

Water Absorption Pattern and Dimensional Stability of Oil Palm Fiber–Linear Low Density Polyethylene Composites

S. Shinoj,¹ S. Panigrahi,² R. Visvanathan³

¹Directorate of Oil Palm Research, Indian Council of Agricultural Research, Pedavegi, Eluru, Andhra Pradesh 534 450, India

²Department of Agricultural and Bioresource Engineering, University of Saskatchewan, 57 Campus Drive, Saskatoon SK S7N5A9, Canada

³Department of Food and Agricultural Process Engineering, Tamil Nadu Agricultural University, Coimbatore, Tamil Nadu 641 003, India

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ABSTRACT: The water absorption pattern and associated dimensional changes and solid loss of oil palm fiber–linear low density polyethylene composites was studied. The effects of fiber size (425–840, 177–425, and 75–177 μ), fiber loading (0, 10, 20, 30, 40, and 50%), and time of immersion (192 h at an interval of 24 h) on these parameters were also studied. Alkali treatment of fibers was done to reduce the hydrophilic nature of the composites and its effect was studied. It was found that the water absorption in most of the combinations followed typical Fickian behavior. The rate of water absorption and swelling increased with fiber loading. However, alkali treatment of the fibers resulted in a reduction of water absorption at higher fiber loadings only, and composites with higher fiber sizes exhibited higher water absorption. A sharp increase in the thickness swelling was observed in the initial days of immersion,

which remained constant thereafter. The thickness swelling also increased with fiber size; however, a constant trend was not observed for the 75–177 μ fiber size. In addition to thickness swelling, composites also expanded linearly during water absorption; however, linear expansion was considerably less than thickness swelling. Higher fiber loading and alkali treatment caused more linear expansion. We observed that maximum solid loss on water immersion occurred with small-sized and also alkali-treated fiber composites. An increase in thickness and a decrease in linear dimension were observed after one sorption–desorption cycle. This irreversible change was also found to be proportional to fiber loading and alkali treatment. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1064–1075, 2010

Key words: polyethylene (PE); composites; biofibers

INTRODUCTION

The incorporation of natural fibers in polymer matrices to obtain desirable material properties has led to the development of an environmental friendly class of materials called *natural fiber composites* (NFCs). The use of natural fibers as fillers in polymeric matrices offers several advantages over conventional inorganic fillers with regard to their lower density, lower abrasiveness to processing equipment, environmentally friendly nature, lower cost, greater deformability, biodegradability, renewable nature, nontoxicity, flexible usage, high specific strength, low energy cost, positive contribution to the global carbon budget, combustibility, ease of recyclability, good thermal and insulating properties, good electrical resistance, good acoustic insulating properties, worldwide availability, and so on.^{1–6} Because of

these advantages, there is growing interest in natural fiber composites for various applications.

Oil palm is an edible oil-yielding crop cultivated in 11 million ha of land in over 42 countries around the world.⁷ An oil palm plantation produces about 55 ton/ha/year of total dry matter in the form of fibrous biomass and 5.5 ton/ha/year of oil.⁸ Among oil palm biomass, empty fruit bunches (EFBs), a waste material obtained after the fruits are stripped from fresh fruit bunches, is the major source of fiber, yielding 73% fiber.⁹ The palm oil industry has to dispose of about 1.1 ton of EFBs for every ton of oil produced.¹⁰ The current uses of this highly cellulosic material are as boiler fuel, in the preparation of fertilizers, or as mulching material.^{11,12} When left on the plantation floor, these waste materials create great environmental problems.^{11,13} The physical properties and chemical composition of the fibers extracted from oil palm EFBs, as reported by earlier researchers, are presented in Tables I and II, respectively.

Linear low density polyethylene (LLDPE) is a popular thermoplastic material used mainly for packaging applications.¹⁵ The low processing temperature (<130°C) of LLDPE makes composite

Correspondence to: S. Panigrahi (sap382@campus.usask.ca).

TABLE I
Physical Properties of the Oil Palm Fiber

Property	Value and reference
Diameter (μm)	150–500 ²⁰
Microfibrillar angle ($^\circ$)	46 ³⁰
Length-weighted fiber length (mm)	0.99 ¹³
Cell-wall thickness (μm)	3.38 ¹³
Fiber coarseness (mg/m)	1.37 ¹³
Fines (<0.2 mm; %)	27.6 ¹³
Rigidity index $[(T/D)^3 \times 10^{-4}]$	55.43 ¹³
Density (g/cc)	0.7–1.55 ²⁰

T , wall thickness; D , diameter.

fabrication possible without partial melting or annealing of the fibers.¹⁶ The high toughness of LLDPE imparts a good impact-resistant to composites. Short processing time, unlimited storage time, and solvent-free processing are other advantages of NFCs based on LLDPE.

One of the disadvantages of NFCs is its hydrophilic nature compared to pure polymers. The hydrophilic nature of natural fibers contributed by the hydroxyl groups cause increased water absorption by NFCs. The absorption of water, through the formation of hydrogen bonding, takes place in the cell wall of lignocellulosic materials, and it subsequently swells the cell wall.¹⁷ This phenomenon is reflected in changes in the dimensions of the composites. The application of NFCs in the automotive, construction, marine, and consumer goods necessitates exposure to water or high-moisture environments. Water absorption may adversely affect the physical properties of composites and also the fiber matrix interactions and may result in changes in the bulk properties, such as the dimensional stability and mechanical and electrical properties.¹⁸ However, there are treatment technologies to improve the hydrophobicity of natural fibers. Treatments used to improve fiber-matrix adhesion include chemical modification of the lignocellulosic biomass (anhydrides, epoxies, isocyanates, etc.), grafting of polymers onto the lignocellulosic biomass, and use of compatibilizers and coupling agents.¹⁹ Various treatment methods onto oil palm fibers are already discussed in detail.^{5,18,20–22} A detailed discussion of various treatments of lignocellulosic fibers in general to improve their properties was also given earlier.²³ John and Anandjiwala²⁴ reviewed developments in the chemical modification and characterization of natural-fiber-reinforced composites and concluded that one of the most common and efficient methods of chemical modification is alkali treatment of the fibers; they reported that this method has been used to treat almost all natural fibers with successful results. Alkali treatment is one treatment technology used to reduce water absorption in composites.¹⁸

Hence, in this study, we examined the time-dependent moisture sorption of oil palm fiber-LLDPE composites and associated swelling and solid loss on sorption. The dimensional stability of the composites on reconditioning of the specimens was also assessed. The effects of fiber loading, fiber size, and alkali treatment on all of these parameters were studied.

EXPERIMENTAL

Materials

Oil palm EFBs were obtained from a local palm-oil mill at Pedavegi, Andhra Pradesh, India. The fresh fruit bunches were steam-treated at a pressure of 294 kPa for 1 h before the fruits were stripped to yield EFBs in a usual process in the palm-oil milling sequence. The initial moisture content of EFB, on the order of 65–70% (wb, wet basis), was brought down to 35–40% in an electrically heated forced convection cabinet drier. Fibers were extracted from dried EFBs with a mechanical decorticator developed by Jayashree et al.,²⁵ where the EFBs were subjected to the action of rotating mechanical beaters. The extracted fibers were washed in distilled water to remove field impurities and dried in a hot-air oven at 50°C for 48 h and stored in airtight containers for the experiments. The fibers used in this experiment contained 47.6% cellulose, 14.1% lignin, 25.7% hemicellulose, and 1.5% ash. LLDPE in powder form was used in the experiments (Exxon Mobil Chemical Canada, Toronto, Canada). The properties of LLDPE were as follows: density = 0.938 g/cm³, melt flow index = 3.3 g/10 min, and melting point = 126.5°C.

Methods

Composite preparation

Alkali treatment was done by immersion of the fibers in a 5% (w/w) NaOH (technical-grade) solution for 1 h and washing thereafter in distilled water until such time that the traces of alkali were removed. An alkali concentration of 5% was selected because the mechanical properties of the composite were reported to be at a maximum at this concentration.²⁶ The washed fibers were further conditioned

TABLE II
Chemical Composition of the Oil Palm Fiber

Property	Value and reference
Cellulose (%)	65 ¹¹
Lignin (%)	19 ¹¹
Ash content (%)	2 ¹¹
Holocellulose (%)	82.4 ¹³
α -Cellulose (%)	44.2 ¹⁴
Hemicellulose (%)	33.5 ¹⁴
Extractives (hot water; %)	10 ¹¹
Solubility in cold water (30°C; %)	8 ¹¹
1% NaOH soluble (%)	20 ¹¹

at $50 \pm 1^\circ\text{C}$ for 48 h in a hot-air oven and stored in airtight containers. The fibers were shredded in a laboratory grinder, and sieve analysis was done to separate the shredded fibers into different fractions in a sieve shaker with ASTM standard test sieves. The fibers were separated into three size fractions, namely, ASTM sieve sizes 20–40 (425–840 μ), 40–80 (177–425 μ), and 80–200 (75–177 μ). The mixing of the LLDPE and palm fibers was done in a mechanical mixer equipped with helical blades rotating at 40 rpm for 10 min. The composite mixture was poured into a mold $200 \times 200 \text{ mm}^2$ in size with a 3-mm board thickness and compression-molded in a hydraulic press equipped with a water-cooling facility. The compression cycle included (1) preheating of the press to 150°C , (2) heating of the mix in a mold for 12 min under 850 kPa pressure, (3) cooling of the mold under the same pressure for 15 min, and (4) cooling of the mold at atmospheric pressure for 15 min. The specimen thickness was maintained at 3 mm.

Fiber surface morphology

The fiber surface morphology was examined with scanning electron microscopy (SEM) imaging on a JEOL JSM 840A scanning electron microscope (Peabody, MA). Fiber samples were mounted flat to double-sided adhesive carbon tape and gold-coated, rotated, and recoated to ensure that all surfaces to be imaged were conductive. The accelerator voltage was set to 20 kV, and the working distance was 15 mm. Images were acquired digitally with Gellar Microanalytical dPICT software.

Water absorption

Test specimens $77 \times 26 \times 3 \text{ mm}^3$ in size were conditioned at 50°C for 48 h, and the initial mass was noted with a precision balance with 0.01 mg of accuracy. The exact sizes of the individual specimen were measured with a digital micrometer with 0.01 mm of accuracy. The specimens were fully immersed in distilled water in a container maintained at a constant temperature of 30°C in a temperature-controlled water bath. Specimens were taken out at regular intervals of 24 h and wiped to remove surface moisture, and measurements of mass, thickness, length, and breadth were recorded for a period of 192 h. The mass gain at the time of measurement, expressed as a percentage of the initial specimen mass, was recorded as the water absorption corresponding to the time of immersion in water.

Dimensional stability

The dimensional stability of the composite specimens on water exposure was quantified in terms of

the change in dimensions. The gain in thickness, expressed as a percentage of the initial specimen thickness, was termed *thickness swelling*. The linear expansion (L_e) was calculated with the following equation:

$$L_e = \left[\frac{\frac{L_t - L_0}{L_0} + \frac{B_t - B_0}{B_0}}{2} \right] \times 100 \quad (1)$$

where L_t and B_t are the length and breadth of the specimen at time t and L_0 and B_0 are the length and breadth of the specimen measured at the beginning of the experiment. After the experiment, the specimens were reconditioned at the same temperature (50°C) and period (48 h) at which specimens were conditioned, and the differences in mass and dimensions were noted. The difference in mass between the conditioned specimens at the beginning of the experiment and the reconditioned specimens after the experiment, expressed as a percentage of the

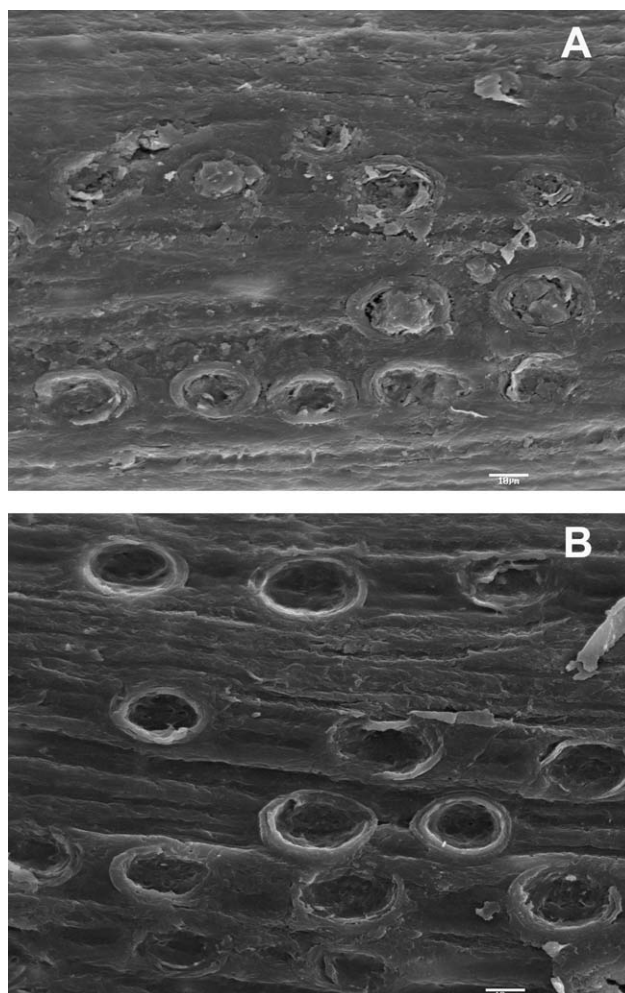


Figure 1 Microstructure of the oil palm fiber surfaces: (A) untreated fiber (750 \times) and (B) alkali-treated fiber (500 \times).

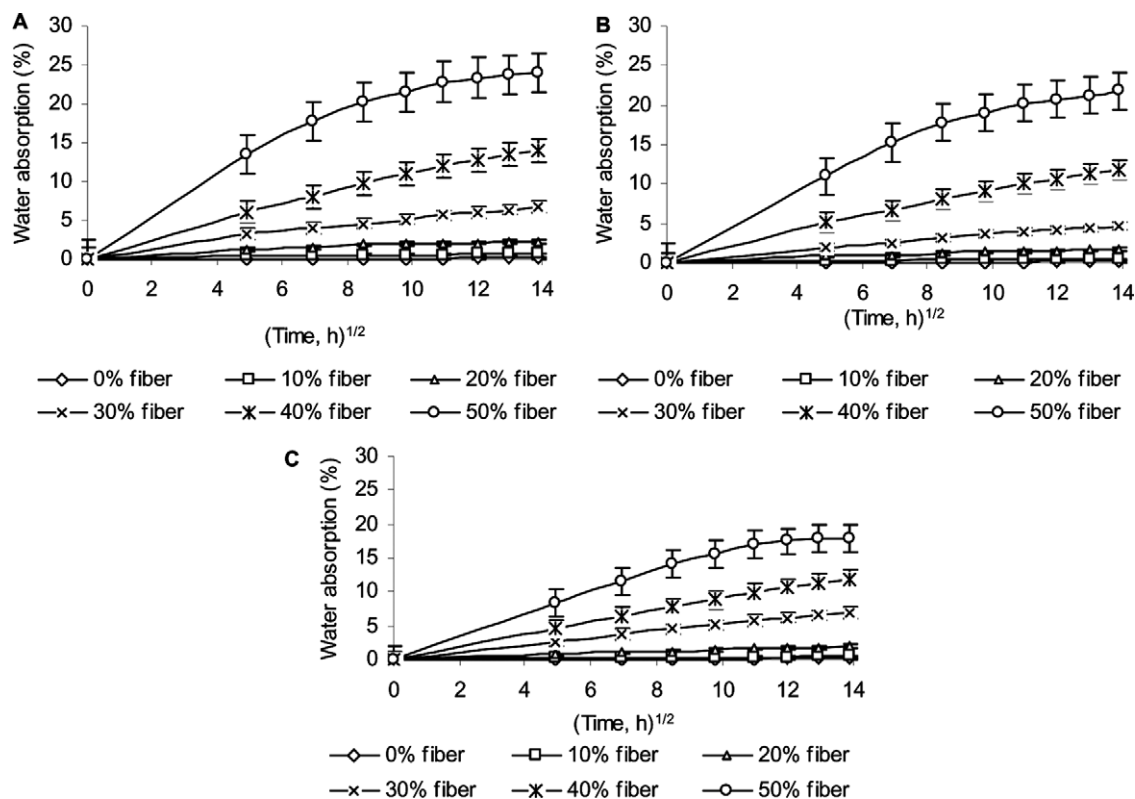


Figure 2 Water absorption of the untreated oil palm fiber-LLDPE composites with fiber sizes of (A) 425–840, (B) 177–425, and (C) 75–177 μ .

initial mass, was termed *solid loss on water absorption*. Similarly, the differences in the thickness and linear dimensions between the specimens before and after the experiment were termed *thickness swelling* during the sorption-desorption cycle and *linear contraction* during the sorption-desorption cycle, respectively. The experiment was repeated for five test specimens, and the average values are reported.

RESULTS AND DISCUSSION

Fiber surface morphology

The microstructure (SEM images) of the alkali-treated oil palm fiber surface in comparison with that of the untreated one is presented in Figure 1. The surface pits became more clear upon alkali treatment as a result of the removal of silica bodies, as reported earlier.¹³ This enhanced the fiber matrix bonding and thereby reduced the water absorption capacity of the composites.

Water absorption

The water absorption of the untreated and alkali-treated oil palm fiber-LLDPE composites at different fiber loadings and fiber sizes are presented in Figures 2 and 3, respectively. The water absorption of

the oil palm fiber-LLDPE composites was less than that of LLDPE-sisal fiber composites reported earlier.²⁷ The water absorption increased linearly with time of immersion in water during the initial days and, thereafter, reached a plateau region and remained constant; this is typical of Fickian behavior, as observed in previous studies on unsaturated polyester-oil palm fiber composites and coir fiber-low-density polyethylene/LLDPE blend composites.^{28,29} The high initial water absorption was contributed by the porous structure of the oil palm fiber, which transported the water via the capillaries in the fiber strands into gaps and flaws at the interfaces between the matrix and fibers.³⁰ The rate of water absorption of the oil palm fiber-LLDPE composites increased with fiber loading. The addition of more hydrophilic oil palm fiber caused a deviation from the hydrophobic nature of the composites, and such deviation was proportional to the amount of fiber added. Generally, composites with a higher proportion of natural fiber absorb more water than those with a lower proportion because of the cellulose, lignin, and hemicellulose contents of the fibers, which possess polar hydroxyl groups in their structure that can form hydrogen bonds with water. A similar trend was observed for natural rubber-oil palm fiber composites by Jacob et al.³¹ In another study, the water absorption of polyurethane-oil

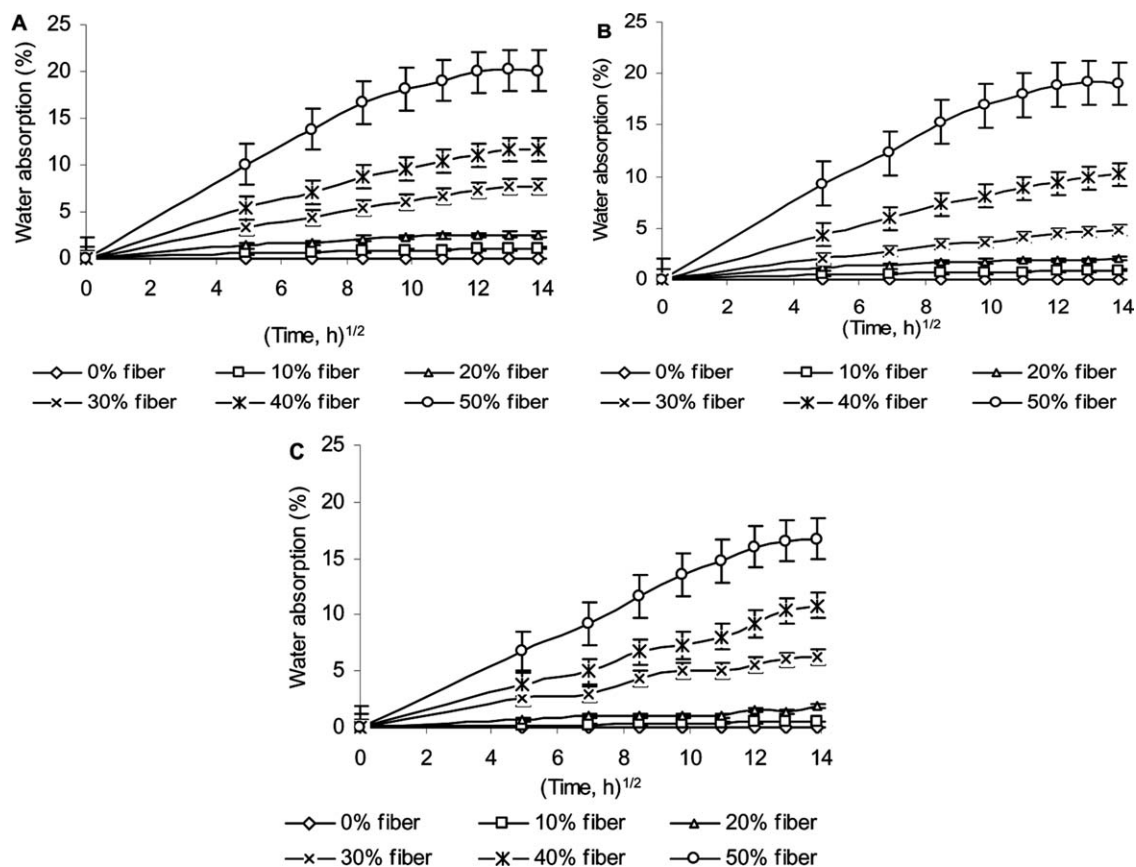


Figure 3 Water absorption of the alkali-treated oil palm fiber-LLDPE composites with fiber sizes of (A) 425–840, (B) 177–425, and (C) 75–177 μ .

palm fiber composites increased sharply on the 1st day of immersion and remained constant for the next 5 days, and the composites with higher fiber contents absorbed more water.³⁰ For the same study, it was also reported that composites with 75% fiber content absorbed 55% water and composites with 65% fiber absorbed 48% water on the 1st day of immersion. In a similar study, it was found that coir fiber-low-density polyethylene/LLDPE composites absorbed 5.5% water at the end of 200 h of immersion in water at 25°C.²⁹

Alkali treatment of the fibers reduced the water absorption of the composites only at the higher fiber loadings of 40 and 50%. However, at low fiber loadings, both the alkali-treated and untreated fiber composites exhibited almost the same water absorption. This finding partially agreed with the opinion of Sreekala et al.¹⁸ that alkali treatment of fibers reduces the water absorption of composites in comparison with other chemical treatments. Alkali treatment of fibers has three effects, namely, fibrillation or breaking down of the fibers into smaller ones, removal of the amorphous waxy cuticle layer, and activation of hydroxyl groups.^{18,31} Fibrillation provides a large surface area, which, coupled with the activation of hydroxyl groups, imparts better me-

chanical interlocking between fiber and matrix and, thus, reduces water absorption. The removal of the waxy cuticle layer, which holds water molecules, also reduces water absorption. However, in case of the oil palm fiber-LLDPE composites, these effects were not significant at low fiber loadings, as the concentration of the fibers were low enough to impart a difference between the alkali-treated and untreated fibers.

Composites with higher fiber sizes exhibited higher water absorption in both the untreated and alkali-treated fiber composites. Interestingly, the difference in water absorption between fiber sizes was predominant in the alkali-treated fiber composites. In case of the untreated fiber composites, fiber size did not cause a difference in the water absorption at lower levels of fiber loading. The void spaces around the fibers due to poor mixing of the composite mixture in the long fibers would have caused the rapid penetration of water, which explained the reason for the high water absorption in the long-fiber composites. A similar trend was observed for wood flour-plastic composites.³² The effect of fiber size coupled with the effect of alkali treatment in the reduction of water absorption may have been the reason for the significant difference in the water absorption

TABLE III
Water Sorption Constants of the LLDPE–Oil Palm Fiber (Alkali-Treated) Composites at Different Fiber Loadings and Fiber Sizes

Fiber content (%)	k	n	R^2	Standard error
Fiber size = 425–840 μ				
10	0.166	0.349	0.997	0.010
20	0.214	0.305	0.951	0.042
30	0.115	0.422	0.991	0.022
40	0.156	0.365	0.986	0.026
50	0.211	0.308	0.945	0.046
Fiber size = 177–425 μ				
10	0.193	0.319	0.990	0.018
20	0.243	0.280	0.941	0.044
30	0.124	0.408	0.995	0.017
40	0.134	0.395	0.990	0.022
50	0.186	0.331	0.956	0.043
Fiber size = 75–177 μ				
10	0.068	0.524	0.986	0.030
20	0.086	0.470	0.782	0.118
30	0.104	0.443	0.967	0.044
40	0.066	0.530	0.989	0.028
50	0.109	0.435	0.983	0.032

between fiber sizes in the alkali-treated fiber composites in this study. The effect of fiber size on water absorption of the untreated fiber composites was not predominant at low fiber loadings, as the concentration of fibers was not high enough to make a difference.

Kinetics of water absorption

Water absorption in polymeric composites is mainly due to the direct diffusion of water molecules into the polymer chains, capillary transport into cracks, flaws in the fiber–matrix interface, and absorption into the exposed fiber strands. In general, water transport behavior in polymer composites can be Fickian diffusion, relaxation controlled and non-Fickian, or anomalous, which can be identified by the shape of the sorption curve represented by the following equation:³³

$$\frac{M_t}{M_m} = kt^n \quad (2)$$

where M_t is the moisture content at time t , M_m is the moisture content at equilibrium, and k and n are constants. The value of k gives an idea about the extent of the polymer–solvent interaction, and the value of n determines the mode of the sorption mechanism.³⁴ For Fickian water transport, $n = 0.5$; for relaxation controlled water transport, $n \geq 1$; and for non-Fickian or anomalous transport, $0.5 < n < 1.0$. To study the kinetic parameters n and k , the experimental water sorption data was fitted into eq. (2) with Sigmaplot 6.0 (Systat-Software, San Jose, CA). The values of n and k obtained for the alkali-treated and untreated fiber composites are summarized in

Tables III and IV, respectively. The composites fabricated with the alkali-treated fibers exhibited Fickian behavior, as evident from n values close to 0.5, except for the composites with 10 and 40% fiber contents (fiber size = 75–177 μ), for which n was found to be between 0.5 and 1, which indicated the water transport to be non-Fickian. Similarly, in the untreated fiber composites, Fickian behavior was also observed, except for some treatments. At 10% loading of 177–425- μ fibers, the water transport behavior was non-Fickian, and interestingly, for 20% fiber loading, a relaxation mechanism was observed. Most authors have reported Fickian diffusion as the predominant mechanism of water transport in composites.^{29,35,36} However, Tsotsis and Weitsman³⁷ reported that the moisture absorption in composites is generally non-Fickian. They also mentioned that in most studies and specifications, this deviation is ignored, although many previous studies on diffusion behavior in polymers and composites have been performed. Deviation from Fickian behavior was also reported for pineapple leaf fiber–polyester composites.³⁸ The deviation from Fickian behavior may be due to the additional mechanism observed as a result of fiber swelling, fiber matrix interface weakening, microcracking, and leaching.³⁶

Water diffusivity

The diffusion coefficient (D_x) represents the ability of water molecules to penetrate into the composite. D_x was determined by the method developed by Shen and Springer,³⁹ which assumes one-dimensional unsteady diffusion through the thickness of the composite sheet, where the flat surface is much

TABLE IV
Water Sorption Constants of the LLDPE–Oil Palm Fiber (Untreated) Composites at Different Fiber Loadings and Fiber Sizes

Fiber content (%)	k	n	R^2	Standard error
Fiber size = 425–840 μ				
10	0.397	0.178	0.976	0.018
20	0.250	0.271	0.977	0.025
30	0.155	0.363	0.997	0.011
40	0.127	0.404	0.997	0.012
50	0.280	0.252	0.952	0.036
Fiber size = 177–425 μ				
10	0.951	0.602	0.999	0.076
20	0.991	1.305	0.999	0.045
30	0.131	0.399	0.991	0.022
40	0.122	0.411	0.997	0.012
50	0.230	0.290	0.957	0.038
Fiber size = 75–177 μ				
10	0.158	0.359	0.980	0.028
20	0.103	0.446	0.993	0.020
30	0.102	0.446	0.998	0.011
40	0.100	0.449	0.998	0.011
50	0.178	0.341	0.960	0.042

TABLE V
Diffusion Parameters and Maximum Linear Expansion of the LLDPE–Oil Palm Fiber (Alkali-Treated) Composites at Different Fiber Loadings and Fiber Sizes

Fiber content (%)	EMC (%)	$D \times 10^{-12}$ (M ² /s)	S	$P \times 10^{-12}$ (M ² /s)	Maximum linear expansion (%)
Fiber size = 425–840 μ					
10	1.030	2.50	0.011	0.027	0.07
20	2.550	2.13	0.029	0.062	0.19
30	7.520	3.35	0.080	0.267	0.87
40	11.420	2.67	0.123	0.329	1.30
50	20.070	2.16	0.204	0.440	2.55
Fiber size = 177–425 μ					
10	0.84	2.15	0.009	0.019	0.19
20	1.95	1.82	0.022	0.040	0.50
30	4.64	3.13	0.050	0.156	0.69
40	9.82	3.11	0.108	0.337	1.30
50	19.01	2.43	0.194	0.470	2.63
Fiber size = 75–177 μ					
10	0.48	4.16	0.031	0.130	0.31
20	1.6	3.14	0.019	0.060	0.68
30	5.95	3.55	0.049	0.173	1.21
40	10.11	4.21	0.099	0.415	1.60
50	16.45	3.57	0.171	0.612	2.00

greater than the thickness. This method uses eq. (3). The analytical solution for this equation for a plane sheet with uniform initial moisture concentration along the thickness is given in eq. (4).⁴⁰

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial z^2} \quad (3)$$

where C is the moisture concentration at time, t along coordinate direction z .

$$M_t = 4M_m \sqrt{\frac{D_x}{\pi h^2}} \sqrt{t} \quad (4)$$

where M_t is the average moisture content of the composite sheet at time t , M_m is the moisture content of the sheet at equilibrium, and h is the thickness of the sheet. A modified equation including a correction for the edge effect is presented as follows.⁴⁰

$$D_x = \pi \left[\frac{\theta}{4M_m} \right]^2 \left[1 + \left(\frac{h}{l} \right) + \left(\frac{h}{b} \right) \right]^2 \quad (5)$$

where θ is the slope of the linear portion of M_t versus $\frac{\sqrt{t}}{h}$ plot and l and b are the length and breadth of the composite sheet, respectively.

The thermodynamic solubility (S) is related to the extent of absorption of water, which is estimated with eq. (6).³⁵

$$S = \frac{W_w}{W_c} \quad (6)$$

where W_w is the mass of water absorbed by the composite sheet at equilibrium and W_c is the initial mass of the composite sheet.

The permeability (P) of the composite specimens, which represents a net effect of diffusion and sorption was estimated with eq. (7)

$$P = D_x \times S \quad (7)$$

Water absorbed at equilibrium (EMC), D_x , S , and permeability (P) values for the alkali-treated and untreated oil palm fiber–LLDPE composites are presented in Tables V and VI, respectively. An increase in fiber loading caused an increase in D_x ; however, a reduction was observed after 40% fiber loading. The values of P and S also increased with fiber loading. At lower fiber loadings, the dispersion of fiber was lower; hence, the D_x , sorption coefficient, and permeability coefficient values were lower. As the fiber content increased, because of the high void content and fiber–fiber interaction, the fiber–matrix adhesion decreased, which increased the D_x , sorption coefficient, and permeability coefficient values.⁴¹ Higher values of D_x were observed for composites fabricated with small fibers; however, the solubility exhibited a reverse trend. Interestingly, the D_x values were slightly higher for the alkali-treated fiber composites than for the untreated composites.

Thickness swelling

Poor absorption resistance of lignocellulosic fibers leads to a moisture build-up in the fiber cell wall (fiber swelling) and also in the fiber–matrix interface. This is responsible for the changes in the dimensions of cellulose-based composites upon immersion in water. The swelling of the fiber induces stress on the surrounding matrix and leads to microcracks, which

TABLE VI
Diffusion Parameters and Maximum Linear Expansion of the LLDPE–Oil Palm Fiber (Untreated) Composites at Different Fiber Loadings and Fiber Sizes

Fiber content (%)	EMC (%)	$D \times 10^{-12}$ (M ² /s)	S	$P \times 10^{-12}$ (M ² /s)	Maximum linear expansion (%)
Fiber size = 425–840 μ					
10	0.680	0.90	0.016	0.014	0.00
20	2.240	1.68	0.024	0.040	0.13
30	6.340	2.54	0.071	0.181	0.29
40	13.480	3.06	0.147	0.450	0.78
50	23.690	1.56	0.242	0.378	1.32
Fiber size = 177–425 μ					
10	0.440	1.78	0.005	0.009	0.05
20	1.630	2.45	0.018	0.045	0.04
30	4.340	3.05	0.049	0.149	0.26
40	11.260	3.16	0.124	0.392	0.57
50	21.260	1.99	0.222	0.442	1.19
Fiber size = 75–177 μ					
10	0.440	2.66	0.005	0.013	0.05
20	1.820	3.63	0.021	0.077	0.07
30	6.570	3.60	0.076	0.274	0.59
40	11.320	3.59	0.124	0.446	0.74
50	17.730	2.52	0.178	0.449	1.84

cause the composite to fail catastrophically. Thus, the fiber–matrix adhesion becomes weak, and the dimensional stability of composites are affected, particularly for outdoor applications.⁴²

Plots of the thickness swelling of the untreated and alkali-treated oil palm fiber–LLDPE composite specimens immersed in distilled water against time are presented in Figures 4 and 5, respectively. A

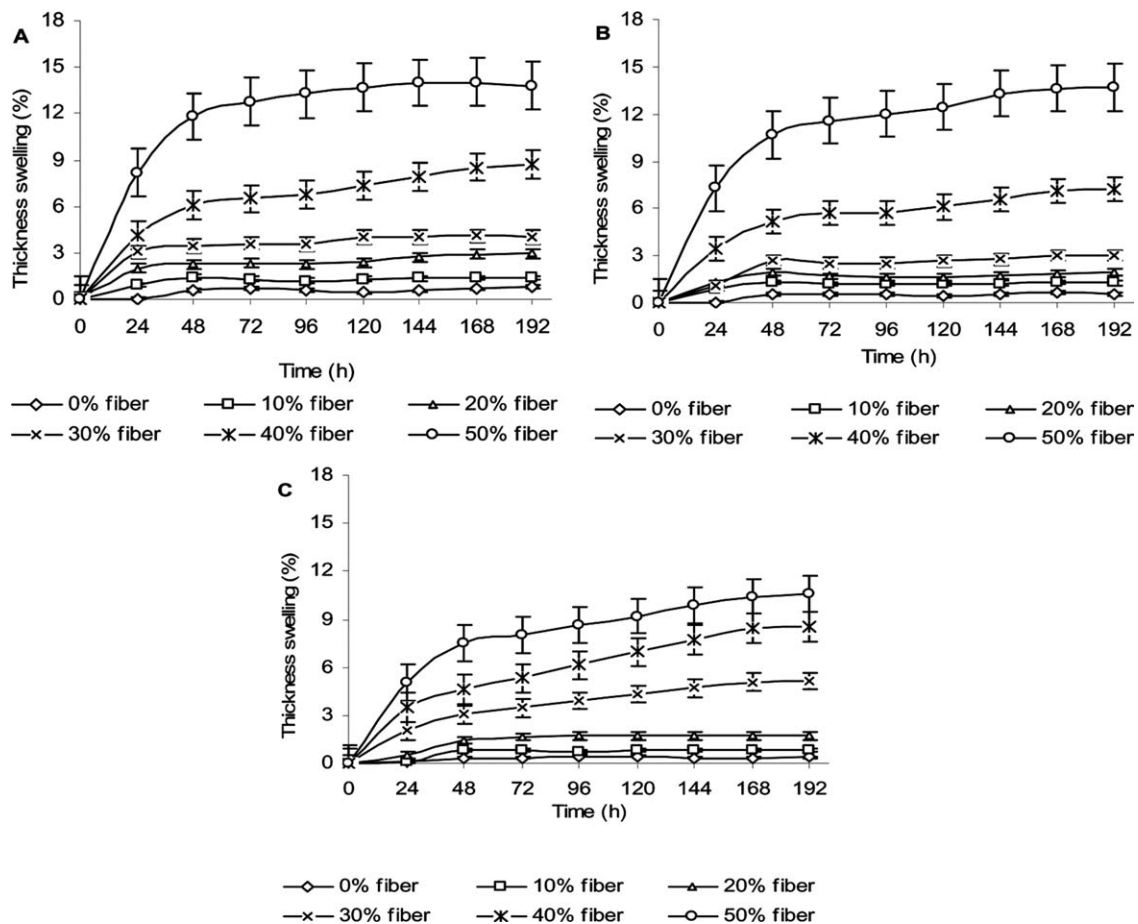


Figure 4 Thickness swelling of the untreated oil palm fiber–LLDPE composites with fiber sizes of (A) 425–840, (B) 177–425, and (C) 75–177 μ .

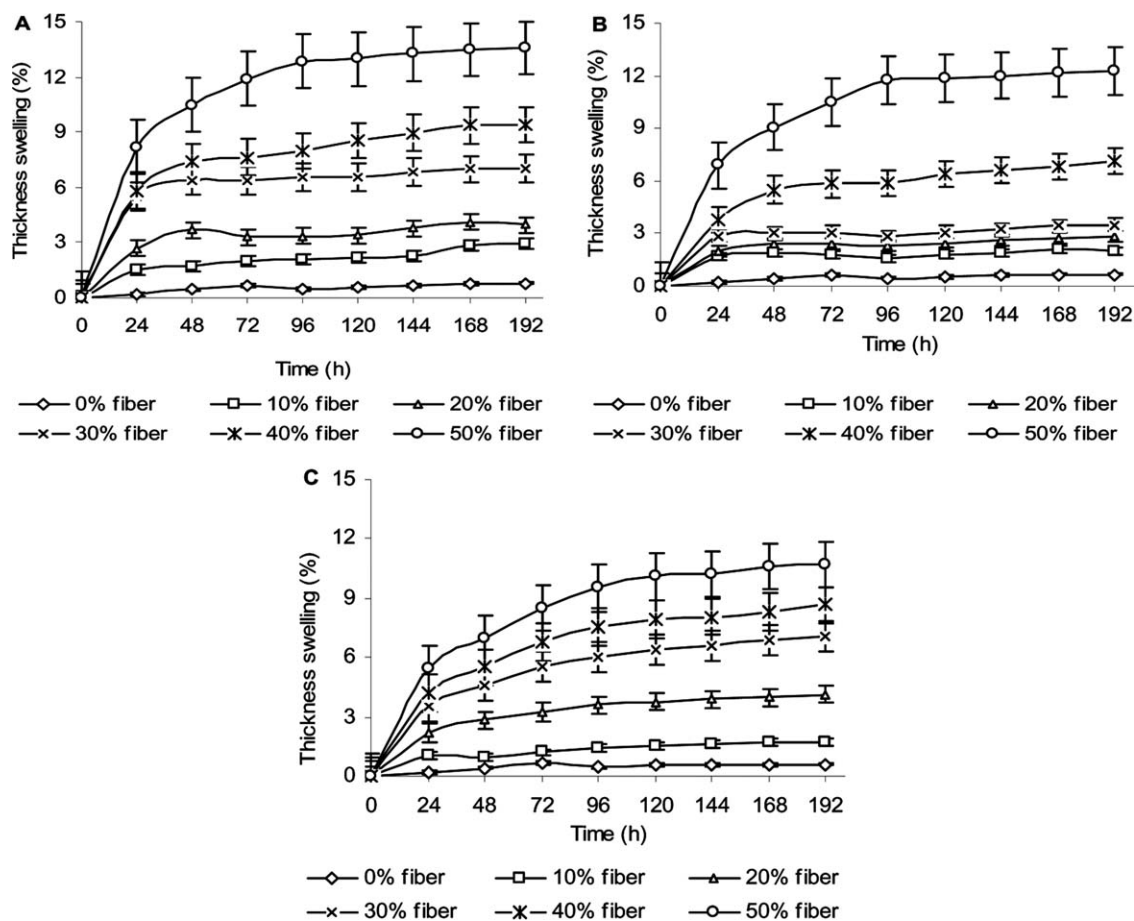


Figure 5 Thickness swelling of the alkali-treated oil palm fiber-LLDPE composites with fiber sizes of (A) 425–840, (B) 177–425, and (C) 75–177 μ .

sharp increase in swelling was observed initially at all fiber loadings, and thereafter, the swelling remained constant. The thickness swelling increased as the percentage fiber loading increased. As the swelling was due to the absorption of water by hydrogen bonding of the lignocellulosic material in the cell wall, the addition of more lignocellulosic material increased the swelling. Interestingly, the composites made from the alkali-treated fibers exhibited more swelling compared to untreated fiber composites at all fiber loadings except 50%, whereas the water absorption was lower for the alkali-treated fiber composites at low fiber loadings. Alkali treatment caused the washing out of the hemicellulosic portion in the fibers, which was responsible for water absorption and resulted in a reduction in the overall water absorption.⁴³ However, the water molecules absorbed in the free space caused by the washing out of the hemicellulose forced cellulose molecules apart and destroyed the rigidity of the cellulose structure, which caused swelling of the fibers. The LLDPE matrix, because of its elastic nature, adjusted fiber swelling and caused an increased overall thickness swelling for the alkali-treated specimens. However, at a fiber loading of 50%, swelling

due to water absorption superseded that caused by alkali treatment.

The thickness swelling of the composites with fiber sizes of 177–425 μ was less than that of composites with fiber sizes of 425–840 μ . The same trend was exhibited by both alkali-treated and untreated fiber composites. The higher water absorption exhibited by the larger size fibers was the reason for the greater thickness swelling, as cell-wall swelling was directly proportional to the quantity of absorbed water. However, no constant trend was observed in the 75–177 μ sized fibers for an unknown reason.

Linear expansion

All of the specimens expanded both along their length and breadth. The linear expansion of the composite specimens, noted at specific time intervals for a period of 192 h, indicated that similar to thickness swelling, the linear expansion also initially increased sharply and became constant thereafter. The linear expansion achieved at equilibrium is termed *maximum linear expansion*, and the values are provided in Tables V and VI for the alkali-treated and untreated composites, respectively. Composite

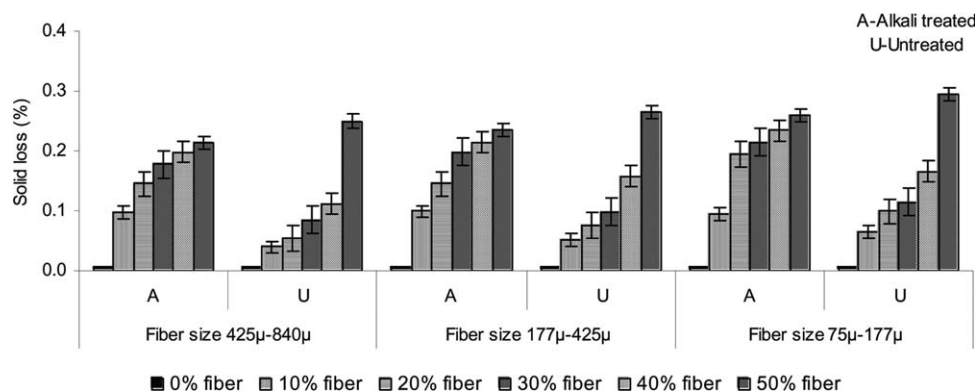


Figure 6 Solid loss from the oil palm fiber-LLDPE composites on water immersion.

specimens with higher fiber loadings exhibited more expansion. Interestingly, linear expansion was considerably less than the thickness swelling. During the compression molding of the thermoplastic composites, the majority of the fibers were suspended in the molten polymer with its long axis parallel to the liquid surface. This led to orientation of fibers parallel to the finished composite surface. Swelling of the palm fiber may have been more perpendicular to the cellulose chains rather than parallel to the fiber axis, as in case of flax fiber.⁴⁴ This caused more thickness swelling compared to linear expansion. Similar to the trend observed for the thickness swelling, the alkali-treated fiber composites exhibited a higher linear expansion at all fiber loadings. The reason for thickness swelling held good for this trend also. However, a constant trend could not be observed for the expansion between different fiber sizes.

Solid loss

We determined the solid loss through the moisture soluble substances by drying the specimen after the water absorption tests in a hot-air oven at 50°C until a constant mass was reached. If the posttest oven-dry mass was lower than the preconditioned mass, the difference was considered as soluble matter lost during the testing process. For such materials, the effective equilibrium moisture content is calculated by the addition of the mass of the moisture-soluble matter to the mass of the specimen at the establishment of effective moisture equilibrium. This corrected equilibrium moisture mass is used to calculate the percentage mass change, and the resulting values are recorded as the equilibrium moisture content.⁴⁵ However, in this case, the solid loss was found to be negligible compared to the equilibrium moisture content, and hence, we did not account for it in the calculations.

The solid loss of the composite specimens after immersion in distilled water for 192 h is presented in Figure 6. The solid loss increased with fiber con-

tent as the fraction of low-molecular-weight soluble materials, such as short-chain hemicellulose, pectin, and other soluble sugars, increased with fiber loading. It was also observed that the maximum solid loss occurred in composites prepared from small-size fibers. The increased surface area of the smaller size fractions exposed the soluble substances to the absorbed water and caused more solid loss. The solid loss from the alkali-treated fiber composites was slightly high compared to untreated fiber composites.

Change in the dimensions during the absorption-desorption cycle.

On reconditioning/drying the specimens after the water absorption experiment, the initial dimensions could not be regained. There was an increase in thickness and a decrease in the linear dimensions from the initial dimensions after one sorption-desorption cycle. Hydrophilic fibers were responsible for the water absorption and swelling/expansion of the composites. On desorption, the fibers contracted and left cavities (Fig. 7) along the fiber matrix interface with its broader axis along the thickness because

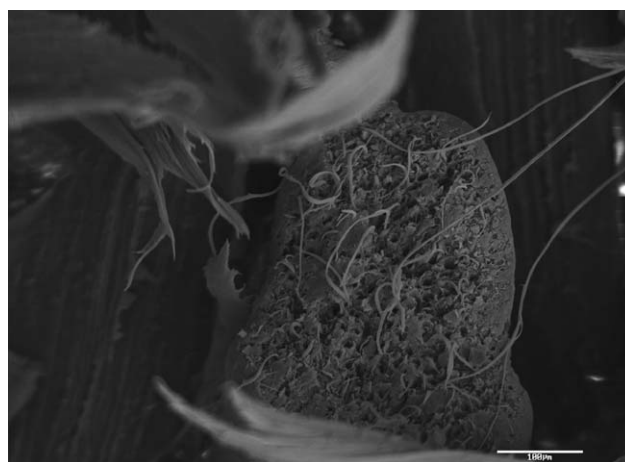


Figure 7 SEM image of the composite sample showing the fiber contraction and resulting void on desorption.

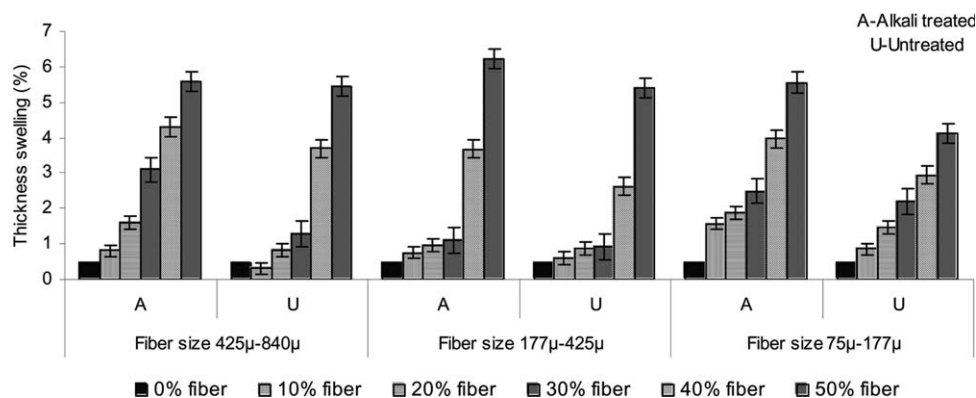


Figure 8 Thickness swelling of the oil palm fiber-LLDPE composites after one sorption-desorption cycle.

of the diametrical swelling of the fibers. Because of this, the composites could not regain their initial thickness. However, the linear expansion was meager compared to the thickness swelling on sorption, which caused a linear contraction. The changes in thickness and linear dimensions on sorption-desorption cycle are presented in Figures 8 and 9, respectively. The change in the dimensions was proportional to fiber loading. The composites made with alkali-treated fibers exhibited more deviation from the original dimensions on desorption, as was evident from the fact that more swelling/expansion was observed for the alkali-treated fiber composites. However, a consistent trend was not observed between fiber sizes, the reason for which is unknown.

CONCLUSIONS

The study of the water absorption pattern and associated dimensional changes of natural fiber composites are important for applications in damp environments, as the addition of natural fibers to polymers increases their hygroscopic nature. Hence, the water sorption and dimensional stability of oil palm fiber-LLDPE composites fabricated by the compression-molding technique were studied. The fiber size (425–840, 177–425, and 75–177 μ), fiber loading (0, 10, 20,

30, 40, and 50%), and time of immersion (192 h at an interval of 24 h) were varied, and the effects of these variables were assessed. Composites fabricated with the alkali-treated fibers exhibited Fickian behavior, as evident from n values close to 0.5. However, for 10 and 40% fiber content (fiber size = 75–177 μ), n was found between 0.5 and 1, which indicated the water transport to be non-Fickian. An increase in fiber loading increased D_{xt} ; however, a reduction was observed after 40% fiber loading. The values of permeability and solubility also increased with fiber loading. The rate of water absorption increased with fiber loading. However, alkali treatment of the fibers resulted in a reduction in the water absorption at higher fiber loadings, whereas not much difference was observed at low fiber loadings. Composites with higher fiber sizes exhibited higher water absorption; the difference in absorption between fiber sizes was predominant for the alkali-treated fibers. A sharp increase in the thickness swelling was observed in the initial days of immersion, and the thickness swelling remained constant thereafter. The thickness swelling increased with fiber loading, and composites made from alkali-treated fibers exhibited more swelling compared to the untreated fiber composites, except at 50% fiber loading. The thickness swelling also increased with fiber size; however, a constant

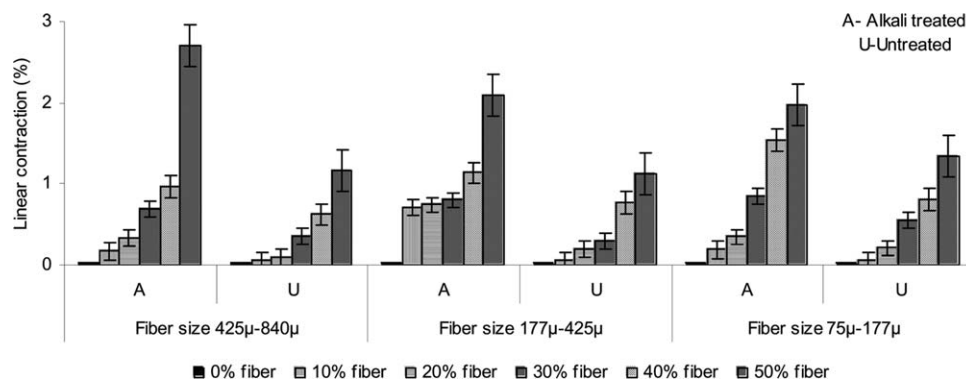


Figure 9 Linear contraction of the oil palm fiber-LLDPE composites after one sorption-desorption cycle.

trend was not observed for the 75–177 μ fiber size. In addition to thickness swelling, the composites expanded linearly during water absorption; however, the linear expansion was considerably less than the thickness swelling. Similar to the thickness swelling, the linear expansion was sharp in the initial days of sorption and leveled off in subsequent days. Higher fiber loading and alkali treatment caused more linear expansion. Maximum solid loss on water immersion occurred for small-sized-fiber-made composites. Alkali treatment of the fibers also increased solid loss. An increase in the thickness and a decrease in the linear dimensions of the composite specimens were observed after one sorption-desorption cycle. This irreversible change was found to be proportional to fiber loading and alkali treatment.

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References

- Raju, G.; Ratnam, C. T.; Ibrahim, N. A.; Rahman, M. Z. A.; Yunus, W. M. Z. W. *J Appl Polym Sci* 2008, 110, 368.
- Rozman, H. D.; Tay, G. S.; Abusamah, A. *J Wood Chem Tech* 2003, 23, 249.
- Yousif, B. F.; El-Tayeb, N. S. M. *Proc Inst Mech Eng Part J: J Eng Tribol* 2008, 222, 637.
- Hill, C. A. S.; Khalil, H. P. S. A. *J Appl Polym Sci* 2000, 78, 1685.
- Sreekala, M. S.; Kumaran, M. G.; Geethakumariam, M. L.; Thomas, S. *Adv Compos Mater* 2004, 13, 171.
- Hariharan, A. B. A.; Khalil, H. P. S. A. *J Compos Mater* 2005, 39, 663.
- Khalil, H. P. S. A.; Siti, M. A.; Ridzuan, R.; Kamarudin, H.; Khairul, A. *Polym Plast Technol Eng* 2008, 47, 273.
- Hasamudin, W.; Soom, R. M. *Malaysian Palm Oil Board Inf Ser* 2002, 171, 1.
- Wirjosentono, B.; Guritno, P.; Ismail, H. *Int J Polym Mater* 2004, 53, 295.
- Karina, M.; Onggo, H.; Abdullah, A. H. D.; Syampurwadi, A. *J Biol Sci* 2008, 8, 100.
- Sreekala, M. S.; Kumaran, M. G.; Thomas, S. *J Appl Polym Sci* 1997, 66, 821.
- Singh, G.; Manohan, S.; Kanopathy, K. In *Proceedings of the 1981 International Oil Palm Conference*; Incorporated Society of Planters: Kuala Lumpur, Malaysia, 1982; p 367.
- Law, K. N.; Daud, W. R. W.; Ghazali, A. *BioResources* 2007, 2, 351.
- Khalid, M.; Ratnam, C. T.; Chuah, T. G.; Ali, S.; Choong, T. S. Y. *Mater Des* 2008, 29, 173.
- Zheng, Y.; Yanful, E. K.; Bassi, A. S. *Crit Rev Biotechnol* 2005, 25, 243.
- Lee, S. G.; Joo, C. W. *Polym Polym Compos* 1999, 7, 195.
- Rozman, H. D.; Lai, C. Y.; Ismail, H.; Ishak, Z. A. M. *Polym Int* 2000, 49, 1273.
- Sreekala, M. S.; Kumaran, M. G.; Thomas, S. *Compos A* 2002, 33, 763.
- Khalil, H. P. S. A.; Ismail, H.; Rozman, H. D.; Ahamad, M. N. *Eur Polym J* 2001, 37, 1037.
- Ibrahim, N. A.; Ilaiwi, F. A.; Rahman, M. Z. A.; Ahmad, M. B.; Dahlan, K. Z. M.; Yunus, W. M. Z. W. *J Polym Res* 2005, 12, 173.
- Sreekala, M. S.; Kumaran, M. G.; Joseph, R.; Thomas, S. *Compos Sci Technol* 2001, 61, 1175.
- Raju, G.; Ratnam, C. T.; Ibrahim, N. A.; Rahman, M. Z. A.; Yunus, W. M. Z. W. *Polym Plast Technol Eng* 2007, 46, 949.
- Belgacem, M. N.; Gandini, A. *Compos Interfaces* 2005, 12, 41.
- John, M. J.; Anandjiwala, R. D. *Polym Compos* 2008, 29, 187.
- Jayashree, E.; Mandal, P. K.; Madhava, M.; Kamaraj, A.; Sireesha, K. In *Proceedings of the 15th Plantation Crops Symposium—Placrosym XV*; Central Coffee Research Institute: Chikmagalur, India, 2002; p 10.
- Joseph, S.; Joseph, K.; Thomas, S. *Int J Polym Mater* 2006, 55, 925.
- Mokoena, M. A.; Djokovi, V.; Luyt, A. S. *J Mater Sci* 2004, 39, 3403.
- Khalil, H. P. S. A.; Azura, M. N.; Issam, A. M.; Said, M. R.; Adawi, T. *J Reinf Plast Compos* 2008, 27, 16.
- Choudhury, A.; Kumar, S.; Adhikari, B. *J Appl Polym Sci* 2007, 106, 775.
- Badri, K. H.; Amin, K. A. M.; Othman, Z.; Manaf, H. A.; Khalid, N. K. *Polym Int* 2006, 55, 190.
- Jacob, M.; Varughese, K. T.; Thomas, S. *Biomacromolecules* 2005, 6, 2969.
- Migneault, S.; Koubaa, A.; Erchiqui, F.; Chaala, A.; Englund, K.; Wolcott, M. P. *Compos A* 2009, 40, 80.
- Espert, A.; Vilaplana, F.; Karlsson, S. *Compos A* 2004, 35, 1267.
- Tay, G. S.; Rozman, H. D. *J Appl Polym Sci* 2008, 108, 995.
- Adhikary, K. B.; Pang, S.; Staiger, M. P. *Chem Eng J* 2008, 142, 190.
- Panthapulakkal, S.; Sain, M. *J Compos Mater* 2007, 41, 1871.
- Tsotsis, T. K.; Weitsman, Y. J. *Mater Sci Lett* 1994, 13, 1635.
- Devi, L. U.; Joseph, K.; Nair, K. C. M.; Thomas, S. *J Appl Polym Sci* 2004, 94, 503.
- Shen, C. H.; Springer, G. S. *J Compos Mater* 1976, 10, 2.
- Gupta, K. M.; Pawar, S. J. *Mater Sci Eng* 2005, 412, 78.
- Sreekumar, P. A.; Albert, P.; Unnikrishnan, G.; Joseph, K.; Thomas, S. *J Appl Polym Sci* 2008, 109, 1547.
- Khalil, H. P. S. A.; Hanida, S.; Kang, C. W.; Fuaad, N. A. N. *J Reinf Plast Compos* 2007, 26, 203.
- Bismark, A.; Askargorta, A. I.; Springer, J. *Polym Compos* 2002, 23, 872.
- Stamboulis, A.; Baillie, C. A.; Garkhail, S. K.; Melick, V. H. G. H.; Peijs, T. *Appl Comp Mater* 2000, 7, 273.
- Leman, Z.; Sapuan, S. M.; Saifol, A. M.; Maleque, M. A.; Ahmad, M. M. H. M. *Mater Des* 2008, 29, 1666.