



**CHARACTERIZATION AND PROPERTIES OF LINEAR
LOW-DENSITY POLYETHYLENE / DATE SEEDS
(LLDPE/DS) BIOCOMPOSITES**

by

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TABLE OF CONTENTS

	PAGE
DECLARATION OF THESIS	i
TABLE OF CONTENTS	iii
LIST OF TABLES	vii
LIST OF FIGURES	ix
LIST OF ABBREVIATIONS	xv
LIST OF SYMBOLS	xvi
ABSTRAK	xvii
ABSTRACT	xviii
CHAPTER 1 : INTRODUCTION	1
1.1 Research Background	1
1.2 Problem Statement	6
1.3 Objectives	7
1.4 Research Scope	8
CHAPTER 2 : LITERATURE REVIEW	11
2.1 Bio-Polymer Composites	11
2.2 Natural Fibers	13
2.2.1 Chemical Composition of Natural Fibers	13
2.2.2 Fruit Seed as a fibers	15
2.2.3 Natural Fibers Properties	16
2.2.4 Date Seeds	22

2.2.5	Natural Fibers Modification	25
2.2.5.1	Chemical Methods	25
2.3	Linear Low- Density Polyethylene	31
2.4	Alkali Treatment	35
2.5	Acids Treatment	36
2.6	Electron beam irradiation (EBR)	38
2.7	Processing Methods	44
CHAPTER 3 : RESEARCH METHODOLOGY		47
3.1	Introduction	47
3.2	Materials	47
3.3	Sample Preparation	55
3.3.1	Date Seeds Preparation	55
3.3.2	Date Seeds Characterization	57
3.3.3	Composite Preparation	57
3.3.4	LLDPE/DS Composites Modification	59
3.3.4.1	Modification with Alkaline	59
3.3.4.2	Modification with Stearic Acid	59
3.3.4.3	Electron Beam Irradiation	60
3.4	Testing and Characterization	60
3.4.1	Fourier Transform Infrared Spectroscopy (FTIR)	61
3.4.2	Tensile Test	62
3.4.3	Flexural Tests	63
3.4.4	Impact test	64
3.4.5	Scanning Electron Microscopy (SEM)	66
3.4.6	Thermogravimetric Analysis (TGA)	66
3.4.7	Differential Scanning Calorimetry	67

3.4.8	Gel content test	67
3.5	Flow chart	69
CHAPTER 4 : RESULTS AND DISCUSSION		70
4.1	The Effects of Date Seeds Size and Content on the Properties of LLDPE/DS Composites	70
4.1.1	Tensile Properties	70
4.1.2	Fractured Surface Morphology	73
4.1.3	Flexural Properties	75
4.1.4	Impact Properties	77
4.1.5	Thermo-Gravimetric Analysis (TGA)	78
4.1.6	Differential Scanning Calorimetry (DSC)	80
4.1.7	Fourier Transform Infrared Spectroscopy (FTIR)	83
4.1.8	Gel Content Test	85
4.2	The Effects of Sodium Hydroxide (NaOH) on the Properties of LLDPE/DS Composites	88
4.2.1	Tensile Properties	88
4.2.2	Fractured Surface Morphology	91
4.2.3	Flexural Properties	93
4.2.4	Impact Properties	96
4.2.5	Thermo-Gravimetric Analysis (TGA)	98
4.2.6	Differential Scanning Calorimetry (DSC)	100
4.2.7	Fourier Transform Infrared Spectroscopy (FTIR)	103
4.2.8	Gel Content Test	105
4.3	The Effects of Stearic Acid (SA) on the Properties of LLDPE/DS Composites	106
4.3.1	Tensile Properties	106
4.3.2	Fractured Surface Morphology	109
4.3.3	Flexural Properties	112

4.3.4	Impact Properties	113
4.3.5	Thermogravimetric Analysis (TGA)	115
4.3.6	Differential Scanning Calorimetry (DSC)	118
4.3.7	FTIR	121
4.3.8	Gel Content Test	122
4.4	The effects of electron beam radiation on the Properties of LLDPE/DS Composites	124
4.4.1	Tensile Properties	124
4.4.2	Fractured Surface Morphology	129
4.4.3	Flexural Properties	134
4.4.4	Impact Properties	135
4.4.5	Thermo-Gravimetric Analysis (TGA)	137
4.4.6	Differential Scanning Calorimetry (DSC)	142
4.4.7	FTIR	146
4.4.8	Gel Content Test	152
CHAPTER 5 : CONCLUSIONS		157
5.1	Conclusions	157
5.2	Recommendations for Future Study	158
REFERENCES		161
LIST OF PUBLICATIONS		178

LIST OF TABLES

	PAGE
Table 2.1 Commercially major fiber sources (Staiger and Tucker, 2008)	14
Table 2.2 Chemical composition of the most common natural fibers (Hattallia et al., 2002; Hoareau et al., 2004; Marti-Ferrer et al., 2006)	15
Table 2.3 Physico-mechanical properties of natural fibers (Hattallia, et al., 2002, Hoareau et al., 2004)	17
Table 2.4 The equilibrium moisture content of natural fiber at 65% relative humidity and 21 °C temperature (Rowell, 2008)	19
Table 2.5 The typical properties of three main thermoplastic polymers (Kwon et al., 2012)	33
Table 3.1 Typical chemical composition of DS (Besbes et al., 2004)	49
Table 3.2 Typical properties of LLDPE (Maddah, 2016)	53
Table 4.1 Thermal degradation of LLDPE and LLDPE/DS composites at different DS size and loading	80
Table 4.2 Thermal properties of LLDPE and LLDPE/DS composites at different DS size and loading	83
Table 4.3 Gel content of LLDPE and LLDPE/DS composites at different DS size and loading	87
Table 4.4 Thermal degradation of untreated and treated LLDPE/DS composites at different NaOH concentration	100

Table 4.5	Thermal properties of untreated and treated LLDPE/DS composites at different NaOH concentration	103
Table 4.6	Gel content of untreated and treated LLDPE/DS composites at different NaOH concentration	106
Table 4.7	Thermal degradation of untreated and treated LLDPE/DS composites at different SA concentration.	118
Table 4.8	Thermal properties of untreated and treated LLDPE/DS composites at different SA concentration.	121
Table 4.9	Gel content of untreated and treated LLDPE/DS composites at different SA concentration	123
Table 4.10	Thermal degradation of treated LLDPE and treated LLDPE/DS composites at 50 and 200 kGy doses of EBR by using TMPTA	139
Table 4.11	Thermal degradation of treated LLDPE and treated LLDPE/DS composites at 50 and 200 kGy doses of EBR by using TPGDA	141
Table 4.12	Thermal properties of the treated LLDPE and treated LLDPE/DS composites at 50 and 200 kGy doses of EBR by using TMPTA	144
Table 4.13	Thermal properties of treated LLDPE and treated LLDPE/DS composites at 50 and 200 kGy doses of EBR by using TPGDA	146
Table 4.14	Gel content of treated LLDPE/DS composites at different EBR doses by using TMPTA	154
Table 4.15	Gel content of treated LLDPE/DS composites at different EBR dose using TPGDA	155

LIST OF FIGURES

	PAGE
Figure 2.1 The structure of a single fiber cell (Gassan et al., 2001).	20
Figure 2.2 Correlation between spiral angle and elastic modulus of a natural fiber (Gassan et al., 2001).	21
Figure 2.3 Date seeds (Stark et al,2004)	23
Figure 2.4 The polymerization process of ethylene to obtain polyethylene.	33
Figure 2.5 The chemical formula of HDPE, LDPE and LLDPE	34
Figure 3.1 (a) LLDPE, (b) DS, (c) NaOH and (d) $C_{18}H_{36}O_2$	48
Figure 3.2 The SEM micrographs of DS at ($\times 100$ and $\times 200$ magnification) for coarse and fine sizes	50
Figure 3.3 Thermal degradation of DS powder.	51
Figure 3.4 FTIR spectra of DS powder of fine size	53
Figure 3.5 High-speed grinder (Model: DF 20)	56
Figure 3.6 Sieving machine	56
Figure 3.7 Rotating twin screw extruder machine	58
Figure 3.8 Injection molding machine (BOY 22M)	58
Figure 3.9 FT-IR instrument (Perkin Elmer-2000)	61
Figure 3.10 Instron Universal Testing Machine	62
Figure 3.11 Tensile test specimen as per ASTM D638	63
Figure 3.12 Flexural test specimen as per ASTM D638-01.	64

Figure 3.13	Izod Impact Tester (Model HT8041B)	65
Figure 3.14	(a) Impact test specimen, and (b) Impact test as per ASTM D256-04.	65
Figure 3.15	Flow chart Process of LLDPE/DS Composites.	69
Figure 4.1	The values of tensile strength of LLDPE/DS composites at different DS size and loading.	71
Figure 4.2	The values of elongation at break of LLDPE/DS composites at different DS size and loading.	72
Figure 4.3	The values of Young's modulus of LLDPE/DS composites at different DS size and loading.	72
Figure 4.4	The SEM micrographs of LLDPE and LLDPE/DS composite at different DS size and loading ($\times 200$ and $\times 1000$ magnification)	74
Figure 4.5	The values of flexural strength of LLDPE/DS composites at different DS size and loading	76
Figure 4.6	The values of flexural modulus of LLDPE/DS composites at different DS size and loading.	76
Figure 4.7	The values of izod impact strength of LLDE/DS composites at different DS size and loading.	78
Figure 4.8	TGA thermogram of LLDPE and LLDPE/DS composites at different DS sizes and loadings	80
Figure 4.9	DSC melting thermograms of LLDPE and LLDPE/DS composites at different DS size and loading	82
Figure 4.10	DSC crystallization thermograms of LLDPE and LLDPE/DS composites at different DS size and loading	82

Figure 4.11	FTIR spectra of (a) LLDPE, and LLDPE/DS composites at (b) DS-FS 10%, (c) DS-MS 10%, (d) DS-CS 10%, (e) DS-FS 20%, (f) DS-MS 20%, (g) DS-CS 20%	85
Figure 4.12	The effect of NaOH on the tensile strength of LLDPE/DS composites at different NaOH concentration	89
Figure 4.13	The effect of NaOH on the elongation at break of LLDPE/DS composites at different NaOH concentration	90
Figure 4.14	The effect of NaOH on the Young Modulus of LLDPE/DS composites at different NaOH concentration.	90
Figure 4.15	The SEM micrographs of untreated LLDPE/DS composite and treated LLDPE/DS composite at different NaOH concentration ($\times 300$ and $\times 1000$ magnification)	92
Figure 4.16	The effect of NaOH on the flexural strength of LLDPE/DS composites at different NaOH concentration	95
Figure 4.17	The effect of NaOH on the flexural modulus of LLDPE/DS composites at different NaOH concentration	95
Figure 4.18	The effect of NaOH on the impact strength of LLDPE/DS composites at different NaOH concentration	97
Figure 4.19	The effect of NaOH on the thermal stability of LLDPE/DS composites at different NaOH concentration	100
Figure 4.20	DSC melting thermograms of untreated and treated LLDPE/DS composites at different NaOH concentration	102
Figure 4.21	DSC crystallization thermograms of untreated and treated LLDPE/DS composites at different NaOH concentration	102
Figure 4.22	FTIR spectra of (a) untreated LLDPE/DS composite and treated LDPE/DS composite at (b) 3%, (c) 6%, and (d) 9% NaOH concentration	104

Figure 4.23	The effect of SA concentration on the tensile strength of LLDPE/DS composites	108
Figure 4.24	The effect of SA concentration on the elongation at break of LLDPE/DS composites	108
Figure 4.25	The effect of SA concentration on the Yong Modulus of LLDPE/DS composites	109
Figure 4.26	The SEM micrographs of untreated LLDPE/DS composite and treated LLDPE/DS composite at different SA concentration ($\times 300$ and $\times 1000$ magnification)	111
Figure 4.27	The effect of SA on the flexural strength of LLDPE/DS composites at different SA concentration	113
Figure 4.28	The effect of SA on the impact strength of LLDPE/DS composites at different SA concentration	115
Figure 4.29	The effect of SA treatment on the thermal stability of LLDPE/DS composites at different SA concentration.	117
Figure 4.30	DSC melting thermograms of untreated and treated LLDPE/DS composites at different SA concentration	119
Figure 4.31	DSC crystallization thermograms of untreated and treated LLDPE/DS composites at different SA concentration	120
Figure 4.32	FTIR spectra of treated LLDPE/DS composite at (a) 3%, (b) 6%, and (c) 9% SA concentration.	122
Figure 4.33	The effect of EBR on the tensile strength of LLDPE/DS composites	128
Figure 4.34	The effect of EBR on the elongation at break of LLDPE/DS composites	128
Figure 4.35	The effect of EBR on the Young modulus of LLDPE/DS composites	129

Figure 4.36	SEM micrographs of LLDPE/DS composite using TMPTA as initiators and LLDPE control at 50 and 200 kGy of EBR ($\times 200$ and $\times 1000$ magnification)	131
Figure 4.37	SEM micrographs of LLDPE control and LLDPE/DS composite using TPGDA at 50 and 200 kGy of EBR ($\times 300$ and $\times 1000$ magnification)	133
Figure 4.38	The effect of EBR on the flexural strength of LLDPE/DS composites	135
Figure 4.39	The effect of EBR on the impact strength of LLDPE/DS composites at different EBR doses by using TMPTA or TPGDA as initiators	136
Figure 4.40	Thermal degradation of treated LLDPE and treated LLDPE/DS composites at 50 and 200 kGy doses of EBR by using TMPTA	138
Figure 4.41	Thermal degradation of treated LLDPE and treated LLDPE/DS composites at 50 and 200 kGy doses of EBR by using TPGDA	141
Figure 4.42	DSC melting thermograms of the treated LLDPE/DS composites at 50 and 200 kGy doses of EBR by using TMPTA	143
Figure 4.43	DSC crystallization thermograms of treated LLDPE and treated LLDPE/DS composites at 50 and 200 kGy doses of EBR by using TMPTA	144
Figure 4.44	DSC melting thermograms of treated LLDPE and treated LLDPE/DS composites at 50 and 200 kGy doses of EBR by using TPGDA	145

Figure 4.45	DSC crystallization thermograms of treated LLDPE and treated LLDPE/DS composites at 50 and 200 kGy doses of EBR by using TPGDA	145
Figure 4.46	FTIR spectra of EBR treated LLDPE/DS composite with TMPTA at (b) 50 kGy, (d) 200 kGy, and LLDPE control with TMPTA at (a) 50 kGy, and (c) 200 kGy	149
Figure 4.47	FTIR spectra of EBR treated LLDPE/DS composite with TPGDA at (b) 50 kGy, (d) 200 kGy, and LLDPE control with TPGDA at (a) 50 kGy, and (c) 200 kGy	152

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
NaOH	Sodium Hydroxide
DS	Date Seeds
SA	Steric Acid
DSC	Differential Scanning Calorimetry
EBR	Electron Beam radiation
TS	Tensile Strength
FTIR	Fourier Transform Infrared Spectrometer
LLDPE	Linear Low Density Polyethylene
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analysis
TMPTA	Trimethylolpropane Triacrylate
TPGDA	Tripropylene Glycol Diacrylate

LIST OF SYMBOLS

H_m	Melting enthalpy
H°	Heat of fusion
H^*	Heat of fusion for semicrystalline
phr	Part per hundred resin
T-5%	Temperature at 5% degradation
T-30%	Temperature at 30% degradation
T_c	Crystalline temperature
T_m	Melting temperature
X_c	Degree crystallinity

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Pencirian dan Sifat-Sifat Biokomposit Polietilena Linear Berketumpatan Rendah / Biji kurma (LLDPE/DS)

ABSTRAK

Potensi biji kurma (DS) sebagai pengisi baru biomas dikaji. DS telah dikumpulkan, dibasuh dan dikisar. Ini diikuti oleh pengasingan DS kepada tiga kategori berlainan berdasarkan partikel saiz iaitu saiz kasar (antara 700-1000 μm), saiz sederhana (antara 250-500 μm) dan saiz halus (antara 1-125 μm). Selepas itu, serbuk DS dicampurkan dengan polietilena berketumpatan rendah linear (LLDPE), sebelum dimasukkan ke dalam ekstruder skru berkembar dan seterusnya ke dalam mesin pengacuan suntikan untuk menghasilkan biokomposit LLDPE/DS. Analisis seperti ujian tensil, lenturan, hentaman, thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FTIR), dan mikroskop penskanan elektron (SEM) telah diuji. Pada objektif pertama, biokomposit LLDPE/DS telah dihasilkan dengan nisbah komposisi 0, 5, 10, 15 dan 20 %. Keputusan kajian menunjukkan bahawa dengan pertambahan jumlah DS sehingga 10 wt%, terutamanya DS bersaiz halus telah terhasilnya peningkatan dalam nilai kekuatan tensil, lenturan dan kestabilan termal pada biokomposit LLDPE/DS. Biokomposit LLDPE/DS pada kandungan DS bersaiz halus juga telah menunjukkan nilai kandungan gel yang tinggi berbanding yang lain. Pada objektif seterusnya, tiga konsentrasi yang berlainan (3, 6 dan 9 %) sodium hidroksida (NaOH) telah digunakan sebagai rawatan berkali pada DS. Keputusan menunjukkan bahawa dengan rawatan pada 3 % NaOH telah meningkatkan kekuatan tensil, kekuatan lenturan dan hentaman biokomposit LLDPE/DS. Dalam terma kristalografi dan kestabilan termal, nilai komposit yang terawat adalah lebih baik berbanding dengan komposit tidak dirawat. Tiga nisbah (iaitu 3, 6, 9 %) asid stearik ($\text{C}_{18}\text{H}_{36}\text{O}_2$) sebagai rawatan asid pada DS telah dikaji pada objektif keempat. Ianya dapat dilihat bahawa, 3% rawatan asid stearik pada DS telah menunjukkan peningkatan pada kesemua nilai mekanikal dan kestabilan termal biokomposit LLDPE/DS. Sementara itu pada objektif kelima, penyaluran radiasi sinar elektron (EBR) telah didedahkan pada biokomposit LLDPE/DS untuk tujuan sambung silang, dengan menggunakan pemecut radiasi sinar elektron berjumlah 1.5 MeV dalam julat dos 0-200 kGy. Trimethylolpropane triacrylate (TMPTA) dan tripropylene glycol diacrylate (TPGDA) telah digunakan sebagai promoter silang. Hasilnya adalah komposit yang ditambah dengan TMPTA menunjukkan sifat tensil yang lebih tinggi, lenturan, hentaman, kandungan gel dan kestabilan termal yang lebih baik berbanding dengan komposit yang ditambah dengan TPGDA. Dalam masa yang sama, biokomposit LLDPE/DS dengan kehadiran TMPTA yang terdedah pada 150 kGy radiasi sinar elektron telah menghasilkan penyerapan optimum dan menunjukkan sifat-sifat mekanikal dan fizikal yang optimum.

Characterization and Properties of Linear Low-Density Polyethylene / Date Seeds (LLDPE/DS) Biocomposites

ABSTRACT

The potential of Date Seeds (DS) as a new biomass filler was studied. DS were collected, washed and grinded. This followed up by sorting the DS into three different categories based on their particle size, i.e. coarse size (between 700-1000 μm), medium size (between 250-500 μm) and fine size (between 1-125 μm). After preparing of DS powder, DS was mixed with linear low-density polyethylene (LLDPE), prior to being fed into a twin-screw extruder and subsequently into an injection moulding machine to produce LLDPE/DS biocomposites. The analyses such as tensile test, flexural, impact, thermal gravimetry analysis (TGA), differential scanning calorimetry (DSC), fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) were conducted. At second objectives, LLDPE/DS biocomposites were produced with composition ratios 0, 5, 10, 15 and 20 wt%. The results showed that the increase of DS loading up to 10 wt%, particularly DS fine size resulted in an increment of the value of tensile, flexural strength and thermal stability of LLDPE/DS biocomposites. The LLDPE/DS biocomposites at high DS content, particularly DS fine size exhibited relatively higher gel content compared to others. At next objectives, three different concentrations (3, 6 and 9 %) of sodium hydroxides (NaOH) were used as alkali treatment for DS. Result indicated that with the 3% NaOH treatment on DS improved the tensile strength, flexural strength and impact of the LLDPE/DS biocomposites significantly. In terms of crystallinity and thermal stability, the treated composites were superior compared with those of the untreated composites. The incorporation of three concentration of stearic acid ($\text{C}_{18}\text{H}_{36}\text{O}_2$) (3, 6, 9 %) different as acid treatment on DS was carried in fourth objectives. It can be seen that, 3% treatment with steric acid (SA) on DS shows improvement of all mechanical value and thermal stability of LLDPE/DS biocomposites. Meanwhile at fifth objectives, the electron beam radiation (EBR) was applied on the composites for crosslinking purposes, using a 1.5 MeV electron beam accelerator within the dosage range of 0–200 kGy. Trimethylolpropane triacrylate (TMPTA) and tripropylene glycol diacrylate (TPGDA) were used as the crosslink promoters. The results showed that the composites added with TMPTA showed higher tensile properties, flexural, impact, gel content and thermal stability compared with composites added with TPGDA. In addition, the LLDPE/DS biocomposites with TMPTA that exposed at 150 kGy improved an optimum value of mechanical and physical properties.

CHAPTER 1 : INTRODUCTION

1.1 Research Background

The interest to incorporate natural fibre has generated huge interest in recent time due to the quest for materials with high durability, biodegradable and has mechanical stability. Especially the demand for improving the performance of materials, such as biodegradability, has led to extensive research and development of new and improved materials, such as biopolymer composite materials, because natural fibre along is highly hydrophilic which is easily destroyed by the environment humidity likewise, the polymer along is hydrophobic. Therefore bringing these such components will yield biodegradable and yet mechanically stable composite. In recent years, natural resources seem to be the outstanding material due to abundance and has capable of replacing the non-renewable and high cost synthetic fibers. Natural fibers such as oil palm, banana, sisal, jute, and coir have been utilized as a reinforced composite for advanced applications. Among different types of fibers, date seed has been limited explored over the past several years, several researchers have proposed incorporating date into polymer and among them Nurazzi et al., 2017 and Wegst et al., 2015. Date seed can be obtained from date fruit. Moreover, a big amount of date fruit is produced in the Gulf region, which generates a significant amount of seed waste. Date seed composites have a bright future due to its renewability and eco-friendly. Hence this work is presenting reinforces of linear low-density polyethylene (LLDPE) composites with date seed powder (DS).

The need to develop biomaterials prepared and mixed with natural fibers is increasing worldwide, especially the material with integrity to be used in various application. Due to natural large variation in properties under different conditions, it becomes a great challenge in using it as a plastic reinforcement. The properties of bio-composites are influenced by different variables such as, the type of fibers, source of fibers, preparation methods, and modification of fiber. Recently there has been a great interest in preparation of bio-composites comprising of natural fillers reinforced with polymers for industrial application (Ahmad et al., 2015).

With their many preferred properties, composites have been used in a wide range of applications in aerospace, electronics, and bio-medical industries, to name just a few. A composite has wide range of properties, some of the properties are; Low density compared to various metals, high strength and stiffness, good impact resistance and toughness, high damping capacity and corrosion resistance (Joshi & Chatterjee, 2016).

Generally, the date seeds are hard natural materials which are waste product in the production of pitted dates, date syrup and date confectionery from date fruit. Due to the hardness, the DS expected to have slow changes in times which will improve the aging. The seeds may also be used as food for ruminant, poultry birds and vegetable oil source. Generally, there is no exact use of DS but sometimes they are used as an organic fertilizer of the soil and/or as livestock feed (Alsewailem and Binkhder, 2010). Normally, DS comprise approximately 78% carbohydrates, 5% moisture, 1.5% ash, 10% oil and 5.5% protein, these compositions are all eco friendly (Andrea et al, 2017). The use of natural fibers in polymer composites serves to improve the toughness and strength of the plastic. Fibers sourced cellulosic materials such kenaf, dates are

considered to be of relatively higher strength, lower density, cheaper, more abundant and renewable. Moreover, the date seed (DS) have been utilised in many different matrix and especially its powder after grinding might be used as natural filler in thermoplastics and DS oil content could be a natural lubricant and improves the mixing and molding process. Earliest study on using DS flour as natural filler for production showed that, in comparison with flax fiber and pistachio shell flour, It was found that DS filler had higher melt flow index compared to flax fiber and shell flour, (Ghazanfari et al., 2005). With high disposal of DS particularly in Middle East countries with no specific use for them, it seems reasonable idea to study the DS powder as natural filler for thermoplastic-based composite.

Although polyethylene has been frequently different applications packaging but unfortunately is creating more environmental issues especially in the agricultural sectors. The area such packaging waste has caused environmental concerns. The use of mulch films in agricultural sector, similarly, gives adverse environmental impacts with a high energy consumption required for the removal and disposal of their waste (Haider et al., 2019). This conventional plastic is a nondegradable plastic and its disposal in the natural environment can cause hazardous impact on the environment (Pavani & Rajeswari, 2014). Khabbaz and Albertsson (2001) reported that polyethylene has a very slow degradation rate of less than 0.5% in 100 years. The rate increases to 1%, if it is exposed to sunlight for 2 years.

The combination of natural fiber with polymer will introduced new composites, the composite class of material that seems to have a good potential in the future as a substitute for plastic based material in several applications. The biodegradability and

mechanical strength provide by most natural fibers make promising reinforcing materials particularly in polymer composites applications. Thus, the incorporation of the date seed in polymer, particularly thermoplastics polymer will promote available of natural material base polymer composite with all needed properties, due to natural and biodegradable fiber, the material has shown the ability to break down easily by biological means and disappear into the environment without any harm. The biodegradable material in polymer blends will help to break up the polymer into small fragments when exposed to microorganisms gradually will change the entire composite biocompatibility with the soil(Khalil et al., 2017, Mendes et al., 2016).

Though the biopolymer composites (polymer / natural fibers) are a material with several advantages and benefits compared to polymer based product such as plastic bags such today, biopolymer composites present some challenges and room for improvement. The combination of a hydrophilic (natural fiber) with hydrophobic (polymer) materials gives different characteristics, which in turn cause issues in the compatibilization process of this composite (Faruk et al., 2012). However, the advantage comes with some difficulties because issue of compatibilization between polar natural fibers and non-polar polymer matrix causes non-uniform dispersion of natural fiber as well as poor interfacial adhesion between natural fiber and polymer matrix (Yusoff et al., 2016). Therefore need careful processing. The poor microbial resistance, which lead to high moisture absorption, relatively inconsistency in length and diameter, and poor thermal stability of natural fiber along with the weak interface between natural fiber and polymer matrix can effect negatively on the properties, particularly the mechanical properties of the composite, which is considered as

ingrained problem in biopolymer composites manufacturing (Ferrero et al., 2017, Sanjay et al., 2018).

To overcome the low interfacial properties between natural fiber and polymer, the chemical modifications of fiber is one of the process used to optimize the interface of fibers. Chemicals can activate the hydroxyl groups of the fiber and also can produce other active site that can crosslink with the polymer matrix. Generally, coupling agents are available and in chemical form which can be used for the treatment of polymer composites. Normally, it contains two functions, the first function is to interlock with functional groups of the polymer matrix while the second function is to interlock with hydroxyl groups of cellulose (Yahaya et al., 2015, Zivkovic et al., 2016). Mercerization or alkaline treatment is one of the chemicals that used widely in chemical modification of natural fibers to reinforce polymer matrix, particularly thermoplastics. The chemical treatment such as alkaline which are considered chemical modification bring disruption of hydrogen bonding in the network structure, thus increasing roughness of the fiber surface, this improve compatibilities. The alkaline treatment can remove a certain amount of lignin addition to the oil and wax covering the exterior surface of the fiber cell wall (Orue et al., 2016). Furthermore, the presence of alkaline chemical, such as sodium hydroxide (NaOH) in natural fiber can improve the bonding between the natural fibre and the polymer (Manalo et al., 2015). Other chemical modification, such as acetylation, Benzoylation, cyanoethylation, peroxide treatments, graft copolymerization (methylmethacrylate, acrylamide, and acrylonitrile), Permanganate treatment, Isocyanate treatment as well as several coupling agents (silane, isocyanate and titanate based compounds), have been considered extensively and reviewed by numerous researchers (Wróbel-Kwiatkowska et al., 2017).

1.2 Problem Statement

The fabrication of polymer composites from polymer matrix and conventional filler or fiber has spread extensively in polymer manufacturing due to the improvement that accrued on the overall properties of the polymer composites as compared with virgin polymers. However, polymer composites from traditional fillers still have disadvantages in terms of the environment issues especially due to the hydrophilic nature of the natural material, it absorb moisture which quickly affect the mechanical strength in outdoor application .

The combination of different natural fibers found to give better physical and mechanical properties than carbon and glass fibres. Date seeds are usually discarded as materials with no specific use or value. Furthermore, these presumably designated waste materials, i.e., date seeds, comprise significant ingredients such as minerals (considerably rich in potassium), oils (up to 10%), and fibers (46.4%), which might be used for specific purposes, such as polymer composites manufacturing.

Nevertheless, several limitations must be overcome in order to exploit the full potential of date seeds as natural fillers. The direct introduction of hydrophilic fillers like most of natural fibers into hydrophobic polymer matrix like thermoplastics mostly caused unwanted agglomerations of filler inside polymer matrix, which in turn lead to the deterioration in the properties, particularly mechanical properties of the resultant composites.