Effects of Sodium Hydroxide Treatment on LLDPE/DS Composites: Tensile Properties and Morphology

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Abstract. In this research, the effect of different sodium hydroxide (NaOH) concentration (3, 6 and 9 wt.%) on the tensile properties of linear low density polyethylene / date seeds (LLDPE/DS) composites were investigated. The size of DS particles was measured at (125 - 250 μm) and the ratio of LLDPE over DS was fixed at 90/10 wt.%. The samples were prepared using extrusion process (screw speed at 60 rpm and barrel and die temperature at 160°C and 165°C respectively) followed by injection moulding process (from feed to exit die zone temperature at 160, 165, 170 and 175°C respectively). Results suggest that the addition of NaOH particularly 3 wt% has improved the tensile strength. Additionally, the elongation at break has improved as well. However, the high concentration of NaOH, particularly 9 wt.% effects negatively on these properties. In contrast, the Modulus shows different trend, which increased as NaOH concentration increased in the composites. The SEM section shows the improvement on DS surface as low NaOH concentration used (3 wt.%) and deterioration on the DS surface as high NaOH concentration used (9 wt.%).
1. Introduction
Generally, polymer composites consist of filler such as fiber as reinforcing materials and polymer as matrix. There are several types of plastic polymers in the literature that were used to form polymer composites, such as low, linear and high density polyethylene, polyether ether ketone, polypropylene and other [1,2]. Traditional fiber, such as glass fiber, silica, carbon, metal oxide, and many others were used extensively as reinforcing components in polymer composites [3-6]. However, the using of natural fiber as reinforcing materials in plastic composites has increased rapidly in the last decade due to the advantages of natural fiber over traditional fiber. These advantages include low cost, low density, recyclability and biodegradability, which in turn have attracted the attention of researchers and engineers and make natural fibers potential replacement for traditional fibers in several applications such as automobile, construction, plastics and packaging [7-9].
However, the low interfacial characteristics between natural fiber and polymer matrix could effect negatively on the properties, particularly the mechanical properties of the polymer composites due to the hydrophilic behavior of natural fibers. Therefore, the chemical modification could be the suitable technique to improve the interface of natural fibers. Several researches were conducted to evaluate the effect of different type of chemical modification of natural fiber on the properties of polymer composites [10,11]. Chemical modification using alkaline is one of the most treatment methods used in thermoplastic, thermoset and elastomer. The alkaline modification improves the properties of polymer itself [12]. Additionally, alkaline modification increases the surface roughness of the fiber due to the disruption of hydrogen bonding in the network structure. Moreover, this type of treatment can remove a part of wax, lignin and oils covering the external surface of the fiber cell wall, depolymerizes cellulose and exposes the short length crystallites [13]. Middle East countries are well known for palm trees and largest producers of date fruit in the world [14]. The nature of Middle East people is consumes date fruit daily and date pits are usually discarded as waste with no use or value. However, this type of waste material, date pits comprise significant constituents such as minerals (rich in potassium), oils (bout 10%) and fibers (up to 46.4%) that may be used for specific purposes. There are limited researches in the literature that studied the potential of date pits as fillers for thermoplastics. Ghazanfari et al. have evaluated the effect of date pits flour with HDPE. Their results showed that date pits have decreased the melt flow index (MFI), and improved the thermal conductivity of the HDPE/date pits composites [15].
In our present research, we have investigated the effect of sodium hydroxide (NaOH) as alkali treatment on the tensile properties of linear low density polyethylene / date seeds powder (LLDPE/DS) composites.

2. Experimental

2.1. Materials
Polymer matrix, LLDPE (density 0.920 g cm\(^{-3}\), melt flow index 1.00 g 10 min\(^{-1}\)) was purchased from PT. Lotte Chemical Titan Nusantara, Banten, Indonesia. The date seeds were obtained from Syarikat Abdul Ghaffar sdn. Bhd., Penang, Malaysia. The Sodium Hydroxide (NaOH) was purchased from Anchor Chemical Co. (M) LTD.

2.2. Fabrication and treatment of the composites
DS were milled using Crasher (RT34) and then sieved using lab sieves to obtain (125 - 250 \(\mu m\)) DS size. After sieving, chemical treatment was applied to sieved DS using sodium hydroxide (NaOH). The DS were treated in 3%, 6% and 9% of NaOH for 24 hours separately. Treated DS powder was dried using vacuum oven at 60°C for 24 hours. Dried DS was mixed with LLDPE and introduced into feeder of twin-screw extruder (JSW-100 tonne) with ratio 90/10 wt.% of LLDPE/DS. The screw speed was 60 rpm and the extruder barrel and die temperature were 160°C and 165°C respectively. The feed amount of the mixture 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 dried using vacuum oven at 60°C for 8 hours.
2.3. Injection molding
The standard tensile dumbbells were prepared using the Battenfell Injection Moulding Machine according to ASTM D638. Different temperature profile was used in this process, 160, 165, 170 and 175°C from feed to exit die zone respectively.

2.4. Tensile properties
The tensile test was conducted for LLDPE/DS composites using Instron Machine (model 5569) according to ASTM D638. The test on dumbbell shaped specimens of 4mm thickness was carried out at a cross-head shape of 50mm/min at 23 ± 2°C. Results such as tensile strength, elongation at break and Young’s modulus were recorded. Five samples were used for each batch and take the average values of the results.

2.5. Scanning electron microscopy
The Tensile fracture surface of treated LLDPE/DS composites was examined using SEM device model JSM-6400, JEOL. All specimens were gold-coated to avoid the effect of electron charging during analysis.

3. Results and Discussion

3.1. Tensile properties
The effect of different NaOH concentration on the tensile strength, elongation at break and young modulus properties of LLDPE/DS composites are shown in Figure 1 a, b and c respectively. The 3 wt.% of NaOH treatment shows highest tensile strength and elongation at break (Figure 1a and b). This is due to the improvement on the fiber surface in presence of NaOH. Jacob et al. evaluated the influence of different NaOH concentration (0.5, 1, 2, 4 and 10%) on the sisal fiber-reinforced composites. Their results concluded that the maximum tensile strength value was 4% of NaOH [16]. Other researcher, such as Mishra et al. found that the 5% of NaOH treated natural fiber-reinforced polyester composite had better tensile strength than 10% NaOH treated composites. This is because at high NaOH concentration, excess delignification of natural fiber occurs which in turn lead to damage of fiber structure [17]. Thus, the tensile strength of LLDPE/DS composite decreased gradually after 3 wt.% of NaOH concentration. However, The high NaOH concentration such as 9 wt.% shows higher modulus than other NaOH concentration. This could be due to the high disruption of hydrogen bonding in the network structure causing increase in surface roughness of the fiber. The increasing of fiber surface roughness can increase the interaction between fiber and polymer matrix, which in turn make composite stiffer and more rigid. Therefore, modulus value increased.

![Graph showing tensile strength vs NaOH concentration](image-url)
Figure 1. The effect of NaOH on the (a) tensile strength, (b) elongation at break and (c) Modulus of LLDPE/DS composites.

3.2. Scanning electron microscopy
The Scanning electron micrographs of the tensile fractured surfaces of treated LLDPE/DS composites at 3 wt.%, 6 wt.% and 9 wt.% are taken to evaluate the fracture behavior and the interaction between date seeds filler and LLDPE matrix (Figure 2 a, b, an c respectively). The SEM micrograph of treated LLDPE/DS composite with low NaOH concentration (3 wt.%) shows relatively smooth DS surface and strong interfacial bonding between DS and LLDPE matrix [18]. However, the high NaOH concentration, particularly (9 wt.%) shows rough surface (Figure 1 c) indicating that the high NaOH concentration, excess delignification of natural fiber occurs which in turn lead to damage of fiber structure [19,20].
Figure 2. The tensile fracture surface of treated LLDPE/DS composite at (a) 3 wt.% NaOH, (b) 6 wt.% NaOH and (c) 9 wt.% NaOH.

4. Conclusion
In conclusion, fabricating polymer (low linear density polyethylene) with natural fiber such as Date seeds could give a new opportunity to the manufacture of green plastic products. However, the mechanical properties of this composite were relatively poor. Therefore, the chemical modification using NaOH was necessary to improve the properties. The using of low concentration (3 wt.%) of NaOH gave better tensile properties compared with control and other NaOH concentration.

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