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

by

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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	TrimethylolpropaneTriacrylate
TPGDA	TripropyleneGylcol Diacrylate

LIST OF SYMBOLS

H_m	Melting enthalpy
H^o	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
Tc	Crystalline temperature
Tm	Melting temperature
Xc	Degree crystallinity

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 beralkali 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 ($C_{18}H_{36}O_2$) 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, particularity 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 ($C_{18}H_{36}O_2$) (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 incooperate natural fibre has generate huge interest in rcent time due quest for materials with high durability, biodegrable 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 firbre along is highly hydrophillics which easily destroyed by the envirement humidity likewise, the polymer along is hydrophobic. Therefore bring these such components will yield biodegrable and yet mechanically stable composoite. 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 incooperating 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 compostions 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 sead (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.

Althiugh polyethylene has been frequently different applications packaging but unfortunately is creating more envirmental issues espescially 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 biodegrabilty 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 compositite 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 carefull processing. The poor microbial resistance, which lead to hgh 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 avaibale 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 considred 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 expecially 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.