STUDIES ON FOAM PROCESSING AND DEGRADATION BEHAVIOUR OF PLA BASED BLENDS AND COMPOSITES

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STUDIES ON FOAM PROCESSING AND DEGRADATION BEHAVIOUR OF PLA BASED BLENDS AND COMPOSITES

by

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Dedicated to my parents

Certificate

This is to certify that the thesis entitled **"Studies on Foam Processing and Degradation Behaviour of PLA based Blends and Composites"** being submitted by **Mr. Sanjeev Kumar** is the report 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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Date:

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Abstract

Foaming in biodegradable polymers is of special concern because of their applications of biomedical importance. The present work focuses on the exploring the foam processing of poly(lactide) to prepare microcellular foams of with a view to be used as biomedical scaffolds. The studies were carried out in terms of the material modifications as well as effect of variation of the processing parameters in order to understand the basic factors which lead to the development of the microstructure in the polymeric bulk.

As an attempt to understand the detailed effect of variation of the d-content in poly(lactide) two grades of PLA, one with the highest crystallinity PLLA (PLA 3001D) and the other with low crystallinity PDLA (PLA 3051D were blended in 0%, 10%, 30%, 50% and 100% ratio to give B00, B10, B30, B50 and B100. As a result d-content differed in different blends which caused remarkable changes in the % crystallinity as well as crystalline structure while mechanical and rheological properties were not affected much. These changes in crystallinity and crystalline structure was found to produce the propound effect of microstructure when the blend samples were subjected to the foam processing by batch process using CO_2 as PBA (Physical Blowing Agent) under different processing conditions.

In order to explore the role of the filler in the foam processing, the composites were prepared by adding HA (Hydroxyapatite) in the PDLA with 0%, 1%, 3% and 5% content, designated as C00, C01, C03 and C05 respectively. While the crystallinity of the various composites did not change significantly their melt properties varied significantly as considerable reduction in melting temperature T_m and the shear viscosity was observed. This in turn produced the remarkable changes in their foam microstructure when foamed by batch foaming process.

The effects of the material modifications as well as the variation of the microstructure on their *in vitro* degradation profile were studied so as to ascertain the synchronization of the growth rate of the target tissue to be healed inside the body with the rate of degradation of scaffold. The foamed samples of blends and composites were subjected to the *in vitro* degradation at 37 °C in PBS (Phosphate Buffer Saline). The degradation profile showed different trends initially up to 14 weeks but after that time the degradation rates approached each other and in the later phase after 48 weeks found to follow the same pattern. The porosity and pore size were also found to influence the degradation profile as well as the pattern of degradation products in de-ionized water at 60 °C temperature.

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List of symbols

T_g	glass transition temperature
T_m	melting temperature
T_c	crystallization temperature
ΔG_{hom}	Gibbs free energy for homogeneous nucleation
ΔG_{het}	Gibbs free energy for heterogeneous nucleation
ΔP	saturation gas pressure
γ_{bp}	interfacial energy at polymer – bubble interface
θ	contact angle at the interface of the polymer and an inorganic filler
N_{hom}	homogeneous nucleation rate
N_{het}	heterogeneous nucleation rate
C_0	concentration of the gas molecules
f_0, f_l	frequency factor of gas molecule joining the nucleus
k	Boltzman's constant
T	temperature in K
c_1	concentration of heterogeneous nucleation sites
k_D	Henry's law constant
P	applied saturation pressure
D	diffusion co-efficient
D_o	diffusion co-efficient constant
ΔE_D	activation energy for diffusion of gas in polymer
R	gas constant
α	observed optical rotation of angle in degree unit
l	path length in dm
c	concentration in g/ml unit
α_D	specific rotation
ΔH_m	melting enthalpy
ΔH°_m	crystalline melting enthalpy of 100 % crystalline PLA
K	Scherrer's constant
B	angular width at half maxima
λ	wavelength
θ	Bragg diffraction angle
N_o	cell density

List of Abbreviations

PLA	poly(lactic acid) or poly(lactide)
PCL	poly(caprolactone)
PGA	poly(glycolic acid)
PHA	poly(hydroxyl alkanoate)
PDXO	poly(1,5-dioxepan-2-one)
PLLA	poly(l-lactic acid)
PDLA	poly(d,l-lactic acid)
TCP	tricalcium phosphate
HA	Hydroxyapatite
PHB	poly(hydroxybutyrate)
CBA	chemical blowing agent
PBA	physical blowing agent
SCF	supercritical fluid
$SrCO_2$	supercritical carbon di-oxide
STP	standard temperature and pressure
BG	bioactive glass
W	wollastonite
TSE	Twin screw extruder
DSC	differential scanning calorimetry
TGA	thermogravimetric analysis
PLOM	polarized light microscopy
DMA	dynamical mechanical analysis
WAXD	wide angle X-ray diffraction analysis
SEM	scanning electron microscopy
TEM	transmission electron microscopy
PBS	phosphate buffer saline
SEC	size exclusion chromatography
GPC	gel permeation chromatography
ESI-MS	elecrto-spray ionization mass-spectroscopy
GC-MS	gas chromatography-mass-spectroscopy