UNIVERSITI PUTRA MALAYSIA

FABRICATION OF PLA/COW DUNG-BASED BIOCOMPOSITE

MOSTAFA YUSEFI

FABRICATION OF PLA/COW DUNG-BASED BIOCOMPOSITE

By

MOSTAFA YUSEFI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

December 2015

Dedicated to My Beloved Parents
And
Nature

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the Degree of Master of Science

FABRICATION OF PLA/COW DUNG-BASED BIOCOMPOSITE

By

MOSTAFA YUSEFI

December 2015

Chairman : Faizah Md. Yasin. PhD
Faculty : Engineering

Various environmental drawbacks such as reduction in land fill space and non-biodegradability lead to systematically investigate the replacing of synthetic composites by using biocomposites. Biocomposites possess suitable characterizations such as light weight, combustible, nontoxic, and biodegradability behavior. However, the final product of the biocomposites carries certain drawbacks in terms of mechanical, physical and thermal properties. In order to determine their characteristic, this research aided to figure out the possibility of applying cow dung (CD) as filler to prepare polylactic acid (PLA) biocomposite. The main objective of this research is to obtain a suitable composition ratio based on the filler and the hosting polymer.

The CD of two different sizes, namely 4.00 mm and 0.5 mm were blended with PLA. PLA/CD biocomposites with different CD ratios (0-60 wt.%) were fabricated using an internal Brabender mixer (W50EHT-3zones) followed by a 40 tones hydraulic compression moulding. The results showed that the addition of CD led to improve flexural properties compared to tensile and impact strength. Biocomposites with 4.00 mm CD (bigger filler) mainly showed higher mechanical properties than those of 0.5 mm CD (smaller filler). Scanning electron microscopy (SEM) of tensile and impact fractured surfaces indicated that the bigger fillers had stronger adhesion and bonding with the matrix. Moreover, the cavities and rough surface of biocomposites increased with the filler content addition. This led to lower mechanical and physical properties of the biocomposites and increased water uptake during water absorption test accordingly. Dynamic mechanical analysis (DMA) technique was also followed to determine both storage and loss modulus of the samples. Neat PLA indicted the lowest storage modulus, while the filler content addition generally improved the storage modulus. Results of thermogravimetric analysis (TGA) indicated that the addition of the filler content prolonged the major degradation temperature. This was due to the higher resistance of the CD filler to the degradation temperature, which induced higher thermal stability of CD compared to the neat PLA.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains.

FABRIKASI BIOKOMPOSIT BERASASKAN PLA/TAHI LEMBU

Oleh

MOSTAFA YUSEFI

Disember 2015

Pengerusi : Faizah Md. Yasin, PhD
Fakulti : Kejuruteraan

Pelbagai kelemahan alam sekitar seperti pengurangan dalam ruang mengisi tanah dan kemerosotan selain daripada segi bio telah menggantikan komposit sintetik dengan menggunakan biokomposit. Biokomposit mempunyai pencirian yang sesuai seperti ringan, mudah terbakar, tanpa toksik, dan kemerosoton dari segi bio. Walau bagaimanapun, produk akhir daripada biokomposit membawa kelemahan tertentu dari segi sifat-sifat mekanikal, fizikal dan terma. Dalam usaha untuk menentukan ciri-cirinya, penyelidikan ini telah dijalankan untuk mengkaji kemungkinan penggunaan tahi lembu (CD) sebagai pengisi untuk menyediakan asid polylactic (PLA) biokomposit. Objektif utama kajian ini adalah untuk mendapatkan nisbah komposisi sesuai berdasarkan pengisi dan polimer hosting.

Terdapat dua saiz CD yang berbeza, iaitu 4.00 mm dan 0.5 mm yang telah dicampur dengan PLA. Biokomposit PLA / CD dengan nisbah CD yang berbeza (0-60 wt.%) telah direka dengan menggunakan pembancuh Brabender dalaman (W50EHT-3zones) diikuti dengan 40 nada pengacuan mampatan hidraulik. Hasil kajian menunjukkan bahawa penambahan CD membawa kepada peningkatan dari segi kelenturan berbanding dengan ketegangan dan kekuatan. Biokomposit bersaiz 4 mm CD (pengisi lebih besar) menunjukkan sifat-sifat mekanik lebih tinggi daripada 0.5 mm CD (pengisi lebih kecil). Mikroskop imbasan elektron (SEM) tegangan dan kesan permukaan patah menunjukkan bahawa pengisi lebih besar mempunyai lekatan yang kuat dan ikatan dengan matriks. Selain itu, rongga dan permukaan kasar biokomposit juga meningkat dengan kandungan pengisi. Ini telah menyebabkan penurunan sifat-sifat mekanikal, fizikal biokomposit dan juga peningkatan pengambilan air semasa ujian penyerapan air. Analisis mekanikal teknik dinamik (DMA) juga digunakan untuk menentukan simpanan dan kehilangan modulus sampel. PLA yang tulen menunjukkan simpanan modulus yang paling rendah, manakala peningkatan kandungan pengisi secara amnya menambah baik modulus simpanan. Keputusan analisis Termogravimetri (TGA) menunjukkan bahawa penambahan kandungan pengisi telah memanjangkan suhu kemerosotan. Ini disebabkan oleh rintangan pengisi CD yang lebih tinggi kepada suhu degradasi, dan menunjukkan kestabilan haba CD yang lebih tinggi berbanding dengan ketulenan PLA.

ACKNOWLEDGEMENTS

An investigation is an arduous job, which requires obligation to achieve the specified objectives. This work has successfully accomplished by patronage of many identities. I am really grateful to all persons who kindly help to finish this research. First and foremost, I would like to express a great appreciation to my advisor Dr. Faizah Md. Yasin for her advices, honest encouragements and supports. I have been absolutely lucky that the wheel of fortune made a perfect opportunity for me to know Prof. Dr. Luqman Chuah Abdullah, Dr. Mohammad Khalid Siddiqui and Dr. Chantara Thevy Ratnam, my supervisory committee. I am very thankful to them that they always respond my questions throughout the research and without their wholehearted support this research was not feasible. I also appreciate the Head of the Department Dr. Mohamad Amran Mohd Salleh for his cooperation and excellent knowledge.

I am very thankful to Mohammad Reza Ketabchi who has cooperated and helped for accomplishing different processes and tests of this research at University of Nottingham Malaysia Campus (UNiM). I must say my sincere gratitude to Mrs. Eli Rashidah Ashari and Mr. Mohd Lufti Mohd Tawi, Mrs Ana Salleza and Mohd Hafizie Manap (INTROP Staff) for their assistance. Also, I would like to say lovely thanks to Kim Tan Hoi Hoi for her supports and helps.

Lastly, I really like to express my honest impression and appreciation to my parents who always have heartily behind me to do my best.

This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of requirement for the degree of Masters of Science. The members of supervisory Committee are as follows:

Faizah Md. Yasin, PhD
Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Luqman Chuah Abdullah, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Mohammad Khalid Siddiqui, PhD
Lecturer
Faculty of Engineering
University of Nottingham Malaysia Campus
(Member)

Chantara Thevy Ratnam, PhD
Senior Research Officer
Malaysian Nuclear Agency
(Member)

BUJANG BIN KIM HUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF NOTATIONS AND ABBRIVATIONS

E*	Storage Modulus
E’	Loss Modulus (E")
l	fiber length
l_c	Critical length
tan δ	Mechanical Damping
σ^*_f	Fiber tensile strength
σ_{fu}	Fiber ultimate strength in tension
τ_y	Interfacial shear stress
ASTM	American Society for Testing and Materials
CD	Cow Dung
DMA	Dynamic Mechanical Analysis
INTROP	Institut Perhutanan Tropika & Produk Hutan
PLA	Polylactic Acid
PLLA	Poly-l-lactic acid
PP	Polypropylene
RGP	Refiner Ground Pulp
RH	Relative Humidity
SEM	Scanning Electron Microscope
TG	Thermogravimetric
TGA	Thermogravimetic Analysis
DTG	Derivative Thermal Gravimetric
FEG	field emission guns
Xc	crystallinity
Tc	temperature of crystallization
ΔHf	heat of fusion
CL	cotton linear
WF	wood fiber
CFs	chicken feathers
C	cellulose
SGC	silane-grafted cellulose

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Overusing of synthetic plastic causes several environmental drawbacks such as reduction in landfill space, natural resources depletion and non-biodegradability. This leads to replacing of the synthetic plastic or composites by using biocomposites. Biocomposites possess suitable characterizations such as lightness in weight, combustible, nontoxic, low cost and low density. However, their final production lacks assemblage of mechanical, thermal and physical properties. In addition, biocomposites have some disadvantages such as low thermal stability during processing, high moisture absorption, ultraviolet light resistance and a relatively high price at the current low volume production. Numerous researchers attempt to develop a natural composite for various applications in the automotive, construction, agriculture, building industries and etc (Auras *et al.*, 2004; Joshi *et al.*, 2004). Recently, researchers have applied new materials and modern manufacturing techniques to improve strength of biocomposites.

Since the 1990s, polylactic acid (PLA) has been known as one of the most compostable and renewable polymers. PLA can be derived from renewable resources like corn, scratch, sugarcane, potato and renewable feedstock by bacterial fermentation. It has excellent properties such as stiffness, low energy consumption, low production temperature and biodegradability (Sawyer & Grubb, 1996). It is a linear aliphatic thermoplastic polyester, which is fabricated either by condensation of lactic acid or the ring-opening polymerization of lactic (Garlotta, 2001). However, PLA has its own disadvantages such as inherent brittleness, weak thermal resistance and limited gas barrier. To use PLA in different applications including biomedical, mulching film, packaging and tissue, its undesirable properties such as inherent brittleness, weak thermal resistance and limited gas barrier have been improved by mixing different kinds of fillers and fibers; flax (Bax & Müssig, 2008), kenaf (Han *et al.*, 2012) and nanoparticles (nanaoclays) (Paul *et al.*, 2005).

After chicken, cattle are the second populous livestock in the world with the approximate number of 1.4 billion. As a 450 kg cow produces around 3 kg dung per day, the daily production of dung is virtually 4.2 million tonnes. In addition, it possesses a wide range of protein, lignocellulose, light weight, low cost, a capability as a good filler and it is an animal based fiber with biodegradability behavior (Reddy *et al.*, 2014). It should be noted that to decrease the problems of unusable cow dung (CD) like environmental damages and pollution to ground water, the CD needs improvement of its physical and chemical structure for usage in various applications.

In this study, biocomposite of PLA/CD is systematically described as a composite derived from 100% renewable resources. The additional effects of the two different sizes of CD filler were studied on the mechanical, physical, morphological and thermal properties of PLA/CD biocomposite.

1.2 Problem Statement

Different ratios of fillers and polylactic acid (PLA) are molded to produce biocomposite materials. Biocomposite materials are broadly utilized in many structural applications such as in panels, parts, boards and sheets. For this aim, the sample's properties play a key role with respect to their applications including compost bags, tea bags, food packaging and also mulch film. Therefore, it is necessary to study the mechanical, thermal and physical properties of the biocomposite materials. PLA has a brittle microstructure and it also has a high cost. Besides that, high amount of un-usable cow dung (CD) results in environmental pollution to ground water. Therefore, to decrease the drawbacks of both PLA and CD, the effect of CD to PLA biocomposite properties is systematically studied in this first hand study.

1.3 Objective

The aim of this study is attempted to prepare suitable biocomposite samples and investigate their mechanical, thermal, and physical properties. The influence of this study will aid to figure out the possibility of applying cow dung (CD) as filler to produce polylactic acid (PLA) biocomposite. The ability of manufacturing development of the biocomposite will be understood from this study as using of CD filler can decrease final price of the PLA biocomposite.

To completely obtain the final objective of this study, the following contributions will be investigated.

1) The fabrication of the biocomposite films at different CD ratios and sizes.

2) The assessment of the mechanical, physical, thermal, and dynamic properties of the fabricated biocomposites.

3) The study of the interfacial interaction using morphological analysis.

This research will evaluate suitable methods to obtain main contributions of the relation between the samples preparation and their characterizations.

1.4 Scope

Using biodegradable substances has become more popular in the modern societies due to increasing of plastic waste and environmental problems. However, a major disadvantage of the biocomposite is poor adhesion between matrix and filler that it leads to weak physical, thermal and mechanical properties. Sorts of natural polymers with different natural fillers have been examined to fabricate strong biocomposite samples. Advantages of natural filler (low cost, light weight and low density) may improve the mechanical, thermal, morphological and dynamic properties of polymer composites with lower cost. The high temperature of biocomposite fabrication influences the mechanical stress that it leads to their thermal and mechanical degradation (Klemm, 1998). This effects the strength of the final biocomposite samples (Gassan & Bledzki, 2001). Polylactic acid (PLA) is comprised of different natural fillers to improve its strength. Cow dung with its sufficient cellulose content can be used as a new natural filler to improve mechanical, thermal, dynamic and morphological properties of PLA composites. In addition, CD with its low cost and biodegradability behavior can decrease the final cost of PLA production.

1.5 Significance of the Study

This research has taken the full advantages of polylactic acid (PLA) matrix and cow dung (CD) filler for PLA/CD biocomposite samples preparation. Low cost of CD and suitable properties of the PLA lead to the obtainment of the low final cost and improvement of the mechanical and dynamic properties of the biocomposite, respectively. Besides, PLA samples comprise of various sizes of CD filler in different content ratios which leads to the improved formulation of PLA/CD biosomposite. Therefore, different biocomposite formulations can be used for all sorts of applications such as mulch film, disposable tableware as well as food container. The consequence of this study will lead to understanding the ability of replacing synthetic composite using PLA/CD biocomposite which is 100 % biodegradable to decline the environmental problems. Therefore, the mechanical, physical, thermal and morphological properties of PLA/CD biocomposite are evaluated, systematically.

1.6 Chapter Outline

Chapter 1 briefly describes introduction, problem statement and objectives of this research.

Chapter 2 is "Literature Review", which explains a review of the previous works on types of composites, natural fiber or filler and polymers. It presents the challenges and suitable properties of different composites and ends with the summary.

Chapter 3 is "Research Methodology", which presents the methodology of this research. It outlines the materials, method of PLA/CD biocomposites preparation and the apparatuses employed for all sorts of mechanical, thermal, physical and morphological analysis and tests.

Chapter 4 is "Results and Discussion", which explains and discusses the results and findings of mechanical, physical, thermal and morphological analysis and tests of PLA/CD biocomposites.

Chapter 5 is "Conclusion", which gives an outline of all the conclusions that have been obtained from this study and also presents the direction for future research.

REFERENCES

Adler, Erich. (1977). Lignin chemistry—past, present and future. *Wood science and technology, 11*(3), 169-218.

Akil, HMl, *et al.* (2011). Kenaf fiber reinforced composites: a review. *Materials & Design, 32*(8), 4107-4121.

Ala Moussawi, Hassan, *et al.* (1993). The silane/sizing composite interphase. *Polymer composites, 14*(3), 195-200.

Alimuzzaman, Shah, *et al.* (2013). Nonwoven polylactic acid and flax biocomposites. *Polymer Composites, 34*(10), 1611-1619.

Auras, Rafael A, *et al.* (2011). *Poly (lactic acid): synthesis, structures, properties, processing, and applications* (Vol. 10): John Wiley & Sons.

Auras, Rafael, *et al.* (2004). An overview of polylactides as packaging materials. *Macromolecular bioscience, 4*(9), 835-864.

Bax, Benjamin, *et al.* (2008). Impact and tensile properties of PLA/Cordenka and PLA/flax composites. *Composites Science and Technology, 68*(7), 1601-1607.

Bleach, NC, *et al.* (2002). Effect of filler content on mechanical and dynamic mechanical properties of particulate biphasic calcium phosphate—polylactide composites. *Biomaterials, 23*(7), 1579-1585.

Bledzki, AK, *et al.* (2004). Unidirectional hemp and flax EP and PP composites: Influence of defined fiber treatments. *Journal of Applied Polymer Science, 93*(5), 2150-2156.

Bledzki, AK, *et al.* (1999). Composites reinforced with cellulose based fibres. *Progress in polymer science, 24*(2), 221-274.

Bledzki, AK, *et al.* (2010). Mechanical performance of biocomposites based on PLA and PHBV reinforced with natural fibres–A comparative study to PP. *Composites science and technology, 70*(12), 1687-1696.

Bledzki, Andrzej K, *et al.* (2009). Mechanical properties of PLA composites with man-made cellulose and abaca fibres. *Composites Part A: Applied science and manufacturing, 40*(4), 404-412.

Bourmaud, Alain, *et al.* (2010). Effects of thermo mechanical processing on the mechanical properties of biocomposite flax fibers evaluated by nanoindentation. *Polymer Degradation and Stability, 95*(9), 1488-1494.

Cantero, Guillermo, *et al.* (2003). Effects of fibre treatment on wettability and mechanical behaviour of flax/polypropylene composites. *Composites science and technology, 63*(9), 1247-1254.

Carens, Joseph H. (2000). *Culture, citizenship, and community: A contextual exploration of justice as evenhandedness*: Oxford University Press.

Chen, Shulin, *et al.* (2003). *Value-added chemicals from animal manure*: Pacific Northwest National Laboratory.

Cheung, Hoi-Yan, *et al.* (2007). A critical review on polymer-based bio-engineered materials for scaffold development. *Composites Part B: Engineering, 38*(3), 291-300.

Cheung, Hoi-Yan, *et al.* (2008). A potential material for tissue engineering: Silkworm silk/PLA biocomposite. *Composites Part B: Engineering, 39*(6), 1026-1033.

Christian, Sarah Jane. (2009). *Mechanical characterization and structural assessment of biocomposites for construction*: ProQuest.

Comyn, John. (2012). *Polymer permeability*: Springer Science & Business Media.

Correlo, Vitor M, *et al.* (2007). Water Absorption and Degradation Characteristics of Chitosan-Based Polyesters and Hydroxyapatite Composites. *Macromolecular bioscience, 7*(3), 354-363.

Corro, Grisel, *et al.* (2013). Generation of biogas from coffee-pulp and cow-dung co-digestion: Infrared studies of postcombustion emissions. *Energy Conversion and Management, 74*, 471-481.

Devi, L Uma, *et al.* (1997). Mechanical properties of pineapple leaf fiber-reinforced polyester composites. *Journal of Applied Polymer Science, 64*(9), 1739-1748.

Drzal, LT, *et al.* (2002). Trends in new filler and reinforcement technologies for plastic composites. *Macromol. Mater. Eng, 1*, 276-277.

Eichhorn, SJ, *et al.* (2001). Review: current international research into cellulosic fibres and composites. *Journal of materials Science, 36*(9), 2107-2131.

El-Mashad, Hamed M, *et al.* (2003). A model of solar energy utilisation in the anaerobic digestion of cattle manure. *Biosystems Engineering, 84*(2), 231-238.

El-Mashad, Hamed M, *et al.* (2005). Rheological properties of dairy cattle manure. *Bioresource technology, 96*(5), 531-535.

Fan, Yao-Ting, *et al.* (2006). Efficient conversion of wheat straw wastes into biohydrogen gas by cow dung compost. *Bioresource Technology, 97*(3), 500-505.

Fay, JJ, *et al.* (1991). Effect of morphology, crosslink density, and miscibility on interpenetrating polymer network damping effectiveness. *Polymer Engineering & Science, 31*(24), 1731-1741.

Folkes, MJ. (2012). *Processing, structure and properties of block copolymers*: Springer Science & Business Media.

Frone, Adriana N, *et al.* (2013). Morphology and thermal properties of PLA–cellulose nanofibers composites. *Carbohydrate Polymers, 91*(1), 377-384.

Gao, ZH, *et al.* (2005). FTIR and XPS study of the reaction of phenyl isocyanate and cellulose with different moisture contents. *Pigment & resin technology, 34*(5), 282-289.

Garkhail, SK, *et al.* (2000). Mechanical properties of natural-fibre-mat-reinforced thermoplastics based on flax fibres and polypropylene. *Applied Composite Materials, 7*(5-6), 351-372.

Garlotta, Donald. (2001). A literature review of poly (lactic acid). *Journal of Polymers and the Environment, 9*(2), 63-84.

Gassan, Jochen, *et al.* (2001). Thermal degradation of flax and jute fibers. *Journal of Applied Polymer Science, 82*(6), 1417-1422.

Gatenholm, P. (1997). Interfacial adhesion and dispersion in biobased composites. Molecular interactions between cellulose and other polymers". *Lignocellulosicplastics composites, AL Leão, FX Carvalho e E. Frollini (ed.), USP/UNESP, São Paulo*.

Gatenholm, P, *et al.* (1994). Biodegradable natural composites. II. Synergistic effects of processing cellulose with PHB. *Journal of applied polymer science, 51*(7), 1231-1237.

Geethamma, VG, *et al.* (2005). Dynamic mechanical behavior of short coir fiber reinforced natural rubber composites. *Composites part A: applied science and manufacturing, 36*(11), 1499-1506.

George, Jayamol, *et al.* (2001). A Review on Interface Modification and Characterization. *Polymer engineering and science, 41*(9).

George, Jayamol, *et al.* (1999). Effect of strain rate and temperature on the tensile failure of pineapple fiber reinforced polyethylene composites. *Journal of Thermoplastic Composite Materials, 12*(6), 443-464.

Goering, H Keith, *et al.* (1970). Forage fiber analyses (apparatus, reagents, prcedures, and some applications). *USDA Agr Handb*.

Göksungur, Yekta, *et al.* (1997). Batch and continuous production of lactic acid from beet molasses by Lactobacillus delbrueckii IFO 3202. *Journal of chemical technology and biotechnology, 69*(4), 399-404.

Gu, Huang. (2009). Dynamic mechanical analysis of the seawater treated glass/polyester composites. *Materials & Design, 30*(7), 2774-2777.

Gupta, AP, *et al.* (2007). New emerging trends in synthetic biodegradable polymers–Polylactide: A critique. *European polymer journal, 43*(10), 4053-4074.

Hahn, Hong T, *et al.* (1980). *Introduction to composite materials* (Vol. 1): CRC Press.

Hamdan, S, *et al.* (2000). Compatibility studies of polypropylene (PP)-sago starch (SS) blends using DMTA. *Journal of Polymer Research, 7*(4), 237-244.

Han, Seong Ok, *et al.* (2012). Understanding the reinforcing mechanisms in kenaf fiber/PLA and kenaf fiber/PP composites: A comparative study. *International Journal of Polymer Science, 2012*.

Hearle, John WS, *et al.* (2008). *Physical properties of textile fibres*: Elsevier.

Huda, Masud S, *et al.* (2005). A study on biocomposites from recycled newspaper fiber and poly (lactic acid). *Industrial & engineering chemistry research, 44*(15), 5593-5601.

Huda, Masud S, *et al.* (2008). Effect of chemical modifications of the pineapple leaf fiber surfaces on the interfacial and mechanical properties of laminated biocomposites. *Composite Interfaces, 15*(2-3), 169-191.

Huda, MS, *et al.* (2006). Woodæfiberæreinforced poly (lactic acid) composites: Evaluation of the physicomechanical and morphological properties. *Journal of Applied Polymer Science, 102*(5), 4856-4869.

Huda, MS, *et al.* (2007). The effect of silane treated-and untreated-talc on the mechanical and physico-mechanical properties of poly (lactic acid)/newspaper fibers/talc hybrid composites. *Composites Part B: Engineering, 38*(3), 367-379.

Huda, MS, *et al.* (2005). "Green" composites from recycled cellulose and poly (lactic acid): Physico-mechanical and morphological properties evaluation. *Journal of Materials Science, 40*(16), 4221-4229.

Ikada, Yoshito, *et al.* (2000). Biodegradable polyesters for medical and ecological applications. *Macromolecular Rapid Communications, 21*(3), 117-132.

Islam, MS, *et al.* (2010). Influence of alkali treatment on the interfacial and physico-mechanical properties of industrial hemp fibre reinforced polylactic acid composites. *Composites Part A: Applied Science and Manufacturing, 41*(5), 596-603.

Jandas, PJ, *et al.* (2011). Effect of surface treatments of banana fiber on mechanical, thermal, and biodegradability properties of PLA/banana fiber biocomposites. *Polymer Composites, 32*(11), 1689-1700.

Jayanarayanan, K, *et al.* (2008). Morphology, static and dynamic mechanical properties of in situ microfibrillar composites based on polypropylene/poly (ethylene terephthalate) blends. *Composites Part A: Applied Science and Manufacturing, 39*(2), 164-175.

Joseph, K, *et al.* (2000). Natural fiber reinforced thermoplastic composites. *Natural Polymers and Agrofibers Composites, 159*.

Joseph, PV, *et al.* (2003). Dynamic mechanical properties of short sisal fibre reinforced polypropylene composites. *Composites Part A: applied science and manufacturing, 34*(3), 275-290.

Joshi, Satish V, *et al.* (2004). Are natural fiber composites environmentally superior to glass fiber reinforced composites? *Composites Part A: Applied science and manufacturing, 35*(3), 371-376.

Kalapakdee, Asama, *et al.* (2014). Mechanical properties of preferentially aligned short pineapple leaf fiber reinforced thermoplastic elastomer: Effects of fiber content and matrix orientation. *Polymer Testing, 37*, 36-44.

Kalia, Susheel, *et al.* (2009). Pretreatments of natural fibers and their application as reinforcing material in polymer composites—a review. *Polymer Engineering & Science, 49*(7), 1253-1272.

Karnani, Rajeev, *et al.* (1997). Biofiber-reinforced polypropylene composites. *Polymer Engineering & Science, 37*(2), 476-483.

Katz, Harry S, *et al.* (1987). *Handbook of fillers for plastics*: Springer Science & Business Media.

Khalid, M, *et al.* (2009). Thermal and Dynamic Mechanical Behavior of Cellulose-and Oil Palm Empty Fruit Bunch (OPEFB)-Filled Polypropylene Biocomposites. *Polymer-Plastics Technology and Engineering, 48*(12), 1244-1251.

Khalid, Marzuki, *et al.* (2008). Comparative study of polypropylene composites reinforced with oil palm empty fruit bunch fiber and oil palm derived cellulose. *Materials & Design, 29*(1), 173-178.

Kimura, Teruo, *et al.* (2004). Compression molding and mechanical properties of green-composite based on ramie/PLA non-twisted commingled yarn. *JOURNAL-SOCIETY OF MATERIALS SCIENCE JAPAN, 53*, 776-781.

Kirk, T Kent, *et al.* (1987). Enzymatic" combustion": the microbial degradation of lignin. *Annual Reviews in Microbiology, 41*(1), 465-501.

Klemm, Richard. (1998). Space-time adaptive processing. *The Institute of Electrical Engineers, London, United Kingdom*.

Landel, Robert F, *et al.* (1993). *Mechanical properties of polymers and composites*: CRC Press.

Lariviere, D, *et al.* (2004). Interfacial properties in commingled yarn thermoplastic composites. Part II: Influence on crack initiation and propagation. *Polymer composites, 25*(6), 589-600.

Lee, Seung-Hwan, *et al.* (2004). Eco-composite from poly (lactic acid) and bamboo fiber. *Holzforschung, 58*(5), 529-536.

Lee, Seung-Hwan, *et al.* (2006). Biodegradable polymers/bamboo fiber biocomposite with bio-based coupling agent. *Composites Part A: Applied Science and Manufacturing, 37*(1), 80-91.

Li, Zhaoqian, *et al.* (2011). Effect of sisal fiber surface treatment on properties of sisal fiber reinforced polylactide composites. *International journal of polymer science, 2011*.

Liu, LinShu, *et al.* (2005). Biodegradable composites from sugar beet pulp and poly (lactic acid). *Journal of agricultural and food chemistry, 53*(23), 9017-9022.

Liu, Wanjun, *et al.* (2007). Influence of processing methods and fiber length on physical properties of kenaf fiber reinforced soy based biocomposites. *Composites Part B: Engineering, 38*(3), 352-359.

Liu, X, *et al.* (1997). Thermal and mechanical properties of poly (lactic acid) and poly (ethylene/butylene succinate) blends. *Journal of environmental polymer degradation, 5*(4), 225-235.

Liu, Xingxun, *et al.* (2010). Effects of hydrophilic fillers on the thermal degradation of poly (lactic acid). *Thermochimica Acta, 509*(1), 147-151.

Lunt, James. (1998). Large-scale production, properties and commercial applications of polylactic acid polymers. *Polymer degradation and stability, 59*(1), 145-152.

Ma, Hongwei, *et al.* (2010). Structure and mechanical properties of jute-polylactic acid biodegradable composites. *Journal of Composite Materials*, 0021998310382316.

Mallarino, Stéphanie, *et al.* (2009). Interphase study in cyanate/glass fibre composites using thermomechanical analysis and micro-thermal analysis. *Composites Science and Technology*, *69*(1), 28-32.

Malo, JE, *et al.* (1995). Establishment of pasture species on cattle dung: the role of endozoochorous seeds. *Journal of Vegetation Science*, *6*(2), 169-174.

Marcovich, Norma E, *et al.* (1998). Dependence of the mechanical properties of woodflour–polymer composites on the moisture content. *Journal of Applied Polymer Science*, *68*(13), 2069-2076.

Mlekuz, Dimitrij. (2009). The materiality of dung: the manipulation of dung in Neolithic Mediterranean caves. *Documenta Praehistorica*, *36*, 219-225.

Mohanty, AK, *et al.* (2001). Surface modifications of natural fibers and performance of the resulting biocomposites: an overview. *Composite Interfaces*, *8*(5), 313-343.

Mohanty, Amar K, *et al.* (2005). *Natural fibers, biopolymers, and biocomposites*: CRC Press.

Mohanty, Smita, *et al.* (2006). Dynamic mechanical and thermal properties of MAPE treated jute/HDPE composites. *Composites Science and Technology*, *66*(3), 538-547.

Molins, Gemma, *et al.* CHICKEN FEATHERS BASED BIOCOMPOSITES: A NEW SUSTAINABLE PRODUCT?

Nair, KC Manikandan, *et al.* (2001). Thermal and dynamic mechanical analysis of polystyrene composites reinforced with short sisal fibres. *Composites Science and Technology*, *61*(16), 2519-2529.

Nampoothiri, K Madhavan, *et al.* (2010). An overview of the recent developments in polylactide (PLA) research. *Bioresource technology*, *101*(22), 8493-8501.

Netravali, Anil N, *et al.* (2003). Composites get greener. *Materials today*, *6*(4), 22-29.

Nishino, Takashi, *et al.* (2003). Kenaf reinforced biodegradable composite. *Composites Science and Technology*, *63*(9), 1281-1286.

Nosbi, Norlin, *et al.* (2011). Behavior of kenaf fibers after immersion in several water conditions. *BioResources*, *6*(2), 950-960.

Ochi, Shinji. (2008). Mechanical properties of kenaf fibers and kenaf/PLA composites. *Mechanics of materials*, *40*(4), 446-452.

Ogawa, Kozo, *et al.* (1992). Dependence on the preparation procedure of the polymorphism and crystallinity of chitosan membranes. *Bioscience, biotechnology, and biochemistry*, *56*(6), 858-862.

Oksman, Kristiina, *et al.* (2003). Natural fibres as reinforcement in polylactic acid (PLA) composites. *Composites science and technology*, *63*(9), 1317-1324.

Park, Sang-Dae, *et al.* (2004). Effect of annealing on the fracture toughness of poly (lactic acid). *Journal of materials science*, *39*(3), 1113-1116.

Park, Sang Dae, *et al.* (2006). Effect of crystallinity and loading-rate on mode I fracture behavior of poly (lactic acid). *Polymer*, *47*(4), 1357-1363.

Paul, M-A, *et al.* (2005). Polylactide/montmorillonite nanocomposites: study of the hydrolytic degradation. *Polymer degradation and stability*, *87*(3), 535-542.

Pejic, Biljana M, *et al.* (2008). The effects of hemicelluloses and lignin removal on water uptake behavior of hemp fibers. *Bioresource technology*, *99*(15), 7152-7159.

Petinakis, Eustathios, *et al.* (2010). Biodegradation and thermal decomposition of poly (lactic acid)-based materials reinforced by hydrophilic fillers. *Polymer Degradation and Stability*, *95*(9), 1704-1707.

Pilla, Srikanth, *et al.* (2008). Polylactide-pine wood flour composites. *Polymer Engineering & Science, 48*(3), 578-587.
Plackett, David, *et al.* (2003). Biodegradable composites based on L-polylactide and jute fibres. *Composites Science and Technology, 63*(9), 1287-1296.
Pothan, Laly A, *et al.* (2003). Dynamic mechanical analysis of banana fiber reinforced polyester composites. *Composites Science and Technology, 63*(2), 283-293.
Rana, AK, *et al.* (1999). Short jute fiber-reinforced polypropylene composites: Dynamic mechanical study. *Journal of Applied Polymer Science, 71*(4), 531-539.
Ray, Dipa, *et al.* (2002). Dynamic mechanical and thermal analysis of vinylester-resin-matrix composites reinforced with untreated and alkali-treated jute fibres. *Composites Science and Technology, 62*(7), 911-917.
Raya, Dipa, *et al.* (2002). Dynamic mechanical and thermal analysis of vinylester-resin-matrix composites reinforced with untreated and alkali-treated jute Ebers. *Compos Sci Technol, 62*, 911-917.
Reddy, T Ranjeth Kumar, *et al.* (2014). Studies on thermal characteristics of cow dung powder filled glass–polyester hybrid composites. *Composites Part B: Engineering, 56*, 670-672.
Rowell, Roger M, *et al.* (1996). *Paper and composites from agro-based resources*: CRC press.
Saheb, D Nabi, *et al.* (1999). Natural fiber polymer composites: a review. *Advances in polymer technology, 18*(4), 351-363.
Sawpan, Moyeenuddin A, *et al.* (2011). Improvement of mechanical performance of industrial hemp fibre reinforced polylactide biocomposites. *Composites Part A: Applied Science and Manufacturing, 42*(3), 310-319.
Sawpan, Moyeenuddin A, *et al.* (2012). Flexural properties of hemp fibre reinforced polylactide and unsaturated polyester composites. *Composites Part A: Applied Science and Manufacturing, 43*(3), 519-526.
Sawyer, Linda C, *et al.* (1996). Polymer applications *Polymer Microscopy* (pp. 174-314): Springer.
Shibata, Mitsuhiro, *et al.* (2003). Biocomposites made from short abaca fiber and biodegradable polyesters. *Macromolecular Materials and Engineering, 288*(1), 35-43.
Shibata, Shinichi, *et al.* (2008). Flexural modulus of the unidirectional and random composites made from biodegradable resin and bamboo and kenaf fibres. *Composites part A: Applied science and manufacturing, 39*(4), 640-646.
Shinde, VB, *et al.* (2014). THERMO GRAVIMETRIC ANALYSIS OF BIOMASS STALKS FOR BRIQUETTING. *Journal of Environmental Research and Development, 9*(1), 151.
Speranza, V, *et al.* (2014). Thermal and hydrolytic degradation kinetics of PLA in the molten state. *Polymer Degradation and Stability, 100*, 37-41.
Stamboulis, A, *et al.* (2000). Environmental durability of flax fibres and their composites based on polypropylene matrix. *Applied composite materials, 7*(5-6), 273-294.
Stamboulis, A, *et al.* (2001). Effects of environmental conditions on mechanical and physical properties of flax fibers. *Composites Part A: Applied Science and Manufacturing, 32*(8), 1105-1115.
Standard, ASTM. (1998). D570-98: Standard test method for water absorption of plastics. *American Society for Testing and Materials: New York, NY, USA*.
Stevens, Eugene S. (2002). *Green plastics: an introduction to the new science of biodegradable plastics*: Princeton University Press.

Summerscales, John, *et al.* (2010). A review of bast fibres and their composites. Part 1–Fibres as reinforcements. *Composites Part A: Applied Science and Manufacturing, 41*(10), 1329-1335.

Tee, Yee Bond, *et al.* (2013). Thermally grafting aminosilane onto kenaf-derived cellulose and its influence on the thermal properties of poly (lactic acid) composites. *BioResources, 8*(3), 4468-4483.

Timbuntam, Walaiporn, *et al.* (2006). Lactic acid production from sugar-cane juice by a newly isolated Lactobacillus sp. *Biotechnology letters, 28*(11), 811-814.

Tjong, SC, *et al.* (1999). Composites based on maleated polypropylene and methyl cellulosic fiber: Mechanical and thermal properties. *Journal of applied polymer science, 72*(13), 1647-1653.

Ugheoke, BI, *et al.* (2011). *The effect of processing methods on some properties of rice husk-polypropylene composite: A preliminary report.* Paper presented at the National Postgraduate Conference (NPC), 2011.

Utracki, LA, *et al.* (1989). *Polymer alloys and blends* (Vol. 4): Marcel Dekker: New York.

Van de Velde, Kathleen, *et al.* (2002). Biopolymers: overview of several properties and consequences on their applications. *Polymer Testing, 21*(4), 433-442.

Van den Oever, MJA, *et al.* (2010). Agrofibre reinforced poly (lactic acid) composites: Effect of moisture on degradation and mechanical properties. *Composites Part A: Applied Science and Manufacturing, 41*(11), 1628-1635.

Way, Cameron, *et al.* (2013). Processing stability and biodegradation of polylactic acid (PLA) composites reinforced with cotton linters or maple hardwood fibres. *Journal of Polymers and the Environment, 21*(1), 54-70.

Weeton, John W, *et al.* (1987). *Engineers' guide to composite materials*: American Society for metals.

Wells, JK, *et al.* (1985). Debonding and pull-out processes in fibrous composites. *Journal of Materials Science, 20*(4), 1275-1284.

Wu, Jingshen, *et al.* (2000). Effect of fiber pretreatment condition on the interfacial strength and mechanical properties of wood fiber/PP composites. *Journal of applied polymer science, 76*(7), 1000-1010.

Yalley, Peter Paa-Kofi, *et al.* (2013). Strength and Durability Properties of Cow Dung Stabilised Earth Brick. *Civil and Environmental Research, 3*(13), 117-125.

Yew, GH, *et al.* (2009). Natural weathering of poly (lactic acid): effects of rice starch and epoxidized natural rubber. *Journal of Elastomers and Plastics, 41*(4), 369-382.

Yokoyama, Hiroshi, *et al.* (2007). Hydrogen fermentation properties of undiluted cow dung. *Journal of bioscience and bioengineering, 104*(1), 82-85.

Yu, Tao, *et al.* (2010). Effect of fiber surface-treatments on the properties of poly (lactic acid)/ramie composites. *Composites Part A: Applied Science and Manufacturing, 41*(4), 499-505.

Yuan, Xiaowen, *et al.* (2002). Plasma treatment of sisal fibres and its effects on tensile strength and interfacial bonding. *Journal of adhesion science and technology, 16*(6), 703-727.

Zhang, Farao, *et al.* (2002). Preparation and mechanical properties of composite of fibrous cellulose and maleated polyethylene. *Journal of applied polymer science, 84*(11), 1971-1980.

Zhang, Qi, *et al.* (2012). Study on poly (lactic acid)/natural fibers composites. *Journal of Applied Polymer Science, 125*(S2), E526-E533.