Effects of Date Seeds Size and Loading on Properties of Linear Low-Density Polyethylene/Date Seeds Powder Composites

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Abstract. In this work, the influences of different date seeds (DS) size, fine size (125 - 250 μm), medium size (250 - 500 μm) and coarse size (500, 1000 μm) and different DS content (5, 10, 15, 20 wt%) on the tensile properties of linear low density polyethylene / date seeds (LLDPE/DS) composites were evaluated. The extrusion and injection molding process were used respectively to form LLDPE/DS composites. Results show that the addition of DS up to 10 wt%, particularly DS fine size has increased the tensile strength (TS) of LLDPE/DS composites. However, high DS content, particularly DS coarse size decreased the TS of the composites. The percentage of elongation at break (Eb) decreased while the modulus increased gradually as DS content increased in LLDPE/DS composites, which made the composite stiffer and less flexible. The SEM shows clearly the good distribution of DS fine size and the agglomeration of DS coarse size.

1. Introduction
Generally, the history using cellulose fiber with plastic to form bio composite started in 1908, later extending to melamine and urea and reaching commodity status with glass fiber / plastics composites [1,2]. In the last decade, the bio plastic composites have been utilized in several applications [3-9]. Biopolymer composites, started to improve novel polymer-based composites that one day could revolutionize the automotive industry. Aims to obtain high-performance biopolymer composites that might reduce the car structures weight. The lightweight of the biopolymer composite will subsequently increase the efficiency of device products such as airplanes, cars, etc.
Polyethylene (PE) is the cheapest and highest production share of any thermoplastic type, representing about 29% of the plastic production in the world [10]. PE is produced through the polymerization of ethylene (C2H4) that obtains macromolecules containing of a repeating monomer unit (CH2-CH2). Linear low-density polyethylene (LLDPE) is the most affordable variant of PE that has poor mechanical properties and high ductility at room temperature among all semi-crystalline polymers [10]. Gu and Raj et al studied the mechanical properties of LLDPE / aspen fibers bio-composites [11].

In a recent research, Mijiyawa et al. studied the thermal degradation of LLDPE/birch but did not analyze the resulting mechanical damage [12]. Date seeds (DS) are by-products of some date processing industries. 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 [13]. Normally, DS comprise approximately 78% carbohydrates, 5% moisture, 1.5% ash, 10% oil and 5.5% protein [14]. The DS 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, DS filler had higher melt flow index compared to flax fiber and shell flour, [15]. 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.

Therefore, the main objective of this work is to investigate the effects of different date seeds powder size and loading on the tensile properties of linear low density polyethylene / date seeds powder (LLDPE/DS) composites.

2. Experimental

2.1. Materials

LLDPE matrix with density 0.920 g cm\(^{-3}\) and melt flow index 1.00 g 10 min\(^{-1}\) was used in this work. It was purchased from PT. Lotte Chemical Titan Nusantara, Banten, Indonesia. The date seeds were purchased from Syarikat Abdul Ghaffar sdn. Bhd., Penang, Malaysia.

2.2. Preparation of LLDPE/DS composites

First, DS were ground and sieved using Crasher Model RT34 and lab sieves respectively. After grinding and sieving, DS powder was dried using vacuum oven at 60°C for 24 h. Dried DS along with LLDPE pellets was mixed and introduced into a twin-screw extruder feeder model JSW-100 tonne with 60 rpm screw speed The extruder barrel temperature was 160°C while the die temperature was 165°C.

The Amount of the feed was fixed at 1,000 g/h. The extrudate was cooled in a water bath to room temperature and pelletized using pelletizer. Pellets were then vacuum dried at 60°C for 8 hours under.

This process was carried out for four different DS loading (5, 10, 15 and 20 wt. %) and three different DS sizes, fine size (125 - 250 μm), medium size (250 - 500 μm) and coarse size (500 - 1000 μm).

2.3. Injection molding

According to (ASTM D638), standard tensile dumbbells were prepared using the Battenfell Injection Moulding Machine with a temperature profile of 160, 165, 170 and 175°C from feed to exit die zone respectively.

2.4. Tensile properties

According to ASTM D638, the tensile test for LLDPE/DS composites was carried out using universal tensile testing machine, Instron Machine model 5569. The test on dumbbell shaped specimens of 4mm thickness was performed at a cross-head shape of 50mm/min at 23 ± 2°C. Tensile strength, elongation at break and Young’s modulus were reported and five specimens were used and take the average values of the results.
2.5. *Scanning electron microscopy*

The Tensile fracture surface of LLDPE/DS composites was analyzed using SEM (JSM-6400, JEOL). All samples were gold-coated to prevent the electron charging effect during test.

3. Results and Discussion

3.1. Tensile properties

The tensile strength (Ts), elongation at break (Eb), Young’s modulus variations of LLDPE /DS composites at different DS size and loading are shown in Figure 1 a, b and c respectively.

It can be clearly observed that the addition of DS up to 10 wt%, particularly DS fine size has increased the tensile strength (TS) of LLDPE/DS composites. This could be due to the synergism effect, which means the interaction between DS filler and LLDPE matrix has exceeded their maximum properties [16, 17]. The increasing of DS content into LLDPE has effected negatively on the tensile strength (TS) of the composites. The TS reduction after 10 wt% of DS, particularly for DS coarser size was due to aggregation phenomena of DS in LLDPE/DS composites, which in turn increased the difficulty of the stress transmission from LLDPE matrix to DS filler [18].

The values of the elongation at break (Eb) have decreased as DS content increased in LLDPE/DS composites causing reduce the chains mobility inside the composite, which in turn decreased the flexibility of the composite. This made the composite harder and stiffer [18]. In conjunction with Eb, the value of modulus increased linearly with increasing of DS content in LLDPE/DS composites. This might be due to the increasing of the adhesion bonding between DS, particularly DS fine size and LLDPE matrix which made the composites stiffer [19].

In general, the fine size of DS showed better tensile properties than DS coarse size at same loading in the composite. This was due to the good dispersion of DS fine size in LLDPE matrix that improved matrix/fiber bonding. This matter explained clearly in SEM micrographs of tensile fracture surface of the composites.
3.2. Scanning electron microscopy
The scanning electron microscopy (SEM) micrographs of tensile fracture surface of LLDPE/DS composite at 10 wt.% DS fine size, 10 wt.% DS coarse size, 20 wt.% DS fine size and 20 wt.% DS coarse size are shown in figure 2a, b, c and d respectively. Results show that the low DS content (10 wt.% DS), particularly DS fine size have numerous tearing lines on the tensile fracture surface indicating that the sample need more energy to break the matrix (Figure 2a). This phenomenon attributed to the high surface area of the date seeds that strongly bonded with LLDPE matrix [17]. By contrast, the high DS content (20 wt.% DS), particularly DS coarse size show DS agglomeration and rough surface causing breakage and pull out of DS particles, which in turn reduce the stress transition from LLDPE matrix to DS filler. Thus, the tensile strength value of high DS content has decreased [20, 21].
4. Conclusion
According to the results of this work, it can be concluded that the fine size of date seeds, particularly at DS 10 wt% exhibited better properties than DS coarse size and other DS content in LLDPE/DS composites due to the high DS distribution in LLDP matrix. However, the high DS content reduced the flexibility and made the composites harder and stiffer.

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