

**STUDIES ON POLY(LACTIC ACID)/JUTE FIBER
BIOCOMPOSITES AND THEIR FOAM PROCESSABILITY**

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**CENTRE FOR POLYMER SCIENCE AND ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JULY 2017**

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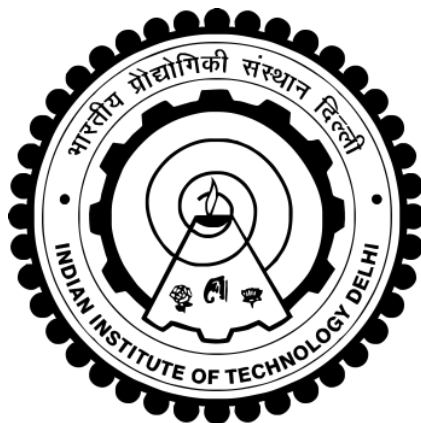
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Submitted

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

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

JULY 2017

Dedicated to my parents

Certificate

This is to certify that the thesis entitled “**Studies on Poly(lactic acid)/Jute Fiber Biocomposites and their Foam Processability**” being submitted by **Mr. Mohammad Tahir Zafar** to the Indian Institute of Technology Delhi, for the fulfillment of award of the degree “**Doctor of Philosophy**” is a record of bonafide research work carried by him under our supervision. This thesis has been prepared in conformity with the rules and regulations of the Indian Institute of Technology Delhi, New Delhi. We further certify that the thesis has attained a standard required for a Ph.D. degree of the institute. The research reported and results presented in the thesis have not been submitted in part or full to any other institute or university for the award of any other degree or diploma.



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Acknowledgements

It gives me immense pleasure to express my deep sense of gratitude to all who have helped me along my way through the doctoral studies and a memorable stay at IIT Delhi.

*I express my profound sense of gratitude and veneration to my supervisors, **Prof. Anup K. Ghosh**, **Prof. S. N. Maiti**, and **Prof. Amar K. Mohanty** for guiding me all the way during my PhD tenure. Their constant inspiration and encouragement have been a great motivation for me behind all the work I have conducted. I appreciate their cool composure and patience which helped me to tide over the difficult situations. I have learnt from them that failures in all doing should motivate one to work harder. They have always boosted me to put in extra efforts and I am indebted to them what I am today. I am also thankful to them for providing me opportunities to handle some short-term projects and assisting them in few industrial projects which enabled me to fortify my skills.*

I express my deep sense of gratitude to my student research committee members, Dr. Bhabani K. Satapaty, Dr. Josemon Jacob and Prof. Bhuvanesh Gupta who have monitored my work and provided me the valuable suggestions. I am also thankful to Prof. Veena Choudhary, Dr. Leena Nebhani, and Dr. Sampa Saha who inspite of their busy schedule have always made themselves available for valuable discussions and support.

I would like to convey my special thanks to Dr. Sanjeev Kumar (Lajpat Rai Post Graduate College, Sahibabad) for keeping him available for me from time to time with his valuable suggestions and encouraging spirit.

This work would not be possible without the support and encouragement from my friends, seniors and juniors. My special thanks go to Dr. Mayank Dwivedi, Dr. Saikat Banerjee, Dr. Satpal Singh, Dr. Manash Jyoti Kashyap, Dr. Satish Kommoji, Dr. Snehi Bharti, Dr. Shikha Jain, Dr. Jutika Goswami, Dr. Priyanka Singh, Dr. Rishi Sharma, Dr. Sunil Kumar, Dr. Rajender Malik, Dr. Pawan Verma, Dr. Rakesh Kumar Kachhap, Mr. Sabapathy Sankarpandi, Miss. Swarna, Mr. Anindya Dutta, Ms. Saheli Bhattacharyya, Ms. Ritima Banerjee, Miss. Prajesh Nayak, Miss. Neetu Singh, Miss. Bariya Qayyum, Miss. Srijita Purkayastha, Ms. Astha Garhwal, Ms. Achala, Ms. Ranjana Nehra, Mr. Rajendra Singla, Mr. Harjeet Singh Jaggi, Ms. Harshita, Miss. Sucharita Sethy, Ms. Savita Meena, Mr. Debang Konwar, Ms. Bhavana Sharma, Miss. Banpreet Kaur, Ms. Meenakshi Verma, Mr. Sampat Singh Chauhan, Mr. V.P. Singh, Mr. Devender Mogha,

Ms. Shilpi Sharma, Miss Pragati Ghalout, Miss Sumbul Hafeez, Miss Ifra, Miss Zeenat Sheerazi, Mr. Agni Kumar Biswal, and Miss Smruti Mishra for their cooperation and friendly attitude.

I am especially thankful to Mr. Ashish Singh, Ms. Priyanka Singh and Mr. Kinshuk Singh for their constant encouragement throughout and immediate help whenever needed.

I owe thanks to laboratory staffs Mr. Ashok Kapoor, Mr. Surender Sharma, Mr. Shiv Kant, Mr. S. S. Bhatnagar, Mr. Ehteshamul Islam and Mr. Gajraj Singh for their timely help and suggestions. I would also like to convey my thanks to Mr. Narender Kumar, Ms. Suchitra Singh, Ms. Shalini Arora, Mr. Sudhir Kumar Pandey and Pramod Kale for their all possible supports. I am grateful to Mr. D. C. Sharma and Mr. Kuldeep Sharma of SEM central facility for teaching and allowing me the SEM of my samples.

I would like to extend my thanks to Prof. Manju Misra, University of Guelph, ON, Canada for their kind support and providing necessary facilities to carry out research in their laboratory.

I wish to acknowledge Council of Scientific & Industrial Research (CSIR), New Delhi, India (File No. 09/086(0913)/2008-EMR-I) and Ministry of Human Resource Development (MHRD), Government of India, for providing me financial assistance to carry out my research work smoothly. I would also like to acknowledge the Department of Foreign Affairs and International Trade (DFAIT), Canada, and the Canadian Bureau for International Education (CBIE) for providing a Graduate Student Exchange Program (GSEP) 2011-2012 fellowship.

I take this opportunity to express my deepest gratitude to my family members. The love from my parents (Mohd. Zafar Ali & Razia Begum) has always given me the strength and confidence to overcome the difficulties and to accomplish the objectives in my life. They always stood by my side with their emotional support, and blessings. My brothers Mr. Md. Javed Zafar, Mr. Md. Khalid Zafar, Mr. Md. Danish Zafar, and sisters Ms. Rabia Zafar, and Miss. Reshima Zafar have always supported me with their unconditional love and care and my deep regards are always with them who have been with me.

Finally and above all, I would like to thank the Almighty God. It would not have been possible for me to reach at this stage of academic pursuit without his grace.

(Mohammad Tahir Zafar)

Date:

Place: New Delhi

Abstract

Jute fibers have immense potential to be used as natural fillers in polymeric matrices to prepare biocomposites. The present research work focuses on the surface treatment of the jute fibers and the biocomposites fabrication of the same with poly(lactic acid)(PLA). Jute fibers were surface treated using i) alkali (NaOH) and ii) alkali followed by silane (NaOH+Silane). The effects of surface treatments on the various properties of the jute fibers were investigated. SEM images showed the presence of various impurities on the surface of untreated jute fibers, while the jute fiber surfaces treated using NaOH were found free from impurities and comparatively rougher. (NaOH+Silane) treated jute fiber surfaces were found to be clean and covered with the polysiloxane layers. Thermogravimetric analysis (TGA) revealed higher thermal stability of the jute fiber treated using both ways NaOH and (NaOH+Silane) than the untreated jute fibers. FT-IR spectra showed the absence of carbonyl stretching peak at 1739 cm^{-1} in case of NaOH treated jute fibers due to the hemicellulose removal and the presence of -Si-O-Si-, -Si-C- and -Si-O-C- peaks at 713 cm^{-1} , 776 cm^{-1} and 1210 cm^{-1} respectively in case of (NaOH+Silane) treated jute fibers. The effect of surface treatment of jute fibers on phase adhesion between PLA and jute fibers were analyzed by performing single fiber pull-out test and were examined in terms of interfacial shear strength (IFSS) and critical fiber length. It was observed that with the increase of extent of surface treatment, the IFSS between PLA and jute fibers increased and the critical fiber length decreased.

Biocomposites based on PLA/jute fibers with untreated and surface treated jute fibers were fabricated using the twin screw extruder in the ratios (95/5, 90/10, 80/20, 70/30 w/w) and subsequently injection molded. The biocomposites thus prepared, were characterized by various

test methods like mechanical (tensile and impact), thermal (TGA, DSC), thermomechanical, rheological (capillary and parallel plate rheometry), hydrophilicity, dimensional stability, and biodegradative analyses.

Microcellular foaming of the selected biocomposites was carried out by single stage batch process in a high pressure vessel at 150 °C, under 17 MPa saturation pressure for 6 h saturation time. The effects of jute fiber content as well as that of matrix-fiber phase adhesion in composites with surface treated jute fibers on the foam microstructure were studied. Prior to the foaming of the biocomposites, neat PLA samples were also foamed at 150 °C and the effect of process parameters such as saturation pressure and saturation time on the foam microstructure of PLA was studied to find the best set of process parameters. Further the effects of the jute fiber content and jute fiber surface treatment were analyzed on the hydrophilicity, dimensional stability, and biodegradation behavior of the foamed biocomposites.

सारांश

बहुलकीय मैट्रिक्स से जैव-कोम्पोजिट्स बनाने हेतु प्राकृतिक रेशों के रूप में जूट के रेशों को उपयोग करने की वृहत संभावनाएं हैं। प्रस्तुत शोध कार्य में जूट-रेशों की सतह को उपचारित कर एवम उन्हें पोली(लैक्टिक अम्ल) (पी-एल-ए) में मिश्रित कर जैव-कोम्पोजिट्स विनिर्माण पर विषयकेंद्रित किया गया है। जूट-रेशों की सतह का उपचार दो प्रकार से किया गया i) क्षार (NaOH) से तथा ii) क्षार तथा तदोपरांत साइलेन (NaOH + साइलेन) से। जूट-रेशों की सतह के उपचार के प्रभाव का उसके विभिन्न गुणधर्मों पर आकलन किया गया। एस-ई-एम छायाचित्रों में जहाँ एक ओर अनउपचारित जूट-रेशों के पृष्ठ पर विभिन्न प्रकार की अशुद्धियों की उपस्थिति पायी गयी वहीं NaOH से उपचारित जूट-रेशों की सतह अशुद्धियों से विमुक्त तथा सापेक्ष रूप से खुरदुरी ज्ञात हुई। (NaOH + साइलेन) द्वारा उपचारित जूट-रेशों की सतह अशुद्धियों से विमुक्त तथा पौलीसाईलोकसेन की परतों से आवरित पायी गयी।

ताप-भारात्मक विश्लेषण (टी-जी-ए) से ज्ञात हुआ कि NaOH तथा (NaOH + साइलेन), दोनों प्रकार से सतह उपचारित जूट-रेशों का ताप स्थायित्व अनउपचारित जूट-रेशों की तुलना में अधिक है। अवरक्त स्पेक्ट्रम (एफ़-टी-आई-आर) में NaOH से उपचारित जूट-रेशों से हेमी-सेलुलोज के विलोपन के कारण 1639 सेमी^{-1} पर पाई जाने वाली श्रृंखला अनुपस्थित थी तथा (NaOH + साइलेन) से उपचारित जूट-रेशों में -Si-O-Si- , -Si-C- और -Si-O-C- से सम्बंधित श्रृंखलाएं कृमशः 1013 सेमी^{-1} , 1066 सेमी^{-1} तथा 1210 सेमी^{-1} पर देखी गयी। जूट-रेशों की सतह के उपचार का पी-एल-ए और जूट-रेशों की प्रावस्था-आसंजन पर प्रभाव का आकलन एकल -रेशा-बहिनिष्क्रमण-परीक्षण द्वारा किया गया और अंतर-पृष्ठीय शियर शक्ति (आई-एफ़-एस-एस) तथा क्रांतिक रेशा लम्बाई ज्ञात कर विश्लेषण किया गया। यह पाया गया कि सतह के उपचार की मात्र में वृद्धि के

साथ-साथ पी-एल-ए एवम जूट-रेशों के बीच अंतर-पृष्ठीय शियर शक्ति में वृद्धि हुई है तथा क्रांतिक रेशा लम्बाई में कमी आयी हैं।

पी-एल-ए/जूट-रेशों पर आधारित विभिन्न प्रकार के जैव-कॉम्पोजिट्स को अनउपचारित तथा सतह उपचारित जूट-रेशों के साथ द्विक-पेंच-मिश्रण-यंत्र में (९५/५, ९०/१०, ८०/२०, ७०/३० भार/भार) अनुपातों में मिश्रित कर विनिर्मित किया गया तथा तदोपरांत बाद में संपीडन साचे द्वारा प्रमाणिक आकार में ढाला गया। इस प्रकार तैयार किए गए जैव-कॉम्पोजिट्स का यांत्रिक (तन्यता और संघट्ट), तापीय (टी-जी-ए, डी-एस-सी), ताप यांत्रिकीय (डी-एम्-ए), रियोलोजिकल (केशिका और समांतर पट्ट रीहोमेट्री), जल-स्नेहकता, आयामी दृढ़ता और जैव-अपघटन जैसे विभिन्न परीक्षणों द्वारा विश्लेषण किया गया।

कुछ विशेष चयनित जैव-कॉम्पोजिट्स को एक उच्च-दाब वाले पात्र में लेकर 150 °C ताप पर एकल चरण बैच प्रक्रिया द्वारा 6 घंटे संतृप्तिकरण समय और 17 मेगा पास्कल संतृप्तिकरण दाब पर माइक्रो-सेलुलर-फोमिंग प्रक्रिया द्वारा फोम किया गया। जूट-रेशों की मात्रा का तथा सतह उपचारित जूट-रेशों वाले कंपोजिट्स में मैट्रिक्स-रेशा प्रावस्था-आसंजन का फोम की सूक्ष्म-संरचना पर प्रभाव का अध्ययन किया गया। जैव-कॉम्पोजिट्स के फोमिंग से पहले, प्रक्रिया मानदंडों का सबसे अच्छा संयोजन प्राप्त करने के लिए विशुद्ध पी-एल-ए के नमूने भी 150 °C ताप पर फोम किए गए जिसमें विशुद्ध पी-एल-ए के फोम की सूक्ष्म-संरचना पर संतृप्तिकरण दाब तथा संतृप्तिकरण समय जैसे प्रक्रिया मानदंडों के प्रभाव का अध्ययन किया गया। तत्पश्चात, जूट-रेशों की मात्रा और जूट-रेशों की सतह उपचार का विश्लेषण फोम जैव-कॉम्पोजिट्स के जल-स्नेहकता, आयामी दृढ़ता और जैव-अपघटन व्यवहार पर किया गया।

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List of Symbols

Symbol	Description
M_n	: Number average molecular weight
M_w	: Weight average molecular weight
T_g	: Glass transition temperature
T_{cc}	: Cold crystallization temperature
ΔH_{cc}	: Enthalpy of cold crystallization
T_m	: Melting temperature
ΔH_m	: Enthalpy of melting
T_{mc}	: Melt crystallization temperature
ΔH_{mc}	: Enthalpy of melt crystallization
ΔH_m^0	: Melting enthalpy of 100% crystalline PLA
S_p	: Slope of the cold crystallization peak
ΔW_d	: Peak width at half height
X_c	: Crystallinity from DSC
W_f	: Weight fraction
I_c	: Crystallinity index
ρ_f	: Jute fiber density
L_c	: Critical fiber length
τ_c	: Inter facial shear strength
σ	: Ultimate tensile strength of jute fibers
L_e	: Embedded length
G'	: Storage modulus
G''	: Loss modulus
η^*	: Complex viscosity
$\tan\delta$	: Loss factor
V_f	: Volume fraction
ϕ	: Expansion ratio
N_f	: Cell density

List of Abbreviations

Abbreviation	Description
PLA	: Poly(lactic acid)
PLLA	: Poly(l-lactic acid)
PDLA	: Poly(d,l-lactic acid)
PCL	: Poly(caprolactone)
PGA	: Poly(glycolic acid)
TSE	: Twin screw extruder
DSC	: Differential scanning calorimetry
TGA	: Thermal gravimetric analysis
DMA	: Dynamic mechanical analysis
SEM	: Scanning electron microscopy
GPC	: Gel permeation chromatography
WAXD	: Wide angle X-ray diffraction
PLOM	: Polarized light optical microscopy
FT-IR	: Fourier transfer infrared spectroscopy
IFSS	: Interfacial shear strength
CBA	: Chemical blowing agent
PBA	: Physical blowing agent