# STUDIES ON PROCESSABILITY AND PHYSICO-MECHANICAL PROPERTIES OF BIODEGRADABLE POLYESTER-BASED BLENDS FOR SCAFFOLD SUBSTRATES

**HARSHAL VINOD PESHNE**

**DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING**
**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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# STUDIES ON PROCESSABILITY AND PHYSICO-MECHANICAL PROPERTIES OF BIODEGRADABLE POLYESTER-BASED BLENDS FOR SCAFFOLD SUBSTRATES

*by*


**HARSHAL VINOD PESHNE**

**Department of Materials Science and Engineering**


*Submitted*
*in fulfilment of the requirements of the degree of*

**Doctor of Philosophy**

*to the*

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***Dedicated to my family***

***Grandparents – Ambika and Vishwanathji Peshne,***

***Nirmala and Nathuji Tidke***

***Parents – Pushpa and Vinod Peshne***

***Sibling – Rutuja Peshne***

**Thank you for your unconditional love.**

# CERTIFICATE

This is to certify that the thesis entitled "**Studies on processability and physico-mechanical properties of biodegradable polyester-based blends for scaffold substrates**" submitted to the Indian Institute of Technology Delhi by **Mr. Harshal Vinod Peshne**, for the award of the degree of **Doctor of Philosophy** in the Department of Materials Science and Engineering, is a bonafide record of original research work carried out by the candidate. The results contained in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree.

I further certify that **Mr. Harshal Vinod Peshne** has fulfilled all the requirements for the submission of the thesis.


Bhabani. K. Satapathy

Professor

Department of Materials Science and Engineering

Indian Institute of Technology Delhi

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*"ॐ गं गणपतये नमः"*

**Harshal Peshne**

# ABSTRACT

The thermo-mechanical, morphological, and rheological properties of blends containing poly(3-hydroxybutyrate) (PHB) and bio-based poly(butylene succinate) (Bio-PBS), as well as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and bio-based poly(butylene succinate) (Bio-PBS), have been comparatively investigated. Differential scanning calorimetry (DSC) analysis indicated that crystallization in both PHB and PHBV is significantly hindered while blending with Bio-PBS, which resulted in a slight thermal stability enhancement. Morphologically, phase immiscibility caused changes from domain-dispersed to co-continuous type, where the domain sizes of the dispersed Bio-PBS phase increased in tune with compositions. Dynamic mechanical analysis (DMA) revealed distinct glass transition peaks of the two components. Wide angle x-ray diffraction (WAXD) demonstrated a sharper decline in PHB crystallization compared to PHBV upon blending with Bio-PBS. Constitutive modelling of complex viscosity indicates the polymer melts to follow the Carreau-Yasuda model, where the zero- shear viscosity decreased with Bio-PBS content, irrespective of the nature of the matrix. The Cox-Merz rule estimates that PHB and PHBV matrices could produce co-continuous morphologies at 35 wt.% and 41 wt.% Bio-PBS, respectively. Therefore, polyhydroxyalkanoates matrices-based blends showed potential for further investigation as bioresorbable scaffolds. Subsequent study examined the non-isothermal melt-crystallization kinetics of PHB/Bio-PBS blends at different Bio-PBS contents at melting temperatures close to the degradation (onset) temperatures of PHB. Further investigations into non-isothermal melt-crystallization dynamics near the degradation onset temperature of PHB highlighted the impact of cooling rates and degradation temperatures on crystallization. The secondary regime had a lower crystallisation rate ($k$) than the primary regime, according to Avrami analysis. The nucleation and growth rate of PHB spherulites is enhanced during the crystallization process when cooling the melt from 260°C, which may be attributed to the higher undercooling ($\Delta T_u$). In order to address the issue of high stiffness and limited deformation in PHB/Bio-PBS blends, the studies conducted additional investigation by incorporating poly(ethylene glycol) (PEG) as a compatibilizer. The physico-mechanical properties of binary and ternary blends of PEG with PHB and Bio-PBS are examined. PHB/PEG blends showed a slight increase in elongation at the break despite the decrease in glass transition temperature ($T_g$). Bio-PBS/PEG blends showed a considerable increase in elongation at break, reaching ~261% at 20 parts per hundred resin (phr) PEG loading due to the miscibility of Bio-PBS and PEG phases, which improves

interfacial adhesion and flexibility. Addition of PEG has improved miscibility of ternary blends by creating a more diffuse interface at domain sites in immiscible PHB/Bio-PBS blends. Mechanical properties of PHB/Bio-PBS/PEG (ternary blends) did not considerably increased due to the complex interplay between enhanced molecular movement and the crystallization process. Moreover, PHB/Bio-PBS blends were electrospun using 2,2,2-trifluoroethanol, resulting in electrospun mats (EMs) with fiber diameters ranging from ~ 534 to ~ 181 nm. $CaCl_2$ addition resulted in the defect-free morphology of PHB and PHB/Bio-PBS blends, except for Bio-PBS at ~20 wt.% concentration. The immiscibility of Bio-PBS in the PHB matrix led to decreased tensile strength (from ~ 4.0 to ~ 2.0 MPa) and tensile modulus (~ 186 to ~ 64 MPa), whereas strain-at-break increased (from ~ 1.5 to ~ 46.5%). Up to 50% Bio-PBS loading of electrospun mats showed optimum ductility, strength, and a tensile modulus comparable to cancellous bone. The blend with ~50 wt.% Bio-PBS exhibited higher hydrophobicity (116°) and reduced swelling (84%) compared to neat PHB (95° and 124%). Overall, this research indicated that the relationship between composition, morphology, and processing conditions in addition of Bio-PBS into Polyhydroxyalkanoates matrices and provided the requisite physico-mechanical characteristics, thus resulting in suitable scaffold substrates for soft bone tissue engineering applications.

# सार

पॉली(3-हाइड्रोक्सीब्यूटाइरेट) (PHB) और बायो-आधारित पॉली(ब्यूटिलीन सुकीनेट) (Bio-PBS), साथ ही पॉली(3-हाइड्रोक्सीब्यूटाइरेट-को-3-हाइड्रोक्सीवैलेरेट) (PHBV) और बायो-आधारित पॉली(ब्यूटिलीन सुकीनेट) (Bio-PBS) के सम्मिश्रण में थर्मो-मैकेनिकल, मोर्फोलॉजिकल, और रियोलॉजिकल गुणों का तुलनात्मक अध्ययन किया गया है। डिफरेंशियल स्कैनिंग कैलोरीमेट्री (DSC) विश्लेषण से पता चला कि Bio-PBS के साथ मिश्रण करते समय PHB और PHBV दोनों में क्रिस्टलीकरण काफी बाधित होता है, जिससे थोड़ी थर्मल स्थिरता में सुधार होता है। मोर्फोलॉजिकली, चरण असंगतता के कारण डोमेन-प्रसारित से सह-निरंतर प्रकार में परिवर्तन होता है, जहां Bio-PBS चरण के फैले हुए डोमेन के आकार रचनाओं के साथ बढ़ते हैं। डायनामिक मैकेनिकल एनालिसिस (DMA) ने दोनों घटकों के स्पष्ट ग्लास ट्रांज़िशन पीक का खुलासा किया। वाइड एंगल एक्स-रे डिफ्रैक्शन (WAXD) ने Bio-PBS के साथ मिश्रण करने पर PHBV की तुलना में PHB क्रिस्टलीकरण में तेजी से कमी का प्रदर्शन किया। जटिल चिपचिपाहट की नियामक मॉडलिंग से पता चला कि पॉलिमर पिघलने में Carreau-Yasuda मॉडल का पालन होता है, जहां शून्य-शियर चिपचिपाहट Bio-PBS सामग्री के साथ कम हो जाती है, चाहे मैट्रिक्स का स्वभाव कोई भी हो। Cox-Merz नियम अनुमान लगाता है कि PHB और PHBV मैट्रिक्स 35 वज़न% और 41 वज़न % Bio-PBS पर सह-निरंतर मोर्फोलॉजी उत्पन्न कर सकते हैं। इसलिए, पॉलीहाइड्रोक्सीअल्कानोएट्स मैट्रिक्स-आधारित सम्मिश्रण बायोरिसॉर्बेबल स्कैफोल्ड्स के रूप में आगे की जांच के लिए संभावित दिखाए गए हैं। इसके बाद के अध्ययन ने विभिन्न Bio-PBS सामग्री के साथ PHB/Bio-PBS मिश्रणों के गैर-समानांतर पिघल-क्रिस्टलीकरण गतिशीलता की जांच की है। PHB के क्षरण (शुरुआत) तापमान के करीब पिघलने के तापमान पर गैर-समानांतर पिघल-क्रिस्टलीकरण गतिशीलता में आगे की जांच ने क्रिस्टलीकरण पर शीतलन दरों और क्षरण तापमान के प्रभाव को उजागर किया। Avrami विश्लेषण के अनुसार, द्वितीयक शासन में प्राथमिक शासन की तुलना में क्रिस्टलीकरण दर (k) कम थी। PHB स्फेरुलाइट्स का नाभिकरण और वृद्धि दर क्रिस्टलीकरण प्रक्रिया के दौरान 260°C से पिघलने पर बढ़ जाती है, जिसे अधिक ठंडक ($\Delta Tu$) के कारण माना जा सकता है। PHB/Bio-PBS सम्मिश्रण में उच्च कठोरता और सीमित विकृति की समस्या को हल करने के लिए, अध्ययन ने Poly(ethylene glycol) (PEG) को एक संगतकारी के रूप में शामिल कर आगे की जांच की। PEG के साथ PHB और Bio-PBS के द्विआधारी और त्रिआधारी सम्मिश्रण के भौतिक-यांत्रिक गुणों की जाँच की गई। PHB/PEG सम्मिश्रण में ग्लास ट्रांज़िशन तापमान ($T_g$) में कमी के बावजूद ब्रेक पर थोड़ा खिंचाव बढ़ गया। Bio-PBS/PEG सम्मिश्रण में ब्रेक पर खिंचाव में काफी वृद्धि हुई, जो कि 20 भाग प्रति सौ रेजिन (phr) PEG लोडिंग पर

~261% तक पहुंच गई, क्योंकि Bio-PBS और PEG चरणों की संगतता, जो इंटरफेसियल एडहेशन और फ्लेक्सिबिलिटी में सुधार करती है। PEG की वृद्धि ने असंगत PHB/Bio-PBS सम्मिश्रण में डोमेन स्थलों पर एक अधिक विभाजित इंटरफेस बनाकर त्रिआधारी सम्मिश्रण की संगतता को बेहतर किया। PHB/Bio-PBS/PEG (त्रिआधारी सम्मिश्रण) के यांत्रिक गुणों में जटिल आणविक गति और क्रिस्टलीकरण प्रक्रिया के बीच के जटिल तालमेल के कारण उल्लेखनीय वृद्धि नहीं हुई। इसके अलावा, PHB/Bio-PBS सम्मिश्रण को 2,2,2-ट्राइफ्लूरोएथेनॉल का उपयोग करके इलेक्ट्रोस्पून किया गया, जिससे फाइबर व्यास के साथ इलेक्ट्रोस्पून मैट्स (EMs) का निर्माण हुआ, जो ~534 से ~181 नैनोमीटर तक थे। $CaCl_2$ के जोड़ ने PHB और PHB/Bio-PBS सम्मिश्रण की दोष-मुक्त मोर्फोलॉजी का निर्माण किया, सिवाय Bio-PBS के ~20 वज़न% सांद्रता पर। PHB मैट्रिक्स में Bio-PBS की असंगतता ने तन्यता ताकत (~4.0 से ~2.0 मेगा पास्कल) और तन्यता मापांक (~186 से ~64 मेगा पास्कल) को कम कर दिया, जबकि ब्रेक पर खिंचाव बढ़ गया (~1.5 से ~46.5%)। इलेक्ट्रोस्पून मैट्स की ~50% Bio-PBS लोडिंग ने इष्टतम नलिका, ताकत और तन्यता मापांक दिखाया, जो कि अस्थि मज्जा के समान थे। ~50 वज़न% Bio-PBS के साथ सम्मिश्रण ने उच्च हाइड्रोफोबिसिटी (116°) और कम सूजन (84%) दिखाई, जो शुद्ध PHB (95° और 124%) की तुलना में बेहतर थे। कुल मिलाकर, इस अनुसंधान ने Bio-PBS को पॉलीहाइड्रोक्सीअल्कानोएट्स मैट्रिक्स में सम्मिलित करने पर संरचना, मोर्फोलॉजी और प्रसंस्करण स्थितियों के बीच के संबंध को उजागर किया और आवश्यक भौतिक-यांत्रिक गुणों को प्रदान किया, जिससे यह मुलायम अस्थि ऊतक इंजीनियरिंग अनुप्रयोगों के लिए उपयुक्त स्कैफोल्ड सब्सट्रेट्स के रूप में उपयोगी साबित हुआ।

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# LIST OF ABBREVIATIONS

| **Abbreviations** | **Full form** |
|---|---|
| 3HB | 3-hydroxybutyric acid |
| ANOVA | Analysis of variance |
| ATBC | Acetyl-tri-n-butyl citrate |
| ATR | Attenuated total reflection |
| BD | 1,4-butanediol |
| BET | Brunauer-Emmett-Teller |
| Bio-PBS | Bio-based poly(butylene succinate) |
| BJH | Barrett–Joyner–Halenda |
| $CaCl_2$ | Calcium Chloride |
| CaP | Calcium phosphates |
| DCP | Dicumyl peroxide |
| DMA | Dynamic mechanical analysis |
| DSC | Differential Scanning Calorimetry |
| DTGA | Differential Thermogravimetric Analysis |
| ECM | Extracellular matrix |
| EM | Electrospun mats or Electrospun fibrous mats |
| FDM | Fused Deposition Modelling |
| FESEM | Fourier enhanced scanning electron microscopy |
| FTIR | Fourier transforms infrared |
| HA | Hydroxyapatite |
| HV | Hydroxyvalerate |
| LiCl | Lithium Chloride |
| mcl-PHA | medium-chain length polyhydroxyalkanoates |
| nHA | Hydroxyapatite nanoparticle |
| P4HB | Poly(4-hydroxybutyrate) |
| PBA | Poly(butylene adipate) |
| PBAT | Poly(butylene adipate-co-terephthalate) |
| PBS | Polybutylene succinate |

| | |
|---|---|
| PCL | Poly(ε-caprolactone) |
| PDCHI | Poly(dicyclohexylitaconate) |
| PDLLA | Poly-D-L-lactic acid |
| PEG | Poly(ethylene glycol) |
| PEKK | Poly(ether ketone ketone) |
| PEO | Polyethylene oxide |
| PGA | Poly(glycolic acid) |
| PHAs | Polyhydroxyalkanoates |
| PHB | Poly(3-hydroxybutyrate) |
| PHBH | poly (3-hydroxybutyrate-co-3-hydroxyhexanate) |
| PHBV | Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) |
| phr | Parts per hundred resin |
| PLA | Poly(lactic acid) |
| PLGA | Poly lactic-co- glycolic acid |
| PLLA | Poly-L-lactic acid |
| PLOM | Polarised Light Optical Microscopy |
| PPC | Poly(propylene carbonate) |
| PVA | Polyvinyl alcohol |
| SA | Succinic acid |
| scl-PHA | short-chain length polyhydroxyalkanoates |
| SEM | Scanning electron microscopy |
| TCP | Tri-calcium Phosphate |
| TFE | 2,2,2- trifluoroethanol |
| TGA | Thermogravimetric Analysis |
| WAXD | Wide Angle X-ray diffraction |
| WCA | Water contact angle |
| wt. | Weight |
| XRD | X-ray diffraction |