Mechanical and Physical Properties of Kenaf-reinforced Poly(lactic acid) Plasticized with Epoxidized Jatropha Oil

Siti Hasnah Kamarudin,[a,b,]* Luqman Chuah Abdullah,[c] Min Min Aung,[d] and
Chantara Thevy Ratnam [e]

Epoxidized jatropha oil (EJO) was investigated as a sustainable alternative to petrochemical-based plasticizers to reinforce the plastics, leading to increased ductility and toughness of kenaf-reinforced poly(lactic acid) (PLA). The EJO was melt-blended into kenaf-reinforced PLA at concentrations from 1 wt% to 5 wt%. The blends were then hot-pressed into sheets to characterize their mechanical and physical properties. Kenaf fibers were treated with 6% sodium hydroxide (NaOH), and the effects thereof on the composites' tensile, flexural, and impact properties, as well as their water absorption and density were stu died. The impact strengths of the kenaf-reinforced PLA composites were improved with the addition of EJO up to 5 wt%, with a maximum over 10 times that of the neat PLA. The flexural strength and modulus increased 4% and 50%, respectively, for treated kenaf-reinforced PLA plasticized with EJO. This increase demonstrated the alkalization treatment's notable improvements to the composites' properties. Furthermore, analysis by scanning electron microscopy (SEM) of the composites' tensile fracture surfaces indicated better interaction adhesion of the treated kenaf-reinforced PLA plasticized with EJO compared with the untreated composites. Compared to untreated 1 wt% EJO biocomposites, the treated 5 wt% EJO biocomposites reduced water absorption from 3.1% to 1.6% after 8 weeks of immersion.

Keywords: Polylactic acid; Kenaf; Epoxidized jatropha oil; Bio-sourced plasticizer; Environmentally friendly

Contact information: a: Laboratory of Biocomposite Technology, Institute of Tropical Forestry and Forest Products, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia; b: School of Industrial Technology, Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia; c: Department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia; d: Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia; e: Radiation Processing Technology Division, Malaysian Nuclear Agency, 43000Bangi, Selangor, Malaysia;
** Corresponding author: sitihas_kam@yahoo.com*

INTRODUCTION

From the last few years, the polymer composites approach is emerging as a promising sector with a considerable potential to capitalize various lignocellulose materials; such technology incorporates plant biomass into a variety of industrially relevant bio-products (Bilal *et al*. 2017; Silalertruksa *et al.* 2017). Moreover, industrial compounds and polymers from natural resources have attracted ever-increasing interest as alternatives to petroleum-based counterparts due to the depletion of fossil resources, increasing emissions of greenhouse gases and toxic wastes, and stringent environmental regulations

(Metzger and Bornscheuer 2006). Lignocellulosic fiber plants have attracted strong interest as potentially renewable feedstocks for a variety of industrial and consumer products, though their potential has not been fully realized (Biermann *et al*. 2000). Plant fibers are used widely in many applications because they can be engineered to offer important advantages over traditional materials. Positive attributes of these fibers include being renewable, biodegradable, CO_2 neutral, and environmentally friendly character, being low in cost and available abundantly in industrial waste, and having antioxidant, antimicrobial, and stabilizing properties. These factors make plant fibers appear to be promising for cost-effective polymer reinforcement. Furthermore, wide ranges of these natural fibers are available for various material applications (Gross and Scholz, 2001). Easily available natural fibers, such as jute, kenaf, sisal, coir, straw, hemp, banana, pineapple, rice husk, and bamboo, have been used to reinforce biodegradable polymers, in contrast with conventional polymer composites reinforced with man-made glass fiber.

Kenaf has been grown commercially in several areas around the world, such as Bangladesh, India, Thailand, parts of Africa, southeastern Europe, and Malaysia. Kenaf fiber has been deemed highly environmentally friendly and has been mainly used in the textile, automotive, construction and packaging industries. Thus, the demand for this fiber as a reinforcement for polymers is expanding. In Malaysia, the planting and harvesting of kenaf plants has become a subject of interest, with encouragement from the government in replacing the tobacco plant. Under the Tenth Malaysia Plan (2011 to 2015), the Plantation Industries and Commodities Ministry has increased its allocation for relevant research and development to RM 65 million. The allocation has been multiplied from RM 12 million to RM 110 million, a nearly ten-fold increase, from the Ninth Malaysia Plan to the Eleventh Malaysia Plan from the government to the National Kenaf and Tobacco Board (LKTN), with an expectation in return of being able to generate income of up to RM 4000 per month in five years on 10 hectares area, as compared with RM 2000 per month in a previous plan. However, drawbacks of using these fibers are their hydrophilic nature and highly polar character, which affect the fiber-matrix bonding and thus limit the potential of the final composites. Consequently, to improve the fiber-matrix interaction and compatibility within the polymer matrices, surface modification and treatment of the fibers are necessary to reduce their hydrophilicity and minimize the interfacial energy with hydrophobic polymer matrices. Thus, one method of effective surface modification is alkali treatment, which has been proposed and used to improve the mechanical performance of composites by several researchers (Mwaikambo and Ansell 2002; Aziz and Ansell 2004; Tawakkal *et al*. 2012). Although there is much research on the use of NaOH-treated fibers as reinforcement in thermoplastics, most of the composites produced are not fully-biodegradable. Therefore, the use of biodegradable polymers or green matrices, such as poly(lactic acid) (PLA), polyhydroxybutyrate (PHB), polycaprolactone (PCL), and polyester amide, was strongly suggested for combination with lignocellulosic fiber in composites (Ray *et al*. 2006).

Among all biodegradable polymers available in the market, PLA is the most promising biopolymer to be developed, as it is versatile and has immense potential for use in various industrial applications. Current research efforts are progressive in developing a new class of fully biodegradable composites, or biocomposites, by combining plant fibers with biodegradable polymers such as PLA. Nevertheless, the limiting properties of PLA, such as brittleness and stiffness, have made it difficult to process for further applications. Hence, the addition of plasticizer is crucial in improving the flexibility, as well as the elongation and impact properties, of composites (Bledzki *et al*. 2009). Currently, realizing the importance of biodegradability and renewability, a feasible biodegradable plasticizer is based on vegetable oil. It is notable that modified vegetable oils, such as corn, olive, canola, cottonseed, linseed, palm, rapeseed, and soybean oils are of renewed interest as substitutes for phthalates and have been applied as plasticizers or stabilizers for polymers (Al-Mulla *et al*. 2011; Robertson *et al*. 2011; Alam *et al*. 2014; Dai *et al*. 2014). However, these oils are categorized as edible oils and could become more expensive, as they may compete for use in the food industry in the long term. Numerous advantages have been reported for the use of epoxidized vegetable oil in the polymer industry, including biodegradability, environmental friendliness, renewability, and potential to reduce costs (Alam *et al*. 2014). Moreover, it has potential for use as an additive in industrial polymers that require properties such as good lubricity, low vitality, high viscosity index, and good solvency (Lathi and Mattiasson 2007).

Hence, the contributions of non-edible oils, such as jatropha, will be useful as plant oil sources for composite production. Jatropha oil having 78.9% unsaturated fatty acids, which is mainly comprised of oleic acid (44.7%) and linoleic acid (32.8%) and higher proportion of unsaturated fatty acids than that of palm oil (56.6%) (Sarin *et al*. 2007). There is a lack of published work on using epoxidized jatropha oil (EJO) as a plasticizer for PLA/natural fiber systems. Accordingly, the aim of this study is to introduce and propose the potential of EJO as a reactive plasticizer together with kenaf as a natural fiber for reinforcement to the PLA composite system. The effects of kenaf treatment and the addition of plasticizer on the mechanical and physical properties of the biocomposites will be discussed.

EXPERIMENTAL

Materials

Poly(lactic acid) polymer resins of grade 2003D were obtained from NatureWorks LLC (Minnetonka, MN, USA), and their properties are listed in Table 1. Meanwhile, crude jatropha oil, not a food-grade material, was supplied by Bionas Sdn Bhd (Kuala Lumpur, Malaysia) and was used as received. Kenaf fiber in the size of 40-µm mesh was obtained from the National Kenaf Tobacco Board (Kelantan, Malaysia). Reagent-grade hydrogen peroxide (30%) and magnesium sulfate were supplied by Merck (Darmstadt, Germany). Sodium hydroxide (NaOH; reagent grade) and formic acid were supplied by Systerm (Shah Alam, Malaysia).

Table 1. Properties of PLA Resin

Property	PLA 2003D	ASTM
Specific gravity	1.2	D792-00
Melt flow at 210 °C (g/10 min)	6.0	D1238-04
Viscosity at 30 °C (Pa.s)	4.0	-
Tensile strength at break (MPa)	53.0	D882-02
Tensile modulus (GPa)	3.6	D882-02
Elongation at break (%)	6.0	D882-02
Notched Izod impact (J/m)	16.0	D256-04
Melting point (°C)	145-160	D256-04
Glass transition temperature (°C)	55.0-66.0	D3418-03
Deflection temperature at 0.46 MPa (66 psi) (°C)	55.0	E2092
Melt temperature for processing (°C)	210	-
D-lactide (%)	4.0 - 4.5	-

Epoxidation of jatropha oil

The epoxidation of jatropha oil was carried out by the *in-situ* epoxidation method described by Goud *et al*. (2007) with a slight modification in the molar ratio of 1:0.6:1.7 (organic acid: double bonds: hydrogen peroxide) at a temperature of 60 °C for 5 h reaction time.

Treatment of kenaf fiber

The delignification and mercerization of kenaf fibers were performed to modify the fibers' surfaces. The fibers were mercerized, or alkali treated, to remove hemicellulose, lignin residue, and wax, thus producing the desired fibers. First, fibers with the size of 40 µm were treated with alkali and soaked in hot distilled water with continuous stirring at 60 °C for 4 h to remove excess wax and other impurities. Then, the treated fibers were washed with distilled water until reaching pH 7 (neutral) and subsequently oven-dried at 60 °C for 24 h.

Preparation of PLA/treated kenaf/EJO (PLA/TK/EJO) biocomposites

Prior to melt blending, PLA and kenaf (KF) were kept in an oven at 60 °C for 24 h to remove moisture content. The PLA/TK/EJO blends were prepared by the melt blending technique. Poly(lactic acid) was premixed with 1 to 5wt% of epoxidized jatropha oil and added with 30 wt% ratio of treated kenaf fiber. The amount 30 wt% of kenaf fiber was chosen as a suitable amount of fiber loading for the reinforcement of PLA with EJO due to the good mechanical interlocking between the kenaf fibers and the matrix. The fibers were well distributed and had a sufficient extent of interaction with the matrix. The amount of matrix was sufficient to wet out the fiber and fully transfer the stress effectively at such fiber loadings. Kenaf fibers were treated with a 6% concentration NaOH, and PLA was plasticized from 1 wt% to 5 wt% EJO. The melt blending was performed using a Brabender internal mixer (Dusburg, Germany) at 170 °C for 10 min at 50 rpm motor speed. The blended materials were then placed in the hot and cold press for compression molding with a pressure of 10.8 MPa at 170 °C for 11 min to produce biocomposite sheets of uniform 1 mm and 3 mm thickness. The biocomposites were then analyzed for characterization of their physical, mechanical, and morphological properties.

Methods

Mechanical tests

The tensile properties of the composites were measured using a Toyoseiki universal testing machine (model Strograph R1; Toyoseiki Kogyo Co. Ltd, Nagano, Japan), with a grip attachment distance of 45 mm and a load cell of 1 kN. Each tensile test was performed at a crosshead speed of 5 mm/min on specimens with dimensions in accordance with the ASTM D638-98 (1999) standard until tensile failure was detected. The three-point bending flexural tests were performed at a crosshead speed of 1.3 mm/min on specimens of rectangular shape with dimensions of 127.00 mm × 12.70 mm × 3.00 mm. The support span length was 48 mm.The specimens were deflected until rupture occurred. Meanwhile, impact strength tests were performed by using an Izod impact tester (International Equipment, Mumbai, India) with a pendulum weighing 453 g (1.0 lb) based on the ASTM D256-10(2010) standard with dimensions of 63.50 mm length, 12.70 mm width, and approximately 3.00 mm thickness. The impact resistance value is the energy required to break the sample (as recorded on the tester machine) divided by the thickness of the sample. The widths and thicknesses of the specimens were measured at three different points, and their averages were calculated. The resultant values for the tensile, flexural, and impact properties of neat PLA and the composites were taken from the averages of seven samples.

Physical tests

Water absorption tests were conducted based on the ASTM D570-98 (1998) standard on specimens with dimensions of 25 mm × 1.5 mm × 3 mm. Prior to immersion, the specimens were oven-dried for 24 hat 60 °C to reach a constant weight and subsequently were cooled in a desiccator for at least 30 min. The initial weights of the dried samples were measured using an electronic balance. The samples were then placed in a test tube and immersed in distilled water at room temperature (approximately 25 °C). The weights of the immersed samples were recorded daily from week 1 until a constant zero increment in mass was obtained. The samples were then removed from the distilled water, and the surface water was wiped off using a tissue at the end of the immersion period. The wet weight of the samples was determined from an average of at least three samples. Furthermore, the densities of the composites were determined based on ASTM D1505 (2003) using an electronic densimeter (model MD-200S; Alfa Mirage Ltd, Osaka, Japan) density determination kit by the water displacement method. A total of three rectangular bar-shaped specimens from each composite sample with thicknesses of 1 mm and an average weight of 1g were tested to determine the average value. The water absorption was calculated using Eq. 1,

$$\textit{Water absorption}\ (\%) = ((W_{\mathrm{w}} - W_{\mathrm{d}}) / W_{\mathrm{d}}) \times 100 \qquad (1)$$

where W_{w} and W_{d} are the weights(unit) of the specimen when wet and when dry, respectively.

Scanning electron microscopy (SEM)

Scanning electron microscopy was conducted to determine the dispersion of EJO in the PLA matrix and the adhesion among kenaf, EJO, and the PLA matrix. The tensile fracture of the specimens was studied using a JEOLJSM-6300F scanning electron microscope (SEMTech Solutions, Massachusetts, USA) with an accelerating voltage of 20 kV. The specimens were coated with gold prior to each test to avoid electrostatic charging during electron irradiation.

RESULTS AND DISCUSSION

Tensile Properties

The values of tensile strength and tensile modulus of the pure PLA, plasticized PLA/untreated kenaf (UTK) composites, and plasticized PLA/treated kenaf (TK) composites are given in Table 2. The table shows that the values of tensile strength and tensile modulus for both plasticized biocomposites (untreated and treated) were much lower when compared with the neat PLA. While the neat PLA polymer exhibited a tensile strength of 50.64 MPa and a tensile modulus of 8.46 GPa, the tensile strength decreased 59% to 20.78 MPa for 5wt% EJO plasticized PLA/untreated kenaf composites, and 51% to 24.93 MPa for 5 wt% EJO plasticized PLA/treated kenaf composites. In both the UTK and TK conditions, the tensile strength reached its lowest value at 5 wt% EJO. From this finding, it is shown in Table 2 that the decrement of the tensile strength was due to the inefficiency of stress transfer from PLA to kenaf fiber, whereby the weak interfacial bonding between the PLA and kenaf fibre led to the restriction of penetration between the polymer onto the fiber surface. Moreover, according to Mwaikambo (2009), a type of short fiber had difficulties supporting stress transfer from PLA and therefore have led to the strength reduction as fiber was added to PLA. Because the kenaf fiber used for this work came from short fiber types, it was anticipated that tensile strength might decrease upon its addition to the composites. The irregular shapes of the fibers induced their inability to support stress transfer from the polymer matrix, and poor interfacial bonding generated spaces between the fibers and the polymer matrix, contributing to a weak structure (Yang *et al*. 2004; Ismail *et al*. 2011).

Table 2. Mechanical Properties of PLA, PLA/UTK/EJO Composites, and PLA/TK/EJO Composites

Material	Tensile Strength (MPa)		Tensile Modulus (GPa)		Flexural Strength (MPa)		Flexural Modulus (GPa)		Impact Strength (J/m)	
Neat PLA	50.64		8.46		62.14		3.05		13.87	
PLA/KF/EJO	UTK	TK	UTK	TK	UTK	TK	UTK	TK	UTK	TK
1 wt% EJO	25.31	36.18	8.17	8.21	61.54	64.90	3.61	4.14	76.36	116.60
2 wt% EJO	25.29	34.78	7.75	8.28	57.04	61.67	3.74	4.28	86.50	141.60
3 wt% EJO	24.10	29.90	6.61	8.72	50.52	51.51	3.66	4.21	108.66	151.13
4 wt% EJO	21.06	29.84	6.43	8.41	43.05	47.61	3.07	4.72	66.91	113.89
5 wt% EJO	20.78	24.93	6.42	8.11	41.46	42.97	3.20	3.21	65.04	104.32

However, the addition of plasticizer with the treated fiber surface succeeded in increasing the tensile strength of composites as compared with the untreated fibers. From this result, several important findings can be highlighted. Alkali treatment of lignocellulosic fibers is a way of fiber surface modification that appeared to be a promising treatment, enhancing the fibers' surface roughness and leading to surface fibrillation (Drzal *et al*. 2002). This observation is supported by John and Anandjiwala (2008), who concluded that the alkali treatment leads to the fibers' fibrillation, breaking down the fiber bundles into smaller fibers. With this in mind, it therefore increases the fibers' surface area available to be adhered with the plasticized matrix.

This explains the reason behind the increase in tensile strength corresponding to the plasticized PLA/treated kenaf composites was due to the alkali treatment subjected to the system. When the fibers were treated with NaOH, the surface was cleaned and later provided a rougher surface. However, at the same time, the treatment also softened the interfibrillar matrix, which negatively affected the stress transfer in the fibers (Thomas and Pothan 2009). In other words, alkali treatment uncovers the fibrils and gives the fibers a rough surface topography (Mwaikambo and Ansell 2002). Furthermore, alkali treatment at a sufficiently high concentration alters the fine structure of native cellulose I to cellulose II by a process known as alkalization (Nevell and Zeronian 1985; Mwaikambo and Ansell 2002; John and Anandjiwala 2008). The reaction of NaOH with cellulose can be explained through Eq. 2:

$$\text{Fiber} - \text{OH} \;+\; \text{NaOH} \longrightarrow \text{Fiber} - \text{O}^{-}\,\text{Na}^{+} \;\_\; \text{H}_2\text{O} + (\text{Surface impurities}) \quad (2)$$

In plasticized PLA/treated kenaf composites, the fibers were treated with NaOH, which removed the undesirable materials; thus, more reactive sites (*i.e*., hydroxyl groups) of cellulose were revealed (Thomas and Pothan 2009). The interaction between the NaOH and kenaf fibers is illustrated in the schematic approach of hypothetical chemical structure, as depicted in Fig. 1.

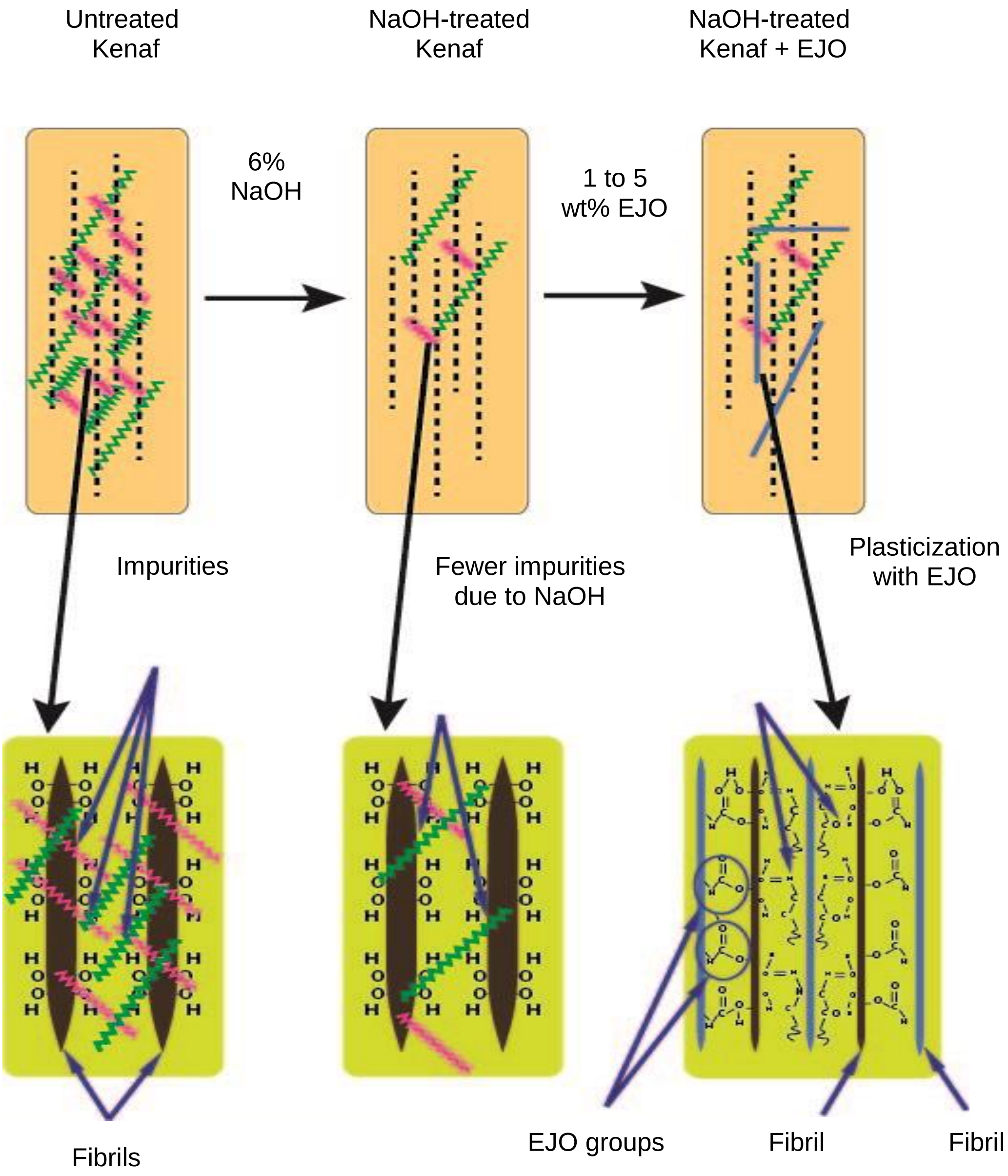

Fig. 1. Hypothetical chemical structure of kenaf fibers treated with 6% NaOH and EJO

The rough surface topography of plasticized PLA/treated kenaf composites can be seen in the SEM micrographs (Fig. 2). From this figure, it is understood that the treatment removed a certain amount of hemicellulose, lignin, wax, oils, and other impurities, hence yielding the rough surface and preventing the leaching and migration of the plasticizer from the polymer. Liu and Dai (2007) reported a similar trend. It can be supported that the treatment altered the strength and reduced the stiffness of the composites. In addition, from the micrograph, it can be seen that the filler-related failures were significantly decreased, and more-embedded fibers and, notably, voids were reduced.

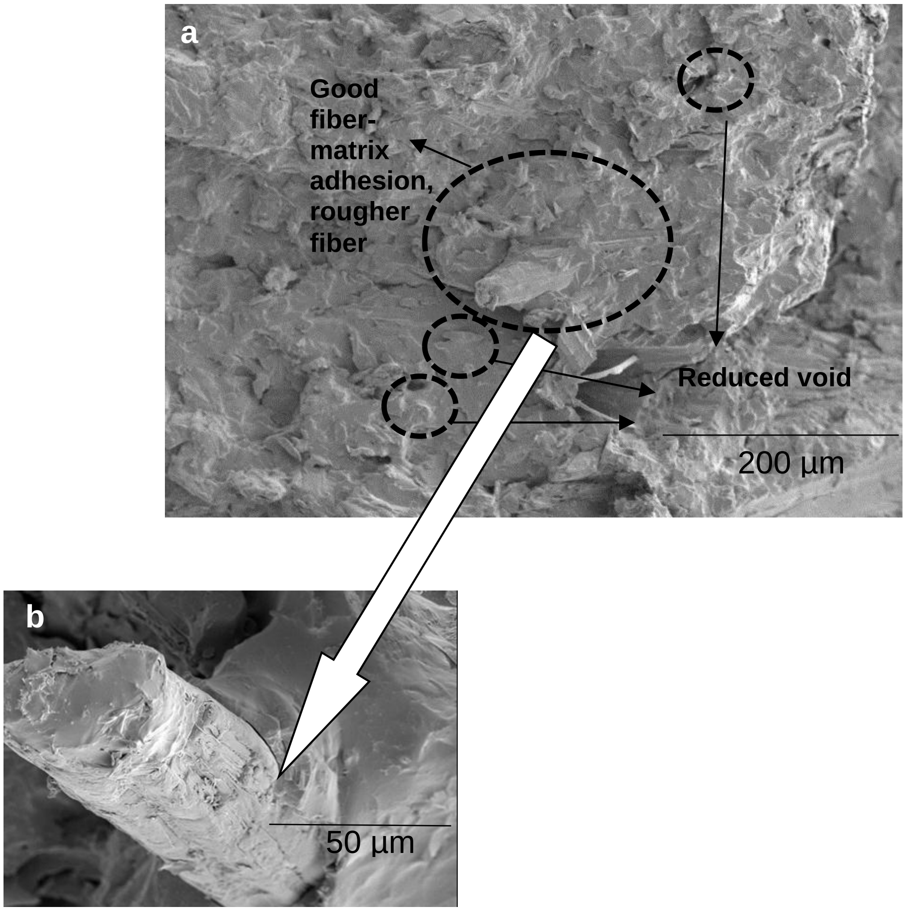

Fig. 2. Scanning electron micrograph of the tensile surface fracture of PLA/TK/EJO composites at (a) 200 µm magnification and (b) 50 µm magnification

The wax and impurities disappeared and were removed after alkaline treatment. The surface treatment facilitated good adhesion between the kenaf and the plasticized PLA matrix through increased surface roughness. Furthermore, kenaf fibers were well trapped by the plasticized PLA matrix. Better stress transfer from the PLA matrix to kenaf fiber was expected due to the thin layer linking the fiber surface to the matrix. Furthermore, better wetting out of the PLA/EJO onto kenaf fibers was observed. Thus, improved adhesion led to a significant increase in tensile properties. Notably, the enhancement in fiber-matrix adhesion explained the improvement in mechanical properties of PLA/TK/EJO compared to the untreated composite.

For plasticized PLA/untreated kenaf composites in Fig. 3, the micrograph of the surface displays a notable gap as compared to the plasticized PLA/treated kenaf composites. In addition, aggregation and fiber breakage are visible. As reported by Li *et al.* (2007), the gaps were probably due to debonding during mechanical testing or poor dispersion during the composites'preparations, which indicated a weak fiber-matrix adhesion. Changes of surface topography and good fiber-matrix adhesion are required for effective stress transfer from the matrix to the fiber (Bachtiar *et al*. 2008). Therefore, alkalization treatment for fibers is needed to modify the surface roughness of the plasticized kenaf composites. It was observable through SEM morphology that alkali treatment had a positive effect on the fiber-matrix adhesion that explained the improvement in mechanical properties.

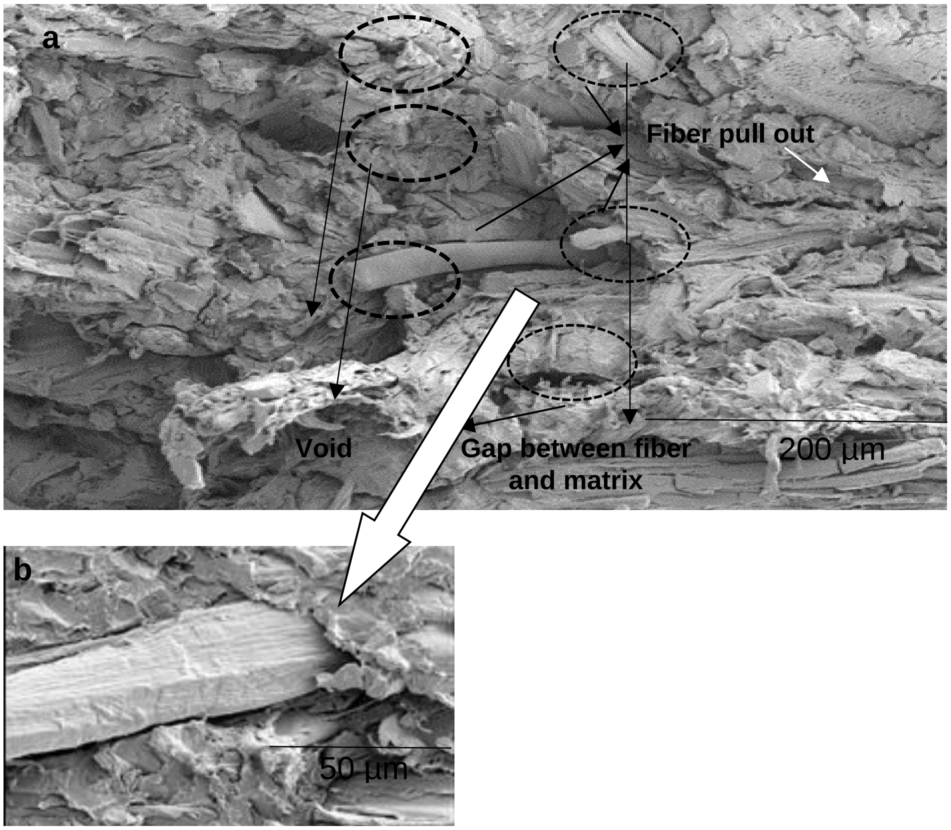

Fig. 3. Scanning electron micrograph of the tensile surface fracture of PLA/UTK/EJO composites at (a) 200 µm magnification and (b) 50 µm magnification

Epoxidized jatropha oil was used in this work to plasticize PLA/KF, thus modifying the brittleness of neat PLA. The use of plasticizer had previously been reported to bring good results for the PLA's properties (Wadhi and Weliam 2014). As the plasticizer was introduced to the system, the PLA became softer and more flexible, which resulted in reduced tensile strength and modulus. Thus, the values of tensile strength and modulus for PLA/UTK/EJO were lower than those of PLA. However, the results for tensile modulus did not differ significantly between PLA (8.46 GPa) and PLA/UTK/EJO 1 wt% (8.17 GPa). Introduction of EJO as a plasticizer into PLA/KFT entails the addition of more free volume and consequently increases the flexibility of polymer chains, lowering the tensile strength and tensile modulus of the polymer (Sears and Darby1982).

Although the tensile modulus was reduced with the addition of EJO, PLA/TKF/EJO had a higher tensile modulus (8.21 GPa) compared with the untreated plasticized biocomposites (8.17 GPa) due to the uniform fiber dispersion in PLA for PLA/TKF with 1 wt% EJO. Additionally, the improvement in tensile modulus indicated an improvement in effectiveness of oriented cellulose fibers due to the removal of the hemicellulose and lignin content, leading to better packing of cellulose chains. As a result, the fibers become relatively ductile after the removal of some hemicellulose and lignin content, resulting in the improvement of the stiffness of the fiber. According to Agarwal *et al*. (2000), the alkalization treatment has a lasting effect on the mechanical behavior of natural fibers, especially on fiber stiffness. Sodium hydroxide solution has the ability to remove natural fats, waxes, and impurities from the fiber surfaces (Sreekala and Thomas 2003). Therefore, the alkalization treatment results in the opening of more hydroxyl groups and other reactive functional groups on the surfaces of the fibers (Islam *et al*. 2011). The increase in tensile modulus for PLA/KFT compared to untreated fiber composites was due to the enhanced surface wettability between fiber and matrix, causing the removal of impurities and waxy substances from the fiber surface and the creation of a rougher surface after the modification.

Flexural Properties

Table 2 also presents the flexural strengths and moduli for virgin PLA and both plasticized biocomposite (untreated and treated kenaf) samples. It shows that the flexural strength of the PLA/UTK/EJO composites decreased upon addition of kenaf fiber and linearly decreased with increasing (1 wt% to 5 wt%) EJO content. However, a slight drop was noticed in the flexural strength value from 4 wt% to 5 wt%. At 4% EJO loading, the matrix-reinforcement ratio reached a critical limit. In other words, when a higher percentage of EJO loading (5%) was added to the system, the value given did not show much difference. It is unsurprising that there was a reduction in the flexural strength with the addition of untreated kenaf fiber to the matrix due to the poor fiber-matrix adhesion, which reduced the ability of the matrix to absorb stress transfer (Razak and Kalam 2012). The fiber-matrix adhesion depends on several factors, such as the natures of the matrix and fiber, the aspect ratio of the fiber, the composition, the method of processing, and the treatment of the fiber (Rozman *et al*. 2001). However, it should be once again highlighted that the treatment of kenaf fiber brought a significant improvement in flexural strength for PLA/TK/EJO (1 wt%). Interestingly, the flexural strength results for all treated plasticized biocomposites had higher values compared to the untreated plasticized biocomposites for all EJO levels (1wt%to5 wt%). The increased flexural strength for treated plasticized biocomposites compared to untreated plasticized biocomposites could be due to the treatment's lasting effects on the fibers' mechanical properties, specifically fiber stiffness (Agarwal *et al*. 2000). Similarly, Huda *et al*. (2008) investigated the improvement of flexural strength for treated kenaf fiber composites. The drop in flexural strength of biocomposites as a result of the addition of EJO plasticizer was possibly due to a reduction of chain mobility, leading to decreased crystallization and decreased free volume in the PLA chain (Shibata *et al*. 2007). Thus, with the higher polymer-plasticizer interaction, it then resulted the incorporation of more free volume, which improved segmental chain mobility and decreased the steric hindrance of polymer chains (Bergquist *et al*. 1999). Without plasticizer molecules, as in the case of the neat PLA, the plastic was tougher and more rigid because the polymer molecules held onto each other more tightly.

Meanwhile, according to the values for the flexural modulus in Table 2, the introduction of plasticized kenaf (both untreated and treated) significantly improved the moduli of biocomposites compared to the neat PLA matrix. The incorporation of fibers had an influence on the modulus as it contributed to the stiffness of the composites. Similarly, positive values of flexural modulus were witnessed for short-sisal-fiber biocomposites (Alvarez *et al*. 2004) and kenaf-fiber biocomposites (Shibata *et al*. 2005). It was demonstrated that incorporation of fibers notably improved the flexural stiffness of the matrix and increased the modulus of the biocomposites. Cañigueral *et al*. (2009) explained that a good fiber dispersion in the composite system could be confirmed by observing an increase in the modulus of composites. Furthermore, the treatment of the fibers steadily improved the modulus, as it restricted the mobility of the polymer chain and therefore hindered the ability of the polymer to deform (Huda *et al*. 2006). Li *et al*. (2011) reported similar findings on the increase of the modulus of treated composites, which was explained as an indication of good interfacial adhesion between the fibers and the matrix. Addition of EJO plasticizer for both untreated and treated plasticized biocomposites show inconsistently reduction of the flexural modulus. The flexural modulus increased with increased amount of plasticizer. The strength of the polymer-plasticizer interaction depended on the concentration of the plasticizer. A compatible plasticizer, especially at low concentration (in this case, 1 wt% to 4 wt% EJO), was difficult to remove, and the molecules cannot move past each other easily. Hence, the increased flexural modulus of plasticized biocomposites were similar to neat PLA. However, as the concentration of EJO plasticizer increased to 5 wt%, the interaction between polymer and plasticizer decreased due to an increased migration rate of the plasticizer. Nevertheless, the flexural moduli of both the untreated (3.20 GPa) and treated (3.21 GPa) plasticized biocomposites of PLA/KF/EJO were much higher than that of the PLA matrix alone (3.05 GPa).

Impact Properties

The effects of various amounts of plasticizer together with kenaf fiber on the impact strength of biocomposites are tabulated in Table 2. Adding kenaf fiber and EJO plasticizer to the PLA matrix significantly contributed to the total impact strength of the biocomposites. The PLA/KF/EJO 3 wt% composites achieved the highest impact strength values for both the untreated (108.66 J/m) and treated (151.13 J/m) plasticized biocomposites, with the latter being over 10 times that of neat PLA. Overcoming the brittleness of PLA by the addition of kenaf and EJO enhanced its impact resistance properties. Impact properties increased with the addition of kenaf fiber and EJO as shown in Fig. 4.

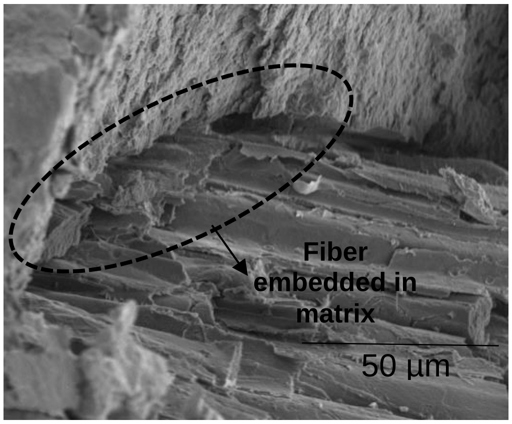

Fig. 4. Scanning electron micrograph of the impact surface fracture of PLA/TK/EJO composites at 50 µm magnification

These results suggested that the presence of kenaf fiber significantly contributed to its capacity to absorb energy and to the composites' toughness. This result could have been due to the incorporation of kenaf fiber into the PLA matrix, which resulted in stress concentration regions that required more energy to initiate cracks. Stress concentration regions are attributable to the fibers' ends, composite defects, and a lack of adhesion between the fibers and the matrix at the interface regions (Huda *et al*. 2006). This phenomenon was further explained by the efficiency of stress transfer from the matrix during sudden impact with the high absorption of kenaf fibers. The stress was transferred from the PLA matrix to the kenaf, which acted as a barrier to transfer the sudden impact load from the small section of the PLA matrix. Thus, more energy is absorbed due to decreased crack propagation and initiation (Huda *et al*. 2006).

As can be seen from Table 2, the impact strength showed significant increase up to 3 wt% of EJO loading in the plasticized biocomposites which supported that even at low plasticizer concentration, the absorption of energy was higher. This is because the addition of EJO up to 3 wt% loading promotes the dispersion become evenly. Thus, it comprised a larger part of the fracture energy during the crack initiation and altered the crack path. The impact resistance is effected by absorption of the energy of formation of the free surface of the rupture. Impact strength properties may have caused visible cracking in some materials. Microcracks may develop into macrocracks, usually resulting in brittle failure. In the presence of plasticizers which function as lubricants," the crazes branch during elongation, the energy of the craze formation is dissipated, and the impact strength increases (Gubeladze 1987). However, it was apparent that there was a slight reduction of impact strength with the further addition of EJO to the biocomposites (4 wt% to 5 wt%). Excess EJO in the plasticized PLA/kenaf composites led to poor dispersion and adhesion between the matrix and plasticizer, which resulted in decreased impact strength for plasticized PLA/kenaf composites above 3 wt% EJO. Furthermore, blends with higher EJO content provided points of stress concentration, hence providing sites for crack initiation. Nevertheless, the blends with 4 wt% and 5 wt% EJO still had greater impact strength than neat PLA. Research done by Vijayarajan (2013) confirmed this phenomenon with a successful investigation of the effects of epoxidized soybean oil (ESO) on the impact strength of PLA sheets, finding that the impact strength increased significantly from 5 wt% to 10 wt% ESO and started dropping off between 15 wt% and 20 wt% ESO. This result could have been attributed to the partial miscibility between PLA and ESO, with ESO forming a dispersed phase that dissipates the fracture energy, resulting in improved impact strength.

Physical Properties

In addition to mechanical properties, including tensile, flexural, and impact properties, water absorption is one of the most important physical properties to consider when dealing with composites. High water absorption tends to be one of the limiting factors for many practical applications of composites, especially when exposed to humidity. Figure 5 presents the water absorption of the neat PLA, the PLA/UTK/EJO composites, and the PLA/TK/EJO composites at various EJO concentrations as percentages of dry weights after 8 weeks of immersion time. The results showed an initial linear relationship between water absorption and immersion time in each sample, which gradually decreased afterwards. It is believed that the change of weight gain for all samples represents typical Fickian diffusion behavior. As shown in Fig. 5, the water absorption of neat PLA was lower than that of the plasticized biocomposites for both the untreated and treated kenaf. The neat PLA had absorbed approximately 1.3% water at the end of the water absorption test. Previous research had reported that the water uptake for PLA levels off at approximately 1%, which is similar to most petroleum-based polymers. (Wang *et al.* 2002; Garlotta 2002; Yew *et al.* 2005). This 1% water represents hydrogen bonding between carbonyl groups of PLA and water molecules (Wang *et al.* 2002; Garlotta 2002; Yew *et al.* 2005).

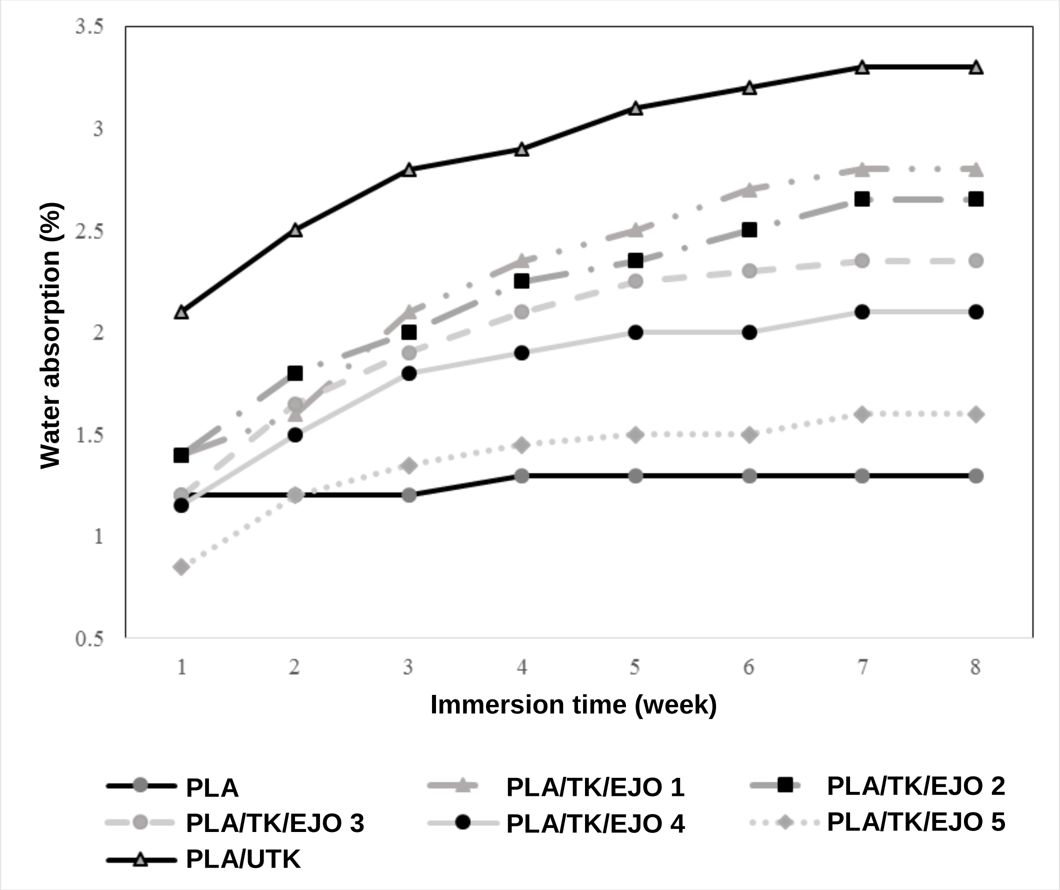

Fig. 5. Water absorption of PLA, PLA/UTK/EJO composites, and PLA/TK/EJO composites

Water absorption of the plasticized kenaf biocomposites decreased with increased EJO content. The results were in the range from 1.6% to3.1% for all untreated and treated plasticized biocomposites for the total absorption time period of 8 weeks. This result was attributed to strong hydrogen bond formation between plasticised matrix and fibre. As a result, it significantly reduced the interaction between water molecules and the intermolecular hydrophilic functional groups of PLA (Sanyang *et al*. 2016). In this case, EJO acted as a hydrophobic type of plasticizer, reducing water absorption and likely contributing to the reduction of water sensitivity of plasticized PLA. Hydrophobic plasticizers may close the microvoids in the film, reduce water sensitivity, and lead to a decrease in water uptake (Vieira *et al*. 2011).

The effect of fiber treatment was noticeable. The removal of hemicellulose, the most hydrophilic component, and lignin from the fiber during the treatment process contributed to the total reduction in moisture absorption for treated biocomposites. Water penetration in natural fiber composites is based on microcracks in the polymer matrix, spaces between the matrix and natural fibers (bad interphase), or exposed natural fibers (edges of samples uncoated by the matrix) (Bledzki *et al.* 2005).

Higher water uptake for untreated fiber composites can also be attributed to gaps between fibers and the matrix, as can be observed in Fig. 3 from the SEM images. As a result, increased water uptake caused more water to penetrate into the fiber, thus causing the fibers' cell walls to swell, leading to crack formation in the composites. The formation of microcracks created pathways for water molecules to diffuse into the composites, hence explaining the higher water uptake for untreated plasticized biocomposites. The first 3 weeks of immersion showed a rapid increase in the level of water absorption of the plasticized kenaf biocomposites.

The next 3 weeks showed a gradual increase in the water uptake, which then slowed until complete saturation or plateau was reached for the rest of the testing period. The results showed that increasing EJO content led to decreasing water sorption of the biocomposites. Despite this trend, treated plasticized biocomposites still showed lower water uptake compared with the untreated plasticized biocomposites. Similar behavior was observed by Dhakal *et al.* (2007) and Tawakkal *et al.* (2012).

In short, increased EJO concentration led to decreased water uptake, and treatment of the fibers reduced the volume by increasing fiber and plasticized matrix adhesion, together with the removal of lignin and hemicellulose. Consequently, the strength and stiffness were expected to be less affected by increased humidity, providing long-term stability to the plasticized PLA. Furthermore, this improvement extends the use of plasticized PLA in various applications that are moisture sensitive.

The effect of EJO concentration on the densities of untreated and treated plasticized PLA kenaf biocomposites is shown in Fig. 6. Incorporating EJO and kenaf fiber into the PLA matrix changed the density of PLA. Neat PLA was less dense (1.38 g/cm^3) compared with the of untreated and treated PLA kenaf biocomposites for lower EJO concentrations (1 wt% to 3 wt%). However, the densities of the biocomposites started to decline when EJO content reached 4 wt% to 5 wt%. Generally, the introduction of plasticizer affects the packing density and free volume of the polymer chain. Free volume can be increased by the combination of decreased molecular weight and increased chain mobility. Therefore, increased plasticizer concentration increases free volume, hence leading to the density reduction visible in Fig. 6.

Low density leads to lighter weight composites. The results are also in agreement with Jusoh *et al.* (2012), who found a decrease in density by increasing the proportion of crude palm oil plasticizer from 1wt%to 5wt% in polypropylene, and Jusoh *et al.* (2012), who found a decrease in density by increasing the proportion of glycerol plasticizer from 15wt% to 40 wt% in the sugar palm starch. Both film sheets were prepared using a dry processing technique (hot pressing).In this study, when the EJO plasticizer was incorporated into the PLA, it caused softening by reducing the intermolecular attractive forces among the chains in the PLA resin system.

Nevertheless, treated plasticized biocomposites had higher densities compared with untreated plasticized biocomposites. As anticipated, the percentage of void content was much lower for the treated plasticized biocomposites compared with untreated plasticized biocomposites. This result was due to the efficiency of the alkaline treatment in improving fiber-matrix adhesion and dispersion in the composites. Thus, it was observed that the treatment of the fiber helped reduce the voids of the PLA matrix interface, as supported by the SEM images in Fig. 2.

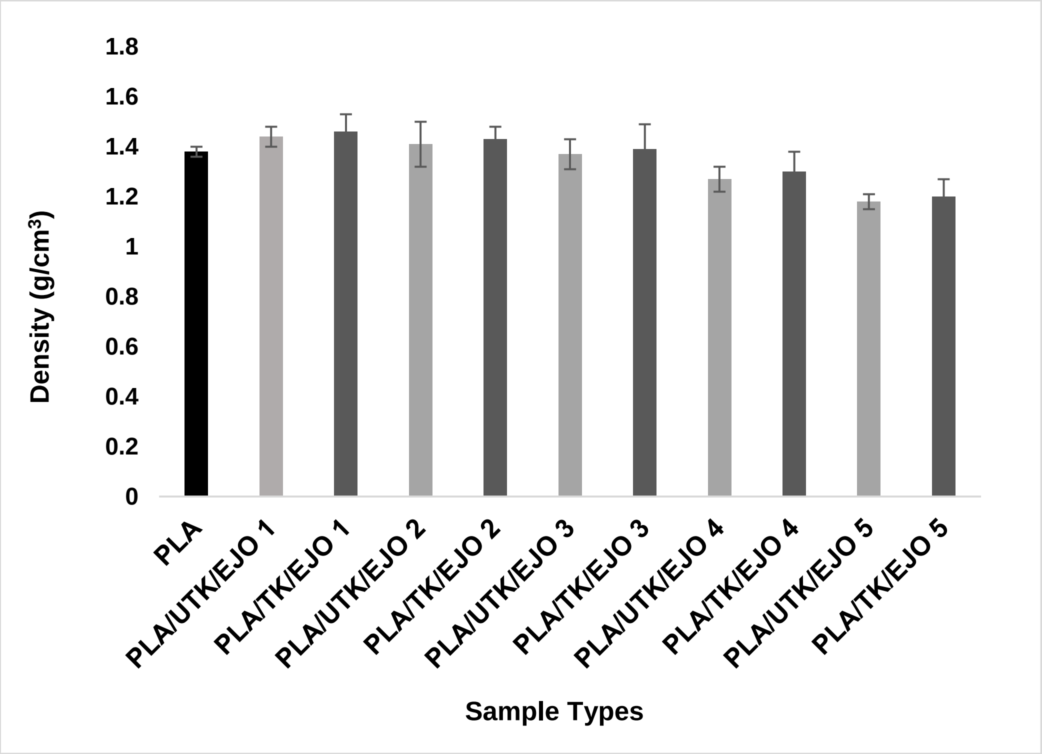

Fig. 6. Density of PLA, PLA/UTK/EJO composites, and PLA/TK/EJO composites

CONCLUSIONS

1. Impact strength was overall significantly improved, while the tensile strength were much lower, for both plasticized biocomposites (untreated kenaf and treated kenaf) as compared with the commercial neat poly(lactic acid) (PLA) polymer. The tensile modulus of the untreated plasticized biocomposites were lower than neat PLA, while the highest tensile modulus was found to be at 3 wt% epoxidized jatropha oil (EJO), which was even higher than neat PLA.
2. Although the biocomposites had greater water uptake than the neat PLA, increasing EJO concentration from 1 to 5 wt% reduced the magnitude of the difference of percentage of water uptake for the untreated and treated plasticized kenaf biocomposites after 8 weeks of immersion, which reflected a significant contribution of EJO.
3. The densities of the biocomposites decreased with increasing EJO.
4. Alkali treatment of the kenaf fibers improved all the properties of the biocomposites, showing good contact between the fibers and the plasticized matrix.

ACKNOWLEDGMENTS

The authors are grateful to the Biocomposite Laboratory, Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, and to the Loji Polymer, Radiation and Processing Technology Division, Nuclear Malaysia, Bangi, for the research facilities and property testing. Additionally, the authors would like to thank the Biopolymer Research Group, Department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia and Universiti Teknologi MARA (UiTM), as well as the Ministry of Higher Education for financial support.

REFERENCES CITED

Agarwal, R., Saxena, N. S., Sharma, K. B., Thomas, S., and Sreekala, M. S. (2000). "Effect of different treatments on the thermal behavior of reinforced phenol–formaldehyde polymer composites," *Journal of Applied Polymer Science* 78(3), 603-608. DOI: 10.1002/1097-4628(20001017)78:3<603::AID-APP150>3.0.CO;2-W

Al-Mulla, E. A. J., Suhail, A. H., and Aowda, S. A. (2011). "New biopolymer nanocomposites based on epoxidized soybean oil plasticized poly(lactic acid)/fatty nitrogen compounds modified clay: Preparation and characterization," *Industrial Crops and Products* 33(1), 23-29. DOI: 10.1016/j.indcrop.2010.07.022

Alam, M., Akram, D., Sharmin, E., Zafar, F., and Ahmad, S. (2014). "Vegetable oil based eco-friendly coating materials: A review article," *Arabian Journal of Chemistry* 7(4), 469-479. DOI: 10.1016/j.arabjc.2013.12.023

Alvarez, V. A., Kenny, J. M., and Vázquez, A. (2004). "Creep behavior of biocomposites based on sisal fiber reinforced cellulose derivatives/starch blends," *Polymer Composites* 25(3), 280-288. DOI: 10.1002/pc.20022

ASTM International. (2001). "Standard test method for density and specific gravity (relative density) of plastics by displacement (D792-00)," West Conshohocken. ASTM International, PA. 2000.

ASTM International. (2004). "Standard test method for melt flow rates of thermoplastics by extrusion plastometer (D1238-04)," West Conshohocken. ASTM International, PA. 2004.

ASTM International. (2002). "Standard test method for tensile properties of thin plastic sheeting (D882-02)," West Conshohocken. ASTM International, PA. 2002.

ASTM International. (2004). "Standard test methods for determining the Izod pendulum impact resistance for plastics (D256-04)," West Conshohocken. ASTM International, PA. 2004.

ASTM International. (2003). "Standard test method for transition temperatures of polymers by differential scanning calorimetry (D3418-043)," West Conshohocken. ASTM International, PA. 2003.

ASTM International. (2013). "Standard test method for distortion temperature in three point bending by thermomechanical analysis (E2092-13)," West Conshohocken. ASTM International, PA. 2013.

ASTM International. (1999). "Standard test method for tensile properties of plastics (D638-99)," West Conshohocken. ASTM International, PA. 1999.

ASTM International. (2010). "Standard test methods for determining the Izod pendulum impact resistance of plastics (D256-10)," West Conshohocken. ASTM International, PA. 2010.

ASTM International. (2003). "Standard test methods for density of plastics by the density-gradient technique (D1505-03)," West Conshohocken. ASTM International, PA. 2003.

ASTM International. (1998). “Standard test methods for water absorption of plastics (D570-98),” West Conshohocken. ASTM International, PA. 1998.

Aziz, S. H., and Ansell, M. P. (2004). “The effect of alkalization and fibre alignment on the mechanical and thermal properties of kenaf and hemp bast fibre composites: Part 1–Polyester resin matrix,” *Composites Science and Technology* 64(9), 1219-1230. DOI: 10.1016/j.compscitech.2003.10.001

Bachtiar, D., Sapuan, S. M., and Hamdan, M. M. (2008). “The effect of alkaline treatment on tensile properties of sugar palm fibre reinforced epoxy composites,” *Materials & Design* 29(7), 1285-1290. DOI: 10.1016/j.matdes.2007.09.006

Bergquist, P., Zhu, Y., Jones, A. A., and Inglefield, P. T. (1999). “Plasticization and antiplasticization in polycarbonates: The role of diluent motion,” *Macromolecules* 32(23), 7925-7931. DOI:10.1021/ma980205g

Biermann, U., Friedt, W., Lang, S., Lühs, W., Machmüller, G., Metzger, J. O., Rüsch gen. Klaas, M., Schäfer, H. J., and Schneider, M. P. (2000). “New syntheses with oils and fats as renewable raw materials for the chemical industry,” *Angewandte Chemie International Edition* 39(13), 2206-2224. DOI: 10.1002/1521-3773(20000703)39:13<2206::AID-ANIE2206>3.0.CO;2-P

Bilal, M., Asgher, M., Iqbal, H. M., Hu, H., and Zhang, X. (2017). “Biotransformation of lignocellulosic materials into value-added products—A review,” *International Journal of Biological Macromolecules* 98, 447-458. DOI: 10.1016/j.ijbiomac.2017.01.133

Bledzki, A. K., Jaszkiewicz, A., and Scherzer, D. (2009). “Mechanical properties of PLA composites with man-made cellulose and abaca fibres,” *Composites Part A: Applied Science and Manufacturing* 40(4), 404-412. DOI: 10.1016/j.compositesa.2009.01.002

Bledzki, A. K., Letman, M., Viksne, A., and Rence, L. (2005). “A comparison of compounding processes and wood type for wood fibre—PP composites,” *Composites Part A: Applied Science and Manufacturing* 36(6), 789-797. DOI: 10.1021/ma980205g10.1016/j.compositesa.2004.10.029

Cañigueral, N., Vilaseca, F., Méndez, J. A., López, J. P., Barberà, L., Puig, J., Pèlach, M. A., and Mutjé, P. (2009). “Behavior of biocomposite materials from flax strands and starch-based biopolymer,” *Chemical Engineering Science* 64(11), 2651-2658. DOI: 10.1016/j.ces.2009.02.006

Dai, X., Xiong, Z., Na, H., and Zhu, J. (2014). “How does epoxidized soybean oil improve the toughness of microcrystalline cellulose filled polylactide acid composites?,” *Composites Science and Technology* 90, 9-15. DOI: 10.1016/j.compscitech.2013.10.009

Dhakal, H. N., Zhang, Z. Y., and Richardson, M. O. W. (2007). “Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites,” *Composites Science and Technology* 67(7-8), 1674-1683. DOI: 10.1016/j.compscitech.2006.06.019

Drzal, L. T., Mohanty, A. K., Tummala, P., and Misra, M. (2002). “Environmentally friendly bio-composites from soy-based bio-plastic and natural fiber,” *Polymeric Materials: Science and Engineering* 87, 117-118.

Garlotta, D. (2002). “A literature review of poly(lactic acid),”*Journal of Polymers and the Environment* 9(2), 63-84. DOI: 10.1023/A:1020200822435

Goud, V. V., Patwardhan, A. V., Dinda, S., and Pradhan, N. C. (2007). “Kinetics of epoxidation of jatropha oil with peroxyacetic and peroxyformic acid catalysed by acidic ion exchange resin," *Chemical Engineering Science* 62(15), 4065-4076. DOI: 10.1016/j.ces.2007.04.038

Gross, R. A., and Scholz, C. (2001). *Biopolymers from Polysaccharides and Agroproteins*, American Chemical Society, Washington, DC, USA. DOI: 10.1021/bk-2001-0786

Gubeladze, K. M. (1987). "The effect of plasticisers on the structure of crosslinked high-elastic materials," *Kauchuk i Rezina* 2, 29.

Huda, M. S., Drzal, L. T., Mohanty, A. K., and Misra, M. (2006). "Chopped glass and recycled newspaper as reinforcement fibers in injection molded poly(lactic acid)(PLA) composites: A comparative study," *Composites Science and Technology* 66(11-12), 1813-1824. DOI: 10.1016/j.compscitech.2005.10.015

Huda, M. S., Drzal, L. T., Mohanty, A. K., and Misra, M. (2008). "Effect of fiber surface-treatments on the properties of laminated biocomposites from poly(lactic acid)(PLA) and kenaf fibers," *Composites Science and Technology* 68(2), 424-432. DOI: 10.1016/j.compscitech.2007.06.022

Islam, M. S., Pickering, K. L., and Foreman, N. J. (2011). "Influence of alkali fiber treatment and fiber processing on the mechanical properties of hemp/epoxy composites," *Journal of Applied Polymer Science* 119(6), 3696-3707. DOI: 10.1002/app.31335

Ismail, H., Omar, N. F., and Othman, N. (2011). "The effect of kenaf fibre loading on curing characteristics and mechanical properties of waste tyre dust/kenaf fibre hybrid filler filled natural rubber compounds," *BioResources* 6(4), 3742-3756.DOI: 10.15376/biores.6.4.3742-3756

John, M. J., and Anandjiwala, R. D. (2008). "Recent developments in chemical modification and characterization of natural fiber-reinforced composites," *Polymer Composites* 29(2), 187-207. DOI: 10.1002/pc.20461

Jusoh, E. R., Ismail, M. H. S., Abdullah, L. C., Yunus, R., and Wan Abdul Rahman, W. A.(2012). "Crude palm oil as a bioadditive in polypropylene blown films," *BioResources* 7(1),859-867.DOI: 10.15376/biores.7.1.859-867

Lathi, P. S., and Mattiasson, B. (2007). "Green approach for the preparation of biodegradable lubricant base stock from epoxidized vegetable oil," *Applied Catalysis B: Environmental* 69(3-4), 207-212. DOI: 10.1016/j.apcatb.2006.06.016

Li, S.-M., Jia, N., Ma, M.-G., Zhang, Z., Liu, Q.-H., and Sun, R.-C. (2011). "Cellulose–silver nanocomposites: Microwave-assisted synthesis, characterization, their thermal stability, and antimicrobial property," *Carbohydrate Polymers* 86(2), 441-447. DOI: 10.1016/j.carbpol.2011.04.060

Li, X., Tabil, L. G., and Panigrahi, S. (2007). "Chemical treatments of natural fiber for use in natural fiber-reinforced composites: A review," *Journal of Polymers and the Environment* 15(1), 25-33. DOI: 10.1007/s10924-006-0042-3

Liu, X. Y., and Dai, G. C. (2007). "Surface modification and micromechanical properties of jute fiber mat reinforced polypropylene composites," *Express Polymer Letters* 1(5), 299-307. DOI: 10.3144/expresspolymlett.2007.43

Metzger, J. O., and Bornscheuer, U. (2006). "Lipids as renewable resources: Current state of chemical and biotechnological conversion and diversification," *Applied Microbiology and Biotechnology* 71(1), 13-22. DOI: 10.1007/s00253-006-0335-4

Mwaikambo, L. Y., and Ansell, M. P. (2002). "Chemical modification of hemp, sisal, jute, and kapok fibers by alkalization," *Journal of Applied Polymer Science* 84(12), 2222-2234. DOI: 10.1002/app.10460

Mwaikambo, L. Y. (2009). “Tensile properties of alkalised jute fibres,” College of Engineering Technology, University of Dares Salaam Research Repository.

Nevell, T. P., and Zeronian, S. H. (1985). *Cellulose Chemistry and Its Applications*, Ellis Horwood, Ltd., Chichester, England.

Ray, S. S., Okamoto, K., and Okamoto, M. (2006). “Structure and properties of nanocomposites based on poly(butylene succinate) and organically modified montmorillonite,” *Journal of Applied Polymer Science* 102(1), 777-785. DOI: 10.1002/app.23940

Razak, N. W. A., and Kalam, A. (2012*).* “Effect of OPEFB size on the mechanical properties and water absorption behaviour of OPEFB/PPnanoclay/PP hybrid composites,” *Procedia Engineering* 41, 1593-1599. DOI: 10.1016/j.proeng.2012.07.355

Robertson, M. L., Paxton, J. M., and Hillmyer, M. A. (2011). “Tough blends of polylactide and castor oil,” *ACS Applied Materials &Interfaces* 3(9), 3402-3410. DOI: 10.1021/am2006367

Rozman, H. D., Tay, G. S., Abubakar, A., and Kumar, R. N. (2001). “Tensile properties of oil palm empty fruit bunch–polyurethane composites,” *European Polymer Journal* 37(9), 1759-1765. DOI: 10.1016/S0014-3057(01)00063-5

Sahari, J., Sapuan, S. M., Ismarrubie, Z. N., and Rahman, M. Z. A. (2012). “Physical and chemical properties of different morphological parts of sugar palm fibres,” *Fibres & Textiles in Eastern Europe* 91(2), 21-24.

Sanyang, M. L., Sapuan, S. M., Jawaid, M., Ishak, M. R., and Sahari, J. (2016). “Effect of sugar palm-derived cellulose reinforcement on the mechanical and water barrier properties of sugar palm starch biocomposite films,” *BioResources* 11(2), 4134-4145. DOI:152.1.0.246

Sarin, R., Sharma, M., Sinharay, S., and Malhotra, R. K. (2007). “Jatropha–palm biodiesel blends: An optimum mix for Asia,” *Fuel* 86(10-11), 1365-1371. DOI: 10.1016/j.fuel.2006.11.040

Sears, J. K., and Darby, J. R. (1982). “Mechanism of plasticizer action,” in: *The Technology of Plasticizers*, J. K. Sears and J. R. Darby (eds.), John Wiley & Sons, Inc., New York, NY, USA, pp. 35-77.

Shibata, S., Cao, Y., and Fukumoto, I. (2005). “Press forming of short natural fiber-reinforced biodegradable resin: Effects of fiber volume and length on flexural properties,” *Polymer Testing* 24(8), 1005-1011. DOI: 10.1016/j.polymertesting.2005.07.012

Shibata, M., Teramoto, N., and Inoue, Y. (2007). “Mechanical properties, morphologies, and crystallization behavior of plasticized poly (L-lactide)/ poly (butylenesuccinate-co-L lactate) blends,” *Polymer* 24(8), 1005-1011. DOI: 10.1016/j.polymertesting.2005.07.012

Silalertruksa, T., Pongpat, P., and Gheewala, S. H. (2017). “Life cycle assessment for enhancing environmental sustainability of sugarcane biorefinery in Thailand,” *Journal of Cleaner Production* 140, 906-913. DOI: 10.1016/j.jclepro.2016.06.010

Tawakkal, I. S. M. A., Talib, R. A., Abdan, K., and Ling, C. N. (2012). “Mechanical and physical properties of kenaf-derived cellulose (KDC)-filled polylactic acid (PLA) composites,” *BioResources* 7(2), 1643-1655. DOI: 10.15376/biores.7.2.1643-1655

Thomas, S., and Pothan, L. A. (2009). *Natural Fibre Reinforced Polymer Composites: From Macro to Nanoscale*, Old City Publishing, Inc., Philadelphia, PA, USA.

Vieira, M. G. A., da Silva, M. A., dos Santos, L. O., and Beppu, M. M. (2011). "Natural-based plasticizers and biopolymer films: A review," *European Polymer Journal* 47(3), 254-263. DOI: 10.1016/j.eurpolymj.2010.12.011

Vijayarajan, S. (2013). *Continuous Blending Approach in the Manufacture of Epoxidized Soybean-plasticized Poly(lactic acid) Sheets and Films for Packaging Applications*, Master's Thesis, Michigan State University, East Lansing, MI, USA.

Wadhi, M. M., and Weliam, R. (2014). "Effect of epoxidized sunflower oil on polylactic acid properties," *Research on Chemical Intermediates* 40(1), 399-406. DOI: 10.1007/s11164-012-0971-5

Wang, Y., Ameer, G. A., Sheppard, B. J., and Langer, R. (2002). "A tough biodegradable elastomer," *Nature Biotechnology* 20(6), 602-606. DOI: 10.1038/nbt0602-602

Yang, F., Xu, C. Y., Kotaki, M., Wang, S., and Ramakrishna, S. (2004). "Characterization of neural stem cells on electrospun poly(L-lactic acid) nanofibrous scaffold," *Journal of Biomaterials Science, Polymer Edition* 15(12), 1483-1497. DOI: 10.1163/1568562042459733

Yew, G. H., Mohd Yusof, A. M., Mohd Ishak, Z. A., and Ishiaku, U. S. (2005). "Water absorption and enzymatic degradation of poly(lactic acid)/rice starch composites," *Polymer Degradation and Stability* 90(3), 488-500. DOI: 10.1016/j.polymdegradstab.2005.04.006

Article submitted: January 3, 2018; Peer review completed: April 22, 2018; Revised version received and accepted: September 18, 2019; Published: September 26, 2019.
DOI: 10.15376/biores.14.4.9001-9020