Chapter 5:
Poly(VAc-t-BA-t-Sty) terpolymer/kaolin clay composites and their characterizations

ABSTRACT

The main goal of this work is report the preparation of a terpolymer of styrene with butyl acrylate and vinyl acetate in emulsion via free radical polymerization and its composites with kaolin clay. The emulsion ter-polymerization was carried out at 70 °C using sodium dodecyl sulfate (SDS) as an emulsifier and potassium persulfate (KPS) as a free radical initiator. The latex obtained in this emulsion polymerization was coagulated to obtain the terpolymer. Thus, the obtained terpolymer was purified and analyzed via NMR analysis for structural evaluation. However, latex was used to prepare a series of terpolymer/kaolin clay composites by mixing with kaolin clay at different weight ratios. The effect of the amount of kaolin on the properties of the terpolymer/clay composites was studied. Surface morphology and crystallinity were also studied for all those prepared composites. It was observed that the incorporation of kaolin clay increases the roughness and crystallinity in the terpolymer/kaolin clay composites. It was also observed that 10% kaolin clay contain composite was show good interaction between clay and polymer matrix among the five set of composites evaluated from FTIR and PXRD analysis. This composites also show more roughness analyzed by SEM.

KEYWORDS: Styrene, Vinyl acetate, Butyl acrylate, Terpolymer, Composite.

5.1. INTRODUCTION

Recently, growth of polymer–inorganic nanocomposites have gained momentum due to these materials scientific and industrial overview of a wide range of application.[150] The key features of these materials are mainly inorganic material behavior such as rigidity and thermally stable and also organic polymer characteristics like flexible product, ductility, and processability.[106] Nowadays, polymer composite give great attention due to the unique properties of which come from the blend of two or more materials of polymeric, metallic or ceramics nature by means of specific ways to link them together.[26] In this research field polymer/clay blends have gained drive after the report on the Nylon-6 and clay nanocomposites blends.[94] Researchers have focused their efforts on the study of these polymer/clay composite materials. They were able to make some remarkable progress in this field using the waste polymer in useful products. Kaolin-based pyrolysis of waste polystyrene, which is a green process can convert waste plastic materials into useful products.[151] There are numerous reports on the preparation of polymer/clay composites and the evaluation of their properties for certain applications. Cazotti et al. reported the preparation of poly(vinyl acetate)/montmorillonite clay nanocomposites. This poly(vinyl acetate) based nanocomposite showed better adhesive properties, and good mechanical and thermal properties.[110] Polymer composites of these types have many applications, they are used in paint and also to recycle papers for better economic improvement.[152,108] The well-known methods used to manufacture of polymer/clay composites such as electrophoresis precipitation, chemical inscription, layer after layer self-assembly, chemical vapor deposition and electrospinning technique,[153] latex blending method.[153] Clays are aluminium phyllosilicate. They are natural inorganic materials and are mostly used as fillers. The most useful layered clay mineral is Kaolinite. Kaolinite is suitable to be used as a functional filler to modify the properties of polymers. There have been several reports on this line. Zhang et al. reported the preparation of SBR/kaolin clay composite by latex blending method.[154] They investigated the improvement of the interaction between the filler particles and the rubber matrix. This composite was projected as an eco-friendly rubber composite for making tires with better wet traction, slip resistance and a low heat build-up. In another work, Qin el al. reported SBR/ kaolinite composite using the same process described the mechanical properties of is improve reinforcement due to the presence of clay intercalation compounds.[155] Hua et al. proposed an experiment to study of the effect of poly (isoprene-random-3-methacryloxypropyltrimethoxysilane) random copolymer on improved the properties dispersed and mechanical strength of kaolin-reinforced styrene-butadiene rubber (SBR).[156] Wu et al. reported unique experiment on synthesis of clay/polymer inorganic dyes useful as synchronous coloring and reinforcing requirements of plastic due to outstanding environmental stability and weather resistance compared with organic dyes.[157] Sarde et al. reported the preparation of a polyester resin/kaolin clay composite. It was aimed to be used as a binder in polymer mortar composites for interior decoration and in construction applications.[158] In another approach, poly(butyl acrylate)/silicon dioxide composite microspheres prepared using ultrasonically initiated emulsion polymerization method described by Guoa et al.[159] Polymer/clay composites like $CsPbBr_3$ perovskite quantum dots/ethylene vinyl acetate composite films were prepared with good properties for use in lighting applications.[109] By solution cast approach, polymer blend of polyvinyl alcohol (PVA)/carrageenan/kaolinite prepared. Such films show antibacterial properties and suitable for food packaging.[160] There have been numerous reports on the preparation of polymer/clay composite by different methods for the improvement of mechanical properties. However, the latex blending method has not been explored much.[161]

In this current investigation, the latex blending method has been used to prepare a series of styrene-based terpolymer/kaolin clay composites. The terpolymer, poly(VAc-*t*-Sty-*t*-BA) was synthesized via free radical polymerization in the emulsion. The resulting terpolymer latex was mixed with various amounts of kaolin clay to prepare some terpolymer/kaolin clay composites. The prepared polymer/clay composites were characterized by several methods to study the possible interactions that exist between the polymer and clay moieties leading to the improvement in properties.

5.2. PREPARATION

5.2.1. Preparation of the terpolymer, poly(VAc-*t*-Sty-*t*-BA)

For the preparation of the terpolymer, SDS (11.37 mmol) and distilled water (9.11 mol) were taken in a dry round bottom flask (RB) equipped with a stirrer, a magnetic bar and a rubber septum. The mixer was stirred till a homogeneous colloidal solution was formed. Then all three monomers, styrene (Sty) (41 g, 0.39 mol), butyl acrylate (BA) (32.8 g, 0.09 mol), and vinyl acetate (VAc) (8.2 g, 0.26 mol) were added to the colloidal solution with continuous stirring. After 30 mins of stirring, KPS (0.656g, 2.42 mmol) was added to the reaction mixture and was sealed the RB with a rubber septum. The polymerization was started by placing the RB in a preheated oil bath at 70 ºC. The stirring speed was maintained at 460 rpm and the polymerization reaction was run for 1hr. Aliquots were taken out at regular intervals to check the progress of the polymerization. The conversion of the monomers was calculated gravimetrically. The polymerization was stopped by exposing the polymerization mixture to atmospheric air. The final monomer conversion was calculated to be 90%. The coagulum formed was found to be 1.58% which was separated before processing. The prepared terpolymer latex was dissolved in THF, re-precipitated in water, and dried in an oven at 60 °C to get the pure terpolymer for further characterization. GPC analysis of this purified terpolymer (Mn(GPC) = 4,43,919 g/mol and PDI = 3.6) showed an unimodal trace (Figure 5.1). UV-Vis analysis was carried out for the latex to estimate the latex’s transparency.

5.2.2. Preparation of Poly(VAc-t-Sty-t-BA) terpolymer/kaolin clay

The basic formulation used in this study is shown in Table 5.1. The terpolymer/clay composites were prepared by direct mixing of the terpolymer latex with kaolin clay at various weight ratios: 5%, 10%, 15%, and 20% w.r.t the weight of the terpolymer used respectively. The mixtures were stirred for 24 hours and then poured into a glass petri dish. It was then dried in an oven at 60ºC to get a thin layer film of the composites. The obtained films of the terpolymer/clay composites were characterized via FT-IR, PXRD and SEM analyses.

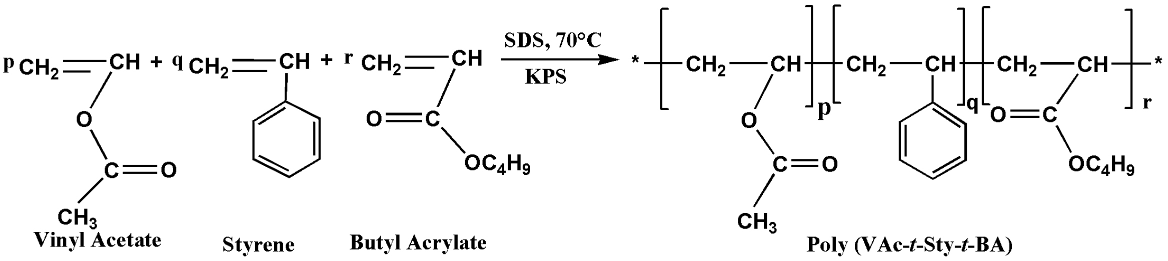
Table 5.1. Compositions of the terpolymer latex and clay in the composites.

Sample Designation	Poly(Sty-t-BA-t-VAc)/Kaolin (wt.%)	Clay% w.r.t terpolymer weight
SV1	50/0	0
SV2	45/2.25	5
SV3	45/4.50	10
SV4	45/6.75	15
SV5	45/9	20

5.3. RESULTS AND DISCUSSION

5.3.1. Analysis of terpolymer latex

Scheme 5.1 shows the ter-polymerization of vinyl acetate (VAc), styrene (Sty) and butyl acrylate (BA) via free radical polymerization. This emulsion polymerization was carried out at 70 ℃ using potassium persulfate (KPS) as an initiator and sodium dodecyl sulfate (SDS) as surfactant.



Scheme 5.1. Free radical emulsion polymerization of (VAc-*t*-Sty-*t*-BA)

Figure 5.1. shows the terpolymer latex prepared by the above method. This latex was stored for a couple of weeks and no macroscopic phase separation was observed during this preservation period.

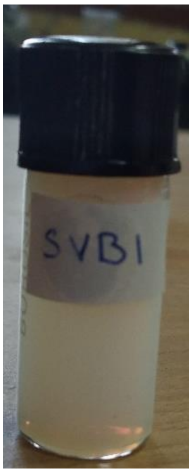


Figure 5.1. Latexes of poly (VAc-*t*-Sty-*t*-BA).

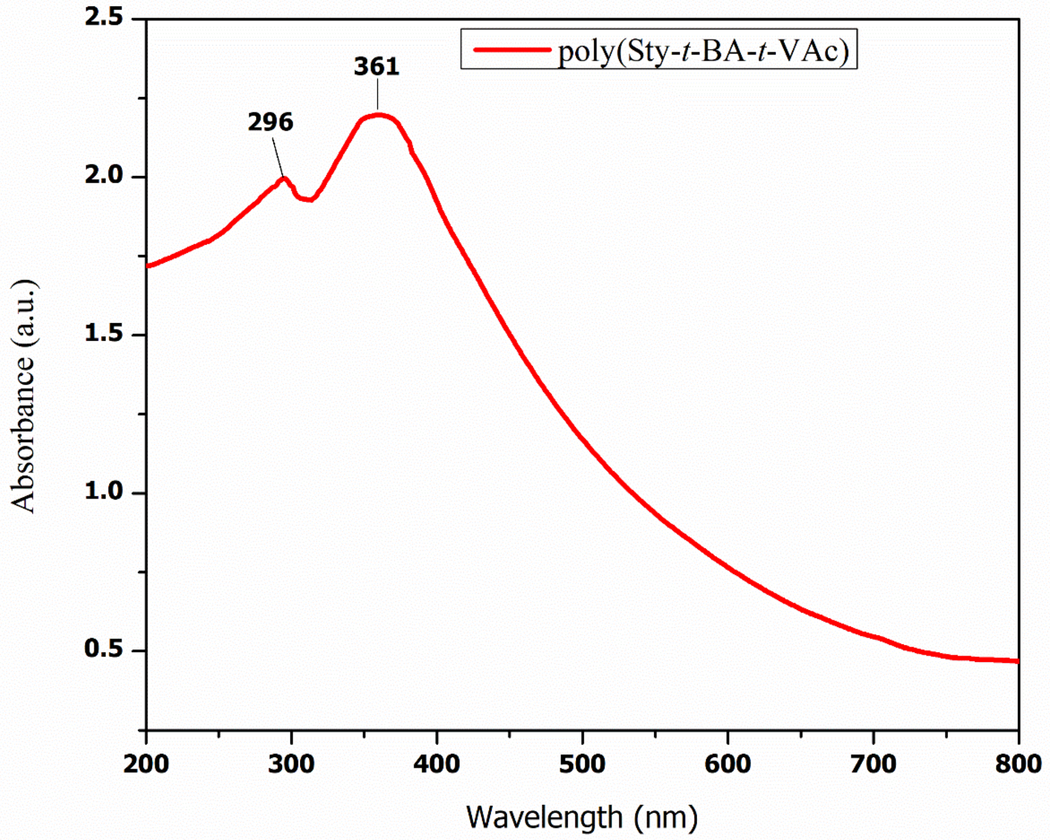


Figure 5.2. UV-Visible spectrum of poly(VAc-*t*-Sty-*t*-BA) polymer latex.

UV-Vis analysis of the terpolymer latex was carried out to extract information about its transparency. Figure 5.2. shows the UV-Vis absorption spectrum of the poly(VAc-*t*-Sty-*t*-BA) terpolymer latex. The λ_{max} at which the terpolymer latex absorbs UV light is 360 nm. This may be attributed to the increase in the number of chromophoric carbonyl groups (C=O) of PBA and PVAc units in the terpolymer latex. The absorption band at 296 nm is observed due to the charge-transfer interaction of the phenyl group present in the terpolymer. Due to the flexibility of the polymer chain, the interaction between phenyl groups is possible which may lead to this absorption band.[162]

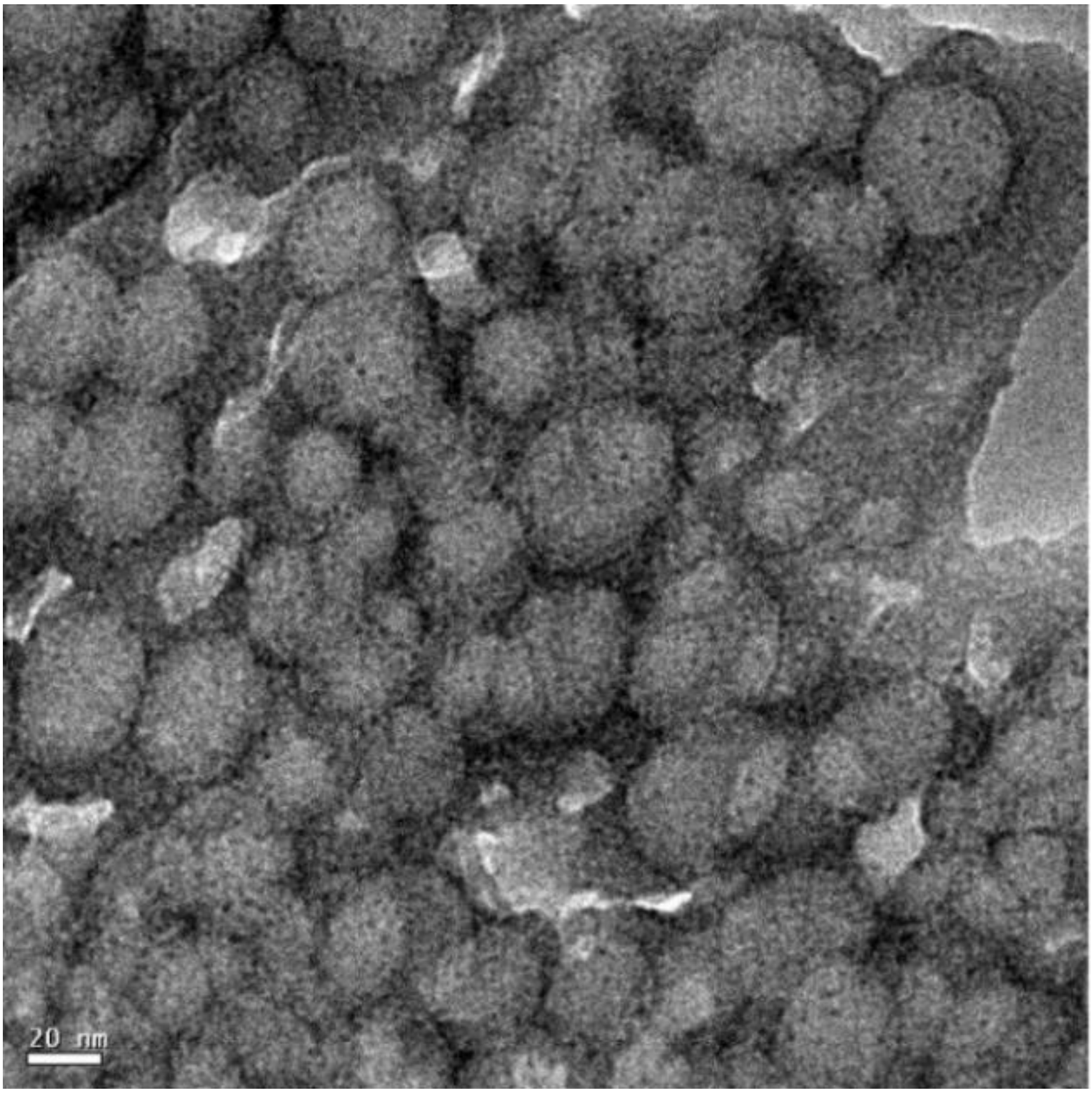


Figure 5.3.(a) TEM images of poly(VAc-*t*-Sty-*t*-BA) terpolymer latex (20nm).

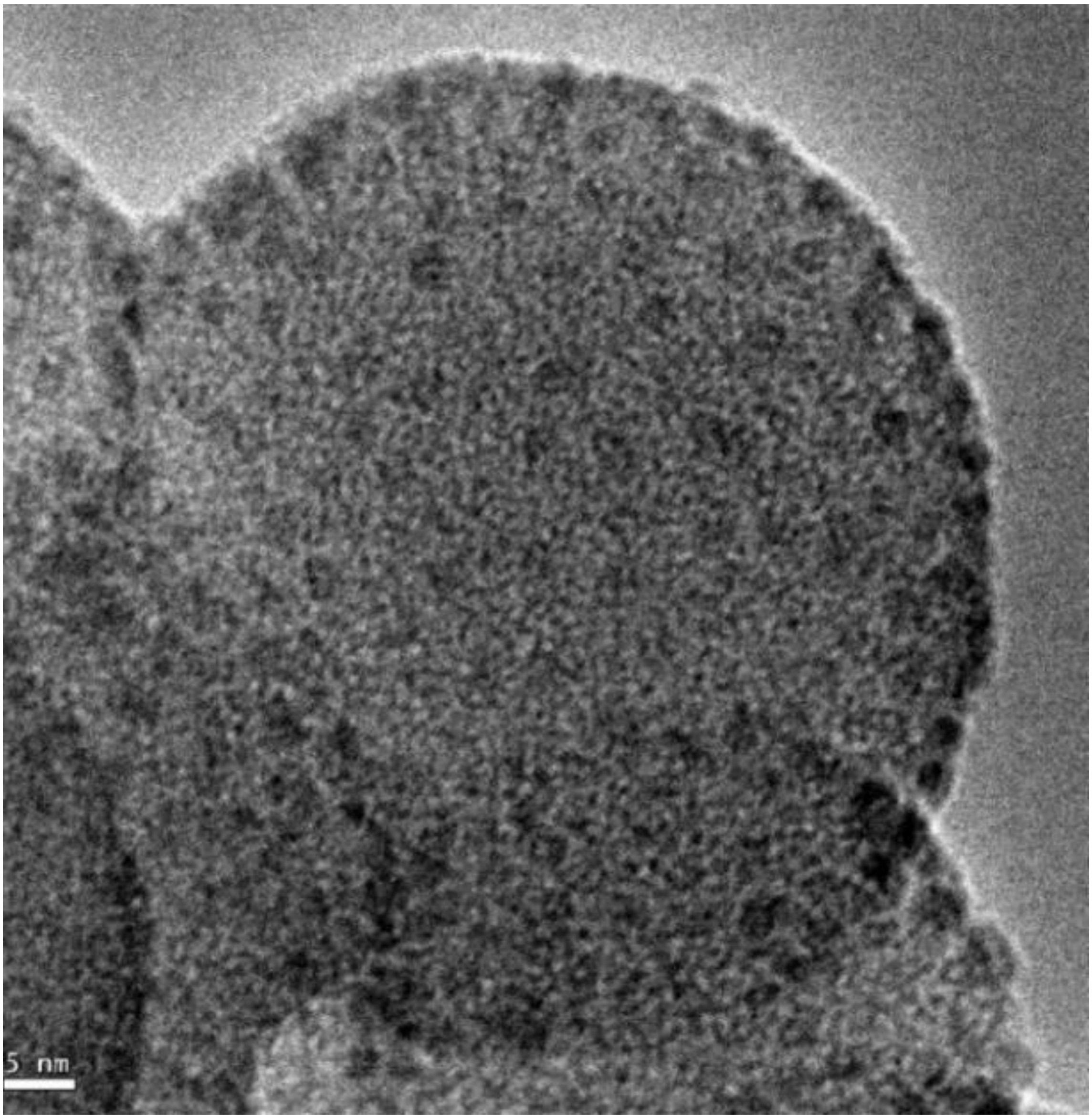


Figure 5.3.(b) TEM images of poly(VAc-*t*-Sty-*t*-BA) terpolymer latex (5 nm).

The morphology of the prepared latex was studied by transmission electron microscopy (TEM) (Figure 5.3.) analysis. The TEM micrographs of terpolymer latex shows that the particles are nearly monodispersed and spherical in shape. From the TEM image, it can be observed that the diameter of terpolymer particles ranges from 21.8 to 22.6 nm, which is calculated using the distribution method. According to the TEM images, the particles are spherical and have good dispersibility.

5.3.2. Analysis of terpolymer (pure)

GPC analysis was carried out to know the molecular weight of the pure terpolymer. The number average molecular weight provided by the GPC analysis was found to be 4,43,919 g/mol with PDI = 3.6. The unimodal GPC trace (Figure 5.4.) of the terpolymer indicates that the terpolymer prepared was free of homo or copolymers of the monomers.

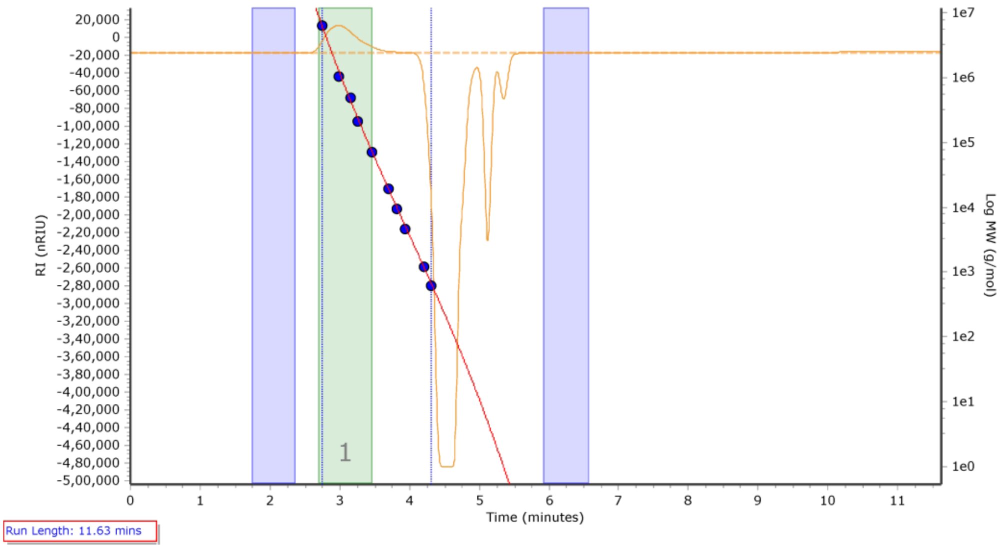


Figure 5.4. GPC trace of the purified terpolymer.

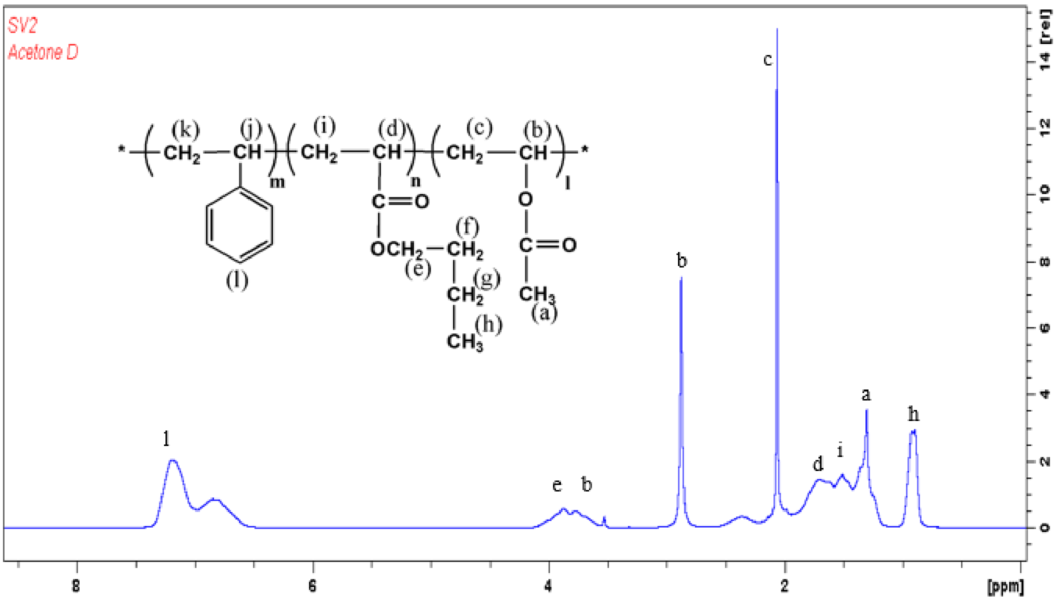


Figure 5.5. ^{1}H NMR spectrum of poly(VAc-*t*-Sty-*t*-BA) terpolymer.

Structural evaluation of the pure terpolymer was carried out by ^{1}H NMR analysis. Figure 5.5. shows the ^{1}H NMR spectrum of the poly(VAc-*t*-Sty-*t*-BA) terpolymer. In Figure 5.5., the methyl and methylene protons of BA were observed at 0.87 (h) ppm and 1.76 ppm respectively, while the —OCH_2— protons were observed at 4.06 (e) ppm. The main backbone protons of —CH— (d) of BA were observed at 1.6 ppm. The peaks at 1.35 (f) ppm and 6.61-7.52 ppm are attributed to the methyl protons (—CH_3) of VAc and the aromatic protons of styrene of the terpolymer respectively. The absence of the NMR peak at 4.6-5.9 ppm for vinyl protons confirms the successful terpolymerization.

5.3.3. Analysis of terpolymer/clay composites

A few terpolymer/clay composites were prepared by mixing the terpolymer latex with different amount of kaolin clay as shown in the Table 5.1. Four different terpolymer/clay composites were prepared by mixing 5%, 10%, 15% and 20% of kaolin clay with the terpolymer latex. Figure 4.6. shows the films prepared from all the five compositions as shown in Table 5.1.

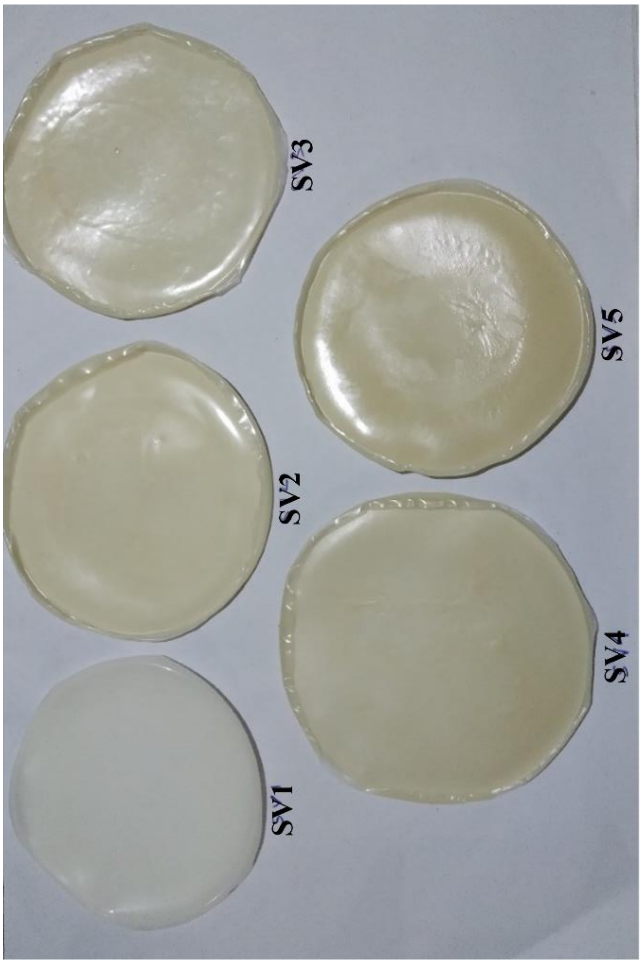


Figure 5.6. Poly(Sty-*t*-BA-*t*-VAc) /clay composite films (SV1, SV2, SV3, SV4 and SV5).

The successful preparation of polymer/clay composite was studied via the FT-IR analysis. Figure 5.7. shows the FT-IR spectra of the pure terpolymer and its composites. In Figure 5.7., it is seen that as the concentration of clay increased, the absorption band of >C=O stretching frequencies shifted 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%, while the Al—O stretching frequencies of kaolin clay in the composites shifted to a higher frequency (479 cm^{-1} in case of 5% clay, 480 cm^{-1} in case of 10% clay, 481 cm^{-1} in 15% clay, and 481 cm^{-1} in 20% clay). This is due to the Van Der Waals force of intermolecular bonding of the interaction of the >Al=O group of the clay layers with the >C=O group of the monomers (>C$^{\delta-}$=O$^{\delta+}$·····$^{\delta-}$Al=O) (Scheme 5.2), which reduces the double bond character of the carbonyl group and hence the stretching frequencies.[163]

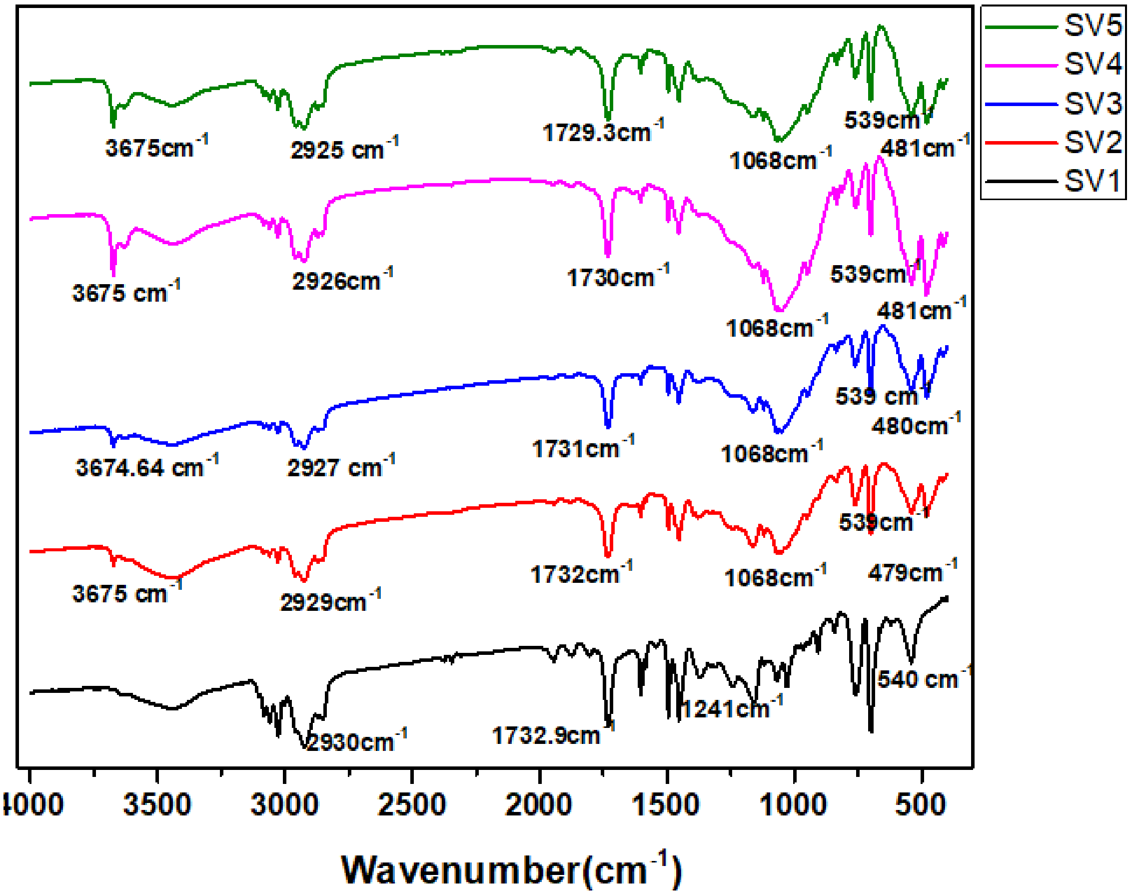
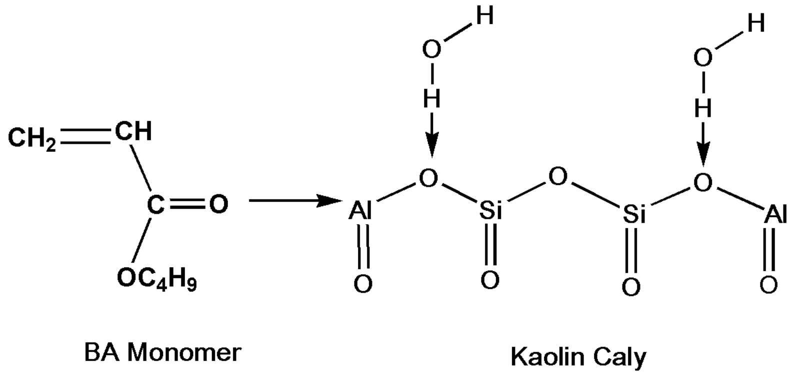


Figure 5.7. FT-IR spectra of poly(VAc-*t*-Sty-*t*-BA) and its composites.



Scheme 5.2. The Chemical interaction of the BA unit with the kaolin clay

The C—H stretching band of the methyl group of the polymer composites SV1, SV2, SV3, SV4, and SV5 is shown at 2930, 2929, 2927, 2926, and 2925 cm^{-1} respectively.[101] In comparison to pure polymer, the C—H stretching band of polymer composites shifted towards lower frequencies (by 1 cm^{-1} in case of 5%, 3 cm^{-1} in case of 10%, 4 cm^{-1} in 15%, and 5 cm^{-1} in 20%). This refers to the adsorption of kaolin clay particles by the polymer latex via hydrogen bonding between the Si—O—H (silanol) of clay and the polymer molecules.[139] The absorption band at 1068 cm^{-1} is attributed to the Si—O group of kaolin clay. The absorption frequency of the Si—O group in kaolin clay is slightly shifted to the lower frequency as a result of the interaction between the polymer molecules and clay particles.[139]

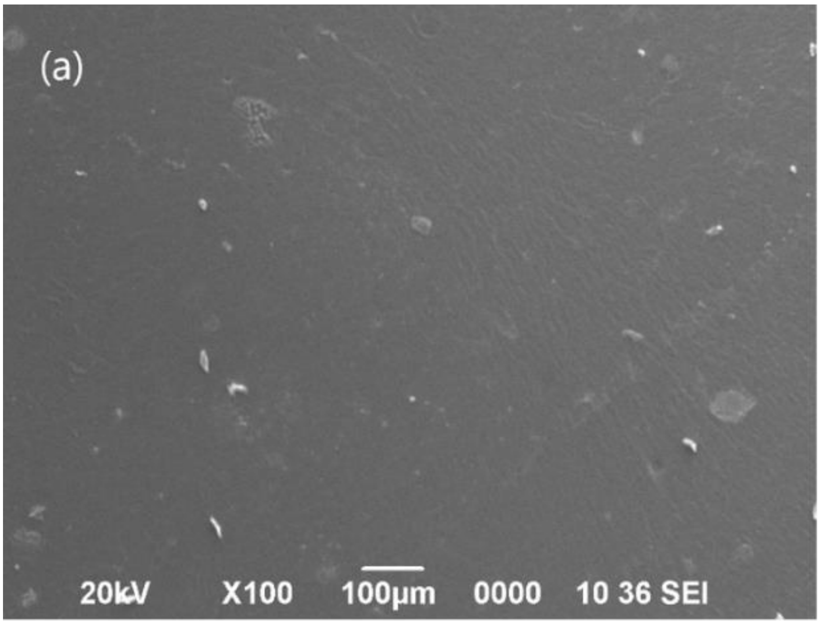


Figure 5.8. SEM images of the terpolymer and terpolymer/clay composites: (a) SV1 at 100 μm.

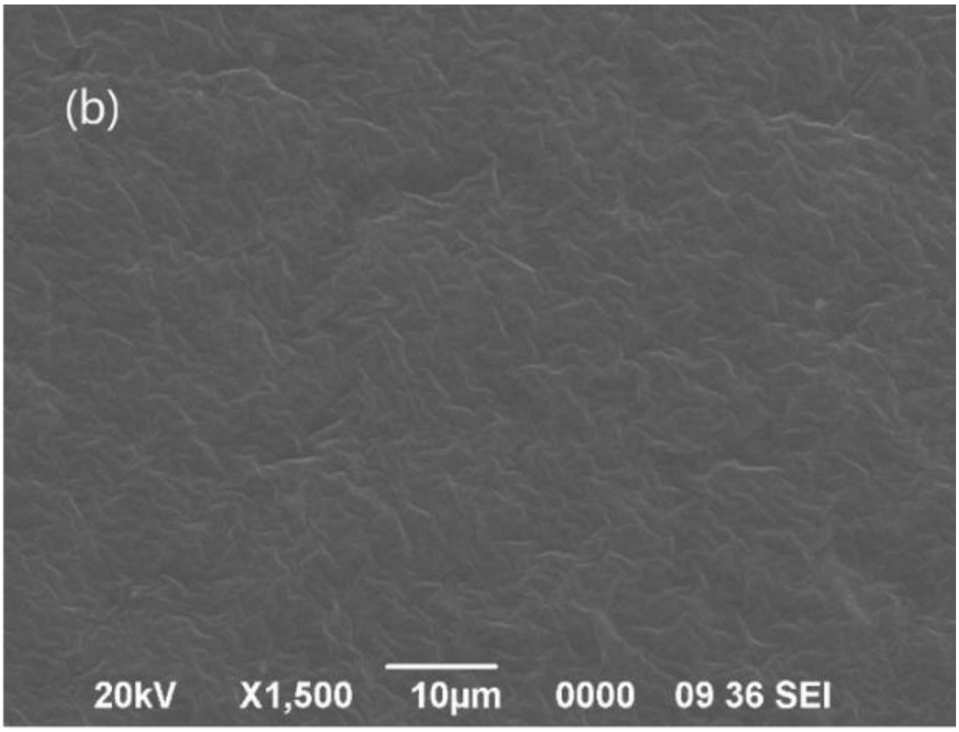


Figure 5.8. SEM images of the terpolymer and terpolymer/clay composites: (b) SV1 at 10 *μm,*

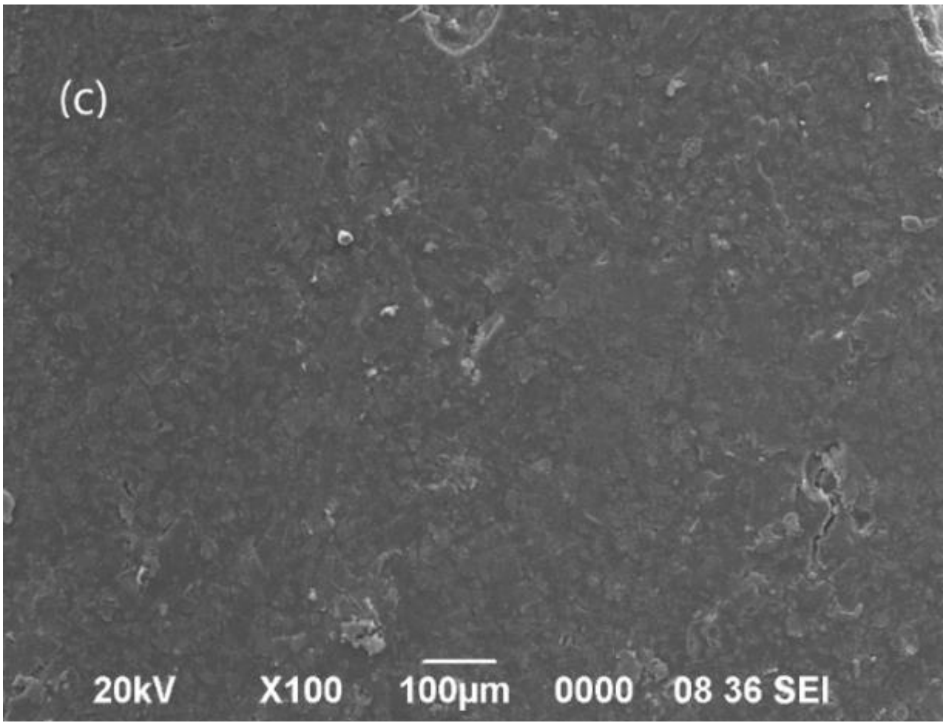


Figure 5.8. SEM images of the terpolymer and terpolymer/clay composites: (c) SV3 at 100 *μm*.

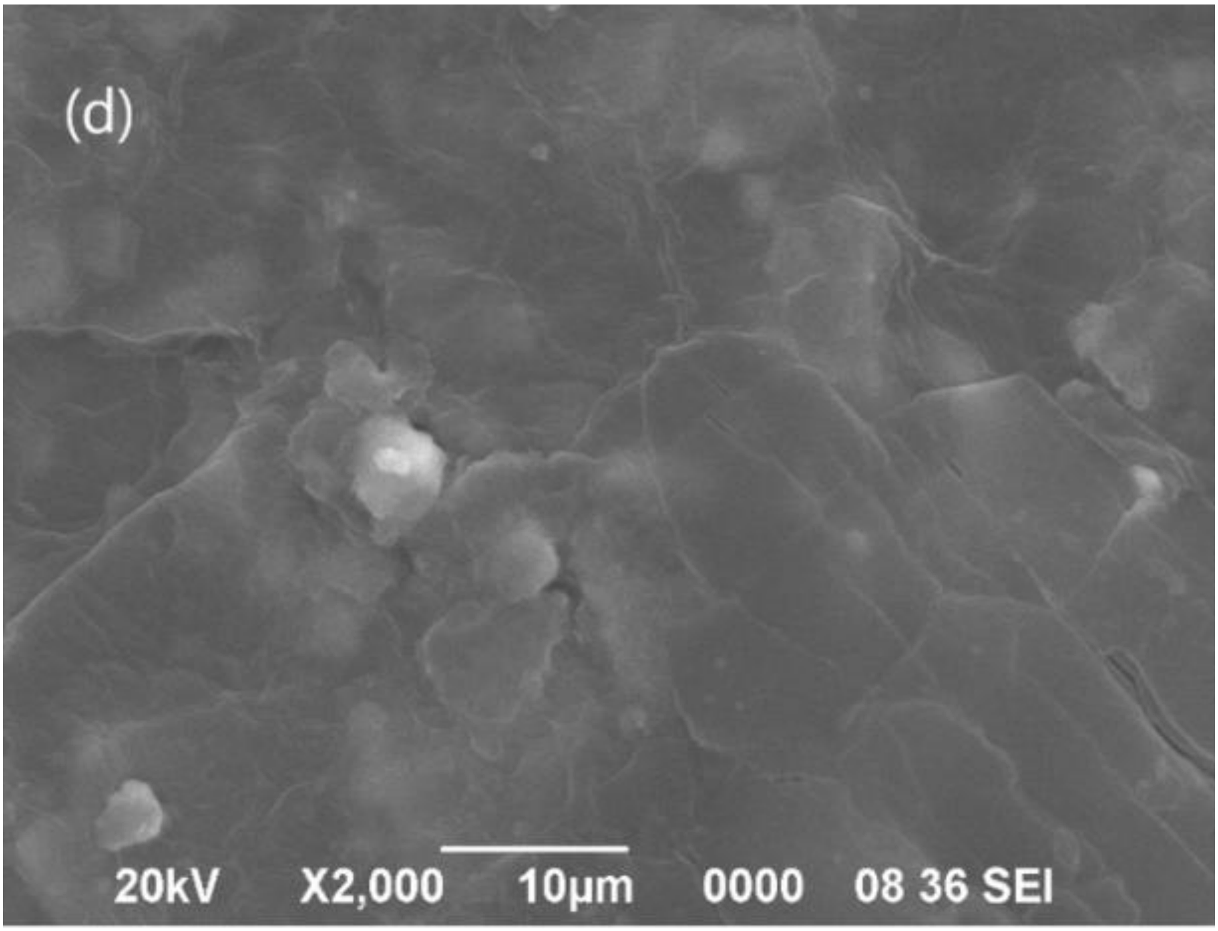


Figure 5.8. SEM images of the terpolymer and terpolymer/clay composites: (d) SV3 at 10 μm.

The surface morphologies of the terpolymer and the terpolymer/clay composites were analyzed by SEM analysis. Figures 5.8. (a) and (b), illustrate the surface morphologies of the terpolymer (SV1), while Figures 5.8. (c) and (d), illustrate the surface morphologies of terpolymer/clay composite (SV3). From the SEM analysis, the surface morphology of the terpolymer/clay composites are observed to be rougher than the neat terpolymer. The dispersion of clay on the polymer matrix and distribution of the aluminum oxide and silicon oxide layers in the polymer. It is estimated based on the above discussion, the FTIR spectra (Figure 6) represented the interaction of polymer and clay.[164] The augmentation of roughness primarily increases with increasing the clay percentage enhancing the polymer/clay composite's degradation nature.[165]

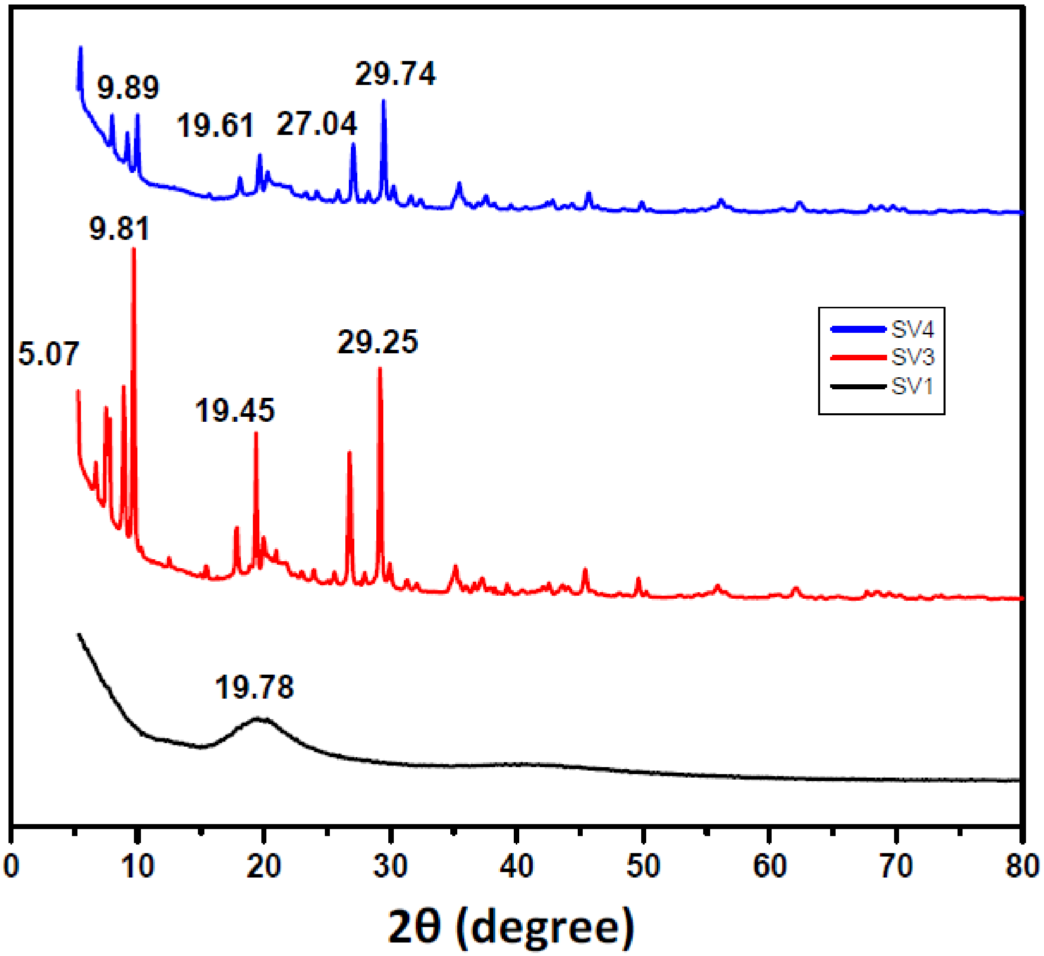


Figure 5.9. PXRD diffractogram of poly(VAc-*t*-Sty-*t*-BA)/kaolin clay composites (SV1, SV3, and SV4).

The crystalline nature of the prepared terpolymer composites were studied by XRD analysis. Figure 5.9. shows the PXRD diffractograms of the terpolymer and the terpolymer/clay composites. The XRD plot of the terpolymer shows a broad peak at 2θ =19.78°, which corresponds to the terpolymer microspheres. In composites SV3 and SV4 shows adsorption peaks at 2θ =9.81°, 19.45°, 29.25° and 9.98°, 19.61°, 29.74° respectively which is mainly presence of more crystalline nature of kaolin clay.[165] The crystalline nature of the polymer/clay composites can be seen in their respective XRD plots. It is expected based on the SEM discussion, roughness increases with increasing the clay amount in the composites and also improve degradation nature with enhancement of crystalline nature. The crystalline nature of the composites increases with the increase in the amount of clay. This also increases roughness in the composites.

5.4. CONCLUSION

Free radical emulsion terpolymerization of styrene, butyl acrylate and vinyl acetate led to the formation of stable latex of the terpolymer, poly(VAc-*t*-Sty-*t*-BA). This polymerization was carried out at 70ºC using KPS as an initiator and SDS as a surfactant. The conversion of the monomers was calculated gravimetrically and found to be 90% after 1 hour of polymerization time. The prepared latex was stable for a couple of weeks and was also found to be transparent as evidenced by the UV-vis analysis. A unimodal GPC trace and ^{1}H NMR spectrum of the purified terpolymer confirmed the successful preparation of the terpolymer. A few terpolymer/clay composites were prepared by direct mixing of this terpolymer latex with kaolin clay at different weight ratios. The prepared terpolymer/clay composites were also characterized by various analytical techniques, like FT-IR, PXRD and SEM. The chemical interaction that exists between the monomer's units and the clay moieties in the composites was established via all those analyses and hence the formation of the true composites was confirmed.