Chapter 2:

Experimental and characterization techniques

2.1. MATERIALS

Vinyl acetate (VAc) (99%, SRL, India), butyl acylate (BA) (99%, Aldrich, USA) acrylic acid (AA) (99%, Loba, India) and styrene (99% Loba, India) were used as monomers. Ammonium persulfate (APS) (98%, Merk, India) and potassium persulfate (KPS) (98%, Avra Synthesis Pvt., India) were used as initiators. Sodium dodecyl sulfate (SDS) (99%, SRL, India) was used as surfactants. Kaolin clay was used as received. 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.

2.2. CHARACTERIZATIONS

2.2.1. UV-visible spectroscopy

UV-visible spectra of the purified poly(VAc-*co*-BA*)* copolymers and poly(VAc-*t*-BA-*t*-AA*)* terpolymers were recorded in the wavelength range of 200-1000 nm on UV-visible spectrophotometer. UV-visible spectra of the poly(VAc-*t*-Sty-*t*-BA*)* terpolymer latex was recorded in the wavelength range of 200-1100 nm on a UV-visible spectrophotometer (electronic India (EI), Mode No. 3375) using water as a reference solvent.

Figure 2.1. UV-visible spectroscopy (Bodoland University).

2.2.2 Nuclear magnetic resonance (NMR) spectroscopy

The ^{1}H NMR spectra of poly(VAc-*co*-BA) copolymers and poly(VAc-*t*-BA-*t*-AA) terpolymers samples were recorded on 400 MHz Bruker NMR spectrometer using $CDCl_3$ as a solvent with tetramethylsilane (TMS) as an internal standard. ^{1}H NMR spectra of the synthesized poly(VAc-*t*-BA-*t*-AA*)* polymer and polymer/clay composites samples were recorded on 600 MHz Bruker NMR spectrometer using chloroform-d ($CDCl_3$**)** as a solvent and tetramethylsilane (TMS) as an internal standard. Bruker Topspin 3.6.1 software was used to examine the generated spectra. Also ^{1}H NMR spectra of the synthesized poly(VAc-*t*-Sty-*t*-BA) terpolymer and terpolymer/clay composites samples were recorded on 400 MHz Bruker NMR spectrometer using $CDCl_3$ as a solvent.

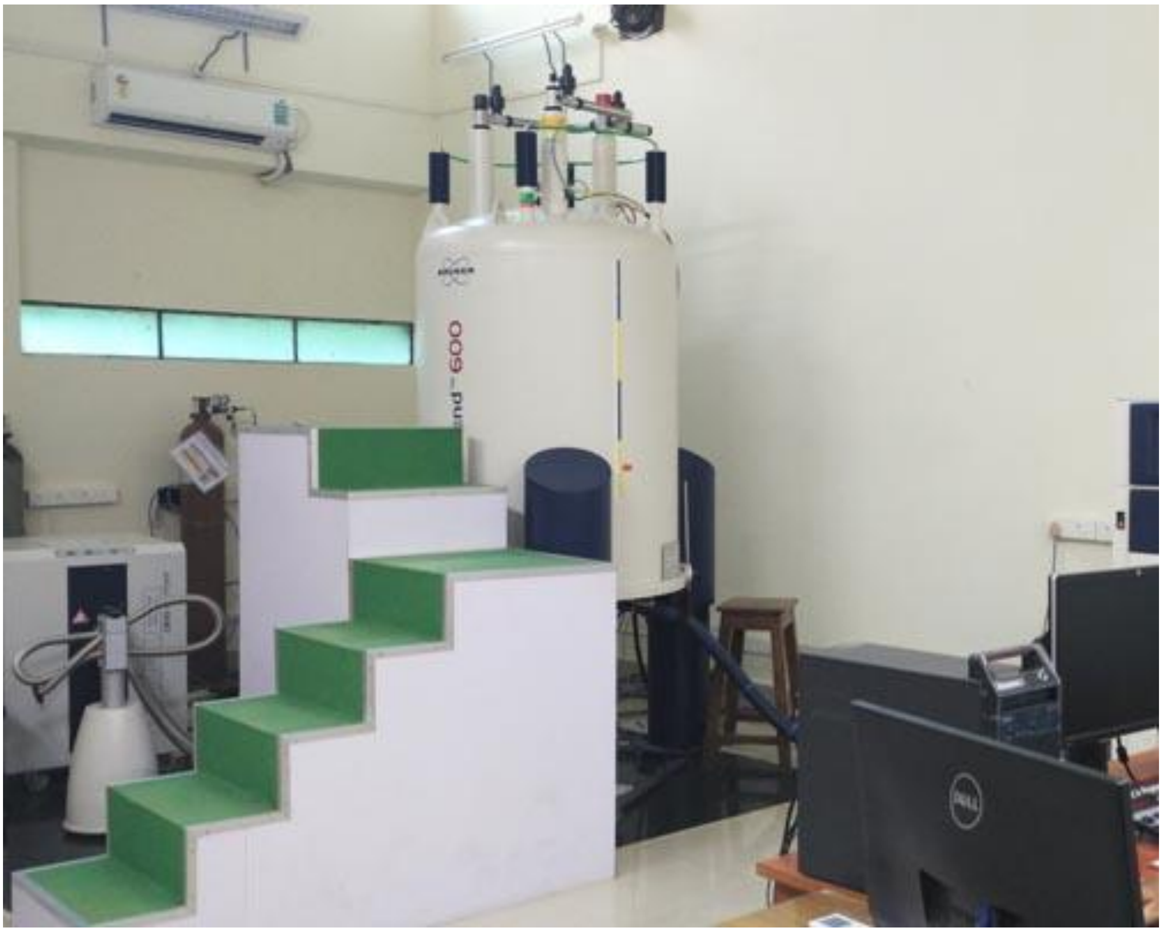

Figure 2.2. Nuclear magnetic resonance (NMR) spectroscopy (CRF IIT Kharagpur).

2.2.3 Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectra of purified poly(VAc-*co*-BA) copolymers 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. Poly(VAc-*t*-BA-*t*-AA) terpolymers samples were recorded with a PerkinElmer (Model spectrum-2) Fourier transform infrared (FTIR) spectrometer for a range of 400 to 4000 cm^{-1} in ATR mode. With a Perkin Elmer (Model spectrum-100) FTIR spectrometer, FTIR spectra of poly(VAc-*t*-Sty-*t*-BA*)* terpolymer and terpolymer/clay composites were recorded for a range of 400 to 4000 cm^{-1}.

Figure 2.3. Fourier transform infrared (FT-IR) spectroscopy (Tezpur University SAIC).

2.2.4 Size exclusion chromatography (SEC)

Size exclusion chromatography (SEC) was carried out in an Agilent Gel permeation chromatography (GPC) system with configuration comprises of a 50 µL manual sampler, Isocratic pump and 1260 infinity II refractive index (RI) detector. GPC analysis of purified poly(VAc-*co*-BA) copolymers, poly(VAc-*t*-BA-*t*-AA) and poly(VAc-*t*-Sty-*t*-BA) terpolymer samples were performed to determine the molecular weight distribution of polymers. The analysis polymers were performed at room temperature and THF was used as an eluent at a flow rate of 1 mL/min in the analysis.

Figure 2.4. Gel permeation chromatography (GPC) (Bodoland University).

2.2.5. Differential scanning calorimetry (DSC)

The Differential scanning calorimetry (DSC) measurements were performed to determine the glass transition temperatures (T_gs) for the poly(VAc-*t*-BA-*t*-AA*)* terpolymer/clay composites prepared, using a TA DSC25 instrument at a heating rate of 10°C/ min from -80.5°C to 200°C. The DSC data for each sample (6-10 mg) was mounted in T_{zero} aluminum hermetic pans and heated under the nitrogen atmosphere.

Figure 2.5. Differential scanning calorimetry (DSC) (https://www.tainstruments.com/dsc-25/).

2.2.6. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of the terpolymer/clay composites were performed in Shimadzu TGA-50 instrument. In this case, a small amount of sample (approx. 15 mg) was heated from room temperature to 700°C at a heating rate of 10°C/min under nitrogen atmosphere.

Figure 2.6. Thermogravimetric analysis (TGA) (https://www.shimadzu.com/an/products/thermal-analysis/thermogravimetric-analysis/tga-50-series/index.html).

2.2.7. Universal testing machine (UTM)

Tensile tests were performed according to ASTM D-412 standard using a Zwick/Roell Universal testing machine (UTM) with a load cell of 500N and cross-head speed of 200 mm/min at room temperature. 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 an average of the three was plotted. Mechanical properties like tensile strength, modulus, and elongation at break of poly(VAc-*t*-BA-*t*-AA)terpolymer/clay composites were recorded.

Hysteresis test of terpolymer/clay composites were also carried out with a Zwick/Roell UTM at room temperature with maximum strain 100% with cross-head speed 200 mm/min in load 500 N with number of cycles 4. The sample preparation was the similar manner as the tensile tests and was subjected with 100% maximum deformation.

Figure 2.7. Universal testing machine (UTM).
https://www.zwickroell.com/industries/plastics/plastics-testing-standards/astm-d412-tensile-test-elastomers/

2.2.8. Rubber process analyzer (RPA)

Rheological properties such as the dynamic melt rheological behavior of the poly(VAc-*t*-BA-*t*-AA) polymer and polymer/clay composites were evaluated using rubber process analyzer (RPA 200000) equipped with biconical dies. 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.

Figure 2.8. Rubber process analyzer (RPA) (CRF IIT Kharagpur).

2.2.9. Field emission scanning electron microscopy (FESEM)

Morphology of the poly(VAc-*t*-BA-*t*-AA) polymer composites was evaluated using field emission scanning electron microscopy (FESEM) (JEOL) micrograph with an accelerating voltage of 5.0 kV. These polymer composite films were divided into small pieces and then attached using double glue tape to the SEM holder. Subsequently, the Pd and Au plasma combination sputtered onto the polymer samples' surface. After that, the polymer samples underwent SEM analysis. The morphology study of the poly(VAc-*t*-Sty-*t*-BA) polymer and polymer/clay composites were estimated using scanning electron microscopy (SEM) (JEOL, Japan, JSM 6390LV) with an accelerating voltage of 20 kV micrograph using JEOL software.

Figure 2.9. Field emission scanning electron microscopy (FESEM) (Tezpur University SAIC).

2.2.10. Transmission electron microscopy (TEM)

The morphology study of the poly(VAc-*t*-Sty-*t*-BA) latex polymer was estimated using transmission electron microscopy (TEM) (TECNAI G2 20 S-TWIN, 200kV, USA) micrograph using TIA software.

Figure 2.10. Transmission electron microscopy (TEM) (Tezpur University SAIC).

2.2.11. X-ray diffraction (XRD) analysis

The X-ray diffraction patron of poly(VAc-*t*-Sty-*t*-BA*)* polymer and polymer/clay composites were recorded on Bruker AXS (Germany) (model D8 Focus) X-ray diffractometer at room temperature. Cu Kα radiation was carried out at 30kV and 30mA, with a scanning rate of 0.05 degrees per second with 2θ range 10° to 70°.

Figure 2.11. X-ray diffraction (XRD) analysis instrument. (Tezpur University SAIC).