

**PROPERTIES AND CHARACTERISATION OF
BAMBOO CELLULOSE NANOFIBRE
REINFORCED POLYLACTIC ACID –
CHITOSAN NANOCOMPOSITES**

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UNIVERSITI SAINS MALAYSIA

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REINFORCED POLYLACTIC ACID – CHITOSAN
NANOCOMPOSITES**

by

OLAIYA NIYI GIDEON

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for the degree of
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TABLE OF CONTENTS

| | |
|---|--------------|
| ACKNOWLEDGEMENT | ii |
| TABLE OF CONTENTS | iii |
| LIST OF TABLES | ix |
| LIST OF FIGURES | xi |
| LIST OF SYMBOLS | xviii |
| LIST OF ABBREVIATIONS | xx |
| ABSTRAK | xxii |
| ABSTRACT | xxv |
| CHAPTER 1 INTRODUCTION | 1 |
| 1.1 General background of the study | 1 |
| 1.2 Problem statement | 5 |
| 1.3 The objective of the study | 7 |
| 1.4 Significance of study | 7 |
| 1.5 Layout of thesis | 8 |
| CHAPTER 2 LITERATURE REVIEW | 10 |
| 2.1 Introduction | 10 |
| 2.2 Biopolymers | 10 |
| 2.3 Classification of biopolymers..... | 11 |
| 2.3.1 Polylactic acid | 13 |
| 2.3.2 Structural analysis of polylactic acid | 15 |
| 2.3.3 Properties of polylactic acid..... | 18 |
| 2.3.3(a) Physical and mechanical properties of polylactic acid..... | 18 |
| 2.3.3(b) Thermal properties of polylactic acid | 20 |

| | | |
|-----|---|----|
| | 2.3.3(c) Degradation properties of polylactic acid..... | 21 |
| 2.4 | Chitosan..... | 23 |
| | 2.4.1 Chitosan structure, production, and use | 23 |
| 2.5 | Review of polylactic acid/chitosan composite | 25 |
| 2.6 | Natural fibres..... | 28 |
| 2.7 | Plant fibres: bamboos and <i>Schizostachyum Brachycladum</i> bamboo Material | 30 |
| | 2.7.1 General properties of bamboo | 36 |
| | 2.7.1(a) Chemical composition | 37 |
| | 2.7.1(b) Physical properties..... | 38 |
| | 2.7.1(c) Mechanical properties..... | 39 |
| 2.8 | Cellulose and cellulose fibre | 40 |
| | 2.8.1 Nanocellulose | 44 |
| | 2.8.2 Cellulose nanofibre | 46 |
| | 2.8.3 Isolation of nanocellulose..... | 48 |
| | 2.8.4 Pre-treatment of lignocellulosic biomass materials | 48 |
| | 2.8.4(a) Physicochemical pre-treatment..... | 52 |
| | 2.8.4(b) Chemical pre-treatment | 52 |
| | 2.8.4(c) Supercritical fluids pre-treatment | 54 |
| | 2.8.4(d) Mechanical pretreatment | 57 |
| 2.9 | Polymer biocomposites | 60 |
| | 2.9.1 Nanocomposites | 63 |
| | 2.9.1(a) Cellulose nanofibre reinforced nanocomposites..... | 64 |
| | 2.9.1(b) Cellulose nanofibre reinforced nanocomposite melt processing technique..... | 65 |
| | 2.9.1(c) Properties of cellulose nanofibre reinforced nanocomposites..... | 72 |
| | 2.9.1(d) Application of cellulose nanofibre based nanocomposites..... | 74 |

| | | |
|---|---|-----------|
| 2.10 | Research gap | 77 |
| CHAPTER 3 MATERIAL AND METHOD..... | | 79 |
| 3.1 | Introduction | 79 |
| 3.2 | Materials..... | 80 |
| 3.3 | Raw material preparation | 80 |
| 3.3.1 | Determination of chemical constituents..... | 81 |
| 3.3.2 | Determination of extractive content..... | 81 |
| 3.3.2(a) | Determination of holocellulose..... | 81 |
| 3.3.2(b) | Determination of α -cellulose | 82 |
| 3.3.2(c) | Determination of lignin..... | 82 |
| 3.3.2(d) | Determination of ash content..... | 83 |
| 3.3.3 | Extraction and isolation of cellulose nanofibre..... | 83 |
| 3.3.3(a) | Soda-AQ pulping | 84 |
| 3.3.3(b) | Alkaline-peroxide bleaching..... | 84 |
| 3.3.3(c) | Isolation of cellulose nanofibre (CNF)..... | 84 |
| 3.3.4 | Characterization of raw bamboo fibre, pulp, bleached pulp, and CNF | 85 |
| 3.3.4(a) | Scanning electron microscopy (SEM) | 85 |
| 3.3.4(b) | Transmission electron microscopy (TEM) | 85 |
| 3.3.4(c) | Fourier transform infrared spectroscopy (FT-IR)..... | 86 |
| 3.3.4(d) | X-ray diffraction analysis (XRD) | 86 |
| 3.3.4(e) | Thermogravimetric analysis (TGA) | 86 |
| 3.3.4(f) | Particle size and zeta potential analysis..... | 87 |
| 3.4 | Preparation and characterisation of chitosan..... | 87 |
| 3.5 | Preparation of PLA/chitosan/CNF nanocomposites | 88 |
| 3.6 | Characterization of CNF reinforced PLA/chitosan-based nanocomposites... | 91 |
| 3.6.1 | Physical test..... | 91 |

| | | |
|------------------|---|-----------|
| 3.6.1(a) | Water absorption..... | 91 |
| 3.6.1(b) | Thickness of swelling | 91 |
| 3.6.1(c) | Moisture content | 92 |
| 3.6.1(d) | Density | 92 |
| 3.6.2 | Mechanical test..... | 92 |
| 3.6.2(a) | Tensile test | 92 |
| 3.6.2(b) | Flexural test | 93 |
| 3.6.2(c) | Izod notched impact test | 93 |
| 3.6.3 | Morphological test..... | 93 |
| 3.6.4 | Thermal test..... | 94 |
| 3.6.4(a) | Thermogravimetric analysis (TGA) | 94 |
| 3.6.4(b) | Differential scanning calorimetry (DSC)..... | 95 |
| 3.6.5 | Structural test..... | 95 |
| 3.6.5(a) | X-ray diffraction analysis (XRD) | 95 |
| 3.6.5(b) | Fourier-transform infrared spectroscopy (FT-IR) | 95 |
| 3.6.6 | Degradation test..... | 96 |
| 3.6.7 | Wettability measurement..... | 97 |
| CHAPTER 4 | RESULTS AND DISCUSSION..... | 99 |
| 4.1 | Properties of raw fibre and alkaline treated bamboo fibre | 99 |
| 4.1.1 | Chemical composition..... | 99 |
| 4.1.2 | Yield | 102 |
| 4.1.3 | Fourier transform infrared spectroscopy (FT-IR) | 102 |
| 4.1.4 | Morphological analysis | 106 |
| 4.1.5 | Crystallinity index | 108 |
| 4.1.6 | Thermal properties | 111 |
| 4.1.6(a) | Thermogravimetric analysis (TGA) | 111 |
| 4.1.6(b) | Differential scanning calorimetry (DSC)..... | 115 |

| | | |
|----------|--|-----|
| 4.2 | Properties of bamboo CNF and commercial CNF | 117 |
| 4.2.1 | Fourier transform infrared spectroscopy (FTIR)..... | 117 |
| 4.2.2 | X-ray diffraction (XRD)..... | 118 |
| 4.2.3 | Thermo-gravimetric analysis (TGA)..... | 120 |
| 4.2.4 | Transmission electron microscope (TEM)..... | 122 |
| 4.2.5 | Particle size analysis..... | 123 |
| 4.2.6 | Zeta potential analysis | 124 |
| 4.3 | Properties of amphiphilic chitosan | 124 |
| 4.4 | Optimisation of the composition variation PLA/chitosan CNF biocomposite | 126 |
| 4.4.1 | Tensile properties | 126 |
| 4.4.1(a) | Tensile strength..... | 126 |
| 4.4.1(b) | Tensile modulus..... | 132 |
| 4.4.1(c) | Tensile elongation..... | 136 |
| 4.4.2 | Flexural properties..... | 140 |
| 4.4.2(a) | Flexural strength | 141 |
| 4.4.2(b) | Flexural modulus | 145 |
| 4.4.2(c) | Impact strength | 149 |
| 4.4.3 | Morphological properties | 154 |
| 4.4.4 | Thermal properties | 164 |
| 4.4.4(a) | Thermogravimetry analysis | 164 |
| 4.4.4(b) | Differential scanning calorimetry | 174 |
| 4.5 | Properties of Bamboo and commercial CNF reinforced in PLA/chitosan composite | 182 |
| 4.5.1 | Physical properties | 183 |
| 4.5.1(a) | Moisture content properties | 183 |
| 4.5.1(b) | Density measurement..... | 185 |
| 4.5.2 | Mechanical properties | 186 |

| | | |
|--|---|------------|
| 4.5.2(a) | Tensile properties..... | 187 |
| 4.5.2(b) | Flexural properties | 190 |
| 4.5.2(c) | Impact properties | 192 |
| 4.5.3 | Morphological properties Field Emission Gun Scanning Electron Microscope | 193 |
| 4.5.4 | Structural properties | 196 |
| 4.5.4(a) | Fourier transform infrared spectroscopy (FTIR) | 196 |
| 4.5.4(b) | X-ray diffraction (XRD) | 197 |
| 4.5.5 | Thermal and degradation characterization | 198 |
| 4.5.5(a) | Thermo-gravimetric analysis (TGA) | 198 |
| 4.5.5(b) | Differential scanning calorimetry (DSC)..... | 200 |
| 4.5.6 | Wettability properties | 201 |
| 4.5.6(a) | Water absorption..... | 202 |
| 4.5.6(b) | Thickness of swelling | 204 |
| 4.5.6(c) | Contact angle properties | 205 |
| 4.5.6(d) | Soil burial analysis..... | 207 |
| CHAPTER 5 CONCLUSION AND RECOMMENDATION | | 214 |
| 5.1 | Conclusion..... | 214 |
| 5.2 | Recommendations | 215 |
| REFERENCES..... | | 217 |
| LIST OF PUBLICATIONS | | |

LIST OF TABLES

| | Page |
|------------|---|
| Table 2.1 | Properties of PLA..... 19 |
| Table 2.2 | Chemical composition of selected bamboo species37 |
| Table 2.3 | Physical characteristics of bamboo species.....38 |
| Table 2.4 | Various sources of nanocellulosic fibres45 |
| Table 2.5 | Types of nano cellulose.....46 |
| Table 2.6 | Various pre-treatment processes of lignocellulosic biomass.51 |
| Table 3.1 | Composition Variation for optimization of PLA/chitosan/CNF biocomposite90 |
| Table 4.1 | Average percentage of the chemical composition of <i>S.</i> <i>Brachycladum</i> 100 |
| Table 4.2 | Main IR peaks and corresponding functional groups of <i>S.</i> <i>Brachycladum</i> 104 |
| Table 4.3 | Range of diameter of raw fibre, pulp and bleached pulp 108 |
| Table 4.4 | Crystallinity percentage of raw fibre, pulp and bleached pulp 111 |
| Table 4.5 | Thermal degradation properties of raw fibre, pulp and bleached pulp..... 113 |
| Table 4.6 | Thermal properties of raw fibre, pulp and bleached pulp 116 |
| Table 4.7 | Differential scanning calorimetry temperatures of neat PLA, and 80:20 samples of PLA/chitosan/CNF biocomposite 176 |
| Table 4.8 | Differential scanning calorimetry temperatures of neat PLA, and 85:15 samples of PLA/chitosan/CNF biocomposite 177 |
| Table 4.9 | Differential scanning calorimetry temperatures of neat PLA, and 90:10 samples of PLA/chitosan/CNF biocomposite 179 |
| Table 4.10 | Differential scanning calorimetry temperatures of neat PLA, and 95:5 samples of PLA/chitosan/CNF biocomposite 181 |

| | | |
|------------|---|-----|
| Table 4.11 | Contact angles of bamboo CNF and commercial CNF biocomposite | 207 |
| Table 4.12 | Biodegradation sample result of neat PLA and biocomposites after 75 days | 208 |
| Table 4.13 | Biodegradation sample result of neat PLA and biocomposites after 150 days | 209 |

LIST OF FIGURES

| | Page |
|-------------|---|
| Figure 2.1 | Classification of Biopolymers 12 |
| Figure 2.2 | Molecular structure of the starting polymer and preparation routes for PLA 14 |
| Figure 2.3 | Types of fibre materials29 |
| Figure 2.4 | Schematic drawing of plant cellulosic fibre hierarchical structure (1) Bark Cambium pith, (2) Cambium (3) mature cell wall, (4) cellulose fibre, and (5) chemical structure of Cellulose.....29 |
| Figure 2.5 | Picture of <i>Schizostachyum Brachycladum</i> bamboo a) Stalk b) clump c) Leaves and fruiting stems d) whole plant cultivated for 2 years31 |
| Figure 2.6 | Classification of agricultural biomass raw materials32 |
| Figure 2.7 | Modulus of rupture for the 13 Malaysian bamboos34 |
| Figure 2.8 | Modulus of elasticity for the 13 Malaysian bamboos34 |
| Figure 2.9 | Schematic diagram of the general structure of bamboo.....36 |
| Figure 2.10 | Transmission Electron Microscopy of <i>S. Brachycladum</i> which is (a) and (b) consist on 1.3k and 10k of magnification for 4-year-old, respectively, while (c) and (d) consist on 1.3k and 10k of magnification for a 2-year old.....39 |
| Figure 2.11 | Chemical structure of cellulose.....42 |
| Figure 2.12 | Schematic diagram of a typical bamboo fibre with internal structure.....43 |
| Figure 2.13 | Schematic drawing showing the crystalline (core micro fibril) and amorphous (surface) region in cellulose44 |
| Figure 2.14 | Schematic of hierarchical cellulose structure to CNC and CNF.....47 |
| Figure 2.15 | Schematic role of biomass pre-treatment.....50 |

| | | |
|-------------|---|-----|
| Figure 2.16 | Schematic diagram of fibre fibrillation by Ultra Turrax rotor-stator homogenizer | 58 |
| Figure 2.17 | Classification of a biocomposite based on the raw material source of matrix and reinforcement. | 61 |
| Figure 2.18 | (a) DSM micro-extruder (DSM) showing the processing chamber and conical screw design; (b) Schematic of a Haake micro extruder with a similar conical screw design. | 67 |
| Figure 2.19 | Schematic diagram of twin-screw extruder operation | 69 |
| Figure 3.1 | Schematic diagram of the experimental methodology for the composite. | 79 |
| Figure 3.2 | Preparation of amphiphilic chitosan, isolation of cellulose nanofibre and preparation of PLA/chitosan/CNF biocomposite. | 89 |
| Figure 3.3 | Mettler-Toledo thermogravimetric analyzer model TGA/DSC | 94 |
| Figure 3.4 | FT-IR Prestige 21 (Perkin-Elmer, PC1600, USA) machine | 96 |
| Figure 3.5 | Schematic drawing of soil burial test set up for molecular biodegradation of neat PLA and bio-composite..... | 97 |
| Figure 3.6 | Contact angle analyser (KSV CAM 101)..... | 98 |
| Figure 4.1 | FT-IR spectrum of <i>S. Brachycladum</i> raw, pulp and bleached fibre. | 103 |
| Figure 4.2 | SEM micrographs of (a, b) raw bamboo fibre; (c, d) pulp fibres and (e, f) bleached pulp fibres..... | 107 |
| Figure 4.3 | X-ray diffractograms of (R) raw fibre; (P) pulp, and (B) bleached pulp..... | 109 |
| Figure 4.4 | TGA thermograms of (R) raw fibre; (P) pulp, and (B) bleached pulp..... | 112 |
| Figure 4.5 | DTG thermograms of (R) raw fibre; (P) pulp, and (B) bleached pulp..... | 112 |
| Figure 4.6 | DSC curves of (R) raw fibre; (P) pulp and (B) bleached pulp..... | 116 |
| Figure 4.7 | FT-IR analysis of bamboo CNF and commercial CNF | 118 |
| Figure 4.8 | XRD analysis of bamboo CNF and commercial CNF..... | 119 |

| | | |
|-------------|--|-----|
| Figure 4.9 | Thermogravimetry analysis (TGA) of bamboo CNF and commercial CNF | 121 |
| Figure 4.10 | Derivative thermogravimetry (DTG) analysis of bamboo CNF and commercial CNF | 121 |
| Figure 4.11 | TEM images of (a) bamboo CNF; (b) commercial CNF, particle size analysis; (c) bamboo CNF; (d) commercial CNF, zeta potential analysis of (e) bamboo CNF; and (f) commercial..... | 123 |
| Figure 4.12 | FT-IR graph of Amphiphilic chitosan and conventional chitosan].. | 125 |
| Figure 4.13 | Preparation and chemical reaction of amphiphilic chitosan | 126 |
| Figure 4.14 | Tensile strength properties of PLA/chitosan/CNF biocomposite for 80:20 set | 127 |
| Figure 4.15 | Tensile strength properties of PLA/chitosan/CNF biocomposite for 85:15 set | 127 |
| Figure 4.16 | Tensile strength properties of PLA/chitosan/CNF biocomposite for 90:10 set | 128 |
| Figure 4.17 | Tensile strength properties of PLA/chitosan/CNF biocomposite for 95:5 set | 128 |
| Figure 4.18 | Tensile modulus properties of PLA/chitosan/CNF biocomposite for 80:20 set | 132 |
| Figure 4.19 | Tensile modulus properties of PLA/chitosan/CNF biocomposite for 85:15 set | 132 |
| Figure 4.20 | Tensile modulus properties of PLA/chitosan/CNF biocomposite for 90:10 set | 133 |
| Figure 4.21 | Tensile modulus properties of PLA/chitosan/CNF biocomposite for 95:5 set | 133 |
| Figure 4.22 | Elongation of PLA/chitosan/CNF biocomposite 80:20 samples | 136 |
| Figure 4.23 | Elongation of PLA/chitosan/CNF biocomposite 85:15 samples | 137 |
| Figure 4.24 | Elongation of PLA/chitosan/CNF biocomposite 90:10 samples | 137 |
| Figure 4.25 | Elongation of PLA/chitosan/CNF biocomposite 95:5 samples | 138 |

| | | |
|-------------|--|-----|
| Figure 4.26 | Flexural strength of PLA/chitosan/CNF biocomposite 80:20 samples..... | 141 |
| Figure 4.27 | Flexural strength of PLA/chitosan/CNF biocomposite 85:15 samples..... | 141 |
| Figure 4.28 | Flexural strength of PLA/chitosan/CNF biocomposite 90:10 samples..... | 142 |
| Figure 4.29 | Flexural strength of PLA/chitosan/CNF biocomposite 95:5 samples..... | 142 |
| Figure 4.30 | Flexural modulus of PLA/chitosan/CNF biocomposite 80:20 samples..... | 145 |
| Figure 4.31 | Flexural modulus of PLA/chitosan/CNF biocomposite 85:15 samples..... | 145 |
| Figure 4.32 | Flexural modulus of PLA/chitosan/CNF biocomposite 90:10 samples..... | 146 |
| Figure 4.33 | Flexural modulus of PLA/chitosan/CNF biocomposite 90:10 samples..... | 146 |
| Figure 4.34 | Impact strength of PLA/chitosan/CNF biocomposite 80:20 samples..... | 149 |
| Figure 4.35 | Impact strength of PLA/chitosan/CNF biocomposite 80:20 samples..... | 150 |
| Figure 4.36 | Impact strength of PLA/chitosan/CNF biocomposite 80:20 samples..... | 150 |
| Figure 4.37 | Impact strength of PLA/chitosan/CNF biocomposite 80:20 samples..... | 151 |
| Figure 4.38 | Scanning electron microscopy of 80:20 samples of PLA/chitosan/CNF biocomposite a) neat PLA @ 500 μm , b) neat PLA @ 50 μm c) P8020 d) P80201 c) P80203 d) P80205 | 155 |
| Figure 4.39 | Scanning electron microscopy of 85:15 samples of PLA/chitosan/CNF biocomposite a) neat PLA @ 500 μm , b) neat PLA @ 50 μm c) P8515 d) P85151 c) P85153 d) P85155 | 158 |

| | | |
|-------------|--|-----|
| Figure 4.40 | Scanning electron microscopy of 90:10 samples of PLA/chitosan/CNF biocomposite a) neat PLA @ 500 μm , b) neat PLA @ 50 μm c) P9010 d) P90101 c) P90103 d) P90105 | 161 |
| Figure 4.41 | Scanning electron microscopy of 90:10 samples of PLA/chitosan/CNF biocomposite a) neat PLA @ 500 μm , b) neat PLA @ 50 μm c) P955 d) P9551 c) P9553 d) P9555 | 163 |
| Figure 4.42 | Thermogravimetry (TG) analysis of neat PLA, and 80:20 samples of PLA/chitosan/CNF biocomposite | 165 |
| Figure 4.43 | Derivative thermogravimetry (DTG) analysis of neat PLA, and 80:20 samples of PLA/chitosan/CNF biocomposite | 167 |
| Figure 4.44 | Thermogravimetry (TG) analysis of neat PLA, and 85:15 samples of PLA/chitosan/CNF biocomposite | 168 |
| Figure 4.45 | Derivative thermogravimetry (DTG) analysis of neat PLA, and 85:15 samples of PLA/chitosan/CNF biocomposite | 169 |
| Figure 4.46 | Thermogravimetry (TG) analysis of neat PLA, and 90:10 samples of PLA/chitosan/CNF biocomposite | 170 |
| Figure 4.47 | Derivative thermogravimetry (DTG) analysis of neat PLA, and 90:10 samples of PLA/chitosan/CNF biocomposite | 171 |
| Figure 4.48 | Thermogravimetry (TG) analysis of neat PLA, and 95:5 samples of PLA/chitosan/CNF biocomposite | 172 |
| Figure 4.49 | Derivative thermogravimetry (DTG) analysis of neat PLA, and 95:5 samples of PLA/chitosan/CNF biocomposite | 173 |
| Figure 4.50 | Differential scanning calorimetry of neat PLA, and 80:20 samples of PLA/chitosan/CNF biocomposite | 175 |
| Figure 4.51 | Differential scanning calorimetry of neat PLA, and 85:15 samples of PLA/chitosan/CNF biocomposite | 176 |
| Figure 4.52 | Differential scanning calorimetry of neat PLA, and 90:10 samples of PLA/chitosan/CNF biocomposite | 179 |
| Figure 4.53 | Differential scanning calorimetry of neat PLA, and 95:5 samples of PLA/chitosan/CNF biocomposite | 180 |

| | | |
|-------------|---|-----|
| Figure 4.54 | Schematic diagram of the effect of supercritical carbon dioxide on bamboo fibre | 183 |
| Figure 4.55 | Moisture content properties of bamboo CNF and commercial CNF reinforced in PLA/chitosan | 185 |
| Figure 4.56 | Density properties of bamboo CNF and commercial CNF reinforced PLA/chitosan | 186 |
| Figure 4.57 | Comparative analysis of tensile strength properties of bamboo CNF and commercial CNF reinforced biocomposite | 187 |
| Figure 4.58 | Comparative analysis of tensile modulus properties of bamboo CNF and commercial CNF reinforced biocomposite | 189 |
| Figure 4.59 | Comparative analysis of tensile elongation properties of bamboo CNF and commercial CNF reinforced biocomposite | 189 |
| Figure 4.60 | Comparative analysis of flexural strength of bamboo CNF and commercial CNF reinforced biocomposite | 191 |
| Figure 4.61 | Comparative analysis of flexural modulus of bamboo CNF and commercial CNF reinforced biocomposite | 192 |
| Figure 4.62 | Comparative analysis of impact strength properties of bamboo CNF and commercial CNF reinforced biocomposite | 193 |
| Figure 4.63 | Comparative analysis of morphological properties of bamboo CNF and commercial CNF reinforced biocomposite | 195 |
| Figure 4.64 | Comparative analysis of FT-IR analysis of bamboo CNF and commercial CNF reinforced biocomposite | 196 |
| Figure 4.65 | Comparative analysis of X-ray diffraction analysis of bamboo CNF and commercial CNF reinforced biocomposite | 198 |
| Figure 4.66 | Comparative analysis of thermogravimetry analysis (TGA) properties of bamboo CNF and commercial CNF reinforced biocomposite | 199 |
| Figure 4.67 | Comparative analysis of Derivative thermogravimetry (DTG) properties of bamboo CNF and commercial CNF reinforced biocomposite | 200 |

| | | |
|-------------|---|-----|
| Figure 4.68 | Comparative analysis of differential scanning calorimetry (DSC) properties of bamboo CNF and commercial CNF reinforced biocomposite | 201 |
| Figure 4.69 | Water absorption properties of bamboo CNF and commercial CNF reinforced biocomposite | 203 |
| Figure 4.70 | Thickness of swelling properties of bamboo CNF and commercial CNF reinforced biocomposite | 205 |
| Figure 4.71 | Biodegradation weight loss percentage of neat PLA and biocomposite | 210 |
| Figure 4.72 | Schematic process of molecular degradation in soil burial test | 212 |

LIST OF SYMBOLS

| | |
|--------------------|--|
| \pm | Plus-minus |
| $<$ | Less than |
| $>$ | Greater than |
| $^{\circ}\text{C}$ | Degree Celsius |
| $^{\circ}$ | Degree |
| ΔE | Total colour difference |
| L^* | Lightness |
| a^* | Colour channel of redness-greenness |
| b^* | Colour channel of yellowness-blueness |
| $\%$ | Percentage |
| mm^2 | Millimetre square |
| Pa | Pascal |
| g | Gram |
| s | Second |
| m^2 | Meter square |
| m | Meter |
| α | Alfa |
| T_m | Melting temperature |
| H_m | Enthalpy of melting |
| T_{onset} | Initial degradation temperature |

| | |
|-----------|------------------------------------|
| T_{max} | Maximum degradation temperature |
| M_o | Initial weight |
| M_f | Final weight |
| l_o | Original length |

LIST OF ABBREVIATIONS

| | |
|-------------------|---|
| AgNPs | Silver nanoparticles |
| ANOVA | Analysis of variance |
| A | Area |
| ASTM | American Society for Testing and Materials |
| AQ | Anthraquinone |
| BBP | Bleached bamboo pulp |
| BC | Bamboo chips |
| BP | Bamboo pulp |
| BS | Bamboo strips |
| CA | Contact angle |
| CaCO ₃ | Calcium carbonate |
| C-MCC | Commercial microcrystalline cellulose |
| CMC | Carboxymethyl cellulose |
| CF | Cellulose fibres |
| CNC | Cellulose nanocrystals |
| CNW | Cellulose nanowhiskers |
| CrI | Crystallinity Index |
| EAB | Elongation at break |
| FT-IR | Fourier Transforms Infrared Spectroscopy |
| F | Forces |

| | |
|--------|---|
| GS-MCC | <i>Schizostachyum Brachycladum-</i> microcrystalline cellulose |
| GPa | Gigapascal |
| HCl | Hydrochloric acid |

**SIFAT DAN PENCIRIAN KOMPOSIT NANO ASID POLILAKTIK
CHITOSAN DIPERKUAT GENTIAN
NANO SELULOSA BULUH**

ABSTRAK

Sifat-sifat mekanikal dan degradasi bahan-bahan polimerik yang berpotensi adalah penting dalam kaedah pembuatan hijau. Asid polilaktid (PLA) telah dilaporkan sebagai biopolimer yang paling sesuai untuk penggantian polimer sintetik utama dalam aplikasi perindustrian kerana persamaan tingkah laku viscoelastik dalam pemrosesan. Walau bagaimanapun, asid polilaktid mempunyai kelemahan dalam kekuatan tegangan dan kekerasan disebabkan sifatnya yang rapuh. Oleh itu, dalam kajian ini, chitosan dan selulosa nanofiber (CNF) telah digabungkan bersama asid polilaktid untuk meningkatkan sifatnya bagi berpotensi sebagai bahan plastik hijau dalam aplikasi industri. Chitosan pertama telah diubahsuai secara kimia kepada chitosan amphiphilic untuk meningkatkan kelarutannya dengan PLA. Selulosa nanofiber (CNF) telah diasingkan daripada buluh *Schizostachyum brachycladum* dengan gabungan kaedah hidrolisis, karbon dioksida genting lampau dan proses homogenisasi tekanan tinggi. Adunan chitosan PLA/amphiphilic (PLA/chitosan) digunakan sebagai matriks dan diperkuatkan dengan selulosa nanofiber menggunakan gabungan ekstruder leburan dan teknik acuan mampatan. Pencirian CNF yang telah diasingkan dianalisis dengan menggunakan transmisi elektron mikroskopi (TEM), FT-IR, analisis termal, diffraction X-ray (XRD), 'zeta potential' dan taburan saiz partikel. FT-IR telah digunakan dalam mengkaji perubahan chitosan dalam penggantian kumpulan berfungsi selepas diubah secara kimia. Chitosan amphiphilic digunakan sebahagian dalam matriks PLA/chitosan dengan kandungan 5%, 10%, 15%, dan 20%.

Matriks PLA/chitosan diperkuat dengan 1%, 3%, dan 5% daripada CNF yang diasingkan daripada buluh (B-CNF). Variasi komposisi optimum biokomposit PLA/chitosan/CNF ditentukan dengan menggunakan sifat mekanikal dan termal. Sifat-sifat mekanikal, termal, fizikal dan degradasi biokomposit yang optimum dibanding dengan biokomposit yang diperkuatkan dengan CNF komersil (C-CNF) dengan komposisi yang sama. Keputusan daripada TEM, FT-IR, 'zeta potential' dan taburan saiz partikel menunjukkan kejayaan pengasingan selulosa nanofiber menggunakan gabungan karbon dioksida genting lampau dan homogenisasi tekanan tinggi. Walau bagaimanapun, analisis XRD dan taburan saiz partikel B-CNF menunjukkan indeks kristal yang lebih tinggi dan saiz yang lebih rendah daripada jenis komersial (C-CNF) kerana perbezaan sumber dan kaedah penghasilan. Analisis FT-IR chitosan amphiphilic mengesahkan penggantian hidrogen dalam kumpulan berfungsi amine chitosan. Ciri-ciri ketegangan, kelenturan dan kekuatan impak biokomposit telah dipertingkatkan untuk semua set sampel berbanding dengan PLA tiada gabungan bahan. Kestabilan termal biokomposit telah dikurangkan dengan penambahan chitosan tetapi meningkat dengan pemuatan CNF; Walau bagaimanapun, ia adalah lebih rendah berbanding dengan PLA tiada gabungan bahan. Sifat-sifat mekanikal dan termal terbaik telah diperolehi dengan nisbah 90:10 (PLA:chitosan) biokomposit dengan muatan CNF tertinggi iaitu 5%. Tambahan pula, sifat-sifat mekanikal dan termal bagi biokomposit 90:10 adalah lebih tinggi berbanding dengan CNF komersial yang menguatkan biokomposite dengan muatan yang sama disebabkan oleh perbezaan saiz partikel dan indeks kristal CNF. Ciri-ciri penyerapan air, kadar pengembangan, dan kandungan kelembapan biokomposit (untuk B-CNF dan C-CNF) meningkat berbanding PLA mungkin disebabkan oleh kehadiran kumpulan berfungsi hidroksida dalam chitosan dan CNF. Walau bagaimanapun, biokomposit diperkuatkan B-CNF

mempunyai ketahanan air yang lebih baik daripada C-CNF kerana indeks kristal yang lebih tinggi. Analisis morfologi menunjukkan kelarutan atau penyebaran CNF yang baik dalam matriks PLA/chitosan dengan sedikit berongga. Sudut sentuhan PLA dikurangkan dengan chitosan dan CNF; tetapi B-CNF mempunyai sudut sentuhan yang lebih tinggi daripada C-CNF disebabkan sifat kristalnya yang mengurangkan kebolehbasahan. Sifat biodegradasi PLA telah dipertingkatkan dengan ketara daripada ujian penguburan tanah. Bio-komposit mempunyai potensi untuk digunakan dalam aplikasi industri yang hijau dan mapan.

**PROPERTIES AND CHARACTERISATION OF BAMBOO CELLULOSE
NANOFIBRE REINFORCED POLYLACTIC ACID – CHITOSAN
NANOCOMPOSITES**

ABSTRACT

Potential polymeric materials' mechanical and degradation properties are significant for green manufacturing. PLA has been reported to be an adaptable biopolymer to replace primary synthetic polymer in industrial applications. However, PLA has poor tensile strength and toughness because of its brittleness. In this study, chitosan and cellulose nanofibre (CNF) was incorporated in PLA to enhance its properties for potential green plastic industrial material applications. First, chitosan was chemically modified to amphiphilic chitosan to enhance its miscibility with PLA. The CNF was isolated from *Schizostachyum Brachycladum* bamboo using combined hydrolysis, supercritical carbon dioxide, and high-pressure homogenisation. PLA/amphiphilic chitosan (PLA/chitosan) blend was used as the matrix and reinforced with CNF using combined melt extrusion and compression moulding technique. The isolated CNF was characterised with transmission electron microscopy (TEM), FT-IR, thermogravimetry analysis, X-ray diffraction (XRD), zeta potential, and particle size analysis. The chitosan substitution reaction was studied with FT-IR analysis. The amphiphilic chitosan was used as part of the matrix PLA/chitosan ranging from 5%, 10%, 15%, and 20%. The PLA/chitosan matrix was reinforced with 1%, 3%, and 5% of the isolated bamboo CNF (B-CNF). The optimum composition variation of the PLA/chitosan/CNF biocomposite was determined using mechanical and thermal properties. The mechanical, thermal, physical, and degradation properties of the optimum biocomposite were compared with corresponding commercial CNF (C-CNF)

reinforced biocomposite with similar loading. The result of the TEM, FT-IR, zeta potential, and particle size results showed successful isolation of cellulose nanofibre using combined supercritical carbon dioxide and high-pressure homogenisation. However, the XRD and particle size analysis of the isolated B-CNF shows a higher crystallinity index and lower size than the commercial type (C-CNF) due to differences in source and production method. The FT-IR analysis of the amphiphilic chitosan confirmed the substitution of hydrogen in the amine functional group of chitosan. The biocomposite's tensile, flexural, and impact properties were enhanced for all sets of samples compared with the neat PLA. The thermal stability of biocomposite was reduced with the addition of chitosan but increased with CNF loading; however, it is lower compared with neat PLA. The best mechanical and thermal properties were obtained with 90:10 (PLA: chitosan) set biocomposite with the highest at 5% CNF loading. Furthermore, the mechanical and thermal properties of 90:10 set biocomposites were higher than commercial CNF reinforced biocomposites of similar loading due to the difference in the particle size and crystallinity index of the CNF. The water absorption, the thickness of swelling, and moisture content of the biocomposite (for both B-CNF and C-CNF) increased compared to PLA, probably due to the presence of hydroxide functional group in the chitosan and CNF. However, the B-CNF reinforced biocomposites had better water-resistant ability than C-CNF due to their higher crystallinity index. The morphological analysis shows good miscibility or dispersion of the CNF in the PLA/chitosan matrix with minor voids. The contact angle (CA) of PLA was reduced with chitosan and CNF, but B-CNF has a higher CA than the C-CNF because of its crystallinity properties which reduced wettability. The biodegradation properties of PLA were significantly enhanced from the study. The bio-composite has the potential for green and sustainable industrial application.

CHAPTER 1

INTRODUCTION

1.1 General background of the study

Synthetic polymers have, over the years, served as a replacement for most metallic and ceramic applications. This set of polymers are derived from crude oil extraction, and several types of polymer have been processed from oil exploration. Several industrial material revolutions have been traced to synthetic polymers for product parts (Alves *et al.*, 2020). Synthetic polymers have been used for several industrial manufacturing processes and applications. The use has been from simple skateboards to complex automobile parts.

One of the significant use of plastics from petroleum products is in packaging. Thousands of plastic product materials used for packaging applications are produced daily (Ahmed and Varshney, 2011). According to statistics, an average of 8.5 tons of plastic products are manufactured daily worldwide. The use of plastics is generally increasing due to increased demand caused by population increase (Borrelle *et al.*, 2020). It has been projected that the use of plastic packaging will continue to increase at an exponential rate.

Synthetic polymers have excellent properties, which are desirable for most applications (Alves *et al.*, 2020). First, most synthetic polymers' mechanical properties are high, which has made them suitable as a replacement for applications where metals are not essentially needed. Furthermore, the toughness and low water permeability have made it useable for the packaging of liquid products. However, synthetic polymers are faced with the challenge of biodegradation. Most synthetic polymers are non-degradable by heat and bioprocess (Siracusa, 2019).

Global statistics on land and marine pollution indicated that plastic waste is the primary cause. The production of plastic-based products has increased, with 300 billion tons of plastics produced each year and about 50% single-use (Borrelle *et al.*, 2020). Reports on marine waste pollution showed that more than 8 million tons of waste plastic are deposited in the ocean (Borrelle *et al.*, 2020). Further analysis of reports on plastic waste revealed that countries with a large population, such as China, the USA, and Germany, are on top of plastic production. Statistical projections predicted that by the year 2050, there would be more plastic waste in the oceans than fish (Kumar *et al.*, 2015; Ma *et al.*, 2020).

Several policies and solutions have been developed to combat the global challenge of plastic waste pollution. Plastic recycling is one of the foremost solutions to plastic waste (Ma *et al.*, 2020). Many government policies encourage the green disposal of plastic waste, and plastic waste disposal has been classified with colour codes (Maraveas, 2020). Also, several disposal symbols have been developed and printed on plastic packaged products by manufacturing companies. Germany is one of the top countries with effective waste disposal. The disposed plastics are then recycled for subsequent production. However, 50% of the synthetic plastic produced cannot be recycled (Borrelle *et al.*, 2020). Owing to this, population growth has overcome the effects of this method as more plastics are produced to satisfy the demand. At present, the most effective solution to plastic waste pollution is the production of alternative biodegradable material for synthetic polymers (Murphy *et al.*, 2018).

Biopolymers are naturally occurring polymers with unique biodegradable properties. Among the most abundant biopolymers are cellulose, chitosan, and starch. Biopolymers are extracted from plant or animal sources and are often biocompatible

with human systems (Murphy *et al.*, 2018). The biodegradability nature of biopolymer has attracted several types of research and has been proposed as a possible replacement for synthetic polymers (Murphy *et al.*, 2018). Biodegradable polymers from renewable sources are more economical than synthetic polymers because they naturally exist (Muthuraj *et al.*, 2019). Most biopolymers are nontoxic, and these properties make them suitable for packaging application

Several types of research have been conducted on synthetic polymers for enhanced bio and thermal degradation (Alves *et al.*, 2020). Synthetic polymers have been blended with natural polymers for improved degradation properties. Common synthetic polymers such as polyethylene, ABS, and PVC have been blended with biopolymers for improved degradability; however, the synthetic-natural blend's biodegradability properties of the hybrid forms are not significantly enhanced (Jawaid and Khalil, 2011).

Further research on the use of biopolymer blends showed poor mechanical properties (Anwer and Naguib, 2016). Biopolymers such as PLA, chitosan, cellulose have been reported to have low mechanical properties (Coltelli *et al.*, 2019). This has discouraged their use for many automobile parts and aerospace applications. The mechanical properties of the proposed biopolymer have been of significant concern to researchers (Sadasivuni *et al.*, 2020).

The use of nanoparticles as reinforcement for materials has restarted research on biopolymers for packaging (Deepa *et al.*, 2016). Nanoparticles of biopolymers such as cellulose and chitosan have been reported to significantly enhance the mechanical properties of many biopolymers (Choo *et al.*, 2016). The isolation of cellulose nanofibre from cellulose has been done using chemical and mechanical methods.

Cellulose nanofibre has been used as reinforcement for most biopolymers for different applications such as biomaterial Research on major biopolymers such as PLA and PBS has been on the front of material research for packaging application (Siakeng *et al.*, 2019).

Cellulose nanofibre has the challenge of miscibility with PLA (Clarkson *et al.*, 2018). This majorly is due to the difference in their nature. Cellulose nanofibre is hydrophilic, while PLA is hydrophobic. Poor miscibility between these two polymers has resulted in low mechanical properties from their blend. PLA/CNF composite has been reported with agglomeration in the microstructure. This challenge often limits the quantity of cellulose nanofibre added to the PLA matrix. The solution to the miscibility challenge of PLA with CNF has been proposed as novel research (Siakeng *et al.*, 2019).

Chitosan has been used as filler in PLA to enhance its properties. Previous studies showed a significant increase though not up to cellulose nanofibre (Nasrin *et al.*, 2017). However, the use of chitosan as a compatibilizer has not been researched. Chitosan has two functional groups: amine and hydroxyl (Aranaz *et al.*, 2009). Previous studies show that the amine group hydrogen makes it more active in substitution reactions such as alkylation and acylation (da Mata Cunha *et al.*, 2020). The substitution of amine hydrogen has been reported to enhance chitosan miscibility with hydrophobic polymers such as PLA (Gupta *et al.*, 2018).

On the other hand, the hydroxyl group of chitosan enhances its solubility in acetic acid, which is often used as its solvent (GLOTOVA *et al.*, 2016; Tikhonov *et al.*, 2008). This makes chitosan miscible with hydrophilic polymers, of which cellulose is not an exemption. This reaction is used in the preparation of amphiphilic chitosan.

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Amphiphilic polymers are polymers with both hydrophilic and hydrophobic nature when mixed with other polymers. Biopolymers such as chitosan exhibited such properties in their modified state (Gupta *et al.*, 2018). Amphiphilic chitosan is a modified form of chitosan in an acylation substitution reaction. Amphiphilic chitosan is different from other modified forms of chitosan because of its ability to mix with hydrophilic and hydrophobic polymers. The amphiphilic properties of chitosan have been reported in the literature (da Mata Cunha *et al.*, 2020). Several reaction mechanisms have been developed to produce amphiphilic chitosan. Many types of research have been conducted on its production due to its application in drug delivery, DNA and other biomedical application. The amphiphilic properties of chitosan were used when it was introduced as a compatibilizer (Gupta *et al.*, 2018). This study isolated CNF from bamboo using the supercritical carbon dioxide method. The isolated CNF was used to reinforce PLA/chitosan hybrid blend. PLA/chitosan/CNF composite was produced using melt extrusion and compression moulding method. The obtained composite's mechanical, thermal, morphological, and wettability properties were studied for improved properties.

1.2 Problem statement

Biopolymers are considered a replacement for synthetic polymers, but the poor mechanical properties of the produced composite have been a significant problem in their application as packaging material (Sadasivuni *et al.*, 2020). Potential biodegradable material's mechanical and degradation properties are of significant concern (Surya *et al.*, 2020).

Cellulose nanofibre has been proposed and used as reinforcement for most biopolymers (Eichhorn *et al.*, 2010). The properties of isolated CNF have been reported to depend on its source and isolation method (Qua *et al.*, 2011). The isolation method majorly determines the homogeneity of the obtained CNF and the miscibility of the CNF with other biopolymers for reinforcement. This determines the hydroxyl group available for hydrogen bonding with another biopolymer. Isolation of cellulose nanofibre with a chlorine-free method has been proposed to improve the interaction of CNF with other biopolymers as more hydroxyl groups can be available for hydrogen bonding (Eichhorn *et al.*, 2010). Isolation of CNF from *S. Brachycladum* bamboo-CNF with supercritical carbon dioxide (a chlorine-free method) has not been reported

Furthermore, isolation of CNF from different sources has been reported to affect the strength of reinforcement of CNF on biopolymers (Ohwoavworhua and Adelakun, 2005). The use of CNF from bamboos has been proposed to improve the strength of CNF reinforcement. The effect of the source of the isolated CNF on its properties has not been fully established. A comparative study is needed to establish the influence of CNF sources on its properties.

Cellulose nanofiber has the challenge of miscibility with PLA. This majorly is due to the difference in their nature. That is, cellulose nanofiber is hydrophilic, while PLA is hydrophobic. Poor miscibility between these two polymers has resulted in low mechanical properties from their blend due to agglomeration in the microstructure. This challenge has not been solved and often limits the use of cellulose nanofiber in the PLA matrix. The solution to the miscibility challenge of PLA with CNF has been proposed as novel research.

An introduction of a compatibilizer has been proposed to improve its properties. Amphiphilic polymers are polymers with both hydrophilic and hydrophobic nature when mixed with other polymers. This study used the amphiphilic properties of chitosan at different composition as a compatibilizer between PLA and CNF. Amphiphilic chitosan was prepared to enhance the miscibility properties between PLA and cellulose nanofiber. Amphiphilic chitosan as a compatibilizer in immiscible biopolymer has not been researched. Furthermore, the reinforcement of PLA/chitosan with cellulose nanofibre has not been reported (Borrelle *et al.*, 2020).

1.3 The objective of the study

The objectives of these study were;

- i. To determine the physicochemical, thermal, and morphological properties of *S. Brachycladum* bamboo cellulose nanofibre (B-CNF) and compared with commercial cellulose nanofibre (C-CNF);
- ii. To characterise the optimum composition variation properties of amphiphilic chitosan compatibilized reinforced CNF-PLA nanocomposite constituent materials;
- iii. To study the effect of different types of CNF reinforcement material on physical, mechanical, morphological, thermal, and biodegradable properties of PLA/chitosan/CNF nanocomposite.

1.4 Significance of study

This significance of these studies was justified from the statement of fact established from this research:

- i. A comparative analysis of the properties of CNF from *S. Brachycladum* Bamboo with commercial CNF has not been reported. The establishment of the effect of the source on the properties of Obtained CNF was a novel contribution
- ii. A previous study on the preparation of CNF from *S. Brachycladum* bamboo combined with alkaline and enzymic hydrolysis has been reported in the literature. However, the Isolation of CNF from *S. Brachycladum* bamboo with supercritical carbon dioxide method has not been reported.
- iii. The literature has not reported reinforcing PLA/chitosan with CNF from bamboo. The reported properties of PLA/chitosan/CNF composite were novel addition to the literature.

1.5 Layout of thesis

- | | |
|-----------|--|
| Chapter 1 | The Chapter consisted of the Introduction to the background of the study. The problem statement established the problem solved and the outlined objectives. The Chapter concluded with the significance of the research, which established the study's novelty and the thesis outline. |
| Chapter 2 | The Chapter reported various definitions, terms, and classifications important to the study. It concluded with detailed previous researches relevant to this study and established the research gap covered. |

- Chapter 3 This Chapter outlined a detailed step-by-step methodology used to achieve the stated objectives. The CNF isolation, composite development, and characterisation were the major highlight of the Chapter.
- Chapter 4 This Chapter reported the isolation of CNF, production of PLA/chitosan/CNF, and characterisation. The Chapter is arranged to answer each of the objectives in Chapter one.
- Chapter 5 This Chapter was a summary of the established trend from Chapter 4. It consisted of conclusions deduced from Chapter 4 based on the study's objectives and the recommendations for further work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This Chapter entails details of in literature which is significant o his study. It comprises of introduction to biopolymer and its classifications. Specific biopolymers such as PLA, chitosan and CNF preparation, properties and application were expressly discussed. A review of literature on the properties of PLA blends with chitosan using melt extrusion techniques and their application was also studied. The Chapter concluded with the research gap and scope of this study

2.2 Biopolymers

Biopolymers consist of biodegradable polymers from renewable sources, biodegradable polymer petroleum sources and non-biodegradable polymers from renewable. Biodegradable polymers are from renewable resources to degrade under certain environmental conditions (Phommachanh, 2013). Based on ASTM standards, biopolymers are polymers that can be degraded by microorganisms like algae, bacteria and fungi (Shimao, 2001). Several processes occur during the degradation of biopolymers, such as hydrolysis, photo degradation and oxidation. There are conditions for each to occur at different stages, depending on environmental factors.

Biopolymers degradation is a chain process that involves photo-degradation, oxidation, and hydrolysis. The biodegradable properties of biopolymers revive the interest of most researchers in polymeric material. At present, there are rising concerns over limited landfill sites, and environmental regulations are being used to cub increasing oil-based plastics (Phommachanh, 2013). Biodegradable polymers can undergo enzymatic decomposition primarily by the action of microorganisms to

produce carbon dioxide, methane etc., after some time (Kolybaba *et al.*, 2006). Biodegradable Plastic Society Japan (BPS, Japan) reports showing that biodegradable polymers could be degraded naturally in soil with normal climate conditions. The process of degradation results in the reduced molecular structure of the biopolymers. This process can be accelerated under specific conditions such as pH, humidity, oxygenation, and sometimes in a degradation catalyst. Biodegradable polymers can also be obtained from bio-resources such as wood, corn using bacterial (Akaraonye *et al.*, 2010).

Biodegradable polymers are sustainable materials with residues and have been used to replace non-degradable polymers, which cause pollution (Phommachanh, 2013). The biodegradable properties of biopolymers are a probable solution to pollution from synthetic polymers. Biopolymers are classified as green materials because of their low impact on the environment. Biopolymer has been used in packaging and agriculture compositing due to this property. Furthermore, some biopolymer has biocompatibility with the human system and is used in biomedical and tissue engineering applications such as scaffolding and temporary organ replacement (Jun *et al.*, 2018). Biopolymers have different categories based on their sources and properties, as reported in previous literature (Akaraonye *et al.*, 2010; Sato *et al.*, 2010).

2.3 Classification of biopolymers

Biodegradable polymers, also called biopolymers, are extracted from renewable and biomass source. Biopolymers such as cellulose can be obtained from agro- biomass by fractionation, dividing larger molecules into smaller ones either by chemical or microorganisms. An example is the fermentation of biomass or plants to obtain monomers. Also, some types of biopolymers can be obtained from

petrochemical products (Jacob and Thomas, 2008). Therefore, biopolymers can be classified into two groups; agropolymers and biodegradable polyesters (Durowaye *et al.*, 2014). Biodegradable polymers that are produced from nature by microorganisms are from renewable sources. The more common and abundant natural biopolymers are cellulose, chitosan starch and cellulose. Examples of the second class of biopolymers (polyester) are proteins, polyhydroxy-alkanoates etc. (Phommachanh, 2013). The schematic diagram of the classification of biopolymers based on their polymer backbone, types of monomer and biodegradability is presented in Figure 2.

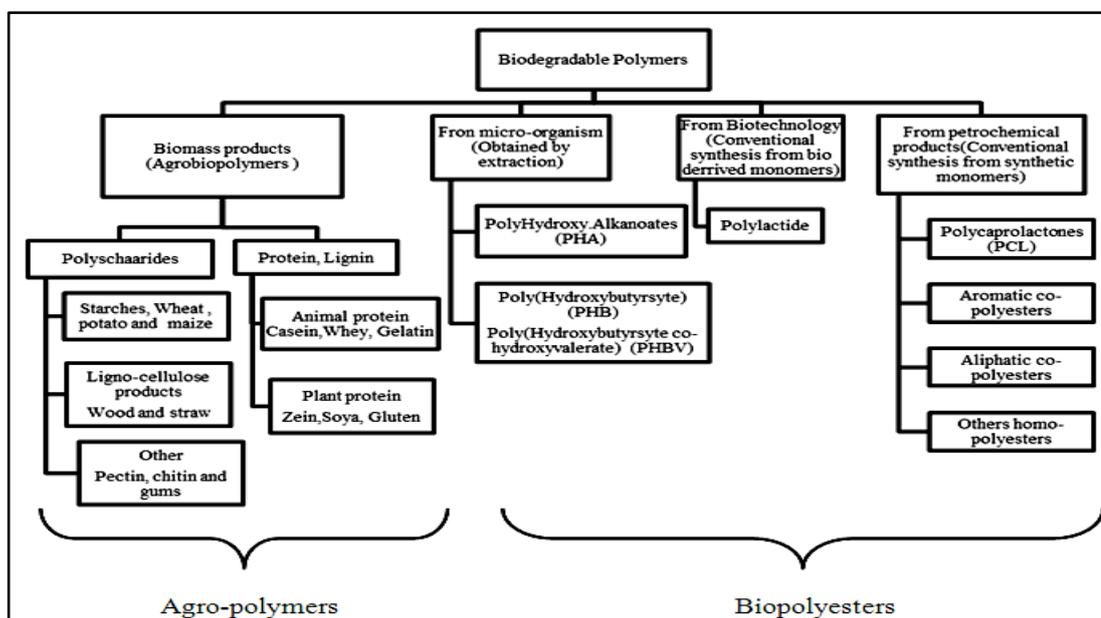


Figure 2.1 Classification of Biopolymers (Kumar and Thakur, 2017).

Biopolymers derived from renewable sources are biodegradable, compostable, and environmentally green (Phommachanh, 2013). Many researchers have increasingly used these polymers because of the projection to close the carbon process cycle; that is, the eventual cycle return of plant-based carbon to the soil. This happens through biodegradation and or composting. Therefore, it reduces environmental pollution. Secondly, it reduces fossil fuel use, emitting carbon dioxide during production and product life cycles (Plackett, 2011). This makes biopolymers classified

as novel materials of the twenty-first century, which significantly contributes to the material world. The biopolymer solution is to grow the environmental issues and the uncertainty of continuity petroleum supply. Biopolymers are now moving into primary use and are competing with conventional plastics in the commercial valorization of more than 30% annually (Mohanty *et al.*, 2018). Besides, the primary reason for the prior interest in biopolymers is their biodegradability, reducing the present waste disposal challenge. The aftermath of this development in biodegradable polymers is its suitability for packaging and storage applications. Biopolymers have fulfilled several performance index criteria. This criterion includes non-toxicity, flexibility, permeability (water and oxygen), moisture, thermal stability, an abundance of starting materials, and ease of production. This has shifted the material production process towards zero-emission and green manufacturing. A concept developed to combat global warming and climatic changes caused by the greenhouse effect. This has resulted in a boost for the production of biodegradable plastics from renewable sources (Sudesh and Iwata, 2008). One of the most researched biodegradable polymers for industrial application is PLA because of its properties close to that of synthetic properties (Ramontja *et al.*, 2009). They are nontoxic and environmentally biodegradable by microorganisms to carbon dioxide (CO₂) and water (H₂O) (Funabashi *et al.*, 2009).

2.3.1 Polylactic acid

PLA is a polymer based on the monomer lactic acid. It is one of the most promising biopolymers produced from renewable sources. PLA is compostable as well as biocompatible. Its processing is similar to standard plastic production (Almenar and Auras, 2010). PLA is industrially produced through direct condensation polymerization of lactic acid and or ring-opening polymerization of cyclic lactide

dimer. Cyclic lactide dimer is a diester of lactic acid obtained from the fermentation process of sugar feedstock. PLA has a chiral molecule in two active forms: L-lactide and D-lactide. These are optically active forms of PLA, and their semi-crystalline form can be produced using the depolymerization of any of the monomers. PLA structure can be easily modified using polymerizing or a controlled mix of optical isomers to form semi-crystalline or amorphous PLA (CT, 2007).

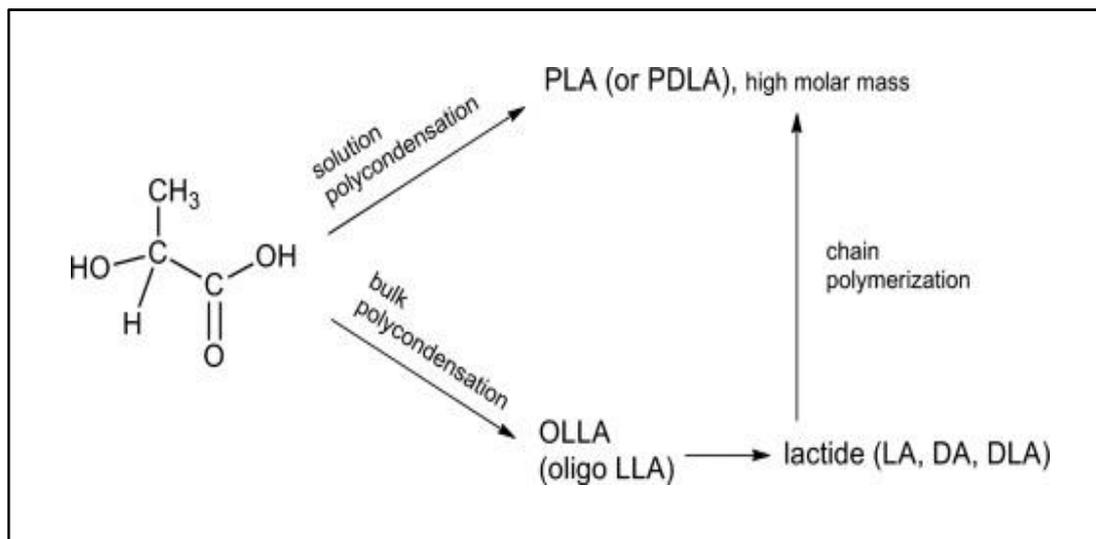


Figure 2.2 Molecular structure of the starting polymer and preparation routes for PLA (Pretula *et al.*, 2016)

PLA has been researched because it has similar properties to PET and Polypropylene (PP) in terms of elasticity. It is regarded as one of the biopolymers with several applications due to its crystallisation ability under stress. It can be thermally crystallized, impact stress modified, reinforced or filled, copolymerized and processed into various forms using minimal processing equipment (Henton *et al.*, 2005). PLA has been reported with excellent organoleptic properties, making it suitable for food packaging applications. PLA has been used in 3D printing due to its lower flow temperature than other biopolymers; it has similar flow properties with most synthetic polymers suitable for the 3D printer laser tip (Phommachanh, 2013). PLA is biodegradable to H_2O and CO_2 , which is not hazardous to the environment. Thus,

making it a green, nontoxic and eco-friendly biomaterial. PLA has been widely used as a material in biomedical engineering to produce clips for the medication (Henton *et al.*, 2005). PLA's properties such as biocompatibility, renewability, plasticity, and transparency make it a suitable replacement for most synthetic polymers (Phommachanh, 2013). Although PLA has been produced in abundance, it has not been adopted in many industries.

PLA has been reported with a prolonged degradation process due to hydrolysis, which takes an extended period. It is brittle with a breaking point of less than 10 % elongation. PLA is a hydrophobic biopolymer with limited gas barrier properties (Chiu *et al.*, 2008; Kiziltas *et al.*, 2016). However, it has been proposed for various applications, which makes researchers work on its drawbacks using modification, reinforcement or blending. PLA has been modified and surface treated with solvent. PLA modification makes it more flexible and crystalline in its chain (Li *et al.*, 2017c).

2.3.2 Structural analysis of polylactic acid

PLA is one of the most extensively studied bioplastics because of its abundance and can easily be obtained from renewable feedstock. PLA is classified as aliphatic polyester, which is made from acids. PLA is produced from lactic acid (i.e., 2-hydroxy propionic acid) using a fermentation process extracted from a resource such as corn starch and sugarcane (Li *et al.*, 2017a). Lactic acid is one of the simplest hydroxyl acids with an asymmetric carbon atom, and it exists in two optically active forms; D (+) lactic acid and L(-) lactic acid. L-isomer type is derived from humans or mammals (Garlotta, 2001). It has a high water-soluble ability and three chiral carbon acids naturally. Both enantiomers (D (+) and L (-)) can also be produced from a bacterial system. However, lactic acid is usually commercially produced by fermentation with selected micro-organisms. However, lactic acid extracted using the chemical process

is a mixture of L- and D- isomers (Garlotta, 2001; Gupta *et al.*, 2018; Gupta *et al.*, 2007).

There are primarily two methods for preparing PLA; the chemical (polymerization of lactic acid) and industrial method (fermentation). PLA characteristics from lactic acid vary, dependent on the distribution ratio between the stereoisomers and comonomers (Södergård and Stolt, 2010). Several polymerization routes have been used to produce PLA. PLA with high molecular weight is mostly prepared using ring-opening polymerization (ROP) of dimer lactide (lactide; 3,6-dimethyl-1,4-dioxane-2,5-dione). This was prepared by depolymerization of a polycondensed lactic acid in 2-hydroxypropanoic acid (Södergård and Stolt, 2010). This route involves a two-step procedure with additional purification, making it cost-intensive. However, PLA produced from polycondensation has poor tensile properties and low molecular weight, making it unsuitable for most applications except reinforcement. The only commercially manufactured PLA to solve this problem of cost-effective approaches is with a high molecular weight. Solvent-assisted polycondensation, melt polycondensation, and solid-state polycondensation has been used to produce high molecular weight PLA (Lim *et al.*, 2008). Another approach that produces high molecular weight LA-based polymers is terminal group prepolymer using linking processes, i.e., a linking agent is employed. The prepolymers are usually composed of one stereoisomer, or a combination of D- and L-lactose units with various ratios, or multifunctional comonomers

Lactic acid can also be produced commercially using fermentation or petrochemical feedstock (Li *et al.*, 2017a). The lactic acid produced by this route is an optically inactive racemic mixture of L- and D-enantiomers. Nowadays, the most

popular route is fermentation, in which corn starch is converted into lactic acid by bacterial fermentation using an optimized strain of lactobacillus (Sin, 2012). All organic lactic acid and the lactic acid produced exist, more than 99.5% of L-isomer (Siakeng *et al.*, 2019). This is one reason why biodegradable polymers from renewable sources are favoured over petrochemical-based ones. PLA was first commercially produced by the fermentation of starch. PLA was discovered around 1932 by Carothers (Zaaba and Jaafar, 2020). He discovered this PLA by heating lactic acid in a vacuum. By this process, the production cost would be relatively high. Nowadays, PLA is made by fermentation of Starch. When manufactured, PLA granules are generally from 1 to 100-micron diameter in size (Wang *et al.*, 2020b).

Many companies use corn starch to produce plastics and can be manufactured for various applications. Today the most popular route is fermentation, in which corn starch is converted into lactic acid by bacterial fermentation using an optimized strain of Lactobacillus (Gupta *et al.*, 2007). PLA produced from fermentation of sugar and (poly)saccharides such as sugar feedstock's and corn, wheat, and other starch sources, either by ring-opening polymerization or by condensation polymerization

Two different polymerisation routes can be followed to produce PLA from lactic acid monomers. Lactic acid is usually condensed and polymerized to obtain low molecular weight glassy but brittle PLA. This type of PLA is mostly un-useable in neat form for any application unless coupled with external agents to increase its molecular weight (Garlotta, 2001; Torres-Hernández *et al.*, 2018). The biopolymer PLA using direction condensation is of low molecular weight because of the challenge of water removal from a viscous mixture (Cavallo *et al.*, 2021).

Furthermore, a controlled polymerization of polymer with low molecular weight can be used to produce lactides that can be purified, and ring-opening polymerization is done (in the presence of a catalyst) to obtain a high molecular weight polymer (Chun *et al.*, 2012). Ring-opening polymerization has two types, that is anionic and cationic ring-opening type. The purification process of the crude lactides is to remove impurities, water and oligomers impurities which could react during polymerization reaction (Cavallo *et al.*, 2021). The ring-opening polymerization involves a solvent-free process adapted for the preparation of PLA. This method produces pure PLA with a high molecular weight (Chiu *et al.*, 2008; Leluk *et al.*, 2021).

2.3.3 Properties of polylactic acid

2.3.3(a) Physical and mechanical properties of polylactic acid

PLA's physical and mechanical properties are often different to a large extent because of its molecular weight, which makes it soft, and elastic plastics or stiff with high strength (Henton *et al.*, 2005). Semi-crystalline PLA is often preferred over amorphous for high mechanical strength applications (Table 2.1). Most significantly, molecular weight is a determinant of the mechanical strength of PLA. An increase in molecular weight increases the mechanical strength because there is an increase in the entanglements of its molecules. Also, previous studies show that an increase in crystallinity increases tensile strength and modulus, but it decreases the percentage elongation of PLA (Tsuji, 2002).

Commercial PLA grade contains a combination of L-lactide and D-lactide copolymers (Sin, 2012). The percentage of these copolymers in PLA determines its optical purity and overall properties. An optically pure PLA is isotactic, which is highly crystalline. A decrease in the optical purity of PLA decreases its crystallinity

because it reduces its stereoregularity; for example, poly(L-lactide) (PLLA) contains more than 15% D-lactide and is amorphous (Hu *et al.*, 2016). PLA can be produced with up to 40% crystalline or amorphous. PLA resins with more than 93% L-lactide is semi-crystalline (Henton *et al.*, 2005; Zhang *et al.*, 2020) (Avérous, 2004), and the formula is indicated as PLLA, PDLA or PDLLA.

Table 2.1 Properties of PLA

| Physical and Mechanical Properties | INGEO 4032D | ASTM Method | References |
|------------------------------------|-------------|-------------|---|
| Specific gravity | 1.24 | D792 | (Zuo <i>et al.</i> , 2015) |
| MFI, g/10 min (210°C, 2.16 kg) | 7 | D1238 | (Zhou <i>et al.</i> , 2018) |
| Tensile strength at break, MPa | 53 | D882 | (Zhang <i>et al.</i> , 2020) |
| Tensile yield strength, MPa | 60 | D882 | (Wang <i>et al.</i> , 2020b) |
| Tensile modulus, GPa | 3.5 | D882 | (Torres-Hernández <i>et al.</i> , 2018) |
| Notched Izod Impact, J/m | 16 | D256 | (Henton <i>et al.</i> , 2005) |
| Mn*,g/mol | 114317 | | (Henton <i>et al.</i> , 2005) |
| Mw*,g/mol | 181744 | | (Henton <i>et al.</i> , 2005) |
| DMM* | 1.59 | | (Henton <i>et al.</i> , 2005) |
| Glass transition (T _g) | 60 – 70 °C | | (Garlotta, 2001) |
| Melting temperature | 155 - 170°C | | (Garlotta, 2001) |
| Processing temperature | 185 - 190°C | | (Garlotta, 2001) |

2.3.3(b) Thermal properties of polylactic acid

The thermal properties of PLA are often studied with thermogravimetry analysis (TGA), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Table 2.1 present the basic thermal properties of PLA. The melting temperature values show good thermal stability (170°C). However, PLA has low mechanical properties, which has prevented its use in neat form for applications(Bhasney *et al.*, 2019). The properties of PLA are dependent on its structure. The polymer architecture and molecular mass determine mechanical strength, melting point, and crystallinity properties. Also, the PLA biodegradation is affected by its molecular mass and degree of crystallinity(Bhasney *et al.*, 2019; Chan *et al.*, 2015). The amorphous form of PLA degrades faster compared to its semi-crystalline form.

Previous studies show that PLA molecular weight is dependent on its heat capacity and density. In solid-state, PLA is either amorphous or semi-crystalline. Its melting point is between 130-230 °C which depends on its structure, and the T_g is around 58 °C. Above the T_g , PLA enters a rubbery state, i.e., liquid form. Below the T_g , PLA is brittle (Chiu *et al.*, 2008; Henton *et al.*, 2005).

In the DSC endothermic process, the curve has high enthalpy because no crystalline structure is forming. However, an exothermic curve is obtained during cold crystallization above T_g . The exothermic curve of the DSC instrument is absent in this process because the ray refracts in exothermic activities. The quench cooling process involves heated PLA cooling down at different rates. This process cooling process does not form crystallite of the PLA such that the DSC curves are easily visible without refraction. The cooling rate may vary between 10, 5 or 1 °C/min. PLA, the crystallinity varies with cooling. In the crystallization process, the alpha crystalline is obtained at

temperatures between 130-140 °C, and the annealing starts at a lesser temperature. The crystal obtained during this cooling process diffracts the X-rays.

2.3.3(c) Degradation properties of polylactic acid

Degradation of PLA involves physical and chemical change depending on the relative environmental factors such as heat, light, moisture, biological activity and chemicals present. Degradation affects the properties of PLA because it involves the breaking of bonds. Degradation affects PLA properties and facilitates cracking, erosion, crazing, discolouration, delamination, or phase separation (Li *et al.*, 2017a). The internal changes include the scission of bonds, the transformation of chemicals, and new functional groups formation (Kiziltas *et al.*, 2016; Montes *et al.*, 2020).

Photo-degradation is the ability to absorb harmful parts of tropospheric solar radiation. This UV-B terrestrial radiation range 295-315 nm and UV-A radiation range 315-400 nm are responsible for photodegradation (photolysis, or initiated photo-oxidation). The visible spectra from sunlight (400 - 760 nm) increase polymeric degradation by causing heat. As an example, Infrared radiation (760-2500 nm) increases thermal oxidation (Yagi *et al.*, 2009). Many plastics usually absorb high-energy radiation from the spectrum's ultraviolet portion, which activates the electrons to higher reactivity, causing oxidation and cleavage (Ghasemi *et al.*, 2018). Photo-degradation reduces the molecular weight of PLA materials to form the C=C double bonds using the Norrish II mechanism (Singh *et al.*, 2018).

PLA thermal degradation process involves molecular reduction by heat. The process involves photo-degradation, thermo-oxidative and biodegradation. The active agent which accelerates the degradation process is the heat from sunlight (UV-light) and oxygen (Karamanlioglu *et al.*, 2017). The microbial process does not require high-

energy agents or radiation. The requirement is not higher than that from normal heat at ambient temperature. However, the rate of Initiation can be slow. A faster or moderate degradation can be obtained by creating or modifying the environmental factors.

In some cases, environmental high-energy is considered acceptable (Brebu, 2020; Zaaba and Jaafar, 2020). Overall the degradation process is acceptable and cheap. The polymer's degradation process can begin with separate (molecular scission) and reaction with one another, which changes the properties of the polymer. The chemical reactions are activated by heat, leading to physical and optical changes in the initially specified properties (Benoit *et al.*, 2017). The thermal degradation is usually accompanied by changes in the polymer's molecular weight distribution, including reduced embrittlement, ductility, colour, chalking, and cracking, a general reduction in its physical properties (Ohkita and Lee, 2006).

The oxo-biodegradation of polymers involves two steps biodegradation; Oxidation and photo-degradation (UV). The UV light degradation is used to degrade the end product. The oxidation process takes time for the heat to break down the chains in the bioplastic. Both steps reduce the molecular weight of the bioplastic to biodegrade (Shah *et al.*, 2008). The biodegradation process is one in which living organisms break down organic substances. This term is used in waste management, ecology, environmental remediation (bioremediation) of plastic materials, and determines their life span. Organic material is both aerobically and anaerobically degradable (Ghasemi *et al.*, 2018). Organic materials can also be converted to minerals, often called bio-mineralization. This process involves converting minerals (Shah *et al.*, 2008). Bioplastics are biodegradable aerobically in the wild but an-

aerobically in the sediments, landfills. However, the process is anaerobic and aerobically in soil and composts. Bioplastic is converted to water and carbon dioxide for aerobic biodegradation, while water, carbon dioxide, and methane are the by-products of anaerobic degradation (Phommachanh, 2013).

2.4 Chitosan

Chitosan can be obtained from fungi, yeast, and the exoskeleton of arthropods in the cell walls of fungi. The primary source of commercial chitosan is shrimp and crab, but chitosan can also be present in squid pens, tubeworms, lobsters, clams, krill, oysters, and fungi (Guan *et al.*, 2013). Chitosan molecular structure consists of molecules arranged in long and small units, like proteins. Chitosan is biodegradable, biocompatible, and nontoxic. It has been used in water treatment, cosmetics, biomedical applications, and agriculture.

Chitosan is a hard powder, white, an inelastic polysaccharide derived from various exoskeletons. Chitosan is the second most abundant polysaccharide after cellulose, and it is one of the most important natural polysaccharides. Structurally it consists of β (1 \rightarrow 4)-linked 2-acetamido-2-deoxy- β -D-glucose (N-acetyl glucosamine) (Younes and Rinaudo, 2015). Chitosan has several derivatives, including monoacetyl chitosan, chitosan, di-butyl chitosan, N-acetyl chitosan, chitosan acetate, etc. The chitosan's major derivative is chitosan, a linear polymer with α (1 \rightarrow 4) linked 2-amino-2-deoxy- β -D-glucopyranose. N-deacetylation obtains it at different degrees depending on the result of the deacetylation (Aranaz *et al.*, 2009).

2.4.1 Chitosan structure, production, and use

Chitosan is a polysaccharide with a nitrogen-containing functional group called an amine. It is usually synthesized chemically from N-acetyl-D-glucosamine (to be

precise, 2-(acetylamino)-2-deoxy-D-glucose). This unit forms a covalent β -(1 \rightarrow 4)-linkage in the glucose units like cellulose (Irvin *et al.*, 2019). Therefore, chitosan is often described as cellulose with hydroxyl and amine groups. The hydroxide functional group allows the formation of hydrogen bonding with adjacent polymers with hydrophilic nature. Chitosan is usually translucent, has high resilience, is pliable, and quite tough in its pure form. Chitosan is present in arthropods. However, it is often used in modified forms like chitosan in composite materials. Chitosan in the skeleton is combined with calcium carbonate, for example, in the shells of molluscs and crustaceans. Chitosan is often used to produce a much tougher and stronger composite. Chitosan-based composite material is described as harder and stiffer than pure chitosan and tougher with less brittle than pure calcium carbonate (Jana *et al.*, 2020). Pure chitosan is different from its composite form in its flexibility and, light especially those extracted from the beetle, which contains a large skeleton (Gilbert, 2009).

Chitosan is present in the wing scales of a butterfly. It is organized in stacks of gyroids with constructed photonic crystals that have several colours used by the butterfly communication and signalling for foraging and mating (Saranathan *et al.*, 2010). Chitosan is estimated annually to be produced second to cellulose. It is utilised for many types of research and cosmetics because of its non-toxic and biocompatibility properties. Recently, the use of chitosan in chemical industries has increased significantly (Olaiya *et al.*, 2020). It has been reported that it has potential application as chitosan with over 200 other derivatives (Kumar, 2000; Kumar *et al.*, 2015). Other applications of chitosan are in food processing, biocatalysis, biomedical, and wastewater treatment. Also, Chung *et al.* (2003) have reported that it has been used in commercial disinfectants due to chitosan derivatives' natural antibacterial and antifungal characteristics.