

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

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INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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MECHANICAL PROPERTIES OF BIODEGRADABLE
POLYESTER-BASED BLENDS FOR SCAFFOLD
SUBSTRATES**

by

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

Doctor of Philosophy

to the



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OCTOBER 2024**

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

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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 (ΔT_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 increase 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. CaCl₂ 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 (ΔT_u) 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 जांच 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 प्लेक्सिबिलिटी 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 जोड़ने PHB और PHB/Bio-PBS सम्मिश्रण की दोष-मुक्त मोर्फोलॉजी का निर्माण किया, सिवाय Bio-PBS के ~20 वजन% सांद्रता पर। PHB मैट्रिक्स में Bio-PBS की असंगतता ने तन्यता ताकत (~4.0 से ~2.0 मेगापास्कल) और तन्यता मापांक (~186 से ~64 मेगापास्कल) 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 वजन% 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 सबस्ट्रेट्स के रूप में उपयोगी साबित हुआ।

Table of Contents

Certificate	ii
Acknowledgements	iii
Abstract	v
Table of Contents	ix
List of Figures	xv
List of Tables	xxi
List of Abbreviations	xxiv
<i>CHAPTER 1 Introduction and Literature Review.....</i>	<i>1</i>
1.1 Introduction.....	1
1.2 Bone Tissue Engineering (Introductory background).....	5
1.2.1 Hierarchical structure of a Bone	7
1.3 Requirements for scaffolds	21
1.4 Methods for fabrication of Scaffolds	22
1.4.1 Melt Molding	24
1.4.2 Solvent casting	24
1.4.3 Salt-leaching	24
1.4.4 Freeze Drying.....	25
1.4.5 Gas Foaming	25
1.4.6 Additive Manufacturing.....	26
1.4.7 Electrospinning	27
1.5 Current Challenges in Scaffold fabrication.....	28

1.6	Research Gaps.....	29
1.7	Thesis format	31
CHAPTER 2 Comparative studies of structural, thermal, mechanical, rheological and dynamic mechanical response of melt mixed PHB/Bio-PBS and PHBV/Bio-PBS blends .34		
2.1	Introduction.....	34
2.2	Experimental.....	37
2.2.1	Preparation of blends	37
2.2.2	Differential Scanning Calorimetry (DSC)	37
2.2.3	Thermogravimetric Analysis (TGA).....	38
2.2.4	Morphological characterization by electron microscopy.....	38
2.2.5	Dynamic Mechanical Analysis	38
2.2.6	Quasi-static mechanical properties	39
2.2.7	Structural characterization by wide angle X-ray (WAXD) diffraction	39
2.2.8	Fourier transforms infrared (FTIR) spectroscopy.....	39
2.2.9	Melt Rheological Measurements	39
2.3	Results and discussion	40
2.3.1	Thermal behaviour of the blends	40
2.3.2	Morphology of blends by electron microscopy	45
2.3.3	Structural characterization by 2D wide angle X-ray diffraction (WAXD)	47
2.3.4	Fourier transform infrared spectroscopy (FTIR) analysis	49
2.3.5	Thermo-mechanical analysis	51
2.3.6	Mechanical properties.....	54
2.3.7	Melt-rheological study of the blends	57
2.3.8	Viscoelastic flow response and complex viscosity of the blends	60
2.3.8.a	Constitutive modeling of the complex viscosity.....	61

2.3.9	Conclusion	66
CHAPTER 3 <i>Insights into understanding the dynamic crystallization behaviour of poly(3-hydroxybutyrate) /poly(butylene succinate) blends: Non-isothermal kinetics approach near the degradation onset temperatures of poly(3-hydroxybutyrate)</i>		
69		
3.1	Introduction.....	69
3.2	Experimental.....	73
3.2.1	Materials and sample preparation of blends	73
3.2.2	Differential Scanning Calorimetry (DSC)	74
3.3	Results and discussion	75
3.3.1	Non-Isothermal Crystallization Behaviour.....	75
3.3.2	Avrami analysis.....	84
3.4	Conclusion	98
CHAPTER 4 <i>Effect of poly(ethylene glycol) content as compatibilizer on blends of poly(3-hydroxybutyrate) and poly(butylene succinate).</i>		
101		
4.1	Introduction.....	101
4.2	Materials and Experimental methods.....	107
4.2.1	Preparation of blends	107
4.2.2	Thermal, structural and rheological characterizations of blends	109
4.2.2.a	Differential Scanning Calorimetry (DSC)	109
4.2.2.b	Thermogravimetric Analysis (TGA).....	109
4.2.2.c	Morphological characterization by electron microscopy.....	109
4.2.2.d	Dynamic Mechanical Analysis	110
4.2.2.e	Structural characterization by wide angle X-ray (WAXD) diffraction.....	110
4.2.2.f	Fourier transforms infrared (FTIR) spectroscopy analysis.....	110

4.2.2.g	Melt rheological measurements	110
4.3	Results and discussion	111
4.3.1	Thermal behaviour of the blends	111
4.3.2	Morphology of blends by electron microscopy	119
4.3.3	Structural characterization by 2D wide angle X-ray diffraction (WAXD) of blends	121
4.3.4	Fourier transform infrared spectroscopy (FTIR) of blends.....	124
4.3.5	Thermo-mechanical analysis of blends.....	127
4.3.6	Mechanical properties of blends	132
4.3.7	Melt-rheological study of the blends	135
4.4	Conclusion	137

CHAPTER 5 Physico-mechanical evaluation of electrospun nanofibrous mats of poly(3-hydroxybutyrate)/poly(butylene succinate) blends with enhanced swelling-dynamics and hydrolytic degradation-kinetics stability for pliable scaffold substrates..... 140

5.1	Introduction.....	140
5.2	Materials and Methods.....	142
5.2.1	Raw materials.....	142
5.2.2	Preparation of electro-spinnable solutions and fabrication of electrospun fibrous mats (EMs).....	142
5.2.3	Thermal characterization	144
5.2.3.a	Differential Scanning Calorimetry (DSC)	144
5.2.3.b	Thermogravimetric Analysis (TGA).....	144
5.2.4	Morphological characterization	144
5.2.5	Rheological characterization and conductivity of electrospinning solutions	144
5.2.6	Microstructural characterization	145

5.2.6.a	Wide-angle X-ray diffraction (WAXD) studies	145
5.2.6.b	BET specific surface area and porosity measurements.....	145
5.2.7	Fourier transform infrared (FT-IR) spectroscopy	145
5.2.8	Quasi-static mechanical properties	146
5.2.9	Water Contact Angle (WCA) studies	146
5.2.10	In-vitro swelling and weight loss studies.....	146
5.2.11	Statistical analyses	146
5.3	Results and discussion	147
5.3.1	Morphological attributes of HBS blends based EMs.....	147
5.3.2	Thermal behavior of HBS blend based EMs	152
5.3.3	Microstructural attributes of HBS blends based EMs.....	155
5.3.4	Fourier transform infrared spectroscopy (FTIR) of HBS blends based EMs	157
5.3.5	Quasi-static mechanical properties of HBS blend-based EMs	157
5.3.6	Water Contact Angle of HBS blends based EMs.....	162
5.3.7	In-vitro swelling and weight loss studies for HBS blends based EMs	163
5.4	Conclusion	168
CHAPTER 6 Conclusion and future scope		172
6.1	Conclusion	172
6.2	Future Scope	175
References		177
Publications.....		210
Appendices.....		212
Appendix A: Supporting Information for Chapter 2.....		212
Appendix B: Supporting Information for Chapter 3.....		212

Biography 213

List of Figures

Figure No.	Caption	Page No.
Figure 1.1	<i>Current status and future roadmap of Biodegradable plastics</i>	2
Figure 1.2	<i>Biodegradable polymers classification based on source.</i>	3
Figure 1.3	<i>Life cycle of Biopolymers.</i>	4
Figure 1.5	<i>Desired properties needed for scaffold materials.</i>	22
Figure 1.6	<i>Characteristic attributes affecting performance & functionality of scaffold materials.</i>	29
Figure 2.1	<i>DSC measurement: crystalline exotherm a) PHB/Bio-PBS c) PHBV/Bio-PBS blends and melting endotherm (b) PHB/Bio-PBS (d) PHBV/Bio-PBS blends.</i>	42
Figure 2.2	<i>TGA traces of a) PHB/Bio-PBS b) PHBV/Bio-PBS blends and DTGA traces of (c) PHB/Bio-PBS (d) PHBV/Bio-PBS blends.</i>	44
Figure 2.3	<i>SEM images of the cryo-fractured specimens (a) PHB (neat) at 2kX (b) Bio-PBS (neat) at 2kX (c) PHBV (neat) at 2kX (d) HBS10 at 5kX (e) HBS30 at 10kX (f) HBS50 at 10kX (g) HVS10 at 10kX (h) HVS30 at 15kX (i) HVS50 at 10kX</i>	46
Figure 2.4	<i>FESEM images at 5kX magnification of the cryo-fractured specimens (a) PHB (neat) (b) Bio-PBS (neat) (c) PHBV (neat) and selectively etched Bio-PBS phase from blends of (d) HBS10 (e) HBS30 (f) HBS50 (g) HBS10 (h) HVS30 (i) HVS50</i>	47
Figure 2.5	<i>WAXD patterns of the (a) PHB/Bio-PBS and (b) PHBV/Bio-PBS blends</i>	48
Figure 2.6	<i>ATR-FTIR spectra of (a) PHB/Bio-PBS and (b) PHBV/Bio-PBS blends.</i>	50
Figure 2.7	<i>DMA plots of the PHB/Bio-PBS and PHBV/Bio-PBS – (a) & (b) storage modulus (E'), (c) & (d) loss modulus (E'') and (e) & (f) $\tan \delta$ versus temperature of blends respectively.</i>	53

Figure 2.8 Stress strain percent curves of (a) PHB/Bio-PBS (b) PHBV/Bio-PBS blends	55
Figure 2.9 Impact strength of (a) PHB/Bio-PBS (b) PHBV/Bio-PBS blends with varying compositions.	56
Figure 2.10 Flexural stress strain percent plot of (a) PHB/Bio-PBS (b) PHBV/Bio-PBS blends	57
Figure 2.11 Melt rheological response: (a) (b) complex viscosity (η^*), (c) (d) storage modulus (G'), (e) (f) loss modulus (G'') as a function of angular frequency (ω).	59
Figure 2.12 Storage and loss modulus variation with angular frequency of (a) PHB (neat) (b) Bio-PBS (neat) (c) PHBV (neat) (d) PHB 10 % PBS (e) PHB 30 % PBS (f) PHB 50 % PBS (g) PHBV 10 % PBS (h) PHBV 30% PBS (i) PHBV 50 % PBS.	60
Figure 2.13 Constitutive modeling response of complex viscosity: Cross model – (a) PHB/Bio-PBS (b) PHBV/Bio-PBS blends, Carreau-Yasuda model – (c) PHB/Bio-PBS (d) PHBV/Bio-PBS blends and Zero shear viscosity response of (e) PHB/Bio-PBS (f) PHBV/Bio-PBS blends	63
Figure 2.14 Dependence of $\eta^*(\omega)$ and $G'(\omega)$ by addition of Bio-PBS in (a), (b) PHB/Bio-PBS and (c),(d) PHBV/Bio-PBS blends at different frequencies, respectively.	64
Figure 2.15 Schematic illustration of developments in PHB/Bio-PBS and PHBV/Bio-PBS blends	68
Figure 3.1 DSC exotherms of neat PHB, PHB/Bio-PBS blends and Bio-PBS at different cooling rates (i.e. 10°C, 20°C and 30°C). PHB is crystallised by cooling the melt from (a) 220°C (b) 240°C (c) 260°C, HBS10 blend is crystallised by cooling the melt from (d) 220°C (e) 240°C (f) 260°C, HBS30 blend is crystallised by cooling the melt from (g) 220°C (h) 240°C (i) 260°C, HBS50 blend is crystallised by cooling the melt from (j) 220°C (k) 240°C (l) 260°C, and Bio-PBS is crystallised by cooling the melt from (m) 220°C (n) 240°C (o) 260°C.	77

Figure 3.2 Temperature-dependent changes of relative crystallinity (X_t) at different cooling rates (i.e. 10°C, 20°C and 30°C) when PHB is crystallised by cooling the melt from (a) 220°C (b) 240°C (c) 260°C, HBS10 blend is crystallised by cooling the melt from (d) 220°C (e) 240°C (f) 260°C, HBS30 blend is crystallised by cooling the melt from (g) 220°C (h) 240°C (i) 260°C, and HBS50 blend is crystallised by cooling the melt from (j) 220°C (k) 240°C (l) 260°C. ___ 85

Figure 3.3 Relative crystallinity versus time-resolved at different cooling rates (i.e. 10°C, 20°C and 30°C) when PHB is crystallised by cooling the melt from (a) 220°C (b) 240°C (c) 260°C, HBS10 blend is crystallised by cooling the melt from (d) 220°C (e) 240°C (f) 260°C, HBS30 blend is crystallised by cooling the melt from (g) 220°C (h) 240°C (i) 260°C, and HBS50 blend is crystallised by cooling the melt from (j) 220°C (k) 240°C (l) 260°C. _____ 88

Figure 3.4 Avrami plots of $\log(-\ln(1-X_t))$ vs $\log t$ during non-isothermal crystallisation at different cooling rates (i.e. 10°C, 20°C and 30°C) when PHB is crystallised by cooling the melt from (a) 220°C (b) 240°C (c) 260°C, HBS10 blend is crystallised by cooling the melt from (d) 220°C (e) 240°C (f) 260°C, HBS30 blend is crystallised by cooling the melt from (g) 220°C (h) 240°C (i) 260°C, and HBS50 blend is crystallised by cooling the melt from (j) 220°C (k) 240°C (l) 260°C _____ 89

Figure 3.5 Half-time of crystallisation $t_{1/2}$ of (a) & (b) PHB, (b) & (c) HBS10, (d) & (e) HBS30 and (g) & (h) HBS50 blends at different cooling rates (i.e. 10°C, 20°C and 30°C) when crystallised by cooling the melt from 220°C, 240°C and 260°C respectively. _____ 97

Figure 3.6 Schematic illustration of possible developments in crystallization structures within a PHB/Bio-PBS blend after undergoing a melting process close to PHB's degradation onset temperatures (Non-isothermal crystallisation kinetics) _____ 100

Figure 4.1 DSC measurement: crystalline exotherm of a) PHB/PEG blends, b) Bio-PBS/PEG blends, (c)-(d) PHB/Bio-PBS/PEG blends, and melting endotherm of (e) PHB/PEG blends, (f) Bio-PBS/PEG blends, and (g)-(h) PHB/Bio-PBS/PEG blends. _____ 114

Figure 4.2 TGA traces of a) PHB/PEG, b) Bio-PBS/PEG blends, (c)-(d) PHB/Bio-PBS/PEG blends, and DTGA traces of (e) PHB/PEG blends, (f) Bio-PBS/PEG blends, and (g)-(h) PHB/Bio-PBS/PEG blends.	117
Figure 4.3 SEM images of the cryo-fractured specimens of (a) PHB (neat), (b) HBS0-G5, (c) HBS0-G10, (d) HBS0-G15, (e) HBS0-G20, (f) Bio-PBS (neat), (g) Bio-PBS-G5, (h) Bio-PBS-G10, (i) Bio-PBS-G15, (j) Bio-PBS-G20, (k) HBS10, (l) HBS10-G5, (m) HBS10-G10, (n) HBS30, (o) HBS30-G5, (p) HBS30-G10, (q) HBS30-G15, (r) HBS30-G20 at 5kX magnification.	121
Figure 4.4 WAXD patterns of the a) PHB/PEG, b) Bio-PBS/PEG blends, (c)-(d) PHB/Bio-PBS/PEG blends	123
Figure 4.5 ATR-FTIR spectra of a) PHB/PEG, b) Bio-PBS/PEG blends, (c)-(d) PHB/Bio-PBS/PEG blends.	126
Figure 4.6 DMA plots of the PHB/PEG, Bio-PBS/PEG blends, and PHB/Bio-PBS/PEG blends – (a)-(d) storage modulus (E'), (e)-(h) loss modulus (E''), and (i)-(l) $\tan \delta$ versus temperature of blends, respectively.	131
Figure 4.7 Stress strain percent curves of a) PHB/PEG, b) Bio-PBS/PEG blends, (c)-(d) PHB/Bio-PBS/PEG blends.	133
Figure 4.8 Complex viscosity (η^*) as a function of angular frequency (ω) response of a) PHB/PEG, b) Bio-PBS/PEG blends, (c)-(d) PHB/Bio-PBS/PEG blends.	136
Figure 4.9 Schematic illustration of development of PHB/Bio-PBS blends compatibilized with PEG	139
Figure 5.1 Schematic illustration of the preparation of PHB/Bio-PBS blends based electrospun mats (EMs)	143

Figure 5.2 FESEM images of EMs (a-e) without CaCl₂ (f-j) with CaCl₂ for HBS0-F (neat PHB), HBS10-F, HBS30-F, HBS50-F, and Bio-PBS-F respectively at 30kX and 5kX magnification (except neat Bio-PBS without salt at 5kX and 500X magnification). _____ 149

Figure 5.3 The average fiber diameter and fiber diameter distribution of EMs of neat PHB, neat Bio-PBS and HBS blends based EMs blended fibers (a) and (c) without salt, and (b) and (d) with salt, respectively. Significant differences found by one way ANOVA ($p \leq 0.05$) are indicated by asterisks. _____ 150

Figure 5.4 (a) Electrical conductivity of neat PHB, neat Bio-PBS, HBS blends based solution and (b) rheological properties of neat PHB, neat Bio-PBS and HBS blends based solution (solution concentration ~ 20 wt. % with CaCl₂). _____ 152

Figure 5.5 DSC plots for electrospun mats of HBS blends a) crystalline exotherm and (b) melting endotherm (with CaCl₂). _____ 153

Figure 5.6 a) TGA and (b) DTGA plots for electrospun mats of HBS blends (with CaCl₂). 154

Figure 5.7 (a) X-ray diffractograms and (b) ATR-FTIR spectra of electrospun mats of HBS blends (with CaCl₂). _____ 155

Figure 5.8 Stress strain curve and morphology of tensile-fractured surfaces of electrospun fibrous mats of HBS blends at 250X and 2kX magnification. _____ 160

Figure 5.9 Mechanical properties of electrospun mats of HBS blends (Bio-PBS-F prepared at ~ 30 kV whereas all the other blends fabricated at ~ 20 kV). Significant differences found by one way ANOVA ($p \leq 0.05$) are indicated by asterisks. _____ 160

Figure 5.10 Tensile testing of (a) HBS30-F and (b) HBS50-F EMs, (c) HBS50-F EM showing layer-by-layer separation or peeling off of the 2D-fibrous continuum under tensile force. _ 161

Figure 5.11 Mechanical properties of (a) HBS0-F based EMs and (b) HBS50-F based EMs, (c) Bio-PBS-F based EMs, post ~ 15 days of incubation in PBS buffer solution. Significant differences found by one way ANOVA ($p \leq 0.05$) are indicated by asterisks. _____ 162

Figure 5.12 Water contact angle measurements for electrospun mats of HBS blends. Significant differences found by one way ANOVA ($p \leq 0.05$) are indicated by asterisks. _____ 163

Figure 5.13 (a) Degree of swelling and (b) weight loss (%) for HBS blends-based EMs post 30 days and 60 days incubation in PBS buffer, respectively. The compositional variations among individual blends were statistically evaluated through a two-way analysis of variance (ANOVA), assessing the mean weight loss data over a 60-day period of hydrolytic degradation and the swelling percentage mean over a 30-day. The analysis revealed statistical significance (****) for both. _____ 164

Figure 5.14 FESEM images of HBS0-F, Bio-PBS-F, and HBS50-F blends based on EMs hydrolytic degradation behaviour post 15, 30, 45, and 60 days incubation in PBS buffer. _ 166

Figure 5.15 Swelling kinetics model-fit plots for (a) first-order kinetics (b) pseudo second-order kinetics and (c) power law models. _____ 167

Figure 5.16 Schematic illustration of development of PHB/Bio-PBS based electrospun nanofibrous mats for pliable scaffold substrates _____ 171

List of Tables

Table No.	Caption	Page No.
Table 1.1	<i>Mechanical properties of bone tissues and scaffold materials for bone tissue.</i>	9
Table 1.2	<i>Benefits and drawbacks of different materials for bone tissue engineering.....</i>	11
Table 1.3	<i>Properties of biodegradable polyester-based materials.....</i>	14
Table 1.4	<i>Studies on biodegradable polyester based materials performance attributes.....</i>	16
Table 2.1	<i>Details of the designation and compositions of blends of (a) PHB/Bio-PBS and (b) PHBV/Bio-PBS.....</i>	40
Table 2.2	<i>Twin screw extrusion processing temperature profile (°C).....</i>	40
Table 2.3	<i>DSC parameters of PHB/Bio-PBS and PHBV/Bio-PBS blends.....</i>	43
Table 2.4	<i>TGA parameters of PHB/Bio-PBS and PHBV/Bio-PBS blends.....</i>	45
Table 2.5	<i>Morphological Parameters of PHB/Bio-PBS and PHBV/Bio-PBS blends.....</i>	46
Table 2.6	<i>Crystallinity percentage and mean crystallite size of blends from WAXD.....</i>	49
Table 2.7	<i>Glass transition temperature (T_g) from Loss modulus vs. temperature curve and by Fox equation.</i>	54
Table 2.8	<i>Tensile properties of (a) PHB/Bio-PBS (b) PHBV/Bio-PBS blends.....</i>	55
Table 2.9	<i>Impact properties of (a) PHB/Bio-PBS (b) PHBV/Bio-PBS blends.....</i>	56
Table 2.10	<i>Flexural properties of (a) PHB/Bio-PBS (b) PHBV/Bio-PBS blends.....</i>	57
Table 3.1	<i>Twin screw extrusion processing temperature profiles.....</i>	74
Table 3.2	<i>Details of PHB/Bio-PBS blend's designation and compositions.....</i>	74
Table 3.3	<i>DSC parameters of crystalline exotherms of (a) PHB (HBS0), (b) HBS10, (c) HBS30 and (d) HBS50 blends at different cooling rates (i.e. 10°C, 20°C and 30°C) when cooling the melt from 220°C, 240°C and 260°C.....</i>	80

Table 3.4 Avrami parameters, such as n and k , for primary, secondary, and overall crystallisation of (a) PHB, (b) HBS10, (c) HBS30 and (d) HBS50 blends at different cooling rates (i.e. 10°C, 20°C and 30°C) when crystallised by cooling the melt from 220°C, 240°C and 260°C, respectively.....	92
Table 4.1 Details of the designation and compositions of blends of (a) PHB/PEG and Bio-PBS/PEG blends (Binary blends)	107
Table 4.2 Details of the designation and compositions of blends of PHB/Bio-PBS/PEG (Ternary blends).....	108
Table 4.3 Twin screw extrusion processing temperature profile (°C).....	108
Table 4.4 DSC parameters of PHB/PEG and Bio-PBS/PEG blends.....	115
Table 4.5 DSC parameters of PHB/Bio-PBS/PEG blends.....	115
Table 4.6 TGA parameters of a) PHB/PEG b) Bio-PBS/PEG blends	118
Table 4.7 TGA parameters of PHB/Bio-PBS/PEG blends.....	118
Table 4.8 Crystallinity percentage of PHB/PEG and Bio-PBS/PEG blends from WAXD....	123
Table 4.9 Crystallinity percentage of PHB/Bio-PBS/PEG blends from WAXD.....	124
Table 4.10 Glass transition temperature (T_g) from Loss modulus vs. temperature curves of PHB/PEG and Bio-PBS/PEG blends.....	131
Table 4.11 Glass transition temperature (T_g) from Loss modulus vs. temperature curves of PHB/Bio-PBS/PEG blends.....	132
Table 4.12 Tensile properties of PHB/PEG and Bio-PBS/PEG blends	134
Table 4.13 Tensile properties of PHB/Bio-PBS/PEG blends.....	135
Table 5.1 Composition and designation of PHB/Bio-PBS blends based EMs.....	143
Table 5.2 Porosity, specific surface area and pore volume of the electrospun mats of HBS blends	150
Table 5.3 DSC data for electrospun mats of HBS blends (with CaCl_2).....	153

Table 5.4 TGA data of electrospun mats of HBS blends (with CaCl ₂).....	154
Table 5.5 Crystallinity percentage and average crystallite size from WAXD.....	156
Table 5.6 Swelling kinetics parameters for first-order kinetics, pseudo second-order kinetics and power law models.	168

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