STUDIES ON CO$_2$-INDUCED CRYSTALLIZATION AND FOAMING BEHAVIOUR OF POLY(LACTIC ACID)/CLAY NANOCOMPOSITES

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by

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DEDICATED TO DIVINE NATURE

Certificate

This is to certify that the thesis entitled **"studies on CO_2-induced crystallization and foaming behaviour of poly(lactic acid)/clay nanocomposites"** being submitted by **Mr. Sabapathy S** to the Indian Institute of Technology Delhi, for the fulfilment of award of the degree **"Doctor of Philosophy"** is a record 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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ABSTRACT

The commercial grades poly(lactic acid) (PLA) are usually based on an L-rich mixture and typically comprise of 95-97 % L-units and 1-2% D-units. PLA exhibits very slow crystallizing behaviour. During foam processing of PLA with CO_2, PLA/CO_2 system exhibits rapid crystallization behaviour which imparts high stable crystalline foam morphology to the final product. This CO_2 induced crystallization process occur at supersaturated/foaming condition is spontaneous in nature. This indicates that like bubble nucleation, crystal nucleation in a CO_2 supersaturated samples is a spontaneous process and it can be enhanced by increasing the degree of supersaturation. The objective of the current thesis is to investigate the crystallization and foaming behaviours of PLA and PLA/clay nanocomposites (PLANCs) at their CO_2 induced supersaturation state for the development of structurally controlled crystalline foam morphologies. The raw material used were PDLA (PLA8032D), nanoclay (Cloisite 30B) and high pressure CO_2 as green plasticizer. PLA and Cloisite 30B were melt compounded in a Prism EUROLAB-16 co-rotating twin screw extruder. PLA based nanocomposites containing 0.5 wt.% (PLANC-0.5), 1 wt.% (PLANC-1), and 2 wt.% (PLANC-2) of nanoclay were prepared. The various characterizations of PLA/clay nanocomposites (PLANCs) were carried out to study the effects of nanoclay content (wt.%) on the thermal, morphological, rheological, mechanical properties and thermo-mechanical properties of the PLANCs. The crystallization behaviour of PLA and PLANCs were studied at saturation and supersaturation condition with CO_2. The distinct differences in the crystal growth behaviour between the two states were investigated. The crystallization behaviour of CO_2 treated PLA and PLANCs at various CO_2 saturation conditions (20, 30 & 50 bar) were performed by using high pressure differential scanning calorimetry (HP-DSC). The crystallization behaviour of CO_2 treated PLA and PLANCs under supersaturated conditions were studied by using high pressure autoclave. The compression moulded amorphous PLANCs samples were saturated with CO_2 at an optimum conditions using high pressure autoclave. In order to achieve various degree of supersaturation, the CO_2 saturated samples were heated to different temperatures (60 °C, 70 °C, 75 °C, 80 °C). The resultant spherulitic structures were investigated by using optical microscopy, scanning electron microscopy, and wide angle X-ray diffraction. In contrast to CO_2 saturated conditions (50 bar), there was an exponential increases in nucleation density of spherulites (from 220 to 4.5×10^3 number/mm^2) at superheated condition (80 °C) was observed. Interestingly, from the morphological analysis, it was established that the superheating process not only enhances nucleation exponentially but also induces transition from 3-D to 2-D crystal growth mechanism in PLA. To establish the correlation between the crystallization and foaming process, concurrent crystallization and foaming behaviour of PLANCs were studied at different superheated conditions (120 °C, 130 °C, 140 °C, and 150 °C). The obtained 2-D crystalline foam morphologies of PLANCs were studied by various characterization techniques such as, SEM, SAXS and WAXD techniques. It was found that the CO_2 induced 2-D crystal growth mechanism of PLANCs with exclusion of CO_2 simply direct the growth of 2-D spherulites into the self-templated regions and in-situly foam the inter-spherulitic amorphous region concurrently, so-called 'instantaneous 2-D crystallization and in-situ foaming processes'. The obtained self-stack 2-D spherulites with in-situ foamed interlayers replicate the 2-D crystalline porous microstructure of nacre biomaterials and thus the rapid biomimetic concept of crystallization of PLANCs occurs at superheated conditions. The subsequent transformation of the amorphous PLA into a self-stacked 2-D spherulitic microstructure and the reinforcing effect of semi-crystalline 2-D spherulites in the novel assembly with in-situ foamed amorphous interface were established by various mechanical studies. This thesis reveals the rapid biomimetic concept of CO_2 induced crystallization and foaming of PLA & PLANCs occurring at superheated conditions and its application in developing bioinspired polymeric materials for structural applications.

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List of Symbols

T_g	Glass transition temperature
T_c	Cold crystallization temperature
ΔH_c	Enthalpy of cold crystallization
T_m	Melting temperature
ΔH_c	Enthalpy of melting
T_m	Melt crystallization temperature
ΔH_m	Enthalpy of melt crystallization
ΔH_{mo}	Melting enthalpy of 100% crystalline PLA
X_c	Crystallinity from DSC
wt.%	Weight fraction
G'	Storage modulus
η^*	Complex viscosity
Tan δ	Loss factor
K	Crystallization kinetic constant
$t_{1/2}$	Crystallization half-time (min)
G	Crystallization rate (1/min)
n	Avrami exponent
r^*_{2D}	Critical radius of disc shaped nucleus
r^*_{3D}	Critical radius of spherical nucleus
ΔG	Gibb free energy

List of Abbreviations

PLA	Polylactide
CO_2	Carbon dioxide
PLANCs	PLA/clay nanocomposites
PLANCCs	Crystallized PLANCs
PLANCCFs	Crystalline foamed PLANCs
SEM	Scanning electron microscopy
WAXD	Wide-angle X-ray Diffraction
SAXS	Small angle X-ray scattering
TEM	Transmission electron microscopy
POM	Polarized optical microscopy
DSC	Differential Scanning Calorimeter
HP-DSC	High pressure DSC
X_t	Relative crystallinity