

Synthesis & Studies of Differential Scanning Calorimetry, Scanning Electron Microscopy and Mechanical Properties of Biodegrade Poly (β -Hydroxy Butyrate), Its Applications and A Comparative Study With Poly Propylene

S. Srilalitha¹, K.N. Jayaveera², S.S. Madhvendra³

¹ Institute of Aeronautical Engineering, Dindigal, Hyderabad – 500043 (A.P), India.

² Department of Chemistry, Jawaharlal Nehru University, Anantapur – 515002(A.P),India.

³ Electron Microscopy Center, Indian Institute of Chemical Technology, Hyderabad -500007 (A.P), India.

ABSTRACT:- Poly hydroxy butyrate (PHB) homo polymer which is a thermoplastic material has been produced from co-polymers of (β -hydroxy butyrate(HB) and β -hydroxy valerate (HV). This family of materials PHBV has much improved properties over the original PHB including reduced brittleness and biodegradability. It has been observed from the studies of DSC and SEM that the melting point, degree of crystallinity and glass transition temperature of PHB is closer to poly propylene, but PHB is stiffer and more brittle than poly propylene. From the studies of mechanical properties it has been observed that the decrease in Young's modulus indicates improved flexibility. As PHBV itself is non-toxic and compatible with living tissue, it can be used internally in humans. As a medical material the most notable features of PHBV are that it is very bio compatible, producing an extremely mild foreign body response, and that biodegradation rate in vivo is slow. As the piezoelectric properties of PHBV are similar to those of natural bone, a bone fracture fixation plate, made from a reinforced PHB composite to match mechanical properties, might actually stimulate bone growth and healing.

Keywords:- Synthesis, Studies, DSC, SEM, Mechanical properties, Biodegradable, PHB, PP.

I. INTRODUCTION

Biodegradation is an event which takes place through the action of enzymes and/or chemical decomposition associated with living organisms (bacteria, fungi, etc) or their secretion products. Biodegradation might be better used as a term only when it is essentially to distinguish clearly between the action of living organisms and other degradation modes (eg. photolysis, oxidation, hydrolysis). The current interest in bio poly esters centers around their environmentally friendly nature, and opposition to extensive use of non-biodegradable plastics.

Baptist, and Werber produced pound quantities of PHB for commercial evaluation and developed articles such as sutures and prosthetic devices. This work was truly pioneering both in terms of reporting on the plastic potential of PHB (1) and in proposing its use as a bio compatible material. As oil prices stabilized, production costs for PHB remained higher than these for poly propylene, so the original idea of developing PHB as a general, high tonnage plastic was put on hold (2).

In the present investigation poly hydroxyl butyrate (PHB) homo polymer which is a thermo plastic material has been produced from copolymers of β -hydroxy butyrate (HB) and β -hydroxy valerate(HV). This family of materials, known as PHBV or Biopol, has much improved properties over the original PHB including reduced brittleness. The melting point, degree of crystallinity and glass transition temperature of PHB have been studied by Differential Scanning Calorimetry and Scanning Electron Microscopy and compared with the properties of poly propylene. Young's modulus and tensile strength of PHB have been studied by mechanical studies.

II. EXPERIMENTAL PROCEDURES

Materials

The polymers used in the present investigation were poly propylene (PP), (Aldrich, USA) and Poly (β -hydroxy butyrate) -which is produced from copolymers of β -hydroxy butyrate (HB) and β -hydroxy valerate(HV). Poly propylene was melted at 200°C and pressed between two heated glass plates, and cooled to about 130°C; spherulites were produced from a number of nucleating centers. Samples of these spherulites were utilized for various studies.

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The DSC studies were performed by Differential Scanning Calorimetry (Perkin-Elmer DSC-7) utilising a Mettler H20 T semi microbalance for weighing samples. All samples weighed 7-20mg were run at constant heating rate, $10^{\circ}\text{C mm}^{-1}$, under N_2 atmosphere.

SCANNING ELECTRON MICROSCOPY (SEM)

The SEM studies were carried out using High resolution scanning electron microscope (Model Hitachi S-520) with the samples of PP and PHB spherulites.

MECHANICAL STUDY

Mechanical studies were performed on the polymer samples with Instron model AGS-10 KNG-Shimadzu (Japan)

III. RESULTS AND DISCUSSION

DSC Study

The variation of melting point, glass transition temperature with composition of PHBV co-polymers was given in the table (I). With increasing concentrations of HV units from 0-25%, there was a decrease in melting point increasing the size of the processing window within which the polymer can be melted without being degraded. The glass transition temperature also decreased, allowing use of these materials at lower temperatures without becoming brittle and glassy.

It has been observed from the DSC studies that the melting point, degrees of crystallinity and glass transition temperatures (T_g) of PP and PHB are almost similar (Table2). PHB is highly viscous and mouldable at temperatures closer to or above the melting point. PHB is both stiffer and more brittle than PP.

SEM Study

The phase morphology of the spherulites of PHB and PP has been observed by SEM studies. The brittleness of PHB is largely due to the presence of large crystals in the form of spherulites, which form upon cooling from the melt, a hot rolling treatment to remove cracks from within the spherulites can reduce the brittle character, allowing production of ductile films. (3).

Mechanical Study

With increasing concentrations of HV units 0-25% , there is a steady decrease in Young's modulus indicates improved flexibility (Table 1). The notched izod impact strength also increases with increasing HV concentration, indicating that the toughness of the material is increased (Table 1).

The ductile films of PHB and PP differ in chemical properties, with PHB having a lower solvent resistance but much better natural resistance to ultraviolet weathering than poly propylene.

Packaging films of PHB had excellent gas barrier properties being four times less permeable to CO_2 than poly ethylene terephthalate (PET) (4) and was as strong as PP film. PHB can be strengthened by addition of a glass fiber filling (5); glass reinforced mouldings were stiffer and tougher than similar nylon parts.

Table 1: Physical Properties of PHB-Co-HV Copolymers

P(H B-co-HV) (mole %HV)	Melting point ($^{\circ}\text{C}$)	Glass transition ($^{\circ}\text{C}$)	Young's modulus (GPa) .	Tensile strength (MPa)	Notched Izod impact (Strength (Jm^{-1}))*
0	179	10	3.5	40	50
3	170	8	2.9	38	60
9	162	6	1.9	37	95
14	150	4	1.5	35	120
20	145	-1	1.2	32	200
25	137	-6	0.7	30	400

* with 1mm radius notch

Table 2: Properties of PHB compared to those of poly propylene(PP)

Property	PHB	PP
Crystalline melting point ($^{\circ}$ C)	175	176
Crystallinity (%)	80	70
Molecular weight (Dalton's)	5×10^5	2×10^5
Glass transition temperature	-4	-10
Density (g cm^{-3})	1.250	0.905
Flexural modulus (GPa)	4.0	1.7
Tensile strength (MPa)	40	38
Extension to break (%)	6	400
Ultraviolet resistance	Good	Poor
Solvent resistance	Poor	Good

IV. FUTURESCOPE AND APPLICATIONS OF BIODEGRADABLE PHB AND PHBV

PHBV is used as biodegradable substitute for poly olefin containers, plastic films and bags (6). The gas barrier properties of PHBV could lead to applications in food packaging or as a replacement for PET for plastic bottles.

As PHBV itself is non-toxic and compatible with living tissue, it can be used internally in humans. For controlled drug release applications in human medicine PHBV is used not as a bolus but as micro capsules, which are injected subcutaneously as a suspension (7) pressed into a pill and administered orally (8). A blood compatible membrane has been proposed with PHBV (9) unlike cotton fibers, bits of PHBV fiber from the swab or dressing can be left in the wound without concern as they will biodegrade.

A high technology futuristic use of PHBV could be as a vascular graft or blood vessel, compared of very fine fibers arranged to form a water impermeable tube of suitable internal diameter (10). Surgical implants of PHBV to join tubular body parts have already been developed (11) as sheets (12) or coils (13) of PHBV to separate tissue in wound healing.

Piezo electric properties of PHBV are similar to those of natural bone. Bone can be strengthened and repaired by electrical stimulation(14), therefore, a bone fracture fixation plate, made for a reinforced PHB composite to match mechanical properties, might actually stimulate bone growth and healing. An added advantage of such a plate is that it would be biodegradable, and could be left in place to be, slowly absorbed by the body, instead of requiring a second operation to remove it.

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