PROPERTIES AND CHARACTERIZATION OF LOW DENSITY POLYETHYLENE/MODIFIED COCKLE SHELL COMPOSITE FILMS

MUHAMMAD HUSNAN BIN MUSTAFFA

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Philosophy

School of Chemical and Energy Engineering
Faculty of Engineering
Universiti Teknologi Malaysia

OCTOBER 2018

To my beloved parents and friends

ACKNOWLEDGEMENT

First and foremost, I would like to express my sincere gratitude to my supervisor, Assoc. Prof Dr. Aznizam Bin Abu Bakar for his continuous support during my research, for his patience, motivation, enthusiasm, and immense knowledge. His guidance has helped me in all time of research and during writing this thesis.

I would also like to express my sincere thanks to all lecturers, technicians and staff of Faculty of Chemical and Energy Engineering, UTM and especially from the Department of Polymer Engineering, UTM whom have directly and indirectly assisted me in the experimental works and the preparation of the thesis.

I thank my fellow laboratory friends and technicians Sakinah Md Tia, Muhammad Hakim, Nur Wahida Che Rahim, Abang Shidi, En. Izzat and En. Suhee Tan for being such the continuous supports and motivations.

Last but not least, I would like to thank my beloved family especially my father Mustaffa Bin Saad, my mother Azizah Binti Ismail and also my brothers for their inspirations and endless love during this research.

ABSTRACT

The objective of this research was to study the mechanical, thermal and morphological properties of low-density polyethylene (LDPE)/cockle shell (CS) composite films. Untreated cockle shells (UCS) and treated cockle shells (TCS) were used as fillers in the composite system with filler loadings of 10 – 50 phr. Stearic acid (SA) was used as a coupling agent to produce the TCS. The composite films were prepared using a co-rotary twin screw extruder machine at temperature 160ºC and screw speed 64 rpm followed by blown film machine. It was found that the increasing of UCS loading reduced the tensile strength and elongation at break for all LDPE/UCS composite films. However, the incorporation of SA coupling agent slightly increased the tensile strength of LDPE/TCS composite films compared to pure LDPE film and LDPE/UCS composite films. Scanning electron microscopy micrographs showed presence of agglomeration at the higher filler loading which probably caused the reduction on the tensile strength of LDPE/40UCS films compared to LDPE/40TCS films. Differential scanning calorimetry results showed that degree of crystallinity (X_c) and melting enthalpy (ΔH_m) of the films slightly increased with the presence of CS loading while melting temperature (T_m) and crystallization temperature (T_c) only showed slight changes for LDPE/UCS and LDPE/TCS formulations. Reduction of X_c and ΔH_m was observed in LDPE/TCS composite. Thermogravimetry analysis showed that the thermal degradation temperature slightly increased with the incorporation of CS and the higher char residue was observed at 50 phr filler loading for both UCS and TCS. The overall result showed that the incorporation of TCS into LDPE/TCS composite films showed better properties, especially in the tensile strength.

ABSTRAK

Penyelidikan ini bertujuan untuk mengkaji sifat mekanikal, haba dan morfologi filem polietilena berketumpatan rendah (LDPE)/cengkerang kerang (CS). Cengkerang kerang yang tidak dirawat (UCS) dan cengkerang kerang yang terawat (TCS) digunakan sebagai pengisi dalam sistem komposit dengan muatan pengisi 10 – 50 phr. Asid stearik (SA) digunakan sebagai agen gandingan untuk menghasilkan TCS. Filem komposit dihasilkan dengan menggunakan penyemperitan skru berkembar putaran pada suhu 160ºC dan kelajuan skru 64 rpm diikuti dengan mesin tiupan filem. Didapati bahawa dengan penambahan kandungan pengisi UCS memberi pengurangan terhadap kekuatan tegangan dan pemanjangan bagi semua formulasi filem komposit LDPE/UCS. Bagaimanapun, dengan penambahan SA sebagai agen gandingan telah meningkatkan sedikit kekuatan tegangan filem komposit LDPE/TCS berbanding dengan filem tulen LDPE dan juga filem komposit LDPE/UCS. Mikrograf oleh mikroskop elektron pengimbas telah menunjukkan terdapat gumpalan pada kandungan pengisi yang tinggi yang mengakibatkan pengurangan pada kesan tegangan filem komposit LDPE/40UCS berbanding dengan filem komposit LDPE/40TCS. Analisis pengimbas pembezaan kalorimeter menunjukkan kadar penghabluran (X_c) dan entalpi lebur (ΔH_m) filem sedikit meningkat dengan kehadiran pengisi CS manakala suhu lebur (T_m) dan suhu penghabluran (T_c) menunjukkan hanya sedikit perubahan yang berlaku untuk formulasi LDPE/UCS dan LDPE/TCS komposit. Pengurangan bagi X_c dan ΔH_m diperhatikan dalam LDPE/TCS komposit. Analisis thermogravimetri menunjukkan suhu degradasi haba sedikit meningkat dengan penambahan CS dan sisa char dapat dilihat meningkat pada kandungan pengisi 50 phr bagi kedua UCS dan TCS. Keputusan keseluruhan menunjukkan gabungan TCS kedalam formulasi filem komposit LDPE/TCS telah menghasilkan sifat-sifat yang lebih baik, terutamanya kekuatan tegangan.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CS	-	Cockle Shells
HDPE	-	High density polyethylene
LDPE	-	Low density polyethylene
LLDPE	-	Linear low density polyethylene
MFI	-	Melt flow index
PE	-	Polyethylene
PET	-	Polyethylene terephthalate
phr	-	Part per hundred resin
PLA	-	Polylactic acid or Polylactide
PP	-	Polypropylene
PVC	-	Polyvinyl chloride
SA	-	Stearic Acid
SEM	-	Scanning Electron Microscope
TCS	-	Treated Cockle Shells
TGA	-	Thermogravimetry Analysis
UCS	-	Untreated Cockle Shells
WVTR	-	Water vapor transmission rate

LIST OF SYMBOLS

cm	-	Centimeter
g	-	Gram
kg	-	Kilogram
ml	-	Milliliter
mm	-	Millimeter
MPa	-	Mega Pascal
$CaCO_3$	-	Calcium Carbonate
CH_4	-	Methane
CO_2	-	Carbon dioxide
N_2	-	Nitrogen
T_c	-	Crystallization temperature
T_g	-	Glass transition temperature
T_m	-	Melting temperature
Wt %	-	Weight percent
X_c	-	Degree of crystallinity
^oC	-	Degrees celsius
^oF	-	Fahrenheit
ΔH_m	-	Melting enthalphy
µm	-	Micrometer
%	-	Percent

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research Background

Calcium carbonate ($CaCO_3$) is considered as one of commercially used and common fillers that usually used as reinforcing fillers in polymer industry. Chemically, $CaCO_3$ from limestone also contain a small amount of $MgCO_3$ and any other impurities such as SiO_2, AlO_3 and Fe_2O_3. In terms of mineralogical, it was classified as trimorphous mineral because it can exist in three distinct crystal structures which are calcite, aragonite and vaterite. However, $CaCO_3$ is widely found in calcite form which come from all limestone and marbles. Since $CaCO_3$ was moderately soft mineral, so it can be ground to a very fine particle sizes to be a particulate fillers.. The versatility of $CaCO_3$ was utilized in a wide variety of products including paper, plastics, rubber and pharmaceuticals (Hariharan *et al.,* 2014)

Incompatibility of fillers into polymer matrix leads to the modification or treatment of the fillers. In the limestone case, the modification by using stearic acid can improve the hydrophobicity level, had better powder flow properties, reduced the cost production by lowering the lubricant and stabilizer level, improvement in low temperature impact strength and also reduced the abrasivity.

Stearate treatment chemically reacts with the limestone surface and usually applied in sufficient quantity to fom a monomolecular layer. The chemical reaction between limestone particles and stearic acid is shown in equation below.

$$2C_{17}H_{35}COOH + CaCO_3 \rightarrow (C_{17}H_{35}COO)_2\,Ca + CO_2\uparrow + H_2O \qquad (1.1)$$

Recent work has been focused on using renewable resources as fillers to be incorporated with polymer composite. Renewable resources are well known sources because of their rich chemical composition and low cost compared to commercial fillers. Recently many works have been studied on the usage of renewable resources like oil palm empty fruit bunches, wood sawdust, rice husk and other agricultural wastes as the reinforcing fillers in polymer composites due to their low cost, high specific strength and modulus and biodegradability. The usage of the current commercial filler to the polymer composites which are high in cost and non-environmental friendly make the researchers extensively investigate and study on the natural fillers as an alternative fillers.

The previous researchers has reported their research work regarding to renewable resources in polymer composite like shrimp shells by Hussein (2011), oyster shells by Shnawa *et al*., (2011) and egg shells by Suhadah *et al.,* (2009). LDPE has been chosen as the main polymer matrix in their study. Similar purpose were noticed from their studies which is to improve the mechanical properties like tensile strength and Young's modulus in the LDPE composite.

The other potential filler was noticed from cockle shells which contain rich chemical composition of $CaCO_3$ which is approximately about 95-98% of $CaCO_3$ (aragonite) and can be applied in the polymer composite field (Kamba *et al*., 2013). Cockles which is known due to its luscious taste has contributed their empty shells dumped and left untreated, mostly in the public area like market places, restaurant and public areas. Hence, this research proposed cockle shells as the alternative natural filler since it contains high composition of $CaCO_3$ that can be incorporated with polymer composite. The research of cockle shells has been widely studied but apparently the usage of cockle shells waste particle as filler in LDPE composite film has not been reported yet in any studies. LDPE has been used as it has good flexibility in terms of application for packaging films as well as the low cost of purchasing the LDPE raw material.

As mentioned before, the addition of additives to the polymer matrix is to enhance its properties for various application. The incompatibility between polymer matrix and filler has become an issue since filler was in polar group and polymer matrix in non-polar group. Hence, the surface modification on the filler is to improve the homogeneity between filler and polymer matrix as well as to increase the compatibility between each other. Thus, there are several studies has been reported in surface modification of fillers by using chemical treatment to increase the hydrophobicity state (Jeong *et al*., 2009).

This present study has proposed the using of petroleum-based plastic materials like polyethylene (PE) as polymer matrix due to its good properties such as light weight, low cost, easy processability and good water barrier properties. However, there are some limitation that restrict their applications in the packaging industry such as low stiffness and tensile strength. Hence, these properties should be improved in order to extend their use in packaging applications (Hong *et al*., 2012).Besides that, the advantages of using LDPE also have been stated which is also due to its flexibility, sealable, transparent and easy to process (Mahaphram *et al.,* 2011).

1.2 Problem Statement

The study on the natural filler in polymer composite has attracted many researchers in recent works. Previous studies have shown that the usage of modified egg shell powder (ESP) as fillers in LDPE has resulted to increasing of Young's modulus but decrease the tensile strength of LDPE/ESP composite (Suhadah *et al*., 2009). The similar finding also spotted when the shrimp shells used as fillers in LDPE composite (Hussein, 2011). The previous study showed that the used of these filler has a potential to be used as the alternative filler but it still need to be studied more in terms of the optimum amount of filler, the modification of the filler and the usage of chemical treatment used in the polymer composite.

Besides that, the other potential natural mineral filler that can be used is cockle shells which is one of the abundant natural resources in Malaysia (Rusnah *et al*., 2014). The expected number of cockle shells produced during Ninth Malaysia Plan was 13000 metric ton and this number might increase by years until now. This statistic is quite worrisome because it will cause unpleasant smell and environment's distraction. On top of that, this present study used cockle shells as the reinforcing fillers in LDPE/CS composite. The previous study also reported that CS filler contain approximately 95-98% of $CaCO_3$ in the form of aragonite crystal (Kamba *et al*., 2013). Thus, in order to utilised the abundant of cockle shell waste, CS was used as the filler in LDPE/CS composite films and reduced the cost of manufacturing of LDPE/CS composite films. However, the poor interaction between LDPE and CS has limit its performance. Thus, the surface modification on the CS filler has been done to improve the compatibility between LDPE matrix and CS filler.

Many studies have been intensively carried out previously in order to develop low cost LDPE composite and also to improve tensile properties and thermal stability. In this context, the influence of filler on the tensile , chemical interaction between filler-matrix and thermal properties have been studied. The addition of $CaCO_3$ as a filler in LDPE matrix has been considered because of its properties like high strength and easy processing during compounding with polymer and eventually can reduce the cost production of LDPE composite and also to improve the tensile properties (Wang *et al*., 2007).

LDPE can be considered as the most common thermoplastics that are currently used for industrial application like packaging field. The low cost of purchasing for raw material LDPE was one of the reason of LDPE has been chosen in this current study. However, since the production of the LDPE is consistently increase, the environmental problem have become a crucial issue as LDPE was not biodegradable (Pedroso *et al.,* 2005).

1.3 Research Objectives

The objectives of this study are:

1. To prepare and characterize the untreated and treated CS filler, pure LDPE film, LDPE/UCS and LDPE/TCS composite films.

2. To determine tensile, thermal and morphological properties of LDPE film, LDPE/UCS composite film and LDPE/TCS composite films with different CS filler loadings.

1.4 Scope of Research

The scope of this study consist of three parts which are the preparation of CS filler, preparation of LDPE/CS composite films and characterization of all samples. The details are described as below:

1. Preparation of CS filler

   i. CS filler was prepared by three main process which are crushing, grinding and sieving by using sand crusher machine, grinder machine and sieve shaker machine respectively. CS filler was prepared by two different class which are untreated and treated CS filler. Treated CS filler was chemically treated by stearic acid (2 wt%) in order to increase the hydrophobicity state of the fillers and to improve the homogeneity of fillers in polymer matrix by improving the filler-matrix interaction.

2. Preparation of pure LDPE film, LDPE/UCS and LDPE/TCS composite films

   i. LDPE matrix and CS fillers were compounded by using a extruder machine. The formulations of LDPE/UCS and LDPE/TCS composite films were incorporated with CS filler loading at 10phr, 20phr, 30phr, 40phr and 50phr.
   ii. Melt flow index (MFI) test was conducted to ensure the flow index within the range of LDPE resin for ease of extrusion blown film process. Blown film machine was used to produce the LDPE/UCS and LDPE/TCS composite films

3. Characterization and analyzing of all samples

   i. The CS filler were characterized by using Fourier transform infrared (FTIR) to analyse the existence of functional groups in the UCS and TCS filler.

ii. Tensile test was carried out to determine the tensile properties such as tensile strength, elongation at break and Young's modulus.
iii. Scanning electron microscopy (SEM) analysis was carried out to study the microstructure of polymer matrix and fillers by using the tensile test specimen.
iv. Thermal properties analysis was carried out by using thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC).
v. Assessment of water vapour transmission rate test was carried out to evaluate the physical properties of the composite films.
vi. Data analysis

REFERENCES

Abdolmohammadi, S., Siyamak, S., Ibrahim, N.A., Yunus, W.M.Z.W., Rahman, M.Z.A., Azizi, S. and Fatehi, A. (2012). Enhancement of Mechanical And Thermal Properties of Polycaprolactone/Chitosan Blend by Calcium Carbonate Nanoparticles. *International journal of molecular sciences*, 13(4), pp.4508-4522.

Adeosun, S.O., Usman, M.A., Akpan, E.I. and Dibie, W.I. (2014). Characterization of LDPE Reinforced With Calcium Carbonate—Fly Ash Hybrid Filler.*Journal of Minerals and Materials Characterization and Engineering*, 2 (04), 334.

Alma, H. (2014). Natural Fibre Composites : Materials, Processes and Properties. Almaya, A. and Aburub, A. (2008). Effect of Particle Size On Compaction of Materials With Different Deformation Mechanisms With and Without Lubricants. *AAPS Pharm Sci Tech*. 9, 414–418.

Ammala, A., Bateman, S., Dean, K., Petinakis, E., Sangwan, P., Wong, S.(2011). An Overview of Degradable and Biodegradable Polyolefins. *Progress in Polymer Science*. 36(8), 1015-1049.

Annepu, R. K. (2012). *Sustainable Solid Waste Management in India*. Columbia University. Master of Science, Columbia University, New York.

Arrakhiz, F.Z., Achaby, M.El., Malha, M., Bensalah, M.O., Fassi-Fehri, O., Bouhfid, R., Benmoussa, K. and Qaiss, A. (2013). Mechanical And Thermal Properties of Natural Fibers Reinforced Polymer Composites: Doum/Low Density Polyethylene. *Materials and Design*. 43, 200–205.

Banat, R., and Fares M.M. (2015). Thermo-gravimetric Stability of High Density Polyethylene Composite Filled with Olive Shell Flour. *American Journalof Polymer Science*. 5(3), 65-74.

Bastide, S., Binda, N. and Crespy, A. (1998). Mechanical Behaviour of Polypropylene Composites Containing Fine Mineral Filler And Effect of Filler Surface Treatment. *Composites Science and Technology*. 3538, 747–752. Bikiaris, D., and Panayiotou, C. (1998). LDPE/Starch Blends Compatibilized with PE-g MA Copolymers. *Journal of Applied Polymer Science*. 70(8), 1503-1521.

Borghei, M., Karbassi, A., khoramnejadian, S., Oromiehie, A., and Javid, A. H. (2010). Microbial Biodegradable Potato Starch Based Low Density Polyethylene. *African Journal of Biotechnology*. 9(26), 4075-4080.

Briston, J. H. (1974). *Plastics Films*. London: Iliffe Books

Buasri, A., Chaiyut, N., Loryuenyong, V., Worawanitchaphong, P. and Trongyong, S., (2013). Calcium Oxide Derived From Waste Shells of Mussel, Cockle, And Scallop As The Heterogeneous Catalyst For Biodiesel Production. *The Scientific World Journal*.

Cardinaud, R. and McNally, T. (2013). Localization of MWCNTs in PET/LDPE Blends. *European Polymer Journal*. 49, 1287–1297.

De La Orden, M.U., Sanchez, C.G., Quesada, M.G. and Urreaga, J.M. (2010). Effect Of Different Coupling Agents On The Browning of Cellulose-Polypropylene Composites During Melt Processing. *Polymer Degradation and Stability*. 95, 201–206.

Deng, C., Zhao, J., Deng, C.L., Lv, Q., Chen, L. and Whang, Y.Z. (2014). Effect of Two Types of Iron MMTs on The Flame Retardation of LDPE Composite. *Polymer Degradation and Stability*. 103, 1–10.

Deshmukh, G. S., Pathak, S. U., Peshwe, D. R., and Ekhe, J. D. (2010). Effect of Uncoated Calcium Carbonate and Stearic Acid Coated Calcium Carbonate On Mechanical, Thermal, and Structural Properties of Poly(butylene terephthalate) (PBT) / Calcium Carbonate Composite. *Indian Academy Sciences*. 33, 277-284.

Doufnoune, R., Haddaoui, N. and Riahi, F. (2008). The Effects of Coupling Agents On The Mechanical, Rheological And Thermal Properties of Calcium Carbonate Filled LDPE Compatibilized With Maleic Anhydride-g-LDPE (PartII). *International Journal of Polymeric Materials*, 57(7), pp.690-708.

Friedrich, K., Zhang, Z. and Schlarb, A.K. (2005). Effects of Various Fillers On The Sliding Wear of Polymer Composites. *Composites Science and Technology*. 65,2329–2343.

Fombuena, V., Bernardi, L., Fenollar, O., Boronat, T. and Balart, R. (2014). Characterization of Green Composites From Biobased Epoxy Matrices And Bio Fillers Derived From Seashell Wastes. *Materials & Design*, 57, pp.168-174.

Ghavidel, A. K., Shabgard, M., Biglari, H. (2006). Microscope And Mechanical Properties Of Semi-Crystalline And Amorphous Polymeric Parts Produced By Laser Cutting. *Journal Of Applied Polymer Science*. 133 (44)

Gulmine, J. V., Janissek, P.R., Hesie, H.M. and Akcelrud, L. (2002). Polyethylene Characterization by FTIR. *Polymer Testing*. 21, 557–563.

Gupta, A. P., Kumar, V. and Sharma, M. (2010). Formulation and Characterization of Biodegradable Packaging Film Derived from Potato Starch & LDPE Grafted with Maleic Anhydride-LDPE Composition. *Journal of Polymers and the Environment*. 18, 484–491.

Hariharan, M., Varghese, N., Cherian, A.B. and Paul, J. (2014). Synthesis and Characterisation of CaCO3 (Calcite) Nano Particles From Cockle Shells Using Chitosan As Precursor. *International Journal of Scientific and Research Publications*. 4(10), 2250-3153.

Hemabarathy, B,M,D and Perimal, E, K. (2014). Mineral and physiochemical evaluation of Cockle shell (Anadara granosa) and other selected Molluscan shell as potential biomaterials. *Sains Malaysiana*, 43(7), 1023-1029.

Hippi, U., Mattila, J., Korhonen, M. and Seppala, J. (2003). Compatibilization of Polyethylene / Aluminum Hydroxide (PE / ATH) And Polyethylene / Magnesium Hydroxide (PE / MH) Composites With Functionalized Polyethylenes. *Polymer*. 44, 1193–1201.

Hoque, M.E., Shehryar, M. and Nurul Islam, K.M. (2013). Processing And Characterization of Cockle Shell Calcium Carbonate (CaCO3) Bioceramic ForPotential Application In Bone Tissue Engineering. *J Material Sci Eng*, 2(4), 132.

Hussein, A., Sultan, A. and Matoq, Q.A. (2011). Mechanical Behaviour of Low Density Polyethylene/Shrimp Shells Composite. *Journal of Basrah Researches Sciences*. 37, 3.

Islam, K. N., Bakar, M. Z., Noordin, M., Hussein, M. Z. and Rahman, N. S. (2011). Characterisation of Calcium Carbonate And Its Polymorphs From Cockle Shells (Anadara Granosa). *Powder Technology*. 213, 188–191

Jeong, S. B., Yang, Y.C., Chae, Y-B. and Kim, B.G. (2009). Characteristics of the Treated Ground Calcium Carbonate Powder with Stearic Acid Using the Dry Process Coating System. *Materials Transactions*. 50, 409–414.

Ju, S., Zhang, H., Chen, M., Zhang, C., Chen, X., and Zhang, Z. (2014). Improved Electrical Insulating Properties of LDPE Based Nanocomposite: Effect of Surface Modification of Magnesia Nanoparticles. *Composites Part A: Applied Science and Manufacturing*. 66, 183–192.

Kamba, A. S., Ismail, M., Ibrahim, T. A. T., Zakaria, Z. A. B. (2013). Synthesis And Characterization Of Calcium Carbonate Aragonite Nanocrystals From Cockle Shell Powder (Anadara Granosa).

Kato T. (2000).Polymer/Calcium Carbonate Layered Thin-Film Composites. *Advanced Materials*, 12(20), 1543-1546.

Kemal, I., Whittle, A., Burford, R., Vodenitcharova, T. and Hoffman, M. (2013). Toughening of Unmodified Polyvinylchloride Through The Addition of Nanoparticulate Calcium Carbonate And Titanate Coupling Agent. *Journal of Applied Polymer Science*. 127, 2339–2353.

Kong, J.S., Lee, D.J. and Kim, H.D. (2001). Surface Modification of Low-Density Polyethylene (LDPE) Film And Improvement of Adhesion Between Evaporated Copper Metal Film And LDPE. *Journal of Applied Polymer Science*. 82, 1677 -1690.

Kumar, S. and S. A. Gaikwad (2004). Municipal Solid Waste Management in Indian Urban Centres: An Approach for Betterment. In K. R. Gupta. *Urban Development Debates in the New Millennium* (100-111)

Kwon, S., Kim, K.J., Kim, H., Kundu, P.P., Kim, T.J., Lee, Y.K., Lee, B.H. and Choe, S. (2002). Tensile Property And Interfacial Dewetting In The Calcite Filled HDPE, LDPE and LLDPE Composites. *Polymer*, 43(25), pp. 6901-6909.

Kyaw, B.M., Champakalakshmi, R., Sakharkar, M.K., Lim, C.S. and Sakharkar, K.R. (2012). Biodegradation of Low Density Polythene (LDPE) by Pseudomonas Species. *Indian Journal of Microbiology*. 52, 411–419.

Landau, L. (2010). Introduction To Industrial Polyethylene. *Journal of Experimental and Theoretical Physics*.

Lafleur, P. G. and Vergnes, B. (2014). Production of Films and Sheets. *Polymer Extrusion* (245-303)

Li, H.Y., Tan, Y.Q., Zhang, L., Zhang, Y.X., Song, Y.H., Ye, Y. and Xia, M.S. (2012). Bio-Filler From Waste Shellfish Shell: Preparation, Characterization, And Its Effect On The Mechanical Properties On Polypropylene Composites. *Journal of hazardous materials*, 217, pp.256-262.

Liu, P., Zhao, M. and Guo, J. (2006). Thermal Stabilities of Poly (vinylchloride) /Calcium Carbonate (PVC/CaCO3) Composites. *Journal of Macromolecular Science*, Part B: Physics, 45(6), pp.1135-1140.

Madera-Santana, T.J., Soto Valdez, H. and Richardson, M.O.W. (2013). Influence of Surface Treatments On The Physicochemical Properties of Short Sisal Fibers: Ethylene Vinyl Acetate Composites. *Polymer Engineering & Science*. 53, 59 -68.

Madera-Santana, T.J., Robledo, D., Azamar, J.A., Rios-Soberanis, C.R., and Freile Pelegrin, Y. (2010). Preparation and Characterization of Low-Density Polyethylene-Agar Biocomposites: Torque-Rheological, Mechanical, Thermal and Morphological Properties. *Polymer Engineering & Science*. 1 - 7

Mareri, P., Bastide, S., Binda, N., and Crespy, A. (1998). Mechanical Behaviour of Polypropylene Composites Containing Fine Mineral Filler: Effect of Filler Surface Treatment. *Composites Science And Technology*. 58, 747-752.

Mark, J. E. (Ed.). (1999). *Polymer Data Handbook. United Kingdom*: Oxford University Press.

Marsh, K. and Bugusu, B. (2007). Food Packaging-Roles, Materials, and Environmental Issues. *Journal of Food Science*. 72(3), 39-55.

McKenzie, M. D. (1999). The Impact of Exchange Rate Volatility on International Trade Flows. *Journal of Economic Surveys*. 13(1), 71-106.

Michael Rubinsstein., Ralph, H.C. *Polymer Physics Book*.

Mohamed, M., Yusup, S. and Maitra, S. (2012). Decomposition Study of Calcium Carboante in Cockle Shell. *Journal of Enginnering Science And Technology*. 7, 1–10.

Morse, J.W., and Arvidson, R.S., Luttge, A. (2007). Calcium Carbonate and Dissolution. *Chemical Reviews*. 107, 342-381.

Morton-Jones, D. (1990). *Polymer Processing*.

Mousa, A., Heinrich, G., and Wagenknecht, U. (2010). Thermoplastic Composite Based on Renewable Natural Resources: Unplasticized PVC/Olive Husk. International *Journal of Polymeric Materials and Polymeric Biomaterials*. 59(11), 843-853.

Nakamura, E.M., Cordi, L., Almeida, G.S.G., Duran, N. and Mei, L.H.I. (2005). Study And Development of LDPE/Starch Partially Biodegradable Compounds. *Journal of Materials Processing Technology*. 162-163, 236–241.

Nasir, R.M. (2013). Lubricated Abrasion Study of Bio-Fibre (Paddy Straw) and Cockle Shell Using Pin-On-Disk Method. *Procedia Engineering*. 68, 116-122.

Nwanonenyi, S.C., Obidiegwu, M.U. and Onuegbu, G.C. (2013). Effects of Particle Sizes , Filler Contents and Compatibilization On The Properties Of Linear Low Density Polyethylene Filled Periwinkle Shell Powder. *The International Journal of Enginnering And Science* (IJES). 2, 1–8.

Osborn, K. R. and Jenkins, W. A. (1992). *Plastic Films*: Technology and Packaging Applications. New York: CRC Press.

Osman, M.A., Atallah, A. and Suter, U.W. (2004). Influence of Excessive Filler Coating On The Tensile Properties of LDPE-Calcium Carbonate Composites. *Polymer*. 45, 1177–1183.

Othman, N., Ismail, H. and Mariatti, M., (2006). Effect of Compatibilisers On Mechanical and Thermal Properties of Bentonite Filled Polypropylene Composites. *Polymer Degradation and Stability*. 91, 1761-1774.

Pandiyaraj, K.N., Deshmukh, R.R., Ruzybayej, I., Shah, S.I., Su, P.G., Halleluyah, J.M. and Halim, A.S. (2014). Influence of Non-Thermal Plasma Forming Gases On Improvement of Surface Properties of Low Density Polyethylene (LDPE). *Applied Surface Science*. 307, 109–119.

Peacock, A.J. (2000). *Handbook Of Polyethylene: Structures, Properties And Application*, 224-225.

Pedroso, A.G. and Rosa, D.S. (2005). Mechanical, Thermal And Morphological Characterization of Recycled LDPE/Corn Starch Blends. *Carbohydrate Polymers*. 59, 1–9.

Premphet, K. and Horanont, P. (1999). Influence of Stearic Acid Treatment of Filler Particles on the Structure and Properties of Ternary-Phase. *Journal of Applied Polymer Science*. 74, 3445–3454.

Premraj, R. and Doble, M. (2005). Biodegradation of Polymers. *Indian Journal of Biotechnology*. 4, 186-193.

Rudnik, E. (2008). *Compostable Polymer Materials*. UK: Elsevier.

Rusnah, M., Reusmaazran, MMY. and Yusof, A. (2014). Hydroxyapatite From Cockle Shell As a Potential Biomaterial For Bone Graft. *Official Journal of TESMA*. 3, 52–55.

Salmah, H., Lim B. Y., and The P.L. (2011). Rheological and Thermal Properties of Palm Kernel Shell – Filled Low Density Polyethylene Composite With Acrylic Acid. *Journal of Thermoplastic Composite Materials*, 1-13.

Selke, S. E. M., Culter, J. D., and Hernandez, R. J. (2004). *Plastics Packaging Properties, Processing, Applications, and Regulations*. Munich, Hanser.

Shanks, R. (2003). *Handbook of Plastic Films*. Technology of Polyolefin Film Production. 5-40.

Shnawa, H.A., Abdulah, N.A. and Mohamad, F.J. (2011). Thermal Properties of Low Density Polyethylene with Oyster Shell Composite : DSC Study. *World Applied Sciences Journal*. 14, 1730–1733.

Shuhadah. S. and Supri, A.G. (2009). LDPE-Isophthalic Acid-Modified Egg Shell Powder. *Journal of Physical Sciences*. 20, 87–98.

Sichina (2000). DSC as Problem Solving Tool: Measurement of Percent Crystallinity of Thermoplastics. *International Marketing Manager*.

Sirin, K., Balcan, M. and Doğan, F. (2012). The Influence of Filler Component on Mechanical Properties And Thermal Analysis of PP-LDPE and PP LLDPE/DAP Ternary Composites. *INTECH*. 345 – 354.

Strong, A. B. (2000). *PLASTICS: Materials and Processing (2nd ed.)*. New Jersey: Prentice Hall, Inc.

Tang, Y., Xia, X., Wang, Y. and Xie, C. (2011). Study on The Mechanical Properties of Cu/LDPE Composite IUDs. *Contraception*. 83, 255–62.

Thumsorn, S., Yamada, K., Leong, Y.W. and Hamada, H. (2011). Development of Cockle Shell-Derived CaCO3 For Flame Retardancy of Recycled PET/Recycled PP Blend. *Materials Sciences and Applications*, 2(02), p.59.

Titow, W. V., 1990. *PVC Plastics Properties, Processing, and Applications*. New York: Elsevier Applied Science Publishers.

Wang, W. Y., Wang, G. Q., Zeng, X. F., Shao, L., and Chen, J. F. (2007). Preparation And Characterization Of Calcium Carbonate/ Low Density Polyethylene Nanocomposite. *Journal Of Applied Polymer Science*. 107, 3609-3614.

Wellett, J.L. (1994). Mechanical Properties of LDPE/Granular Starch Composites. *Journal Applied Polymer Science*. 54, 1685-1695.

Xia, M.S., Yao, Z.T., Ge, L.Q., Chen, T. and Li, H.Y. (2015). A Potential Bio-Filler: The substitution Effect of Furfural Modified Clam Shell For Carbonate Calcium In Polypropylene. *Journal of Composite Materials*, 49(7), pp.807 -816.

Yao, Z., Xia, M., Li, H., Chen, T., Ye, Y. and Zheng, H (2014). Bivalve Shell: Not An Abundant Useless Waste But A Functional And Versatile Biomaterial. *Critical Reviews in Environmental Science and Technology*, 44(22), pp.2502-2530.