STUDIES ON POLYLACTIDE BASED BLENDS AND NANOCOMPOSITES

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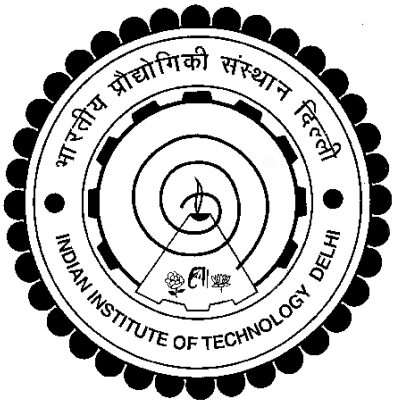

DEPARTMENT OF MATERIAL SCIENCE AND ENGINEERING

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STUDIES ON POLYLACTIDE BASED BLENDS AND NANOCOMPOSITES

by

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CERTIFICATE

This is to certify that the thesis entitled "**Studies on polylactide based blends and nanocomposites**" being submitted by **Ms. Ranjana Nehra,** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in the Department of Material Science and Engineering, is a record of bonafide research work carried out by her. This thesis has been prepared in conformity with the rules and regulations of the Indian Institute of Technology Delhi, New Delhi. The thesis, in our opinion, is worthy of consideration for award of the degree of Doctor of Philosophy in accordance with the regulations of the Institute.

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.

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Date ***Ranjana Nehra***

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ABSTRACT

Biobased polymers have received a great deal of attention because of their superior eco-friendliness and advantages to minimize the usage of petrochemical resources. Polylactide (PLA) is a biodegradable, linear aliphatic thermoplastic polyester which is derived from renewable plant origins. PLA possesses good transparency, high tensile strength and modulus making it a possible alternative for petroleum-based plastics such as poly(ethylene terephthalate), polystyrene and polypropylene. However, due to its brittleness, difficult processability, low thermal stability and toughness, neat PLA finds limited applications.

In order to toughen PLA mainly plasticization, blending and copolymerization methods are used. PLA was melt mixed with poly(ethylene glycol) (PEG) with molecular weight of 4000 g/mol in various PEG concentrations (5-30 wt%). Tensile strength and modulus of PLA decreased in a linear fashion with increasing PEG content. PEG improved the flexibility and plastic deformation of PLA by reducing the intermolecular forces. The impact strength remained almost constant at low PEG content and enhanced significantly at maximum PEG concentration. However, PEG improved the impact strength properties at the cost of tensile strength. Differantial scanning calorimetry (DSC) showed PEG incorporation reduced the T_g of PLA significantly. The melt crystallinity of PLA enhanced with increase in PEG content. The effect of PEG incorporation on thermal stability of PLA was characterised by thermo gravimetric analysis (TGA). Thermomechanical behaviour of the blends was studied by dynamic mechanical analysis (DMA). The shear viscosity of PLA decreased significantly with increase in PEG content.

Blending with a thermoplastic elastomer like poly(styrene-b-ethylene-co-butylene-b-styrene)-g-maleic anhydride copolymer (SEBS-g-MA) can be an effective way to toughen PLA. SEBS-g-MA improves impact strength and flexibility of brittle polymers with minimum decrease in stiffness. PLA was melt blended with SEBS-g-MA copolymer in varied

concentration (5-40 wt%). The blends thus prepared, were characterized by various test methods such as mechanical (tensile and impact), thermal (TGA, DSC), thermomechanical, rheological (capillary and parallel plate rheometry), morphological and fracture analyses. SEBS-g-MA incorporation enhanced elongation-at-break and Izod impact strength with minimum decrease in tensile strength and modulus. Theoretical models were employed to analyze the tensile properties of the blends in order to evaluate the blend structure. The microstructural attributes were characterized by scanning electron microscopy (SEM) of cryofractured, impact fractured and tensile fractured surfaces.

Sepiolite nanoclay is used as reinforcing agent for PLA/SEBS-g-MA 90/10 (w/w) blend. Effects of sepiolite on thermal behaviour, morphology and thermo-mechanical properties of PLA/SEBS-g-MA blend were investigated. The nanocomposite exhibited increase in the tensile modulus and toughness as compared to the blend matrix. Tensile strength and impact strength properties were almost unaffected with sepiolite incorporation. Field emission scanning electron microscopy and transmission electron microscopy images exhibited sepiolite induced morphological changes and dispersion of sepiolite in both PLA and SEBS-g-MA phases. DMA and wide angle X-ray diffraction presented evidences in support of the reinforcing nature of sepiolite and phase interaction between the filler and the matrix.

In future, PLA/SEBS-g-MA/sepiolite ternary nanocomposites can be explored for applications in services e.g. wares, folded cartons, durable goods, laptop and mobile housing, packaging and automotives. PLA/PEG blends can be inducted to nondurable applications in short term molded applications.

सार

जैव आधारित पॉलिमर को पेट्रोकेमिकल संसाधनों के उपयोग को कम करने के लिए उनके श्रेष्ठ पर्यावरण-मित्रता और फायदों के कारण बहुत ध्यान दिया गया है। पोलिलाक्टाइड (पीएलए) एक बायोडिग्रेडेबल, रैखिक एलिफैटिक थर्मोप्लास्टिक पॉलिएस्टर है जो नवीकरणीय पौधे की उत्पत्ति से लिया गया है। पीएलए में अच्छी पारदर्शिता, उच्च तन्यता ताकत और मॉड्यूलस है जो इसे पॉली (एथिलीन टेरेफेथलेट), पॉलीस्टाइरिन और पॉलीप्रोपाइलीन जैसे पेट्रोलियम-आधारित प्लास्टिक के लिए एक संभावित विकल्प बनाता है। हालांकि, इसकी कठिन प्रक्रियाशीलता, कम थर्मल स्थिरता, कठोरता और भंगुरता के कारण, साफ पीएलए सीमित अनुप्रयोगों को पाता है।

पीएलए को सख्त करने के लिए मुख्य रूप से प्लास्टाइजेशन, मिश्रण और कोपोलिमेराइजेशन विधियों का उपयोग किया जाता है। पीएलए को विभिन्न पॉली (एथिलीन ग्लाइकोल) (पीईजी) सांद्रता (5-30 वजन%) में 4000 ग्राम/मोल के आणविक वजन के साथ पीईजी के साथ मिश्रित पिघल गया था। पीएलए की तन्यता ताकत और मॉड्यूलस पीईजी वजन% बढ़ने के साथ एक रैखिक फैशन में कमी आई है। पीईजी ने आणविक बलों को कम करके पीएलए की लचीलापन और प्लास्टिक विरूपण में सुधार किया। कम पीईजी भार पर प्रभाव शक्ति लगभग स्थिर रही और अधिकतम पीईजी भार पर उल्लेखनीय रूप से वृद्धि हुई। हालांकि, पीईजी तन्य शक्ति की लागत पर प्रभाव शक्ति गुणों में सुधार हुआ। अंतरकारी स्कैनिंग कैलोरीमेट्री (डीएससी) ने दिखाया कि पीईजी समावेश ने पीएलए के टीजी को काफी कम कर दिया है। पीएलए की पिघलने वाली क्रिस्टलीयता पीईजी भार में वृद्धि के साथ बढ़ी है। पीएलए की थर्मल स्थिरता पर पीईजी समावेश का प्रभाव थर्मो ग्रेविमेट्रिक विश्लेषण (टीजीए) द्वारा वर्णन किया गया था। मिश्रणों के थर्मोमेकेनिकल व्यवहार का अध्ययन गतिशील यांत्रिक विश्लेषण (डीएमए) द्वारा किया गया था। पीएलए की अपरूपण श्यानता में पीईजी भार में वृद्धि के साथ उल्लेखनीय रूप से कमी आई है।

पीएलए को सख्त करने एक प्रभावी तरीका पॉली(स्टायरिन-ब्लॉक-एथिलीन-सह-ब्यूटिलीन-ब्लॉक-स्टायरिन)-ग्राफ्टेड-मैलेइकएनहाइड्राइड कोपोलिमर (एसईबीएस-जी-एमए) जैसे थर्मोप्लास्टिक इलास्टोमर के साथ मिश्रण हो सकता है। एसईबीएस-जी-एमए भंगुर बहुलकों की कठोरता में न्यूनतम कमी के साथ इम्पैक्ट ताकत और लचीलापन में सुधार करता है। विभिन्न सांद्रता (5-40 वजन%) में एसईबीएस-जी-एमए कोपोलिमर के साथ पीएलए मिश्रित पिघलाया गया था। इस प्रकार तैयार किए गए मिश्रणों को यांत्रिक (तन्यता और इम्पैक्ट), थर्मल (टीजीए, डीएससी), थर्मोमेकेनिकल, रियोलॉजिकल (केशिका और समांतर प्लेट रियोमेट्री), मॉर्फोलॉजिकल और फ्रैक्चर विश्लेषण जैसे विभिन्न परीक्षण विधियों द्वारा निरूपण किया गया था। एसईबीएस-जी-एमए निगमन में तन्यता शक्ति और मॉड्यूलस में

न्यूनतम कमी के साथ बढ़ी हुई लम्बाई और आईजोड इम्पैक्ट शक्ति बढ़ी। सैद्धांतिक मॉडल मिश्रणों के तन्य गुणों का विश्लेषण करने के लिए नियोजित किए गए थे ताकि मिश्रण संरचना का मूल्यांकन किया जा सके। सूक्ष्म संरचनात्मक गुणों को क्रायफ्रैक्चरर्ड, इम्पैक्ट फ्रैक्चरर्ड और तन्यता फ्रैक्चर सतहों के इलेक्ट्रॉन माइक्रोस्कोपी (एसईएम) से स्कैन करके जांच किए गए थे।

सेपियोलाइट नैनोक्ले पीएलए/एसईबीएस-जी-एमए 90/10 (भार/भार) मिश्रण के लिए प्रबल करने वाले एजेंट के रूप में प्रयोग किया जाता है। थर्मल व्यवहार, मोर्फोलॉजी और पीएलए/एसईबीएस-जी-एमए मिश्रण के थर्मो-मैकेनिकल गुणों पर सेपियोलाइट के प्रभाव की जांच की गई। मिश्रण मैट्रिक्स की तुलना में नैनोकंपोजिट्स ने तन्यता मॉड्यूलस और कठोरता में वृद्धि देखी। तन्यता शक्ति और प्रभाव शक्ति गुण सेपियोलाइट निगमन के साथ लगभग अप्रभावित थे। फील्ड उत्सर्जन स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी और ट्रांसमिशन इलेक्ट्रॉन माइक्रोस्कोपी छवियों ने पीएलए और एसईबीएस-जी-एमए अवस्थाओ में सेपियोलाइट प्रेरित मॉर्फोलॉजिकल परिवर्तन और सेपियोलाइट का फैलाव प्रदर्शित किया। डीएमए और चौड़े कोण एक्स-रे विवर्तन ने सेपियोलाइट की सुदृढ बनाने कि प्रकृति और फिलर और मैट्रिक्स के बीच अवस्थाओ के परस्पर क्रिया के समर्थन में साक्ष्य प्रस्तुत किए।

भविष्य में, पीएलए/एसईबीएस-जी-एमए/सेपियोलाइट टर्नरी नैनोकंपोजिट्स का उपयोग सेवाओं में अनुप्रयोगों के लिए लिया जा सकता है, जैसे की फोल्ड किए गए डिब्बे, टिकाऊ सामान, लैपटॉप और मोबाइल हाउसिंग, पैकेजिंग और ऑटोमोटिव इत्यादि। पीएलए/पीईजी मिश्रणों को अल्पकालिक मोल्डेड अनुप्रयोगों में काम में लिया जा सकता है।

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List of abbreviations & symbols

ASTM	American Society for Testing Materials
CSM	Chlorosulfonated polyethylene rubber
CTOD	Crack tip opening displacement
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
d-TGA	First derivative thermogravimetric analysis
D_w	Weight average particle diameter
EWF	Essential work of fracture
FESEM	Field emission scanning electron microscopy
HDPE	High density polyethylene
IFPZ	Inner fracture process zone
MFI	Melt flow index
MMT	Montmorillonite
OPDZ	Outer plastic deformation zone
PA	Polyamide
PC	Polycarbonate
PLA	Polylactide/ poly(lactic acid)
POM	Poly(oxy methylene)
PP	Polypropylene
PS	Polystyrene
iPP	Isotactic polypropylene
SBS	Styrene-butadiene-styrene block copolymer
SEBS	Styrene-(ethylene-butylene)-styrene block copolymer
SEBS-g-MA	Maleic anhydride grafted styrene-(ethylene-butylene)-styrene

TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
T_{cc}	Cold crystallization temperature
T_f	Final decomposition temperature
T_g	Glass transition temperature
T_m	Melting temperature
T_{max}	Temperature at maximum rate of weight loss
T_{onset}	Onset degradation temperature at 5% weight loss
WAXD	Wide-angle X-ray diffraction
X_m	Degree of melt crystallinity
X_{cc}	Degree of crystallinity because of cold crystallization
ΔH_m	Heat of melting
α	Stress concentration factor
β	Plastic shape factor
δ	Phase angle
Φ_d	Volume fraction of SEBS-g-MA
E_b	Tensile modulus of blends
Ed	Tensile modulus of the disperse phase i.e. SEBS-g-MA
Ep	Tensile modulus of PLA
E	Tensile modulus
E'	Storage modulus
E''	Loss modulus
ε_b	Elongation-at-break of the blends
ε_p	Elongation-at-break of PLA
G*	Complex modulus

G'	Elastic modulus
G''	Viscous modulus
K	Phase interaction constant
L	Flexibility coefficient
σ_b	Tensile strength of blends
σ_P	Tensile strength of PLA
τ	Matrix ligament thickness
η^*	Complex viscosity
W_e	Essential work of fracture
W_p	Non-essential work of fracture