

STUDIES ON POLY(LACTIC ACID) BASED BLENDS AND COMPOSITES

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**CENTRE FOR POLYMER SCIENCE AND ENGINEERING
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STUDIES ON POLY(LACTIC ACID) BASED BLENDS AND COMPOSITES

by

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Submitted

In fulfillment of the requirements of the degree of Doctor of Philosophy

to the



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Dedicated To

My Late Father & My

Family

CERTIFICATE

This is to certify that the thesis entitled “**Studies on poly(lactic acid) based blends and composites**” being submitted by **Mr. Rajendra Kumar Singla** to the **Indian Institute of Technology Delhi** for the award of the degree of **Doctor of Philosophy**, in the **Centre for Polymer Science and Engineering**, is a record of original and bonafide research work carried out by him. Rajendra Kumar Singla has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The research reported and results presented in this thesis are original and 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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ABSTRACT

In recent years increasing scarcity of oil resources, energy crisis, and white pollution urge researchers to replace conventional petroleum based plastics with renewable, bio-based and bio-degradable materials. Poly(lactic acid) (PLA) has drawn attention of researchers due to high strength, high stiffness, good bio-compatibility, excellent transparency and complete biodegradability. However, PLA suffers from major disadvantages notably brittleness (low strain-at-break and high modulus), low heat distortion temperature (HDT, $<60^{\circ}\text{C}$), poor impact strength, low rate of crystallization and poor processability. These shortcomings significantly restrict industrial applications of PLA particularly for durable applications such as in automotive and electronics. The blending of bio-degradable polymers with fillers or elastomers is thought to be a cheaper and less time consuming process of modifying polymer properties.

PLA/lignin green biocomposites at varying concentrations of lignin from 0-30 wt.% without use of compatibilizer were prepared which showed improved biodegradability and tensile modulus. Increased tensile modulus indicated significant phase interaction. Tensile strength decreased with increase in lignin in the PLA matrix. Because of stress concentrations, mechanical restraints and phase adhesion the matrix ductility decreases at large deformations resulting in the decrease of elongation-at-break as well. In the present study to understand the phase interaction between PLA and lignin, tensile properties are analyzed employing predictive models.

However, increased embrittlement of the biocomposite affected tensile strength, elongation, and impact strength properties moderately. Therefore, to widen applications of PLA an elastomeric copolymer ethylene-co-vinyl acetate (EVA) was blended with PLA. Blends of

PLA with various concentrations of EVA (vinyl acetate content 50 wt.%) were prepared to modify mechanical properties. Incorporation of EVA co-polymer into PLA decreased the crystallinity and substantially enhanced its flexibility. The tensile modulus and strength decreased while toughness and ductility increased significantly. The impact strength of PLA enhanced significantly making the blend super tough. Tensile properties of the blends were described and correlated with theoretical models. Morphological analysis of impact tested samples demonstrated various fracture mechanisms such as crazing/micro-cracks formation, fibrillation, and shear yielding.

Rheological studies of the blends were performed on a capillary rheometer in which shear stress increased with increase in the volume fraction of the blending polymer, Φ_d , as well as shear rate. Melt viscosity of the blends increased with increase in Φ_d and decreased with rise in temperature. Power law relationship was followed by the blends. Power law index, n , decreased with increase in Φ_d , while the trend was opposite with increase in temperature. Consistency index values increased with Φ_d . The values of the consistency, K , decreased with rise in temperature for a particular blend composition. The activation energy increased with increase in Φ_d which may be due to the enhanced phase adhesion between PLA and EVA. The frequency sweep data of parallel plate rheology indicated monotonous increase in storage modulus, loss modulus and complex viscosity with EVA concentration due to strong phase interaction.

The optimized PLA/EVA super tough blend with 30 wt. % of EVA was further modified with varying concentrations (0.4-9.1 wt.%) of halloysite nanotubes (HNT). TGA study indicated that incorporation of HNT improved the thermal stability of the nanocomposites remarkably. Enhanced tensile modulus and impact strength demonstrated the strengthening

and toughening effect of halloysite in the nanocomposites, simultaneously. The impact fractured surface morphologies and halloysite induced morphological changes of the nanocomposites were evaluated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. FTIR investigation revealed interactions between HNT and PLA. Glass transition behaviour of the nanocomposites, as shown by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC), presents strong evidence in favour of phase interaction and reinforcing effect of halloysite. Enhanced tensile strength and elongation-at-break demonstrated toughening effect of halloysite.

In the future, PLA/EVA/HNT ternary nanocomposites can be explored for applications in services e.g. as wares, folded cartons, durable goods, laptop, computer and mobile housing, packaging and automotive components. PLA/lignin composites are suitable for nondurable applications in short term products, mulch films, as well as grocery and composting bags, trays, bottle and other indoor applications.

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List of Abbreviations & Symbols

ASTM	American Society for Testing and Materials
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
D_w	Weight average particle size
EVA	Ethylene-co-vinyl acetate
FT-IR	Fourier transform infra red spectroscopy
G^*	Complex modulus
G'	Elastic modulus
G''	Viscous modulus
HNT	Halloysite nanotube
MFI	Melt flow index
PLA	Poly(lactic acid)
TGA	Thermogravimetric analysis
T_m	Melting temperature
T_{cc}	Cold crystallization temperature
T_{onset}	Onset of degradation temperature
T_g	Glass transition temperature
WAXD	Wide Angle X-ray Diffraction
X_c	Degree of crystallinity
ΔE	Activation energy
E_c	Tensile modulus of composite
E_p	Tensile modulus of PLA

ΔH_m	Heat of melting
Φ_f	Filler volume fraction
Φ_d	Volume fraction of EVA
σ_c	Tensile strength of composites
σ_P	Tensile strength of PLA
τ	Matrix ligament thickness
τ_w	Shear stress
η^*	Complex viscosity
α	Stress concentration factor
δ	Phase angle