Carbohydrate Polymers 101 (2014) 11–19

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Characteristics of starch-based biodegradable composites reinforced with date palm and flax fibers

Hamdy Ibrahim[a,*], Mahmoud Farag[b], Hassan Megahed[a], Sherif Mehanny[a]

[a] Department of Mechanical Design and Production, Faculty of Engineering, Cairo University, Giza 12613, Egypt
[b] Department of Mechanical Engineering, School of Sciences and Engineering, The American University in Cairo, New Cairo, Cairo 11835, Egypt

ARTICLE INFO

Article history:
Received 25 January 2013
Received in revised form 15 August 2013
Accepted 20 August 2013
Available online 28 August 2013

Keywords:
Biodegradable composites
Date palm fibers
Flax fibers
Starch matrix
Hybrid composites

ABSTRACT

The aim of this work is to study the behavior of completely biodegradable starch-based composites containing date palm fibers in the range from 20 to 80 wt%. Hybrid composites containing date palm and flax fibers, 25 wt% each, were also examined. The composites were preheated and then hot pressed at 5 MPa and 160 °C for 30 min. SEM investigation showed strong adhesion between fibers and matrix. Density measurements showed very small void fraction (less than 0.142%) for composites containing up to 50 wt% fiber content. Increasing fiber weight fraction up to 50 wt% increased the composite static tensile and flexural mechanical properties (stiffness and strength). Composite thermal stability, water uptake and biodegradation improved with increasing fiber content. The present work shows that starch-based composites with 50 wt% fibers content have the optimum mechanical properties. The hybrid composite of flax and date palm fibers, 25 wt% each, has good properties and provides a competitive eco-friendly candidate for various applications.

1. Introduction

Recent research has shown that composites of bio-based polymers reinforced with natural fibers provide an eco-friendly alternative to composites of non-renewable petroleum-based polymers and non-degradable fibers (Satyanarayana, Arizaga, & Wypych, 2009).

Starch based polymers represent the most extensively studied biodegradable polymer (Satyanarayana et al., 2009). Starch is a natural hydrophilic carbohydrate material which is renewable, biodegradable and inexpensive. After plasticizing with water and glycerol, starch exhibits polymerization properties for extrusion, injection and compression molding (Curveloa, Carvalhoa, & Agnelli, 2001; Liu, Xie, Yu, Chen, & Li, 2009; Rodriguez-Gonzalez, Ramsay, & Favis, 2003). Gelatinization is the basic endothermic process of converting the semi-crystal structure of native starch to amorphous state before transforming to thermoplastic starch (Liu et al., 2009). The gelatinization process depends mainly on the water content and heating temperature of the starch (Atwell, Hood, Lineback, Varriano, & Zobel, 1988). The addition of glycerol reduces both the melting point and glass transition temperature (Tg), in addition to delaying the starch aging process and consequently reducing the final product embrittlement resulting from retrogradation (Dufresne & Vignon, 1998; Jagannath, Jayaraman, Arya, & Somashekar, 1998; Satyanarayana et al., 2009).

Wollerdorfer and Bader (1998) investigated the influence of adding lignocellulosic fibers such as flax, jute, oil palm and ramie fibers on the mechanical properties of biodegradable polyester, polysaccharides and a blend of thermoplastic starches (TPSs). The maximum fiber content added was about 20–35% depending on the type of the polymer. The addition of the fibers increased the tensile strengths of all the polysaccharides and TPSs. For example, the tensile strength of TPS increased from 8.9 MPa to 36.4 MPa with the addition of 20% flax fibers.

Several studies used hybrid natural and synthetic fibers to reinforce non-biodegradable polymers with some increase in strength (Abdul Khalil, Hanida, Kang, & Nik Fuaad, 2007; Mishra et al., 2003; Panthapulakkal & Sain, 2007).

Prachayawarakorn, Sangnitidej, and Boonpasith (2010) found that the addition of cotton fibers to thermoplastic rice starch (TPRS) improved the mechanical properties and the thermal stability of the TPRS composite. For example the decomposition temperature of TPRS increased from 300.9 °C to 304.6 °C for TPRS with 5% cotton fibers.

There are more than 100 million date palm trees all over the world which are widely spread in the Middle East, United States, Pakistan and India. Most of the byproducts of the date palm trees are currently used in low value products. Alawar, Hamed, and Al-Kaabi (2009) showed that the raw date palm fibers contain about 20%

* Corresponding author at: Faculty of Engineering, Cairo University, Building 14, Giza 12613, Egypt. Tel.: +20 100 44 105 28.
E-mail addresses: Hamdy.m.elsayed@gmail.com, h.m.elsayed@aucegypt.edu (H. Ibrahim), mmfarag@aucegypt.edu (M. Farag), hssnmegahed@yahoo.com (H. Megahed), smehanny@aucegypt.edu (S. Mehanny).

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http://dx.doi.org/10.1016/j.carbpol.2013.08.051

lignin and have a density about 0.917 g/cm^3 and thermal stability up to 250 °C. Their tensile strength varies from 60 to 275 MPa and Young's modulus from 2 to 12 GPa (Al-Khanbashi, Al-Kaabi, and Hammami, 2005).

Xue, Tabil, and Satyanarayan (2007) chemically treated the lignocellulosic fibers to modify their surface and to improve their adhesion with matrix. In the case of date palm fibers, Al-Khanbashi et al. (2005) found that treated fiber surface and better fibrillation were achieved with 5% NaOH concentration for 2 h at 100 °C.

Flax fibers have better mechanical properties than other natural fibers and comparable to those of glass fibers (Frederick & Norman, 2004; Mohanty, Misra, & Hinrichsen, 2000) and their water absorption is small compared with other natural fibers (about 7%) (Satyanarayana & Wypych, 2007).

The objective of this study is to study the effect of the fiber content on the mechanical behavior, thermal stability, water absorption and biodegradation of starch-based composites. The composites contained date palm fibers in the range from 20 to 80 wt%. Hybrid composite containing 25 wt% date palm and 25 wt% flax fibers were also examined.

2. Experimental methods

2.1. Materials

Long hackled flax strands were donated by the Egyptian Industrial Center E.I.C. The fruit bearing branches of date palm trees were supplied by a palm plantation in Egypt and commercial corn starch was produced by Aro Sheri Company in Egypt. The inherent moisture content of the starch was measured as 2 wt%, this moisture content was considered in further preparations for the starch blends. Glycerin with 99.7% purity was purchased from El-Gomhouria Company in Egypt and used as a plasticizer. Sodium hydroxide (NaOH) with molecular weight 40.00 was used for alkaline treatment of fibers and steric acid with assay 98% was used as a mold-releasing agent.

2.2. Preparation

2.2.1. Fiber preparation

Date palm fibers from fruit bearing branches were retted by soaking in water at room temperature for 2 days, cut transversely to lengths of 20–30 mm and then given mechanical treatment in a home use blender. The fibers were then soaked in 5% NaOH solution at 90 °C for 3 h and stirred in home-use mixer for 30 min at temperature from 80 to 90 °C. The treated fibers were washed several times in cold water to remove most of separated lignin before dipping in 5% acetic acid solution to remove any excess NaOH from the fiber surfaces and then given a final wash in cold water before drying at 120 °C for 3 h.

The flax fibers were soaked in 5% NaOH solution at room temperature for 3 h and then washed thoroughly in cold water before dipping in 5% acetic acid solution to remove any excess NaOH from the fiber surfaces and then given a final wash in cold water before drying at 120 °C for 3 h. Treated flax fibers were cut manually into lengths of 15–30 mm.

2.2.2. Thermoplastic starch preparation

Native corn starch was mixed with 30 wt% glycerin and 20 wt% distilled water at a temperature range of 60–80 °C. Water plays the essential role in the gelatinization process of starch. According to Hulleman, Janssen, and Feil (1998), adding 20 wt% water to corn starch gives the optimum tensile stain at break with no significant change in the tensile strength. Adding glycerin improves processability and reduces embrittlement by inhibiting the retrogradation process after processing (Forssell, Mikkila, Moates, & Parker, 1997). Thermoplastic starch (TPS) blend was then kept in polyethylene bags overnight to enhance its flow properties (Forssell et al., 1997).

2.2.3. Composite preparation

Positive-type mold was coated by steric acid to work as a releasing agent. The chopped fibers were then carefully distributed in the mold. The (TPS) was emulsified in water with ratios of (TPS:water) equal to (1:1, 1:2, 1:2, 1:3, 1:4 and 1:8) for (0, 20, 40, 50, 60 and 80 wt%) fiber content respectively then poured on the fibers. The mold was then closed and placed in a Carver Laboratory press (Model C) and preheated at 140 ± 3 °C for 30 min to remove excess water from the emulsion. This was followed by hot pressing at 5 MPa and 160 ± 3 °C for 30 min (Guimarães, Wypych, Saul, Ramos, & Satyanarayana, 2010; Ochi, 2006) and then cooled at a rate of about 2 °C/min.

2.3. Characterization

2.3.1. Fiber characterization

2.3.1.1. Density measurement. Due to the porous nature of lignocellulosic fibers, their density is affected by the applied pressure (Facca, Kortschot, & Yan, 2006). In the present work, fiber densities were measured before treatment, after treatment and after treatment and compression at 5 MPa for 30 min at 160 °C. Mittler Toledo densitometer was used with xylene (relative density = 0.86) as the immersing liquid.

2.3.1.2. Tensile testing. The tensile strength of the fibers was measured using the procedure given by (Ochi, 2006). The tensile testing of the individual fibers was done at a gauge length of 50 mm using Instron 3382 universal testing machine at 50% RH, 18 °C and strain rate of 0.01 per min. The machine capacity is 100 kN with 1:100 kN force ranges (it uses the load cell to 1% of its capacity with no loss of its accuracy). The reported tensile properties are the average of at least 10 individual fibers.

2.3.2. Matrix and composite characterization

2.3.2.1. Density. Density of the prepared matrix and composites was measured using the Mittler Toledo densitometer. Xylene rather than distilled water was used as the immersing liquid due to the hydrophilic nature of the starch based composites. At least 5 samples were tested for each condition.

2.3.2.2. Tensile testing. Tensile and flexural specimens of dimensions 80 mm × 8 mm × 2 mm were prepared according to ASTM D5083-10 and D7264/D7264M-07 respectively and kept in polyethylene bags at room temperature 20 °C and 50% RH for 3 days before mechanical testing. An Instron 3382 universal testing machine was used at room temperature. The machine capacity is 100 kN with 1:100 kN force ranges (it uses the load cell to 1% of its capacity with no loss of its accuracy). A tensile strain rate of 0.1 per min and a deflection rate of 2 mm/min were used for the tensile and flexural tests, respectively.

2.3.2.3. SEM investigation. The fiber surfaces and composite fracture surfaces were investigated using ZEISS-SEM microscope operating at a vacuum pressure 1e−4 mbar and 8 kV. The samples were viewed without any surface preparation.

2.3.2.4. Thermal analysis. Thermo-gravimetric analysis (TGA) tests were carried out using 60 Hz detector and under 20 ml/min flow of nitrogen atmosphere. The tests were carried out at temperature range from 0 to 600 °C for the matrix and composites with 10 °C/min heating rate.

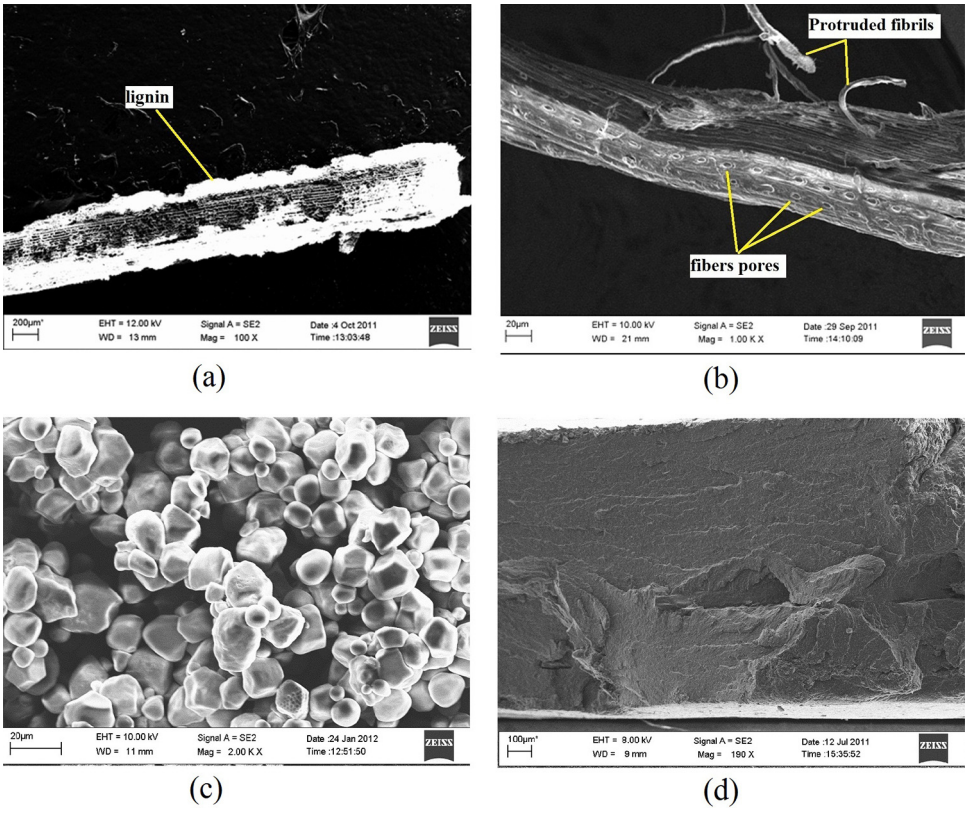

Fig. 1. Date palm fibers and starch SEM investigation: (a) raw date palm fibers are covered with much lignin; (b) NaOH-treated date palm fibers with clean surface and protruded fibrils; (c) overnight-stored plasticized corn starch; (d) compression molded thermoplastic starch by emulsion technique.

2.3.2.5. Water uptake test. A humidity chamber (desiccator) was set up at 100%RH using distilled water at room temperature. Specimens of dimensions (40 mm × 8 mm × 2 mm) were dried at 100 °C for 4 h, weighted and were then placed in the humidity chamber. The weight difference was measured daily until the mass of the samples was almost constant. Then water uptake was calculated using the following equation:

$$\text{Water uptake}\,\% = \left(\frac{M_f - M_i}{M_i}\right) \times 100 \quad (1)$$

where (M_f) is the final sample mass and (M_i) is the initial sample mass.

2.3.2.6. Biodegradation as a result of burial in soil. Samples of the starch matrix and composites of dimensions 40 mm × 8 mm × 2 mm were buried at about 10 cm depth in a mixture of 50% sand and 50% soil. The temperature was maintained at 30 ± 2 °C. The water content of the soil and sand mixture was kept in range of 30–40% by adding 400 ml water to each 1250 g of mixture every 3 days, following the procedure outlined by Franco, Cyras, Busalmen, Ruseckaite, and Vazquez (2004) and Kaith, Jindal, Jana, and Maiti (2010). Four sets of experiments were made for predetermined intervals: 1, 2, 4 and 6 weeks. Samples of the fibers were also treated in the same way. After every predetermined period, samples were carefully cleaned with water before being dried at 80 °C for 24 h and then weighed to determine the weight loss using the following equation:

$$\text{Weight loss}\,\% = \left(\frac{M_i - M_f}{M_i}\right) \times 100 \quad (2)$$

where (M_i) is the initial sample mass and (M_f) is the final sample mass after being dried.

The followed method is easy and reliable in showing the effect of fiber content in the biodegradation rate of the starch-based composites.

3. Results and discussions

3.1. Fibers

3.1.1. Density and dimensions

The average length of the date palm fibers was 13.8 mm, average diameter 196 μm and the aspect ratio 70. The average density of untreated date palm fibers was 0.67 g/cm^3. The density of fibers after the alkaline treatment increased to 1.35 g/cm^3, which can be attributed to the removal of most of the low density lignin and hemicellulosic structure surrounding the cellulosic structure of the fibers (Kalia, Kaith, & Kaur, 2009). Compressing a mass of fibers to simulate the conditions of composite preparation was found to slightly increase their density to 1.37 g/cm^3. This latter value is used in the calculations of composite densities in Eqs. (3) and (4).

3.1.2. Fiber morphology

Untreated date palm fibers are shown in Fig. 1a. The raw date palm fiber is cylindrical in shape and most of the fiber surface is covered with lignin and hemicellulosic structure. Fig. 1b gives the NaOH-treated fibers and shows that the treatment removed most of the lignin and hemicellulosic structure of the fiber surface and caused fiber fibrillation, which is expected to increase the mechanical anchoring of the fibers with the matrix and improve the composite mechanical properties.

3.1.3. Tensile testing

The average ultimate tensile strength and modulus of elasticity of the treated fibers were measured as 195 ± 28.8 MPa and

Table 1
Theoretical and measured date palm fibers composites densities.

Weight fraction of fibers W_f (%)	Volume fraction of fibers V_f (%)	Theoretical density (g/cm^3)	Measured density (g/cm^3)	Void fraction (%)
20	20.8	1.432	1.431	0.07
40	41.21	1.416	1.415	0.07
50	51.25	1.409	1.407	0.142
60	61.19	1.402	1.336	4.71
80	80.79	1.389	1.254	9.72

8.8 ± 1.5 GPa, respectively. Generally, the treated fibers exhibited better mechanical properties than untreated fibers. The average values for untreated fibers ultimate tensile strength and modulus of elasticity were 95 ± 30.8 MPa and 7.8 ± 2.7 GPa, respectively. These values are within the range observed by Al-Khanbashi et al. (2005), where the strength ranged between 60 and 275 MPa and the modulus of elasticity between 2 and 12 GPa.

3.2. Matrix

3.2.1. Density and morphology

TPS emulsion-based matrix average density was 1.45 g/cm^3. The morphology of native commercial corn starch showed irregular shape and sizes with particle size varied from 4.9 to 33 μm and the average size about 16 μm, which is consistent with the values found in Averous (2004). The particles of the plasticized corn starch (TPS) particles are agglomerated and connected together, as shown in Fig. 1c.

The fracture surface of compression molded thermoplastic starch (TPS) matrix made by emulsion technique showed smooth fracture surface and cleavage like regions, as shown in Fig. 1d.

3.2.2. Mechanical properties

The measured tensile strength and Young's modulus of the TPS matrix were 3.8 and 378 MPa, respectively, with 5.25% maximum strain, while the flexural strength and modulus were 8.7 and 685 MPa, respectively. These values are consistent with those reported by Hulleman et al. (1998).

3.3. Composites

3.3.1. Density

Fiber volume contents were calculated based on inverse rule of mixtures (IROM), Eq. (3), and the theoretical composites densities (ρ_c) were calculated in Table 1 based on rule of mixtures (ROM), Eq. (4):

$$V_f = \frac{\rho_m W_f}{\rho_m W_f + g r_f W_m} \tag{3}$$

$$\rho_c = \rho_f V_f + \rho_m (1 - V_f) \tag{4}$$

where (V_f) is the fiber volume fraction, (ρ_m) and (ρ_f) are the matrix and fiber densities, respectively, (W_f) and (W_m) are the fiber and matrix weight fractions, respectively.

The void fraction is calculated form the difference between the calculated values (ρ_c) and the experimentally measured valued (ρ_{exp}) according to the following equation:

$$\text{Void fraction}\,\% = \frac{\rho_c - \rho_{exp}}{\rho_c} \times 100 \tag{5}$$

Table 1 shows that for composites with 20, 40, and 50 wt% fiber weight content, the measured densities were very close to the calculated theoretical densities and the void fractions less than 0.15%. On the other hand, composites with 60 wt% and above have large differences between the measured and theoretical densities and void fractions more than 4%. This increase in porosity can be attributed to insufficient matrix to cover all the fiber surfaces, as will be shown in Fig. 2e.

The 50 wt% hybrid composite (25 wt% flax, 25 wt% date palm fibers) measured density equals to 1.403 g/cm^3 with void fraction about 2.9% which is higher than that for 50 wt% date palm fibers composite (0.142%). This increase in the hybrid composite void fraction is due to the addition of flax fibers which have smaller diameter, thus more fibers surface area and more matrix content is needed to cover all the fibers. These results are consistent with 50 wt% date palm fibers composite results and the 50 wt% flax fibers measured density (1.402 g/cm3) and void fraction (4.95%) found in previous work (Elsayed, Farag, Mehanny, & Megahed, 2012).

3.3.2. Fracture surface morphology

Fig. 2(a–f) shows the fracture surface morphology of date palm fibers TPS-based composites from 40 till 80 wt% fiber content. Fig. 2a shows a fiber pull out void and uniform distribution of fibers in the matrix. Fig. 2b shows good adhesion between fibers and matrix. Fig. 2c shows the fracture surface of date palm fiber, where the fiber cellular and porous structure is clearly shown. Fig. 2d shows more fibers pull outs and large voids for 60 wt% composite due to the increase in void fraction. The lack of matrix to cover all the surfaces of the fibers is observed in the 80 wt% composite Fig. 2e.

Fracture surface of 50 wt% hybrid composite containing (25 wt% flax, 25 wt% date palm fibers) is shown in Fig. 2f. Date palm and flax fibers are uniformly distributed and mixed.

The SEM investigation of starch-based composites shows three types of failure mechanisms: matrix failure, fiber fracture and fiber-matrix interfacial failure. The three types of failure mechanisms took place simultaneously for all fiber contents composites. Fiber fracture failure mechanism is predominant relative to fiber–matrix interfacial failure in composites with fiber contents up to 50 wt%. Good adhesion between fibers and matrix can be attributed to the hydrophilic character of TPS and the effect of the alkaline treatment of the fibers (Vilaseca et al., 2007; Yu, Dean, & Li, 2006).

3.3.3. Tension test results

Fig. 3 shows the tensile strength and modulus of the date palm–TPS composites. Both tensile strength and modulus of composites increase with increasing fiber content to reach their maximum values of 31 MPa and 2.8 GPa respectively at 50 wt% fiber content. Increasing fiber content from 20 to 50 wt% increased the composite tensile strength about three times and the tensile modulus about two times. The decrease in strength and modulus of composites containing 60 and 80 wt% fibers can be attributed to the increased porosity.

Generally, the obtained tensile properties are comparable with those of starch-based matrix with different types of natural fibers. For example, the strength of rice starch-based matrix with 40% w/w palm pressed fibers (about 28 wt%) is reported as 16.26 MPa (Phattaraporn, Waranyou, Fazilah, & Thawien, 2010). While the

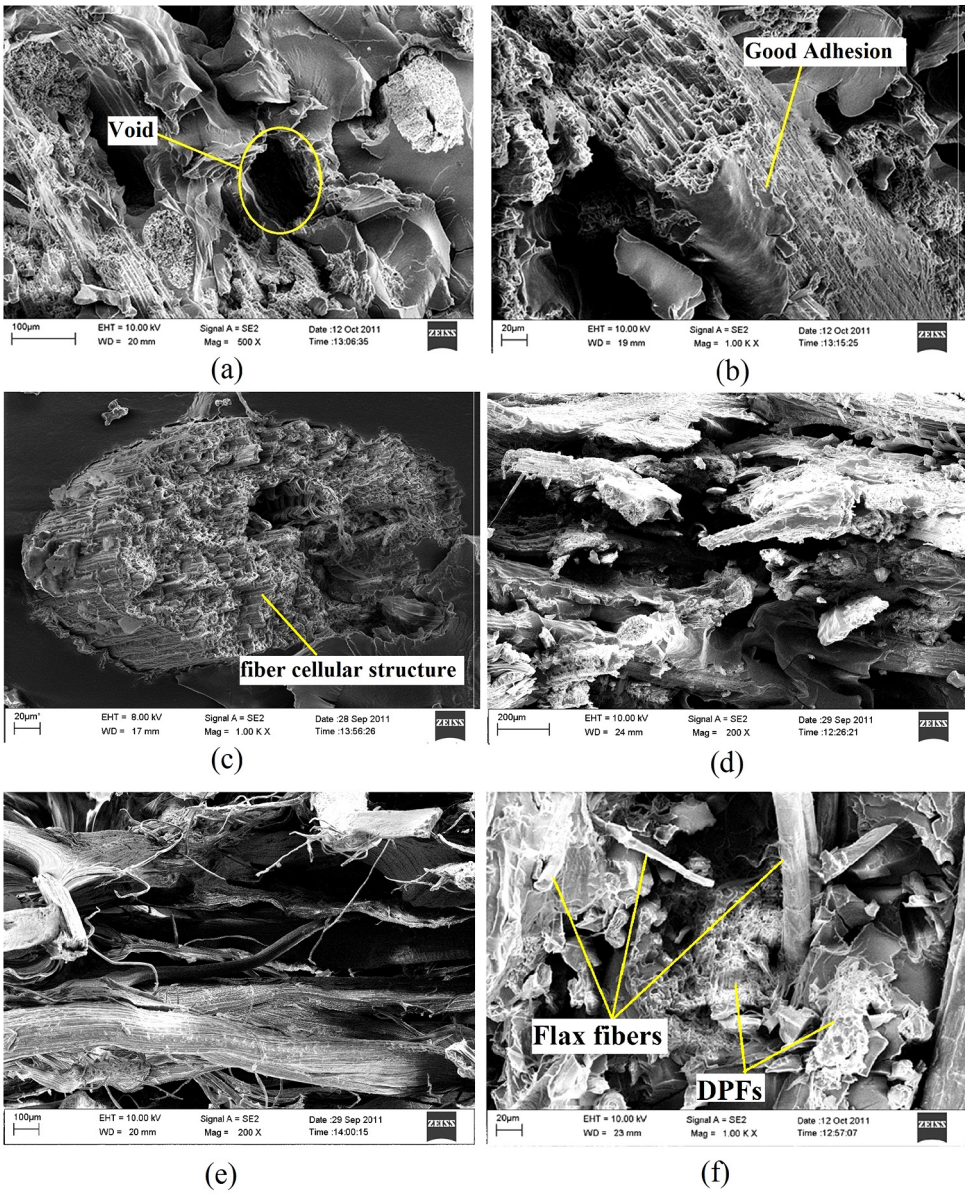

Fig. 2. SEM investigation of tensile fracture surface of date palm fibers TPS-based composite: (a) good fiber distribution, fracture and some pull out voids; (b) good fibers matrix adhesion; (c) fiber fracture and its cellular structure; (d) more fibers pull outs for 60 wt% composite; (e) bad wetting and much pull outs for 80 wt% composite; (f) good flax and date palm fibers distribution and mixing.

tensile strength for TPS reinforced with 65 wt% bagasse fibers was 26.77 MPa (Cao, Shibata, & Fukumoto, 2006).

3.3.3.1. Mathematical analysis of the tensile strength and modulus results. An attempt has been made to predict the tensile strength of composites using mathematical models. The rule of mixtures (ROM) (Eq. (6)) was used to estimate a maxumum value of the tensile strength and Eq. (7) was used to estimate a minimum value in the longitudinal direction.

$$\sigma_L = \sigma_F V_F + \sigma_M V_M \tag{6}$$

$$\sigma_T = \sigma_M \tag{7}$$

where σ_F is the fiber tensile strength (195 MPa), σ_M is the matrix tensile strength (3.8 MPa), V_F is the fibers volume fraction (0–80%) and V_M is the matrix volume fraction ($V_M = 1 - V_F$)

The ROM and inverse rule of mixtures (IROM) equations ((8) and (9)) represent the simplest model that can be used to predict the elastic modulus of a composite. ROM eqn. to predict the upper limit of the elastic modulus:

$$E_L = E_F V_F + E_M V_M \tag{8}$$

And IROM eqn. to predict the lower limit of the elastic modulus:

$$E_T = \left(\frac{E_F E_M}{E_F V_M}\right) + E_M V_F \tag{9}$$

where E_F is the fibers modulus of elasticity, E_M is the matrix modulus of elasticity, V_F is the fibers volume fraction and V_M is the matrix volume fraction. For the present work E_F is 8811 MPa and E_M is 378 MPa.

Kelly and Tyson (Eqs. (10) and (11)) proposed an approach to deal with discontinuous-unidirectional fiber and to overcome the problem of unequal strain in the fibers and the matrix by assuming perfect bonding between fibers and matrix and that both fibers and matrix behave as linear elastic materials. If the fibers are shorter

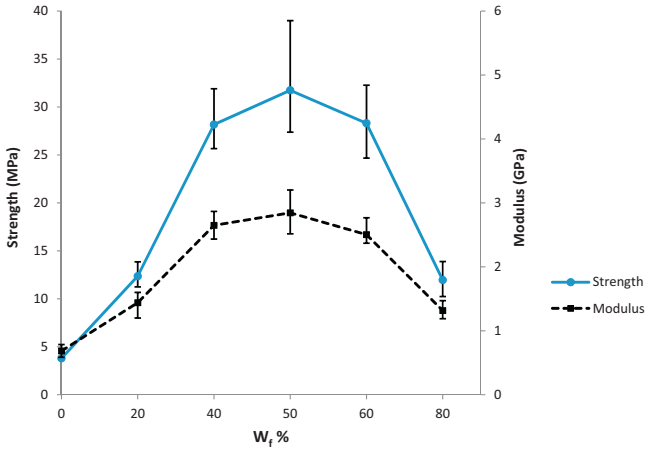

Fig. 3. Composite measured tensile properties: tensile strength and tensile Young's modulus.

than the critical length (L_c) they cannot be loaded to their failure stress and the strength of the composite is then determined by the strength of the fiber/matrix bond, not by the fiber strength, so for fibers length greater than (L_c) the composite tensile strength can be calculated as follows (Harris, 1999).

The critical length and composite strength can be calculated as following:

$$L_c = \sigma_F \left(\frac{d}{2\tau}\right) \tag{10}$$

$$\sigma_c = \left(\frac{1 - L_c}{2L}\right) \sigma_F V_F + \sigma_M V_M \tag{11}$$

where d is fibers average diameter, τ is the shear strength of fiber/matrix bond (about 0.5 of matrix strength), σ_F is the fibers tensile strength, L_c is the critical length, L is the fibers average length, σ_M is the matrix tensile strength, V_F is the fibers volume fraction and V_M is the matrix volume fraction. For the present work, d is 0.2 mm, σ_F is 195 MPa, L_c is 10.1 mm, L is 13.9 mm and σ_M 3.8 MPa.

The Halpin–Tsai equation is used to describe some of the mechanical properties of 2-phase composites such as elastic modulus. In uniform discontinuous fibers model, it assumes that fibers are uniform, discontinuous, cylindrical, and transversely isotropic. The resulting composite is therefore transversely isotropic. The composite elastic modulus in longitudinal direction (E_L) can be obtained as following (Harris, 1999; http://www.mscsoftware.com/training_videos/patran/Reverb_help/index.html#page/Functional%2520Assignments/materials_forms.5.6.html#ww1195).

$$E_L = \frac{E_M(1 + \xi_L \eta_L V_F)}{1 - \eta_L V_F} \tag{12}$$

where (ξ) is a factor depends on the shape and distribution of the reinforcement. The parameter (η) is a function of the ratio of the relevant fiber and matrix moduli with respect to the reinforcement factor (ξ). In this model they can be obtained calculated by the following formulas:

$$\eta_L = \frac{E_F - E_M}{E_F + \xi_L E_M} \tag{13}$$

$$\xi_L = 2\left(\frac{l}{d}\right) + 40 V_F^{10} \tag{14}$$

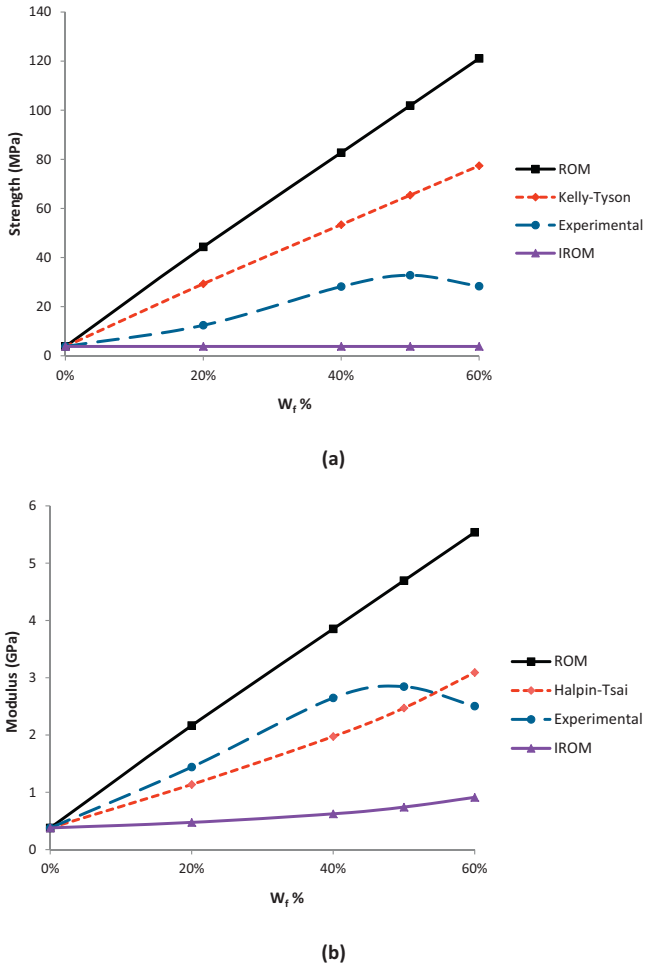

Fig. 4. Composite measured and predicted tensile properties: (a) tensile strength; (b) tensile modulus.

Also, the composite elastic modulus in transversal direction (E_T) can be obtained as following:

$$E_T = \frac{E_M(1 + \xi_T \eta_T V_F)}{1 - \eta_T V_F} \tag{15}$$

where

$$\eta_T = \frac{E_F - E_M}{E_F + \xi_T E_M} \tag{16}$$

$$\xi_T = 2 + 40\, V_F^{10} \tag{17}$$

The two previous moduli are for oriented fibers, the following equation is a result of an averaging process made by Tsai and Pagano (Piggott, 1980) to predict the modulus of an isotropic composite (E_c) based on random fibers reinforcement.

$$E_C = \left(\frac{3}{8}\right) E_L + \left(\frac{5}{8}\right) E_T \tag{18}$$

Fig. 4a compares the present experimental tensile strength with the predictions of various models. The significant discrepancies between experimental and predicted results when using modified Kelly–Tyson model can be attributed to the assumption of alighned chopped fibers in the model. Also the assumption of perfect adhesion between fibers and matrix caused the model to overestimate the tensile strength of the composites.

Halpin–Tsai model underestimated the tensile modulus of date palm fibers composite as shown in Fig. 4b, this may be due to the complex geometry of date palm fibers and fibrillation after the

Table 2
Thermal degradation of date palm fibers composites.

Fiber content (wt%)	Temp. at 10% weight loss (°C)	Temp. at 50% weight loss (°C)	Weight% loss at 100 (°C)	Residual weight% at 600 (°C)
0	192	313	4.8	2.3
50	232	324	2.6	1.4
80	250	351	3.8	0.14

alkaline treatment, hence difficulties in measuring fibers diameter accurately that affect in the calculations of the shape parameter (ξ) (Eq. (14)), thus the final predicted modulus out of the model.

The 50 wt% hybrid composite (25 wt% flax, 25 wt% date palm fibers) exhibited consistent tensile strength (42.2 MPa) in-between the tensile strengths of 50 wt% flax composite about 62 MPa (Elsayed et al., 2012) and 50 wt% date palm fibers composite about 32 MPa. This proves that the fabrication method of mixing and distribution of fibers is successful in producing hybrid composites that combine the properties of 50 wt% flax and 50 wt% date palm fibers as in tensile strength.

3.3.4. Bending test results

The flexural test results follow the same trend as the tensile test, where the optimum flexural strength and modulus were found at 50 wt% fiber content. The flexural strength and modulus increased from 35 MPa and 2.5 GPa respectively at 20 fiber wt% composite to 73.6 MPa and 5 GPa respectively at 50 fiber wt% composite.

Flexural strength and modulus were significantly higher than tensile strength and modulus, which is consistent with the literature. According to a statistical-strength theory based on a Weibull distribution, the higher strength in bending test than tension is due to difference in stress nature. In bending test, composite fail gradually and the generated stress has a gradient that results in increase in the measured strength of the half exposed to tensile stresses, while in tension test all composite cross section being under uniform stress (Whitney & Knight, 1980; Wisnom, 1992).

3.3.5. Thermal analysis

Thermal degradation of the thermoplastic starch (TPS)-based matrix is an important issue to indentify the limits of processing, treatment or operating temperatures. Fig. 5a shows the TGA/DTA curves obtained for the hot pressed TPS-based matrix by emulsion technique, where the percentage loss of the sample weight and the derivative of the weight loss due to the volatilization of the degradation products are monitored as a function of temperature. It can be seen that there are two weight loss phases. The first phase is a weight loss of 9.4% up to 174 °C due to the presence of hydrated/adsorbed water and glycerin. The second weight loss phase corresponds to the thermal decomposition of starch (burning of starch organic matter). The total weight loss in the second phase was about 88.4% between 175 and 530 °C, while most of starch weight loss (about 60%) was between 280 and 340 °C that was associated with peak derivative of the weight loss at 316 °C. Similar results of starch systems thermal analysis were reported in Liu et al. (2009) and Prachayawarakorn et al. (2010). The remaining 2.3% is due to the presence of inorganic materials in the hot pressed TPS-based matrix that included during matrix processing or sample preparation.

In the temperature range between 280 and 340 °C, where most of weight loss takes place, the decomposition process was associated with two endothermic peaks: the first one (1) at about 295 °C due to the evaporation (boiling) of glycerin content, and the second one (2) at about 320 °C which is much greater due to the higher energy needed to burn and cause decomposition of starch content. These DTA results are consistent with published literature (Guimarães et al., 2010).

The TGA and DrTGA curves for date palm fibers reinforced TPS-based composites (0, 50 and 80 wt%) are shown in Fig. 5b. The results show that increasing date palm fibers content improved the composite thermal stability. This improvement is due to the increase in the amount of the cellulosic matter that has higher thermal stability relative to starch. For example, the temperature causing 50% loss of composite weight, increased from 313 °C for 0% to 351 °C for 80 wt% composite.

It can be noticed from DrTGA curves that composites show two major peak regions: the first set of peaks (1) at 316 °C for decomposition of starch and the second (2) at 356 °C for the decomposition of date palm fibers (cellulosic matter). The peaks of starch decomposition become smaller by increasing fiber content. Also DrTGA curves show a broad decomposition of lignin at all temperatures with a significant peak region at higher temperature around 468 °C (Brebu & Vasile, 2010).

From Table 2 it can be seen that the weight loss at 100 °C (mostly of water content) for matrix and all composites varied between 2.6 and 4.8 wt% which confirms that most of water added in the preparation of composites by emulsion technique evaporated during preheating and hot pressing processes. Also the residual weights of most composites at 600 °C was less than 2.3% which reveals that the alkaline treatment successfully removed most of date palm fibers lignin content, where generally about 60% of lignin weight begins to decompose above 700 °C (Satyanarayana et al., 2009; Brebu & Vasile, 2010). Also the composites residual weight decreases as

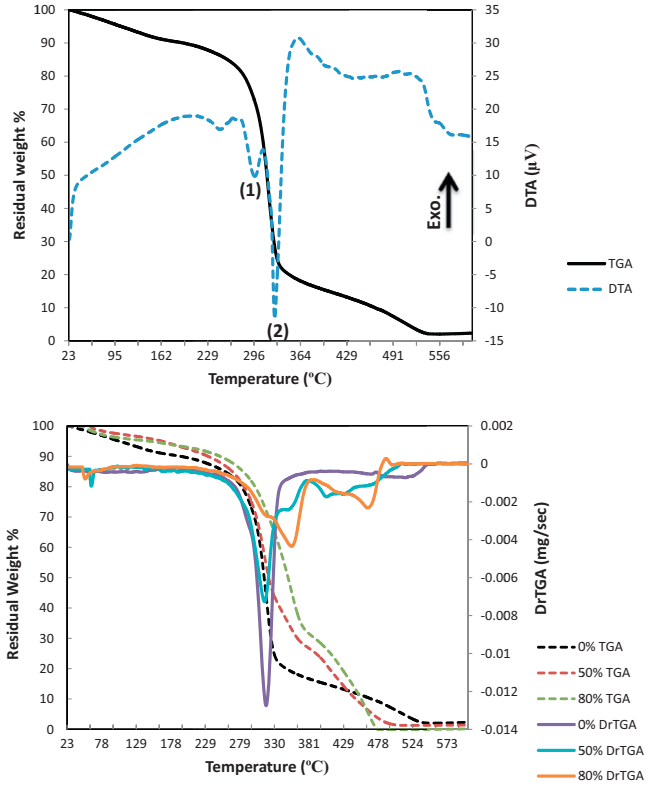

Fig. 5. Thermal analysis: (a) TGA/DTA curves obtained for hot pressed TPS-based matrix; (b) TGA/DrTGA curves obtained for composites with different fiber contents.

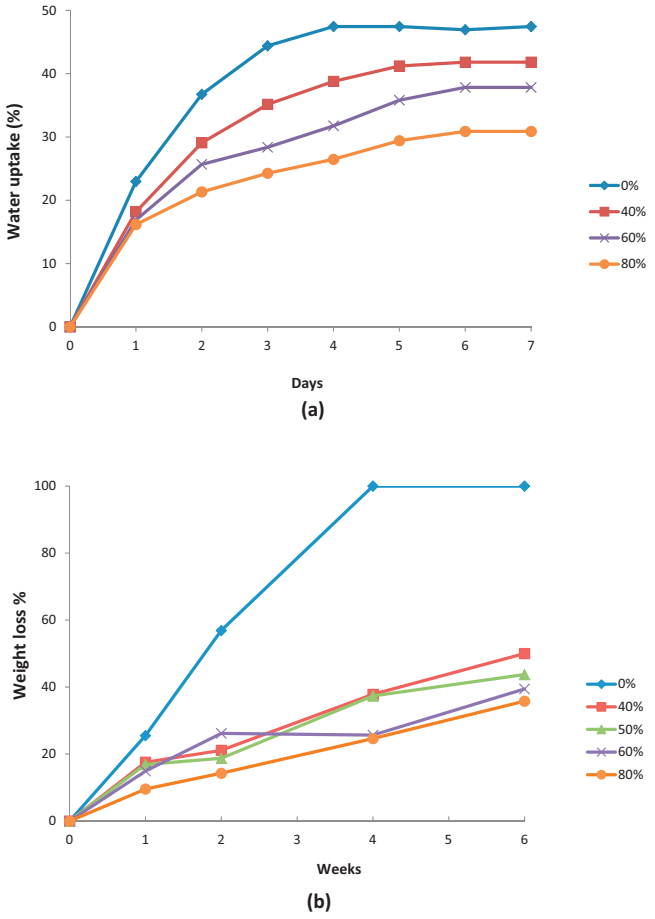

Fig. 6. (a) Composites water uptake with different fiber contents; (b) composites biodegradation with different fiber contents.

the fiber content increases, which implies that starch-based matrix contains more inorganic inclusions.

The hybrid composite showed a thermal behavior consistent with the reported analysis in Elsayed et al. (2012) and with the previously stated analysis of date palm fibers TPS-based composited.

The enhancement in thermal stability of TPS-based composited by increasing date palm fibers implies the good adhesion between fibers and TPS matrix (Prachayawarakorn et al., 2010).

The onset of degradation of the date palm fibers-TPS composites (174 °C) is higher than some petroleum based polymers such as polyethylene (PE) and polypropylene (PP) that have melting temperatures 120–130 °C and 160–166 °C, respectively, which indicated better thermal stability.

3.3.6. Water uptake

Water uptake test of the composites at 100% RH showed a reduction in the percentage of absorbed water with the addition of the date palm fibers, see Fig. 6a. The results show that the water uptake of composite decreases with the increase in fiber content. For example, the water uptake decreased from about 48% for TPS matrix to about 38% for composites with 60 wt% date palm fibers. This is attributed to the cellulosic structure of the fibers, which is less hydrophilic than the TPS matrix. In addition, the composites took longer time to reach the equilibrium weight.

After water uptake test followed by drying, the tensile strength of date palm composites were found to decrease to about half of their values before the water uptake test. This is attributed to the differences in water uptake of fibers and matrix which lead to dimensional changes and weaker adhesion between matrix and fibers (Bismarck et al., 2002).

3.3.7. Biodegradation as a result of burial in soil

Biodegradation of the date palm fibers-TPS composites as a result of microorganisms was determined by weight loss after burying in soil, as shown in Fig. 6b. Increasing the date palm fibers reduced the composites degradation rate, which can be attributed to the lower degradation rate of the date palm fibers (cellulose) compared to the carbohydrate matrix (starch). For example, 50 fiber wt% composite lost about 40% of its initial weights by the fourth week while the TPS matrix lost about 60% of its initial weight by the second week and completely vanished before the fourth week. This is in agreement with the results of Satyanarayana et al. (2009) and Kaith et al. (2010).

4. Conclusions

1. Composites containing 20, 40, and 50 wt% date palm fibers have lower void fractions while composites with 60 and 80 wt% have higher void fractions as the matrix was insufficient to cover all the fiber surfaces.
2. Three types of failure mechanisms have been identified: matrix failure, fiber fracture and fiber-matrix interfacial failure. Fiber fracture was predominant in composites with fiber content up to 50 wt%.
3. The tensile strength and modulus increased from about 3.8 MPa and 0.4 GPa, respectively, for the starch-based matrix to maximum values of 32.7 MPa and 2.8 GPa, respectively, for the 50 wt% date palm fibers composite. Flexural strength and modulus showed similar behavior. At 60 wt% fiber content and above, the mechanical properties deteriorated as a result of the increase in the composites porosity.
4. The 50 wt% hybrid composite of starch-based matrix reinforced with 25 wt% flax and 25 wt% date palm fibers was successfully prepared with a tensile strength of 43 MPa.
5. The modified Kelly–Tyson model overestimated the tensile strength of date palm fibers composite; this can be attributed to the assumption of aligned chopped fibers in the model. Halpin–Tsai model underestimated the tensile modulus of date palm fibers composite; this may be due to fibers fibrillation and their complex geometry.
6. Thermal stability increased as the fiber content increased. The temperature needed for 10% weight loss for date palm fibers composite increased from 192 °C for the starch-based matrix to 232 °C for the 50 wt% fiber composite.
7. The date palm fiber–TPS composites are biodegradable and hydrophilic. Water uptake and rate of biodegradation decrease as the fiber content increases.

Acknowledgment

Authors wish to acknowledge the financial support by the Yousef Jameel Science and Technology Research Center (YJ-STRC) at The American University in Cairo for funding this work and allowing us to use its facilities.

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