

**BIODEGRADATION AND RECYCLING OF POLYETHYLENE INTO COMPOSITE
BUILDING MATERIALS**



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By:

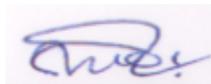
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Dedication

I sincerely, dedicate this thesis to my late father (Azeko Salifu Apeningo Asaberiko), whose immeasurable efforts in my life and academia cannot be overlooked. May Almighty Allah reward and grant him a good place in heaven and the hereafter. Amen!!

Abstract

This work presents the results of experimental and theoretical studies of the biodegradation of polyethylene, recycling of polyethylene into strong and tough earth-based composite building materials and the statistical distribution and particle size analysis of the polyethylene composites. *Serratia marcescens subsp. marcescens* and its supernatants are able to biodegrade linear low density polyethylene (LLDPE). The results show that the cell-free extracts degrade LLDPE faster than the bacterium. The mechanisms of degradation are also elucidated using Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC) and Fourier Transform Infra-Red Spectroscopy (FTIR). These methods show that the bacterium and its supernatant both degrade LLDPE. There was also an increase in the concentrations of the carbonyl groups (new peaks) after the microbial degradation of LLDPE. Waste PE can be recycled and used as reinforcement in laterite bricks for sustainable building materials. The bricks are produced with different volume percentages (0-30 volume percent) of PE. The flexural/compressive strengths and fracture toughness values of the composite blocks were compared with those of mortar (produced from river sand and cement). The composite containing 20 vol. % of PE had the best combination of flexural/compressive strength and fracture toughness. The flexural/compressive strengths and fracture toughness values then decreased, respectively, to minimum values for 30 vol. % of PE. The trends in the measured strengths and fracture toughness values are explained using composites and crack bridging models. Different particle sizes of the PE composites were shown to have statistical variations in flexural/compressive strengths and fracture toughness. The statistical variations in the flexural/compressive strengths and fracture toughness are shown to be well characterized by the Weibull distributions.

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Preface

The work carried out in this dissertation is the original property of Salifu Tahiru Azeko. This work was carried out from January 2012 to July 2015 for the fulfillment of the Doctor of Philosophy Degree in Materials Science and Engineering Department at the African University of Science and Technology, Abuja, Nigeria. I was the lead investigator and this work is solely own by me. All major activities including concept formation, data collection, experiments, data analysis as well as manuscript preparation and composition were carried out by me. Dr. Olushola. S. Odusanya was my co-supervisor. He helped me significantly in the early stages of the concept formation as well as editing and proofreading of manuscripts and thesis. Prof. Winston Oluwole Soboyejo was my supervisor. He entirely participated throughout the work especially in concept formation and manuscript composition as well as editing and proofreading of accepted manuscripts and thesis. Prof. Alfred B.O. Soboyejo was part of my committee members and he was actively involved in editing of manuscripts as well as providing useful concepts in the statistical analysis carried out in the work.

Biodegradation and recycling of polyethylene (PE) into composite building materials are presented in this dissertation. Locally available bacterium (*Serratia marcescens marcescens*) was used in biodegrading PE. PE were processed into powders and incorporated into readily available laterite for sustainable building applications. The new composite bricks produced were found to have improved mechanical properties as compared to conventional blocks. The statistical variations in the flexural/compressive strengths and fracture toughness values in the composite are shown to be well characterized by the Weibull distributions.

As at the time this dissertation was submitted, two of its chapters (4 and 5) were published in the journal of materials in civil engineering and the other chapter (3) was under review in the waste and biomass valorization journal.

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Peer Review Publications in PhD Focus

1. **Salifu T. Azeko**, Kabiru Mustapha, Ebenezer Annan, Olushola S. Odusanya and Winston O. Soboyejo. Recycling of Polyethylene into Strong and Tough Earth-Based Composite Building Materials. J. Mater. Civ. Eng., 10.1061/(ASCE)MT.1943-5533.0001385, 04015104.
2. **Salifu T. Azeko**, K. Mustapha, E. Annan, O. S. Odusanya, A.B.O. Soboyejo and W.O. Soboyejo. Statistical Distributions of the Strength and Fracture Toughness of Recycled Polyethylene-Reinforced Laterite Composites. Journal of Materials in Civil Engineering, 2015 (MTENG-3744) (**In press**)
3. K. Mustapha, E. Annan, **Salifu T. Azeko**, M.G. Zebaze Kana and W.O. Soboyejo. Strength and fracture toughness of earth-based natural fiber-reinforced composites. Journal of Composite Materials (2015): 0021998315589769.
4. **S.T. Azeko**, O. S. Odusanya, G.A. Etuk-Udo, S. Dozie-Nwachukwu, K. Malatesta, N. Anuku and W.O. Soboyejo. Biodegradation of Linear Low Density Polyethylene by *Serratia marcescens subsp. marcescens* and Its Cell Free Extracts. Journal of Waste and Biomass Valorization, 2015 (WAVE-D-15-00088) (**In Press**)
5. K. Mustapha, **Salifu T. Azeko**, E. Annan, M.G. Zebaze Kana, Leo Daniel and W.O. Soboyejo. Pull-out Behavior of Natural Fiber From Earth-based Matrices. Journal of Composite materials. (2015) (**Under Review**)

List of Conference Proceedings/Book of Abstract

1. **S. T. Azeko**, E. Annan, K. Mustapha, O.S. Odusanya, N. Anuku and W.O. Soboyejo. Strength and Fracture of Polyethylene-Reinforced Laterite for Building Materials. The 7th International Conference of the Africa Materials Research Society, Addis Ababa, Ethiopia, December 8-13, 2013.
2. **S. T. Azeko**, E. Annan, K. Mustapha, O.S. Odusanya and W.O. Soboyejo. Recycling of Waste Polyethylene as Reinforcement for Building Materials. The 12th Annual Proceedings of the Materials Science and Technology Society of Nigeria (NIMACON), Vol II, Nov 25-29, 2013, Abuja, Nigeria.
3. **S.T. Azeko**, O. S. Odusanya and W.O. Soboyejo. Bacterial Degradation of Low Density Polyethylene. The 12th Annual Proceedings of the Materials Science and Technology Society of Nigeria (NIMACON), Vol II, Nov 25-29, 2013, Abuja, Nigeria.
4. **S.T. Azeko**, K. Mustapha and W.O. Soboyejo. . Strength and Fracture of Polyethylene-Reinforced Laterite for Building Materials. The 12th Annual Proceedings of the Materials Science and Technology Society of Nigeria (NIMACON), Vol II, Nov 25-29, 2013, Abuja, Nigeria.
5. E. Annan, K. Mustapha, **S. T. Azeko**, O.S. Odusanya, K. Malatesta and W.O. Soboyejo. Flow Statistics and the Scaling of Ceramic Water Filters. The 12th Annual Proceedings of the Materials Science and Technology Society of Nigeria (NIMACON), Vol II, Nov 25-29, 2013, Abuja, Nigeria.
6. K. Mustapha, E. Annan, **S. T. Azeko**, M.G. Zebaze Kana and W.O. Soboyejo. Fracture Toughness and Resistance-Curve Behavior of Earth-Based and Natural Fiber-Reinforced Composites. The 12th Annual Proceedings of the Materials Science and Technology Society of Nigeria (NIMACON), Vol II, Nov 25-29, 2013, Abuja, Nigeria.
7. S. A Mensah, D. Dodoo-Arhin, E. K. Arthur and **S. T. Azeko**. Synthetic Coarse Aggregates as A Substitute in Conventioanal Concrete: A Case Study Of Used Car Tyres. The 12th Annual Proceedings of the Materials Science and Technology Society of Nigeria (NIMACON), Vol II, Nov 25-29, 2013, Abuja, Nigeria.

8. E. K. Arthur, J. D. Obayemi , **S. T. Azeko** , Y. Danyuo. Development of Aqueous Processing Routes for the Removal of Aluminum Impurity from Metallurgical-Grade Silicon (Mg-Si). The 12th Annual Proceedings of the Materials Science and Technology Society of Nigeria (NIMACON), Vol II, Nov 25-29, 2013, Abuja, Nigeria

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CHAPTER ONE

1.0 Introduction

1.1 Background

Plastics are synthetic organic heteroatomic polymers which originate from oil, coal and natural gas [1, 2]. Plastics are generally non-biodegradable in the presence of enzymes or microbes [3] and their pile up leads to prolonged environmental changes [4]. This has led to environmental concerns as approximately 140 million tons of man-made polymers produced worldwide are found in food packaging, detergents, clothing, shelter, transportation and chemical substances with an increasing annual rate of 12% [5, 6]. These plastics include polyethylene (LLPE, LDPE, MDPE and HDPE), polypropylene (PP), polystyrene (PS), Polyvinyl Chloride (PVC) and polyethylene terephthalate (PET) [5, 7, 8, 9].

Plastics have been used extensively due to their attractive combination of stability [10], thermal properties [6] and mechanical properties [11]. PE consumption is the largest among polymers produced worldwide, recording a total of over 90 million metric tons per annum (The Plastics Portal). The high production of PE hinders the implementation of an efficient disposal system [6]. However, PE can be degraded by chemical, thermal, photo and biological means. The current mechanisms that are used in the biodegradation of PE include hydro-degradation [7] and oxo-biodegradation [7, 12]. Hydro-biodegradation involves the degradation of PE plastics by the decomposition of water molecules into protons and hydroxide anions, while oxo-

biodegradation produces molecular fragments and smaller molecules which are converted by microorganisms into carbon dioxide, water and biomass [13].

Recent literature [6, 13,14,15,16] have shown that microbes, such as *Rhodococcus spp*, *Penicillium simplicissimum*, *Brevibacillus*, *Fusarium sp. AF4* and *Pseudomonas spp* are able to biodegrade PE, in particular Low Density Polyethylene (LDPE). The microbes use LDPE as sole carbon and energy source. Plants and plant-based microorganisms have also been shown to degrade polyethylene [17]. The crystalline structure, molecular weight and mechanical properties of polyethylene are initially altered, prior to microbial biodegradation [18].

Before the colonization of Africa, most of the houses in Africa were constructed from clay and silt [19]. However, the shrinkage of clays and the effects of mechanical loads due to wind loading can induce cracking in such structures [20]. Cracking can also be exacerbated by the effects of thermal cycling and the environment [21, 22]. Similar failure phenomena have been observed in cement-based structures that have been used more recently across the world [23]. However cement production is associated with 5% of the global CO₂ emission [24]. There is, therefore, a need to reduce the amount of cement that is used in building materials.

Alternatives to cement include: laterite [19, 25, 26]; recycled materials such as blast furnace slag [27] and polyethylene [28]. Laterites are products of the chemical weathering of naturally occurring rocks [26]. The weathering process may take several of years before the soil (a type of clay) is produced [26]. The soil formed is usually rusty-red or reddish brown, due to the presence of iron in the oxides [26]. It is often found in tropical regions, especially in wet and hot areas. Laterites have been recommended for the construction of roads and dams, as well as applications as fillers for soil reclamation [29]. The uniform distribution and availability of well graded

particle sizes of laterites, as well as their compressibility enable the moulding of bricks with improved mechanical properties [19]. However, the use of laterites alone in bricks does not provide the required strengths for load-bearing structures [25]. There is, therefore a need to mix them with binders, especially cement or lime, to enhance their mechanical properties [25]. However, such binders (cements) are relatively expensive, approximately (4 cents per pound), which increases the cost of concrete buildings across the world.

Hence in an effort to reduce the cost of building materials, significant efforts have been made to replace cement with industrial and agricultural waste materials [30]. Industrial waste materials include blast furnace slag [27], while agricultural waste materials include natural fibres from sisal [31, 32, 33], banana trunk [34], eucalyptus trees [35], sugar cane bagasse [36, 37, 38] and millet [39]. These have all been shown to have improved strengths [40, 41, 42] and fracture toughness [40, 41, 42]. Composite theories [43, 44] and crack-tip shielding concepts have also been used, respectively, to explain the observed improvements in strength and fracture toughness of the resulting composites. In contrast, there have been relatively few efforts to incorporate plastics into blocks, although plastics are often recycled into pipelines that are often used in buildings. Such recycling of plastics could facilitate the reduction in the cost of building blocks that are produced from laterite and concrete. They could also improve the strength and fracture resistance of laterite and cement matrix composites.

The mechanical properties of composites are known to depend on the volume fraction [45] of their constituents, as well as the reinforcement shapes and orientations [46, 47, 48]. Composites also exhibit statistical variations in their mechanical properties [49], which are often

due to differences in the reinforcement shapes, sizes and distributions [48, 49]. However, most composites contain synthetic fibers and particulate reinforcements, which are often too expensive for widespread applications in most building materials [50]. There is, therefore, a need for lower cost composites that can strengthen and toughen building materials without inducing excessive variations in their mechanical properties. Within this context, natural fiber-reinforced cement matrix composites have been developed for applications in sustainable buildings [51]. These include; cement matrix composites reinforced with natural fibers such as sisal [52], eucalyptus fibers [53], banana trunk fibers [54] and bamboo fibers [55, 56].

Ductile phase reinforcements, such as steel fibers [57, 58] and polyethylene particles [58] have also been incorporated into concrete matrices [57, 58] and laterite/concrete matrices [59] in recent years. Although these have been shown to strengthen and toughen the resulting composites [59], the steel composites are relatively expensive due to the processing costs associated with the production of steel fibers [60]. In contrast, the use of recycled polyethylene reinforcements has been shown to offer a low cost alternative to the development of robust composite building materials with lower cost than steel-reinforced composites.

As is the case for most engineering composites, the strengths and fracture toughness values of construction composites are expected to exhibit significant statistical variations. These are due to differences in particle size/shape, and the variations in defect/crack sizes that are introduced during materials processing and manufacturing. Such variations have been characterized by Weibull distributions (weak link statistics) [61, 62], Gaussian (normal) distributions [63, 64], log-normal distributions [65] and entropy functions [66]. However, although these techniques have been applied extensively to the study of brittle ceramic matrix composites, they are yet to

be applied to the study of concrete or, earth-based composites for applications in sustainable buildings.

The poor durability performance and associated short service life of earth-based bricks reduces the sustainable use of the material [67]. A review of existing work has revealed the lack of a systematic approach to fabricating compressed earth-based bricks that recognizes the inter-connection between the bricks structural performance over the service life of the resulting building system and sustainability [68]. According to Conway [69], it should be borne in mind that the most important property of a brick is not its strength in most circumstances but its durability or weather resistance. Therefore, erosion resistance is the main criterion in tropical and subtropical climates, as rain and wind are restricting climate factors. Finding minimum but sufficient strength and porosity of bricks which permit them to resist their erosion by rain and/or wind is another reason that justifies our study.

1.2 Problems of Plastic Waste

PE consumption is the largest among polymers produced worldwide, recording a total of over 90 million metric tons per annum (The Plastics Portal). The high production of PE hinders the implementation of an efficient disposal system. However, PE can be degraded by chemical, thermal and photo methods. The above methods are relatively expensive and not environmentally friendly. Hence, there is the need to use biological methods that are relatively inexpensive and environmentally friendly.

Successfully wealth generation systems have taken advantage of abundant materials found in the environment, with little or no competing use for them. Plastics qualify for such

applications and their incorporation into composite building materials would provide for them a steady use that would mop up their pile up in the environment. Most composites contain synthetic fibers and particulate reinforcements, which are often too expensive for widespread applications in most building materials. Therefore, there is the need to use recycled PE plastic bags in reinforcing composite building materials. PE is recycled into particles that are mixed with laterite and cement matrices to produce laterite/cement matrix composites.

1.3 Unresolved Research Questions

However, although prior studies have attempted to examine the role of various microorganisms in the biodegradation process, the biodegradation of PE is not yet fully understood. Furthermore, there has been no prior study of the mechanisms of biodegradation of PE by the soil-based bacterium, *Serratia marcescens* subsp. *marcescens* (*S. marcescens marcescens*).

There have been relatively few efforts to incorporate plastics into blocks, although plastics are often recycled into pipelines that are often used in buildings. Such recycling of plastics could facilitate the reduction in the cost of building blocks that are produced from laterite and concrete.

Also, the statistical variations in the mechanical properties (compressive strength, flexural strength and fracture toughness) of sustainable building materials need to be addressed.

1.4 Primary Goals

There have been a lot of plastic generations worldwide. These plastic produced from industries becomes readily available on the environment as wastes, and these wastes pollute the environment. This thereby, causes water pollution, fills up landfills, and reduces soil fertility as

well as posing dangers to animal lives. With regard to this, the current study is focus on reducing polyethylene (PE) wastes on the environment. The primary goals are to reduce some of these PE wastes by biological means as well as recycling the waste PE as reinforcement into earth-based composites used in sustainable building applications. The methods used in this study are cost effective and environmental friendly as compared to other techniques used in the reduction of plastics wastes.

1.5 Scope of Work

The main objective of this work is to reduce the generation of PE wastes pileups on the environment through biological means and also recycling into earth-based composites for sustainable building applications. The following procedures were used in the study to ensure that the primary goals of the work were achieved:

- Linear Low Density Polyethylene (LLDPE) were collected, washed and processed into powder. The isolation of the bacterium, *Serratia marcescens*, *marcescens* was achieved through the culture enrichment techniques. The powdered PE and the supernatants as well as the bacterium were inoculated for one and three months, respectively. Fourier Transform Infra-red was used as an evidence of biodegradation on the PE powders for both the supernatant and the bacterium.
- The rule of mixtures was applied in the processing of the earth-based composites. The PE powder was mixed in volume percentages of 10, 20 and 30 with the laterite matrix and cement. The results clearly showed an increase in flexural and compressive strengths as well as the fracture toughness values of the resulting earth-based composites in 20

vol. % of PE particles as compared to 10 vol. % and 30 vol. % of PE. Small scale and large scale bridging models were used to predict the trend in the toughening behavior in the earth-based composites.

- The Gaussian/Normal and the three parameter Weibull distributions were used to predict the statistical variations in strengths and particles size of the resulting earth-based composites. The statistical variations in the particles size, flexural/compressive strengths as well as the fracture toughness values were shown to be well characterized by the Weibull distribution.
- This thesis work is recommended in the fields of bioremediation and the building and construction industries. The study of the environmental degradation of the earth-based composites will be elucidated using erosion test such as the bulletin 5 spraying test. These are clearly some of the challenges for future work.

1.6 References

- [1] Seymour, R. B., 1989. Polymer science before & after 1899: notable developments during the lifetime of Maurtis Dekker, J. Macromol Sci, Pure Appl Chem 26, 1023-1032.
- [2] Scott, G., 1999. Polymers in modern life; Polymers and the Environment, the Royal Society of Chemistry, Cambridge.
- [3] Mueller, R. J., 2006. Biological degradation of synthetic polyesters-enzymes as potential catalysts for polyester recycling, Proc Biochem 41, 2124-8.

- [4] Sivan, A., 2011. New perspectives in plastic biodegradation, *Curr Opin Biotechnol* 22,422-426.
- [5] Shah, A.A., Hasan, F., Hameed, A., Ahmed, S., 2008. Biological degradation of plastics: A comprehensive review, *Biotechnology advances* 26, 246-265.
- [6] Nanda, S., Sahu, S.S., 2010. Biodegradability of polyethylene by *Brevibacillus*, *Pseudomonas*, and *Rhodococcus* spp. *New York Science Journal* 3(7), 95-98.
- [7] Rivard, C., Moens, L., Roberts, K., Brigham, J., Kelley, S., 1995. Starch esters as biodegradable plastics: effects of ester group chain length and degree of substitution on anaerobic biodegradation, *Enzym Microb Technol* 17:848-852.
- [8] Zheng, Y., Yanful, E. K., 2005. A review of plastic waste biodegradation, *Critical Reviews in Biotechnology* 25, 243–250.
- [9] Sangale, M. K., Shanawaz, M., Ade, A. B., 2012. A Review on Biodegradation of polythene: the Microbial Approach, *J. Bioremed Biodeg* 3,164
- [10] Singh B., Sharma N., 2008. Mechanistic implications of plastic degradation, polymer degradation and stability 93(3), 561-584.
- [11] Bonhomme, S., Cuer, A., Delort, A.M., Lemaire, J., Sancelme, M., Scott, G., 2003. Environmental biodegradation of polyethylene., *Polym Degrad Stab* 81, 441–52.

- [12] Witt, U., Einig, T., Yamamoto, M., Kleeberg I., Deckwer, W. D., Müller, R.J., 2001. Biodegradation of aliphatic–aromatic copolyesters: evaluation of the final biodegradability and ecotoxicological impact of degradation intermediates. *Chemosphere* 44, 289–99.
- [13] Hoffmann J, Reznicková I, Kozáková J, Ružicka J, Alexy P, Bakoš D, Precnerová L.,2003. Assessing biodegradability of plastic based on poly(vinyl alcohol) and protein wastes. *Polym Degrad Stab* 79 511-519
- [14] Kawai F., 1995. Breakdown of plastics and polymers by microorganisms. *Adv Biochem Eng Biotechnol* 52,151–94.
- [15] Hadad, D., Geresh, S., Sivan, A., 2005. Biodegradation of polyethylene by thermophilic bacterium *Brevibacillus borstelensis*. *J. Appl Microbiol* 98, 1093-1100.
- [16] Mahalakshmi, V., Siddiq, A., Andrew, S.N., 2012. Analysis of polyethylene degrading potentials of microorganisms isolated from compost soil, *International Journal of Pharmaceutical & Biological Archives* 3(5), 1190-1196.
- [17] Aamer A.S, Fariha Hasan A.H, and Javed I.A., 2009. Isolation of *Fusarium* sp. AF4 from sewage sludge, with the ability to adhere the surface of 45 polyethylene. *African. Journal Microbiology Research* 3 10, 658-663.
- [18] Bikiaris D, Aburto J, Alric I, Borredon E, Botev M, Betchev C., 1999. Mechanical properties and biodegradability of LDPE blends with fatty-acid esters of amylase and starch. *J Appl.Polym.Sci* 71 1089-100.

- [19] James, A I., 2009. Study of compressive strengths of laterite-cement mixes as a building material. *AU .J.T* 13(2) 114-120.
- [20] Liu, Y.Y., McCabe, M.F., Evans, J.P., van Dijk, A.I.J.M., de Jeu, R. A. M. and Su, H., 2010. Influence of cracking clays on satellite observed and model simulated soil moisture. *Hydrol. Earth Syst. Sci. Discuss.*, 7, 907–927.
- [21] Sultan, N., Delage, P. and Cui, Y.J., 2002. Temperature effects on the volume change behavior of Boom clay. *Engineering Geology*, 64: 135-145
- [22] Robinet, J.C., Rahbaou, A., Plas, F. and Lebon, P., 1996. A constitutive thermomechanical model for saturated clays. *Engineering Geology*, 41(1):145-169.
- [23] Hoskovs, S., Kapickova, O., Trtik, K., Vodak, F., 2001. Effect of Thermal Cycling on the Strength and Texture of Concrete for Nuclear Safety Structures. *Acta Polytechnica* Vol. 41 No. 2.
- [24] Ernst, W., Lynn, P., Nathan, M., Chris H., and Leticia, O.M., 2001. Carbondioxide emissions from the global cement industry. *Annu. Rev. Energy Environ* 26:303–29
- [25] Okeke, O.C and Ekere, J.T., 2012. Effects of variations of sand and laterite mixtures on the comprehensive strength of cement-stabilized laterite bricks. *Journal of Applied and the Environment*, vol. 3, pp 49-53, 2012.

- [26] Patrick, N.L., Uphie, F., Chinje, M., Elie, K., and Arlin, B.T., 2011. Laterite Based Stabilized Products for Sustainable Building Applications in Tropical Countries: Review and Prospects for the Case of Cameroon. *Sustainability*, 3, 293-305; doi:10.3390/su3010293
- [27] Prasanta, K.P., Alok, S., Anand M.N., 2013. Processing, characterization, and wear analysis of short glass fiber-reinforced polypropylene composites filled with blast furnace slag. *Journal of Thermoplastic Composite Materials*; doi:10.1177/0892705713486142.
- [28] de Carvalho Neto, A.G.V., Ganzerli, T.A., Cardozo, A.L., Fávaro, S.L., Pereira, A.G.B., Giroto, E.M. and Radovanovic, E., 2014. Development of composites based on recycled polyethylene/sugarcane bagasse fibers. *Polym Compos*, 35: 768–774. doi: 10.1002/pc.22720
- [29] Gidigas, M. A., 1976. *Laterite soil Engineering*, Elsevier Scientific Publication, New York.
- [30] Zaiton, Y., Nadia, F.M., Ahmad Faiz A.R., Zainab, Z., Mohamad, R.M.R., Husnul N.H., Natash, a K., Mohamat N.M.N., Wan Faizal, I.W.A., Nurul A.A.R., Suryani, A., 2010. Comparison Study on Oil Palm Trunk and Oil Palm Fruit Bunch Fibre Reinforced Laterite Bricks. *Canadian Centre of Science and Education*, Vol. 4, No. 7
- [31] Yan, Li, Yiu-Wing, M., Lin, Ye., 2000. Sisal fibre and its composites: a review of recent developments. *Composites science and Technology*, volume 60, issue 11, pages 2037-2055.
- [32] Kuruvilla, J., Romildo, D., Toledo, F., Beena, J., Sabu, T., Laura H. de Carvalho., 1999. A Review on Sisal Fiber Reinforced Polymer Composites. *Revista Brasileira de Engenharia Agrícola e Ambiental*, v.3, n.3, p.367-379.

- [33] Zhong, J.B., Lv, J., Wei, C.,2007. Mechanical properties of sisal fibre reinforced urea-formaldehyde resin composites. *eXPRESS Polymer Letters* Vol.1, No.10 681–687, DOI: 10.3144/expresspolymlett.2007.93.
- [34] Sapuan, S.M., Harun N., Abbas, K.A.,2007. Design and fabrication of a multipurpose table using a composite of epoxy and banana pseudostem fibres. *Journal of Tropical Agriculture* 45 (1-2): 66–68.
- [35] Tonolia, G.H.D., Savastano, H., Fuentec, Jr.b., E., Negroc, C., Blancoc, A., Rocco L.F.A., 2010. Eucalyptus pulp fibres as alternative reinforcement to engineered cement-based composites. *Industrial Crops and Products* 31, 225–232.
- [36] Ghazali, M.J., Azhari, Abdullah, C. H., Omar, S.M.Z., 2008. Characterisation of Natural Fibres (Sugarcane Bagasse) in Cement Composites. *Proceedings of the World Congress on Engineering 2008 Vol II WCE 2008, July 2 - 4, London, U.K.*
- [37] Monteiro, S.N., Rodriquez, R.J.S., De Souza, M.V., 1998. Sugar cane bagasse waste as reinforcement in low cost composites. *Advanced performance materials* 5, 183-191.
- [38] Teixeira, R.S., Tonoli, G.H.D., Santos, S.F., Fiorelli, J., Savastano, H. Jr, Rocco L.F.A., .2012. Extruded Cement Based Composites Reinforced With Sugar Cane Bagasse Fibres. *Key Engineering Materials* Vol. 517, pp 450-457.
- [39] Adegunwa, M.O., Ganiyu, A.A., Bakare, H.A., Adebowale, A.A., 2014. Quality evaluation of composite millet-wheat Chinchin. *Agric. Biol. J. N. Am.*, 5(1): 33-39

- [41] Maleque, M. A., Bela, F. Y., 2007. Mechanical properties study of pseudo-stem banana fiber reinforced epoxy composite. *The Arabian Journal for Science and Engineering*, Volume 32, Number 2B.
- [42] Pavithran, C., Mukherjee, P. S., Brahmakumar, M., Damodaran, A.D., 1987. Impact properties of natural fibre composites. *Journal of Materials Science Letters*, London, v.6, p.882-884.
- [43] Pavithran, C., Mukherjee, P. S., Brahmakumar, M., Damodaran, A.D., 1988. Impact performance of sisal – polyester composites. *Journal of Materials Science Letters*, London, v.7, p.825-826.
- [44] Ritchie, R. O., 1988. Mechanisms of Fatigue Crack Propagation in Metals, Ceramics and Composites: Role of Crack Tip Shielding. *Materials Science and Engineering, A* 103, 15-28.
- [45] Lewis, T.B. and Nielsen, L.E., 1970. Dynamic mechanical properties of particulate-filled composites. *J. Appl. Polym. Sci.*, 14: 1449–1471. doi: 10.1002/app.1970.070140604
- [46] Masenelli-Varlot, K., Reynaud, E., Vigier, G., Varlet, J., 2002. Mechanical properties of clay-reinforced polyamide. *J. Polym. Sci. B Polym. Phys.*, 40: 272–283. doi: 10.1002/polb.10088
- [47] Gupta, M. and Wang, K.K., 1993. Fiber orientation and mechanical properties of short-fiber-reinforced injection-molded composites: Simulated and experimental results. *Polym Compos*, 14: 367–382. doi: 10.1002/pc.750140503

- [48] Brockenbrough, J.R., Subra S., Wienecke H. A., 1991. Deformation of metal-matrix composites with continuous fibers: geometrical effects of fiber distribution and shape." *Acta metallurgica et materialia* 39.5 : 735-752.
- [49] Van Mier, J.G.M., Van Vliet M.R.A., Wang T.K., 2002. Fracture mechanisms in particle composites: statistical aspects in lattice type analysis." *Mechanics of Materials* 34 (11) 705-724.
- [50] Jawaid, M.H.P.S., and Abdul Khalil, H.P.S., 2011. Cellulosic/synthetic fibre reinforced polymer hybrid composites: A review." *Carbohydrate Polymers* 86.1 (2011): 1-18.
- [51] Savastano, Jr. H, Warden, P.G., and Coutts, R.S.P., 2000. Brazilian waste fibres as reinforcement for cement-based composites." *Cement and Concrete Composites* 22 (5): 379-384.
- [52] Zhong, J.B., Lv, J., Wei C., 2007. Mechanical properties of sisal fibre reinforced urea-formaldehyde resin composites. *Express Polym Lett* 2007; 1(10):681–687.
- [53] Sapuan, S.M., Harun, N., Abbas, K.A., 2007. Design and fabrication of a multipurpose table using a composite of epoxy and banana pseudostem fibres. *J Trop Agric* 45 (1-2):66–68.
- [54] Tonoli G.H.D., Savastano, Jr. H, Fuentec, E., Negroc, C., Blancoc, A., Rocco Lahr, F. A., 2010. Eucalyptus pulp fibres as alternative reinforcement to engineered cement-based composites. *Industrial Crops and Products* 31, 225–232.

- [55] Okubo, K., Toru F., and Yuzo Y., 2004. Development of bamboo-based polymer composites and their mechanical properties. *Composites Part A: Applied science and manufacturing* 35 (3) 377-383.
- [56] Deshpande, Abhijit P., Bhaskar R.M., and Lakshmana R.C., 2000. Extraction of bamboo fibers and their use as reinforcement in polymeric composites. *Journal of Applied Polymer Science* 76(1) 83-92.
- [57] Nataraja, M.C., Dhang, N., and Gupta, A.P., 1999. Stress–strain curves for steel-fiber reinforced concrete under compression. *Cement and concrete composites*, 21 (5), 383-390.
- [58] Chen, P.W., and Chung, D.D.L., 1996. Comparative study of concretes reinforced with carbon, polyethylene, and steel fibers and their improvement by latex addition. *ACI materials journal*, 93(2).
- [59] Udoeyo, F.F., Udeme, H.I, and Obasi, O.O., 2006. Strength performance of laterized concrete. *Construction and Building Materials*, 20 (10):1057-1062.
- [60] Johnston, C.D., 1974. Steel fiber reinforced mortar and concrete: a review of mechanical properties. *ACI Special Publication* 44.
- [61] Sakin, R., and Ay, I.,2008. Statistical analysis of bending fatigue life data using Weibull distribution in glass-fiber reinforced polyester composites. *Materials & Design*, 29(6), 1170-1181.

- [62] Alqam, M., Bennett, R.M., & Zureick, A.H., 2002. Three-parameter vs. two-parameter Weibull distribution for pultruded composite material properties. *Composite Structures*, 58(4), 497-503.
- [63] Soroushian, P., and Lee, C.D., 1990. Distribution and orientation of fibers in steel fiber reinforced concrete. *ACI Materials Journal*, 87 (5), 1990.
- [64] Phoenix, S.L., Ibnabdeljalil, M., and Hui, C.Y., 1997. Size effects in the distribution for strength of brittle matrix fibrous composites. *International Journal of Solids and Structures*, 34(5), 545-568.
- [65] Mirza, S.A., and MacGregor, J.G., 1979. Variations in dimensions of reinforced concrete members. *Journal of the Structural Division*, 105(4), 751-766.
- [66] Karlin, I.V., Ferrante, A., & Öttinger, H.C., 1999. Perfect entropy functions of the lattice Boltzmann method. *EPL (Europhysics Letters)* 47(2), 182.
- [67] Garavaglia, E., Lubelli, B., & Binda, L. (2000). Service life modelling of stone and bricks masonry walls subject to salt decay. *Proc. of Integrated Life-Cycle Design of Materials and Structures*, A. Sarja Ed., RILEM/CIB/ISO, Pro, 14, 367.
- [68] Lacasse, M. A., Haagenrud, S. E., & Sjöström, C. (2004, March). Guide and bibliography to service life and durability research for building materials and components. CIB.
- [69] Conway, J. T. (1985). Durability of brick masonry: a review of the literature. In *Masonry, Research, Application, and Problems: Symposium Sponsored by ASTM Committees C-7 on*

Lime, C-12 on Mortars for Unit Masonry, and C-15 on Manufactured Masonry Units, Bal Harbour, FL, 6 Dec. 1983 (Vol. 871, p. 202). ASTM International.

CHAPTER TWO

2.0 Literature Review

2.1 Degradation of Polymers

Polymer degradation involves the physical or chemical change that occurs due to heat, light, moisture or biological activities. The above factors cause the polymer to alter its properties and this aid in degradation. Mechanical, optical and electrical features in cracking and phase separation occur as a result of changes in material properties including scission, chemical transformation and creation of new functional groups [1].

The degradation of polymers can occur due to the effects of photons, heat and biological organisms. Photosensitivity is the ability of polymers to absorb photons. This can induce photolysis, which involves the breakdown of polymer chains. The factors responsible for photolysis and photo-oxidation include the UV-B terrestrial radiation and UV-A radiation with wavelengths of (~295–315 nm) and (~315–400 nm) respectively. The sunlight that reaches the earth with wavelength of 400-760 nm can be used to speed up the degradation of polymers by heating. Thermal oxidation can also be increased by infrared radiation (760-2500 nm) [2].

Majority of polymers are able to absorb radiation with high energy in the ultraviolet part of the electromagnetic spectrum. This triggers their electrons to higher reactivity and leads to oxidation, cleavage and other degradation mechanisms [3]. Degradation of polymers by thermal effects is due to overheating. The constituents of the long chain strength of the polymer starts to detached at greater temperatures and react with each other to alter the polymer properties. Thermal degradation deals with changes in molecular weight and distribution of the polymer. These

changes involves the reduction of ductility and “embrittlement”, variations of color, “chalking”, “cracking” and the lessening of other required physical properties [4].

The two methods used in Oxo-biodegradation in the initiation of biodegradation include; photo-degradation (U V) and oxidation. The photo-degradation uses ultra violet light which aid in the degradation of the final product. Time and heat is used in the oxidation process for easy breakage of the plastic molecules. The two methods described above decreases the weight of the plastic molecules and permits biodegradation [5]. Biodegradation involves the breaking down of organic substances by bacteria. It is used mostly in ecology, waste management and bioremediation. Biodegradation also applies to plastics and this is due to their long existence on the environment. Organic materials can be degraded with or without oxygen and also organic matter is changed into minerals by a process called bio-mineralization [6].

Biodegradation of plastics with oxygen (aerobic) occurs in harsh environment and in sediments and landfills plastics are biodegraded without oxygen (anaerobic) and partially aerobic and anaerobic in soil and composts. The by-products of aerobic biodegradation involve Carbon dioxide and water while that for anaerobic biodegradation consists of water and methane [7]. Mostly, bulk polymers can be broken down to carbon dioxide which requires a lot of different organisms. Some groups of organism breakdown the polymer into its different components and others utilize the monomers and release waste compounds as by-products [8].

2.1.2 Degradation of Plastics

Processes that induce changes in polymer properties (deterioration of functionality) due to chemical, physical or biological reactions resulting in bond scission and subsequent chemical transformations (formation of structural in homogeneities) have been categorized as polymer

degradation. Degradation has been reflected in changes of material properties such as mechanical, optical or electrical characteristics, in crazing, cracking, erosion, discoloration, phase separation or delamination. The changes include bond scission, chemical transformation and formation of new functional groups [9]. The degradation will either be photo, thermal or biological. Sensitivity of polymers to photo-degradation is related to the ability to absorb the harmful part of the tropospheric solar radiation. This includes the UV-B terrestrial radiation (~295– 315 nm) and UV-A radiation (~315–400 nm) responsible for the direct photo-degradation (photolysis, initiated photo-oxidation). Visible part of sunlight (400–760 nm) accelerates polymeric degradation by heating. Infrared radiation (760– 2500 nm) accelerates thermal oxidation [2, 9]. Most plastics tend to absorb high-energy radiation in the ultraviolet portion of the spectrum, which activates their electrons to higher reactivity and causes oxidation, cleavage, and other degradation [10].

Thermal degradation of polymers is ‘molecular deterioration as a result of overheating’. At high temperatures, the components of the long chain backbone of the polymer can begin to separate (molecular scission) and react with one another to change the properties of the polymer. The chemical reactions involved in thermal degradation lead to physical and optical property changes relative to the initially specified properties. Thermal degradation generally involves changes to the molecular weight (and molecular weight distribution) of the polymer and typical property changes include; reduced ductility and embrittlement, chalking, color changes, cracking and general reduction in most other desirable physical properties [10].

2.1.3 Biodegradation of Plastics

Natural and synthetic plastics can be degraded by fungi and bacteria [7]. The properties of soils affect the growth conditions of microorganisms. These different microorganisms which aid in the degradation of plastics will therefore have different biodegradation rate [11]. This may be attributed to their different optimum growth conditions in the soil and as well affect their biodegradation properties. Different microorganisms use plastics as their potential substrates and this help in plastic degradation [11]. The following factors can affect the biodegradation of polymers. These include; the polymer physical features, method of pretreatment, molecular weight, tacticity, crystallinity, nature of functional groups and substituents, the addition of plasticizers and the kind of microorganism used [12,13].

Monomers conversion is the first step in polymer degradation. These converted monomers are then mineralized and depolymerized to smaller monomers before absorbing and biodegrading within the cells of the microbes. The first step in the breakdown of a polymer can induce changes in the physical factors such as heating, cooling, freezing, wetting or drying and biological forces [14]. The physical factors can cause cracking as a result of mechanical damage in the polymer [7]. The continuous growth of several fungi on the polymer could cause small scale swelling and bursting. This is because; the fungi would penetrate through the polymer thereby causing it to burst [15]. Poly-caprolactone, an artificial polymer [16, 17] is depolymerized by enzymes in the microbes. This is then preceded by the absorption of the monomers into microbial cells followed by biodegradation [18].

Abiotic hydrolysis is the most significant reaction for initiating the environmental degradation of man-made polymers [19] such as poly-carboxylates [20], poly (ethylene

terephthalate) [21], polylactic acids and its copolymers [22, 23], poly (α -glutamic acids) [24], and polydimethylsiloxanes, or silicones [25]. In general, an increase in the molecular weight of a polymer results in weakening of the degradability of the polymer by microorganisms. In contrast, monomers, dimers, and oligomers of a polymer's repeating units are much easily degraded and mineralized. Higher molecular weights of polymers result in a sharp decrease in solubility. This makes them unfavorable for microbial attack since microbes require the substrate to be assimilated through the cellular membrane and then further degraded by cellular enzymes. They are two groups of enzymes that are actively involved in biodegradation of polymers. These include; extracellular and intracellular de-polymerases [10, 25]. In the degradation process, exo-enzymes from bacteria breakdown complex polymers and thereby reducing them to short chainlike molecules with smaller structures. Examples include; oligomers, dimers, and monomers and these are smaller enough to pass through the semi-permeable outer microbial membranes, which are then utilized as sources of carbon and energy in a process known as de-polymerization.

The degradation of polymers with end products of CO_2 , H_2O , or CH_4 is known as mineralization [27, 28]. The bio-deterioration and bio-degradation of polymers barely reach 100% completion due to the conversion of smaller portions into microbial biomass, humus and other natural products [29, 30]. Environmental settings usually affect the principal groups of microorganisms and the degradative pathways associated with the degradation of polymers. Aerobic bacteria are mostly responsible for destruction of complex materials, with microbial biomass, CO_2 , and H_2O as the final products. In contrast, in the absence of O_2 , anaerobic consortia of microorganisms are responsible for deterioration of the polymer resulting to

microbial biomass, CO₂, CH₄ and H₂O as by-products under methanogenic (anaerobic) conditions [31] (e.g. landfills/ compost).

2.1.4 Enzymatic Degradation of Polymers

Hydrolysis is a two step-wise process which occurs in the enzymatic degradation of polymers. Firstly, the enzyme sticks to the substrate of the polymer and afterwards catalyzes a hydrolytic cleavage. Poly (3-hydroxybutyrate) (PHB) can be degraded by the action of intra-cellular and extra-cellular de-polymerases in PHB-degrading bacteria and fungi. Intra-cellular degradation is the hydrolysis of an endogenous carbon reservoir by accruing the bacteria themselves while extra-cellular degradation involves the exploitation of an exogenous carbon source not essentially by the accruing microbes. During degradation, extra-cellular enzymes from bacteria breakdown complex polymers and this produces short chains with smaller molecules. Examples include; oligomers, dimers, and monomers, and these are smaller enough to penetrate through the semi-permeable outer bacterial membranes. These short chain-like structures of molecules are then mineralized into finish products. During the process, CO₂, H₂O, or CH₄ are utilized as sources of carbon and energy [32].

2.1.5 Biodegradation of Polyethylene

Man-made polyolefin are inactive materials and their backbones consist of only long chains of carbon. Polyolefin has features which makes them non-susceptible to microbial degradation. However, a wide-ranging study of polyolefin biodegradation has proven the availability of some microorganisms utilizing polyolefin with low molecular weight [33], and then deriving their energy and carbon sources from it. The biodegradation of polyolefin is often followed by photo

and chemical degradation. Polyethylene (PE) is one of the artificial polymers that have high molecular weight as well as high hydrophobicity. It is non-biodegradable in its natural state. PE is used in the production of many materials and their improper disposal systems and non-biodegradability causes' serious treats to the environment, leading to dangerous environment problems [34]. PE can be biodegradable by reducing the molecular weight, modifying its crystalline level and mechanical properties that are responsible for PE resistance towards degradation [35]. This can be achieved by improving PE hydrophilic level and/or reducing the chain length of the polymer by oxidation which can be accessed for microbial degradation [36].

PE degradation can occur by different molecular mechanisms; chemical, thermal, photo and biological degradation. Studies carried out by researchers [32, 37, 38, 39] have assessed the biodegradability of some novel films by measuring the variations in physical properties and observing the microbial growth after exposure to biological or enzymatic environments by CO₂ evolution. Since PE is extensively used as packaging material, significant work on biodegradable PE as well as biodegradation of PE has been shown [40, 41]. The outcomes of these studies show that PE was biodegraded and subsequently photo-degradation and/or chemical degradation took place. PE biodegradation can occur by two mechanisms: hydro- and oxo-biodegradation [40]. These two mechanisms reach agreement with the modifications due to the two additives, starch and pro-oxidant is used in the synthesis of biodegradable PE. Starch blend PE has uninterrupted starch phase that makes the material hydrophilic and therefore, catalyzed by amylase enzymes. Bacteria will easily access, attack and eliminate this part. Thus the hydrophilic PE with matrix remains to be hydro-biodegraded. In case of pro-oxidant additive, biodegradation occur following photo-degradation and chemical degradation. If the pro-oxidant is a metal

combination, after transition, metal catalyzed thermal peroxidation, biodegradation of low molecular weight oxidation products occurs sequentially [33, 40, 42].

Research carried out by EI-Shafei et al. 1998 [42] examined the ability of fungi and Streptomyces strains to attack degradable PE comprising of disposed PE bags with starch content of 6% . He isolated 8 dissimilar strains of Streptomyces and two *fungi Mucor rouxii* NRRL 1835 and *Aspergillus flavus*. In another study, Low density polyethylene (LDPE) parts were buried in the soil, and mixed with sewage sludge. These were subsequently examined after 10 months with the aid of a microscope. There were attachments of fungi on the surface of the LDPE, demonstrating the possible utilization of LDPE as a source of nutrient (carbon and energy source) [43]. The isolated fungal strains were identified as *Fusarium sp. AF4*, *Aspergillus terreus AF5* and *Penicillium sp. AF6*. The ability of the fungal strains to form a biofilm on PE surface was attributed to the continuing decrease in hydrophobicity of its surface [44]. The structural changes in the form of voids and erosions were detected through the scanning electron microscopy and this indicated surface damage of PE incubated with *Fusarium sp. AF4*. This suggested that, *Fusarium sp. AF4*, was able to stick to the surface of LDPE. [43].

Bonhomme et al. 2003 [40], revealed the presence of bacteria build up on the surface of the polymer through SEM imaging. Upon the elimination of the microbes, the surface of the PE became physically pitted and eroded. The surface of the polymer after microbial attack was physically weaken and readily disintegrates under slight pressure. Otake et al. 1995 [45] described the fluctuations like whitewashing of the degraded area and small holes on the surface of PE film after soil burial for 32 years. LDPE film biological degradation was also stated as 0.2% weight loss in 10 years [46]. Ohtaki et al. 1998 [47] examine LDPE bottles exposed in

aerobic soil for over 30 years. They detected that some parts were degraded under SEM imaging as well as a reduction in molecular weight by Time of Flight Mass Spectrometry (TOF-MS). Yamada-Onodera et al. 2001 [33] isolated *Penicillium simplicissimum* YK to biologically degrade PE without additives. Ultra violet sensitizer, an example of oxidizing agents was used to activate PE at the commencement of the experiment. Nitric acid was used to treat the PE at 80 °C for 6 days before cultivation with introduced functional groups of PE that were susceptible to microorganisms. Bonhomme et al. 2003 [40] showed that PE with molecular weights of 4000 Da to 28,000 Da were degraded to smaller molecular weights of 500 Da after three months of liquid cultivation. This was due to the fungi activity on the PE and hence biodegradation occurred on the PE surface. In another study portions of PE were treated upon exposure to UV light and nitric acid. This pretreated PE was then treated by *Fusarium sp. AF4* in a medium containing mineral salt and the PE serves as the sole source of nutrients for *Fusarium sp. AF4*. FTIR was used to observe the structural changes in the treated PE. There were indications of polymer chain breakdown and the existence of oxidation products of PE. The Polyethylene that was not degraded exhibited almost zero absorbance at those wave numbers. Absorbance at 1710–1715 cm⁻¹ (carbonyl groups), 1640 cm⁻¹ and 830–880 cm⁻¹ (alkenes), which appeared after the treatment of UV and nitric acid, decreased during cultivation with bacterial consortia [49].

In general, PE degradation follows both photo- and biological degradation process, either by exposure to UV light or heat treatment. Also, selected thermophilic bacteria degrade low molar mass oxidation products to complete the biodegradation [40].

2.1.6 Starch/Polyethylene Blends Degradation

PE is known to be an inert polymer and for this reason, it has a strong resistance to bacterial actions [49]. An increase in the molecular weight of the polymer decreases the rate of biodegradation [50]. Many microorganisms can utilize linear paraffin molecules not more than 500 Da [51]. Scott 1990 [52] conducted an experiment on the bacterial attack on PE and concluded that, it was a secondary process. In this process, an initial oxidation step results in the reduction of molecular size smaller enough for biodegradation to occur. The addition of readily biodegradable compounds, such as starch, to a LDPE matrix may enhance the degradation of the carbon-carbon backbone [53]. Researchers have investigated on the biodegradability of starch/PE blends, and chemically modified samples of blends [54]. The biodegradability of starch-filled polymer blends with and without oxygen has also been investigated. It was noticed that the removal of carbon from the starch/PE blend was smaller as compared to pure starch. However, under aerobic conditions, the removal rate of carbon was higher than anaerobic process. Biodegradation of starch PE films consisting of a pro-oxidant with 6% starch exhibited evidence of PE degradation in the presence of lignin degrading bacteria *Streptomyces* and white-rot fungus *Phanerochaete chrysosporium* [37]. The rate of degradation of starch-filled PE is dependent on the starch content as well as conditions in the environment [51]. Impurities such as fats and oils during oxidation can affect PE biodegradation. The creation of reactive oxygen species such as peroxides is a likely source of initiators for molecular breakdown even though other radicals may be involved [55].

The degradation of 11 commercially produced degradable starch/PE blended compost bags was assessed in a composite containing municipal waste [54] by chemical-, photo- and bio-

degradation of each product. The concentration of oxygen at the surface of the films was observed to be the rate-limiting component. A pro-oxidant additive (transition metal) was critical in the promotion of oxidative degradation of PE. Numerous researchers have investigated the use of modified starch in starch/LDPE blends [56]. The modified starches improved the miscibility and adhesion of starch in those blends. However, the biodegradation of the modified starches were and hence, showed a very slow biodegradation rate as compared with unmodified starch/PE blends. Other studies have been carried out to assess the biodegradability of films containing starch and PE [57]. The results indicated that rapid and significant starch depletion led to deterioration of the mechanical properties of the films. This, therefore, leaves a rather weak matrix which is prone to extra physical interference by biotic and abiotic factors.

2.2 Characterization Techniques

2.2.1 Differential Scanning Calorimetry (DSC)

DSC is a technique used to determine the heat flow between a sample and a reference especially when the material is heated or cooled or under isothermal [58]. DSC is used in the analysis of semi-crystalline plastics such as polyolefin, polyethylene (PE), among others [59]. DSC can be used to distinguish different types of PE from their melting points and endotherms. In DSC application, temperature difference is converted into energy measurement per unit mass that is related to the transition in which the temperature difference occurred [58]. At concentration less than 5%, DSC may not be able to detect transitions within materials. The percent crystallinity of a polymer can be calculated using the following expression:

$$P_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_{100\%}} \quad (1)$$

where P_c is the percent crystallinity, ΔH_m is the enthalpy of fusion (determined by the area under the melting exotherm), ΔH_c is the enthalpy of crystallization (determined by the area under the crystallization exotherm) and $\Delta H_{100\%}$ is the heat of fusion for 100% crystalline PE. This is ~ 287.3 J/g [60, 61].

2.2.2 Thermogravimetric Analysis (TGA)

TGA is a technique that measures the quantity and the materials weight change with respect to temperature or time in an atmosphere which is well controlled [58]. Volatilization or decomposition can reduce the weight of the material. Also, gas absorption or reactions that involve chemicals can increase the weight content of the material. In polymeric materials, TGA gives important information concerning the composition and thermal stability. The data obtained comprises volatiles and inorganic filler contents, thermal decomposition onset and antioxidants [62].

2.2.3 Gel Permeation Chromatography (GPC)

GPC is a technique used in determining the molecular weight distribution of polymers. It is sometimes called the size exclusion chromatography and uses packed column to separate various constituents of the polymer [58]. Detectors are used in identifying the changes in molecular weight and the results obtained correspond to the actual molecular weight and molecular weight distribution of the polymer. The polymer produces molecular weight distribution in a histogram and the average molecular weight can be obtained. GPC uses small sample size of about 30 to 120 μg for complete analysis of plastics [63]. However, this technique requires sophisticated instrumentation and usually difficult to interpret results.

2.2.4 Fourier Transform Infra-red Spectroscopy (FTIR)

Fourier spectroscopy” is a general term that describes the analysis of any varying signal into its constituent frequency components. The mathematical methods named after J.B.J. Fourier are extremely powerful in spectroscopy and have been discussed in detail [64, 65, 66]. Fourier transforms can be applied to a variety of spectroscopies including infrared spectroscopy known as Fourier transform infrared (FT-IR), nuclear magnetic resonance (NMR), and electron spin resonance (ESR) spectroscopy. FT-IR spectroscopy includes the absorption, reflection, emission, or photo acoustic spectrum obtained by Fourier transform of an optical inter-ferogram. The power of the method derives from the simultaneous analysis of many frequency components in a single operation. When Fourier concepts are applied to various terms of spectroscopy, the resultant technology creates a spectrometer that gives the entire spectrum in the amount of time that a conventional spectrometer (using dispersive elements like prism and grating) would need to scan across just a single line in the spectrum. Fourier spectrometers utilizing interferometers are thus faster by a factor equal to the number of resolvable elements in the spectrum. Fourier-based methods are used over a wide spectral range [67, 68, 69, 70]. FT spectroscopy can be employed for a long range of frequencies varying over ultraviolet, visible, near infrared, mid infrared and even far infrared regions by selecting different beam splitters and detectors for the required. FT-IR spectroscopy requires some study because its principles are different from those of dispersive spectroscopy techniques and uses interferometers in the spectrometers. In a conventional or continuous wave spectrometer, a sample is exposed to an electromagnetic radiation and usually the intensity of transmitted radiation is monitored. The energy of the incident radiation is varied over the desired range and the response is plotted as a function of

frequency of the incident radiation. At certain resonant frequencies, which are characteristic of the sample, the radiation will be absorbed resulting in a series of peaks in the spectrum, which then can be used to identify the sample.

Different FT-IR spectrometers use different interferometers, such as the Michelson interferometer, lamellar grating interferometer, and Fabry-Perot interferometer. The spectrometers utilizing Fabry-Perot interferometers have low resolving power as compared to the two beam interferometers, namely the Michelson and lamellar grating interferometers. Both of the two beam with the basic difference being that in the Michelson interferometer division of wave amplitude takes place, whereas in the lamellar grating spectrometer division of wavefront takes place. The Michelson interferometer is often favored over the lamellar grating interferometer because of its easy construction and operation. Most of the commercially available FT-IR spectrometers use the Michelson interferometer. These have a number of advantages over the other techniques, such as high energy throughput, multiplexing, and high precision in frequency measurement. These will be discussed in detail in later sections. The principal disadvantage of FT-IR spectrometer is that from the interferometer, an interferogram is produced first rather than a spectrum, and little information is available from the interferogram without further processing. The conversion of the interferogram to a spectrum by Fourier analysis requires the use of a computer. Tremendous progress made in computer technology has allowed the method of Fourier spectroscopy to blossom. There is at present no serious technical reason that would prevent the numerical transformation of a large number of data points. Even for 10⁶ sample transformations, the computation time is hardly a few seconds.

Nowadays, the main difficulty in performing Fourier spectroscopy depends upon the correct realization of the interferogram. FT-IR spectroscopy has been used as the dominant technique for measuring the infrared (IR) absorption and emission spectra of most materials [71].

The major advantage of the FT-IR technique over dispersive spectroscopy methods is that practically all compounds show characteristic absorption/emission in the IR spectral region, therefore, they can be analyzed both quantitatively and qualitatively. Although Fourier spectroscopy has been expanded in the last two decades, it still remains a new spectroscopic approach [70]. The interpretation of the effects observed in the spectrum due to features occurring in the interferogram often needs a lot of calculations in addition to Fourier transformation. The most important of these operations are apodization, phase correction, Fourier self-deconvolution and curve fitting [72, 73, 75, 75, 76]. The far infrared region also plays an important role in the studies of low frequency molecular vibrations, derivation studies of molecular parameters via the observation of pure rotational spectra and research on molecular interactions in the solid state. The conventional IR spectrometers are not of much use for far IR region (20–400 cm^{-1}) as the sources are weak and detectors have lower sensitivity. FT-IR spectroscopy has made this energy limited region more accessible [77, 78].

2.3 Recycling of polymers and plastics

2.3.1 Fiber reinforced plastics

Fiber reinforced plastics (FRP) is used broadly as a high strength material in modern times. FRP is used in the petro-chemistry, construction, automobiles and aircraft industries as well as environmental businesses. This is because; it is heat-resistant, has anti-corrosive properties and

mechanical strength. Glass fiber reinforced plastic (GFRP) composite is produced by laminating unsaturated polyester resin with glass fiber and fillers. Carbon fiber reinforced plastic (CFRP) contains carbon fiber and epoxy resin. FRP is one of the most challenging materials to apportion into elemental components such as fiber, filler and polymers. This, therefore, result in the incineration or landfill used of FRP materials without any efforts in recycling it.

Sugeta et al. 2001 [79] and Okajima et al. 2002 [80] reported on the decomposition of FRP in sub- and supercritical water with the aid of a batch-type reactor. FRP was nearly completely decomposed at 653 K in 5 min. Kamimura et al. 2006 [81] treated FRP comprising glass fiber in supercritical methanol in the existence of a catalytic amount of N, N dimethylaminopyridine (DMAP). As an initial experiment, unsaturated polyesters were nearly completely disintegrated in supercritical methanol. 60% soluble oil of MeOH, 39% soluble solid of CHCl_3 and 1% residue at 548 K, 10 MPa and 5 h were produced as the final products. Similar results were obtained from supercritical ethanol. However, the results gotten for unevenly ground waste FRP in methanol at 548 K, 11 MPa, and 6 h were 28.2% soluble oil of MeOH, 16.2% soluble solid of CHCl_3 and 62.6% residue. Since the remains were not up to 3% of organics, the organic polymer phase was almost totally decomposed. This suggests that, the rate and efficiency of degradation depends on the amount of DMAP. Fukuzawa et al. 2002 [82, 83] examined the dissolution process of the resin part of FRP using ambient pressure dissolving method. Different solvents were used with/without catalysts to develop a recycling technology for FRP. They realized the catalyst and solvent had an influence on the de-polymerization of FRP. The maximum conversion was detected when K_3PO_4 was used as a catalyst and diethylene glycol mono-methylether (DGMM) as a solvent.

2.3.2 Durable plastics recycling

Automobiles, computers and its accessories, household appliances as well as carpet and fabrics are all made from durable plastics. These plastics are produced from many industries and are often discarded once they are used. Durable plastics tend to have a life of about 3 or more years [84]. The applications of durable plastics have been increasingly used due to its performance, low cost and design benefits. For these reasons, design engineers, manufactures as well as consumers rely on its properties. The recovery of plastics from these durable goods is usually complex. They are often integrated with several other plastic and non-plastic components. The separation, recovery, as well as the purification of durable plastics often involves numerous procedures and these usually lead to smaller volumes of the materials being recovered [85]. Nevertheless, a lot of efforts are been put in place to recycle such products after their lifetime. The companies producing these products are mandated to re-use the waste materials and this improves the total usage of the materials. Manufactories involve in business equipment and computer and/or its accessories are recently working on the recovery of plastic housings and other components. Automotive companies have major efforts in recycling of plastics and for these, they try using materials having recycled plastics content.

Considering the US as a case study, carpets consume above 2 billion pounds of polymers, and these include nylon 66, nylon 6 or polyesters. Carpet constructions contain almost 50% of fibers [86]. A complex process is achieved in the recovery of the fiber in its pure form that is free from fillers and others. New technologies are put in place by manufacturers to help in the recovery of carpet fibers and underlay and this contains preparation of pure monomers and its intermediates. A number of studies and pilot programs in durables recycling are under way to

investigate the technical, economic and ecological aspects of the recycling process. Automotive shredder residue (ASR), can be used as an extensive investigation concerning its potential use for impact modification of concrete as well as a fuel in energy plants. ASR which consists of waste products from end-of-life (EOL) economic modeling has been used in many experimental researches. These include; the assessment of system economies for today's automobile recycling infrastructure and project the impact of dissimilar material and energy recovery options [87].

2.3.3 Polymer modified Cement

In recent times, the exceptional performance of polymer-modified cement mortar (PCM) has attracted increasing attention ranging from the scientific to the engineering societies. In the course of hardening of mortar, polymer can fill up the pores and voids in the cement matrix and this can improve the bonding between aggregates and cement paste [88]. PCM have low permeability, good freeze–thaw resistance and relatively higher flexural strength and bonding strength as compared to ancient concrete. This therefore, allow the material to be used successfully as concrete repairing materials, concrete bridge and road covering materials and waterproof materials [89, 90, 91]. PCM has a polymer to cement ratio of about 15-20%. The large addition of the polymer in the PCM is a major concern and there is the need to address it.

This causes an incremental change in the price of the material and also reduces its industrial applications. In normal-strength cement-based materials, cracks and voids usually occur in the interfacial zone between aggregates and hardened cement paste. These are governed by the physical and mechanical properties [92]. Some concrete based techniques such as the Sand Enveloped with Cement (SEC) concrete were designed to cater for strengthening the interfacial zone [93]. Increasing a polymer concentration within the interfacial zone adversely increases the

microstructure, physical and mechanical properties of the cement mortar. Uniform distribution of polymer in the whole composite provides less strength as compared to those within the interfacial zone materials [94]. PCM with steels have improved physical and mechanical properties such as flexural strength, ductility and adhesion as compared to normal cement mortars. Therefore, PCM have been largely used in different antiseptic projects as well as a repairing material for concrete structure and pavement [92]. Currently, more research has been focused on the properties of PCM such as strength, durability and fine pore structure [89]. More research can highlight on the use of PCM with silica fume (SF).

2.3.4 Mechanical Recycling of Plastics

Mechanical recycling of plastics consists of melting, shredding or granulation of waste plastics. Plastics must be sorted prior to mechanical recycling. Technologies are being put in place to automatically sort out plastics, using x-ray fluorescence, infrared and near infrared spectroscopy, electrostatics and flotation. Following sorting, the plastics are either melted down directly and molded into a new shape, or melted down after being shredded into flakes and then processed into granules called re-granulate. Zhang and Forssberg 1999 [95] studied the liberation and its impact on the separation of personal computer (PC) scrap and printed circuit board (PCB) scrap. Some unique equipment such as shape separator and aspirator were used in the classification of electronic scrap. Yarahmadi et al. 2001 [96] showed that properties and durability are among the most essential tasks in the evaluation of the possibility of mechanical recycling of waste plastics of rigid PVC. Also, Ambrose et al. 2002 [97] performed the mechanical recycling of 100% post-consumer of waste plastic into high-quality products. The chemical and physical properties of these recycled materials were comparable to similar products

manufactured from virgin resins. The properties of a blow-molded bottle gotten from 100% post-consumer high-density polyethylene (HDPE) indicated that the recycled polymer surpassed the materials specifications for virgin plastics designs. Similarly, a sample of thermoplastic polyolefin (TPO, 100% polypropylene), obtained completely from shredder residue (SR), exhibited sufficient material strength for future separation and reprocessing. Researchers [98] reported on the thermo-mechanical recycling of polyethylene terephthalate (PET) bottles. The studies show that PET can be used as a composite material in many engineering applications.

Yarahmadi et al. 2003 [99] reported that unwanted PVC floorings can be mechanically recycled without the addition of new plasticizer as well as not upgrading. Paula et al. 2005 [100] prepared blends from polymers and this was followed by mechanical recycling as well as characterizing LDPE/Al residues from cartooned packaging with recycled HDPE/LDPE and virgin PE resins. The end result showed that the compositions of blends are dependent on processability, mechanical properties, chemical resistance and water absorption.

2.3.5 Recycling of Plastics as fillers

Waste generated from plastics can be used as fillers with virgin resins in building applications such as concrete structures and also in road construction. In such applications, chemical composition of the polymer is generally not very significant. It is the simplest method in recycling thermosets in the second grade applications. Waste from thermoplastics are usually melted and coextruded or co-injected into moldings with virgin resins. These virgin resins with unique properties are forced into the boundary of the mold. Those plastics that are recycled with low-grade properties are injected in the middle of the mold [101]. Plastic wastes can be used effectively as a partial replacement of inorganic aggregates in concrete structures and building

applications to decrease the dead weight of structures. Similarly, recycled rubber may be used in asphaltic concrete mixes [102] or as a fill material in road construction [103]. The addition of recycled rubber to the asphalt mix increases the skid resistance under icy conditions, improved flexibility and crack resistance as well as reduced traffic noise.

Many researchers studied the use of scrap tire/rubber as reinforcement in cement mortar and concrete and these gave interesting results as describe by Siddique and Naik 2004 [104]. A system was developed by Remias et al. 2000 [105] that utilize nitrogen oxides and dioxygen to break down and oxidize polyethylene. The principal non-gaseous products were succinic, glutaric, adipic and pimelic acids. Masuda et al. 2001 [106] established a new reactor system for recovery fuels from the waste plastic mixture in steam atmosphere. This system composed of three types of reactors that were connected in series. One reactor was filled with stirred heat medium particles, and this increases the heat transfer rate and holdup as well as good contact of the melted plastics with steam. The second one was the tank reactor, while the last one was a fixed bed reactor with FeOH catalyst particles, that showed the catalysis in steam for the decomposition both of a wax and sublimate materials generated by the degradation of plastics.

Cavalieri and Padella 2002 [107] showed that a polymer milling process with liquid CO₂ was applied to polymeric mixed waste, and a powder material was achieved and successfully utilized as a matrix for a new composite material. Established materials have intriguing mechanical properties, and this can easily improve the material performance. Investigations on selected mixtures of PP and PE clearly showed evidence of chemical compatibilization. Shen et al. 2002 [108] examined the floatability of seven plastics (POM, PVC, PET, PMMA, PC, PS and ABS) in the presence of methyl cellulose (MC) and sorting of plastics mixtures. The plastics were

separated into three groups by using the wetting agent MC. Also, the flotation selectivity for the plastics is controlled not only by wettability of plastics, but also by particle size, density and shape. Miskolczi et al. 2004 [109] reported that fuel-like exploitation is one way of chemical recycling of liquids from waste polymers. Hall and Williams 2007 [110] studied three plastic fractions from a commercial waste electrical and electronic equipment (WEEE) processing plant for the possibility of recycling them by batch pyrolysis.

2.3.6 Chemical Modification of Plastics

Plastic can be recycled through chemical modification as well as de-polymerization [111]. Hydrolysis involving chemical decomposition and pyrolysis which consist of thermal decomposition are the two ways in de-polymerization. For example, polyethylene terephthalate (PET) can be chemically modified to produce unsaturated polyester and thermoset polyester applied in bathtubs, boat hulls as well as the exterior panels of automobiles. Also, there is thermal decomposition of acrylic wastes into methyl methacrylate (MMA) and this is used in aircraft windows and neon signs. The technology of depolymerizing single condensation polymers such as urethanes, PET, nylon, and polymethyl methacrylates is relatively simple. However, it is much more complicated to chemically modify mixed plastics to produce useful and economical chemical feed stocks [112].

2.3.7 Thermal processing of Plastics

Thermal reprocessing involves the heating of a thermoplastic at extremely high temperatures, thus enabling the flow of the plastics [113]. This then convert the plastics into a new product as it cools and solidifies. The method does not primarily consist of the modification

of chemical composition of the plastics. For instance, PET which is thermoplastic polyester can be heated and reprocessed into building panels, fence posts, or fibers for carpeting. This process cannot be repeated forever since repeated thermal reprocessing may adversely have an effect on the mechanical properties of the plastics. Thermal reprocessing is quite forthright when applied to relatively clean thermoplastics. However, thermal reprocessing could not be applied to cross linked polyesters due to its inability to soften at high temperatures without degrading. Thermal reprocessing becomes much more involved if various thermoplastics are diversified. One way of doing is to sort the plastics. Separation of different plastics can be simple or difficult and this depends on the method of waste collection. The other way to thermally reprocess varied plastics is to use unique equipment that incorporate the different thermal properties or makes few demands on the melting behavior of the plastic wastes and does not require meticulous removal of non-plastic wastes.

Mechanisms have been produced to reprocess mixed or commingled waste plastics with lower melting point plastics acting as the matrix and this carries other plastics and contaminants into the mold. Compatibilizers, a chemical agent could be used to improve the adherence between different polymer phases [114, 115]. Currently, recycled plastics have gain grounds as an alternative to some wood products used in the manufacturing industries [116]. These new replacements can be cut, sawn, and nailed like wood. They are also more resistant to moisture but more sensitive to differences in temperature than wood. Such construction products include fence posts, large cable reels, park benches and railroad ties among others. However, these products are very expensive, costing between 2 to 4 times more than the same product made

from wood. A lot of commercially available machines are available in handling certain commingled plastic wastes of varying compositions [116].

2.3.8 Plastics and Natural Fiber Composites

The mixture of plastics and fibers gives good properties in the resulting composite. The plastics which serve as the matrix are usually soft and flexible as compared to fibers used as the reinforcement. Hence, their combination results in a high strength-to-weight ratio to in the composite produced. Cellulose fibers are usually highly polar in nature, and this makes them incompatible with non-polar polymers. Also, their poor resistance to the absorption of moisture does not permit natural fibers for exterior applications, thus, making them less attractive. Composites properties strongly depend on the type of the matrix and fiber used as well as their interfacial compatibility. Researches carried out [117, 118, 119, 120] showed that different types of polymers have been used as matrices in the processing of natural fiber composites. The most frequently used polymers include; polyester epoxies and phenolics, which are all thermoset in nature. Polyethylene (PE), polystyrene (PSI and polypropylene (PP) have also been used as matrices in the production of composites [18, 118]. These polymers have dissimilar affinity towards the fiber due to the difference in their chemical structure. Some studies reported that sisal/LDPE composites exhibited a better reinforcing effect due to high matrix ductility and high strength/modulus ratio of sisal in respect to that of LDPE matrix [119].

Some studies [117] highlighted on the tensile properties of polystyrene reinforced with short sisal fiber and benomylated sisal fiber. This showed improved tensile properties in the composite. The integration of sisal fiber significantly reduced the glass transition temperature (T_g) of polystyrene. Joseph, et al. 1996 [119] observed a high tensile and flexural properties as

well as high interfacial bonding in phenolic composites as compared to epoxy and polyester resin composites. The studies also proved that the reinforcing ability of sisal fiber in PP matrix is less. Also, the *Pueraria lobata* extracted from vines and banana strands have prospective economic value with polyester and this can be used in making commercial fabric woven on power looms [120, 121]. The flexural behavior of coir, straw and jute fibers in polyester have been studied and analyzed by different researchers [122, 123]. The potential of sun-hemp/polyester composites with respect to tensile and impact properties has been investigated by Zadorecki and Flodin 1986 [124]. In this work, cellulose fibers in the form of paper sheets were used in reinforcing unsaturated polyester composites. Numerous studies carried out by Kokta and co-workers used chemo-thermomechanical pulp in different thermoplastics [125, 126]. Crystallization kinetic studies were carried out by Chen and Porter on polyethylene and kenaf fiber composites, extracted from the bust of the *Hibiscus cannabinus*. The environmental performance of flax fiber mat reinforced polypropylene was studied by observing the moisture absorption and swelling. They also measured the residual mechanical properties of the samples at different moisture levels [127]. The effects of filler content and size on the mechanical properties of PP/oil palm wood flour composites has been reported by Zaini et al. 1996 [128]. The transfer of stress at the interface between two different phases can be determined by the degree of adhesion. It was noticed that a strong adhesion at the interfaces is needed for an effective stress transfer and load distribution throughout the interface. Hence, there is the need for strategy developments for the surface modification of cellulosic surfaces. Coatings are usually applied upon improving the mechanical properties of composites. These coatings generally consist of coupling agents or compatibilizing agents that introduce chemical bonds between the fiber and matrix. Research

work [129, 130] has reported on the effects of coupling agents on cellulosic fiber reinforced thermoplastic composites and their influence on the composite mechanical properties. Vanna et al. 1996 [131] reported on the effect of organotitanate, zirconate, silane and N-substituted methacrylamide on the properties of sisal fibers reinforced polyester composites. The studies showed that, reinforcing fibers can be modified by physical and chemical methods.

2.4 References

- [1] Pospisil, J., Nespurek S., 1997. Highlights in chemistry and physics of polymer stabilization. *Macromol Symp*, 115:143–63
- [2] Gugumus, F., 1990. In: Pospisil J, Klemchuk PP, editors. Photooxidation of polymers and its inhibition. . Oxidation inhibition in organic materialsCRC press. p. 29–162
- [3] Cumpston, B. H., Parker, I. D., & Jensen, K. F. (1997). In situ characterization of the oxidative degradation of a polymeric light emitting device. *Journal of Applied Physics*, 81(8), 3716-3720.
- [4] Olayan, H.B., Hamid, H.S., Owen, E.D., 1996. Photochemical and thermal crosslinking of polymers. *J MacromolSci Rev MacromolChemPhys*, 36:671–719.
- [5] Rabek, J. F., & Rabek, J. F. (1996). Photodegradation of polymers (p. 77). Berlin: Springer.
- [6] Guillen-Jimenez, E., Alvarez-Mateos, P., Romero-Guzman, F., & Pereda-Marin, J. (2000). Bio-mineralization of organic matter in dairy wastewater, as affected by pH. The evolution of ammonium and phosphates. *Water Research*, 34(4), 1215-1224.

- [7] Gu J.D., Ford, T.E., Mitton, D.B., Mitchell, R., 2000. Microbial corrosion of metals. In: Revie W, editor. The Uhlig Corrosion Handbook.2nd Edition. New York: Wiley, p. 915–27
- [8] Panda, A. K., Singh, R. K., & Mishra, D. K. (2010). Thermolysis of waste plastics to liquid fuel: A suitable method for plastic waste management and manufacture of value added products—A world prospective. *Renewable and Sustainable Energy Reviews*, 14(1), 233-248.
- [9] Pospisil, J., Nespurek, S., 1997. Highlights in chemistry and physics of polymer stabilization. *Macromol Symp*, 115:143–63.
- [10] Shang, J., Chai, M., & Zhu, Y. (2003). Solid-phase photocatalytic degradation of polystyrene plastic with TiO₂ as photocatalyst. *Journal of Solid State Chemistry*, 174(1), 104-110.
- [11] Glass JE, Swift G. Agricultural and Synthetic Polymers, Biodegradation and Utilization, ACS Symposium Series, 433. Washington DC: American Chemical Society; 1989. p. 9–64.
- [12] Artham T, Doble M. Biodegradation of Aliphatic and Aromatic Polycarbonates. *Macromol Biosci* 2008;8(1):14–24 January.
- [13] Swift G. Non-medical biodegradable polymers: environmentally degradable polymers. In: Domb AJ, Kost J, Wiseman DM, editors. *Handbook of Biodegradable Polymers*.Amsterdam:HarwoodAcademic; 1997. p. 473–511

- [14] Kamal MR, Huang B. Natural and artificial weathering of polymers. In: Hamid SH, Ami MB, Maadhan AG, editors. Handbook of Polymer Degradation. New York, NY: Marcel Dekker; 1992. p. 127–68.
- [15] Griffin GJL. Synthetic polymers and the living environment. Pure Appl Chem 1980;52:399–407
- [16] Toncheva V, Bulcke AVD, Schacht E, Mergaert J, Swings J. Synthesis and environmental degradation of polyesters based on poly (ϵ -caprolactone). J Environ Polym Degrad 1996;4:71–83.
- [17] Jun HS, Kim BO, Kim YC, Chang HN, Woo SI. Synthesis of copolyesters containing poly(ethylene terephthalate) and poly(ϵ -caprolactone) units and their susceptibility to *Pseudomonas* sp. Lipase. J Environ Polym Degrad 1994;2:9–18.
- [18] Goldberg D. A review of the biodegradability and utility of poly (caprolactone). J Environ Polym Degrad 1995;3:61–8.
- [19] Göpferich A. Mechanisms of polymer degradation and elimination. In: Domb AJ, Kost J, Wiseman DM, editors. Handbook of Biodegradable Polymers. Amsterdam: Harwood Academic; 1997. p. 451–71.
- [20] Winursito I, Matsumura S. Biodegradability, hydrolytic degradability, and builder performance in detergent formulations of partially dicarboxylated alginic acid. J Environ Polym Degrad 1996;4:113–21.

- [21] Heidary S, Gordon B. Hydrolyzable poly(ethylene terephthalate). *J Environ Polym Degrad* 1994;2:19–26.
- [22] Hiltunen K, Seppälä JV, Itävaara M, Härkönen M. The biodegradation of lactic acid-based poly (ester-urethanes). *J Environ Polym Degrad* 1997;5:167–73
- [23] Nakayama A, Kawasaki N, Arvanitoyannis I, Aiba S, Yamamoto N. Synthesis and biodegradation of poly(γ -butyrolactone-co-L-lactide). *J Environ Polym Degrad* 1996;4:205–11.
- [24] Fan K, Gonzales D, Sevoian M. Hydrolytic and enzymatic degradation of poly (g-glutamic acid) hydrogels and their application in slow-release systems for proteins. *J Environ Polym Degrad* 1996;4:253–60
- [25] Xu S, Lehmann RG, Miller JR, Chandra G. Degradation of silicone polymer as influenced by clay minerals. *Environ Sci Technol* 1998;32:1199–206
- [26] Doi Y. *Microbial Polyesters*. New York: VCH Publishers; 1990
- [27] Frazer AC. O-methylation and other transformations of aromatic compounds by acetogenic bacteria. In: Drake HL, editor. *Acetogenesis*. New York: Chapman & Hall; 1994. p. 445–83
- [28] Hamilton JD, Reinert KH, Hogan JV, Lord WV. Polymers as solid waste in municipal landfills. *J Air Waste Manage Assoc* 1995;43:247–51
- [29] Atlas RM, Bartha R. *Microbial Ecology: Fundamentals and Applications*. 4th Ed. Menlo Park, CA: Benjamin/Cummings Publishing Company; 1997.

- [30] Narayan R. Biodegradation of polymeric materials (anthropogenic macromolecules) during composting. In: Hoitink HAJ, Keener HM, editors. Science and Engineering of Composting: Design, Environmental, Microbiological and Utilization Aspects. Washington, OH: Renaissance Publishers; 1993. p. 339–62.
- [31] Barlaz MA, Ham RK, Schaefer DM. Mass-balance analysis of anaerobically decomposed refuse. *J Environ Eng* 1989;115:1088–102
- [32] Gu JD. Microbiological deterioration and degradation of synthetic polymeric materials: recent research advances. *Int Biodeterior Biodegrad* 2003;52:69–91.
- [33] Yamada-Onodera K, Mukumoto H, Katsuyaya Y, Saiganji A, Tani Y. Degradation of polyethylene by a fungus. *Penicillium simplicissimum* YK. *Poly Degrad Stab* 2001;72:323–7.
- [34] Kwpp LR, Jewell WJ. Biodegradability of modified plastic films in controlled biological environments. *Environ Technol* 1992;26:193–8.
- [35] Albertsson AC, Barenstedt C, Karlsson S. Abiotic degradation products from enhanced environmentally degradable polyethylene. *Acta Polym* 1994;45:97–103
- [36] Bikiaris D, Aburto J, Alric I, Borredon E, Botev M, Betchev C. Mechanical properties and biodegradability of LDPE blends with fatty-acid esters of amylase and starch. *J Appl Polym Sci* 1999;71:1089–100
- [37] Lee B, Pometto AL, Fratzke A, Bailey TB. *Appl Environ Microbiol* 1991;57: 678–85.

- [38] Glass JE, Swift G. Agricultural and Synthetic Polymers, Biodegradation and Utilization, ACS Symposium Series, 433. Washington DC: American Chemical Society; 1989. p. 9–64.
- [39] Imam SH, Gould JM, Gordon SH, Kinney MP, Ramsey AM, Tosteson TR. Fate of starch-containing plastic films exposed in aquatic habitats. *Curr Microbiol* 1992;25:1–8.
- [40] Bonhomme S, Cuer A, Delort AM, Lemaire J, Sancelme M, Scott C. Environmental biodegradation of polyethylene. *Polym Degrad Stab* 2003;81:441–52.
- [41] Wang YZ, Yang KK, Wang XL, Zhou Q, Zheng CY, Chen ZF. Agricultural application and environmental degradation of photo-biodegradable polyethylene mulching films. *J Poly Environ* 2004;12:7–10.
- [42] EI-Shafei H, EI-Nasser NHA, Kansoh AL, Ali AM. Biodegradation of disposable polyethylene by fungi *Streptomyces* species. *Polym Degrad Stab* 1998;62:361–5.
- [43] Shah, A.A., Role of microorganisms in biodegradation of plastics, Ph. D. thesis. Quaid-i-Azam University, Islamabad, Pakistan, 2007
- [44] Gilan I, Hadar Y, Sivan A. Colonization, biofilm formation and biodegradation of polyethylene by a strain of *Rhodococcus ruber*. *Appl Microbiol Biotechnol* 2004;65:97–104.
- [45] Otake Y, Kobayashi T, Ashabe H, Murakami N, Ono K. Biodegradation of lowdensity polyethylene, polystyrene, polyvinyl-chloride, and urea-formaldehyde resin buried under soil for over 32 years. *J Appl Polym Sci* 1995;56:1789–96

- [46] Albertsson AC. The shape of the biodegradation curve for low and high density polyethylenes in prolonged series of experiments. *Eur Polym J* 1980;16:623–30.
- [47] Ohtaki A, Sato N, Nakasaki K. Biodegradation of poly- ϵ -caprolactone under controlled composting conditions. *Polym Degrad Stab* 1998;61:499–505.
- [48] Hasan F, Shah AA, Hameed A, Ahmed S. Synergistic effect of photo and chemical treatment on the rate of biodegradation of low density polyethylene by *Fusarium* sp. AF4. *J Appl Polym Sci* 2007;105:1466–70.
- [49] Weiland M, Daro A, David C. Biodegradation of thermally oxidized polyethylene. *Polym Degrad Stab* 1995;48(2):275–89.
- [50] Tung FD, Wiles M, Cermak BE, Gho JG, Hare CWJ. Addcon'99 Conference, Prague, Czechoslovakia; 1999. p. 207. [October 27–28].
- [51] Albertsson AC, Karlsson S. Aspects of biodeterioration of inert and degradable polymers. *Int Biodeterior Biodegrad* 1993;31:161–70.
- [52] Scott G. Photo-biodegradable plastics: their role in the protection of the environment. *Polym Degrad Stab* 1990;29:135–54
- [53] Griffin, J.L., Biodegradable Synthetic Resin Sheet Material Containing Starch and a Fatty Material. Coloroll Limited, assignee. C08 J 003/20. 1977. United States patent 4016117.
- [54] Johnson E, Pometto AL, Nikolov ZL. Degradation of degradable starch– polyethylene plastics in a compost environment. *Appl Environ Microbiol* 1993;59:1155–61

- [55] Cornell JH, Kaplan AM, Rogers MR. Biodegradation of photooxidized polyalkylenes. J Appl Polym Sci 1984;29:2581–97
- [56] Evangelista RL, Nikolov ZL, Sung W, Jane JL, Gelina RJ. Effect of compounding and starch modification on properties of starch-filled low density polyethylene. Ind Eng Chem Res 1991;30:1841–6
- [57] Shogren R, Thompson AR, Felker FC, Harry-O'Kuru RE, Gordon H, Greene RV, et al. polymer compatibility and biodegradation of starch-poly(ethyleneco- acrylic acid)-polyethylene blends. J Appl Polymer Sci 1992;44:1971–8.
- [58] Jeffrey A. Jansen, Stork Technimet, Inc. Characterization of Plastics in Failure Analysis. The madison group
- [59] Martin J. Forrest. Analysis of Plastics. Rapra Review Reports. Report 149. Volume 13, Number 5, 2002
- [60] Wundelick, B., Cormier, C.M., 1967. J Polym. Sci. Part A-2: Polym. Phys. 5, 987
- [61] Mirabella, F.M., Bafna, A., 2002. A. J Polym. Sci. Part B: Polym. Phys. 40, 1637
- [62] J. Scheirs, Compositional and Failure Analysis of Polymers, John Wiley & Sons, 2000, p 109, 138, 153, 393, 415
- [63] Polymer Characterization: Laboratory Techniques and Analysis,” Noyes Publications, 1996, p 15

- [64] Ghatak, A.K., Goyal, I.C. & Chua, S.J. (1995) *Mathematical Physics* New Delhi: MacMillan Academic Press
- [65] Harper, C. (1993) *Introduction to Mathematical Physics* New Delhi: Prentice-Hall of India Private Ltd.
- [66] Arfken, G. (1985) *Mathematical Methods for Physicists* Orlando: Academic Press, Inc.
- [67] Lee, J.P. & Comisarow, M.B. (1987) *Appl. Spectrosc.* 41, 93-98.
- [68] Steward, E.G. (1983) *Fourier Optics: An Introduction* New York: John Wiley & Sons
- [69] Banwell, C.N. & McCash, E.M. (1999) *Fundamentals of Molecular Spectroscopy* New Delhi: Tata McGraw-Hill Publishing Co. Ltd.
- [70] Guelachvili, G. (1981) *Spectroscopic Techniques; G. A. Vanasse; Volume II* New York: Academic press
- [71] Bacsik, Z., Mink, J. & Keresztury, G. (2004) *Appl. Spectrosc. Reviews* 39, 295-363.
- [72] Codding, E.G. & Horlick, G. (1973) *Appl. Spectrosc.* 27, 85-92
- [73] Lipp, E.D. (1986) *Appl. Spectrosc.* 40, 1009-1011.
- [74] Kawata, S., Noda, T. & Minami, S. (1987) *Appl. Spectrosc.* 41, 1176-1182.
- [75] James, D.I., Maddams, W.F. & Tooke, P.B. (1987) *Appl. Spectrosc.* 41, 1362-1370
- [76] Kauppinen, J.K., Moffatt, D.J., Mantsch, H.H. & Cameron, D.G. (1981) *Appl. Spectrosc.* 35, 271-276.

- [77] Aruldas, G. (2004) *Molecular Structure and Spectroscopy* New Delhi, Prentice- Hall of India Private Ltd
- [78] Green, D.W. & Reedy, G.T. (1978) *Fourier Transform Infrared Spectroscopy Applications to Chemical Systems* Vol. 1, Ferraro, J.R. & Basile; L.J., p18–38 New York, Academic Press.
- [79] T. Sugeta, S.Nagaoka, K. Otake, T. Sako, Decompositon of fiber reinforced plastics using fluid at high temperature and pressure, *Kobunshi Ronbunshu* 58 (2001) 557–563.
- [80] I. Okajima, K. Yamada, T. Sugeta, T. Sako, Decomposition of epoxy resin and recycling of CFRP with sub- and supercriticalwater, *Kagaku Kogaku Ronbunshu* 28 (2002) 553–558.
- [81] A. Kamimura, K. Yamada, T. Kuratani, Y. Taguchi, F. Tomonaga, Effective depolymerization waste FRPs by treatment with DMAP and supercritical alcohol, *Chem. Lett.* 35 (2006) 586–587.
- [82] H. Fukuzawa, K. Shibata, H. Izawa, Proc. 13th Conference of the Japan Society of Waste Management Experts, 2002, p. I: 428.
- [83] H. Fukuzawa, K. Shibata, H. Izawa, A. Matsuo, Proc. Int. Symp. Feedstock Recycling 2002, 2002, p. A30
- [84] Lang, R. W., Stern, A., & Doerner, G. (1997). Applicability and limitations of current lifetime prediction models for thermoplastics pipes under internal pressure. *Die angewandte makromolekulare Chemie*, 247(1), 131-145.

- [85] Al-Salem, S. M., Lettieri, P., & Baeyens, J. (2009). Recycling and recovery routes of plastic solid waste (PSW): A review. *Waste management*, 29(10), 2625-2643.
- [86] Subramanian, P. M. (2000). Plastics recycling and waste management in the US. *Resources, Conservation and Recycling*, 28(3), 253-263.
- [87] Kang, H. Y., & Schoenung, J. M. (2005). Electronic waste recycling: A review of US infrastructure and technology options. *Resources, Conservation and Recycling*, 45(4), 368-400.
- [88] S. Chandra, Y. Ohama, *Polymers in Concrete*, CRC Press, 1994.
- [89] J.-H. Kim, R.E. Robertson, Prevention of air void formation in polymer- modified cement mortar by pre-wetting, *Cem. Concr. Res.* 27 (2) (1997) 171–176.
- [90] L.A. Kuhlmann, Using styrene– butadiene latex in concrete overlays, *Transp. Res. Rec.* 1204 (1988) 52–58.
- [91] D.G. Walters, Latex hydraulic cement additives, *Transp. Res. Rec.* 1204 (1988) 71–76
- [92] S. Diamond, S. Mindess, F.P. Glasser, J.P. Roberts, L.D. Skalny, L.D. Wakeley (Eds.), *Microstructure of cement-based system, Bonding and Interfaces in Cementitious Materials*, Vol. 370, Proceedings of MRS Symposium, Boston, 1994, Pittsburgh, 1995.

- [93] Y. Higuchi, Coated-sand technique produces high-strength concrete, *Concr. Int.* 2 (5) (1980) 75–76.
- [94] S.H. Okba, A.S. El-Dieb, M.M. Reda, Evaluation of the corrosion resistance of latex modified concrete (LMC), *Cem. Concr. Res.* 27 (6) (1997) 861– 868.
- [95] Zhang, S., Forssberg, E., 1999. Intelligent liberation and classification of electronic scrap. *Powder Technology* 105 (1–3), 295–301.
- [96] Yarahmadi, N., Jakubowicz, I., Gevert, T., 2001. Effects of repeated extrusion on the properties and durability of rigid PVC scrap. *Polymer Degradation and Stability* 73 (1), 93–99.
- [97] Ambrose, C.A., Hooper, R., Potter, A.K., Singh, M.M., 2002. Diversion from landfills: quality products from valuable plastics. *Resources, Conservation and Recycling* 36 (4), 309–318.
- [98] Avila, A.F., Duarte, M.V., 2003. A mechanical analysis on recycled PET/ HDPE composites. *Polymer Degradation and Stability* 80 (2), 373–382.
- [99] Yarahmadi, N., Jakubowicz, I., Martnsson, L., 2003. PVC floorings as post-consumer products for mechanical recycling and energy recovery. *Polymer Degradation and Stability* 79 (3), 439–448
- [100] Paula, M.M.da.S., Rodrigues, F.B.B.M., Bernardin, A.M., Fiori, M.A., Angioletto, E., 2005. Characterization of aluminized polyethylene blends via mechanical recycling. *Material Science and Engineering* 403 (1–2), 37–41.

- [101] Curlee, T.R., 1986. *The Economic Feasibility of Recycling: A Case Study of Plastic Wastes*. Praeger, New York.
- [102] McQuillen, J.L., Takallou, H.B., Hicks, R.G., Esch, D., 1998. Economic analysis of rubber modified asphalt mixes. *Journal of Transportation Engineering, ASCE* 114 (3), 259–277.
- [103] Eldin, N.N., Senouci, A.B., 1992. Use of scrap tires in road construction. *Construction Engineering Management, ASCE* 118 (3), 561–576.
- [104] Siddique, R., Naik, T.R., 2004. Properties of concrete containing scrap tire rubber – an overview. *Journal of Waste Management* 24 (6), 563–569
- [105] Remias, J.E., Pavlosky, T.A., Sen, A., 2000. Oxidative chemical recycling of polyethene. *Comptes Rendus de l'Académie des Sciences – Series IIC – Chemistry* 3 (7), 627–629
- [106] Masuda, T., Kushino, T., Matsuda, T., Mukai, S.R., Hashimoto, K., Yoshida, Shu-ichi, 2001. Chemical recycling of mixture of waste plastics using a new reactor system with stirred heat medium particles in steam atmosphere. *Chemical Engineering Journal* 82 (1–3), 173–181
- [107] Cavalieri, F., Padella, F., 2002. Development of composite materials by mechanochemical treatment of post-consumer plastic waste. *Waste Management* 22 (8), 913–916.
- [108] Shen, H., Forsberg, E., Pugh, R.J., 2002. Selective flotation separation of plastics by chemical conditioning with methyl cellulose. *Resources Conservation and Recycling* 35 (4), 229–241

- [109] Miskolczi, N., Bartha, L., Deák, G., József, B., 2004. Thermal degradation of municipal plastic waste for production of fuel-like hydrocarbons. *Polymer Degradation and Stability* 86 (2), 357–366
- [110] Hall, W.J., Williams, P.T., 2007. Analysis of products from the pyrolysis of plastics recovered from the commercial scale recycling of waste electrical and electronic equipment. *Journal of Analytical and Applied Pyrolysis* 79 (1–2), 375–386.
- [111] George, J., Sreekala, M. S., & Thomas, S. (2001). A review on interface modification and characterization of natural fiber reinforced plastic composites. *Polymer Engineering & Science*, 41(9), 1471-1485.
- [112] Rebeiz, K.S., Craft, A.P., 1995. Plastic waste management in construction: technological and institutional issues. *Resources, Conservation and Recycling* 15, 245–25
- [113] Williams, G., & Lord, H. A. (1975). Mold- filling studies for the injection molding of thermoplastic materials. Part I: The flow of plastic materials in hot- and cold- walled circular channels. *Polymer Engineering & Science*, 15(8), 553-568.
- [114] Barlow, J.W., Paul, D.R., 1987. The compatibility of mixed plastic scrap. Reclamation of Plastic Waste Research Report-Phase I. Plastic Institute of America, pp. 137–148.
- [115] Stein, R.S., 1992. Miscibility in polymer recycling-emerging technologies in plastics recycling, ACS Symposium Series 513, American Chemical Society, pp. 39–48

- [116] Barlaz, M.A., Haynie, F.H., Overcash, M.F., 1993. Framework for assessment of recycle potential applied to plastics. *Journal of Environmental Engineering, ASCE* 119 (5), 798–810.
- [117] K. C. M. Nair and S. Thomas, *J. Appl Polym Sci.* 60, 1483 (1996)
- [118] J. George, N. Prabhakaran, S. S. Bhagawan and S. Thomas, *J. Appl Polym Sci*, 57, 871 (1995).
- [119] K. Joseph, S. Varghese, G. Kalaprasad, S. Thomas, L. Prasannakumari, P. Koshy and C. Pavithran., *Eur. Polym J.*, 32, 1243 (1996).
- [120] U. S. Prokop and A. Tanner, *J. Sci Ind. Res.*, 55, 381 (1996).
- [121] W. H. Zhu, B. C. Tobias and R. S. P. Coutts., *J. Mater. Sci.* 14, 508 (1995)
- [122] N. M. white and M. P. Ansell. *J. Ma& Sci*, 18, 1549 (1983).
- [123] A. N. Shah and S. C. Lakkad, *Fiber. Sci. Technol*, 15, 41 (1981).
- [124] P. Zadorecki and P. Flodin, *Polyym Compos.*, 7, 170 (1986)
- [125] D. Beshay, B. V. Kokta and C. Daneault, *Polym Com- ICCM- 12*, 5-9 July, Paris (1999).
pos. 6, 261 (1985)
- [126] B. V. Kokta, C. Daneault and A. D. Beshay, *Polyym Compos.*, 7, 251 (1986)
- [127] T. Peijs, S. Garkhail, R. Heijenrath, M. Oover and H. Bos, *MacromoL Symp.*, 127, 193 (1998).

[128] M. J. Zainy, M. Y. A. Fuad, 2. Ismail, M. S. Mansor and J. Mustafah. *Po4m International* 40.51 (1996)

[129] J. M. Felix and P. Gatenholm. *J. Appl Polym. Sci*, 42, 609 (1991).

[130] J. George, S. S. Bhagawan and S. Thomas, *Comp. Interfaces*, 5, 201 (1998)

[131] B. Singh, M. Gupta and A. Varma, *Polym. Compos.*, 17, 910 (1996)

CHAPTER THREE

3.0 Biodegradation of Linear Low Density Polyethylene by *Serratia marcescens* subsp. *marcescens* and Its Cell Free Extracts

3.1 Introduction

Plastics are synthetic organic heteroatomic polymers that originate from oil, coal and natural gas [1, 2]. They are generally non-biodegradable in the presence of enzymes or microbes [3] and their accumulation leads to prolonged environmental changes [4]. This has led to environmental concerns, since approximately 140 million tons of man-made polymers, including polyethylene (PE), are produced annually across the world [5-7]. These are used typically in food packaging, detergents, clothing, shelter, transportation and chemical substances, with an increasing annual rate of 12% [8, 9] and recently 16% in India [10]. These plastics include: polyethylene (LLPE, LLDPE, MDPE and HDPE), polypropylene (PP), polystyrene (PS), Polyvinyl Chloride (PVC) and polyethylene terephthalate (PET) [5, 11-14].

Plastics have been used extensively in many applications due to their attractive combinations of stability [15], thermal properties [6] and mechanical properties (also physical properties) [16]. PE consumption is the largest among polymers produced worldwide, recording a total of over 90 million metric tons per annum (The Plastics Portal). The high production of PE hinders the implementation of an efficient disposal system [6]. However, PE can be degraded by chemical [17, 18], thermal [10, 19], photo [10, 19] and biological methods [20-22]. The current methods that are used for the biodegradation of PE include: hydro-biodegradation [11] and Oxo-biodegradation [11, 22].

Recent literature has shown that microbes [6, 19, 23-25] and fungi [16,26,27], such as *Rhodococcus spp* [6], *Penicillium simplicissimum* [27] *Brevibacillus* [6, 24], *Fusarium sp. AF4* [28] and *Pseudomonas spp* [6, 7, 23] are able to biodegrade PE. These microbes use PE as their sole carbon and energy source [12, 14, 24, 29-31]. The crystalline structure, molecular weight and mechanical properties of PE are altered during the microbial biodegradation [32].

However, although prior studies [6, 19, 23, 25] have attempted to examine the role of various microorganisms in the biodegradation process, the biodegradation of PE is not yet fully understood. Furthermore, there has been no prior study of the mechanisms of biodegradation of PE by the soil-based bacterium, *Serratia marcescens subsp. marcescens* (*S. marcescens marcescens*). In this study, *S. marcescens marcescens* is shown to degrade powdered Linear Low Density Polyethylene (LLDPE) as well as films of LLDPE. The degradation mechanisms are elucidated via weight loss measurements, Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC) and Fourier Transform Infra-Red Spectroscopy (FTIR). The implications of the results are then discussed for the degradation of LLDPE found in the waste materials.

3.2 Experimental Procedures

3.2.1 Production of PE Powder

LLDPE packages that were produced for the packaging of portable water called ‘‘pure water’’ in Abuja, Nigeria, were obtained. These were dissolved using AGO kerosene fuel obtained from the Niger Delta Development Commission (NDDC), Nigeria, at 140°C (AGO fuel is a trademark of NDDC of Nigeria). The solvent was heated up to 140°C, before adding the

fragments of LLDPE under constant stirring conditions until the solvent became saturated with LLDPE. The temperature was maintained at 140°C until LLDPE was fully dissolved. The resulting slurry and the saturated solution were cooled by immersing the beaker in an ice-bath (-5°C). The solvent was then filter-separated from the slurry using muslin cloth (BDH). The resulting plastic particles were air dried for 3-5 hours and solvents recycled for future use in subsequent processing of LLDPE fragments into PE powder.

3.2.2 Culture Enrichment Techniques

For the microbial growth medium, one gram of the LLDPE powder was added to 100 mL of minimal media augmented with 100 mg g yeast extract and 0.1 g of corn steep liquor (CAS66071-94-1, ShangHai Yuanye Biotechnology Co., Ltd, Shanghai, China). The constitution of the media was as follows: 0.5 % $(\text{NH}_4)_2\text{HPO}_4$; 0.1 % malt extract; 0.001 % CaCl_2 ; 0.01 % NaCl and 0.001 % FeCl_3 . The mixture was autoclaved in a 250 mL conical flask at 121 °C for 20 minutes. 100 mL of this medium and 2 g of LLDPE powder or discs (obtain using office hole puncher) were added (after surface sterilization with tween 80 and sodium dodecyl sulphate) to a 20% solution of sodium hypochlorite for 20 minutes. After decanting the solution, the remaining material was rinsed several (5-10) times with sterile distilled H_2O in a laminar flow hood (Labconco, Kansas city, Missouri, USA). This was done to remove the remaining traces of hypochlorite from the LLDPE, leaving the LLDPE as the sole source of carbon.

In order to obtain a source of microbes, 1 g of soil was obtained from the grounds at Sheda Science and Technology Complex (SHETSCO) in the Federal Capital Territory, Abuja, Nigeria. This was mixed with 10 mL of sterile distilled water. The mixture was then shaken and

thoroughly mixed (for 5 minutes) and transferred to a boiling tube. Following the sedimentation of the sand to the bottom of a boiling tube, 2 mL of the water from the mixture was used to inoculate the beaker containing the nutrients and LLDPE. The soil microorganisms, which were already mixed with the water, thus provided inoculum for the LLDPE-nutrient mixture. The inoculated material was then charged into a temperature-controlled rotary shaker (Labconco, Kansas city, Missouri, USA) that was set at 150 revolutions per minute (rpm) and 30°C. Incubation was continued for duration of 4 weeks. During this time, 5 mL of sterilized nutrient medium was added to the cultures every 4 weeks to provide necessary nutrients to support microbial growth. This process was repeated for a period of 12 weeks. A control without inoculum was also prepared with 4 replicates.

To confirm microbial growth, four independent separate experimental sets were considered. These include: set 1: Nutrient media+ Polymer; set 2: Nutrient media + Polymer + Microbial cell; set 3: Nutrient media; and set 4: Nutrient media + Microbial cell. 1 mL of the experimental fluids (set 1 – set 4) were obtained under sterile conditions (in a laminar flow hood) and spread on Petri dishes containing Nutrient Agar (N8500, US Biological, Burlington, Vermont, Canada) and Potato Dextrose Agar (PDA, P5200, US Biological, Burlington, Vermont, Canada). The Petri dishes were incubated for 2 days to facilitate microbial growth. Microorganisms grew very well on growth media (nutrient agar + Potato Dextrose Agar) coming from both set 2 and set 4 condition because yeast extract is a growth stimulating agent. However, the microbial count was higher in set 2 compared to set 4. 8 similar populations (based on topography, colony and color) were observed in the inoculated cultures, while the controls (set 1 and 3) did not show any signs of microbial growth.

Among the bacterial growth, colonies showing red coloration were isolated and grown in pure culture using microbial streaking techniques [33, 34]. The resulting red-pigmented microorganism was then sent to German Collection of Microorganism and Cell Cultures (DSMZ), Brunswick, Lower Saxony, Germany, for identification. The results obtained via a combination of mRNA studies and protein profile analysis revealed 99% similarity of the isolate to *Serratia marcescens subsp. marcescens*. The red-pigment bearing microbe now positively identified as *Serratia marcescens subsp. marcescens* (*S. marcescens marcescens*) was then used in the biodegradation of LLDPE having been found capable of using LLDPE as carbon source. Table 3.1 shows the results obtained from the biochemical tests that were used to identify for the *S. marcescens marcescens*.

3.2.3 Media Preparation and Inoculation

The nutrient medium (without carbon source) was prepared in a 1 L conical flask with half strength Murashige and Skooge medium (M9500, US Biological, Burlington, Vermont, Canada) [35], that is usually used for plant growth support [35, 36]. Seven empty conical flasks and the nutrient media were covered with sterile cotton wool and aluminum foil in a manner that permits sterile air exchange with the enrichment. The covered flasks and media were then autoclaved at 121°C for 15 min, before moving them into a laminar flow hood (Labconco, Kansas city, Missouri, USA).

2 g of sterilized LLDPE powder were added to six different beakers containing 100 mL sterile nutrient medium. 5 mL of the nutrient broth containing *S. marcescens marcescens* were then added to each of the six flasks, which were corked tightly with sterile cotton wool and

aluminum foil, with one flask serving as a control. The control contained the LLDPE and nutrient medium without inoculation with micro-organism. After inoculating the *S. marcescens marcescens* with the LLDPE, the samples were incubated in a rotary shaker. The shaker was operated at 30°C and 150 rpm, for ten weeks, to observe the degradation of LLDPE. During the degradation period, 5 mL of sterile nutrient medium was added to the mixture to enrich the bacterial cultures, after every 4 weeks of culture.

3.2.4 Weight Loss Experiments

LLDPE plastic bags were shredded and washed in a solution with an excess of 70% ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) - 30% water (H_2O). The shredded bags were then rinsed with distilled water and allowed to air-dry for 30 minutes. The LLDPE was also cut into 5 mm diameter circular disks with an office hole puncher (circular holes). The disks were cut from plastic films that were supported with hard paper to ensure a clean cut. 2 g of the LLDPE disks were then added to each of the two empty autoclaved conical flasks. These were placed in the laminar flow hood (Labconco, Kansas city, Missouri, USA). 100 mL of the nutrient medium was then poured into both flasks, while 5 mL of the nutrient broth containing the *S. marcescens marcescens* was introduced into one flask and corked tightly. The other flask, also corked tightly, served as a control (without *S. marcescens marcescens*). Without contamination (not exposed to air), the samples were later incubated in a shaker incubator at 30°C and 150 rpm, for four weeks, in order to determine the weight loss and the degradation of the LLDPE during exposure to the medium.

3.2.5 Supernatant Experiment

In an effort to determine the effects of supernatant (cell-free extracts/cultures) from the *S. marcescens marcescens*, the LLDPE powder and disks were exposed to the supernatant (by centrifugation and filtration of cultures) for a period of 4 weeks. First, five empty conical flasks were sterilized (autoclaved) and moved to the laminar flow hood (Labconco, Kansas city, Missouri, USA). The biodegraded LLDPE, previously exposed to the *S. marcescens marcescens* for four weeks, was separated from the supernatant using a 0.22 μm filter under a vacuum of 34.5- 62.0 kPa. 50 mL of the supernatant (by centrifugation and filtration) was then added to each of the four conical flasks with 50 mL of nutrient medium, while the remaining flask, containing 100 mL of nutrient medium, served as a control. 2 g of LLDPE powder or LLDPE disks were then introduced into each flask. The flasks were then corked tightly with sterile cotton wool and aluminum foil. The corked flask was then incubated in a rotary shaker that was operated at 30°C and 150 rpm for four weeks.

3.2.6 Scanning Electron Microscopy (SEM)

The surfaces of the powdered LLDPE and the LLDPE disks were observed at different stages of exposure in a Zeiss Evo MA variable pressure Scanning Electron Microscope (SEM) (Carl Zeiss STM AG, Jena, Thuringia, Germany). The smooth surfaces, as well as the surfaces impregnated with actively growing cultures, were carefully mounted on aluminum stubs. Semi-quantitative information on the specimen surfaces was also obtained during SEM examination using an Energy Dispersive X-ray Spectrometer (EDS) system with INCA software analyser (Carl Zeiss STM AG, Oberkochen, Baden-Wurttemberg, Germany).

3.2.7 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) was performed on the LLDPE powder using a DSC system (Q2000 V24.4 Build 116, Elmer system (Boston, MA, USA). All the DSC measurements were carried out on 5 mg samples at atmospheric pressure. The temperature was increased linearly from room temperature (28 °C) to 160 °C, at a rate of 5 °C/min. This was done under a stream of Argon (~50 sccm) to reduce the extent of oxidation. The percent crystallinity was then calculated using the following expression:

$$P_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_{100\%}}$$

where P_c is the percent crystallinity, ΔH_m is the enthalpy of fusion (determined by the area under the melting exotherm), ΔH_c is the enthalpy of crystallization (determined by the area under the crystallization exotherm) and $\Delta H_{100\%}$ is the heat of fusion for 100% crystalline PE. This is ~287.3 J/g [37, 38].

3.3 Results and Discussion

3.3.1 Biodegradation of LLDPE

After the first 4 weeks of inoculation of *S. marcescens marcescens*, it was observed that the inoculated mixture (*S. marcescens marcescens* + LLDPE powder + nutrient medium) became turbid, with signs of microbial activity indicated by the occurrence of gas bubbles. The turbidity increased steadily with time throughout the experiment. At the end of 10 weeks, it was observed that the control beaker without inoculum (without *S. marcescens marcescens*) remained clear, while the inoculated beakers (with *S. marcescens marcescens*) were turbid. In addition to the

occurrence of turbidity, the LLDPE in the inoculated flasks sank to the bottom of the beaker, unlike the controls, where LLDPE remained floating. This indicates that, the bacterium uses LLDPE as its energy and carbon source, hence, a sign of the bacterium feeding on the LLDPE.

The appearance of a red pigment in the samples is a characteristic of prodigiosin expression by *S. marcescens marcescens* [39-42]. This was associated with a progressive decrease of the weight of LLDPE in the medium containing *S. marcescens marcescens* (Figure 3.1). This shows that the extent of biodegradation was very limited during the first two weeks. However, the rate of degradation increased significantly for longer exposures, suggesting an increasing role of extra-cellular enzymatic decomposition of LLDPE [12, 13].

Also, the weight decrease could correspond to the consumption of LLDPE by *S. marcescens marcescens*, utilizing LLDPE as its sole source of carbon and energy [12, 14, 29-31]. In contrast, as expected, the weight of the LLDPE in the control (unexposed to *S. marcescens marcescens*) remained unchanged. Furthermore, the increase in the weight amount of degradation products was proportional to the exposure time of the medium to *S. marcescens marcescens*, as shown in Figure 3.2. The average biodegradation of LLDPE by *S. marcescens marcescens* showed a significant rise of 36%, for an incubation period of 70 days (Figure 3.3). This percentage rise is consistent with work carried out by Nanda *et al* 2010, where pseudomonas biodegraded PE for 8 weeks and the percentage rise was 46.2% and 29.1%, respectively, for both natural and synthetic PE. Furthermore, the observations suggested that the *S. marcescens marcescens* used LLDPE as a source of nutrients (carbon) [12, 14, 29-31].

Figure 3.4 shows a loss of a mass of 0.63 g of LLDPE, after four weeks of incubation in the presence of the supernatant. This shows that the rate of degradation in the supernatant was greater than that in the *S. marcescens marcescens*. This average increase in the amount of biodegraded products was ~ 31.5% over a period of 28 days (Figures 3.4, 3.5 and 3.6), unlike the *S. marcescens marcescens* with 36% over a period of 70 days.

The results presented in Figures 5 and 6 suggest that the average mass of biodegraded products of LLDPE exposed to supernatant decrease significantly, when compared to those exposed to *S. marcescens marcescens* (Figure 3.1 and 3.3). Furthermore, the weight of biodegradation products of LLDPE produced in the presence of supernatant was greater than that produced in the presence of the *S. marcescens marcescens*.

3.3.2 Modeling of Polyethylene (PE) Biodegradation using Student T-Test

A student T-test was used to determine whether the *S. marcescens marcescens* or the supernatant was responsible for the weight changes that were measured in the experiments. The null hypothesis (H_0) stated that the mean of the degradation produced by the supernatant from *S. marcescens marcescens* was responsible for the biodegradation of LLDPE. The alternative hypothesis (H_a) stated that the mean of the degradation produced by the supernatant from the *S. marcescens marcescens* was not responsible for the biodegradation of LLDPE. These hypotheses were tested at a significance level of 0.05.

The results obtained using the Minitab software package (Minitab Model 15, Princeton, New Jersey, USA) with a one sample T and a 95% confidence interval, are presented in Table 3.2. These show that, from the one sample T, the p-value of 0.063 obtained for the weight is

greater than the significance level of 0.05. Hence, the test statistic is not significant and we fail to reject the null hypothesis. Moreover, the T-value of -2.55 is less than the critical value of 2.78 shown in the distribution plot in Figure 3.7. Again, the test statistic is not significant and we fail to reject the null hypothesis at the 95% confidence interval (CI), since it lies within the critical region. The lack of evidence leads to the rejection of H_a , therefore, it can be concluded that, the mean of the degradation produced by the supernatant from *S. marcescens marcescens* is responsible for biodegradation of LLDPE.

3.3.3 Degradation Mechanisms

Figures 3.8a and 3.8b present SEM images of the untreated samples of LLDPE without carbonless medium (Figure 3.8a) and untreated samples of LLDPE exposed to the carbonless medium (Figure 3.8b). These show that the carbonless medium had no visible effect on the LLDPE. However, the LLDPE exposed to *S. marcescens marcescens* for one month exhibited voids and pits (Figure 3.9a). This suggests that the LLDPE was eroded by the *S. marcescens marcescens*.

Further evidence of the effect of the *S. marcescens marcescens* is presented in Figures 3.10a and 3.10b. Figure 3.10a show voids in LLDPE films exposed to *S. marcescens marcescens* for one month, while no voids are observed in virgin material exposed to carbonless medium (Figure 3.10b). This result further reinforces the observation and the degradation is as a result of microbial action.

Figures 3.11a and 3.11b show micrographs of a LLDPE film that was exposed to *S. marcescens marcescens* for one month, without rinsing. Large discontinuities are observed at relatively low magnifications (Figure 3.11a). However, at higher magnifications, rod-like shapes

are observed as shown in Figure 3.11b. These correspond to *S. marcescens marcescens* bacteria that are still present on the sample (Figure 3.11b).

Furthermore, following the direct exposure of the LLDPE to the supernatant, a higher incidence of voids and pits was observed (Figure 3.9b) than those observed in the presence of *S. marcescens marcescens* (Figure 3.9a). The results suggest that the supernatant has the ability to degrade LLDPE faster than the bacterium (*S. marcescens marcescens*).

3.3.4 Differential Scanning Calorimetry

Figures 3.12a and 3.12b correspond, respectively, to the superposition of the DSC first and second scans of LLDPE before and after microbial degradation. Figure 3.12a shows the DSC results obtained from untreated samples of LLDPE exposed to carbonless medium. It reveals the enthalpy of crystallization and heat of fusion are 97.34 J/g and 84.28 J/g, respectively. Also, Figure 3.12a presents the melt and crystallization temperatures of 123.4°C and 111.32°C, respectively. In contrast, Figure 3.12b shows a decrease in the enthalpy of crystallization and heat of fusion to 84.22 J/g and 75.65 J/g, respectively after LLDPE exposure to *S. marcescens marcescens* for 70 days. A decrease was also observed in the melt and crystallization temperatures of 115.2°C and 103.71°C, respectively. The overall percentage of crystallinity of LLDPE also decreased from 65% to 56% after biodegradation with *S. marcescens marcescens* for 70 days. This 9% decrease in the percentage of crystallinity of LLDPE is comparable to research carried by Sudhakar *et al.*, 2008. In his research [43]; *Bacillus Sphericus GC subgroup IV* was able to biodegrade LDPE for a year with an overall decrease in the percentage of crystallinity of 8%.

Research findings have shown that, there is an initial increase in the percent crystallinity of PE after microbial degradation [43-48]. Microbes generally degrade the amorphous portions of the PE first [43-45, 47, 48], before disrupting the crystalline order [46, 49]. Therefore, there is an overall decrease in the percent crystallinity after biodegradation of LLDPE. Also, the broadening of the endotherms in Figure 3.12b is attributed to the erosion of crystalline regions of the LLDPE after biodegradation. Further work is clearly needed to determine the erosion rates of crystalline and amorphous components of LLDPE. These are clearly some of the challenges for future work.

3.3.5 Fourier Transform Infra-Red Spectroscopy

Fourier Transform Infra-Red Spectroscopy (FTIR) was used to determine the introduction/occurrence of new functional groups or change in the quantity of existing functional groups. The FTIR spectra were obtained for virgin LLDPE and LLDPE with bacterium (*S. marcescens marcescens*). New peaks were identified after ten weeks of biodegradation of LLDPE with *S. marcescens marcescens*. The functional groups on the new peaks identified include an alkene (3046.58 cm^{-1} and 904.11 cm^{-1}), alcohol (1249.32 cm^{-1}) and carboxylic acid (1249.32 cm^{-1} and 2915.07 cm^{-1}), as shown on Figure 3.13b. Hence, the results of the current study revealed an increase in the peak wavenumbers of LLDPE following exposure to *S. marcescens marcescens* (Figure 3.13b). Peak wavenumbers of 3408.22 cm^{-1} and 2926.03 cm^{-1} (Figure 3.13a) for the LLDPE increased significantly to 3441.10 cm^{-1} and 2975.34 cm^{-1} (Figure 3.13b), respectively, for LLDPE without and with *S. marcescens marcescens*. The increase in concentrations of these functional groups (carbonyl groups), resulting in new peaks, is due to the availability of microbes on the LLDPE surface [47, 50, 51]. Also, the appearance (increase in concentrations) of double

bonds (Alkene) is due to the presence of the bacteria (*S. marcescens marcescens*) on the PE surface [44, 50-54]. The new functional groups and increment in wavenumbers is due to the effective biodegradation of LLDPE by the bacteria (*S. marcescens marcescens*) [25]. Also, special interest was focused on the following peaks: carbonyl bond at 1740 cm^{-1} , keto-carbonyl bond at 1715 cm^{-1} , vinyl double bond at 1650 cm^{-1} and internal double bond at 908 cm^{-1} with respect to methylene bond at 1465 cm^{-1} . The bond indexes were calculated from the IR spectra and were found to be as follows: Keto-carbonyl bond index (KCBI) = I_{1715}/I_{1465} ; Ester-carbonyl bond index (ECBI) = I_{1740}/I_{1465} ; Vinyl bond index (VBI) = I_{1650}/I_{1465} and Internal double bond index (IDBI) = I_{908}/I_{1465} . These bond indexes results are consistent with research work carried out by Albertsson et al., 1987 [55], Harshvardhan and Jha, 2013 [56] and Devi et al., 2015 [57].

However, a recent review [31] showed that, PE biodegradation follows a very difficult pattern that can differ from one microorganism to the other. Some researchers [24, 44, 52, 53, 55], also suggest a decrease in the carbonyl group of PE surface, upon exposure to microbes, while others report a decrease in the number of double bonds [27, 43, 58].

3.4 Implications

The above results show that the supernatant from *S. marcescens marcescens* is more effective at degrading LLDPE than the bacterium itself. The degradation results in significant weight loss of LLDPE during the four weeks or ten weeks of exposure. However, the actual enzymes in the supernatant that are associated with the degradation are yet to be identified. Furthermore, the degradation by-products are yet to be determined. Nevertheless, it is clear from

the SEM results that the interactions between the LLDPE and the supernatant result in the formation of voids that suggest the occurrence of erosion during exposure of LLDPE to the supernatant. Further work is clearly needed to ascertain why some regions in the LLDPE are more susceptible to void formation than others. These might be due to microbial activity on the amorphous portions of LLDPE [44-48]. Further work is clearly needed to verify such speculation.

Nevertheless, the significant weight losses due to exposure to *S. marcescens marcescens* suggest that the bacterium and its supernatant could be scaled up to promote the biodegradation and bio-deterioration of LLDPE. Further work is clearly needed to ascertain the level of scaling that can be achieved. There is also a need to assess the potential environmental impacts of the biodegradation products. These are clearly some of the challenges for future work.

3.5 CONCLUSIONS

This study shows that LLDPE powder and film can be degraded by exposure to *S. marcescens marcescens* and its supernatant for periods of 4-10 weeks. However, the rate of LLDPE biodegradation and bio-deterioration is faster in the supernatant than in the presence of *S. marcescens marcescens*. Direct exposure to the supernatant also results in a microvoid formation that is consistent with an erosion mechanism. The overall decrease in the percentage crystallinity of LLDPE (9%) suggests that, the *S. marcescens marcescens* and its supernatant degrade the amorphous and crystalline regions of LLDPE.

3.6 References

- [1] Seymour, R. B.: Polymer science before & after 1899: notable developments during the lifetime of Maurtis Dekker, J. Macromol Sci, Pure Appl Chem 26, 1023-1032 (1899).
- [2] Scott, G.: Polymers in modern life; Polymers and the Environment, the Royal Society of Chemistry, Cambridge (1999).
- [3] Mueller, R.: Biological degradation of synthetic polyesters-enzymes as potential catalysts for polyester recycling, Proc Biochem 41, 2124-8 (2006).
- [4] Sivan, A.: New perspectives in plastic biodegradation, Curr Opin Biotechnol 22,422-426 (2011).
- [5] Shah, A.A., Hasan, F., Hameed, A., Ahmed, S.: Biological degradation of plastics: A comprehensive review, Biotechnology advances 26, 246-265 (2008).
- [6] Nanda, S., Sahu, S.S.: Biodegradability of polyethylene by Brevibacillus, Pseudomonas, and Rhodococcus spp. New York Science Journal 3(7), 95-98 (2010).
- [7] Nanda, S., Sahu, S.S., Abraham, J.: Studies on the biodegradation of natural and synthetic polyethylene by Pseudomonas spp. J. Appl. Sci. Environ. Manage 14(2) 57-60 (2010).
- [8] Orhan, Y., Buyukgungor, H.: Enhancement of biodegradability of disposable polyethylene in controlled biological soil, Int. Biodeterior. Biodegrad. 45, 49-55 (2000).
- [9] Shima, M.: Biodegradation of plastics, Curr Opin Biotechnol 12, 242-247 (2001).

- [10] Ghosh, S.K., Pal, S., Ray, S.: Study of microbes having potentiality for biodegradation of plastics, *Environ Sci Pollut Res* (2013). Doi: 10.1007/s11356-013-1706-x.
- [11] Rivard, C., Moens, L., Roberts, K., Brigham, J., Kelley, S.: Starch esters as biodegradable plastics: effects of ester group chain length and degree of substitution on anaerobic biodegradation, *Enzym Microb Technol* 17:848-852 (1995).
- [12] Pospisil, J., Nespurek, S.: Highlights in chemistry and physics of polymer stabilization, *Macromol Symp* 115, 143-63 (1997).
- [13] Zheng, Y., Yanful, E. K.: A review of plastic waste biodegradation, *Critical Reviews in Biotechnology* 25, 243–250 (2005).
- [14] Sangale, M. K., Shanawaz, M., Ade, A. B.: A Review on Biodegradation of polythene: the Microbial Approach, *J. Bioremed Biodeg* 3,164 (2012).
- [15] Singh B., Sharma N.: Mechanistic implications of plastic degradation, polymer degradation and stability 93(3), 561-584 (2008).
- [16] Bonhomme, S., Cuer, A., Delort, A.M., Lemaire, J., Sancelme, M., Scott, G.: Environmental biodegradation of polyethylene., *Polym Degrad Stab* 81, 441–52 (2003).
- [17] Johnson, E., Pometto, A.L., Nikolov, Z.L.: Degradation of degradable starch–polyethylene plastics in a compost environment. *Appl Environ Microbiol* 59,1155–61 (1993).
- [18] Mahalakshmi, V., Andrew, S.N.: Assessment of physicochemically treated plastic by fungi. *Annals of Biological Research* 3 (9), 4374-4381 (2012).

- [19] Kawai F.: Breakdown of plastics and polymers by microorganisms. *Adv Biochem Eng Biotechnol* 52,151–94 (1995).
- [20] Augusta, J., Müller, R.J., Widdecke, H.: A rapid evaluation plate-test for the biodegradability of plastics. *Appl Microbiol Biotechnol* 39, 673–8 (1993).
- [21] Witt, U., Müller, R.J., Deckwer, W.D.: Biodegradation behavior and material properties of aliphatic/aromatic polyesters of commercial importance. *J. Environ Poly Degrad* 15, 81–9 (1997).
- [22] Witt, U., Einig, T., Yamamoto, M., Kleeberg I., Deckwer, W. D., Müller, R.J.: Biodegradation of aliphatic–aromatic copolyesters: evaluation of the final biodegradability and ecotoxicological impact of degradation intermediates. *Chemosphere* 44, 289–99 (2001).
- [23] Hoffmann, J., Rezníková I., Kozáková, J., Ružicka, J., Alexy, P., Bakoš, D., Precnerová, L.: Assessing biodegradability of plastic based on poly(vinyl alcohol) and protein wastes. *Polym Degrad Stab* 79, 511-519 (2003).
- [24] Hadad, D., Geresh, S., Sivan, A.: Biodegradation of polyethylene by thermophilic bacterium *Brevibacillus borstelensis*. *J. Appl Microbiol* 98, 1093-1100 (2005).
- [25] Mahalakshmi, V., Siddiq, A., Andrew, S.N.: Analysis of polyethylene degrading potentials of microorganisms isolated from compost soil, *International Journal of Pharmaceutical & Biological Archives* 3(5), 1190-1196 (2012).
- [26] Albertsson, A.C.: The shape of the biodegradation curve for low and high density polyethylenes in prolonged series of experiments, *J. Eur.Polym* 16, 623-30 (1980).

- [27] Yamada-Onodera, K., Mukumoto, H., Katsuyaya, Y., Saiganji, A., Tani, Y.: Degradation of polyethylene by a fungus. *Penicillium simplicissimum* YK, *Poly Degrad Stab* 72, 323-7 (2001).
- [28] Aamer, A.S., Hasan, F., Hameed, A., Javed, I. A.: Isolation of *Fusarium sp. AF4* from sewage sludge, with the ability to adhere the surface of 45 polyethylene, *African J. Microbiology Research* 3(10), 658-663 (2009).
- [29] Gu, J.D., Ford, T.E., Mitton, D. B., Mitchell, R.: Microbial degradation and deterioration of polymeric materials. In Review editor: the Uhlig Corrosion Handbook.2nd Edition. New York, Wiley, 439–60 (2000).
- [30] Gu, J.D.: Microbiological deterioration and degradation of synthetic polymeric materials. *Recent Res. Adv. Int. Biodeterior. Biodegrad.* 52: 69-91 (2003).
- [31] Restrepo-Flórez, J.–M., Bassi, A., Thompson, M.R.: Microbial degradation and deterioration of polyethylene - A review. *Int. Biodeterior. Biodegrad.* 88, 83-90 (2014).
- [32] Bikiaris, D., Aburto, J., Alric, I., Borredon, E., Botev, M., Betchev, C.: Mechanical properties and biodegradability of LLDPE blends with fatty-acid esters of amylase and starch, *J. Appl.Polym.Sci* 71, 1089-100 (1999).
- [33] Olsen, R.A., Bakken, L.R.: Viability of soil bacteria: Optimization of plate-counting technique and comparison between total counts and plate counts within different size groups, McGinnis and Jagdish Rughani from the Institute of Microb. *Ecol* 13, 59–74 (1987).

- [34] Kleinheinz, G.T., Bagley, S.T.: A filter-plate method for the recovery and cultivation of microorganisms utilizing volatile organic compounds. *Journal of Microbiological Methods* 29, 139–144 (1997).
- [35] Touno, K., Harada, K., Yoshimatsu, K., Yazaki, K., Shimomura, S.: Derivative formation on the stem of cultured shoots in *Lithospermum*, K. *Plant Cell Reports* vol. 19 issue 11 November 14, p. 1121 – 1126 (2000).
- [36] Murashige T., Skoog, F.: A revised medium for rapid growth and bioassays with tobacco tissue cultures. *Physiologia Plantarum* 15 (3), p. 473-497 (1962).
- [37] Wundelick, B., Cormier, C.M.: *J Polym. Sci. Part A-2: Polym. Phys.* 5, 987 (1967).
- [38] Mirabella, F.M., Bafna, A.: *J Polym. Sci. Part B: Polym. Phys.* 40, 1637 (2002).
- [39] Williams, R.F., Gott, C.L., Qadri, S.M.H., Scott, R.H.: Influence of temperature of incubation and type of growth medium on pigmentation in *Serratia marcescens*. *J Bacteriol.* 106: 438-443 (1971).
- [40] Rjazantseva, I.N., Andreeva, I.N., Ogorodnikova, T.I.: Effect of various growth conditions on pigmentation of *Serratia marcescens*. *Micmbios.* 79: 155- 16 1 (1984).
- [41] Hejazi, A., Falkiner, F.R.: *Serratia marcescens*. *J. Med. Microbiol.* 46: 903-912 (1997).
- [42] Venil, C.K., and Lakshmanaperumalsamy, P.: An insightful overview on microbial pigment, prodigiosin. *Electronic Journal of Biology.* 5: 49-61 (2009).

- [43] Sudhakar, M., Doble, M., Murthy, P.S., Venkatesan, R.: Marine microb-mediated biodegradation of low- and high-density polyethylenes. *Int. Biodeterior. Biodegrad.* 61, 203-213 (2008).
- [44] Raghavan, D., Torma, A.E.: DSC and FTIR characterization of biodegradation of polyethylene. *Polym. Eng. Sci.* 32, 438-442 (1992).
- [45] Albertsson, A.-C., Barensted, C., Karlsson, S., Lindberg, T.: Degradation product pattern and morphology changes as means to differentiate abiotically and biotically aged degradable polyethylene. *Polymer* 36, 3075-3083 (1995).
- [46] Manzur, A., Cuamatzi, F., Favela, E.: Effect of the growth of *Phanerochaete Chrysosporium* in a blend of low density polyethylene and sugar cane bagasse. *J. Appl. Polym. Sci.* 66, 105-111 (1997).
- [47] Volke-Sepulveda, T., Saucedo-Castañeda, G., Gutierrez-Rojas, M., Manzur, A., Favela-Torres, E.: Thermally treated low density polyethylene biodegradation by *Penicillium pinophilum* and *Aspergillus niger*. *J. Appl. Polym. Sci.* 83, 305-314 (2002).
- [48] Santo, M., Weitsman, R., Sivan, A.: The role of the copper-binding enzyme - laccase - in the biodegradation of polyethylene by the actinomycete *Rhodococcus ruber*. *Int. Biodeterior. Biodegrad.* 208, 1-7 (2012).
- [49] Khabbaz, F., Albertsson, A.C., Karlsson, S.: Chemical and morphological changes of environmentally degradable poly(ethylene) films exposed to thermo-oxidation. *Polymer Degradation and Stability* 63, 127–138 (1999).

- [50] Balasubramanian, V., Natarajan, K., Hemambika, B., Ramesh, N., Sumathi, C., Kottaimuthu, R., Rajesh Kannan, V.: High-density polyethylene (HDPE)- degrading potential bacteria from marine ecosystem of Gulf of Mannar, India. *Lett. Appl. Microbiol.* 51, 205-211 (2010).
- [51] Nowak, B., Pająk, J., Drozd-Bratkowicz, M., Rymarz, G.: Microorganisms participating in the biodegradation of modified polyethylene films in different soils under laboratory conditions. *Int. Biodeterior. Biodegrad.* 65, 757-767 (2011).
- [52] Gilan, I., Hadar, Y., Sivan, A.: Colonization, biofilm formation and biodegradation of polyethylene by a strain of *Rhodococcus ruber*. *Appl. Microbiol. Biotechnol.* 65, 97-104 (2004).
- [53] Manzur, A., Limón-González, M., Favela-Torres, E.: Biodegradation of physicochemically treated LLDPE by a consortium of filamentous fungi. *J. Appl. Polym. Sci.* 92, 265-271 (2004).
- [54] Chiellini, E., Corti, A., D'Antone, S.: Oxo-biodegradable full carbon backbone polymers - biodegradation behaviour of thermally oxidized polyethylene in an aqueous medium. *Polym. Degrad. Stab.* 92, 1378-1383 (2007).
- [55] Albertsson, A.-C., Andersson, S.O., Karlsson, S.: The mechanism of biodegradation of polyethylene. *Polym. Degrad. Stab.* 18, 73-87 (1987).
- [56] Harshvardhan, K., & Jha, B. Biodegradation of low-density polyethylene by marine bacteria from pelagic waters, Arabian Sea, India. *Marine pollution bulletin*, 77(1), 100-106 (2013).

- [57] Devi, R. S., Kannan, V. R., Nivas, D., Kannan, K., Chandru, S., & Antony, A. R. Biodegradation of HDPE by *Aspergillus* spp. from marine ecosystem of Gulf of Mannar, India. *Marine pollution bulletin*, 96(1-2), 32-40 (2015).
- [58] Artham, T., Sudhakar, M., Venkatesan, R., Madhavan Nair, C., Murty, K., Doble, M.: Biofouling and stability of synthetic polymers in sea water. *Int. Biodeterior. Biodegrad.* 63, 884-890 (2009).

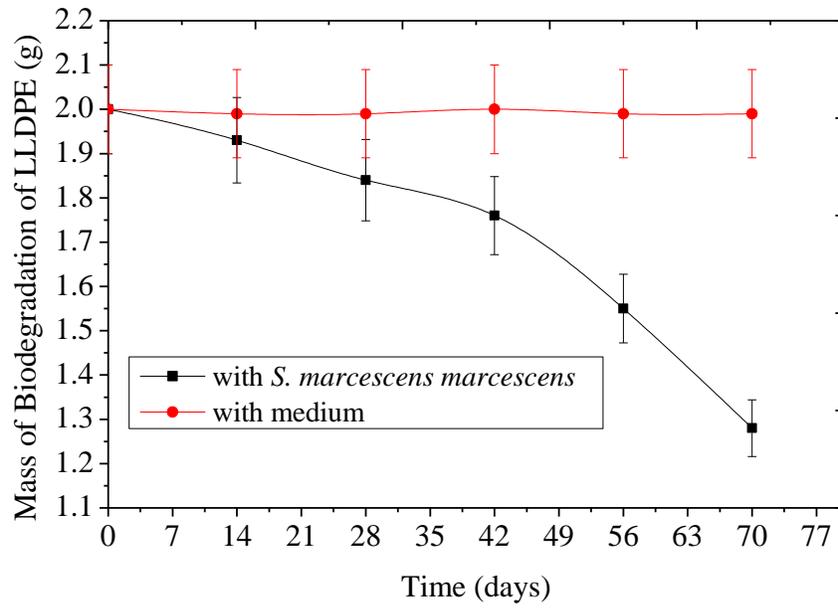


Figure 3.1: Mass of biodegradation of LLDPE during ten weeks of incubation in the presence of *S. marcescens marcescens*

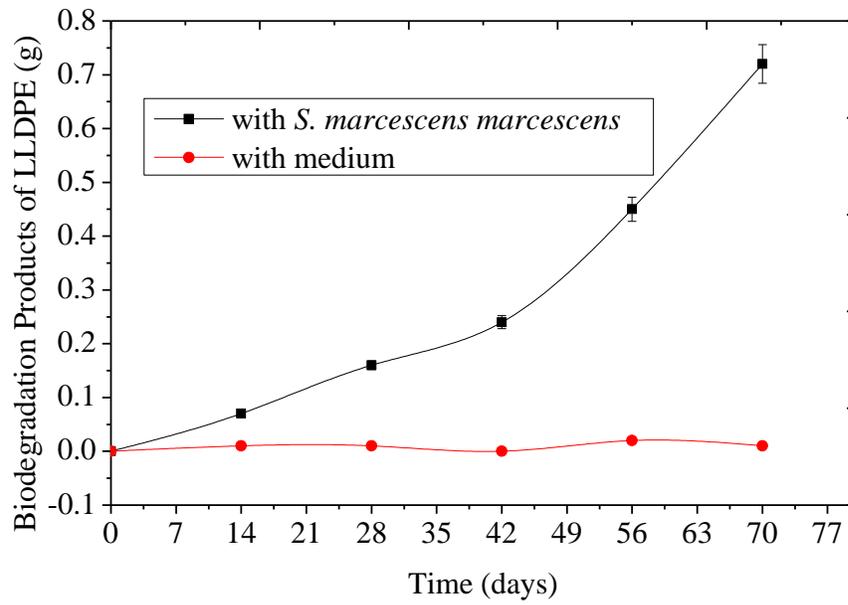


Figure 3.2: Mass of biodegradation products of LLDPE during ten weeks of incubation in the presence of *S. marcescens marcescens*

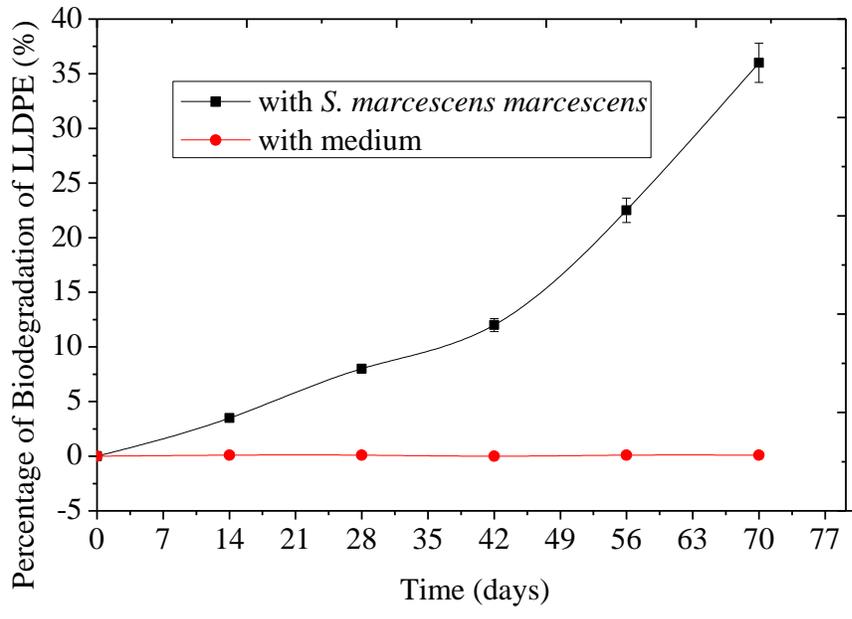


Figure 3.3: Percentage of biodegradation of LLDPE during ten weeks of incubation in the presence of *S. marcescens marcescens*

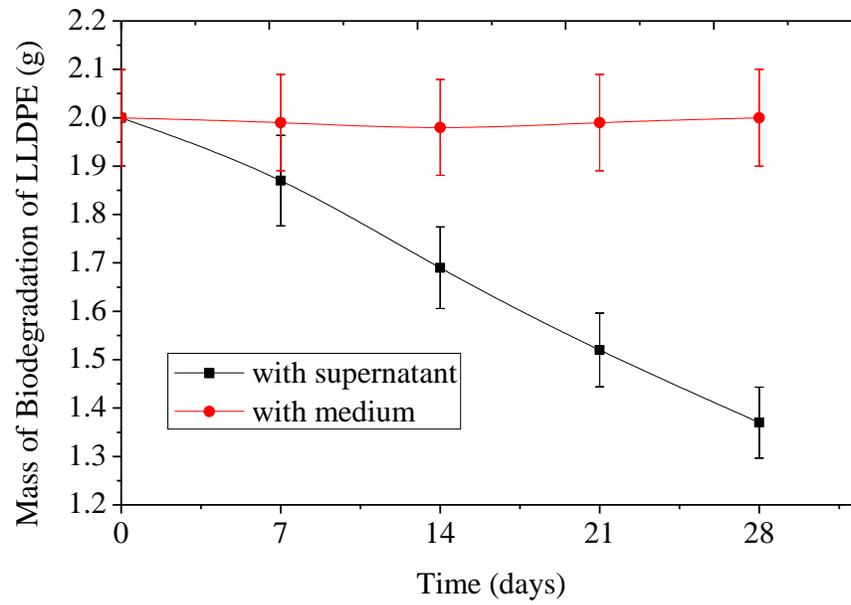


Figure 3.4: Mass of biodegradation of LLDPE during four weeks of exposure to the cell-free supernatant

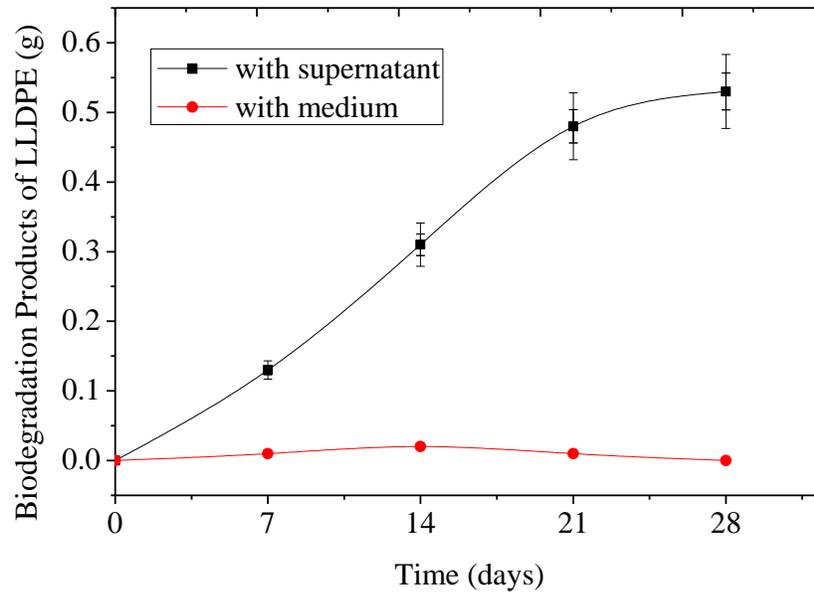


Figure 3.5: Mass of biodegradation products of LLDPE during four weeks of exposure to the cell-free supernatant

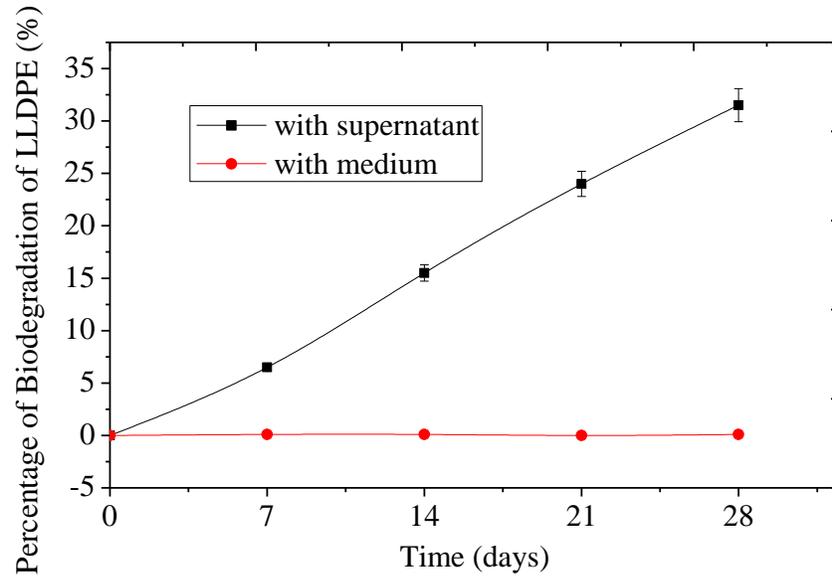


Figure 3.6: Percentage of biodegradation products of LLDPE during exposure to the cell-free supernatant for four weeks

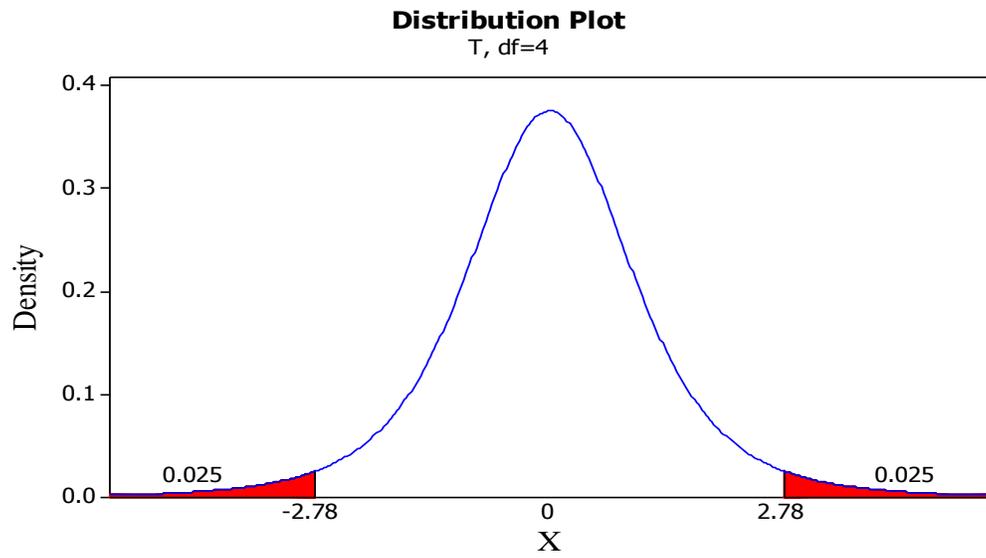


Figure 3.7: Two tail probability distribution plot at $\alpha/2 = 0.025$ for T-test

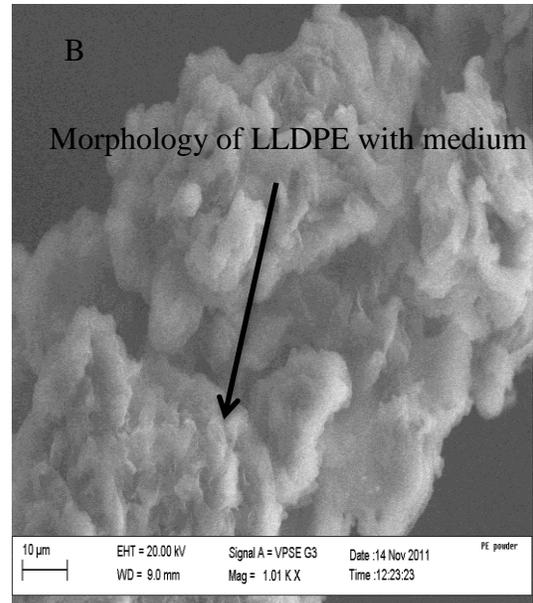
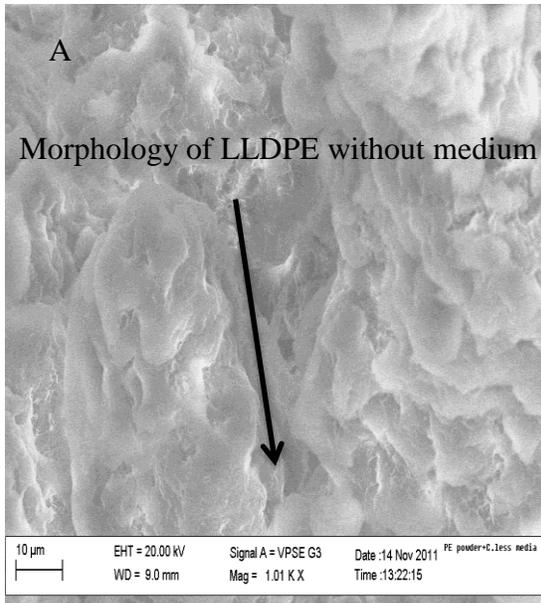


Figure 3.8: SEM micrographs of: (a) Untreated samples of LLDPE without carbonless medium and (b) Untreated samples of LLDPE with carbonless medium

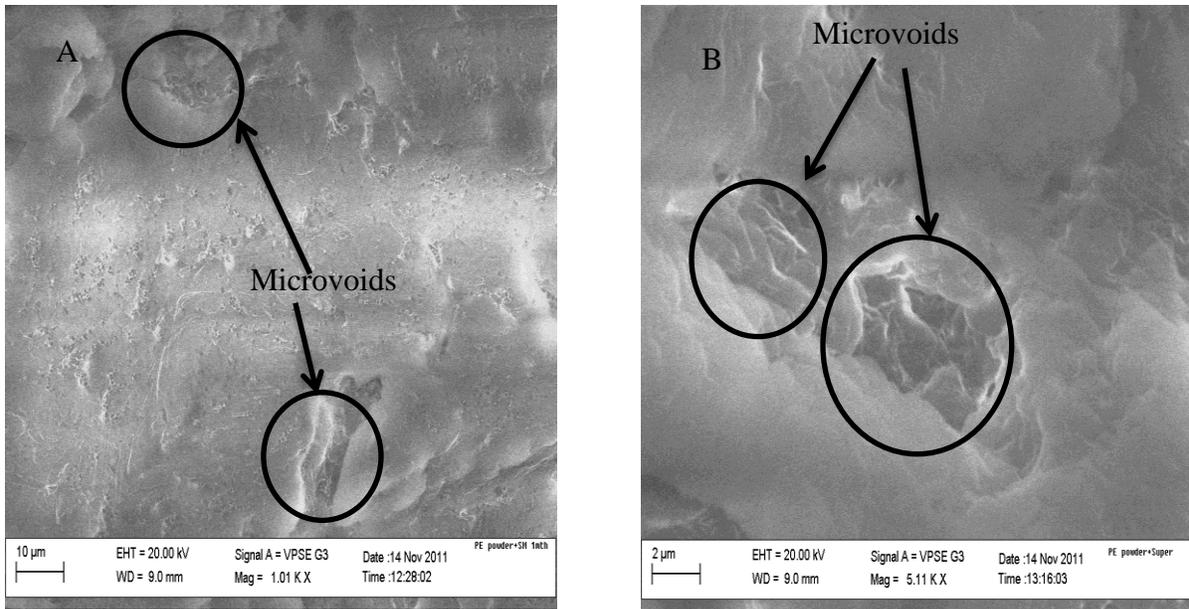


Figure 3.9: SEM micrograph of LLDPE powder (a) exposed to *S. marcescens marcescens* and (b) exposed to supernatant

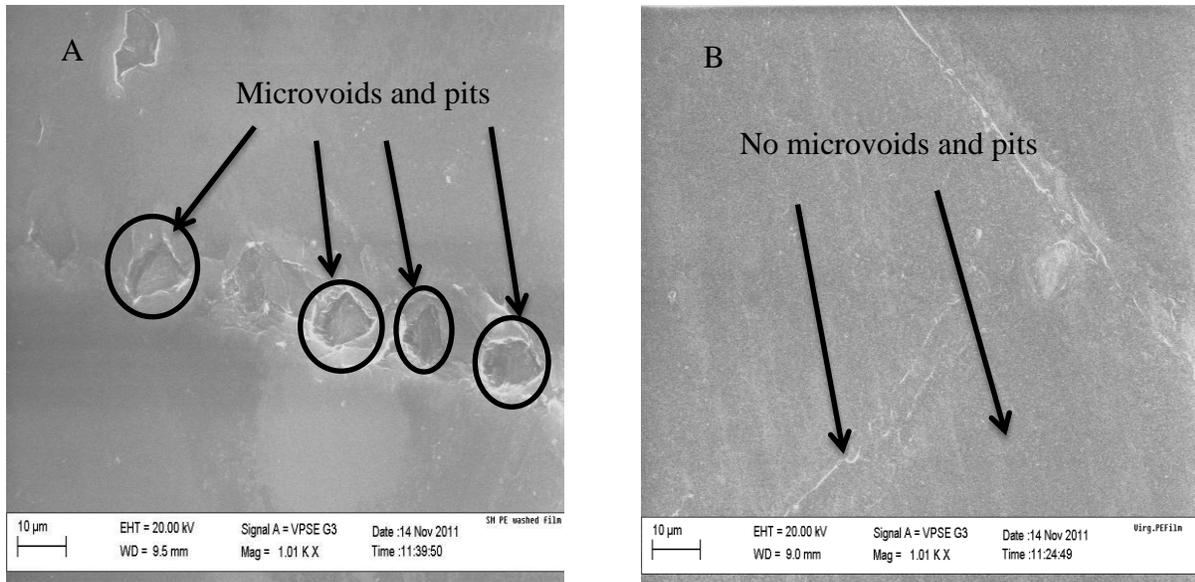


Figure 3.10: SEM micrograph of LLDPE film exposed to (a) *S. marcescens marcescens* and (b) carbonless medium

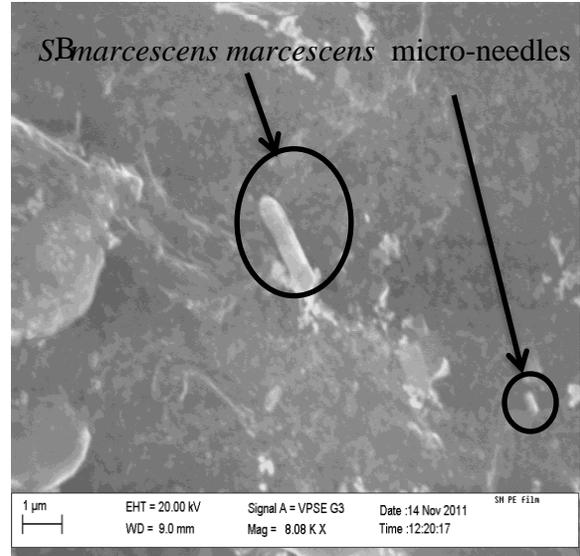
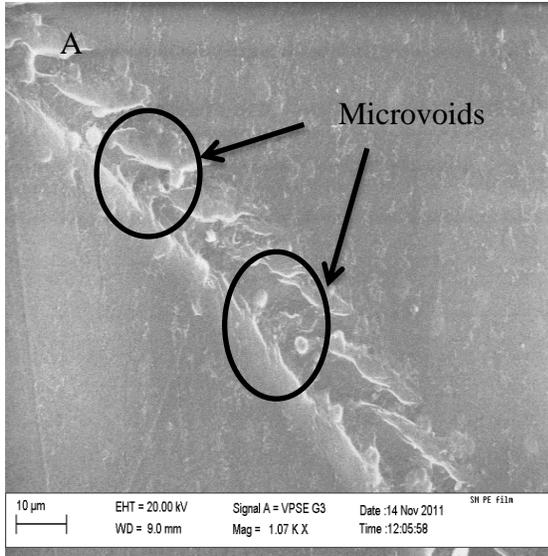


Figure 3.11: SEM micrographs of LLDPE film exposed to *S. marcescens marcescens* without washing (a) at lower magnification and (b) at higher magnification

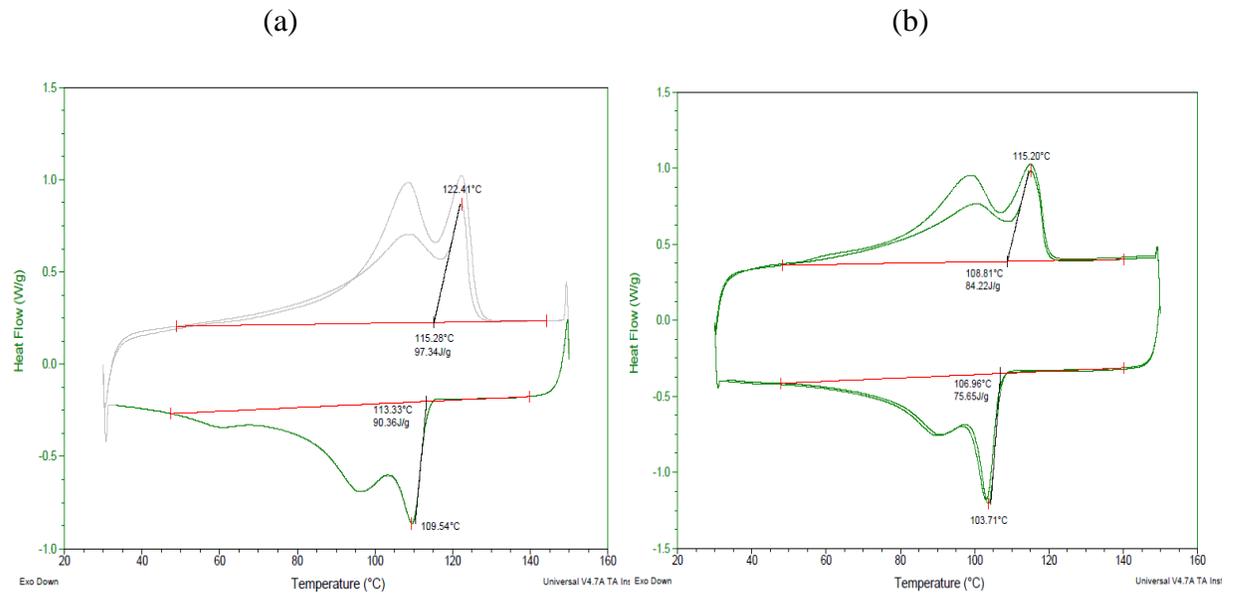


Figure 3.12: DSC analysis of LLDPE (a) without *S. marcescens marcescens* (b) with *S. marcescens marcescens*

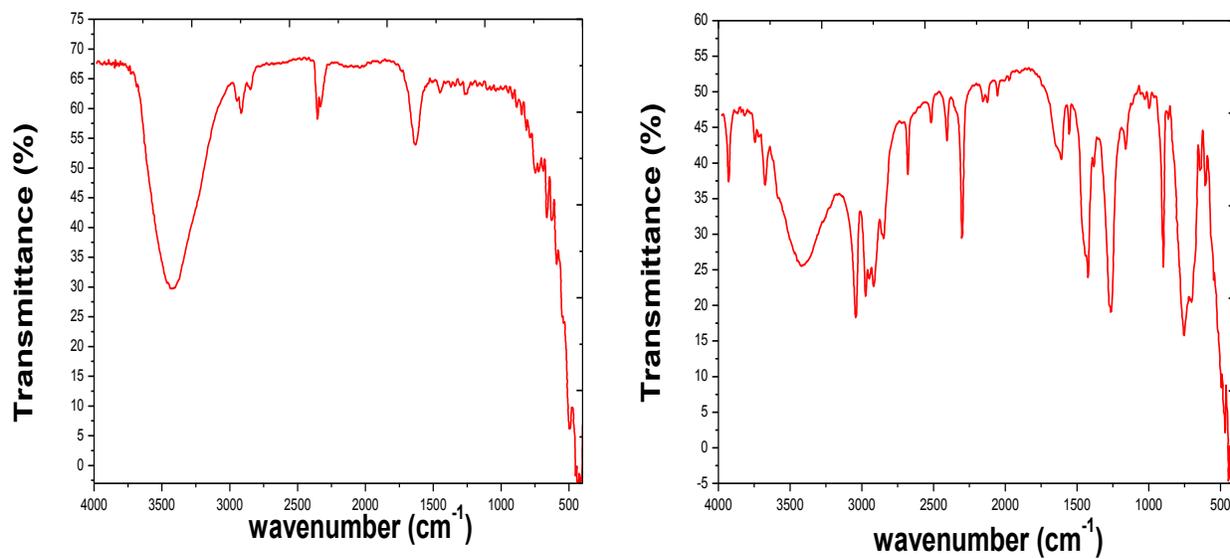


Figure 3.13: FTIR analysis of LLDE (a) without *S. marcescens marcescens* (b) with *S. marcescens marcescens*

Table 3.1: Biochemical Test for *S. marcescens marcescens*

Test	Result
Gram reaction	-ve, rods
Reactivity	
β -gal	+ve
β -glu	+ve
Urease	+ve
Indole production	-ve
Hydrogen Sulfide	-ve
Fermentation test	
Glucose	+ve
Sucrose	+ve
Glycerol	+ve
Fructose	+ve
Sorbitol	+ve
Alanine	+ve
Citrate	+ve
Cellulose	-ve
Lactose	-ve
Pigment	Absorb at UV range
Reaction with FeCl ₃	Precipitate
pH Optimum	6.5
Temperature optimal	28-32 °C

Table 3.2: One-Sample T: Mass (grams), Time (days)

Variable	N	Mean	St Dev	SE Mean	95% CI	T	P
Mass (g)	5	1.656	0.302	0.135	(1.281, 2.031)	-2.55	0.063

CHAPTER FOUR

4.0 Recycling of Polyethylene into Strong and Tough Earth-Based Composite Building Materials

4.1.0 Introduction

Plastics are synthetic organic heteroatomic polymers that are often synthesized in large quantities from oil, coal and natural gas [1]. They are generally non-biodegradable in the presence of enzymes or microbes [2]. This has led to environmental concerns, since almost 30% of plastics produced worldwide are found in food packaging, detergents and chemical substances, with this sector of the global economy growing at an annual rate of 12% [3]. These plastics include: polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET).

Approximately 140 million tons of man-made polymers, including PE, are produced annually across the world, with a utility rate of 12% [4]. This hinders the implementation of an efficient disposal system. Even though PE can be degraded by chemical, thermal, photo-degradation and biodegradation [5, 6], there is a need to recycle it into other functional materials [7].

Before the colonization of Africa, most of the houses in Africa were constructed from clay and silt [8]. However, the shrinkage of clays and the effects of mechanical loads due to wind loading can induce cracking in such structures [9]. Cracking can also be exacerbated by the effects of thermal cycling and the environment [10, 11]. Similar failure phenomena have been observed in cement-based structures that have been used more recently across the world [12].

However, cement production is associated with 5% of the global CO₂ emission [13]. There is, therefore, a need to reduce the amount of cement that is used in building materials.

Alternatives to cement include: laterite [8, 14, 15]; recycled materials such as blast furnace slag [16] and polyethylene [17]. Laterites are products of the chemical weathering of naturally occurring rocks [15]. The weathering process may take several of years before the soil (a type of clay) is produced [15]. The soil formed is usually rusty-red or reddish brown, due to the presence of iron in the oxides. It is often found in tropical regions, especially in wet and hot areas [15]. Laterites have been recommended for the construction of roads and dams, as well as applications as fillers for soil reclamation [18]. The uniform distribution and availability of well graded particle sizes of laterites, as well as their compressibility enable the moulding of bricks with improved mechanical properties [8]. However, the use of laterites alone in bricks does not provide the required strengths for load-bearing structures. There is, therefore a need to mix them with binders, especially cement or lime, to enhance their mechanical properties [14]. However, such binders (cements) are relatively expensive, approximately (4 cents per pound), which increases the cost of concrete buildings across the world.

Hence, in an effort to reduce the cost of building materials, significant efforts have been made to replace cement with industrial and agricultural waste materials [19]. Industrial waste materials include blast furnace slag [16], while agricultural waste materials include natural fibres from sisal [20, 21, 22], banana trunk [23], eucalyptus trees [24], sugar cane bagasse [25, 26, 27] and millet [28]. These have all been shown to have improved strengths [29, 30, 31] and fracture toughness [29, 30, 31]. Composite theories [32, 33] and crack-tip shielding concepts have also

been used, respectively, to explain the observed improvements in strength and fracture toughness of the resulting composites.

In contrast, there have been relatively few efforts to incorporate plastics into blocks, although plastics are often recycled into pipelines that are often used in buildings. Such recycling of plastics could facilitate the reduction in the cost of building blocks that are produced from laterite and concrete. They could also improve the strength and fracture resistance of laterite and cement matrix composites. In this work, low density polyethylene plastic bags are recycled into particles that are mixed with laterite and cement matrices to produce laterite/cement matrix composites. This paper is divided into five (5) sections. Following introduction, composites strengthening models are presented along with ductile phase toughening concepts in section 2. The experimental procedures are then described in section 3, before presenting the results obtained from the experiments and models in section 4. Salient conclusions arising from this work are summarized in section 5.

2. Modeling

2.1 Strength

The compressive and flexural strengths of the composites can be estimated from the simple rule – of– mixtures (ROM) [34]. This gives

$$\sigma_c = V_m \sigma_m + V_f \sigma_f \quad (1)$$

where σ_c is the composite strength, σ_f is the fiber strength, V_f is the fiber volume fraction, σ_m is the matrix strength and V_m is the matrix volume fraction. An example of the ROM compressive strength calculations for 10 vol. % of PE is as follows:

$$\sigma_c = (0.9 \times 2.4 \text{ MPa}) + (0.1 \times 13.5 \text{ MPa}) = 3.51 \text{ MPa}, \text{ where } V_m = 0.9, \sigma_m = 2.4 \text{ MPa (Table 1), } V_f = 0.1 \text{ and } \sigma_f = 13.5 \text{ MPa.}$$

2.2 Toughening Due to Crack Bridging

Crack bridging models have been developed to quantify the crack-tip shielding effects of brittle [35, 36, 37] or ductile [35, 36, 38] reinforcements. Depending on the shapes [34, 35] and the constrained nature of plasticity in ductile reinforcements, ductile reinforcements can promote the bridging of cracks by plastically deformed reinforcements within a bridging zone. This can result in small-scale bridging (SSB) [39, 40] and large-scale bridging (LSB) [36, 38, 41, 42] mechanisms. In the case of SSB, the shielding due to bridging ΔK_{SSB} is given by:

$$\Delta K_{SSB} = V_b \sqrt{\frac{2}{\pi}} \int_0^L \alpha \frac{\sigma_y}{\sqrt{x}} dx \quad (2)$$

Where V_b is the volume fraction of bridging phase that intercepts the dominant crack, α is a constraint/triaxiality parameter [38, 39, 41], σ_y is the yield strength, x is the horizontal distance along the crack and L is the bridge length, which is the distance from the crack tip to the last unfractured ductile reinforcement. SSB generally applies to cracks lengths that are less than $\sim 0.5\text{--}1.0$ mm [34], while in the case of LSB, the bridge lengths are generally greater than $\sim 0.5\text{--}1.0$ mm [34]. Under LSB conditions, the shielding due to crack bridging [34] can be

estimated from models that account for the effective tractions across the bridged cracks, as shown in Figure 1. These give the shielding due to LSB to be [34].

$$\Delta K_{LSB} = \int_0^L \alpha \sigma(x) h(a, x) dx \quad (3)$$

where L is the length of the bridging zone, α is a constraint/triaxiality factor, $\sigma(x)$ is a traction function along the bridge zone, and $h(a, x)$ is a weight function, given by Fett and Munz to be [42]:

$$h(a, x) = \sqrt{\frac{2}{\pi a}} \frac{1}{\sqrt{1-\frac{x}{a}}} \times \left[1 + \sum_{(v,\mu)} \frac{A_{v\mu} \left(\frac{a}{W}\right)}{\left(1-\frac{a}{W}\right)} \left(1 - \frac{x}{a}\right)^{v+1} \right]$$

(4)

where a , is the crack length and W is the specimen width. Hence, the stress intensity factor associated with the resistance-curve behavior, K_R , can be estimated from [34, 41]:

$$K_R = K_i + \Delta K_b \quad (5)$$

where K_i is the initiation toughness [41] and ΔK_b is the shielding due to crack bridging. The latter may correspond to ΔK_{SSB} for SSB or ΔK_{LSB} for LSB, depending on the lengths of the bridging zones. The above models will be used to estimate the fracture toughness/resistance-curve behavior of laterite-polyethylene composites in this paper.

4.3 Experimental Methods

4.3.1 Processing of Low Density Polyethylene (LDPE)

LDPE plastics that are often used for the packaging of pure water in Africa were obtained from the African University of Science and Technology (AUST) in Abuja, Nigeria. The LDPE plastics were dissolved at 140°C using AGO kerosene fuel obtained from the Niger Delta Development Commission (NDDC), Nigeria (AGO fuel is a trademark of NDDC of Nigeria). Prior to dissolution, the solvent was heated up to 140°C. The LDPE films were then added, and stirred in solution, until the solvent became saturated with the LDPE. The resulting slurry was then quenched to room-temperature by immersing the beakers containing the slurry into an ice-bath that was maintained at ~4°C. The resulting powders were filtered from the slurry using muslin cloth (BDH) obtained from Finlab Nigeria Limited, Abuja, Federal Capital Territory, Nigeria. The resulting LDPE powders (reinforcement) were dried and sieved into finer particles with an average particle size of $\sim 800 \pm 0.04 \mu m$.

4.3.2 Matrix and Composite Processing

Laterite was obtained from the Julius Berger Company, Gwagwalada, Abuja, Federal Capital Territory, Nigeria. This laterite was air-dried and crushed into smaller particles with the aid of a mortar and pestle (Model MP-003, Fukai Stone Co., Ltd., Shandong, China). The particles obtained were then sieved into particles with an average size of $800 \pm 0.04 \mu m$. The grain size distributions of the laterite are shown in Figure 4.2. The laterite obtained had a clay content of ~13%. Portland cement produced by Dangote Portland Limestone Cement Industry, Obajana, Kogi State, Nigeria, was used as a binder in the laterite matrix.

The laterite/cement matrix (matrix material) was mixed with PE powder with volume percentages of 10%, 20% and 30%. These were mixed with 200 mL of water in a mixer (JN500 Pan Mixer, Henan Zplus International Trade Company, Shandong, Linyi, China). Mixing was carried out for 10 minutes at 80 revolutions per minute (rpm). The resulting mixtures were then poured into wooden moulds with dimensions of 100 mm × 25 mm × 12.5 mm. Uniform pressure was then applied to the moulds for 5 minutes to produce composites with compositions presented in Table 4.1. Similar procedures were used for the moulding of the matrix material containing 80 vol. % of laterite and 20 vol. % of cement.

Similarly, river sand, with average particle of $800 \pm 0.04 \mu\text{m}$, was mixed with 20 vol. % of Dangote Portland Limestone Cement and 200 mL of water, to produce cement mortar, which was tested as a control. A total of one hundred and eighty (180) samples was produced for flexural and compressive testing, thus, making thirty composite specimens for each composite composition.

4.3.3 Compressive/Flexural Strength Testing

After drying the samples for eight weeks, the flexural/compressive strengths and the fracture toughness/resistance-curve behavior were measured with a Universal Mechanical Testing Machine (TIRAtest Model 2810, Schalkau, Thuringia, Germany). The compressive tests were carried out under displacement control at a displacement rate of 0.02 mm/s and a strain rate of 0.01/s. The specimens were loaded monotonically until failure occurred by separation into two or more pieces. Prior to testing, the actual dimensions of the specimens were measured using a pair of Vernier callipers. The compressive strengths (σ_c) were calculated from:

$$\sigma_c = \frac{F_q}{A_o} \quad (6)$$

where F_q is the force at the onset of failure and A_o is the initial cross-sectional area.

The flexural tests were conducted on moulded specimens with dimensions of 100 mm × 25 mm × 12.5 mm. The specimens were loaded under three-point bending in a Universal Mechanical Testing Machine. The specimens were loaded under displacement control until failure occurred by fracture into 2 or more pieces. The flexural strength was calculated from [43]:

$$\sigma_f = \frac{3F_Q L}{2BW^2} \quad (7)$$

where F_Q is the load at the onset of failure, L is the distance between the support points, B is the breadth of the specimen and W is the width of the specimen. Thirty (30) composite specimens were tested for each composite composition.

4.3.4 Fracture Toughness/Resistance-Curve Experiments

The fracture toughness/resistance-curve experiments were carried out on Single Edge Notched (SEN) bend specimens with dimensions of 100 mm × 25 mm × 12.5 mm. These had notch widths of ~ 4 mm. The fracture toughness was calculated from [34]:

$$K = f\left(\frac{a}{W}\right) \times \sigma \sqrt{\pi \times a} \quad (8)$$

$$f\left(\frac{a}{W}\right) = \frac{3(a/W)^{1/2}}{2(1+2(a/W)(1-a/W)^{1/2})} \times \left[1.99 - (a/W) \left(1 - a/W \times 2.15 - 3.93 \times a/W + 2.7 a^2/W^2 \right) \right] \quad (9)$$

and K is the stress intensity factor, $f\left(\frac{a}{W}\right)$ is a function of crack length, a , and specimen width, W . As before, the specimens were produced by moulding in lab air (28°C). They were then tested in a Universal Mechanical Testing System. The fracture toughness tests were conducted under load control at a stress intensity factor increase rate, K , of $0.01 \text{ MPa}\sqrt{\text{m}} \text{ s}^{-1}$. Monotonic loading was continued until fracture occurred by separation into 2 or more pieces. The specimens were then examined in a scanning electron microscope (Carl Zeiss STM AG, Jena, Thuringia, Germany) that was operated at 20 kV in the secondary imaging mode.

In an effort to identify the crack-tip shielding mechanisms, the resistance-curve behavior was also studied using the same type of SEN bend specimens that was used for the fracture toughness tests. The specimens were loaded incrementally in steps of $0.02 \text{ MPa}\sqrt{\text{m}}$ until cracks were observed to initiate from the notches with a Digital Microscope, (AY11336, Barska, Pomona, California, USA). SEN bend specimens with a notch depth of 4 mm were placed in an Instron Senohydraulic Testing Machine (Model 3360, Norwood, Massachusetts, USA). An initial load of 20 kN was then applied to the SEN specimens at a loading rate of 5 N/s and a strain rate of 0.01/s. The initiation and propagation of cracks was observed using a PC Digital Microscope (AY11336, Barska, Pomona, California, United States).

4.4 Results and Discussion

4.4.1 Microstructure

The microstructures of the laterite/cement matrix and the three composites are presented in Figures 4.3a-4.3d. These optical images show uniform distribution of polyethylene (PE) particles in the composites reinforced with 10 and 20 vol. % of PE (Figures 4.3b-4.3c). However, some aggregation of the PE was observed in the case of the composites reinforced with 30 vol. % of PE (Figure 4.3d).

Semi-quantitative Energy Dispersive X-ray Spectroscopy (EDS) analyses of the laterite revealed the presence of aluminum, iron, oxygen and titanium in the laterite powder (Figure 4.4a). EDS of the as-processed matrix (Figure 4.4b) also confirmed the presence of calcium, silicon, silica, aluminum, iron, calcium oxide, oxygen and potassium in the laterite and Portland cement after 2 months of hydration.

4.4.2 Compressive Strength

The measured compressive strengths are presented in Table 4.1. They show that the 100% laterite specimen had a compressive strength of $1.2 \pm 0.01 \text{ MPa}$. This increased to $\sim 2.4 \pm 0.02 \text{ MPa}$ for laterite with 20 volume percentage of Portland cement. This composition was considered to be the “matrix” material for the composite. The compressive strength of the PE-reinforced composites increased with increasing PE volume percentage for volume percentages of up to 20%. The highest strengths of $\sim 4.1 \pm 0.03 \text{ MPa}$ were obtained for the composite reinforced with 20 vol. % of PE. This is attributed to the effective arresting of cracks by the PE particles in the composite.

Lower strengths of $1.9 \pm 0.03 \text{ MPa}$ were obtained for composites reinforced with PE volume percentages up to 30% of PE. This is attributed to the stress concentration due to the clustering of PE particles. Such clustering of PE particles results in weak interfaces, and lower composite strengths.

The trends in the measured compressive strengths are presented in Figure 4.5a. It is of interest to compare the compressive strengths of the PE-reinforced composites and the laterite/laterite-cement matrix to those of mortar produced using river sand and 20% volume of the same Portland cement (Dangote Portland Limestone Cement, Obajana Plant, Kogi State, Nigeria) that was used in the fabrication of the matrix and laterite-PE composite materials.

Figure 4.5a shows that the cement mortar was much stronger than 100% laterite. However, the cement mortar was weaker than the matrix and the laterite-PE composite materials. The compressive strengths of all of the PE composites were also much greater than those of the conventional cement mortar material, consisting of 80 vol. % river sand and 20 vol. % of cement. This is because the PE particles bridge the cracks in the composite materials.

The measured compressive strengths of the composites (obtained from experiments) were comparable to rule-of-mixture (ROM) estimates, as shown in Figure 5b. Reinforcements with a PE volume percentage of 20% resulted in an increase in compressive strength of $\sim 3\%$. Also, PE volume percentages of 10 % and 30% resulted in percentage increases in compressive strength of $\sim 3\%$ and $\sim 4\%$, respectively.

4.4.3 Flexural Strength

The flexural strengths of the materials are presented in Figure 4.6a and Table 4.2. The river sand-cement mortar had relatively high flexural strengths that were much greater than those of the matrix material and that of the 100% laterite. However, the flexural strengths of the cement-river sand mortar were comparable to those of the laterite-PE composites, which increased with increasing PE volume percentage, for volume percentages up to 20%.

However, composites reinforced with 30 vol. % of PE had lower flexural strengths than river sand-cement mortar. This is attributed to the effects of the stress concentration associated with the clustering of PE particles. Such clustering of PE particles weakens the interfaces, thereby resulting in the lower flexural strengths of the composites reinforced with 30 vol. % PE. Similar trends were observed in the compressive strength data, for which the peak strengths corresponded to composites reinforced with 20 volume percentage of PE.

The measured flexural strengths of the composites were comparable to the ROM estimates, as shown in Figure 4.6b. The 100% matrix had a flexural strength of 4.3 ± 0.02 MPa. Although ROM suggested that each 10 vol. % of polyethylene should result in strength decrement of $\sim 2\%$, the actual measurements revealed a decrease in flexural strength for a PE volume percentage of 30%, compared to that of the composite reinforced with 20 vol. % of PE.

4.4.4 Fracture Toughness and Fracture Modes

The measured fracture toughness values are presented in Figure 4.7 and Table 4.3. The matrix material (80 vol. % laterite and 20 vol. % cement) had higher fracture toughness than the 100% laterite or the river sand and cement mortar. The fracture toughness of the laterite-PE

composites also increased with increasing PE volume percentage, for PE volume percentages up to 20 vol. % ($\sim 0.76 \pm 0.04 \text{ MPa}\sqrt{m}$). However, the composite with 30 vol. % had the lowest composite fracture toughness of $\sim 0.54 \pm 0.03 \text{ MPa}\sqrt{m}$, which was close to the fracture toughness of $\sim 0.46 \pm 0.01 \text{ MPa}\sqrt{m}$ obtained for the 100% matrix material. Again, the trend in the fracture toughness of the composite reinforced with 30 vol. % of PE is attributed to the stress concentration due to the clustering of PE particles. Such clustering of PE particles results in weak interfaces that reduce the fracture toughness values of the composites reinforced with 30 vol. % PE.

The typical fracture modes associated with the different materials are presented in Figures 4.8a-4.8d. These were obtained from SEM images of the fracture surfaces. The SEM images revealed faceted (Figure 4.8a) and smooth transgranular (Figure 4.8c) fracture modes, with some incidence of secondary cracking within the different composites (Figures 4.8a-4.8c). A higher incidence of secondary cracking was also observed on the fracture surfaces of the cement mortar consisting of river sand and cement (Figure 4.8d).

The R-curve behavior for the PE-reinforced laterite is presented in Figures 4.9a-4.9d for the matrix material (Figure 4.9a) and the composites reinforced respectively with 10%, 20% and 30% of PE (Figures 4.9b-4.9d). These show improved fracture resistance of the composites, compared to that of the matrix material. The improved crack growth resistance was associated with crack/microstructure interactions, as shown in Figure 4.10a for the laterite-cement matrix and Figures 4.10b-4.10d the laterite–polyethylene composites.

The images of the crack/microstructure interactions revealed that the cracks were bridged by the PE particles (Figures 4.10b-4.10d). Typical ranges of crack bridging parameters are summarized in Table 4.4. These were incorporated into the small-scale bridging (SSB) and large-scale bridging (LSB) models (Equations 2 and 3) to obtain theoretical predictions of the resistance-curves. The predictions are presented along with the experimental results in Figures 4.9a-4.9d.

In general, the R-Curves obtained for the predicted and experimental data were in close agreement in the SSB regime. However, some differences were observed between the experimental and predicted R-curves in the LSB regime. This is because of the evolution of steady state crack bridging conditions, with increasing crack growth (Table 4.5). Such steady-state conditions represent the upper-bound fracture toughnesses that can be achieved in the different matrix materials and composites that were examined in this study.

4.5 Implications

The current research shows that recycled PE can be used as a reinforcement material in cement-stabilized laterite. Hence, the use of PE can reduce the amount of river sand and cement that are used in the fabrication of building blocks. Furthermore, the results clearly show that improved mechanical properties of the laterite/PE composites can be engineered by applying simple rule-of-mixtures and crack-tip shielding/crack bridging models.

The best balance of compressive/flexural strength and fracture toughness/resistance curve behavior was observed in the composite reinforced with 20 vol. % PE. This has the potential for applications in infrastructure materials such as sustainable housing and roofing tiles. However,

there is a need to study the potential environmental degradation phenomena that can occur due to exposure to water, erosion and sunlight. These are clearly some of the challenges for future work.

4.6 Conclusions

1. Polyethylene plastic bags can be recycled into reinforcements in laterite-cement matrices for sustainable buildings. The resulting building materials have attractive combinations of compressive/flexural strength and fracture toughness/resistance–curve behavior that vary with reinforcement volume fraction.
2. The compressive/flexural strengths of polyethylene–reinforced laterite composites are well predicted by simple rule–of–mixtures. The measured fracture toughness and resistance–curve behavior are also consistent with predictions from small– and large–scale crack bridging models. The models also predict steady–state fracture values that are independent of specimen size.
3. The composite reinforced with 20 vol. % of PE particles was found to exhibit the best combinations of compressive/flexural strength and fracture toughness/resistance–curve behavior. Higher levels of PE reinforcement were found to promote the clustering of particles, which resulted in composites with lower compressive/flexural strengths and fracture toughness/resistance–curve behavior.
4. The PE–reinforced laterite composites have much higher strengths and fracture toughness than concrete mortar produced from river sand and Portland cement. This suggests that PE–reinforced laterite blocks can replace conventional cement blocks produced from river sand and cement. Further work is needed to determine the potential

effects of environmental degradation on the mechanical properties of PE–reinforced laterite composites.

4.7 References

- [1] Seymour RB. Polymer science before & after 1899: notable developments during the lifetime of Maurtis Dekker. *J. Macromol Sci Chem* 1989; 26:1023–1032.
- [2] Mueller RJ. Biological degradation of synthetic polyesters-enzymes as potential catalysts for polyester recycling. *Proc Biochem* 2006; 41:2124–2128.
- [3] Orhan Y, Buyukgungor H. Enhancement of biodegradability of disposable polyethylene in controlled biological soil, *Int Biodeterior Biodegrad* 2000; 45: 49-55.
- [4] Albertsson AC. The shape of the biodegradation curve for low and high density polyethylenes in prolonged series of experiments. *Eur Polym J* 1980; 16: 623–630.
- [5] Ghosh SK, Pal S, Ray S. Study of microbes having potentiality for biodegradation of plastics. *Environ Sci Pollut Res.* 2013; 20(7):4339-4355.
- [6] Witt U, Einig T, Yamamoto M, Kleeberg I, Deckwer WD, Müller RJ. Biodegradation of aliphatic–aromatic copolyesters: evaluation of the final biodegradability and ecotoxicological impact of degradation intermediates. *Chemosphere* 2001; 44(2): 289–299.
- [7] Yang BX, Pramoda KP, Xu GQ, Goh SH. Mechanical reinforcement of polyethylene using polyethylene-grafted multiwalled carbon nanotubes. *Adv Funct Mater* 2007; 17(13): 2062-2069.

- [8] James IG. Study of compressive strengths of laterite-cement mixes as a building material. *AU JT* 2009; 13(2): 114-120.
- [9] Liu YY, McCabe MF, Evans JP, van Dijk AIJM, de Jeu RAM, Su H. Influence of cracking clays on satellite observed and model simulated soil moisture. *Hydrol Earth Syst Sci Discuss* 2010; (7): 907–927.
- [10] Sultan N, Delage P, Cui YJ. Temperature effects on the volume change behavior of Boom clay. *Eng Geol* 2002; (64): 135-145.
- [11] Robinet JC, Rahbaou A, Plas F, Lebon P. A constitutive thermomechanical model for saturated clays. *Eng Geol* 1996; 41(1):145-169.
- [12] Hoskova S, Kapickova O, Trtik K, Vodak F. Effect of thermal cycling on the strength and texture of concrete for nuclear safety structures. *Acta polytechnica* 2001; 41(2): 17-19.
- [13] Worrell E, Price L, Martin N, Hendriks C, Meida LO. Carbon dioxide emissions from the global cement industry. *Annu Rev Energy Environ* 2001; 26: 303–329.
- [14] Osula DOA. A comparative evaluation of cement and lime modification of laterite. *Eng Geol* 1996; 42(1):71-81.
- [15] Lemougna PN, Melo UFC, Kamseu E, Tchamba AB. Laterite Based Stabilized Products for Sustainable Building Applications in Tropical Countries: Review and Prospects for the Case of Cameroon. *Sustainability* 2011, 3, 293-305.

- [16] Savastano Jr. H, Warden PG, Coutts RSP. Ground iron blast furnace slag as a matrix for cellulose-cement materials. *Cement Concrete Compos* 2001; 23: 389-397.
- [17] de Carvalho Neto AGV, Ganzerli TA, Cardozo AL, Fávaro SL, Pereira AGB, Giroto EM, Radovanovic E. Development of composites based on recycled polyethylene/sugarcane bagasse fibers. *Polym Compos* 2014; 35:768–774.
- [18] Gidigas MD. *Laterite soil Engineering: Pedogenesis and Engineering Principles*. Elsevier Scientific Publication Company, New York, 1976.
- [19] Savastano Jr. H, Warden PG, Coutts RSP. Potential of alternative fiber cement as building materials for developing areas. *Cement Concrete Compos* 2003; 25:585-592.
- [20] Yan L, Yiu-Wing M, Lin Y. Sisal fibre and its composites: a review of recent developments. *Compos Sci Technol* 2000; 60:2037-2055.
- [21] Joseph K, Dias R, Filho T, James B, Thomas S, de Carvalho LH. A review on sisal fiber reinforced polymer composites. *R Bras Eng Agric Ambiental* 1999; 3(3):367-379
- [22] Zhong JB, Lv J, Wei C. Mechanical properties of sisal fibre reinforced urea-formaldehyde resin composites. *Express Polym Lett* 2007; 1(10):681–687.
- [23] Sapuan SM, Harun N, Abbas KA. Design and fabrication of a multipurpose table using a composite of epoxy and banana pseudostem fibres. *J Trop Agric* 2007 45 (1-2):66–68.

- [24] Tonoli GHD., Savastano Jr. H, Fuentec E, Negroc C, Blancoc A, Rocco Lahr F.A. Eucalyptus pulp fibres as alternative reinforcement to engineered cement-based composites. *Industrial Crops and Products* 31 2010;225–232.
- [25] Ghazali MJ, Azhari C.H, Abdullah S, Omar MZ. Characterisation of natural fibres (Sugarcane Bagasse) in cement composites. *Proceedings of the World Congress on Engineering* 2008; Vol II WCE, London, 2008, p 1307-1309.
- [26] Monteiro SN, Rodriquez RJS, De Souza MV. Sugar cane bagasse waste as reinforcement in low cost composites. *Adv Perform Mater* 1998; 5:183-191.
- [27] Teixeira RS, Tonoli GHD, Santos SF, Fiorelli J, Savastano Jr. H, Rocco Lahr FA. Extruded cement based composites reinforced with sugar cane bagasse fibres. *Key Eng Mater* 2012; 517: 450-457.
- [28] Adegunwa MO, Ganiyu AA, Bakare HA, Adebowale AA. Quality evaluation of composite millet-wheat Chinchin. *Agric. Biol. J. N. Am.* 2014; 5(1): 33-39.
- [29] Maleque MA, Belal FY, Sapuan SM. Mechanical properties study of pseudo-stem banana fiber reinforced epoxy composite. *Arabian J Sci Eng* 2007; 32(2B): 359-364.
- [30] Pavithran C, Mukherjee PS, Brahmakumar M, Damodaran AD. Impact properties of natural fibre composites. *J Mater Sci Lett* 1987; 6(8): 882-884.
- [31] Pavithran C, Mukherjee PS, Brahmakumar M, Damodaran AD. Impact performance of sisal – polyester composites. *J Mater Science Letters*, London 1988; 7:825-826.

- [32] Ritchie RO. Mechanisms of fatigue crack propagation in metals, ceramics and composites: Role of crack tip shielding. *Mater Sci Eng A* 1988; 103: 15-28.
- [33] Evans AG. Perspective on the development of high toughness ceramics. *J. Am. Ceram. Soc.* 1990; 73 (2): 187-206.
- [34] Soboyejo WO. *Mechanical properties of engineered materials*, Marcel Dekker, Inc. New York 2002.
- [35] Bloyer DR, Venkateswara Rao KT, Ritchie R.O. Resistance curve toughening in ductile/brittle layered structures: behavior in Nb/Nb₃Al laminates. *J Mater Sci Eng A* 1996; 216(1): 80-90.
- [36] Bloyer DR, Venkateswara Rao KT, Ritchie R.O. Fatigue-crack propagation behavior of ductile/brittle laminated composites. *Metall Mat Trans A* 1999; 30a: 633-642.
- [37] Bloyer DR, Venkateswara Rao KT, Ritchie R.O. Fracture toughness and r-curve behavior of laminated brittle-matrix composites. *Metall Mater Trans A* 1998; 29a: 2483-2496.
- [38] Kung E, Mercer C, Allameh S, Popoola O, and Soboyejo W.O. An investigation of fracture and fatigue in a metal/polymer composite. *Metall Mater Trans A* 2001; 32A:1997-2010
- [39] Budiansky B, Amazigo J C, Evans AG. Small-scale crack bridging and the fracture toughness of particulate-reinforced ceramics. *J. Mech Phys Solids* 1988; 36(2):167-187.

[40] Soboyejo WO, Ye F, Chen L-C, Bahtish N, Schwartz DS, Lederich RJ. Effects of reinforcement morphology on the fatigue and fracture behavior of MoSi₂/Nb composites. R.J., Acta Mater. 1996; 44: 2027–2041.

[41] Lou J, Ye F, Li M, Soboyejo WO. Ductile layer toughening of brittle intermetallic composites: J Mater Sci 2002; 37(14): 3023 – 3034

[42] Fett T, Munz D. “Stress intensity factors and weight functions for one-dimensional cracks” (Institut für Material-forschung, Kernforschungszentrum, Karlsruhe, Germany, 1994).

[43] Callister Jr. WD. The 7th edition, introduction to materials science and engineering, John Wiley and Sons, Inc. 2007.

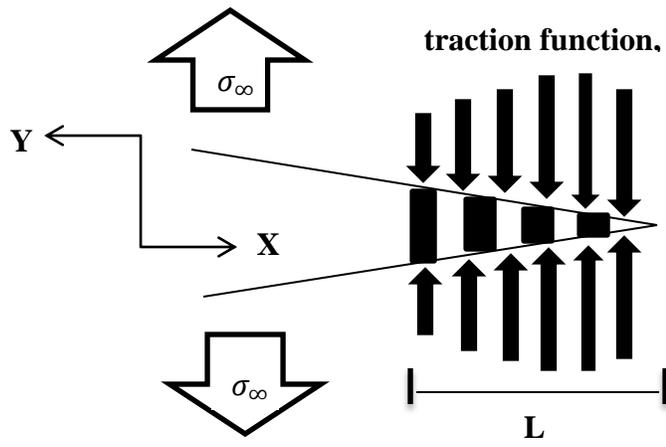


Figure 4.1: Schematic representation of a large-scale bridging model (After Bloyer et al., 1998)

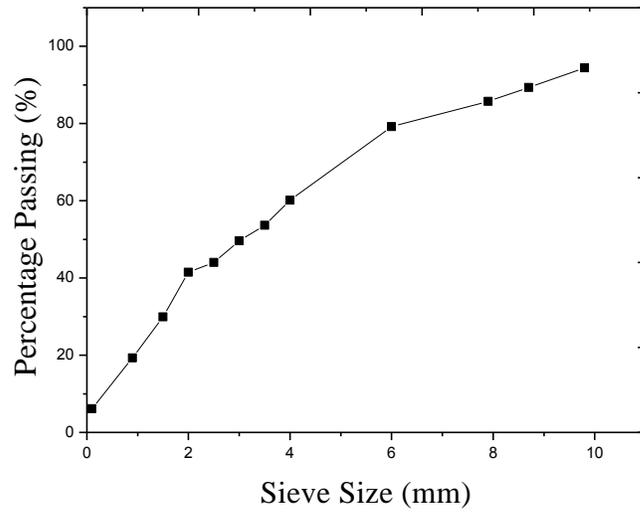


Figure 4.2: Grain Size Distribution Curve of Laterite

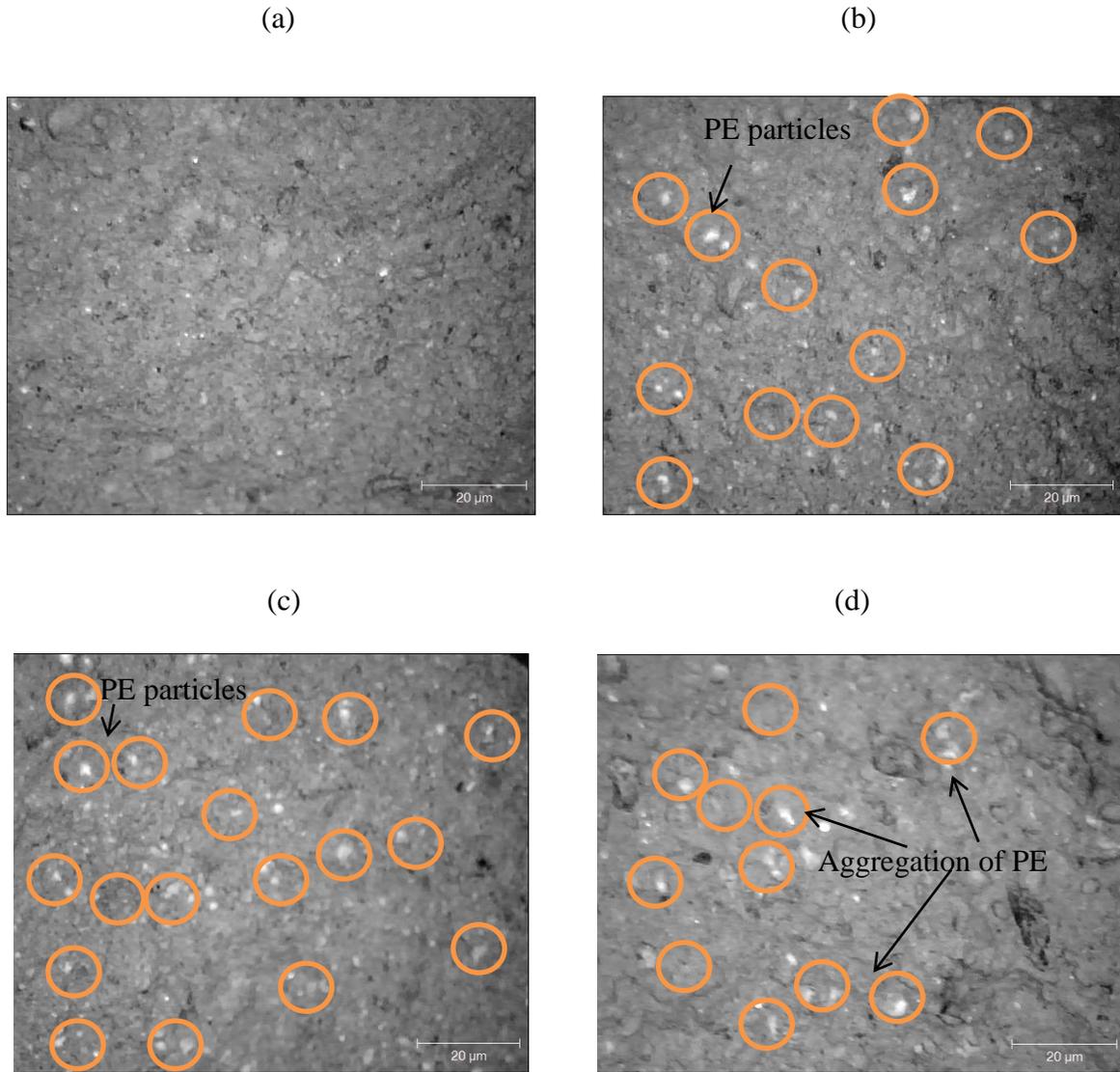
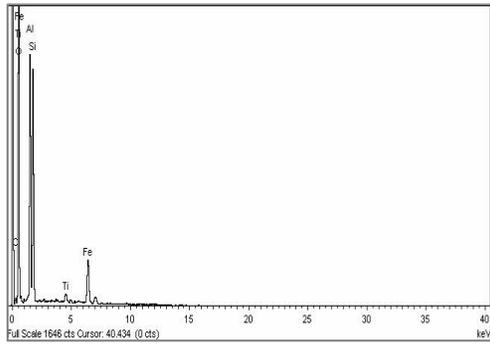


Figure 4.3: Microstructures of (a) laterite/cement matrix, (b) 10% reinforced PE, (c) 20% reinforced PE and (d) 30% reinforced PE

(a)



(b)

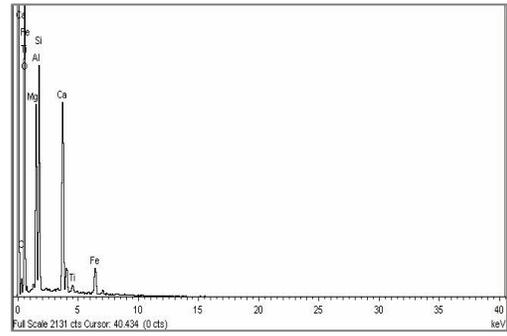
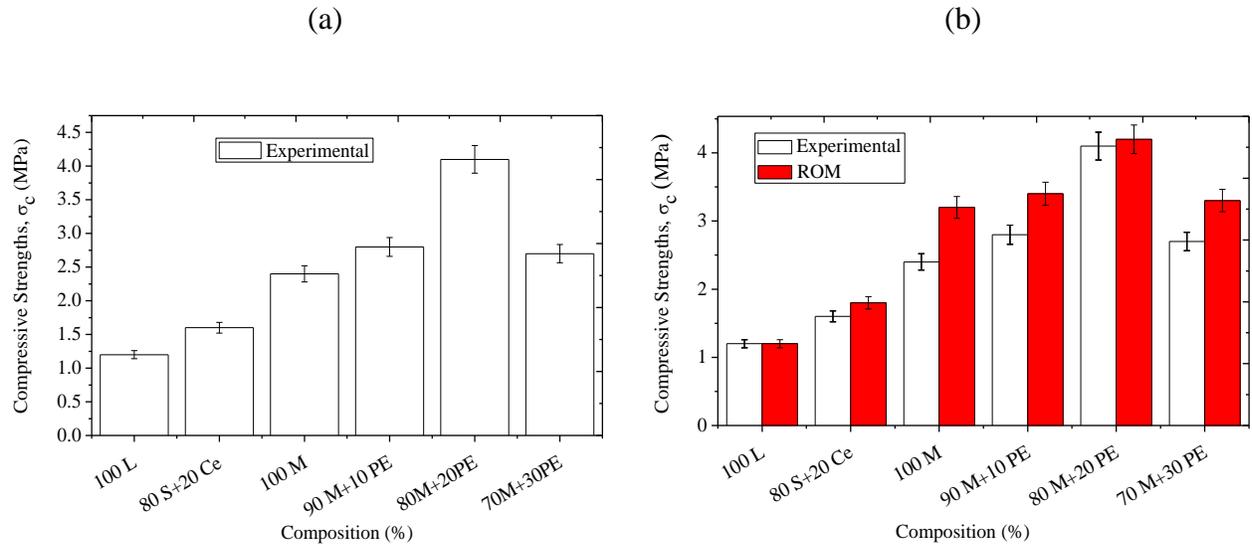


Figure 4.4: Energy Dispersive X-ray Spectroscopy Results obtained for (a) Laterite and (b) Laterite and Portland Cement



Note: L = Laterite, M= Matrix, Ce = Cement, PE= Polyethylene, S = River Sand

Figure 4.5: Compressive strengths (a) obtained for different composition, (b) compared with rule-of-mixture estimates

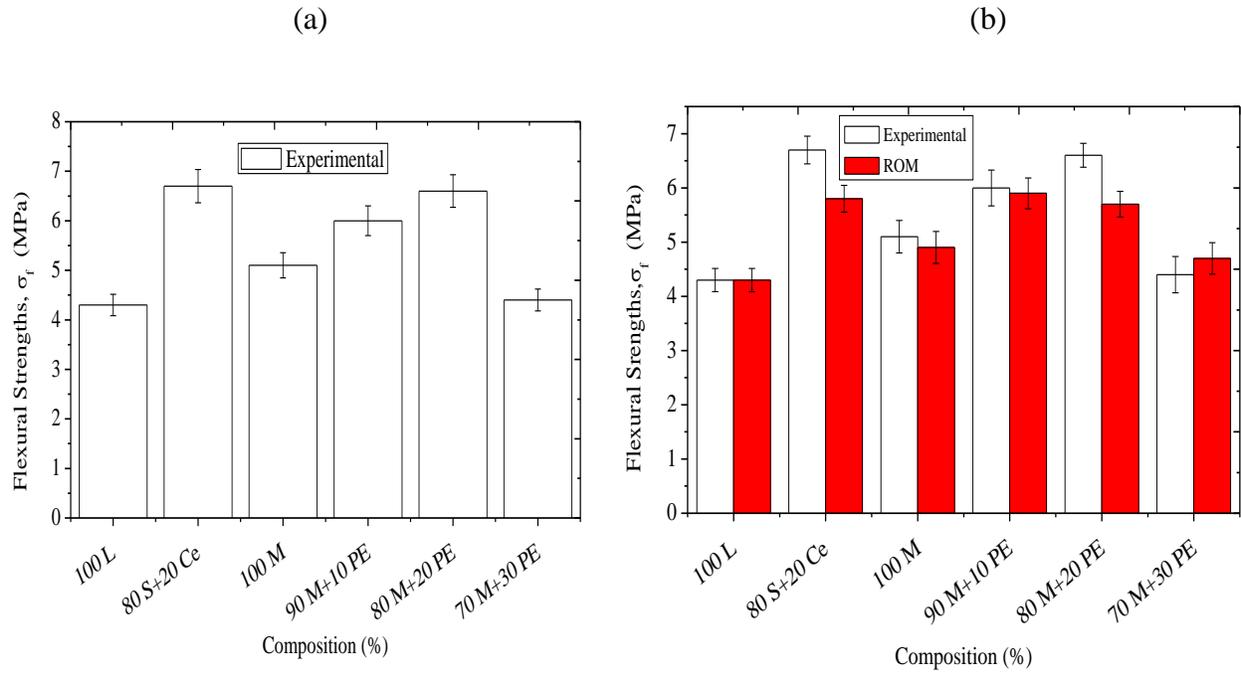


Figure 4.6: Flexural strengths (a) obtained for different composition, (b) compared with rule-of-mixture estimates

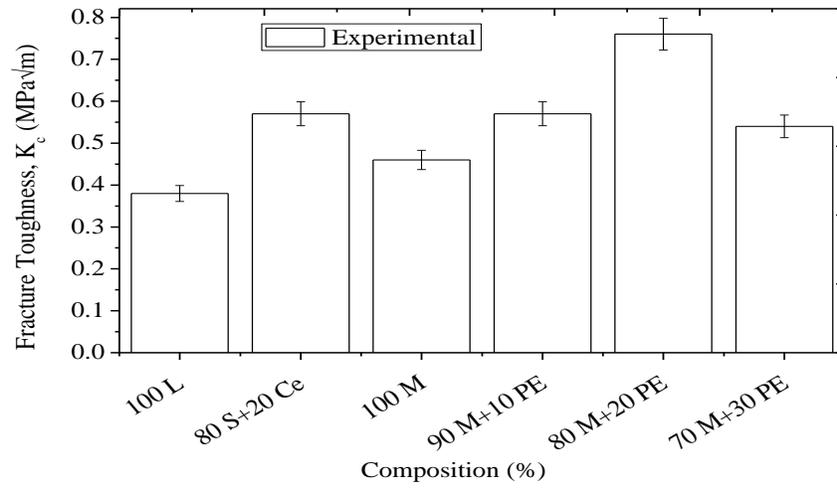
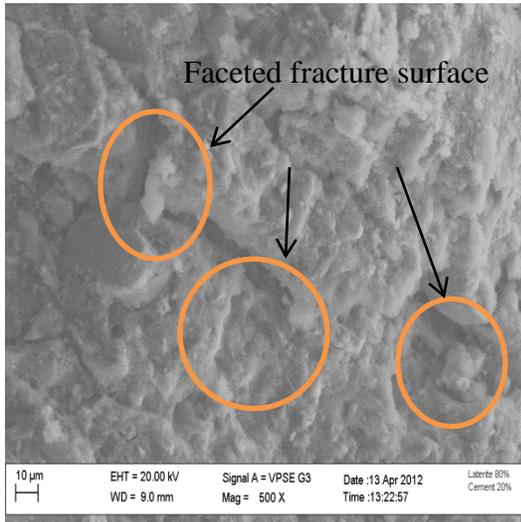
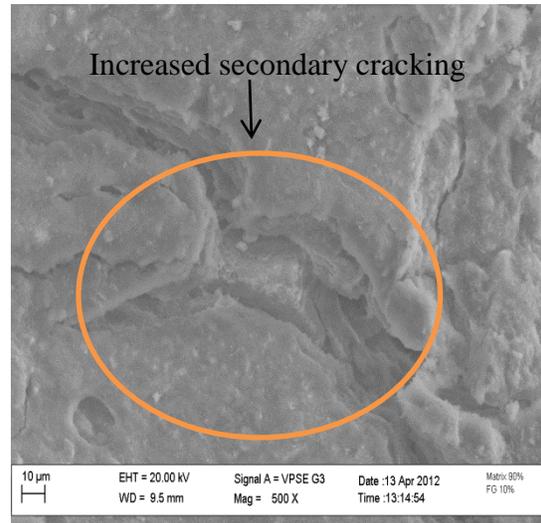


Figure 4.7: A plot of fracture toughness for single edge notch versus composition

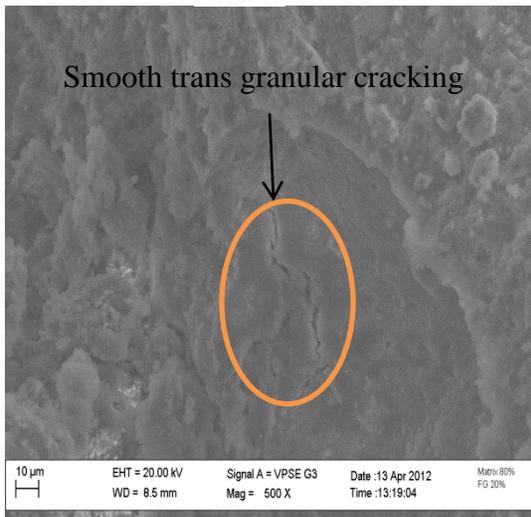
(a)



(b)



(c)



(d)

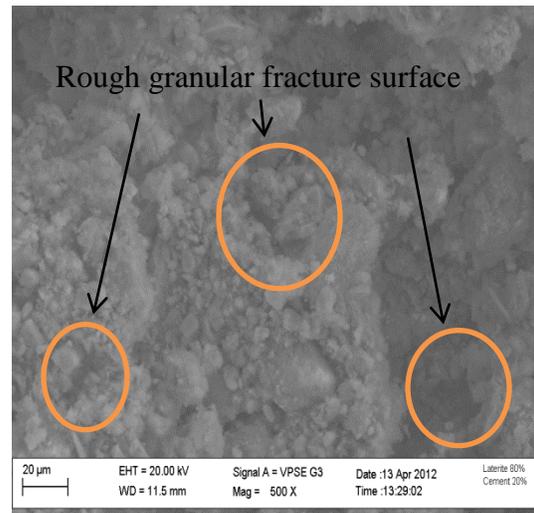


Figure 4.8: SEM micrographs of (a) faceted fracture surface with high incidence of secondary cracks in 100% matrix, (b) Increased secondary cracking in 10% PE composite, (c) Smooth trans-granular cracking in 20% PE composite and (d) Rough granular fracture surfaces with high incidence of secondary cracking in mortar from river sand and cement

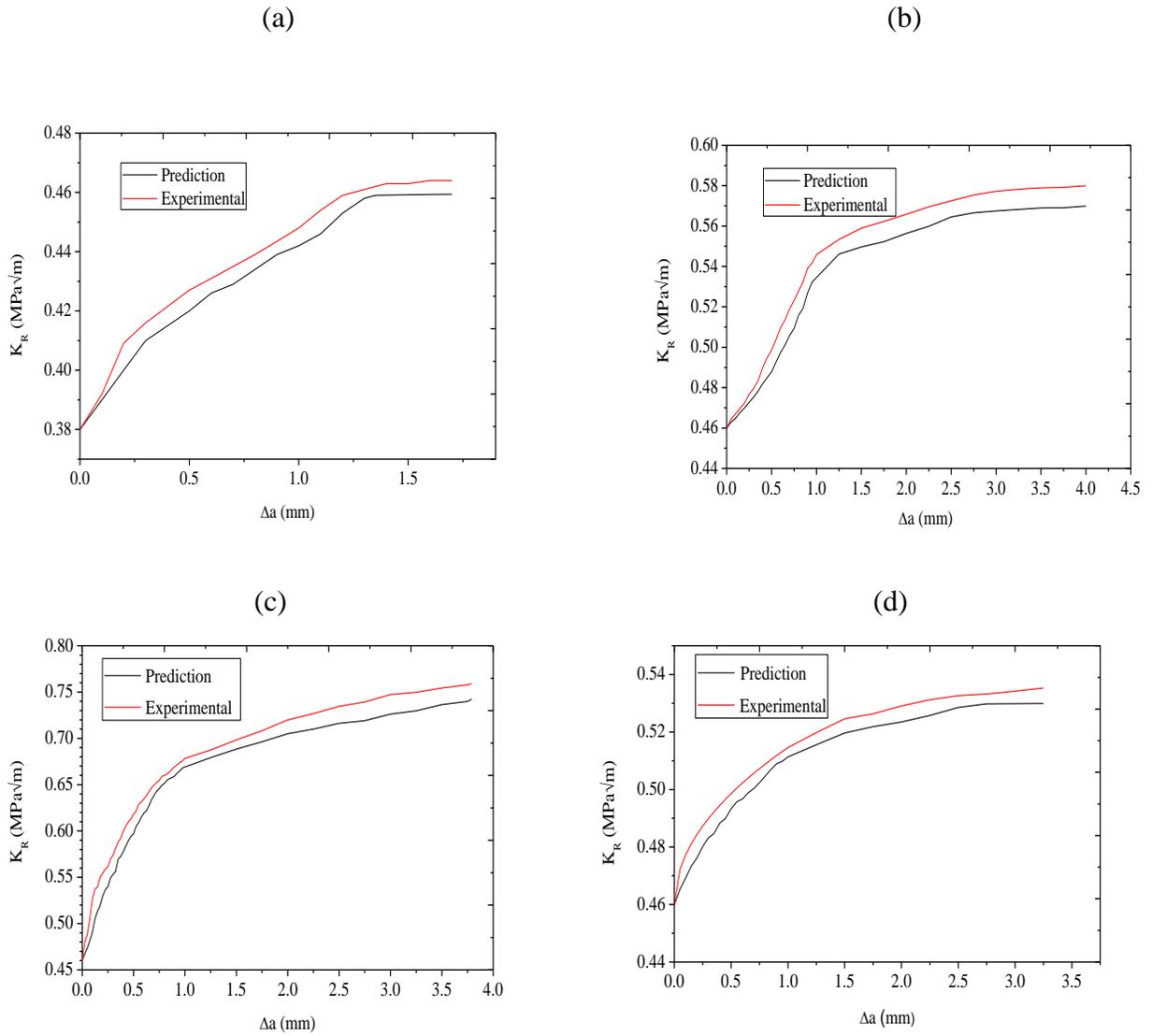


Figure 4.9: R-curves with (a) 100% matrix material, (b) 90% Matrix + 10% PE, (c) 80% Matrix + 20% PE, (d) 70% Matrix + 30% PE

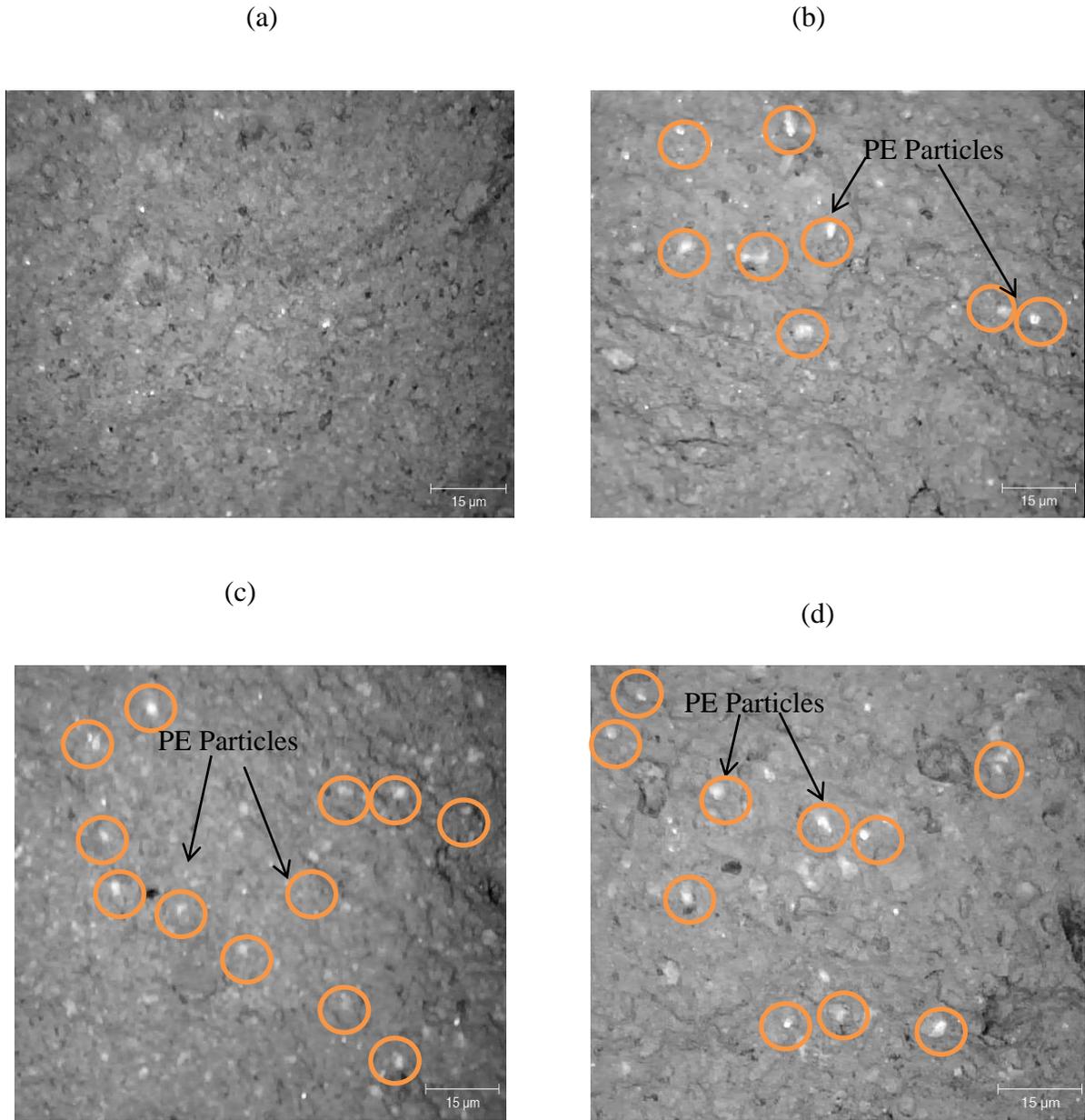


Figure 4.10: Images with Evidence of Bridging of (a) 100% matrix material, (b) 10% reinforced PE, (c) 20% reinforced PE and (d) 30% reinforced PE

Table 4.1: Compressive Strength Measurements

Samples	Composition	$\sigma_{max}(MPa)$
A	100% L	1.2±0.01
B	100% M (80%L + 20%Ce)	2.4±0.02
C	90% M (L +Ce) + 10% PE	2.8±0.04
D	80% M (L +Ce) + 20% PE	4.1±0.03
E	70% M (L +Ce) + 30% PE	1.9±0.03
F	80% S + 20% Ce	1.6± 0.02

Note: L = Laterite, M= Matrix, Ce = Cement, PE= Polyethylene, S = River Sand

Table 3.2: Flexural/Bending Strength Measurements

Samples	Composition	$\sigma_{max}(MPa)$
A	100% L	4.3±0.02
B	100%M (80%L + 20%Ce)	5.1±0.01
C	90% M (L +Ce) + 10% PE	6.0±0.03
D	80% M (L +Ce) + 20% PE	6.6±0.02
E	70% M (L +Ce) + 30% PE	4.4±0.04
F	80% S + 20% Ce	6.7±0.03

Note: L = Laterite, M= Matrix, Ce = Cement, PE= Polyethylene, S = River Sand

Table 4.3: Fracture Toughness of a Single Edge Notched Bend Specimen

Samples	Composition	$K_c(MPa\sqrt{m})$
A	100% L	0.38±0.03
B	100% M (80% L + 20% Ce)	0.46±0.02
C	90% M(L+ Ce)+10% PE	0.57±0.02
D	80% M(L +Ce)+20% PE	0.76±0.04
E	70% M(L +Ce)+30% PE	0.54±0.03
F	80% S + 20% Ce	0.57±0.03

Note: L = Laterite, M= Matrix, Ce = Cement, PE= Polyethylene, S = River Sand

Table 4.4: Fett and Munz (1994) Parameters Used for Single-Edged Notched Bend Specimen
 Subjected to Weighted Crack Bridging Fractions

		μ				
v		0	1	2	3	4
	0	0.4980	2.4463	0.0700	1.3187	-3.067
	1	0.5416	-5.0806	24.3447	-32.7208	18.1214
	2	-0.19277	2.55863	-12.6415	19.7630	-10.9

Table 4.5: Steady State Fracture Toughness Values

Composition	K_{ss} Experimental ($MPa\sqrt{m}$)	K_{ss} Prediction ($MPa\sqrt{m}$)
100% M (80% L + 20% Ce)	0.47	0.46
90% M (L + Ce) + 10% PE	0.58	0.57
80% M (L + Ce) + 20% PE	0.76	0.74
70% M (L + Ce) + 30% PE	0.54	0.53

Note: L = Laterite, M= Matrix, Ce = Cement, PE= Polyethylene, S = River Sand

CHAPTER FIVE

5.0 Statistical Distributions of the Strength and Fracture Toughness of Recycled Polyethylene-Reinforced Laterite Composites

5.1 Introduction

The mechanical properties of composites are known to depend on the volume fraction (Lewis and Nielsen 1970) [1] of their constituents, as well as the reinforcement shapes and orientations [2, 3, 4] (Brockenbrough *et al.*, 1991; Gupta and Wang 1993; Masenelli-Varlot *et al.*, 2002). Composites also exhibit statistical variations in their mechanical properties [5] (Van Mier *et al.*, 2002) which are often due to differences in the reinforcement shapes, sizes and distributions [2, 5] (Brockenbrough *et al.*, 1991; Van Mier *et al.*, 2002). However, most composites contain synthetic fibers and particulate reinforcements, which are often too expensive for widespread applications in most building materials [6] (Jawaid and Abdul Khalil 2011). There is, therefore, a need for lower cost composites that can strengthen and toughen building materials without inducing excessive variations in their mechanical properties. Within this context, natural fiber-reinforced cement matrix composites have been developed for applications in sustainable buildings [7] (Savastano *et al.*, 2000). These include; cement matrix composites reinforced with natural fibers such as sisal [8] (Zhong *et al.*, 2007), eucalyptus fibers [9] (Sapuan *et al.*, 2007) banana trunk fibers [10] (Tonoli *et al.*, 2010) and bamboo fibers [11, 12] (Okubo *et al.*, 2004; Deshpande *et al.*, 2000).

Ductile phase reinforcements, such as steel fibers [13, 14] (Nataraja *et al.*, 1999; Chen and Chung 1996) and polyethylene particles [14] (Chen and Chung 1996) have also been

incorporated into concrete matrices [13, 14] (Chen and Chung 1996; Nataraja *et al.*, 1999) and laterite/concrete matrices [15] (Udoeyo *et al.*, 2006) in recent years. Although these have been shown to strengthen and toughen the resulting composites [15] (Udoeyo *et al.*, 2006), the steel composites are relatively expensive due to the processing costs associated with the production of steel fibers [16] (Johnston 1974). In contrast, the use of recycled polyethylene reinforcements has been shown to offer a low cost alternative to the development of robust composite building materials with lower cost than steel-reinforced composites.

As is the case for most engineering composites, the strengths and fracture toughness values of construction composites are expected to exhibit significant statistical variations. These are due to differences in particle size/shape, and the variations in defect/crack sizes that are introduced during materials processing and manufacturing. Such variations have been characterized by Weibull distributions (weak link statistics) [17, 18] (Alqam *et al.*, 2002; Sakin and Ay 2008), Gaussian (normal) distributions [19, 20] (Soroushian and Lee 1990; Phoenix *et al.*, 1997), log-normal distributions [21] (Mirza and MacGregor 1979) and entropy functions [22] (Karlin *et al.*, 1999). However, although these techniques have been applied extensively to the study of brittle ceramic matrix composites, they are yet to be applied to the study of concrete or, earth-based composites for applications in sustainable buildings.

This paper explores the statistical variations in the mechanical properties (compressive strength, flexural strength and fracture toughness) of sustainable building materials. These include; polyethylene-reinforced concrete and earth-based composites. The statistical variations in the measured mechanical properties are characterized with statistical distributions that best fit

the measured variations. The implications of the results are then discussed for the design of robust buildings from concrete and earth-based composites reinforced with polyethylene particles.

5.2 Modeling

5.2.1 Statistical Distribution

Normal/Gaussian and Weibull statistics are the two most widely used statistical distributions for analyzing the strength distributions of ceramic matrix composites [18, 20] (Phoenix *et al.*, 1997; Sakin and Ay 2008). These distributions have also been used to describe the fracture toughness, as well as the fatigue behavior of brittle matrix composites [23, 24] (Bergman 1984; Soboyejo 2002). The two parameter Weibull distribution is given by [25] (Danzer *et al.*, 2007):

$$F(\sigma_u) = 1 - e^{-\left[\left(\frac{\sigma_u}{\sigma_o}\right)^m\right]} \quad (1)$$

where F is the probability of the material failure under uniaxial tensile stress, σ_u , m is the Weibull modulus or shape parameter and σ_o is a scale parameter. The value of m is related to scatter in the data. It is a measure of the homogeneity of the strength data [24, 26] (Evans 1983; Soboyejo 2002). Typical values of m range between 1 and 10 for ceramics such as silicon carbide, alumina, and silica [24] (Soboyejo 2002). Larger values of m are generally associated with less variable strength data, which would be expected from increased homogeneity. Conversely, smaller values of m would be associated with increased variability or inhomogeneity. Therefore, the lower the m value, the higher the dispersion of fracture stress and vice-versa [24] (Soboyejo 2002). Multiple experiments (usually between 20 and 50 experiments) are needed to determine

the Weibull parameters. As the number of experiments increases, the average estimates obtained from the Weibull distribution approach their true values [23, 27] (Bergman 1984; Soboyejo *et al.*, 2001).

The normal/Gaussian distribution is mostly often used to characterize the variations in large samples of experimental data [24, 27] (Soboyejo *et al.*, 2001; Soboyejo 2002). This normal/Gaussian distribution has a bell-shaped curve and is symmetrical about the mean. The normal distribution has an equal mean, mode and median. Its probability density function is given by [27] (Soboyejo *et al.*, 2001):

$$f_{\mu, \sigma^2} = \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^x e^{-(x-\mu)^2/2\sigma^2} dx \quad (2)$$

where μ is population mean and σ^2 is the variance of the population. The log normal distribution is also used to characterize the variations in strength and fracture toughness. The log normal distribution is a continuous distribution in which the logarithm of a variable is normally distributed. A log normal distribution results if the variable is the product of a large number of independent, identically distributed variables in the same way that a normal distribution results if the variable is the sum of a large number of independent, identically distributed variables.

5.2.2 Probabilistic Modeling

The different particle/grain sizes can be summed for n different particles. Thus, the size of each particle with a size of Y_i (for $i=1,2,3,\dots,n$, where n denotes the total population of particles) is measured within microstructures with different volume fractions of PE. The sum of all possible values of Y_i , can then be expressed as:

$$X = \sum_{i=1}^n Y_i \quad (3)$$

The population mean and standard deviation of the different particle/grain size are denoted by μ_X and σ_X , respectively. These are given by the following expressions [27, 28, 29] (Hoel 1962; Soboyejo *et al.*, 2001; Soboyejo 2007):

$$\mu_X = \frac{1}{n} \sum_{i=1}^n Y_i = \frac{X}{n} \quad (4)$$

$$\sigma_X = \sqrt{\frac{1}{N} \sum_{i=1}^N (Y_i - \mu_Y)^2} \quad (5)$$

5.2.3 Weibull and Normal/Gaussian Distribution

The variabilities in the strengths of most ductile phases are often well characterized by Gaussian distributions. The frequency of failure, $f(x)$ for such materials at a given stress level, x , is given by [24, 29] (Soboyejo 2002; Soboyejo 2007):

$$f_{\bar{x},\mu}(x) = \frac{1}{\mu\sqrt{2\pi}} e^{\left[-\frac{1}{2}\left(\frac{x-\bar{x}}{\mu}\right)^2\right]} \quad (6)$$

where \bar{x} is the mean strength, and μ is the standard deviation. The function $f_{\bar{x},\mu}(x)$ may be integrated to obtain an expression for the probability of failure, $P_f(x)$, at a given stress level, x (Soboyejo 2002; Soboyejo 2007) [24, 27]. This gives:

$$P_f(x) = \int_{-\infty}^{\sigma} f(x) dx \quad (7)$$

where $P_f(x)$ represents the cumulative density function and $f(x)$ corresponds to the probability density function. Conversely, the probability of survival $P_s(x)$ can be determined from the following expression [24, 30] (Weibull 1951; Soboyejo 2002):

$$P_s(x) = 1 - P_f(x) = \int_x^{\infty} f(x) dx \quad (8)$$

The statistical variations in the strengths of most brittle materials (strong and stiff fibers) often do not often follow the Gaussian distribution. Most brittle materials exhibit strength variations that are well characterized by Weibull distribution [24, 27] (Soboyejo 2001; Soboyejo 2002). This gives the probability of survival, $P_s(V)$, of a stressed volume, V , subjected to a stress level, x , by the following expression [24] (Soboyejo 2002):

$$P_s(V) = e^{\left\{ -\frac{V}{V_0} \left(\frac{X - X_\mu}{X_0} \right)^m \right\}} \quad (9)$$

where V is the sample volume, V_0 is a reference volume, X is the applied stress, X_μ is the stress corresponding to zero probability of failure, X_0 is the mean strength and m is the Weibull modulus. Conversely, the probability of failure may be obtained from the following expression [24] (Soboyejo 2002):

$$P_f(V) = 1 - P_s(V) = e^{\left\{ -\frac{V}{V_0} \left(\frac{X - X_\mu}{X_0} \right)^m \right\}} \quad (10)$$

Taking double natural logarithms of eq. 9 gives:

$$\ln \ln \frac{1}{P_s(V)} = m \ln X + C_1 \quad (11)$$

where X is the applied stress and $C_1 = \ln V - \ln V_0 - m \ln X_0$. The value of m can be determined by plotting $\ln \ln \frac{1}{P_s(V)}$ versus $\ln X$ on Weibull paper. The Weibull modulus may thus be determined from the slope of the Weibull plot.

5.2.4 Statistical Modeling of Fracture

Assuming linear elastic fracture mechanics conditions, the stress distribution, σ_{ij} ahead of a dominant crack that causes failure in the polymer-reinforced composite may be estimated from [24] (Soboyejo 2002):

$$\sigma_{ij} = \frac{K}{\sqrt{2\pi r}} f(\theta) \quad (12)$$

where K is the stress intensity factor, r and θ are the polar coordinates from the crack-tip, and $f(\theta)$ depends on mode of loading [24] (Soboyejo 2002). If we also assume that the size distribution of polymer reinforcement is comparable to a size distribution of inclusions ahead of the crack-tip, then the local conditions for cracking interfacial decohesion is given by [31] (Curry and Knott 1979):

$$\sigma_c = \frac{\pi E_m G_m}{(1-\nu_m^2) d_c} \quad (13)$$

where E_m is the Young's modulus, G_m is the fracture energy of the matrix, ν_m is the poisson's ratio of the matrix and d is the critical diameter of the particle. Hence, since the variations in the sizes of the particles are known from experimental measurements, the variations in the particle strengths can be related directly to the variations in particle strength.

Furthermore, since the statistical analysis has revealed that the variations in particle size are well characterized by Weibull (Figures 5, 6 and 8), weakest link statistics may be used to determine the failure or survival probability within the fracture process zone. The failure probability within the process zone is given by [32] (Rice and Johnson 1970):

$$\delta\phi = 1 - \exp \left[-\delta v \int_0^{\sigma} g(s) ds \right] \quad (14)$$

where δv is the incremental volume, $g(s)$ is the strength distribution, S is the strength and σ is the applied stress. Hence, survival probability is given by:

$$\Phi = 1 - \exp \left[-\int_0^v dv \int_0^{\sigma} g(s) ds \right] \quad (15)$$

where v is the volume of the process zone and $g(s) ds$ is the elemental strength distribution proposed by Weibull [33] (Weibull 1953) and given by Evans 1983 to be:

$$\int_0^{\sigma} g(s) ds = \left(\frac{\sigma - \sigma_u}{\sigma_0} \right)^m fN \quad (16)$$

where m is the Weibull modulus or shape parameter, σ_u is the lower bound particle strength, f is the fraction of particles that participates in the fracture process and N is the number of particles per unit volume. Hence, since the size distribution of particles is known along with the stress distribution within the process zone, the failure probabilities can be estimated directly from equations 5. In the case of brittle fracture under linear elastic fracture conditions, Lin *et al.*, 1986 [34] have obtained the failure probability for linear elastic conditions. For elastic-plastic

conditions, where Hutchinson-Rice-Rosengreen (HRR) conditions apply, then the crack-tip field is given by:

$$\frac{\sigma_{ij}}{\sigma_{ys}} = \left[\frac{EJ}{\alpha\sigma_{ys}^2 I_n r} \right]^{\frac{1}{n+1}} \tilde{\sigma}_{ij}^{n+1}(n, \theta) \quad (17)$$

where E is the Young's modulus, J is the J integral, σ_{ys} is the yield stress, n is the strain hardening exponent, I_n is an integration constant that is dependent on n and stress state. If we now assume that weak link statistics prevail, the survival probability in the elemental volume is given by [33] (Weibull 1953):

$$P_s(\bar{\sigma}_i) = \exp \left[-\delta v_i \left(\frac{\bar{\sigma}_i - \sigma_u}{\sigma_0} \right)^m \right] \quad (18)$$

where δv_i is the volume of the plastic zone, σ_u is the lower bound strength, σ_0 is the mean strength and $\bar{\sigma}_i$ is the average stress component in the annular element. Also as, δv_i approaches zero, the average stress equals σ at r.

Now, if the probability of survival in the first annular element is P_1 , and that in the second annular element is P_2 and so on, then we may estimate the probability of survival in the fracture process zone with k annular volumes as:

$$P_s(k) = P_s(1).P_s(2).P_s(3)...P_s(k) \quad (19)$$

Hence, substituting equation 18 into 19 gives:

$$P_s(k) = \prod_{i=1}^k \exp \left[-\delta v_i \left(\frac{\sigma_i - \sigma_u}{\sigma_o} \right) \right]^m \quad (20)$$

or

$$P_s(k) = \exp \left[-\delta v_i \sum_{i=1}^k \left(\frac{\sigma_i - \sigma_u}{\sigma_o} \right)^m \right] \quad (21)$$

Hence, the total survival probability may now be expressed in integral form to be:

$$P_s(r) = \exp \left[-2B\beta fN \int_0^{r_p} \int_0^{\pi} \left(\frac{\sigma - \sigma_u}{\sigma_o} \right)^m r dr d\theta \right] \quad (22)$$

where r_o is the radial distance at which HRR stresses are truncated by crack-tip blunting and r_p is the plastic zone size which is given by:

$$r_p = \lambda \left(\frac{K_I}{\sigma_{ys}} \right)^2 \quad (23)$$

where K_I is the mode I stress intensity factor and σ_{ys} is the yield stress. The crack tip opening displacement (CTOD), δ , is given by:

$$\delta = d_n \sigma_{ys} K_I^2 / E' \quad (24)$$

where $E' = E / (1 - \nu^2)$ for plain strain conditions and $E' = E$ for plane stress conditions. The parameter d_n is given by:

$$d_n = 2\tilde{\mu}_{ij}(\pi, n) \left[\frac{\alpha\sigma_y}{E'} (\tilde{\mu}_x(\pi, n) + \tilde{\mu}_y(\pi, n)) \right]^{\frac{1}{n}} \quad (25)$$

where $\tilde{\mu}_x(\pi, n)$ and $\tilde{\mu}_y(\pi, n)$ are functions of n , and the other constants have their usual meanings. Using a typical value of d_n of 0.5 and substituting equation 13 into 12 gives:

$$r_p = \lambda \frac{E\delta}{d_n(1-\nu)\sigma_{ys}} \quad (26)$$

Hence, the total failure probability, Φ , is given by:

$$\Phi = 1 - P_s(r) = 1 - \exp \left[-2B\beta fN \int_0^{\pi} \int_{r_o}^{r_p} \left(\frac{\sigma - \sigma_u}{\sigma_o} \right)^m r dr d\theta \right] \quad (27)$$

If we now assume for simplicity that $\sigma_u = 0$, since the lower bound particle strength should be close to zero, equations 10 and 11 should provide estimates of the survival and failure probabilities at distances ahead of an advancing crack-tip. Hence, $P_s(k) = P_f(k) = 0.5$ corresponds to the mean survival or failure probabilities and so on.

The values of the CTOD, δ , corresponding to the survival or failure probabilities may, thus be obtained from:

$$\delta = \left(\frac{\ell n 2}{2B(k) f N I_1 I_2} \right)^{\frac{n+1}{m}} \left(\frac{\sigma_o}{\sigma_{ys}} \right)^{n+1} \left(\frac{\alpha I_n d_n \sigma_{ys}}{E} \right) \quad (28)$$

where $I_1 = \int_0^{\pi} \tilde{\sigma}_{ij}^{m(n+1)}(n, \theta) d\theta$

and

$$I_2 = \int_{r_o}^{r_p} r^{\frac{n+1-m}{n+1}} dr$$

The above expressions can be used to determine the parameters for substitution into equation 27 for the determination of the failure probability as a function of particle size. Hence, using the measured variations in particle size, strengths and fracture toughness, the failure and survival probabilities can be characterized as a function of distance from the crack-tip.

5.3 Experimental Methods

5.3.1 Processing of Polyethylene

LDPE plastics are often used for the packaging of pure water in Africa. The LDPE plastic bags that were used in this study were obtained from the African University of Science and Technology (AUST) in Abuja, Nigeria. These were dissolved at 140°C using AGO kerosene fuel supplied by the Niger Delta Development Commission (NDDC), Nigeria (AGO fuel is a trademark of NDDC of Nigeria). Prior to dissolution, the solvent was heated up to 140°C. The LDPE films were then added, and stirred in solution until the solvent became saturated with the LDPE. The resulting slurry was then quenched to room-temperature (~25°C) by immersing the beakers containing the slurry into an ice-bath that was maintained at ~4°C. The resulting powders were then filtered from the slurry using muslin cloth (BDH) obtained from Finlab

Nigeria Limited, Abuja, Federal Capital Territory, Nigeria. The LDPE powders (reinforcement) were then air dried and sieved into different particles with average particle size of $\sim 300\pm 0.02 \mu\text{m}$, $\sim 600\pm 0.03 \mu\text{m}$, $\sim 900\pm 0.03 \mu\text{m}$, $\sim 1200\pm 0.02 \mu\text{m}$ $\sim 1500\pm 0.04 \mu\text{m}$ and $\sim 1800\pm 0.03 \mu\text{m}$.

5.3.2 Matrix and Composite Processing

Laterite was obtained from the Julius Berger Company, Gwagwalada, Abuja, Federal Capital Territory, Nigeria. The laterite was air dried for 7 hours and pounded into smaller particles with the aid of a mortar and pestle (Model MP-003, Fukai Stone Co., Ltd., Shandong, China). The particles obtained were then sieved into particles with an average size of $\sim 300\pm 0.02 \mu\text{m}$, $\sim 600\pm 0.03 \mu\text{m}$, $\sim 900\pm 0.03 \mu\text{m}$, $\sim 1200\pm 0.02 \mu\text{m}$, $\sim 1500\pm 0.04 \mu\text{m}$ and $\sim 1800\pm 0.03 \mu\text{m}$.

Portland cement produced by Dangote Portland Cement Industry, Ajaokuta, Kogi State, Nigeria was used as a binder in the laterite matrix. The laterite/cement matrix was mixed with PE powder with volume percentages of 10 vol. %, 20 vol. % and 30 vol. %. These were mixed for 10 minutes with 200 mL of water at 80 revolutions per minute (rpm), in a pan mixer (JN500 pan mixer, Henan Zplus international Trade Company, Shandong, Linyi, China). The mixtures were then poured into wooden moulds with dimensions of 100 mm \times 25 mm \times 12.5 mm. Uniform pressure was then applied to the moulds for 5 minutes to produce composites with different compositions. The matrix material (80 vol. % of laterite and 20 vol. % of cement) was also moulded under the same conditions that were used for the moulding of the composites. A

total of ninety (90) samples was produced for flexural, compressive and fracture toughness testing for each particle sizes.

5.3.3 Compressive/Flexural Strength Testing

After drying the samples for eight weeks, the flexural/compressive strengths and the fracture toughness/resistance-curve behavior were measured with a Universal Mechanical Testing Machine (TIRAtest model 2810, Schalkau, Thuringia, Germany). The compression tests were carried out under displacement control at a displacement rate of 0.02 mm/s. The specimens were loaded monotonically until failure occurred by separation into two or more pieces. Prior to testing, the actual dimensions of the specimens were measured using a pair of Vernier callipers. The compressive strengths (σ_c) were calculated from:

$$\sigma_c = \frac{F_q}{A_o} \quad (29)$$

where F_q is the force at the onset of failure and A_o is the initial cross-sectional area. The flexural tests were conducted on moulded specimens with dimensions of 100 mm \times 25 mm \times 12.5 mm. The specimens were loaded under three-point bending in a Universal mechanical Testing Machine. The specimens were loaded under displacement control until failure occurred by fracture into 2 or more pieces. The flexural strengths, σ_f , were calculated from [35] (Callister and Rethwisch 2012):

$$\sigma_f = \frac{3F_Q L}{2BW^2} \quad (30)$$

where F_Q is the load at the onset of failure, L is the distance between the support points, B is the breadth of the specimen and W is the width of the specimen. Thirty (30) composite specimens were tested for each composite composition and particle sizes.

5.4 Results and Discussion

5.4.1 Compressive Strength

The measured compressive strengths obtained for the different particle sizes of laterite and PE are presented in Figures 1a-1c. These show the strengths obtained for the different particle sizes of laterite (Figures 1a-1c). Also, composite reinforcement with 10 vol. %, 20 vol. % and 30 vol. % PE resulted in different strengths. The 20 vol. % PE had a maximum strength of $\sim 4.2 \pm 0.02 \text{ MPa}$, while the least strength of $\sim 1.9 \pm 0.03 \text{ MPa}$ was recorded for 30 vol. % PE. The reduction in strength for 30 vol. % PE is due to the clustering of PE particles in the composite.

However, for composites reinforced with 20 vol. % PE, the highest strength was associated with particle size of $\sim 900 \pm 0.03 \mu\text{m}$, while the least strength occurred for a particle size of $\sim 1800 \pm 0.03 \mu\text{m}$. This pattern was similar to 10 vol. % and 30 vol. % PE. However, the composites reinforced with 10 vol. % PE had strength values that were intermediate between those composites reinforced with 20 vol. % and 30 vol. % PE.

5.4.2 Flexural Strength

The flexural strengths of the PE-laterite composites are presented in Figures 2a-2c. The different particle sizes of laterite did not significantly affect the strengths of the PE-laterite

composites (Figures 2a-2c) The composites reinforced with 20 vol. % PE and particle sizes of $\sim 900 \pm 0.02 \mu m$ had the best flexural strength of $\sim 6.6 \pm 0.02 MPa$ (Figure 2b). The PE-laterite composites reinforced with 30 vol. % PE and particle sizes of $\sim 1800 \pm 0.03 \mu m$ had the lowest flexural strengths of $\sim 4.3 \pm 0.04 MPa$. This is because, the particle sizes of PE are too big to fill the voids and as a result, clustering of PE particles occurred.

5.4.3 Fracture Toughness

The measured fracture toughness values are presented in Figure 3. The measured fracture toughness of PE-laterite composites also increased with increasing PE vol. %, for PE vol. percentages up to 20 vol. % ($\sim 0.76 \pm 0.04 MPa\sqrt{m}$). The measured fracture toughness values of the PE-laterite composites again increased with increasing particle size up to $\sim 900 \pm 0.02 \mu m$. The fracture toughness then decreased gradually, with increasing particle size up to $\sim 1800 \pm 0.03 \mu m$.

5.4.4 Statistical Variations

The probability density function plots that are obtained for the compressive/flexural composite strengths and fracture toughness values are presented, respectively, in Figures 4a-4f and 5a-5f. They show that the strength distributions of the PE-laterite composites are well characterized by Weibull distributions (Figure 5a-5f). This can be attributed to the shape of the strengths and fracture toughness values in the predicted and measured plots of the probability density functions.

The cumulative density functions (CDFs) are presented in Figures 6a-6f. They show that the distribution that best fit the different particle sizes of PE in the PE-laterite composites is the Weibull distribution. This is consistent with the brittle nature of the matrix materials in which variations in PE particle size are likely to include notch like-effects that are described by weak-link statistics.

The probability plots for the PE-laterite composites for the strength models are shown in Figures 7a-7f and 8a-8f. They further show that the PE-laterite composite was best characterized by the Weibull distribution (Figure 8a-8f). This was due to its lower Anderson Darling statistics and the probability values greater than the significance level of 0.05.

The total survival and failure probabilities of PE-laterite composites are presented in Figures 9 and 10. These show that, the PE-laterite composites for particle sizes of 900 μm can survive for at least 10 mm before reasonable failure occurs (Figures 9 and 10). However, the other different particle sizes can survive for at least 4 mm before reasonable failure occurs (Figures 9 and 10).

5.5 Implications

The current research shows that different particle sizes of recycled PE can be used as a reinforcement material in cement-stabilized laterite. The optimum strengths and fracture toughness of recycled PE were also comparable to those of regular building materials.

Hence, the use of PE can reduce the amount of river sand and cement that are used in the fabrication of building blocks. The composite reinforced with 20 vol. % PE and particles sizes of $\sim 900 \mu\text{m}$ were found to exhibit the best combinations of compressive/flexural strength and

fracture toughness. The lower strengths and fracture toughness obtained from the composite reinforced with 30 vol. % are attributed to the stress concentration due to the clustering of particles in these composites. Higher levels of PE reinforcement were found to promote the clustering of particles, which resulted in composites with lower compressive/flexural strengths and fracture toughness. The strengths and fracture toughness values of PE-laterite composite are best characterized by the Weibull distributions. This has the potential for applications in infrastructure materials such as sustainable housing, roofing tiles and pavements. However, there is a need to study the potential environmental degradation phenomena that can occur due to exposure to water, erosion and sunlight. These are clearly some of the challenges for future work.

5.6 Summary and Concluding Remarks

1. Polyethylene bags can be recycled into reinforcements in laterite-cement matrices for sustainable buildings. The resulting building materials have attractive combinations of compressive/flexural strength and fracture toughness that vary with reinforcement volume fraction and particle sizes.
2. The compressive/flexural strengths and fracture toughness values increase with increasing polyethylene volume fractions up to 20 vol. % and increasing particle size up to $\sim 900 \mu m$. However, beyond 20 vol. %, the compressive/flexural strengths.
3. The compressive/flexural strengths and fracture toughness values of PE-reinforced laterite composites are well characterized by Weibull distributions. The measured statistical distributions of strength and fracture toughness can be incorporated into a

probabilistic framework for the modelling of the failure or survival probabilities associated with composites reinforced with different average particle sizes.

5.7 References

- [1] Lewis, T. B., Nielsen, L. E. (1970). Dynamic mechanical properties of particulate-filled composites. *J. Appl. Polym. Sci.*, 14, 1449–1471.
- [2] Brockenbrough, J. R., Subra S., Wienecke , H. A. (1991) "Deformation of metal-matrix composites with continuous fibers: geometrical effects of fiber distribution and shape." *Acta metallurgica et materialia* 39 (5), 735-752.
- [3] Gupta, M., Wang, K. K. (1993). Fiber orientation and mechanical properties of short-fiber-reinforced injection-molded composites: Simulated and experimental results. *Polym Compos*, 14, 367–382.
- [4] Masenelli-Varlot, K., Reynaud, E., Vigier, G., Varlet, J. (2002). Mechanical properties of clay-reinforced polyamide. *J. Polym. Sci. B, Polym. Phys.*, 40, 272–283.
- [5] Van Mier, J. G. M., van Vliet, M. R. A., Wang T. K. (2002). "Fracture mechanisms in particle composites: statistical aspects in lattice type analysis." *Mechanics of Materials* 34(11), 705-724.
- [6] Jawaid, M. H. P. S., Abdul Khalil, H. P. S. (2011). "Cellulosic/synthetic fibre reinforced polymer hybrid composites: A review." *Carbohydrate Polymers* 86 (1), 1-18.

- [7] Savastano, Jr. H., Warden, P. G., Coutts, R. S. P. (2000). "Brazilian waste fibres as reinforcement for cement-based composites." *Cement and Concrete Composites* 22(5), 379-384.
- [8] Zhong, J. B., Lv, J., Wei C. (2007). Mechanical properties of sisal fibre reinforced urea-formaldehyde resin composites. *Express Polym Lett.*, 1(10), 681–687.
- [9] Sapuan, S. M., Harun, N., Abbas, K. A. (2007). Design and fabrication of a multipurpose table using a composite of epoxy and banana pseudostem fibres. *J Trop Agric.*, 45 (1-2), 66–68.
- [10] Tonoli, G. H. D., Savastano, Jr. H., Fuentec, E., Negroc, C., Blancoc, A., Rocco Lahr, F. A. (2010). Eucalyptus pulp fibres as alternative reinforcement to engineered cement-based composites. *Indus Crops and Products*, 31,225–232.
- [11] Okubo, K., Toru F., Yuzo Y. (2004). "Development of bamboo-based polymer composites and their mechanical properties." *Composites Part A: Applied science and manufacturing* 35(3), 377-383.
- [12] Deshpande, A. P., Bhaskar, R. M., Lakshmana R. C. (2000). "Extraction of bamboo fibers and their use as reinforcement in polymeric composites." *Journal of Applied Polym Sci.*, 76(1), 83-92.
- [13] Nataraja, M. C., Dhang, N., Gupta, A. P. (1999). Stress–strain curves for steel-fiber reinforced concrete under compression. *Cement and concrete compos.*, 21(5), 383-390.

- [14] Chen, P. W., Chung, D. D. L. (1996). Comparative study of concretes reinforced with carbon, polyethylene, and steel fibers and their improvement by latex addition. *ACI materials journal*, 93(2).
- [15] Udoeyo, F. F., Udeme H. I., Obas,i O. O. (2006). "Strength performance of laterized concrete." *Construction and Building Materials*, 20(10), 1057-1062.
- [16] Johnston, C. D. (1974). "Steel fiber reinforced mortar and concrete: a review of mechanical properties." *ACI Special Publication 44*.
- [17] Alqam, M., Bennett, R. M., Zureick, A. H. (2002). Three-parameter vs. two-parameter Weibull distribution for pultruded composite material properties. *Composite Structures*, 58(4), 497-503.
- [18] Sakin, R., Ay, I. (2008). Statistical analysis of bending fatigue life data using Weibull distribution in glass-fiber reinforced polyester composites. *Materials & Design*, 29(6), 1170-1181.
- [19] Soroushian, P., Lee, C. D. (1990). Distribution and orientation of fibers in steel fiber reinforced concrete. *ACI Materials Journal*, 87(5).
- [20] Phoenix, S. L., Ibnabdeljalil, M., Hui, C. Y. (1997). Size effects in the distribution for strength of brittle matrix fibrous composites. *International Journal of Solids and Structures*, 34(5), 545-568.
- [21] Mirza, S. A., and MacGregor, J. G. Variations in dimensions of reinforced concrete members. *Journal of the Structural Division*, 105(4), 751-766, 1979.

- [22] Karlin, I. V., Ferrante, A., Ottinger, H. C. (1999). Perfect entropy functions of the lattice Boltzmann method. *EPL (Europhysics Letters)*, 47(2), 182.
- [23] Bergman, B. (1984). On the estimation of the Weibull modulus. *Journal of Materials Science Letters*, 3(8), 689-692.
- [24] Soboyejo, W.O. (2002). *Mechanical Properties of Engineering Materials*, Marcel Dekker, New York, NY, pp. 1 – 583
- [25] Danzer, R., Supancic, P., Pascual, J., Lube, T. (2007). Fracture statistics of ceramics– Weibull statistics and deviations from Weibull statistics. *Engineering Fracture Mechanics*, 74(18), 2919-2932.
- [26] Evans, A.G. (1983). Statistical aspects of cleavage fracture in steel *Metall. Trans. A*, Vol. 14A, pp. 1349-1355.
- [27] Soboyejo, A.B.O., Orisamolu, I.R., Soboyejo, W.O. (2001). *Probabilistic Methods in Fatigue and Fracture*, Trans Tech Publishers Ltd, Zurich, Switzerland; for the American Society of Mechanical Engineers Materials Division, ISSN 1013-9826.
- [28] Hoel P.G. (1962). *Introduction to Mathematical Statistics*, 3rd Edition, J. Wiley and Sons, New York.
- [29] Soboyejo, A.B.O. (2007). *Probabilistic Methods in Engineering and Bio-systems Engineering*; *Probabilistic Methods in Engineering Design*, access and retrieved from <http://hcg1.eng.ohio-state.edu/~fabe735/>.

- [30] Weibull, W. (1951) A statistical distribution function of wide applicability, *Journal of applied mechanics*, 293-297.
- [31] Curry, D. A., & Knott, J. F. (1979). Effect of microstructure on cleavage fracture toughness of quenched and tempered steels. *Metal Science*, 13(6), 341-345.
- [32] Rice, J. R., Johnson, M.A. (1970). *Inelastic Behavior of Solids*, McGraw-Hill, New York, pp. 641-672.
- [33] Weibull, W. (1953). *J. App. Mech.*, Vol. 18, pp. 293-297
- [35] Lin, T., Evans, A. G., & Ritchie, R. O. (1986). A statistical model of brittle fracture by transgranular cleavage. *Journal of the Mechanics and Physics of Solids*, 34(5), 477-497.
- [34] Callister, W.D., Rethwisch, D.G. (2012). *Fundamentals of materials science and engineering: an integrated approach*. John Wiley & Sons.

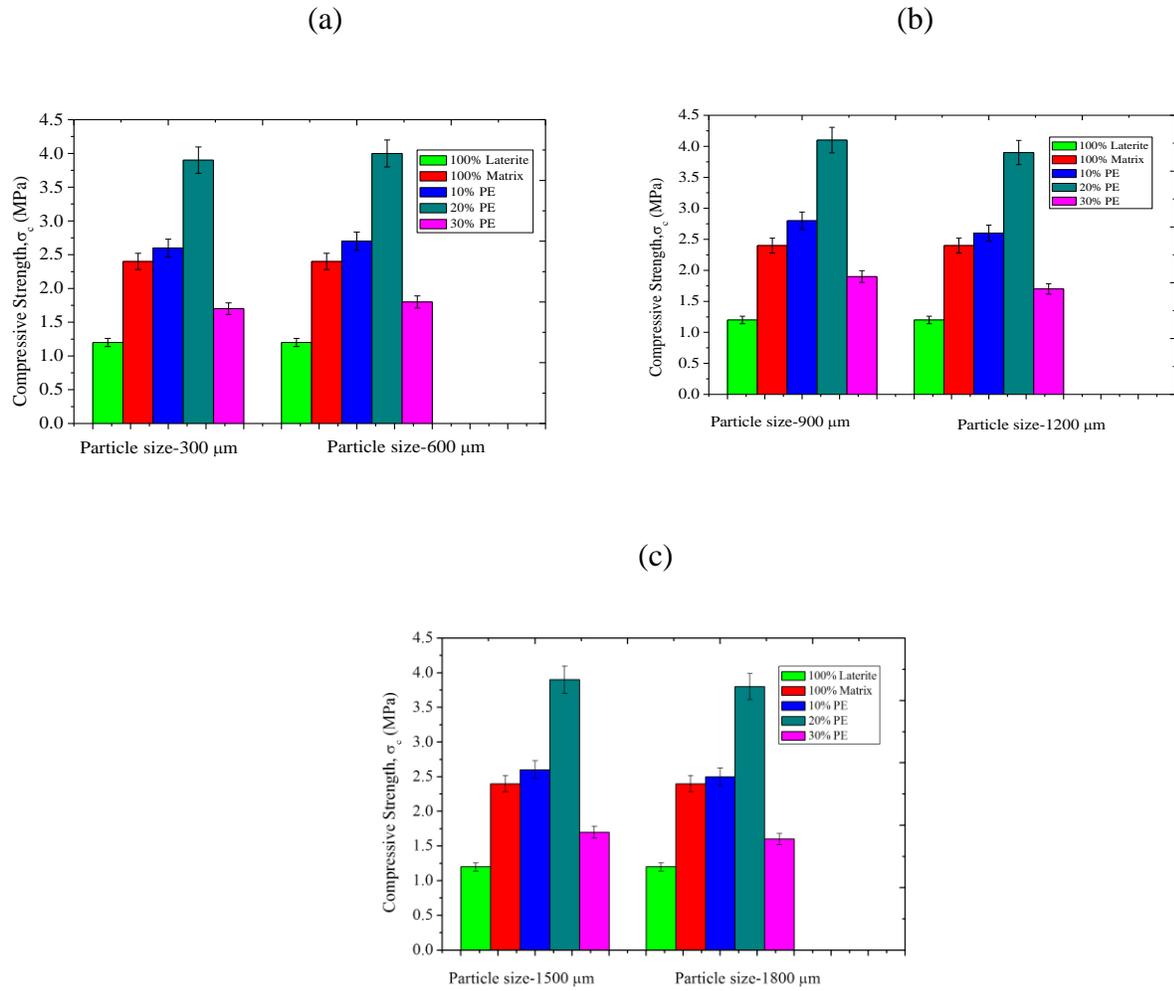


Figure 5.1: Compressive Strengths of PE-laterite composite with Particle Sizes of (a) 300 μm and 600 μm (b) 900 μm and 1200 μm , and (c) 1500 μm and 1800 μm

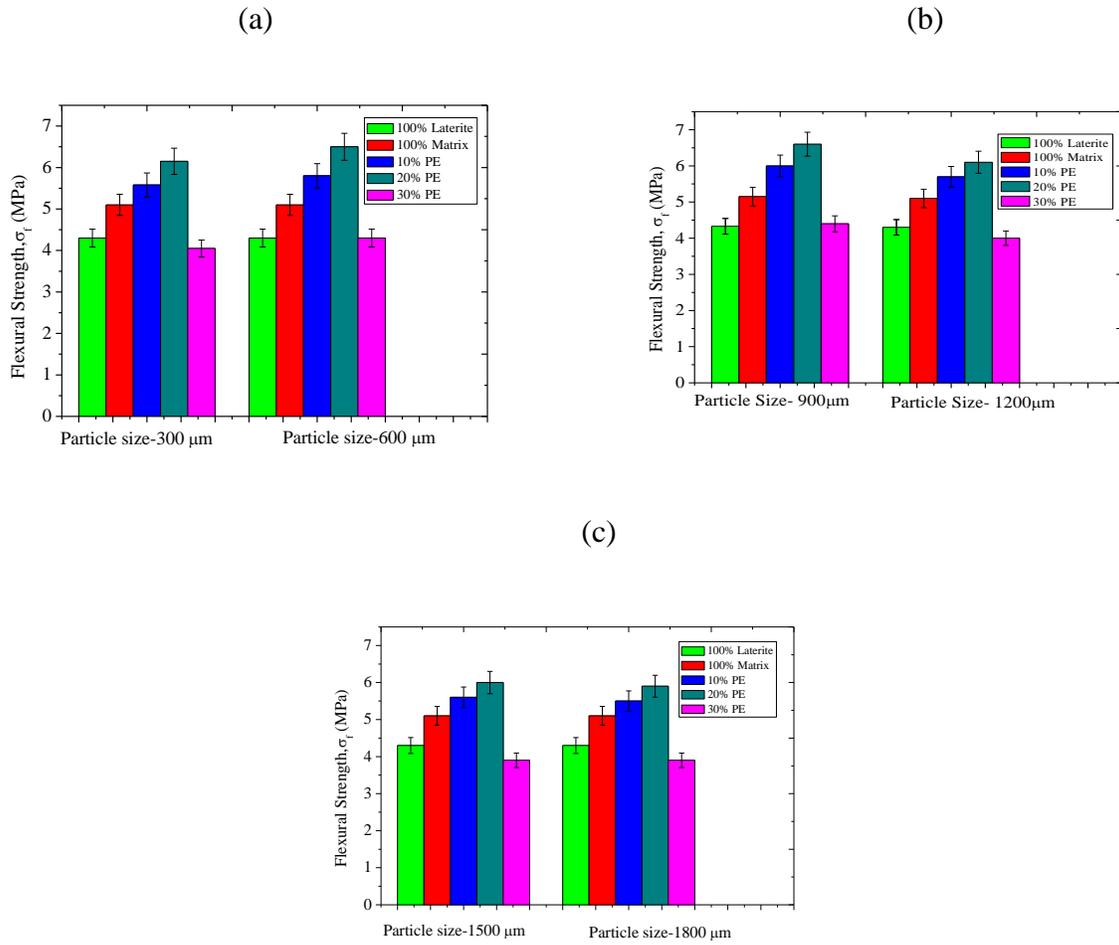


Figure 5.2: Flexural Strengths of PE-laterite composite with Particle Sizes of (a) 300 μm and 600 μm (b) 900 μm and 1200 μm , and (c) 1500 μm and 1800 μm

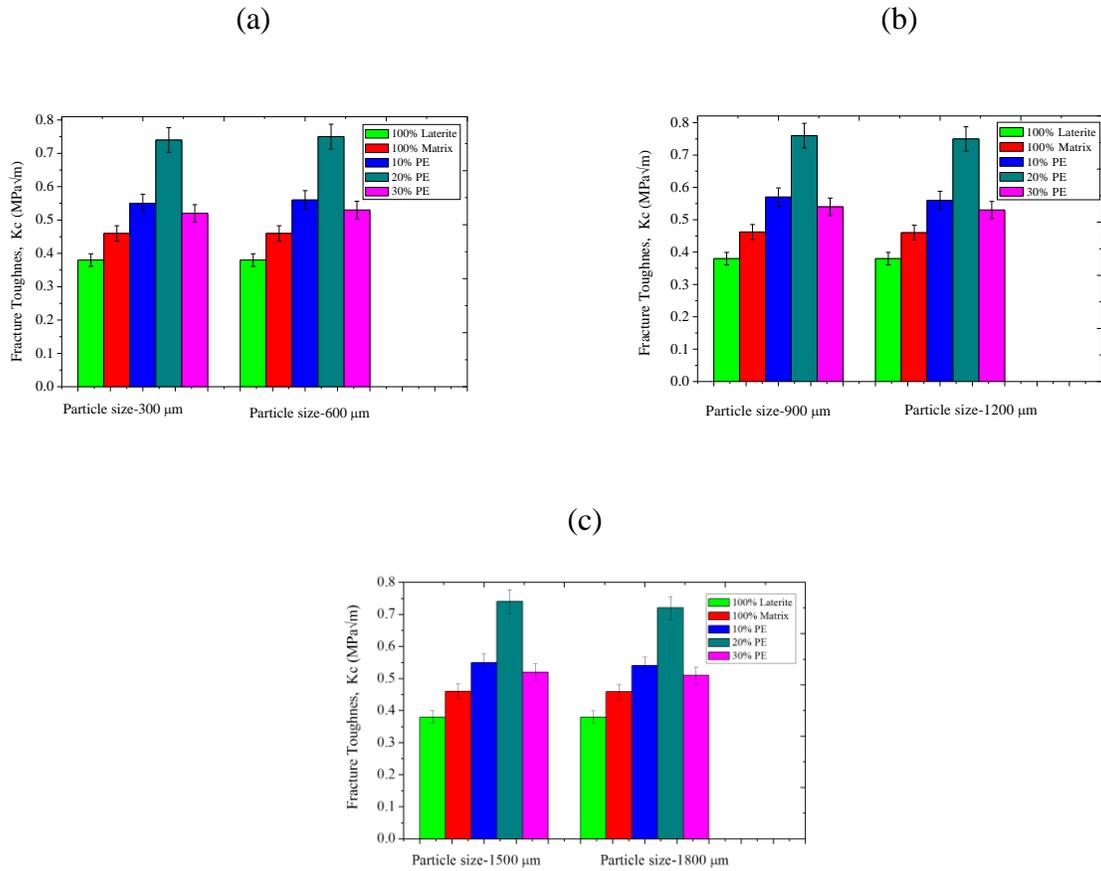


Figure 5.3: Fracture Toughness of PE-laterite Composites with Particle Sizes of (a) 300 μm and 600 μm , (b) 900 μm and 1200 μm , and (c) 1500 μm and 1800 μm

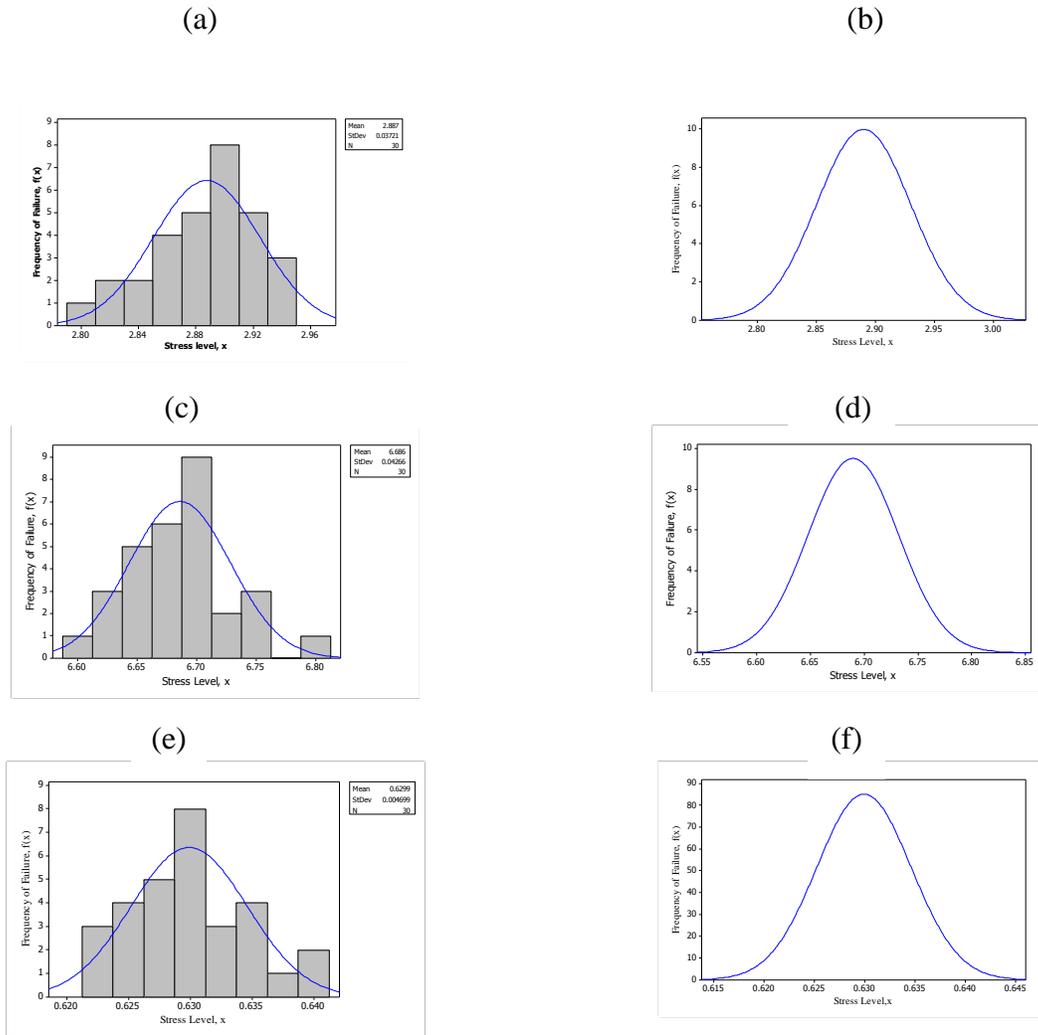


Figure 5.4: Gaussian Distribution Probability Density Functions of PE-laterite composites for (a) Experimental Compressive Strength, (b) Predicted Compressive Strength, (c) Experimental Flexural Strength, (d) Predicted Flexural Strength, (e) Experimental Fracture Toughness and (f) Predicted Fracture Toughness

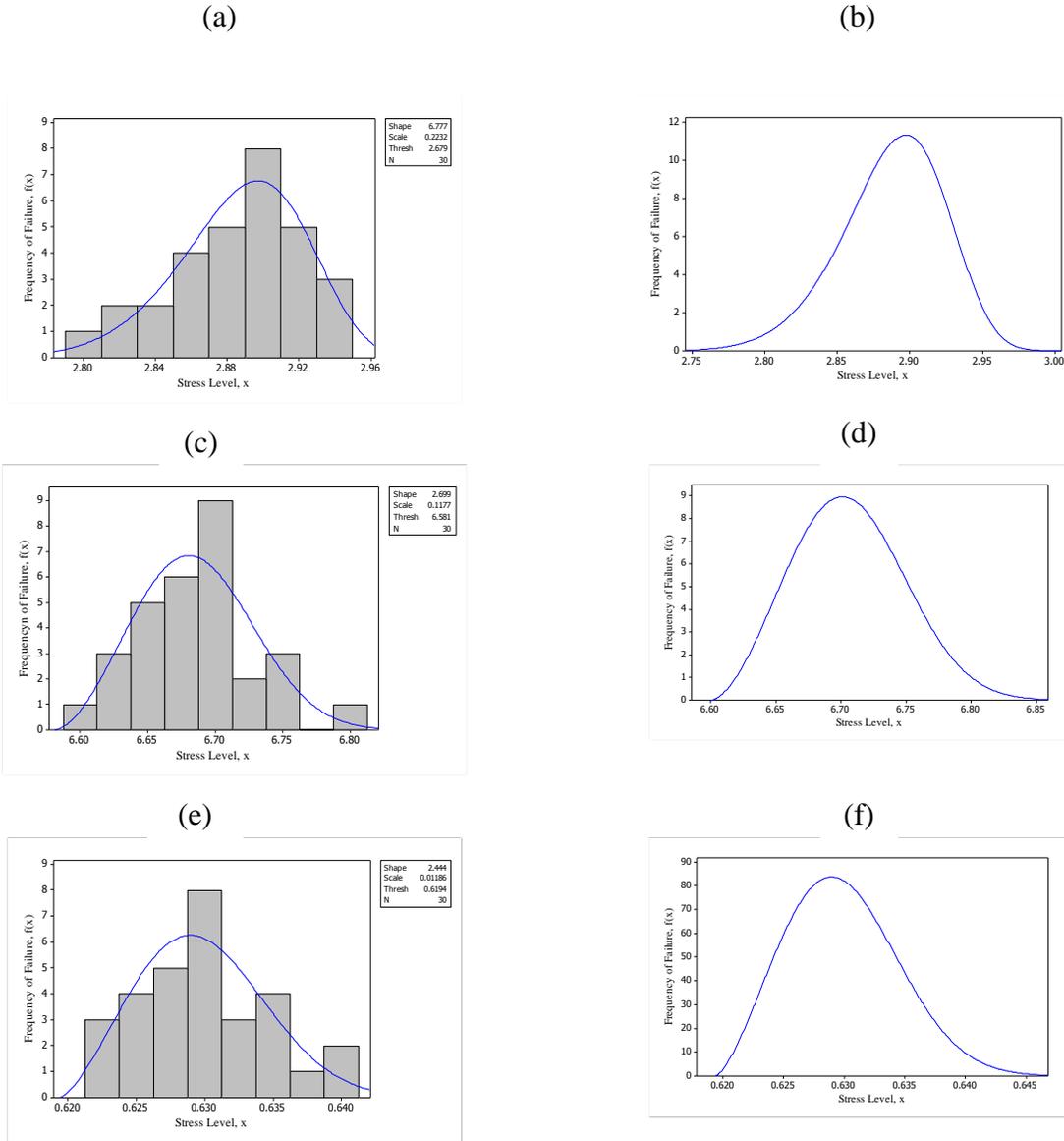


Figure 5.5: Weibull Distribution Probability Density Functions of PE-laterite composites for (a) Experimental Compressive Strength, (b) Predicted Compressive Strength, (c) Experimental Flexural Strength, (d) Predicted Flexural Strength, (e) Experimental Fracture Toughness and (f) Predicted Fracture Toughness

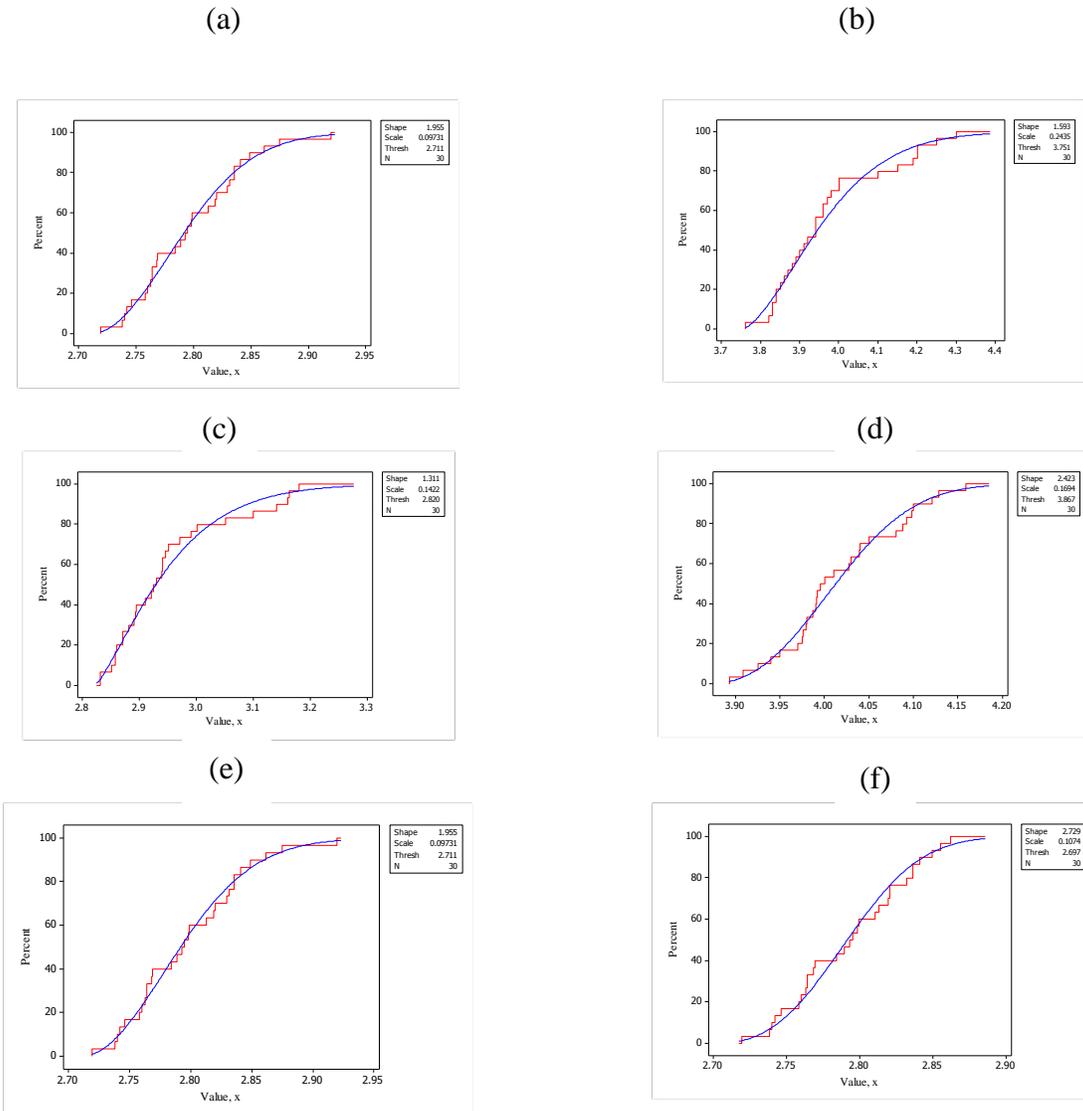


Figure 5.6: Fitted Empirical Cumulative Distribution Functions of PE-laterite composites for Weibull Distribution with Probability Density Functions of PE at (a) 300 μm (b) 600 μm (c) 900 μm (d) 1200 μm (e) 1500 μm (f) 1800 μm

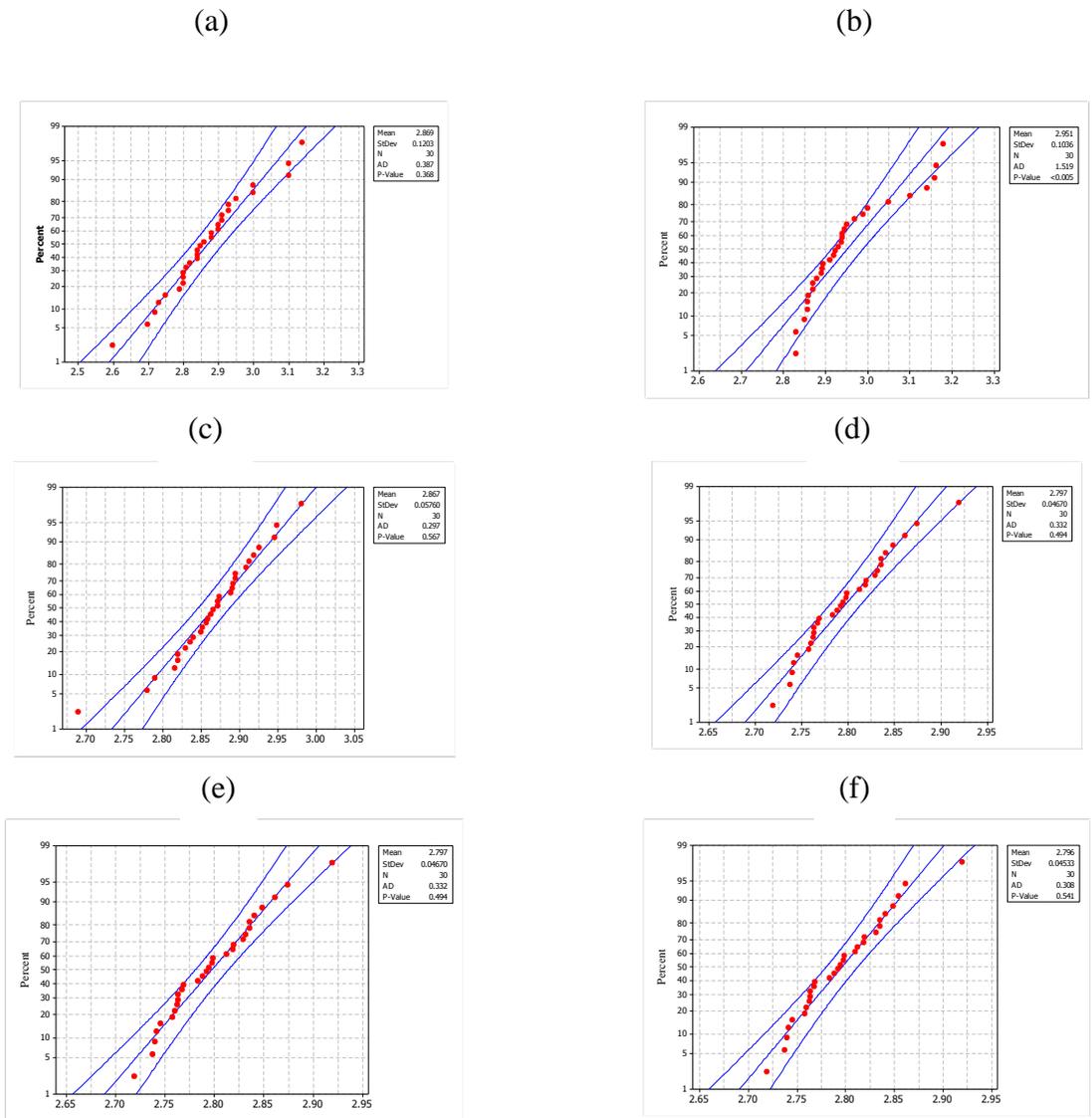


Figure 5.7: Probability Plots of PE-laterite Composites for Normal Distribution of PE at (a) 300 μm (b) 600 μm (c) 900 μm (d) 1200 μm (e) 1500 μm (f) 1800 μm

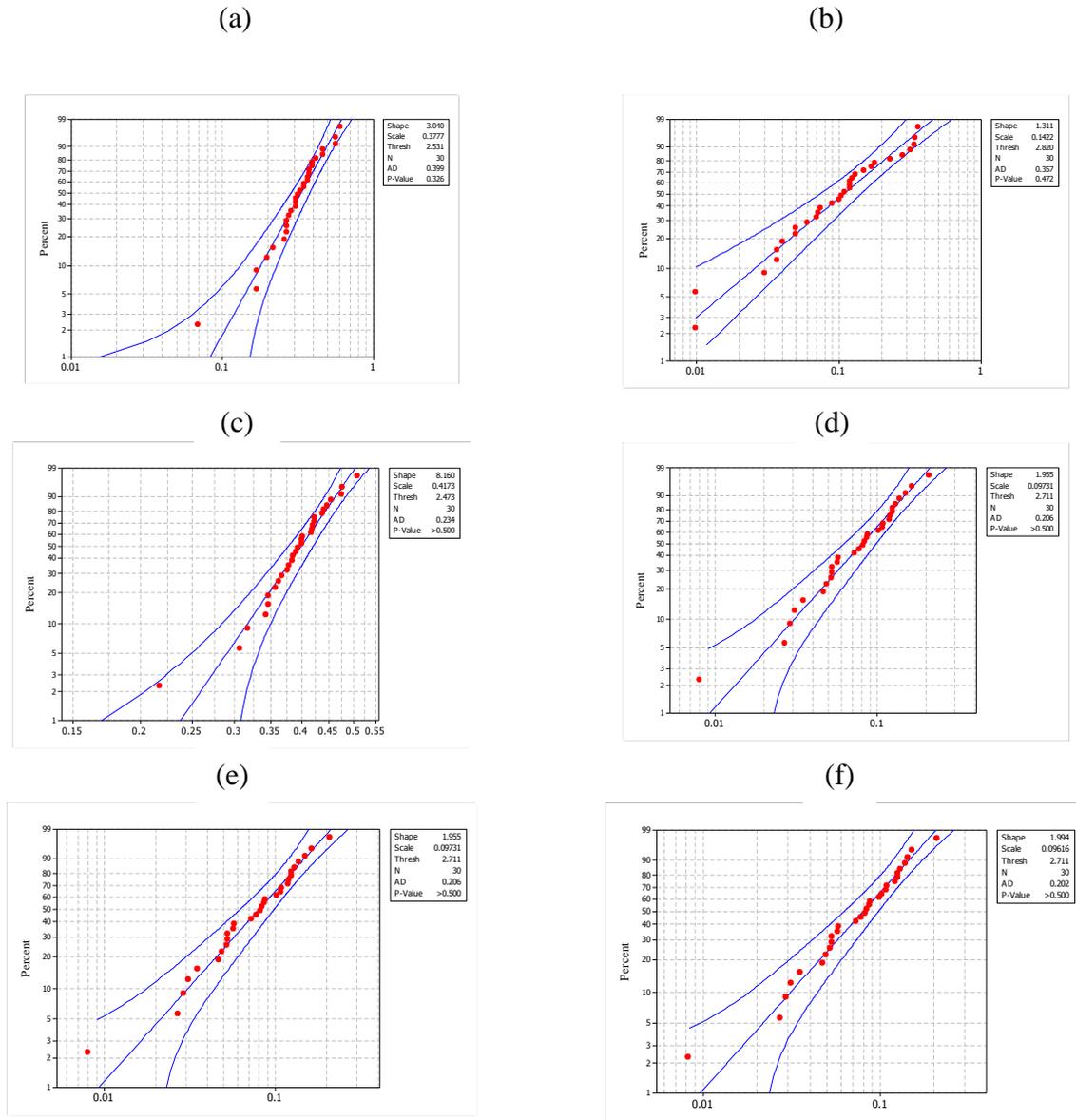


Figure 5.8: Probability Plots of PE-laterite Composites for Weibull Distribution of PE at (a) 300 μm (b) 600 μm (c) 900 μm (d) 1200 μm (e) 1500 μm (f) 1800 μm

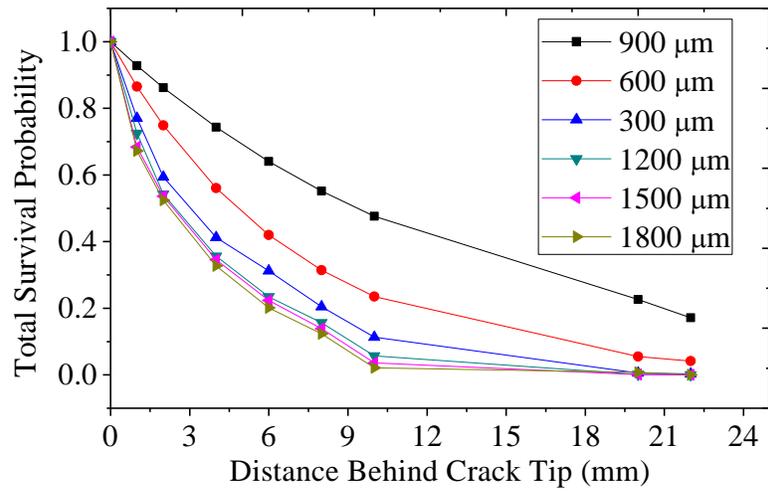


Figure 5.9: Total Survival Probability Plots for different Particle Sizes of PE in the PE-laterite Composites

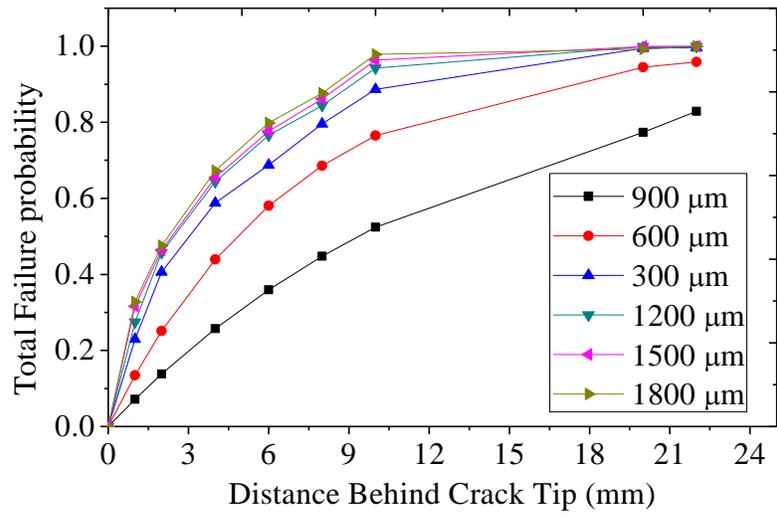


Figure 5.10: Total Failure Probability Plots for different Particle Sizes of PE in the PE-laterite Composites

CHAPTER SIX

6.0 Summary and Concluding Remarks

6.1 Introduction

This thesis presents the results of experimental and theoretical studies of the biodegradation of polyethylene, recycling of polyethylene (PE) into strong and tough earth-based composite building materials and the statistical distributions of the strength and fracture toughness of recycled polyethylene-reinforced laterite composites.

Plastics have been used extensively due to their attractive combination of stability, thermal properties and mechanical properties. PE has an annual production of approximately 140 million tons. This hinders the implementation of an efficient disposal system. However, PE can be degraded by chemical, thermal and photo methods. The above methods are relatively expensive and not environmentally friendly. Hence, there is the need to use biological methods that are relatively inexpensive and environmentally benign.

The poor durability performance and associated short service life of earth-based bricks reduces the sustainable use of the material. A review of existing work has revealed the lack of a systematic approach to fabricating compressed earth-based bricks that recognizes the inter-connection between the bricks structural performance over the service life of the resulting building system and sustainability. The most important property of a brick is not its strength in most circumstances but its fracture toughness, durability or weather resistance. Therefore, erosion resistance is the main criterion in tropical and subtropical climates, as rain and wind are restricting climatic factors. Also, most composites contain synthetic fibers and particulate

reinforcements, which are often too expensive for widespread applications in most building materials. Therefore, there is the need to use recycled PE in reinforcing composite building materials by taking advantage of its relative abundance and low competing use.

6.2 Summary of Work

This work consists of six different chapters. Chapter one emphasizes on the introduction, problems of plastic waste, unresolved research questions, objectives and scope of the work. This presents the problems plastics waste poses on the environment and the need to remediate or reduce its pile-ups as well as recycling polyethylene into useful building materials. Chapter two is focused on related work carried out by researchers in the field. This includes their findings, loopholes and recommendations for improving existing literatures. Chapter three present the results of the isolation of a locally available bacterium (*Serratia marcescens marcescens*) in degradation linear low density polyethylene. From the results obtained in this chapter, the supernatant from the bacterium aid in faster degradation of polyethylene than the bacterium itself. Recycling of polyethylene in strong and tough earth-based composite building materials is presented in chapter four. The results obtained showed that, polyethylene can actually improve upon the flexural/compressive strengths as well as the fracture toughness of the resulting earth-based composites. The polyethylene particles were observed to bridge the cracks in the composites. These were shown clearly by the use of small scale and large scale bridging models as well as images from a digital ProScope imaging device. Chapter five describes the statistical variations of the different particles sizes in the earth-based composites. The results clearly show that, the Weibull distribution best characterized the statistical variations in the earth-based composites than the Gaussian distribution. Finally, chapter six presents the summary and

conclusion as well as the future work for the thesis. This chapter has outlined the use of *Serratia marcescens marcescens* in degrading linear low density polyethylene (LLDPE) as well as using polyethylene as reinforcement in composite building materials.

6.3 Conclusions of Thesis

The conclusions of the thesis will be based on the findings presented in the different chapter papers. The first study shows that LLDPE powder and film can be degraded by exposure to *S. marcescens marcescens* and its supernatant within periods of 4-10 weeks. However, the rate of LLDPE biodegradation and biodeterioration is faster with the supernatant devoid of bacteria than in the presence of *S. marcescens marcescens*. Direct exposure of the polyethylene to the supernatant also results in a microvoid formation that is consistent with an erosion mechanism. The overall decrease in the percentage crystallinity of LLDPE (9%) suggests that, the *S. marcescens marcescens* and its supernatant disrupts the morphology of LLDPE.

The second study concluded that, polyethylene bags can be recycled into reinforcements in laterite-cement matrices for sustainable buildings. The resulting building materials have attractive combinations of compressive/flexural strength and fracture toughness/resistance–curve behavior that vary with reinforcement volume fraction. The compressive/flexural strengths of polyethylene–reinforced laterite composites are well predicted by simple rule–of–mixtures. The measured fracture toughness and resistance–curve behavior are also consistent with predictions from small– and large–scale crack bridging models. The models also predict steady–state fracture values that are independent of specimen size.

The third study concluded that different particle sizes of recycled PE can be used as a reinforcement material in cement-stabilized laterite. The optimum strengths and fracture toughness of recycled PE were also comparable to those of regular building materials. Polyethylene bags can be recycled into reinforcements in laterite-cement matrices for sustainable buildings. The resulting building materials have attractive combinations of compressive/flexural strength and fracture toughness that vary with reinforcement volume fraction and particle sizes. The compressive/flexural strengths and fracture toughness values increase with increasing polyethylene volume fractions up to 20 vol. % and increasing particle size up to $\sim 900 \mu m$. However, beyond 20 vol. % of PE, the compressive/flexural strengths as well as the fracture toughness values decrease.

The compressive/flexural strengths and fracture toughness values of PE-reinforced laterite composites are well characterized by Weibull distributions. The measured statistical distributions of strength and fracture toughness can be incorporated into a probabilistic framework for the modelling of the failure or survival probabilities associated with composites reinforced with different average particle sizes.

6.4 Recommendation for Future Work

The first part of the thesis illustrates the potential use of locally available bacteria (*S. marcescens marcescens*) in degrading “pure water sachets” (Linear Low density Polyethylene). However, there is the need to perform an experiment on the molecular weight and molecular weight distribution of the polyethylene before and after degradation. Gel permeation chromatography (GPC) should be used in determining the molecular weights of the

polyethylene. The GPC will give us information about the number average molecular weight, weight average molecular weight and the poly-dispersity of the polyethylene before and after degradation. Molecular weight determination is very important in polymer chemistry and biodegradation. The molecular weight of the polyethylene will change after being subjected to biodegradation. Also, there is the need to determine the specific enzyme(s) in the supernatant responsible for the biodegradation of polyethylene. This could be achieved by performing protein characterization techniques such as SDS-Polyacrylamide Gel Electrophoresis (SDS-PAGE) on the supernatant. This method will help in discovering the enzyme(s) responsible in degrading polyethylene. Lastly, there is the need to Study the time-dependent degradation at different temperatures as well as performing bioreactors experiments for scale-up. The different temperatures will establish kinetic models and reasons for degradation of the polyethylene.

The second and third part of the thesis illustrates the use of recycled polyethylene in reinforcing building materials. However, there is a need to study the potential environmental degradation phenomena that can occur due to exposure to water, erosion and sunlight. Modified Bulletin 5 Spraying Erosion Test can be used to test for erosion in the composite. This method involve spraying the test samples (bricks) with water for at least one hour or until failure occurs under control pressure. Furthermore, waste oyster shells found in our locality, especially along the coast, could be used in reinforcing building materials. Also, there is a need to combine recycled polyethylene and cement and determine their mechanical properties. These are clearly some recommendations for future work.