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MATHEMATICAL MODELING AND KINETICS OF CRYSTALLIZATION OF POLY LACTIC ACID (PLA) NANOCOMPOSITES

Soumya Ranjan Kar*1

*1Associate Professor, Mechanical, Swami Vivekananda School Of Engineering And Technology, Bhubaneswar, Odisha, India.

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ABSTRACT

Poly Lactic Acid (PLA) is a promising substitute for conventional petroleum based polymer materials because of its benign quality. There are also some problems in properties of PLA such as brittleness, low heat deflection temperature, low melt viscosity and high cost which prevent it from using in wide range of application. PLA is now considered most because of its biomedical and pharmacological use. Hundreds of research papers and patents have appeared in the literature. But some data are lacking as the rate constants for initiation, propagation and termination of polymerization. It is extremely difficult to experimentally find the accurate values of different rate constants. So there is a need for mathematical modeling which when used with the readily available experimental data can predict the polymerization rate with greater accuracy.

The article embodies a brief introduction about the need for PLA and why mathematical modeling of PLA is used in the ring opening polymerization of PLA. The efficiency of the model has been done by comparing the predicted results on molecular weight and molecular weight distribution with those available in the literature.

Keywords: PLA, Investigation, Mathematical Modeling, Ring Opening Polymerization, Organoclays, Melt Intercalation.

I. INTRODUCTION

Poly Lactic Acid (PLA) is produced mainly from sugar obtained from maize, sugarcane, sweet potato by polymerizing lactic acid whose structure contains there carbon atoms. These carbon are derived from the carbon dioxide in the atmosphere so that the absolute amount of carbon in the atmosphere does not affect weather. It is biodegraded or incinerated. Hence PLA is said to be a carbon neutral material.

The main objective of this study is to prepare PLA nanocomposite using three organoclays by using melt intercalation technique and to investigate the influence of the type of clay on structural, thermal, physical and mechanical properties of the nanocomposite. Here PLA and three different organoclays (CLOSITE 25A, CLOSIE 93A and CLOSITE 15A are used to produce nanocomposite by melt intercalation. The incorporation of organoclays into the polymer matrix shows considerable improvement in structural and physical properties. Need For Mathematical Modeling of the Ring Opening Polymerization Of PLA. Hundreds of research papers and patents have been published since the synthesis of PLA . But there is a lack of data concerning the rate constants for initiation, propagation and termination steps of PLA polymerization. Also it is extremely difficult to experimentally find the absolute values of different rate constants. Thus there is a need for mathematical modeling can predict the polymerization rate constants with sufficient accuracy in a short time.

The article consists of the following parts.

1) Mathematical modeling of PLA
2) Incorporation of organoclays (CLOSITE 25A, CLOSITE 93A and CLOSIE 15A) into the PLA polymer matrix by melt intercalation technique.
3) Investigate the influence of types of nanoclay on the intercalation and properties of PLA nanocomposite.

II. METHODOLOGY

2.1 MATHEMATICAL MODELING OF PLA

The progress of lactide polymerization has been modeled by assuming a ring opening reaction technique. Appropriate differential involving the rate controlling reaction has been developed. The resulting differential equation has been solved using a numerical technique. The efficiency of the model is tested by comparing the predicted results on molecular weight of those available in the published literature.

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The kinetic rate constants are obtained for various PLA polymerization catalysts. A mechanistic model is developed to stimulate the ring opening polymerization of PLA for a batch reactor. To verify the correctness of the solutions in the limiting case of Poisson distribution a number of checks are made. Here we are considering the molecular weight change as a function of polymerization time in a homogeneous ring opening polymerization of PLA. The results of the simulations performed on the model developed is compared with experimental data of various catalysts. The sensitivity of the technique is discussed with rate constants for initiation, propagation and termination.

2.2. PREPARATION AND CHARACTERIZATION OF PLA NANOCOMPOSITE BY MELT INTERCALATION BASED ON CLAY TYPE

PLA and different organoclays as Closite 25A, Closite 93A and Closite 15A are used to produce Nano composite by melt-intercalation. The structural, thermal, physical and mechanical properties are characterized by using X-ray diffraction (XRD) and differential Scanning Calorimetry (DSC) on an Instron Universal Testing Machine.The first XRD peaks for all three nanocomposites are observed to shift to lower angles, indicating that intercalation has occurred. The extent of intercalation depended on the type of organoclay and was exhibited in the sequence of Closite 25A > 93A > 15A. Glass transition temperatures and the melting temperatures are investigated by DSC. The Radial Exapansion Ratio (RER), unit density, BSI Bulk Spring Index (BSI), bulk compressibility, youngs modulus, tensile strength, impact strength, DMA,HDT and flexural strength are influenced significantly with the addition of different organoclays. Melt intercalation is a better approach because of its versatility, compatibility with the polymer processing equipment and because of its environmental friendly process that requires no solvent . in melt intercalation technique, the clay and polymer are added together above the melting temperature of the polymer, held for some period of time and then put under shear to fasten the intercalation and exfoliation of the clay.

Poly Glycolic Acid (PGA) was synthesized in early 1970's. Then it followed by synthesis of high-molecular weight PLA and copolymers of PLA and PGA. PLA has been working as an alternative to PET,HIPS, PVC and cellulose in high clarity packaging activities. PLA is being used in candy wrap, optically enhanced films and shrink labels. Considerable attention has been paid on its mechanical properties with the increasing applications of PLA. A comparision has been done about the biaxial oriented films and barrier performances of PLA and some other polymers which is shown in Table 1.

2.3. PROCEDURE

Semi crystalline PLA resin of molecular weight number 85,000 was produced by Harita NTI LTD, Chennai, India. It contained approximately 93% L - Lactide, 2% D – Lactide and 5% mesolactide. It is in the form of sphere , size ranging from 2- 4 mm. The thermal properties is measured by DSC is shown by glass transition temperature of 70 ^{0}c and a melting temperature of 174 ^{0}c. The true density of PLA resin is 1.22 g/cm^3. 10 % PLA is blended with 0.5 % sodium bicarbonate, 0.5 % citric acid and 3 % clay in a Hobert Mixer (Model C-100, Hobart Corporation, Troy, OH) and is stored in plastic jars prior to extrusion. 10% PLA is taken for experimentation. It is observed that the foams possessed highest spring index and intermediate compressibility and youngs modulus values. Sodium bicarbonate and citric acid were added to degrade the biodegradable polymer into chains between 1000 and 100000 Daltons or approx. 500 to 50000 monosaccharide groups to promote expansion. Three commercial clays namely Closite 15A, Closite 25A and Closite 93A were purchased from Southeren Clay Products Inc (Gonzalez, TX) and used as nanofillers. Hereafter these clays are referred as 15A, 25A and 93A respectively. They are organically Modified Montmorillonite (MMT) also known as organoclays. The ammonium cations of organoclays were dimethyl benzyl hydrogenated tallow quartenery ammonium for Closite 15A, dimethyl hydrogenated tallow 2- ethylhexyl quarternary ammonium for Closite 25A and methyl dehydrogenated tallow quartenery ammonium for Closite 93A. The characteristics of the clays used in this work are summerised in Table 3 and Table 4.

III. RESULTS AND DISCUSSIONS

3.1. MELT INTERCALATION TECHNIQUE

During melt intercalation , the insertion of polymer to the organoclays forces the patelets apart and increases the d- spacing resulting in the shift of the diffraction peak to lower angles. In all three nanocomposite, the first

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diffraction peaks are observed to shift to lower angles and are compared to those of the original organoclays. The intercalation of PLA polymer into the organoclay layers increase the door spacing which causes the clay to swell by 43 %. The degree of enlargement of the door spacing decreases incase of the nanocomposite. The degree of enlargement of the door spacing with organoclay 25A is found to be 9.79 A^0 , 8.64 A^0 and 3.46 A^0. The degree of swell of PLA with 25A,PLA with 93A and PLA with 15A nanocomposite are found to be 33.5 %, 27 % and 10.9 % respectively. The interactions between polymer and organoclays depend on the compatibility of the surface polarities of the polymer and clay.

3.2. MECHANICAL PROPERTIES OF NANOCOMPOSITE

Highest Bulk Spring Index (BSI) was obtained for PLA with 93A nanocomposite. It is found to be 0.960. The lowest BSI was obtained for PLA with 93A nanocomposite. It is found to be 0.944. Higher deformations means higher is the youngs modulus. It is observed for PLA with 25A composite and PLA with 15A nanocomposite that the youngs modulus is higher than PLA with 93A nanocomposite. Tensile test data indicate that PLA with Closite 15A nanocomposite of 5% shows better tensile results than PLA with Closite 15A nanocomposite of 3 %. Tensile strengths test and the elongation at break of PLA nanocomposites are shown in Table 3.

PROPERTIES OF BIAXIAL ORIENTED FILMS

Table 1

MATERIAL	PLA	PP	PET	NYLON	CELLOPHANE
Density g/cc	1.25	0.9	1.4	1.2	1.45
Haze %	2.1	1 -4	2 – 5	2 -3	1 – 2
Tensile Strength psi	15,950	27,550	29,725	36,250	13,050
Tensile Modulus psi	478,500	348,000	551,000	264,625	594,500
Ultimate Elongation %	160	110 a	140[a]	125[a]	23 u
Tear g/mil	15	4 – 6	18	13	4

MD – Machine Direction

a – Median of a range of values

BARRIER PERFORMANCES OF CLEAR RESINS

Table 2

Polymer	MVTR	Oxygen Permeation	CO_2 Permeation
PLA	21	40	183
HIPS	10	300 – 400	NA
Nylon 6	23	3	NA
PET	1	3 – 6	15 – 25
PP	0.7	150	NA
PVC	2	5 – 20	20 – 50

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Table 3

Material	Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation at break (%)
V – PLA	38	3522.97	2.91
PLA + 3% C15 A	25.08	3707.38	1.14
PLA + 5% C15 A	18.70	3517.23	2.17
PLA + 3% C25 A	34.42	4121	3.7
PLA + 5% C25 A	28.86	4192.54	2.87
PLA + 3% C93 A	45.47	3983.45	3.01
PLA + 5% C93 A	35.15	4063.96	2.55

Material	Impact Strength (J/M)
V – PLA	24.20
PLA + 3% C15A	18.83
PLA + 5% C15A	15.53
PLA + 3% C25A	20.03
PLA + 5% C25A	17.73
PLA + 3% C93A	21.93
PLA + 5% C93A	20.93

IV. CONCLUSION

The discussion on the need of mathematical modeling of the ring opening polymerization of PLA is done. The process of lactide polymerization has been modeled by assuming a ring opening reaction mechanism comprising of chain initiation, chain propagation and chain termination. Appropriate differential equations have been developed incorporating the rate controlling reaction. A mechanistic model to stimulate the ring-opening polymerization of PLA for a batch reactor is developed. A number of checks are made to verify the correctness of the solutions in the limiting case of poisson distribution. Investigation on the influence of nanoclays on the intercalation and properties of PLA nanocomposite is done. The nanoclay addition showed great improvement in structural, thermal and mechanical properties. The tensile strength, impact strength, HDT and flexural strength are influenced significantly with the addition of different organoclays into the PLA matrix. The comparision about the properties of biaxial oriented films and barrier performances of clear resins of Poly Lactic Acid (PLA) with other polymers as PP, PET, Nylon and cellophane are done successively and is being observed that PLA proved to be a alternative to PET,HIPS , PVC and Cellulose because of its good mechanical properties and optically enhanced films. The radial expansion ratio unit, bulk spring index, density and bulk compressibility data were analysed using general linear models (GLM) in SAS analysis program (SAS Institute Inc, Cary, NC). From the melt intercalation of the polymer with organoclays it is concluded that the greater the door spacings , the greater the intercalation of the polymer molecular chain with clay layered silicate. BSI was significantly influenced by the addition of different organoclays into the polymer matrix. The lowest value of BSI in PLA with 93A nanocomposite has softest foam. The low value is because of organoclay 93A being compatible with PLA molecules. The strong interactions increased the strength of the cell walls making the nanocomposite more rigid and resulting in low bulk compressibility.

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