

**STUDIES ON GRANULAR TAPIOCA STARCH AND
JACK WOOD FLOUR REINFORCED
POLY(ϵ -CAPROLACTONE) BASED BIOCOMPOSITES**

ACHLA



**DEPARTMENT OF MATERIALS SCIENCE
AND ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
MARCH 2018**

©Indian Institute of Technology Delhi (IITD), New Delhi, 2018

**STUDIES ON GRANULAR TAPIOCA STARCH AND
JACK WOOD FLOUR REINFORCED
POLY(ϵ -CAPROLACTONE) BASED BIOCOMPOSITES**

by

ACHLA

Department of Materials Science and Engineering

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the



Indian Institute of Technology Delhi

MARCH 2018

*Dedicated to
my family*

CERTIFICATE

This is to certify that the thesis entitled “*Studies on granular tapioca starch and jack wood flour reinforced poly(ϵ -caprolactone) based biocomposites*” being submitted by **Ms. Achla**, to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in the Department of Materials Science and Engineering, is a record of bonafide research work carried out by her. Ms. Achla has worked under my guidance and supervision and fulfilled all the requirements for the submission of the thesis.

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 or diploma.

Prof Josemon Jacob

Professor

Department of Materials Science and Engineering

Indian Institute of Technology Delhi

New Delhi-110016

India

Prof. S. N. Maiti

Emeritus Professor

Department of Materials Science and Engineering

Indian Institute of Technology Delhi

New Delhi-110016

India

ACKNOWLEDGEMENTS

With deep sense of gratitude and sincere regards, I would like to acknowledge the guidance and encouragement given by my supervisors, Prof. S. N. Maiti and Prof. Josemon Jacob for this research work. They have always been a source of inspiration and have been extremely generous in providing advice, guidance and inputs despite their busy schedules and multiple pre-occupations.

I shower my gratefulness to my PhD SRC members, Prof. A. K Ghosh, Dr. B. Satapathy and Dr. Samrat Mukhopadhyay for their kind support towards completion of my work. My special appreciation to Dr. Veena Choudhary for her support for my study here at CPSE, IIT Delhi. I gratefully acknowledge the help and suggestions by Dr. Leena Nebhani and Dr Sampa Saha as and when required.

I am thankful to the staff members Mr. Surender Sharma, Mr. Ashok Kapoor, Mr. Shiv Kant and Mr. Islam of the Centre for Polymer Science and Engineering, for extending a helping hand whenever needed. Also, I thank the staff members of the laboratories of Textile Department for providing me the facilities to carry out the SEM study.

I am extremely thankful to all my seniors, friends and colleagues Dr. Manisha, Savita Meena, Dr. Rishi Sharma, Dr. Rakesh Kr. Kachhap, Mohd. Tahir Zafar, Shilpi, Sampat, Vishavpratap Singh, Debanga B. Konwar, Bhavana Sharma, Banpreet Kaur, Reshu, Pragati, Neetu, Prajesh, Devendra, Swarna, Sumbul Hafeez, Smruti, Agni Kr. Biswa, Anindya Dutta, Ritima Banerjee, from IIT Delhi for their constant encouragement. It's my fortune to gratefully acknowledge the support of my friends, Astha Garhwal, Ranjana Nehra, Shalini Singh, Dr. Pawan Verma, Dr. Harjeet Singh Jaggi, Dr. Abhishek Gandhi, Dr. Rajendra Singla, Bindu Manchanda, Sabapathi, Dr. Meenakshi Verma, and Deepika Malpani for their support and generous care throughout the research tenure. They were always beside me during the happy and hard moments to push me and motivate me. Special thanks are extended to Astha Garhwal, Ranjana Nehra, and Deepika Malpani.

Finally, I acknowledge the people who mean a lot to me, my parents, Shri Harindra Kishor Tiwari and Smt. Pushpa Devi. I salute you for the selfless love, care, pain and sacrifice you did

to shape my life. Although you hardly understood what I researched on, you were willing to support any decision I made. I would never be able to pay back the love and affection showered upon by my parents. Also I express my thanks to my brothers Mr. Nitesh Tripathi and Mr. Punit Tripathi for showing faith in me and giving me liberty to choose what I desired. I also want to thank my sister-in-laws, Mrs. Pooja Tripathi and Mrs. Jyotika Tripathi for their support and with their unconditional love and care. I am also thankful to my lovely nephew Athrav, and my beautiful niece Medhya and Pihu, for allowing me to enjoy lifetime happiness, always being cheerful and chirpy out all my tensions by their sweet smiles.

I express my special thanks to my younger brother Vinay as he deserves a special mention for consistent support, help and affection throughout my research work.

I am extraordinarily fortunate to have the blessings of my father-in-law, Shri Kailash Tiwari and mother-in-law, Smt. Pushpa Tripathi who always bless me with the shower of their love, providing inner strength, and emotional support for my successful career. I am also thankful to my brother-in-law, Shailendra Tripathi and sister-in-law, Mrs. Vijay laxmi Tripathi, and Dr. Rajani Tripathi for their support to complete this task.

I owe thanks to a very special person, my husband, Dr. Deepak Tripathi for his continued and unfailing love, support and understanding during my pursuit of Ph.D degree that made the completion of thesis possible. You were always around at times I thought that it is impossible to continue, you helped me to keep things in perspective. I greatly value his contribution and deeply appreciate his belief in me. I appreciate my baby, my little son Tanmay for abiding my ignorance and the patience he showed during my thesis writing. Words would never say how grateful I am to both of you. I consider myself the luckiest in the world to have such a lovely and caring family, standing beside me with their love and unconditional support.

I would like to acknowledge the financial assistance received from “MHRD” which has helped me to pursue my PhD without any stress.

Finally, I thank the ‘ALMIGHTY GOD’ for his blessings and further seek him to provide me blessings, patience and strength to accomplish newer goals.

ACHLA

Abstract

The development of biodegradable polymers has emerged as an active field of research in order to reduce plastic littering on landfills which causes environmental pollution such as soil erosion and loss of soil biological activity. Biocomposites based on biodegradable matrices and natural bio-fillers such as wood fibers, wood flour, starch and the like degrade totally in soil without production of pollutants and toxic end products. Poly(ϵ -caprolactone) (PCL) is one of the most studied biodegradable semicrystalline aliphatic polyester. Some advantageous properties of PCL are high toughness, high ductility, good processability, and biodegradability. However, extensive application of PCL remains limited because of some of its inherent inferior properties like low melting point, low melt strength, low modulus, poor barrier properties, and high cost. In order to overcome its poor modulus property PCL is blended with various bio-fillers.

Two different types of biocomposites containing 0-35 wt % granular tapioca starch (GTS) (0-0.36 volume fraction, Φ_f) and 0-35 wt % of jack wood flour (JWF) (0-0.34 volume fraction, Φ_f) and were prepared by melt compounding using twin screw extruder (TSE). In first section of this work, effect of granular tapioca starch (GTS) as reinforcing bio-based filler on various properties of PCL is investigated. The observed marginal decrease in onset degradation temperature studied suggests that the incorporation of GTS does not compromise thermal stability by thermo-gravimetric analysis (TGA). The maximum tensile modulus observed at $\Phi_f = 0.36$ was 225.8 MPa while a decrease in tensile yield strength with the value 12.44 MPa was observed during mechanical testing. From SEM micrographs, homogeneous dispersion of GTS particles was observed in PCL matrix. The nonisothermal crystallization behavior of PCL, in presence of varying concentrations of GTS is studied. Various crystallization parameters were studied by DSC at four different cooling rates and these parameters were analysed employing

Avrami, Jeziorny, and Liu models. Kissinger method was used to estimate the activation energy (ΔE) of the PCL/GTS composites. The effects of GTS on the melt rheological behavior of PCL were investigated by means of capillary and parallel plate rheometers. The complex viscosity increased with the Φ_f as compared to neat PCL. The loss modulus results suggest an enhancement in the energy dissipation ability of the PCL/GTS biocomposites. The dynamic rheological experiments showed a typical pseudo-plastic behavior of PCL while composites exhibit non-Newtonian behavior over the whole frequency region. Elastic behavior of the system is observed at greater than 10 wt. % GTS content. The fracture toughness based on post-yield fracture mechanics (PYFM) concept was investigated by essential work of fracture (EWF) methodology. The essential work of fracture (w_e) is reduced on incorporation of GTS while increase in the non-essential work of fracture (βw_p) is observed. The composites with 20 wt% of GTS showed 121% increase in the βw_p due to reduced interspherulitic region while 35 % decrease in the parameter is registered for highest GTS content (35 wt. %). The biocomposites were investigated for biodegradation studies in composting conditions for 0, 7, 15, 25, 40, 55, and 75 days of burial time. It was found from disintegration studies that neat PCL starts degrading after PCL/GTS composites

Reinforcing materials which have high aspect ratio, such as platelets, fibers and flakes are used to form composites. Further, JWF was incorporated as reinforcing biodegradable filler into PCL matrix by melt compounding in a TSE. The tensile modulus increases by 80.48 % at the highest $\Phi_f = 0.34$ though marginal increment (13.71 %) in the yield strength was registered. A sharp reduction in notched Izod impact strength (85 %) was observed with increasing JWF content. The phase adhesion parameter obtained from micromechanical analysis of tensile properties suggesting the mechanical interlocking and interaction between PCL and JWF. A

uniform dispersion of JWF was observed in all the samples. Thermal characterization of PCL in presence of JWF was done using DSC and TGA. DSC results revealed marginal increment in the melting temperature (T_m) and peak crystallization temperature in presence of JWF while decreases the crystallization of the matrix. Nonisothermal crystallization kinetics of PCL/JWF composites was also investigated. The fracture toughness of the prepared biocomposites based on PYFM concept was investigated by EWF methodology. Incorporation of JWF into PCL matrix diminishes the essential work of fracture (w_e) while increasing the non-essential work of fracture (βw_p). The effect of JWF on melt and solid state rheological response of composites was investigated using parallel plate rheometer and dynamic mechanical analysis respectively. Incorporation of JWF in the polymer matrix resulted in an increases of storage modulus and loss modulus of PCL corresponding to elastic and viscous response of composites respectively. Pristine PCL, PJWF5 and PJWF10 exhibit typical Newtonian characteristic in the low frequency region while at higher frequencies non-Newtonian behavior was observed which suggest pseudo-plastic nature of the system. Biodegradability test in vermi-compost is also examined for PCL/JWF composites films.

सार

जैव अभकनीय पॉलिमर का विकास शोध के एक सक्रिय क्षेत्र के रूप में उभरा है ताकि जमीन के फर्श पर प्लास्टिक के कचरे को कम किया जा सके जिससे मिट्टी की क्षरण और मिट्टी जैविक गतिविधि के नुकसान जैसे पर्यावरण प्रदूषण हो। बायोकाइम्पोजिट्स बायोडिग्रेडबल मैट्रिक्स और प्राकृतिक जैव-फिलर जैसे कि लकड़ी फाइबर, लकड़ी का आटा, स्टार्च और जैसे-जैसे प्रदूषक और जहरीले उत्पादों के उत्पादन के बिना मिट्टी में पूरी तरह से नीचा दिखाना। पॉली(ε-कैपोलैक्टोन) (पीसीएल) एक सबसे अधिक अध्ययन योग्य बायोडिग्रेडबल अर्धुष्मलीय एलीफाइड पॉलिएस्टर है। पीसीएल के कुछ लाभप्रद गुणों में उच्च क्रूरता, उच्च लचीलापन, अच्छी प्रोसेसिबिलिटी और बायोडेग्रेडेबिलिटी है। हालांकि, पीसीएल का व्यापक अनुप्रयोग सीमित है क्योंकि इसकी कुछ अंतर्निहित अवर के गुणों की वजह से कम गलनांक, कम पिघलता शक्ति, कम मापांक, खराब बाधा गुण और उच्च लागत शामिल है। अपने गरीब मॉड्यूलस संपत्ति को दूर करने के लिए पीसीएल विभिन्न जैव-फिलर के साथ मिश्रित है।

दो अलग-अलग प्रकार के बायोकाइम्पोसाइट्स जिनमें 0-35 wt% दानेदार टैपिओका स्टार्च (जीटीएस) (0-0.36 मात्रा अंश, एफएफ) और जैक लकड़ी का आटा (जेडब्ल्यूएफ) का 0-35 वजन % (0-0.34 मात्रा अंश, फ़ाई) और थे जुड़वां पेंच extruder (टीएसई) का उपयोग कर पिघल मिश्रित द्वारा तैयार इस काम के पहले भाग में, पीएलएल के विभिन्न गुणों पर जैव-आधारित भराव को मजबूत बनाने के रूप में दानेदार टैपिओका स्टार्च (जीटीएस) का प्रभाव जांच की जाती है। अध्ययन की शुरुआत में गिरावट के तापमान में देखा गया सीमांत कमी से पता चलता है कि जीटीएस का समावेश थर्मो-ग्रेमीमैट्रिक विश्लेषण (टीजीए) द्वारा थर्मल स्थिरता से समझौता नहीं करता है। फ़ाई = 0.36 में अधिकतम तन्यता मापांक 225.8 एमपीए था, जबकि मैकेनिकल टेस्टिंग के दौरान मूल्य 12.44 एमपीए के साथ तन्यता पैदा करने की शक्ति में कमी आई थी। एसईएम माइक्रोग्राफ से, पीसीएल मैट्रिक्स में जीटीएस कणों की सजातीय फैलाव मनाया गया था। जीएसटी के अलग-अलग सांद्रता की उपस्थिति में, पीसीएल के गैर-स्पेशलाइजेशन व्यवहार का अध्ययन किया जाता है। विभिन्न क्रिस्टलीकरण मापदंडों को डीएससी द्वारा चार अलग-अलग ठंडा दरों में अध्ययन किया गया था और इन पैरामीटरों का विश्लेषण किया गया था जो एविरामी, जैज़ोरनी, और लियू मॉडल का इस्तेमाल किया गया था। किसिंजर विधि का प्रयोग पीसीएल / जीटीएस कंपोजिट के सक्रियण ऊर्जा (एईई) के अनुमान के लिए किया गया था। पीसीएल के पिंडित रियोलॉजिकल व्यवहार पर जीटीएस के प्रभाव की केशिका और समानांतर प्लेट रियरमीटर के माध्यम से जांच की गई। स्वच्छ पीसीएल के मुकाबले जटिल चिपचिपाहट को एफएफ के साथ बढ़ाना हानि मापांक के परिणाम पीसीएल / जीटीएस बायोकोमोसाइट्स की ऊर्जा अपव्यय क्षमता में वृद्धि का सुझाव देते हैं। गतिशील rheological प्रयोगों पीसीएल के एक विशिष्ट छद्म प्लास्टिक के व्यवहार दिखाया, जबकि कंपोजिट पूरे आवृत्ति क्षेत्र पर गैर न्यूटनियन व्यवहार प्रदर्शन। प्रणाली का लोचदार व्यवहार 10 से अधिक wt पर मनाया जाता है। % जीटीएस सामग्री फ्रैक्चर (ईडब्ल्यूएफ) की कार्यप्रणाली के जरिए फ्रैक्चर यांत्रिकी (पीवायएफएम) की अवधारणा की जांच की गई थी। अस्थिभंग (β_{wp}) के गैर-आवश्यक कार्य में वृद्धि

करते समय फ्रैक्चर के आवश्यक काम को जीटीएस को शामिल करने पर कम किया जाता है। जीटीएस के 20 वेट % के साथ कंपोजिट्स ने बीएसडब्ल्यूपी में 121% वृद्धि की वजह से इंटरसफार्मेटिक क्षेत्र घटित किया जबकि पैरामीटर में 35% कमी उच्चतम जीटीएस सामग्री (35 वेट%) के लिए पंजीकृत है। द्विआधारी समय के लिए 0, 7, 15, 25, 40, 55, और 75 दिन के लिए कंपोस्टिंग स्थितियों में जैव-वर्गीकरण अध्ययन के लिए जांच की गई।

कंपोजिट बनाने के लिए प्लेटलेट्स, फाइबर और फ्लेक्स जैसे उच्च आकृति अनुपात वाले रीनॉर्फिंग सामग्री का उपयोग किया जाता है इसके अलावा, जेएसडब्ल्यूएफ को टीएसई में पिघल गए पीसीएल मैट्रिक्स में बायोडिग्रेडेबल भराव को मजबूत करने के रूप में शामिल किया गया था। उच्चतम फ़ाई = 0.34 पर तन्यता मापांक 80.48% बढ़ता है, हालांकि उपज ताकत में सीमांत वेतन वृद्धि (13.71%) दर्ज किया गया था। जेडडब्ल्यूएफ कंटेंट बढ़ने के साथ इज़ोड प्रभाव शक्ति (85%) में तेज कमी देखी गई। चरण आसंजन पैरामीटर, तन्यता गुणों के माइक्रोमकेनिकल विश्लेषण से प्राप्त होता है जो पीसीएल और जेडडब्ल्यूएफ के बीच मैकेनिकल इंटरलॉकिंग और इंटरैक्शन का सुझाव देता है। सभी नमूनों में जेडडब्ल्यूएफ का एक समान फैलाव मनाया गया था। जेएसडब्ल्यूएफ की उपस्थिति में पीसीएल के थर्मल लक्षण वर्णन डीएससी और टीजीए का उपयोग किया गया था। डीएससी परिणाम मैट्रिक्स के क्रिस्टलीकरण को कम करते हुए जेडडब्ल्यूएफ की उपस्थिति में पिघलने के तापमान (टीएम) और पीक क्रिस्टलीकरण तापमान में सीमांत वृद्धि का पता चला है। पीसीएल / जेडडब्ल्यूएफ कम्पोजिट्स के गैर-थिस्स्थार्मल क्रिस्टलीकरण कैनेटीक्स की जांच भी की गई। पीवाईएफएम अवधारणा के आधार पर तैयार जैव-पोषक तत्वों की फ्रैक्चर क्रूरता की जांच ईडडब्ल्यूएफ पद्धति द्वारा की गई थी। पीएलएल मैट्रिक्स में जेडडब्ल्यूएफ को शामिल करना फ्रैक्चर (β_{wp}) के गैर-आवश्यक काम में वृद्धि करते समय फ्रैक्चर (हम) के आवश्यक काम को कम करता है। जेडडब्ल्यूएफ के पिघल और ठोस अवस्था के रेजोलॉजिकल रिजोल्यूशन पर असमान प्लेट प्लेट रेमोमीटर और गतिशील मैकेनिकल विश्लेषण का उपयोग करके क्रमशः जांच की गई। पॉलिमर मैट्रिक्स में जेडडब्ल्यूएफ के शामिल होने से भंडारण मापांक और हानि मो की वृद्धि हुई।

Contents

<i>Chapter</i>	<i>Title</i>	<i>Page No.</i>
	<i>Certificate</i>	
	<i>Acknowledgements</i>	
	<i>Abstract</i>	i–iii
	<i>List of Figures</i>	x–xv
	<i>List of Tables</i>	xvi–xviii
	<i>List of abbreviations and symbols</i>	xix–xx
CHAPTER 1	<i>Introduction and Literature survey</i>	1–30
1.1	Introduction	2
1.2	Biodegradable polymers or bio-plastics	2
1.3	Poly(ϵ -caprolactone)	3
1.3.1	Advantages of poly(ϵ -caprolactone)	4
1.3.2	Limitations of PCL	5
1.3.3	Applications of PCL	5
1.4	Polymer blends and composites	6
1.4.1	Definition and importance of a composites	7
1.5	PCL composites - A literature survey	8
1.6	Tapioca starch as a filler	10
1.6.1	Applications of starch	11
1.7	PCL/starch composites	11
1.8	Wood flour as a filler	15
1.8.1	Classification of wood based fillers	15
1.8.2	Composition of wood flour	17
1.9	Jack wood flour (JWF) as filler	18
1.9.1	Wood plastic composites (WPC)	19

	1.10	Lignocellulosic fillers based PCL biocomposites	20
	1.11	Problem Statement	23
	1.12	Research objective	23
	1.13	Thesis format	24
		References	25
CHAPTER 2		<i>Experimental: Materials and Methods</i>	31–48
	2.1	Introduction	32
	2.2	Materials and methods	32
	2.2.1	Raw materials details	32
	2.2.2	Preparation of PCL/GTS and PCL/JWF) composites	32
	2.3	Testing and measurement techniques	35
	2.4	Characterization techniques for PCL/GTS and PCL/JWF composites	35
	2.4.1	Thermal characterization	35
	2.4.1.1	Differential scanning calorimetry (DSC)	35
	2.4.1.2	Nonisothermal crystallization behavior	36
	2.4.1.3	Thermo-gravimetric analysis (TGA)	36
	2.4.2	Particle size analysis	37
	2.4.3	Mechanical properties	38
	2.4.3.1	Tensile properties	38
	2.4.3.2	Fracture toughness	39
	2.4.3.2.1	Essential work of fracture	39
	2.4.3.2.2	Approach for essential work of fracture	40
	2.4.3.3	Izod impact test	42
	2.4.3.4	Dynamic mechanical analysis (DMA)	43
	2.4.4	Rheological characterization	43
	2.4.4.1	Parallel plate rheology	43
	2.4.4.2	Capillary rheometer	43
	2.4.5	Morphological characterization	45
	2.4.5.1	Scanning electron microscopy (SEM)	45
	2.4.5.2	Polarized light optical microscopy (PLOM)	45

2.4.6	Structural characterization	45
2.4.6.1	Fourier-Transform infrared (FTIR)	45
2.4.7	Disintegration studies	46
	References	47
CHAPTER 3	<i>Effect of GTS on Thermal, Mechanical, Morphological, and Crystallization Behavior of PCL</i>	49–92
3.1	Overview of the chapter	50
3.2	Results and discussion	51
3.2.1	Degree of crystallinity	51
3.2.2	Nonisothermal crystallization kinetics of PCL and PCL/GTS composites	53
3.2.2.1	Avrami analysis	59
3.2.2.2	Jeziorny corrections	64
3.2.2.3	Liu analysis	65
3.2.2.4	Nucleation activity	69
3.2.2.5	Activation energy	71
3.2.3	Thermo-gravimetric analysis	73
3.2.4	Mechanical properties	75
3.2.4.1	Tensile stress-strain curves	75
3.2.4.1.1	Tensile modulus	77
3.2.4.1.2	Tensile strength	80
3.2.4.2	Impact Strength	82
3.2.5	Scanning Electron Microscopy	84
3.2.6	Fourier-Transform infrared (FTIR)	86
3.2.7	Polarized light optical microscopy (PLOM)	87
3.3	Conclusions	89
	References	91
CHAPTER 4	<i>Effect of GTS On Thermomechanical, Rheological, Fracture and Biodegradation behavior of PCL</i>	93–123
4.1	Overview of the chapter	94

4.2	Results and Discussion	95
4.2.1	Dynamic mechanical analysis	95
4.2.1.1	Estimation of the volume of the immobile segments in PCL/GTS composites	98
4.2.2	Capillary rheometer	100
4.2.2.1	Flow curves (Shear stress vs. shear rate curves)	100
4.2.2.2	Melt viscosity curves	102
4.2.2.3	Power law index (n)	103
4.2.2.4	Consistency coefficient (K)	104
4.2.3	Dynamic rheological behavior	105
4.2.4	Fracture behavior of PCL/GTS biocomposites	110
4.2.4.1	Load displacement curves	110
4.2.4.2	Crack resistance behavior	113
4.2.5	Disintegration test in composting condition	117
4.3	Conclusions	121
	References	122
CHAPTER 5	<i>Effect of JWF on Thermal, Mechanical, Morphological, and Crystallization Behavior of PCL</i>	124–154
5.1	Overview of the chapter	125
5.2	Results and discussion	126
5.2.1	Differential scanning calorimetry	126
5.2.1.1	Nonisothermal crystallization kinetics of PCL/JWF composites	128
5.2.1.1.1	Ozawa analysis	132
5.2.1.1.2	Liu analysis	134
5.2.1.1.3	Activation energy	136
5.2.2	Thermo-gravimetric analysis	138
5.2.3	Mechanical properties	140
5.2.3.1	Tensile stress-strain curves	140
5.2.3.1.1	Tensile modulus	142

5.2.3.1.2	Tensile yield strength	145
5.2.3.2	Impact Strength	148
5.2.4	Fracture surface morphology	149
5.3	Conclusions	151
	References	153
CHAPTER 6	<i>Effect of JWF on Thermomechanical, Rheological, Fracture and Biodegradation behavior of PCL</i>	155–183
6.1	Overview of the chapter	156
6.2	Results and Discussion	158
6.2.1	Dynamic mechanical analysis	158
6.2.1.1	Estimation of the volume of the immobile segments in PCL/JWF composites	161
6.2.2	Dynamic rheological behavior	165
6.2.3	Fracture behavior of PCL/JWF biocomposites	170
6.2.3.1	Load displacement curves	170
6.2.3.2	EWF parameters	171
6.2.4	Fracture surface morphology	175
6.2.5	Biodegradation test in composting condition	177
6.2.6	Conclusions	180
	References	182
CHAPTER 7	<i>Summary, Conclusions and Future Scope</i>	184–189
7.1.	Summary of thesis	185
7.2.	Conclusions	188
7.3.	Future scope	189
	List of Publications	
	Biodata	

List of figures

<i>Figure No.</i>	<i>Title</i>	<i>Page Number</i>
Figure 1.1	Chemical structure of PCL	4
Figure 2.1	Particle size distribution curve for granular tapioca starch	37
Figure 2.2	SEM micrograph of JWF	38
Figure 2.3	A typical DENT specimen	40
Figure 3.1	DSC (a) cooling and (b) heating scans for PCL and PCL/GTS composites at a heating rate of 10 °C/min	52
Figure 3.2	DSC exotherms for: PGTS0 (a), PGTS5 (b), PGTS10 (c), PGTS20 (d), and PGTS35 (e), at different cooling rates	55
Figure 3.3	Relative crystallinity versus temperature for: PGTS0 (a), PGTS5 (b), PGTS10 (c), PGTS20 (d), and PGTS35 (e)	57
Figure 3.4	Relative crystallinity versus time for: PGTS0 (a), PGTS5 (b), PGTS10 (c), PGTS20 (d), and PGTS35 (e)	58
Figure 3.5	Avrami plot of $\ln[-\ln(1-X_T)]$ versus $\ln t$ for: PGTS0 (a), PGTS5 (b), PGTS10 (c), PGTS20 (d), and PGTS35 (e)	60
Figure 3.6	Liu plot of $\ln R$ versus $\ln t$ for: PGTS0 (a), PGTS5 (b), PGTS10 (c), PGTS20 (d), and PGTS35 (e)	68
Figure 3.7	The plot $\ln (R/T_p^2)$ versus $1/T_p$ to calculate the nucleation activity of GTS	70
Figure 3.8	Crystallization activation energy of pristine PCL and PCL/GTS composite by Kissinger method	72
Figure 3.9	(a) TG and (b) DTG traces of PCL/GTS composites in nitrogen atmosphere [Heating rate 20 °C/min]	74
Figure 3.10	Stress-Strain curves for PCL and PCL/GTS composites	76
Figure 3.11	Variation of tensile modulus of PCL/GTS composites with crystallinity and Φ_f	77

<i>Figure No.</i>	<i>Title</i>	<i>Page Number</i>
Figure 3.12	Normalized relative tensile modulus, $(E_c/X_c)/(E_m/X_m)$, of PCL/GTS composites (*) and the predictive models according to the ‘‘Einstein (with adhesion)’’ (····), Eq. (3.13) and ‘‘Guth-Smallwood’’(·-·-·) Eq. (3.14), against Φ_f	79
Figure 3.13	Variation of tensile yield strength of PCL/GTS composites with crystallinity and Φ_f	80
Figure 3.14	Normalized relative tensile yield strength, $(\sigma_c/X_c)/(\sigma_y/X_m)$, of PCL/GTS composites (*)and the predictive model according to the ‘‘Bela-Pukanszky’’ model (····) with $B_a = 4.27$ Equation 3.15),against Φ_f	81
Figure 3.15	Variation of impact strength of PCL/GTS composites with crystallinity and Φ_f	83
Figure 3.16	Normalized relative notched Izod impact strength, $(I_c/X_m)/(I_m/X_m)$, of PCL/GTS composites	84
Figure 3.17	SEM micrographs of (a) GTS (b) PCL and PCL/GTS composites at varying Φ_f (c) 0.05 (d) 0.10 (e) 0.20 (f) 0.36	85
Figure 3.18	FTIR scans of PCL and PCL/GTS composites	86
Figure 3.19	Polarized light optical micrographs of neat PCL at 30 °C	87
Figure 3.20	Polarized light optical micrographs of PGTS0 (a), PGTS5 (b), PGTS10 (c), PGTS20 (d), and PGTS35 (e) at 30 °C	88
Figure 4.1	Variation of storage modulus of PCL and PCL/GTS composites with temperature	95
Figure 4.2	Variation of loss modulus of PCL and PCL/GTS composites with temperature	97
Figure 4.3	Variation of $\tan \delta$ of PCL and PCL/GTS composites with temperature	98
Figure 4.4	Comparison of $\tan \delta$ vs. temperature curves for rule of mixture (red sphere) and PCL/GTS composites (black square): (a) $\Phi_f=0.0$ (b) $\Phi_f=0.06$ (c) $\Phi_f=0.10$ (d) $\Phi_f=0.20$ and (e) $\Phi_f=0.36$	101

Figure No.	Title	Page Number
Figure 4.5	A plot of τ_w against at $\dot{\gamma}_w$ 170 °C in PCL/GTS composites at varying Φ_f : (■) 0, (◆) 0.05, (▲) 0.10, (▼) 0.20, and (◇) 0.36	102
Figure 4.6	A plot of $\log \eta_a$ against at $\log \dot{\gamma}_w$ at 170 °C for PCL/GTS composites at varying Φ_f	104
Figure 4.7	Variation of complex viscosity of PCL and PCL/GTS composites with frequency	106
Figure 4.8	Variation of elastic modulus of PCL and PCL/GTS composites with frequency	107
Figure 4.9	Variation of viscous modulus of PCL and PCL/GTS composites with frequency	108
Figure 4.10	The vGPs for PCL and PCL/GTS composites	109
Figure 4.11	The Han plots for PCL and PCL/GTS composites	110
Figure 4.12	Load displacement curves of PCL and PCL/GTS composites (a) PGTS0, (b), PGTS5, (c) PGTS10, (d) PGTS20, and (e) PGTS35 with increasing ligament length (3-7 mm) during EWF test	111
Figure 4.13	Hill's analysis plot: Variation of net section stress (σ_n) with ligament length	112
Figure 4.14	Variation of specific work of fracture (w_f) with ligament length	113
Figure 4.15	Variation of plane stress fracture parameters with various GTS concentrations	114
Figure 4.16	SEM micrographs at the tip of the fracture surface of test specimen during (a) PGTS0, (b), PGTS5, (c), PGTS10, (d), PGTS20, and (e) PGTS35 fractured sample during EWF test at 5 Kx	116

Figure No.	Title	Page Number
Figure 4.17	Digital images of PCL and PCL/GTS composite films corresponding to different incubation times in composting conditions at $\pm 30\text{ }^{\circ}\text{C}$	119
Figure 4.18	SEM images pristine PCL and PCL/GTS biocomposites before and after disintegration in composting condition at $\pm 30\text{ }^{\circ}\text{C}$ for different times (5 kx)	120
Figure 5.1	DSC (a) cooling and (b) heating scans for PCL and PCL/JWF composites at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$	127
Figure 5.2	DSC exotherms for: PJWF5 (a), PJWF10 (b), PJWF20 (c), and PJWF35 (d), at different cooling rates	129
Figure 5.3	Relative crystallinity versus temperature for: PJWF5 (a), PJWF5 (b), PJWF5 (c), and PJWF5 (d), at different cooling rates	131
Figure 5.4	Relative crystallinity versus time for: PJWF5 (a), PJWF10 (b), PJWF20 (c), and PJWF35 (d), at different cooling rates	132
Figure 5.5	Ozawa plots of $\ln[-\ln(1-X_T)]$ versus $\ln R$ for: PJWF0 (a), PJWF5 (b), PJWF10 (c), PJWF5 (d), and PJWF20 (e), at different temperatures	133
Figure 5.6	Liu plot of $\ln R$ versus $\ln R$ for: PJWF5 (a), PJWF10 (b), PJWF20 (c), and PJWF35 (d)	135
Figure 5.7	Crystallization activation energy of PCL/JWF composites by Kissinger method	137
Figure 5.8	(a) TG and (b) DTG traces of PCL/JWF composites in nitrogen atmosphere [Heating rate $20\text{ }^{\circ}\text{C}/\text{min}$]	139
Figure 5.9	Stress-Strain curve for PCL and PCL/JWF composites	141
Figure 5.10	Plot of (a) tensile modulus of PCL/JWF composites versus Φ_f (b) relative tensile modulus versus Φ_f (c) correlation of relative tensile modulus with theoretical models (d) normalized relative tensile modulus versus Φ_f	144

<i>Figure No.</i>	<i>Title</i>	<i>Page Number</i>
Figure 5.11	Plot of (a) tensile yield strength of PCL/JWF composites versus Φ_f (b) relative tensile yield strength versus Φ_f (c) correlation of relative tensile yield strength with theoretical models (d) normalized relative tensile yield strength versus Φ_f	147
Figure 5.12	Plot of (a) notched Izod impact strength and (b) relative normalized notched Izod impact strength of PCL/JWF composites versus Φ_f	148
Figure 5.13	SEM micrographs of (a) JWF (b) PCL and PCL/JWF composites at varying Φ_f (c) 0.05 (d) 0.10 (e) 0.18 (f) 0.34	150
Figure 6.1	Variation of storage modulus of PCL and PCL/JWF composites with temperature	159
Figure 6.2	Variation of storage modulus of PCL and PCL/JWF composites with temperature	160
Figure 6.3	Variation of $\tan \delta$ of PCL and PCL/JWF composites with temperature	162
Figure 6.4	Comparison of $\tan \delta$ vs. temperature curves for rule of mixture (red sphere) and PCL/JWF composites(black circle): (a) $\Phi_f = 0.0$ (b) $\Phi_f = 0.05$ (c) $\Phi_f = 0.10$ (d) $\Phi_f = 0.18$ and (e) $\Phi_f = 0.34$	164
Figure 6.5	Variation of complex viscosity of PCL and PCL/JWF composites with frequency	166
Figure 6.6	Variation of elastic modulus of PCL and PCL/JWF composites with frequency	167
Figure 6.7	Variation of loss modulus of PCL and PCL/JWF composites with frequency	168
Figure 6.8	Phase angle (δ) as a function of complex modulus (G^*), the vGPs, for PCL and PCL/JWF composites	169
Figure 6.9	The Han plots for PCL and PCL/JWF composites	170
Figure 6.10	Load displacement curves of PCL/JWF composite with increasing ligament length during EWF test a varying Φ_f values: (a) 0 (b) 0.05 (c) 0.10 (d) 0.18, and (e) $\Phi_f = 0.34$	172

<i>Figure No.</i>	<i>Title</i>	<i>Page Number</i>
Figure 6.11	Hill's analysis plot: Variation of net section stress (σ_n) with ligament length	173
Figure 6.12	Variation of specific work of fracture (w_f) with ligament length	174
Figure 6.13	Variations of plane stress fracture parameters against Φ_f	174
Figure 6.14	SEM micrographs at the tip of the fracture surface of test specimen during EWF test (a) $\Phi_f = 0$ (b) $\Phi_f = 0.05$ (c) $\Phi_f = 0.10$ (d) $\Phi_f = 0.18$ (e) $\Phi_f = 0.34$ (f) Fractured sample during EWF test	176
Figure 6.15	Digital images of PCL and PCL/JWF composite films corresponding to different incubation times in compositing conditions at ± 30 °C	178
Figure 6.16	SEM images of pristine PCL and PCL/JWF biocomposites before and after before and after disintegration in composting conditions at ± 30 °C for different times (5 kx)	179

List of tables

<i>Table No.</i>	<i>Title</i>	<i>Page Number</i>
Table 1.1	Comparison of typical PCL properties with different thermoplastic resins	4
Table 1.2	PCL/GTS biocomposites and their key findings	14
Table 1.3	Composition of wood flour in soft and hard wood	17
Table 1.4	PCL/JWF biocomposites and their key findings	22
Table 2.1	Raw material specifications	33
Table 2.2	Temperature profile used during extrusion at screw speed of 75 rpm	33
Table 2.3	(a) Temperature profile set in injection molding machine (b) Processing conditions used in injection molding	34
Table 2.4	Compositions and sample designations of PCL/GTS biocomposites	34
Table 2.5	Compositions and sample designations of PCL/JWF biocomposites	35
Table 3.1	DSC crystallization parameters for of PCL and PCL/GTS composites	53
Table 3.2	Nonisothermal crystallization parameters of PCL and PCL/GTS composites	56
Table 3.3	Avrami parameters during nonisothermal crystallization kinetics for PCL and PCL/GTS composites	63
Table 3.4	Jeziorny parameters for PCL and PCL/GTS composites at various cooling rates	66
Table 3.5	Liu parameters for PCL and PCL/GTS composites at various fractions of relative crystallinity values	69
Table 3.6	Nucleation activity for PCL and PCL/GTS composites at different cooling rates	71
Table 3.7	Crystallization activation energy of pristine PCL and PCL/GTS composites	73

<i>Table No.</i>	<i>Title</i>	<i>Page Number</i>
Table 3.8	TG/DTG results of PCL, GTS and PCL/GTS composites in nitrogen atmosphere [Heating rate 20 °C/min]	75
Table 3.9	Values of phase adhesion parameter B_a calculated from Equation 3.9	82
Table 4.1	Storage modulus (MPa) of PCL/GTS biocomposites at different temperatures	96
Table 4.2	Volume fractions of immobilized polymer chains of PCL/GTS biocomposites	99
Table 4.3	Values of consistency coefficient (K) and Power law index (n) at 170 °C, at varying Φ_f	105
Table 4.4	Slope of $\log G'$ and $\log G''$ vs. $\log \omega$ for PCL and PCL/GTS composites	107
Table 5.1	DSC crystallization parameters for of PCL and PCL/JWF composites	127
Table 5.2	Nonisothermal crystallization parameters of PCL/JWF composites	130
Table 5.3	Liu parameters for PCL and PCL/JWF composites at various fractions of relative crystallinity values	136
Table 5.4	Crystallization activation energy of PCL/JWF composites	137
Table 5.5	TG/DTG results of PCL, JWF and PCL/JWF composites in nitrogen atmosphere [Heating rate 20 °C/min]	140
Table 5.6	Mechanical properties and crystallinity (%) of PCL and PCL/JWF composites	142
Table 5.7	Values of phase adhesion parameter B_a calculated from Equation 5.4	148
Table 6.1	Storage modulus of PCL/JWF biocomposites (MPa) at different temperatures	159

<i>Table No.</i>	<i>Title</i>	<i>Page Number</i>
Table 6.2	Volume fractions of immobilized polymer chains of PCL/GTS biocomposites	162
Table 6.3	Slope of log G' and log G'' vs. log ω for PCL and PCL/JWF composites	167

List of abbreviations and symbols

DENT	-	Double-edge-notched-tension
DIC	-	Digital image correlation
DMA	-	Dynamic mechanical analysis
DSC	-	Differential scanning calorimeter
E	-	Young's modulus
E'	-	Storage modulus
E''	-	Loss modulus
EWF	-	Essential work of fracture
FPZ	-	Frontal process zones
FTIR	-	Fourier transform infra red spectroscopy
G'	-	Melt storage modulus
G''	-	Melt loss modulus
HDPE	-	High density polyethylene
IFPZ	-	Inner fracture process zone
l	-	Ligament length
LDPE	-	Linear density polyethylene
N-EWF	-	Non-essential work of fracture
OPDZ	-	Outer plastic deformation zone
PLA	-	Poly lactide
PGA	-	Polyglycolide
PPC	-	Poly(propylene carbonate)
PCL	-	Poly(ϵ -caprolactone)
PYFM	-	Post-yield fracture mechanics
SEM	-	Scanning electron microscopy
$Tan \delta$	-	Tangent delta
T_c	-	Crystallization temperature
T_g	-	Glass transition temperature
TGA	-	Thermogravimetric analysis
T_m	-	Melting temperature
w_e	-	Essential work of fracture
W_f	-	Total work of fracture
w_f	-	Specific total work of fracture
X_c	-	Degree of crystallinity

XRD	-	X-ray diffraction
β	-	Plastic zone shape factor
βw_p	-	Non-essential work of fracture
ε_b	-	Elongation at break
ρ	-	Density
σ_s	-	Tensile strength
σ_y	-	Yield stress