

CHAPTER THREE

MATERIALS AND METHODS

3.0 Experimental:

The primary aims of this research were to blend PHB with PVAc.

3.1 Materials

Poly(3-hydroxybutyric acid) (PHB) was supplied by Sigma Aldrich. The average molecular weights are $M_n = 150,000 \text{ g mol}^{-1}$ and $MW = 86 \text{ g mol}^{-1}$ (Referred to polystyrene calibration standards). Its melting temperatures (T_m) are 175-180 °C and glass transition temperatures (T_g) 5 °C. Poly(vinyl acetate) (PVAc) bead was also purchased from Sigma Aldrich chemical, with an average molecular weight of 100,000 g mol^{-1} . All chemicals were used without purification and newly prepared solutions were used in all experiments.

Table 3.1 shows the specifications of poly(3-hydroxybutyric acid) (PHB) and polyvinyl acetate (PVAc) polymers.

Properties	PHB	PVAc
Physical form	Powder	Beads
Color	Beige	Colorless
Melting point (°C)	175	230
Solubility	Very soluble in chloroform	Very soluble in chloroform
Chemical formula	$[\text{COCH}_2\text{CH}(\text{CH}_3)\text{O}]_n$	$(\text{C}_4\text{H}_6\text{O}_2)_n$
Density (g ml^{-1}) at 25 °C	1.056	1.191

3.2 Procedures

PHB is brittle polymers. To improve their mechanical properties, it is mixed with other biodegradable materials. PHB was dissolved in chloroform, then poured into a mixed solvent of n- hexane and methanol (1:1 v/v %). PVAc was dissolved in chloroform or any aromatic hydrocarbons. Figure 3.1 shows structure of PHB and PVAc.

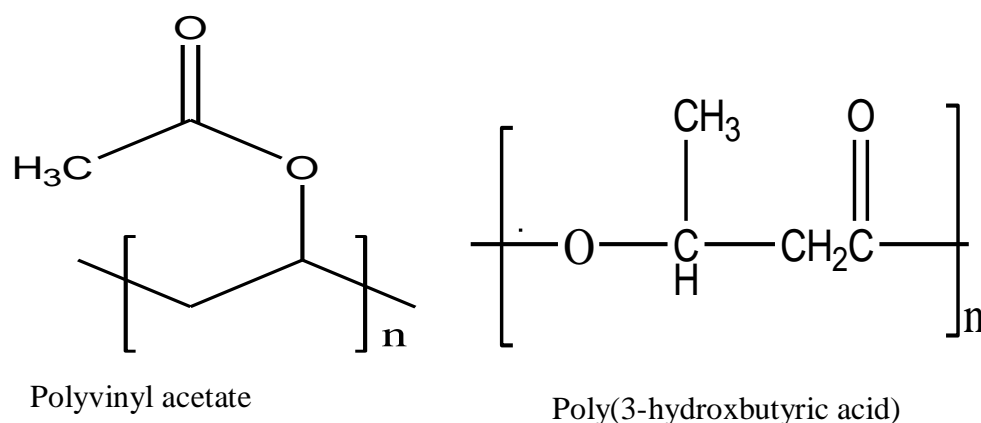


Figure 3.1: Structure details of PHB and PVAc.

3.2.1 Preparation of the solutions

The PHB and PVAc samples were fully dissolved in chloroform and then cast in glass dishes as a film by evaporating the solvent and kept in a vacuum-dried oven at 55 °C for 24 hours and cooled down to room temperature. Solution of PHB was prepared by completely dissolving 5 g of PHB in 500 ml of chloroform (0.1 M) followed by mild stirring using magnetic stirrer and then stirring for 1 h under heating at 40 °C, then poured into a mixed solvent of n- hexane and methanol (1:1 v/v%) as surfactant (Wada et al., 2007) and filtered under vacuum. PVAc was prepared by completely dissolving 5 g in 500 ml of chloroform, under magnetic stirring, at temperature 40 °C The solution was further stirred and kept at about 40 °C for 2 h.

3.2.2 Preparation of the blended solutions

The blended solutions of PHB/PVAc were prepared by adding the PVAc solutions (5 ml, 10 ml, 15 ml, 20 ml, 25 ml, 30 ml and 35 ml) drop by drop to PHB solutions (95 ml, 90 ml, 85 ml, 80 ml, 75 ml, 70 ml and 65 ml) respectively, with continuously a magnetic stirring, at about 40 °C and the further stirred at a moderate speed for 2 h. After that, the composition kept in mechanical stirring for around 3 h. The composition of PHB to PVAc (PHB/PVAc) in the range (5-35 ml) 95/05 to 65/35 (v/v) are shown in **Table 3.2**, which presents the various compositions for all solutions prepared.

Table 3.2 Compositions of the PHB and PVAc mixtures

Solution Ratio	V _{PHB} v/v %	V _{PVAc} v/v %
PHB/PVAc 100/0	100	0
PHB/PVAc 0/100	0	100
PHB/PVAc 95/5	95	5
PHB/PVAc 90/10	90	10
PHB/PVAc 85/15	85	15
PHB/PVAc 80/20	80	20
PHB/PVAc 75/25	75	25
PHB/PVAc 70/30	70	30
PHB/PVAc 65/35	65	35

3.2.3 Preparation of the blended films

The preparation of the blended films of PHB and PVAc was carried out at various proportions. All samples were prepared in the form thin films of circular shape with a diameter equal to 55 mm and thickness of 1 mm. The PVAc solution was added drop by drop to the PHB solution, under magnetic stirring at 40 °C in many proportions by volume. PVAc and PHB solutions were then mixed together by stirring for 1 day and stirring under homogenizer for 2 h. The solvent was allowed to evaporate at room temperature in a hood. Both the PHB and PVAc were dried in a vacuum to remove any moisture prior to use. All the samples were subsequently dried in a vacuum oven for 2 days at 55 °C. The range of the added PVAc for PHB solution was varied in the range of 0-35 v/v%. Continuous stirring was performed for 35 min. After adding, all films obtained were dried at 60 °C under vacuum overnight to eliminate residual solvent and were allowed to dry and solidify. The solvent was evaporated from the circular glass dish at room temperature and solidify for 48 h in the hood at room temperature. Film of the yielded homogeneous solution was obtained by casting prescribed amount of the solution onto glass circular dishes followed by drying at 60 °C. The films were peeled off and stored under evacuated desiccators over fresh silica gel. All films obtained were transparent and free of air bubbles. Similar films from pure PHB and PVAc were prepared using the same casting procedure and used as references (Murakami et al.). polymer blending has been used to modify PHB and improves its properties, and also lower production costs

3.2.4 Film thickness

The film thickness was measured with a digital micrometer (Mitutoyo, Japan) with 0.001 mm resolution. Numerous thickness measurements were taken at various positions on each specimen and average value was determined.

3.3 Methods and equipment

3.3.1 Viscosity Measurements

The rheological measurements were performed on a Brookfield digital viscosity, model DV-II+Pro, with an attached UL adapter. The viscosity was determined in 20 ml of the sample and the shearing time was 30 seconds. For the storage time measurements, solutions were kept at room temperature in glass bottles. All measurements were recorded as an average value of ten readings when a constant shear rate (20 S^{-1}) was applied.

3.3.2 Fourier Transform Infrared Spectroscopy (FTIR Measurements)

The FTIR spectrum was recorded spectrometer by Perkin Elmer, model 2000, USA. The spectra were obtained at a frequency range of $4000 - 400 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} and 4 times scanning.

3.3.3 Field Emission Scanning Electron Microscopy (FESEM) Measurements

In this work, FESEM measurement was carried out to study the surface morphology and to study the compatibility of the blended films. The film surface was observed at a voltage of 10 kV to examine the phase morphology using Field Emission Scanning Electron Microscope (FEI QUANTA 450 FEG. EDX-OXFORD).

3.3.4 Thermal properties

In this work, two techniques have been employed as follows:

3.3.4.1 Thermogravimetric Measurements (TGA)

The samples were heated from room temperature. TGA will be used to evaluate the thermal stability and determine the decomposition temperature of PHB and its blends. Thermogravimetric analysis (TGA) was done on a Perkin-Elmer Pyris Diamond thermal instrument TGA 4000. TGA runs were carried out in a temperature range of $50-700^\circ\text{C}$ under nitrogen atmosphere and a heating rate of $20^\circ\text{C min}^{-1}$. Approximately 3-10 mg of

sample was weighed, then sealed into pan and analyzed by the TGA. A curve of weight loss against temperature was constructed from the data obtained by the instrument. The conversion rate curve was produced to indicate the mass loss conversion (%) during the time.

3.3.4.2 Differential Scanning Calorimetry Measurements (DSC)

The thermal properties such as glass transition temperature (T_g), purity, crystallization and melting temperature (T_m) were being investigated by DSC Mettler- Toledo (model. DSCC822e) instrument in the range started from 25 °C to 230 °C and cooling to 230 °C to 25 °C, under N_2 at a flow rate of $20 \text{ cm}^3 \text{ min}^{-1}$ and a scan rate of 10 °C min^{-1} . The DSC measurement is particularly useful the study of crystallization because it enables direct measurement of thermodynamic properties, melting temperature and heat of fusion. The most common instrument used in polymer studies is the differential scanning calorimeter, which uses two pans; one containing the sample and an empty pan acting as a reference. The two aluminum pans are heated or cooled at a constant rate. The samples were weighed in an aluminum pan and measured against an empty pan as reference. Approximately 3-10 mg of sample was weighed and then encapsulated in an aluminium pan. The pan was then placed in a TA Instruments. The samples were scanned under a nitrogen atmosphere at a constant rate of 10 °C per min . The experiment consisted of two runs. Following protocol: first and second heating from 25 °C to 230 °C. The glass transition temperature (T_g) of pure PHB can't be detected by a conventional DSC measurement owing to its high crystallization (Mousavioun el al., 2013).

3.3.5 X-ray diffraction (XRD)

X-ray diffraction (XRD) analyses were performed with a PANalytical diffractometer operated at unit 40 kV, $\lambda = 1.524 \text{ \AA}$ and 40 mA using Cu-K α radiation with graphite diffracted beam monochromator. The thin films of pure PHB and pure PVAc and its compositions were investigated by X-ray thin film diffraction and recorded in a diffraction angle (2θ) using a step size of 0.03° under time of 98s. XRD patterns were recorded in a 2θ range of $5^\circ - 80^\circ$ at scanning speeds of 2° min^{-1} on a PANalytical diffractometer.

3.3.6 Biodegradability of poly(PHB/PVAc) film

Biodegradable plastics are an attractive route to environmental waste management and can replace conventional polymers when recovery for recycling or incineration is difficult and/or not cost-effective. Research has focused on both the addition of biodegradable polymers to common thermoplastics and on purely biodegradable, natural and synthetic polymers (Park et al., 2001). All the samples were washed in NaOH solution (0.1 N), then washed in water and put it in oven at (110°C) for overnight. After that, samples were buried in the soil (pH= 6.2, moisture =2.2) around 8 weeks, the weight of samples was measured before and after degradation processing while FTIR and TGA were measured every week during this period (Wada *et al.*, 2007).

3.3.6.1 Burial Method

Testing the biodegradability of poly(PHB/PVAc) was also done using burial methods, by using On the spot tester " Soil pH & Moisture tester", model DM-15. A lot of studies deal with poly(β -hydroxyalcanoate) (PHA). All samples were put in soil and studied after first, second, third, fourth, fifth, sixth, seventh and eighth week after washing by NaOH (0.1 N).

References

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