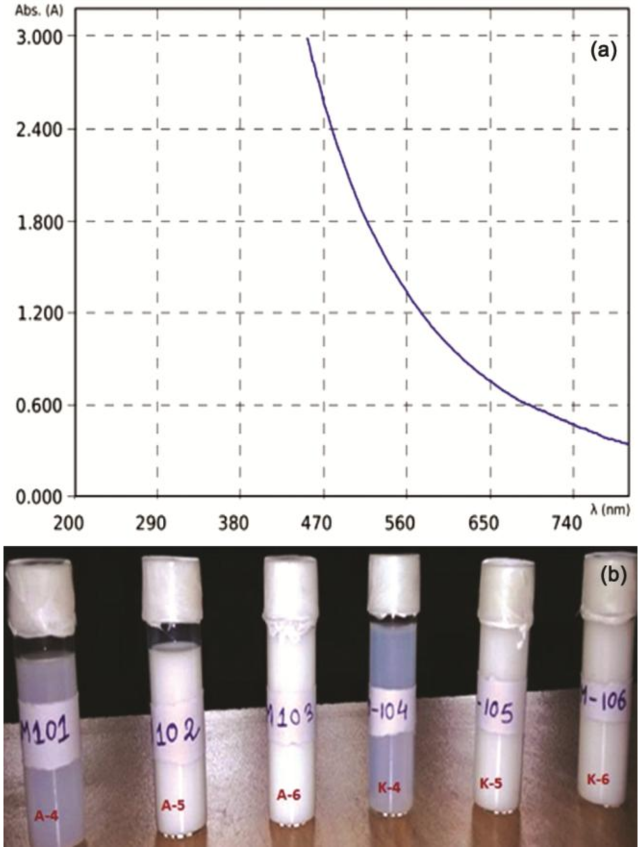


Fig. 1(a-b) — (a) UV-Visible spectrum of latex of copolymer [0.0117/0.0056, BA/VAc] (A-1)&(b) UV-Visible spectrum of latex of copolymer [0.0078/0.0113, BA/VAc] (A-2).

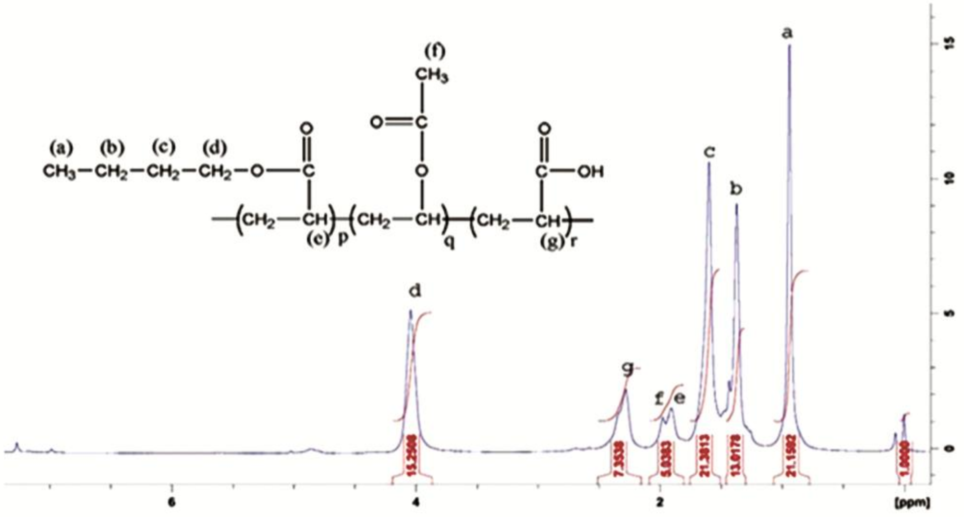


Fig. 2(a-b) — (a) ^{1}H NMR spectrum of Poly (BA-VAc) (A-1) & (b) ^{1}H NMR spectrum of Poly (BA-VAc-AA) (A-4).

Table 3 — Calculated monomer compositions in copolymer by ^{1}H NMR

Sample Number	Conversion (mol %)	Composition in feed (mol%)		Composition in copolymer$^{\#}$ (mol %)	
		BA	VAc	BA	VAc
*A-1	87	67.6	32.4	75.6	24.4
A-2	97	40.8	59.2	72.7	27.3
A-3	98	18.6	81.4	8.1	91.9

*A refers to APS and K refers to KPS
$^{\#}$Calculated by ^{1}H NMR

Table 4 — Calculated monomer compositions in ter-polymer by ^{1}H NMR

Sample Number	Conversion (mol %)	Composition in feed (mol%)			Composition in copolymer$^{\#}$ (mol %)		
		BA	VAc	AA	BA	VAc	AA
*A-4	93	65	26.7	8.3	62.8	6.9	30.3
A-5	97	65	19.4	15.6	62.3	9.4	28.3
A-6	99	65	12.2	22.8	57.1	36.7	6.2

*A refers to APS and K refers to KPS
$^{\#}$Calculated by ^{1}H NMR

=1.37, 1.60 and 4.04 ppm were assigned to the protons of –CH$_2$– (b), –CH$_2$– (c) and –O–CH$_2$– (d) of BA respectively. Signal at δ =1.90 and 2.28 ppm corresponding to the backbone protons of –CH– (e) and –CH– (g) of BA and AA respectively. In table 3 and table 4 the percentage of molar composition of different monomers in feeds as well as in the prepared copolymers and ter-polymer is shown. The monomer composition in the prepared copolymer and ter-polymer were determined by ^{1}H NMR spectroscopy by the following equation:

$$F_{BA} = \frac{A_{BA}}{A_{BA} + A_{VAc} + A_{AA}} \times 100\ \%$$

where

A_{BA}= the integrated peak area for one proton in poly(butyl acrylate) unit.

A_{VAc}= the integrated peak area for one proton in poly(vinyl acetate) unit.

A_{AA}=the integrated peak area for one proton in poly(acrylic acid)unit.

The formation of copolymer was confirmed by FT-IR spectroscopic analysis. A shift in the C-O-C asymmetric stretching vibration of BA and -CH$_3$ symmetric stretching vibrations of VAc were observed at 1242 cm^{-1} and 2850 cm^{-1} respectively in the FTIR spectra of copolymer of BA and Vac

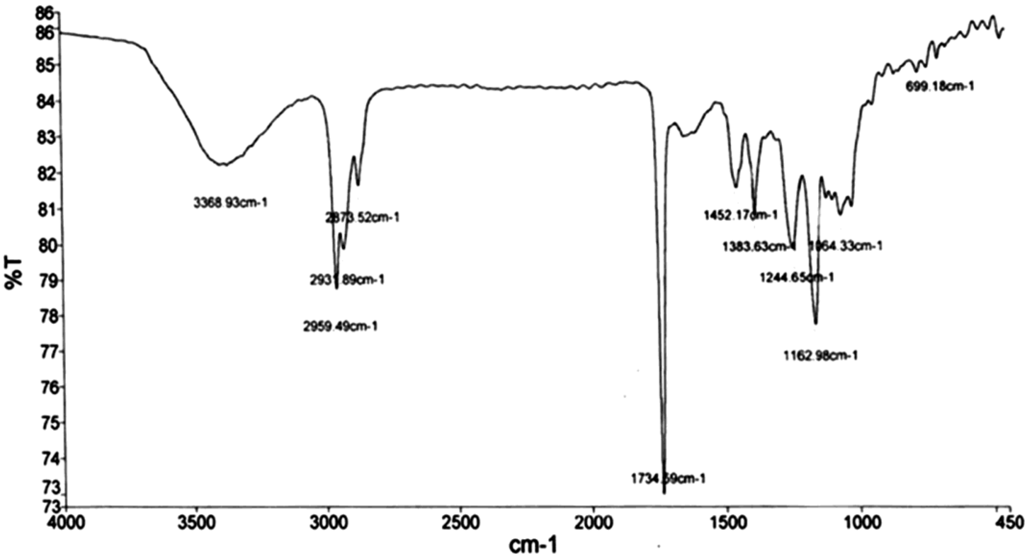


Fig. 3 — FT-IR spectrum of poly (BA-VAc) (A-1).

(Fig. 3). Similarly, the shift in >C=O symmetric stretching vibration of BA and VAc was observed at 1738 cm^{-1} and a shift in the trans -CH wag bending vibration was observed at 946 cm^{-1} in the FTIR spectra of copolymer which confirms the successful preparation of copolymer of BA with VAc. The results confirm that all monomers had participated in the emulsion polymerization reaction.

The synthesized copolymers were purified and analysed by GPC to know their molecular weight. The number average molecular weights of the copolymers were found to be very high with high PDIs. However, uni-modal GPC traces of the copolymers indicated that the prepared copolymers were free from homopolymers.

Conclusion

Colloidal lattices of co-polymer (BA-*co*-VAc) and ter-polymer (BA-*co*-VAc-*co*-AA) of BA were prepared successfully by using free radical emulsion polymerization. To initiate the co-polymerization reaction, two types of thermal initiators APS and KPS were used. All the prepared latexes are found to be stable even after few weeks. The prepared latexes are nearly transparent as evident by UV-Visible analysis. In the UV-Visible plot of absorbance versus wavelength, a shift towards higher wavelength is observed due to the increase in BA content in the copolymer.^{1}H NMR analysis is carried out to know the copolymer and ter-polymer composition via the calculations of areas under the characteristic peaks of the different repeating units present in the copolymer and ter-polymer. FTIR analysis confirmed the successful incorporation of co-monomer in the co-polymer composition. GPC analysis shows a uni-model GPC traces which indicates the successful preparation of co-polymer free from homo-polymers of individual monomers units.

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Effect of Addition of Various Amounts of Kaolin Clay on the Properties of a Terpolymer of Vinyl Acetate (VAc), Butyl Acrylate (BA), and Acrylic Acid (AA)

Maromi Roy [1], Uddhab Kalita [2], Nabendu B. Pramanik [3], Madhabi Bhattacharjee [4], Jayanta Barman [5], Dhruba J. Haloi [6,*]

[1] Bodoland University, Kokrajhar, Assam-783370, India
[2] Indian Institute of Technology Kharagpur, West Bengal-721302, India
[3] Institute of Chemical Technology Mumbai –IOC Odisha Campus, Bhubaneswar-751013, India
[4] Bodoland University, Kokrajhar, Assam-783370, India
[5] A.D.P College, Nagaon, Assam, India
[6] Tezpur University, Tezpur, Assam-783370, India
* Correspondence: dhruba2k3@gmail.com;

Scopus Author ID 35275016000

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Abstract: This study describes preparing and characterizing poly(vinyl acetate) (PVAc) based terpolymer/kaolin clay composites. Conventional free-radical emulsion polymerization was used to prepare a terpolymer of vinyl acetate (VAc), butyl acrylate (BA), and acrylic acid (AA). ^{1}H NMR analysis confirmed the successful preparation of the terpolymer. The conversion of the monomers was calculated gravimetrically and found to be 90 % after one hour of polymerization time. Different amounts of kaolin clay were added to the terpolymer latex and were mixed to prepare the terpolymer/kaolin clay composites. NMR, FT-IR, TGA, DSC, and FESEM analyses were used to characterize the terpolymer and terpolymer/clay composites. Mechanical properties such as tensile strength, modulus, and elongation at the break of the prepared terpolymer/clay composites were also evaluated. A rubber process analyzer (RPA) was used to study the rheological properties of the polymer composites. All the analyses establish the presence of strong clay-polymer interaction in the composite for which the prepared composites exhibit improved thermal properties.

Keywords: vinyl acetate; emulsion polymerization; clay composite.

1. Introduction

In recent years, the research on synthesizing inorganic-organic polymer hybrid materials such as layer silicate/polymer nanocomposites has attracted great interest due to their wide superior physical, mechanical, and thermal properties compared to the other composites [1-3]. The development of emulsion polymers combined with free radical polymerization (FRP), which usually involves two or more monomers in polymerization, has always been of great industrial importance because of its simple preparation methods and wide range of applications [4]. The FRP method is used to produce millions of tons of polymers worldwide [5]. This is due to the wide variety of functional groups well-suited to free radicals [6]. Terpolymers, which are made up of three different monomers that are polymerized together to form a single polymer, have several advantages[7] and applications[7-9] over other polymers as different properties can be combined into a single polymer if the monomers are chosen carefully [7]. Many studies have been published on producing and characterizing various terpolymers and their films with multiple properties for various applications [7,10,11]. Urrtabizkaia *et al.* investigated the use of VAc, methyl methacrylate (MMA), and BA monomers to synthesize emulsion polymerization. Their kinetics, terpolymer composition, and the total number of polymer particles were also evaluated [7]. Unzue *et al.* used different polymerizable surfactants to perform semicontinuous emulsion polymerization of poly(styrene-co-BA-co-AA). The emulsion polymer latices' particle size, surface tension, and stability against electrolyte solutions were reported [12]. Carter *et al.* investigated VAc, 2-Methylene-1, and 3-Dioxepane emulsion polymers with various properties of novel classes of recyclable, upcyclable, or biodegradable polymers [13]. Elmahdy *et al.* synthesize poly(vinyl chloride-co-vinyl acetate-co-2-hydroxypropyl acrylate) terpolymer and study the enhancement of specific capacitance containing tetrabutylammonium tetrafluoroborate ionic liquid [14]. Nanofibers are produced from copolymers and terpolymers of vinyl phosphonic acid, acrylonitrile, methyl acrylate, and vinyl acetate [15]. Shabnam *et al*. investigated the effect of the third monomer on the polymerization of lauryl methacrylate and MMA in emulsions. They discovered that the nature of the third monomer strongly influences the polymerization rate, polymer properties, and latex properties [16].

A composite is a microscopic blend of two or more polymeric, metallic, or ceramic materials that are linked together in specific ways [17]. Clay composites (organic/inorganic hybrid materials) are made up of clay intercalated with a liquid polymer, with the intercalation group consisting of aluminosilicates of the smectite group [18]. Clays are naturally occurring, readily available silicate minerals. This has led to their widespread use in novel chemical processes, owing to the material's low cost and environmentally friendly nature. Few studies have described how different clays, such as montmorillonite, mica, hectorite, bentonite, or laponite, can be used to stabilize emulsion colloidal latex using the emulsion polymerization technique and clay minerals colloidal latex [19,20]. Sheeted of stable aqua silicates of aluminum, iron, and magnesium, sheeted tape, and mixed-sheeted structures are found in the structure of the clays. Due to this structural feature, clay has a high dispersity, hydrophilicity, sorption ability, ion exchangeability, and the highest tendency to adsorb various organic compounds [21]. Kaolin is a clay mineral commonly used for filling and paper coating [22]. With the chemical formula $Al_2Si_2O_5(OH)_4$, it is a one-of-a-kind phyllosilicate mineral. One tetrahedral SiO_4 silica is linked through an oxygen atom to one octahedral $Al_2(OH)_4$ alumina plate in the 1:1 di-octahedral structure of kaolin clay [23]. Kaolin improves paper appearance and printability by improving properties such as gloss, smoothness, brightness, and opacity [24]. The use of a suitable coupling agent to modify kaolinite can result in good filler particle compatibility and dispersibility in a specific polymer matrix [25].

Despite the fact that the chemistry of polymer intercalation with clay has been known for a long time, the research field of polymer/clay nanocomposites has gained momentum only after the report on the Nylon-6/clay nanocomposites by the Toyota research group [26,27]. Several polymer/clay nanocomposites have recently been created using various monomers [28]. Polymer/clay nanocomposites combine the benefits of organic materials, such as flexibility and moldability, with the strength and heat stability of inorganic materials [29]. Clay particles play a leading role in the polymer stabilizer [30]. These changes are usually the result of the important role of silicate layers (on the dimension and the degree of dispersion). Clay dispersion in the polymer matrix inhibits polymer chain movement, resulting in a significant reinforcing effect [31].

The intercalation of polyvinyl acetate (PVAc) with clay improved the composite properties and has some interesting applications. Compared to pure polyvinyl acetate, Mohsen-Nia *et al*. found that PVAc/montmorillonite nanocomposites have a higher glass transition temperature and thermal stability [32]. Mrah *et al*. investigated polymer/Maghnite nanocomposites that improve thermal stability and mechanical and electrical (electrical conductivity increases) properties, which are useful in materials in flexible electronics and conductive coatings [33]. Rubber/poly (ethylene-co-vinyl acetate) nanocomposite materials have maximum mechanical properties and the lowermost loss factor, which is applied as reuse of tires in the rubber industry [34]. Recently, quantum dots/ethylene VAc copolymer composite films for lighting applications and flexible displays were reported by Li *et al*. [35]. Poly(ethylene-co-VAc) composites with silver-calcined scallop shell powder have good antibacterial properties and could be used in food packaging and biomedical sample storage [36]. Vinyl acetate is a superiorly green monomer, and their copolymers prepared using various methods have a variety of applications [37-40], indicating the potential eco-friendliness of this study of a novel type of terpolymer composites [41]. The Kaolin clay was chosen because of its non-toxicity, ease of availability, and affordability. It may be used to enhance filler particle compatibility and dispersibility in a particular polymer, improve its biodegradation nature, and enhance the barrier properties. Kaolin enhances the barrier properties of water vapor. Kaolin increases the biodegradation nature of polymer/clay composites. That makes polymer/clay composites more suitable as film [42]. This study uses emulsion polymerization to synthesize terpolymer, a simple and environmentally friendly experiment [41].

In recent times, an effort has been made to progress on the preparation of tailor-made polymer-clay composites that illustrate the random distribution of the single-layered silicate and offer additional control over the polymer design [43]. If the monomers are chosen carefully, then terpolymers of vinyl acetate overcome some disadvantages of homopolymer, which makes it unique. As a result of the prospectus of various applications and the green aspect of using vinyl acetate monomer, future research in this field is of great interest.

In this study, we used emulsion polymerization to make poly(VAc-co-BA-co-AA) terpolymers, and five batches of polymer/clay composites were made using different clay loadings. To the best of our knowledge, this is the first account in the study of the effect of kaolin clay on poly(VAc-co-BA-co-AA) terpolymers. The composites were characterized using various analytical techniques such as ^{1}H NMR, FT-IR, DSC, TGA, and SEM. Tensile testing was used to evaluate the mechanical properties of the terpolymer composites. RPA was employed to investigate the rheological behavior of the polymer/clay composites. The synthesis terpolymer/clay composites show better modulus or reinforcement properties than other copolymer/clay composites.

2. Materials and Methods

2.1. Materials.

Vinyl acetate (VAc) (99%, SRL, India), Butyl acrylate (BA) (99%, Aldrich, USA), and Acrylic Acid (AA) (99%, Loba, India) were used after the removal of stabilizing agents present. Potassium persulfate (KPS) (98%, Avra Synthesis Pvt., India), Sodium dodecyl sulfate (SDS) (99%, SRL, India), and Kaolin Clay (Oxford Lab fine Chem LLP) were used as received. Distilled water was used for all the experiments.

2.2. Synthesis of poly(vinyl acetate-co-butyl acrylate-co-acrylic acid).

In a typical terpolymerization reaction, distilled water (164 g, 9.11 mol) and the surfactant SDS (3.28 g, 11.37 mol) were combined in a dry round bottom flask (RB) with a stirrer, magnetic bar, and rubber septum. After 15 minutes of stirring, different compositions of VAc/BA/AA monomers (total 82 g) were injected into the RB. After another 30 minutes of stirring, initiator KPS (0.656 g, 2.42 mmol) was added to the reaction mixture and stirred for an hour. After that, the RB was sealed, and nitrogen gas was passed through the mixture for 60 minutes to remove any dissolved oxygen. Then, the reaction RB was placed in a preheated oil bath with a reflux condenser, and the polymerization reaction was allowed to run for 60 minutes at 470 rpm at 70°C. The conversion was determined gravimetrically after the aliquot was removed at the end of the polymerization.

2.3. Preparation of terpolymer/kaolin clay film.

The prepared terpolymer latex was stirred at 540 rpm for 24 hours at room temperature to obtain a uniform latex. Filtering the solution separates the coagulum from the solution, and the coagulum percentage was calculated to be 3.2 percent. The stable latex was mixed with kaolin clay in various ratios of 5%, 10%, 15%, and 20%, respectively concerning latex. After 36 hours of stirring at 540 rpm, the latex mixtures were transferred to a glass petri dish. The latex mixtures were dried for two days at 60°C in an oven to make a uniform film. NMR, FTIR, DSC, and TGA analyses were performed on the obtained films (terpolymer/clay composites). The prepared terpolymer/clay composites were also evaluated for mechanical properties such as tensile strength, modulus, elongation at break, and hysteresis. The RPA was used to assess the rheological properties of the polymer composites.

2.4. Characterization.

On a 600 MHz Bruker NMR spectrometer, ^{1}H NMR spectra of the terpolymer and the terpolymer/clay composites were recorded using chloroform-d ($CDCl_3$) as a solvent and tetramethylsilane (TMS) as an internal standard. Bruker Topspin 3.6.1 software was used to evaluate the spectra.

With a PerkinElmer (Model spectrum-2) FTIR spectrometer, FTIR spectra of terpolymer and terpolymer/clay composites were recorded for a range of 400 to 4000 cm^{-1} in ATR mode.

The glass transition temperatures (T_g) of the terpolymer and terpolymer/clay composites were determined using a TA DSC25 instrument at a heating rate of 10°C/min from –80°C to 200°C measurements. TGA of the terpolymer/clay composites was performed in the Shimadzu TGA-50 instrument. Under a nitrogen atmosphere, a small sample (approximately 15 mg) was heated from room temperature to 700°C at a heating rate of 10°C/min.

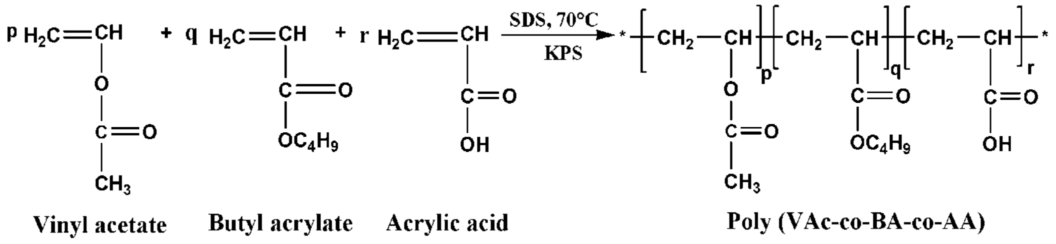
Tensile tests were carried out in a Zwick/Roell Universal testing machine (UTM) with a load cell of 500N and a cross-head speed of 200 mm/min, according to ASTM D412 standards. The polymers were cast over a Teflon Petri dish, dried in a vacuum, and then cut into dumbbell-shaped specimens (thickness 0.85-2.52mm) with the proper dimensions (width 3-3.15 mm). The test was performed on three specimens from the same sample, and the average of all results is shown here. Mechanical properties of terpolymer/clay composites were measured, including tensile strength, modulus, and elongation at break. Hysteresis tests of terpolymer/clay composites were also performed with a Zwick/Roell UTM at 100 percent maximum strain, 200 mm/min cross-head speed, 500 N load, and 4 strain cycles. The samples were prepared in the same way as the tensile tests.

RPA 200000 equipped with biconical dies was used to evaluate rheological properties, such as the dynamic melt rheological behavior of the terpolymer/clay composites. The specimens were thoroughly loaded between the dies, which were kept at 100°C, and the test was performed in both strain and frequency sweep modes. To establish the linear viscoelastic (LVE) region, the strain sweep mode was used from 7 to 200 percent at a constant frequency of 0.50 Hz, and the frequency sweep mode was used to vary the frequency range from 0.7 to 200 Hz at a constant strain amplitude of 7 percent. To ensure that the rheological nature was in the linear viscoelastic region, a strain of 7% was chosen. The rheological properties of the composites were measured, including storage modulus (G′), loss modulus (G″), loss factor (tanδ) on strain amplitude at a constant frequency, and complex modulus (G*), storage viscosity (η') and complex viscosity (η*) on the frequency at constant strain amplitude.

The morphology of the polymer composites was evaluated using a Field Emission Scanning Electron Microscope (FESEM) (JEOL) micrograph with an accelerating voltage of 5.0 kV.

3. Results and Discussion

The poly(VAc-*co*-BA-*co*-AA) terpolymer (Scheme 1) of VAc, BA, and AA monomers was prepared by FRP using an emulsion polymerization technique. The reaction was carried out at 70°C for 60 minutes at 470 rpm. For the synthesis of terpolymer latex, the KPS initiator was combined with the SDS surfactant in an emulsion polymerization process. The monomer conversion for the polymerization was determined by gravimetric analysis and was found to be 90% after 1 hour. The latex was found to be stable even after a few weeks of storage, as evidenced by UV-visible analysis. The molecular weight of the terpolymer was determined by GPC analysis and was already reported in our earlier research publication [41]. The number average molecular weight for this terpolymer was found to be 100 217 g/mol. Various amounts of kaolin clay were added to this terpolymer latex to prepare the polymer/kaolin clay composites. Table 1 summarizes the compositional breakup of the ingredients involved in making the polymer/kaolin clay composites.



Scheme 1. Terpolymerization of vinyl acetate, butyl acrylate, and acrylic acid.

Table 1. The details of the preparation of the polymer/kaolin clay composites.

Sample Name	Polymerization System	Mole Ratio	Conversion %	Polymer Latex(g)/ Kaolin Clay (g)	% of Kaolin Clay
*V-1				55/0	0
V-2				45/2.25	5
V-3	VAc / BA/AA	0.15/ 0.51/0.14	90	45/4.5	10
V-4				45/6.75	15
V-5				33/6.6	20

* V-1 indicate for poly(VAc-*co*-BA-*co*-AA) and V-2, V-3, V-4, V-5 for poly(VAc-*co*-BA-*co*-AA)/clay composites with 5%, 10%, 15%, 20% respectively.

3.1. Nuclear magnetic resonance spectrometry (^{1}H NMR) analysis.

The 1H NMR spectrum confirmed the incorporation of the monomers. The ^{1}H NMR spectra of poly(VAc-*co*-BA-*co*-AA) and poly(VAc-*co*-BA-*co*-AA)/clay composites are shown in Figures 1 and 2, respectively. In Figure 1, the signal at δ =0.96 (a) and 1.99 (f) ppm are attributed to the BA and VAc methyl protons, respectively. Signals at δ =1.39, 1.62, and 4.06 ppm are assigned to the protons of —CH$_2$— (b), —CH$_2$— (c), and —O—CH$_2$— (d) of BA, respectively. Signals at δ =1.92 and 2.36 ppm correspond to the backbone protons of —CH— (e) and —CH— (g) of BA and AA, respectively. The ^{1}H NMR spectra of poly(VAc-*co*-BA-*co*-AA)/clay composites with different kaolin clay ratios are shown in Figure 2.

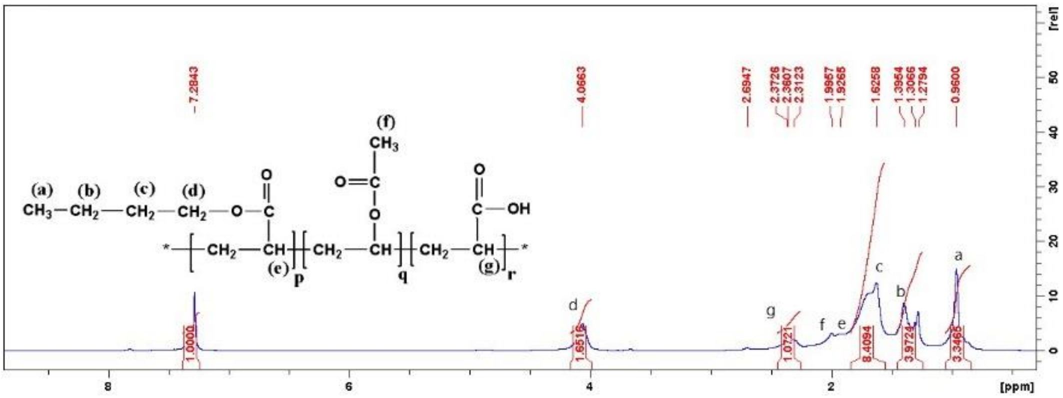


Figure 1. ^{1}H NMR spectrum of poly(VAc-*co*-BA-*co*-AA) terpolymer.

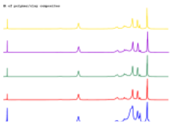


Figure 2. ^{1}H NMR spectra of poly(VAc-*co*-BA-*co*-AA)/clay composites.

3.2. Fourier transform infrared spectroscopy (FTIR) analysis.

The FT-IR spectra for the carbonyl group absorption of terpolymer in the presence of different clay concentrations, t_c, was shown in Figure 3(a). In this spectrum, it was seen that as t_c increases, the absorption band position of >C=O stretching shifts to a lower frequency range (by 1 cm^{-1} in case of 5%, 2 cm^{-1} in case of 10%, 3 cm^{-1} in 15%, and 4 cm^{-1} in 20%). Figure 3(b) shows that with increasing clay amount, Al—O stretching frequencies of kaolin clay shifted to a higher frequency (473.83 cm^{-1} in case of 5% clay, 476.34 cm^{-1} in case of 10% clay, 477.06 cm^{-1} in 15% clay, 478.85 cm^{-1} in 20% clay). It means that when the >Al=O group of the clay layers interacts with the >C=O group of the acrylate monomer ($>C^{\delta-}=O^{\delta+}\cdots\cdots{}^{\delta-}Al=O$) (Scheme S1), the double bond nature of the carbonyl group is reduced, and the absorption band frequency decreases [42]. Figure 3(a) shows C—H stretching of polymer composites at 2961, 2960, 2959, 2958, and 2957 cm^{-1} [18]. In comparison to pure polymer, the C—H stretching band of polymer composites shifted towards a lower frequency (by 1 cm^{-1} in case of 5%, 2 cm^{-1} in case of 10%, 3 cm^{-1} in 15%, and 4 cm^{-1} in 20%). This refers to the adsorption of polymer and kaolin clay particles via hydrogen bonding between the Si—O—H (silanol) of clay and the polymer molecules [43]. Figure 3(b) shows the bands at 1061 and 1070 cm^{-1}, corresponding to Kaolin clay's Si—O stretching frequencies. Similarly, the shift in kaolin's Al—O—Si stretching frequencies was observed at 536, 533 cm^{-1} [44]. The frequency of Si—O groups in kaolin is slightly reduced as a result of polymer molecules interacting with clay particles [43].

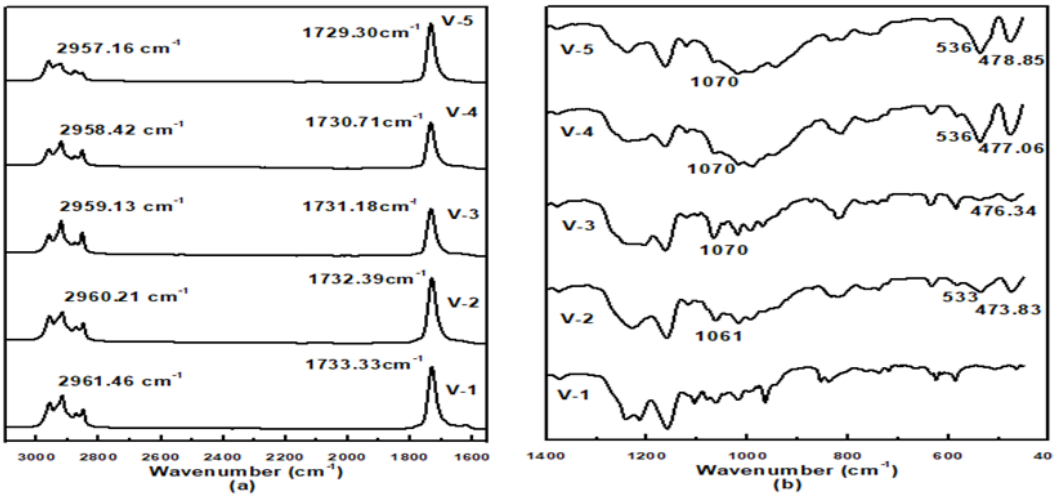
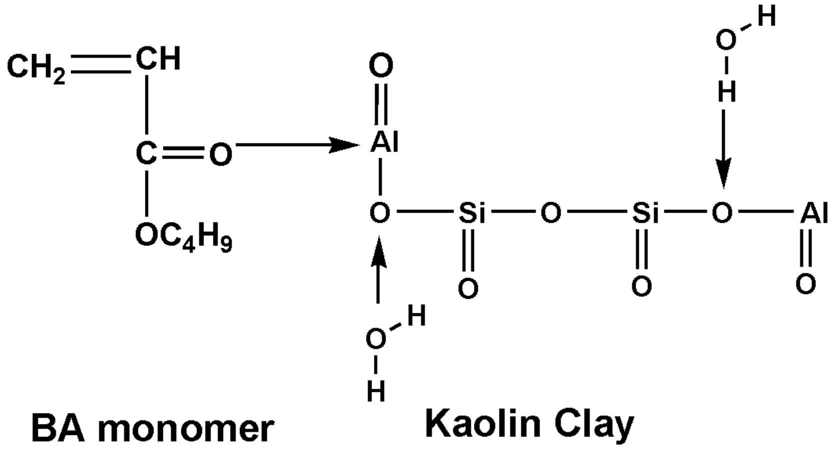


Figure 3. FTIR spectra of terpolymer and terpolymer/clay composites in **(a)** absorption; **(b)** transmittance mode.



Scheme 2. Schematic presentation of chemical interaction of >C=O groups of BA with -Al=O groups of clay.

3.3. Differential scanning calorimetry (DSC) analysis.

The T_g of the terpolymer/clay composites was determined using DSC measurements. The T_g values of V-1, V-2, V-3, V-4, and V-5 terpolymer/clay composites were found to be –42, –41, –40, –39, and –38°C respectively, as shown in Figure 4, and the same also have been summarized in Table 2. With an increase in the amount of clay, the T_g values shifted toward higher temperatures. The presence of clay in the polymer matrix decreases the free segmental motion of the polymer chains and hence increases the glass transition temperature [2]. The reported *Tg* of polyvinyl acetate/ montmorillonite nanocomposite is 32.2°C to 36.2°C [45,31], which is much higher than the *Tg* of terpolymer/clay composites prepared in this work. Low *Tg* indicates the amorphous nature of the composites.

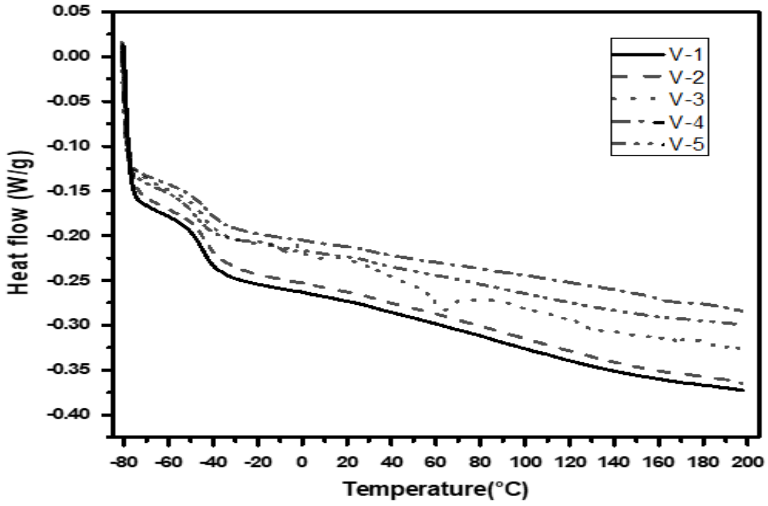


Figure 4. DSC plots of terpolymer and terpolymer/clay composites.

3.5. Thermogravimetric analysis (TGA) analysis.

The thermal stability of the terpolymer/clay composites was investigated using TGA. The different TGA and Derivative thermogravimetry (DTG) curves of terpolymer and terpolymer/clay composites are shown in Figures 5(a) and 5(b). The degradation temperature of terpolymer and terpolymer/clay composites is summarized in Table 2. It shows that terpolymer/clay composites have higher thermal stability than pure terpolymer. The stability of polymer clay composites improves as the amount of clay in the composites increases. This is due to the chemical attachment of the kaolin clay particles to the polymer chains [2]. Batistella *et al.* studied ethylene-VAc/kaolinite composites and observed a two-stage degradation in TGA curves [46], whereas, in this work, a single-stage degradation pattern is observed. The T_{max} values (highest is 540°C) reported in this work are also comparatively higher than the values reported by Batistella *et al.*

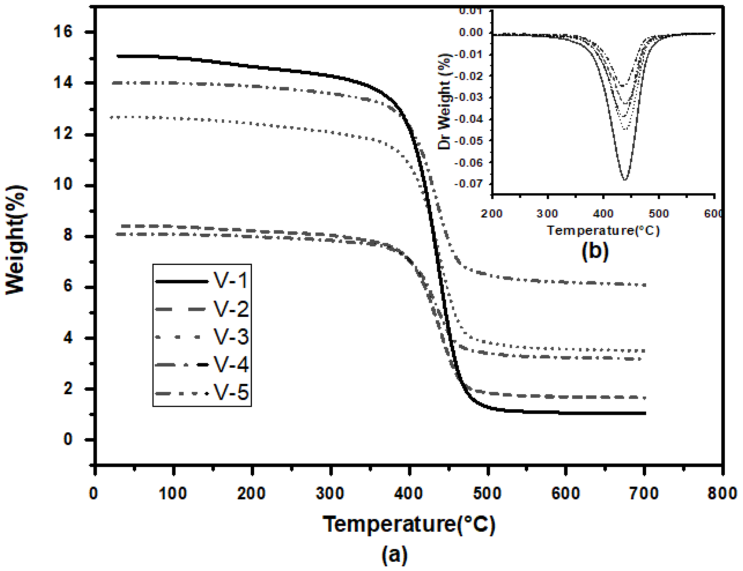


Figure 5. (**a**) TGA; (**b**) DTG plot of terpolymer and terpolymer/clay composites.

Table 2. Thermal properties of terpolymer and terpolymer/clay composites.

Sample	**Kaolin loading (%wt w.r.t. polymer wt)**	**T_{onset} (°C)**	**T_{max} (°C)**	**T_g (°C)**
V-1	Nil	293	508	-42
V-2	5	314	518	-41

Sample	**Kaolin loading (%wt w.r.t. polymer wt)**	**T_{onset} (°C)**	**T_{max} (°C)**	**T_g (°C)**
V-3	10	329	523	-40
V-4	15	331	527	-39
V-5	20	338	540	-38[2]

3.6. Physico-mechanical properties of terpolymer/clay composites.

Mechanical properties such as tensile strength, modulus, and elongation at the break of the terpolymer have been listed in Table 3. Table 3 shows that in the case of composites, the reinforcement of clay in terms of tensile modulus at 50%, 100%, 200%, and 300% elongation increased with increasing the surface area of the kaolin clay (or increase of the percentage of kaolin clay) in the compositions up to V-4, after which it decreased with further increase of clay loading. The tensile strength of the composites decreased as the amount of kaolin clay in the mixture increased to a very high extent. The composites' strength was reduced due to clay aggregation at very high clay loading [47]. Elongation at break decreased as the percent of kaolin clay (or the surface area of composites) increased up to V-3, after which it decreased (in the composite V-5). This is due to the improved polymer reinforcement and internal plasticizing effect imparted by the clay present in the polymer. In contrast, elongation was reduced due to the aggregation tendency of clay at higher clay loading [48]. The reinforcement parameter refers to the physico-mechanical properties of the materials. As a result, as the amount of clay in the composites increases, the physico-mechanical properties of the polymer increase.

Table 3. Physico-mechanical properties of terpolymer and terpolymer/clay compositions.

Sample name	**a_0 (mm)**	**b_0 (mm)**	**Modulus at 50% (MPa)**	**Modulus at 100% (MPa)**	**Modulus at 200% (MPa)**	**Modulus at 300% (MPa)**	**Tensile Strength (MPa)**	**Elongation at break (%)**	**Wa (Nm)**	**F-max (MPa)**
V-1	2.52	3.15	0.065	0.098	0.175	0.276	1.290	962.6	1.43	1.290
V-2	2.14	3.00	0.122	0.167	0.258	0.354	0.830	821.8	0.81	0.832
V-3	1.20	3.00	0.139	0.187	0.295	0.378	0.211	508.8	0.19	0.440
V-4	0.85	3.00	0.175	0.187	0.189	0.188	-	-	-	0.193
V-5	1.30	3.00	0.170	0.171	0.166	0.160	0.050	995.1	0.17	0.175[3]

3.7. Hysteresis test.

The hysteresis loss of polymer compounds is compared in Figure 6 with composite films' thickness (1.3 mm- 2.30 mm) and width (3 mm). The hysteresis loss, known as the Mullins effect, is a stress-softening technique. The Mullins effect describes the amount of energy generated when a cyclic deformation occurs. In terms of viscoelastically and hydrodynamically, the hysteresis of polymer composites increases as the amount of clay or the specific surface area of clay increases. The different specific surface area of polymer/clay blends impacts clay minerals [48]. The amount of hysteresis loss area under the curve was calculated using Origin 8 computer software. Meneghetti *et al.* reported that the hysteresis loop created by short glass fiber and polypropylene increased with the number of cycles [49]. Figure 5 shows that cyclic energy loss is lower in the first cycle than in the second cycle and that the fourth cycle has the highest hysteresis energy loss. The hysteresis loss increased with the number of cycles in the loop, indicating that energy losses increased with the number of cycles in the loop. This is clearly due to the low filler–filler or terpolymer-clay interaction that takes place at a higher specific surface area filled polymer compound with the increase in the number of cycles. This indicates that the energy dissipation of the polymer composite with clay was more effective through the loading and unloading cycles. This could be due to the reason for the destruction and delayed restoration of the interactions among the clay particles and the polymer at different strain amounts during the cycles [50].

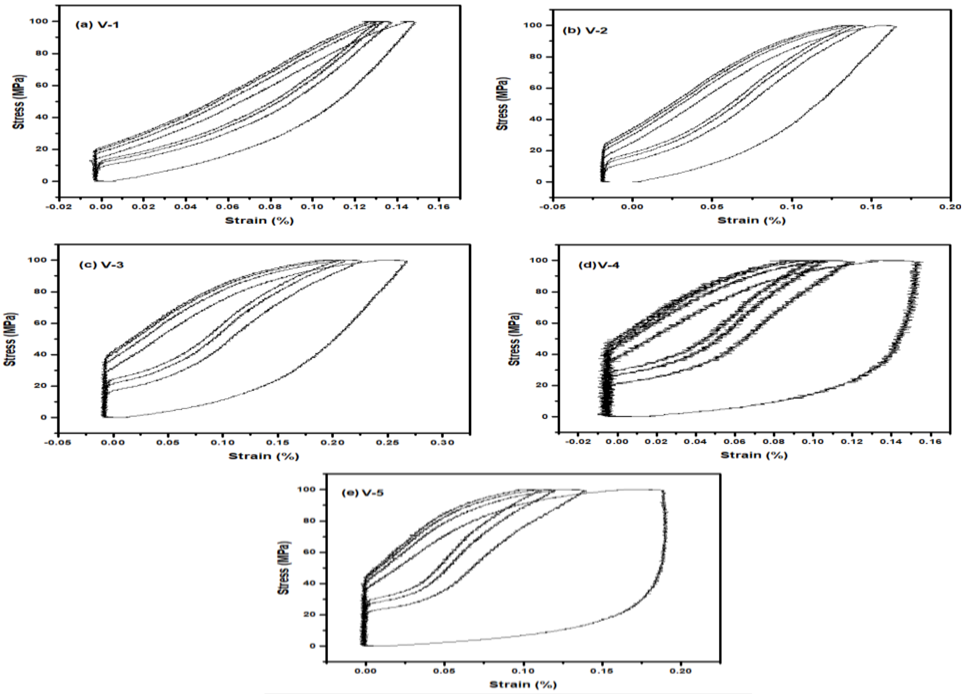


Figure 6. Hysteresis loops for terpolymer and terpolymer/clay composites **(a)** V-1; **(b)** V-2; **(c)** V-3; **(d)** V-4; **(e)** V-5.

3.8. Rheological properties of terpolymer/clay composites analysis.

Using an RPA, the melt rheological properties of the polymer composites were assessed. Dynamic viscoelastic properties of the polymer composites were characterized by storage modulus (G′), loss modulus (G″), and loss factor (tan δ = G″/G′) of the terpolymer and its clay composites under strain sweep and are shown in Figures 7(a), 7(b) and 7(c). Figure 7(a) depicts the terpolymer/clay composites storage modulus (G′) curve, which shows a non-linear viscoelastic behavior, and the modulus decreases with enhancing strain. This demonstrates that there was a structural breakdown. According to Datta *et al.*, in the study of (S–B–S) copolymer of vinyl-styrene, butadiene, and styrene, the modulus decreases with enhancing strain. This is mainly when the temperature rises to 120°C when subjected to increased strain, which causes the uncoiling of polybutadiene units to occur quickly and the fragmentation of polystyrene units into smaller pieces [51]. This is similar to what we found in our research. With increasing strain percent, there is less confrontation in both elastic deformation and viscous flow due to these changes. As a result, the curves showed a sigmoidal decrease in the character [51]. The storage modulus reduction was caused by increasing clay amounts in the composite samples. This may be due to the filler influence of clays and successive interactions with polymer chains in these composites. In fact, the low strain percent of the storage modulus was high for a high clay amount, which features a good dispersion of clay in the polymer matrix. The outcome is useful for estimating the capacity of clay dispersion in the polymer composite matrix. The curve of loss modulus (G″) versus strain percent is shown in Figure 7(b). The loss modulus decreases as the strain percent increases because the materials crack into smaller units. Datta *et al.* also reported that the loss modulus of (S–B–S) copolymer of vinyl styrene, butadiene, and styrene decreased at a certain point with increased strain due to the materials cracking into slighter units. The approximately same type of findings can be found in our polymer composites [51]. As a result, composites exhibit a flow nature. However, the enhancement of loss modulus in the low-frequency region with an increase in the concentration of clay. This performance and magnitude of modulus development may be due to more interaction of clay and polymer chains because of additional effective dispersion given by clay. Figure 7(c) shows the plot of loss factor (tan δ) versus strain % for terpolymer/clay composites, which shows that as the clay content increased, the strain% and the tan δ also increased. The improved flow behavior (or enhancement of viscous property) in the direction of the shear strain helped by the polymer composites in the molten state may be the reason for the high value of tan δ for more clay amount composites [52]. The loss factor increases with the increase in the clay concentration, mainly due to the interaction of polymer and clay. Concisely, the rheological report indicates that there is a stronger interaction between kaolin clay and terpolymer chains. Frequency sweep experiments were used to investigate the melting behavior of the terpolymer/clay composite samples. The plot of complex modulus (G*) on frequency is shown in Figure 8. Throughout the frequency range, the modulus decreases as the frequency increases.

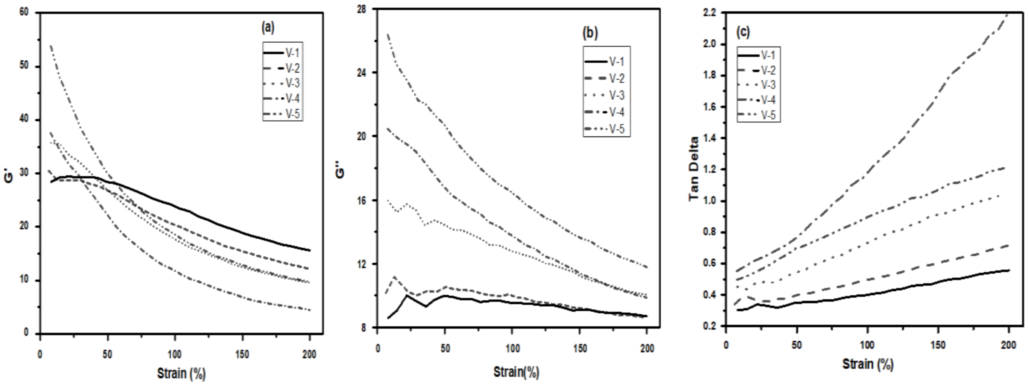


Figure 7. (a) Storage modulus; **(b)** loss modulus; **(c)** loss tangent plots for the terpolymer and its composites.

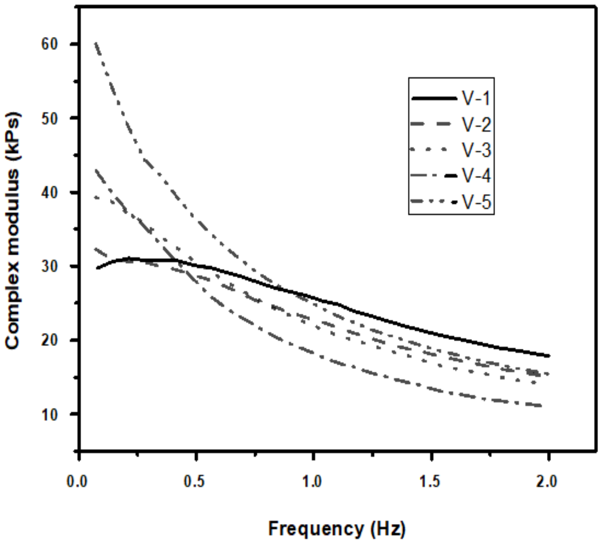


Figure 8. Complex modulus as a function of frequency (Hz) of terpolymer and terpolymer/clay composites.

Figure 9(a) depicts the relationship between storage viscosity (dynamic viscosity) and frequency. The results show that storage viscosity (η') decreases as the frequency of storage increases. According to Datta *et al.*, the real component of the complex viscosity ($\eta^* = \eta' - i\eta''$) is called the storage viscosity for the melt as a fluid in the theory of viscoelasticity. The loss modulus G'' is represented by ($\eta' = G''/\omega$), whereas η'' is the imaginary component representing the melt elasticity, and the relation between η'' and the storage modulus G'' is $\eta'' = G'/\omega$ [51].

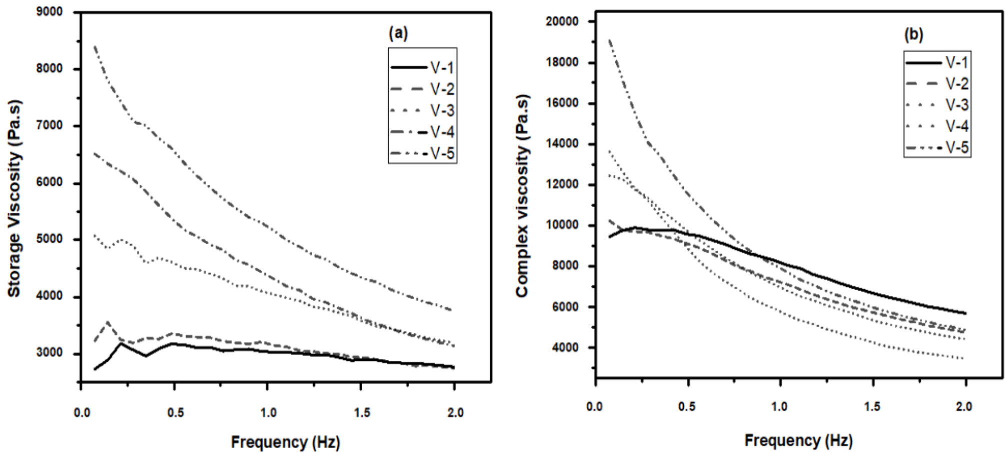


Figure 9. (**a**) Storage viscosity; (**b**) complex viscosity of terpolymer and terpolymer/clay composites.

In frequency sweep mode, the complex modulus of sample V-1 was higher than that of sample terpolymer/Clay composites V-2. It is presented that the incorporation of clay eagerly decreases the modulus from 27.08 kPs for sample V-1 to 24.4 kPs for sample V-2 at a frequency of 83.17 %. In the comparison of the outcomes of the complex modulus for terpolymer and terpolymer/clay composites samples with increasing the clay concentration, indications that terpolymer/clay composites have a more pronounced filler effect using clay of its low molecular weight and, therefore, the low quantity of melt viscosity. This performance and modulus development at the low-frequency region may be due to the higher interaction of clay and polymer chains for more effective clay dispersion [53]. Figure 9(b) shows the plot of complex viscosity as a function of frequency for polymer/clay composites. The results showed that as the shear rate or frequency range increases, all samples' complex viscosity (η^*) decreases. This is due to the fact that all polymer composites exhibit pseudoplastic or non-Newtonian fluid behavior. As a result, the polymer composites have good processing characteristics [52]. The storage viscosity increases with an increase in the clay amount. The complex viscosity decreases with the increase in clay amount. These rheological responses indicate a stronger interaction between kaolin clay and terpolymer chains.

3.9. Morphological study.

FESEM was used to examine the surface morphologies of the polymer and the polymer/clay composites. The micrographs for polymer V-1 and polymer/clay V-2 composites are shown in Figure 10.

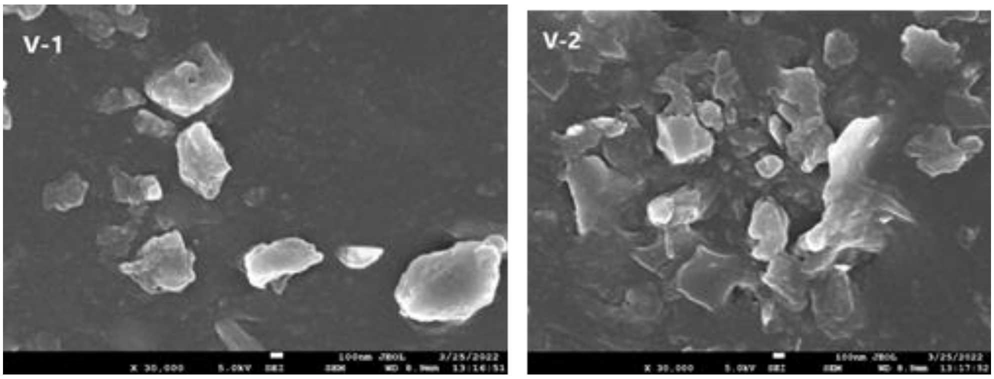


Figure 10. FESEM images of terpolymer (V-1) and terpolymer/clay composite (V-2).

According to these micrographs, polymer composites have a smaller particle size than that of polymer/clay composites. The particle size grows when the clay is added, and agglomeration occurs [54]. This led to a change in the particle size in the terpolymer.

4. Conclusions

Conventional free-radical emulsion polymerization of VAc, BA, and AA yields PVAc-based terpolymer latex. The emulsion polymerization was successfully carried out at 70°C using KPS as an initiator and SDS as a surfactant. The conversion of the monomers after one hour of polymerization was calculated gravimetrically and found to be 90%. The successful incorporation of co-monomers in the terpolymer was confirmed by ^{1}H NMR analysis. A requisite amount of clay is mixed directly with the terpolymer latex to prepare the composites. FT-IR studies reveal a distinct interaction between the >Al=O groups of the clay and that of the carbonyl group in the polymer. The bonding of clay to the polymer chain was confirmed by DSC analysis, where an increase in T_g of the composites was observed with clay loading. According to the TGA and DTG analyses, degradation temperature rises as clay content increases, indicating that clay increases the thermal stability of the composites. As a result, the thermal properties of the composites have improved. The interaction between the polymer and clay was also confirmed via tensile measurements. The tensile strength decreased as the percentage of kaolin composites increased. With the increase of filler loading, the uniform dispersion and adhesion of clay into the polymer matrix increases, which increases the tensile modulus. As a result, clay-based composites improve the physicomechanical properties of polymer films. It was observed that clay's presence enhances the polymer composites' viscous properties in the molten state using an RPA in strain sweep mode. Experiments with frequency sweeps show that the complex viscosity of all composites decreases as the frequency range increases. As a result, polymer composites exhibit pseudoplastic or non-Newtonian fluid behavior. Thus, it can be concluded that the polymer composites have good processing characteristics and may have several potential applications as adhesives.

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Conflicts of Interest

The authors declare no conflict of interest.

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