STUDIES ON POLY(LACTIC ACID) BASED BLENDS AND TALC REINFORCED COMPOSITES

SHIKHA JAIN

CENTRE FOR POLYMER SCIENCE AND ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

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STUDIES ON POLY(LACTIC ACID) BASED BLENDS AND TALC REINFORCED COMPOSITES

by

SHIKHA JAIN

Centre for Polymer Science and Engineering

Submitted

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DEDICATED

TO MY

PARENTS

CERTIFICATE

This is to certify that the thesis entitled, ***"Studies on Poly(lactic Acid) based Blends and Talc Reinforced Composites"*** *submitted by* ***Ms. Shikha Jain*** *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 out by her under our supervision and guidance. 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. To the best of our knowledge, the results embodied in the thesis have not been submitted to any other University or Institute for the award of any other Degree or Diploma.

(Amar K. Mohanty)
Professor
Department of Plant Agriculture & School of Engineering
University of Guelph,
Ontario, Canada, N1G 2W1

(Anup K. Ghosh)
Professor
Centre for Polymer Science and Engineering
Indian Institute of Technology Delhi
Hauz Khas, New Delhi-110016, India

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Date ***Shikha Jain***

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Abstract

Increasing environmental concern and limited resources of petroleum has necessitated the use of biodegradable plastics for various applications. Polymers poly(lactic acid) (PLA) is renewable resource based polyester with superior mechanical properties (tensile strength, modulus), optical properties (gloss, transparency) and biodegradability. PLA is associated with some challenges such as low elongation, low impact strength, slow crystallization rate and low melt strength. Elongation of PLA can be increased by blending of PLA with another flexible biodegradable polymer. Polycaprolactone (PCL) is a synthetic biodegradable polymer having high elongation and toughness and flexibility. Blending of PCL into PLA is a promising approach to increase elongation and toughness of PLA. Extent and rate of crystallization can enhance by adding nucleating agent in to PLA. Talc works as nucleating agent as well as reinforcing filler and increase thermal and mechanical properties and crystallinity of polymer matrix.

The objective of the present study was to study the effect of PCL and talc on structure, processability and properties of PLA and to investigate thermal, morphological, mechanical, rheological and barrier properties in detail. In the present work, PLA/talc composites, PLA/PCL blends and PLA/PCL/talc composites were developed by melt-mixing in twin screw extruder followed by blown film processing and injection molding. Developed PLA based blends and composites were analyzed by using various characterization techniques including thermal, rheological, morphological, barrier, tensile, biodegradability etc.

Isothermal and nonisothermal crystallization kinetics of PLA was studied in presence of talc at different crystallization temperatures and different cooling rates and analyzed by using Avrami equation. Talc worked as nucleating agent and increased degree of crystallinity 30% in neat PLA to 35% in PLA/talc composites. Talc has accelerated the crystallization of PLA and significantly

reduced crystallization half time ($t_{1/2}$) where it was 9.5 min in neat PLA and 1.1 min in PLA/talc-5 composites at 120 ºC. Activation energy barrier (ΔE_a) of crystallization was also reduced significantly in presence of talc and ΔE_a for neat PLA was -0.8 KJ/mol and -23.2 KJ/mol for PLA/talc-5 composite. Spherulite morphology of PLA/talc composites showed that talc filled system has increased nucleation density and reduced spherulite radius compared to that of neat PLA. Morphology of PLA/talc composites showed random dispersion of talc particles in PLA matrix. Tensile properties evaluation results that talc reinforced composites has increased modulus compared to neat PLA. Water vapor permeability and biodegradability of PLA did not change significantly in presence of talc. PLA/PCL blend showed typical domain-bulk phase morphology where minor phase PCL was dispersed as discrete domains in continuous phase of PLA matrix. PCL blends have increased elongation and toughness with a decrease in tensile modulus and strength. Strain at break in neat PLA was 13% and increased upto 322% in PLA/PCL blend whereas PCL content was 60 wt% in the blend. PLA/PCL blend has increased degree of crystallinity, increased water vapor barrier properties and increased biodegradability compared to neat PLA films.

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Abbreviations

M_n = number average molecular weight

M_w = weight average molecular weight

wt% = weight percentage

W_f = weight fraction

D_n = number average diameter of domains (μm)

G = spherulite growth rate (μm/min)

$R_{s\text{-}avg}$ = average spherulite radius (μm)

N = nucleation density (μm^{-3})

T_g = glass transition temperature (˚C)

T_{m1} = temperature at first melting peak (˚C)

T_{m2} = temperature at second melting peak (˚C)

T_m = melting temperature (˚C)

T_p = crystallization peak temperature from cooling exotherm (˚C)

$T_{cc\text{-}onset}$ = onset temperature of cold crystallization (˚C)

T_{ccp} = cold crystallization peak temperature (˚C)

T_c = Temperature for isothermal crystallization conditions (˚C)

ΔH_m = melting enthalpy (J/g)

$\Delta H_{m\text{-}100}$ = melting enthalpy for 100% crystalline polymer (J/g)

ΔH_c = enthalpy of crystallization (J/g)

ΔH_{cc} = enthalpy of cold crystallization (J/g)

X_m = degree of crystallinity for melting endotherm (%)

X_c = degree of crystallinity from cooling exotherm (%)

X_{cc} = degree of crystallinity from cold crystallization peak (%)

ΔW_{cc} = width of cold crystallization peak at half height (˚C)

ΔW_m = width of melting peak at half height (˚C)

α = relative crystallinity (%)

K_a = crystallization rate constant from Avarmi equation (min^{-1})

n = Avrami exponent

$t_{1/2}$ = crystallization half time (min)

Δt = time where crystallization reaches maximum (min)

ΔE_a = activation energy barrier (KJ/mol)

t_p = crystallization time at peak (min)

t_{max} = maximum time for crystallization (min)

φ = heating rate (˚C/min)

R^g = gas constant (J/mol/K)

T_{onset} = temperature at 5 % weight loss (˚C)

T_{max} = temperature at 50 % weight loss (˚C)

T_{end} = temperature at 90 % weight loss (˚C)

DTG-$T_{p\text{-}PLA}$ = degradation peak of PLA in DTG curve (˚C)

DTG-$T_{p\text{-}PCL}$ = degradation peak of PCL in DTG curve (˚C)

G’ = Storage modulus (MPa)

G” = loss modulus (MPa)

tanδ = damping behavior (G”/G’)

η^* = complex viscosity (η’-iη”) (Pa.s)

n = power law index