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

ACHLA

DEPARTMENT OF MATERIALS SCIENCE

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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

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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

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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 Φ_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 अभ्रकनीय 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 बायोडिग्रैडबल 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 बायोडिग्रेएबल अर्धुष्मलीय एलीफाइट 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 बायोकॉम्पोसाइट्स 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 शुरूआत में गिरावट के तापमान में देखा गया सीमांत कमी से पता चलता है कि जीटीएस का समावेश थर्मा-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 (βwp) 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 इंटर्सफार्मिटिक 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 रीनॉर्फ़िंग 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 जेडब्ल्यूएफ के बीच मैकेनिकल इंटरलॉकिंग और इंटरैक्शन का सुझाव देता है। सभी नमूनों में जेडब्ल्यूएफ 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 जेडब्ल्यूएफ की उपस्थिति में पिघलने के तापमान (टीएम) और पीक क्रिस्टलीकरण तापमान में सीमांत वृद्धि का पता चला है। पीसीएल / जेडब्ल्यूएफ 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 ईडब्ल्यूएफ पद्धति द्वारा की गई थी। पीएलएल मैट्रिक्स में जेडब्ल्यूएफ को शामिल करना फ्रैक्चर (βwp) के गैर-आवश्यक काम में वृद्धि करते समय फ्रैक्चर (हम) के आवश्यक काम को कम करता है। जेडब्ल्यूएफ 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 जेडब्ल्यूएफ के शामिल होने से भंडारण मापांक और हानि मो की वृद्धि हुई।

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List of abbreviations and symbols

DENT	-	Double-edge-notched-tension
DIC	-	Digital image correlation
DMA	-	Dynamic mechanical analysis
DSC	-	Differencial 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	-	Polylactide
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