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

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by

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Submitted

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to the

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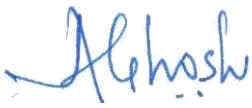
Dedicated to my parents

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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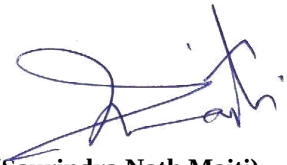

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(Mohammad Tahir Zafar)

Date:
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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 rehometry), hydrophillical, 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 hydrophillicity, 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 हैं। 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 ओ र अनउपचारित जूट-रेशों के पृष्ठ पर विभिन्न प्रकार की अशुद्धियों की उपस्थिति पायी गयी वहीँ NaOH से उपचारित जूट-रेशों की सतह अशिद्धियों से विमुक्त तथा सापेक्ष रूप से खुरदुरी ज्ञात हुई। (NaOH + साइलेन) द्वारा उपचारित जूट-रेशों की सतह अशुद्धियों से विमुक्त तथा पौलीसाईलोक्सेन 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 (ऍफ़-टी-आई-आर) में NaOH से उपचारित जूट-रेशों से हेमी-सेलुलोज के विलोपन के कारण १७३९ 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 ७१३ सेमी$^{-1}$, ७७६ सेमी$^{-1}$ तथा १२१० 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-ऍफ़-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-ऍम-ऐ), 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 जिसमे विशुद्ध पी-एल-ए के फोम की सूक्ष्म-संरचना पर संतृप्तिकरण दाब तथा संतृप्तिकरण समय जैसे प्रक्रिया मान दंडों 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 Equations

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^0_m	:	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