Tensile, Thermal and Water Absorption Properties of Corn Stalk Filled Low Density Polyethylene Composites: Effect of Coconut Oil Coupling Agent

(Sifat Tegangan, Terma dan Penyerapan Air Komposit Batang Jagung Terisi Polietilena Ketumpatan Rendah: Kesan Agen Pangganding Minyak Kelapa)

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ABSTRACT

In this study, the corn stalk (CS) had been utilized as natural filler in low density polyethylene (LDPE). The effect of CS loading and coconut oil coupling agent (COCA) on tensile, thermal and water absorption properties of LDPE/CS composites were investigated. The increases of CS decreased the tensile strength and elongation at break of LDPE/CS composites, but increased in Young's modulus. The incorporation of CS also contributed to high water uptake of LDPE/CS composites. However, the presence of CS has increased the crystallinity of composites and LDPE matrix due to nucleating effect. The addition of COCA has significantly increased the tensile strength, elongation at break, water resistivity and crystallinity of LDPE/CS composites, but slightly reduced in Young's modulus. The scanning electron microscope (SEM) also evidence the presence of COCA improved the adhesion between CS and LDPE matrix.

Keywords: Coconut oil coupling agent; composites; corn stalk; low density polyethylene

ABSTRAK

Dalam kajian ini, batang jagung (CS) telah digunakan sebagai pengisi semula jadi dalam polietilena berketumpatan rendah (LDPE). Kesan pembebanan pengisi CS dan agen pengganding minyak kelapa (COCA) ke atas sifat kekuatan tensil, haba dan penyerapan air komposit LDPE/CS telah dikaji. Peningkatan pembebanan pengisi CS telah mengurangkan kekuatan tegangan dan pemanjangan pada takat putus komposit LDPE/CS, tetapi modulus Young meningkat. Penambahan CS juga menyumbang kepada penyerapan air yang tinggi bagi komposit LDPE/CS. Walau bagaimanapun, kehadiran CS telah menyebabkan penghabluran matriks LDPE yang tinggi, ia disebabkan oleh kesan penukleusan. Penambahan COCA telah meningkatkan kekuatan tegangan, pemanjangan pada takat putus, rintangan terhadap air dan penghabluran komposit LDPE/CS, tetapi modulus Young didapati berkurang. Mikroskop imbasan elektron (SEM) juga menunjukkan bukti kehadiran COCA meningkatkan lekatan antara CS dan matriks LDPE.

Kata kunci: Agen pengganding minyak kelapa; batang jagung; komposit; poletilena ketumpatan rendah

INTRODUCTION

Nowadays, the agricultural by-product become alternative sources of material in several industrials, including wood plastic composites (WPC), textiles, pulp and paper (Flandez et al. 2012). Currently, the WPC industries have interest in producing WPC from agricultural by-products instance of wood flour due to the increase of environmental impact and ecological concerns and new legislations. The main benefits of using agricultural waste as alternative filler in composites are low cost, readily abundant and widely available and renewable (Chun & Husseinsyah, 2014a). The agricultural waste based composites are applicable in construction, furniture, packaging, household and automotive products (Panthapulakkal & Sain 2006). For example, decking, window fitting, car panelling, rear shelves, packaging tray and tableware (Chun & Husseinsyah 2014a; Chun et al. 2013a, 2013b; Panthapulakkal & Sain 2006).

Corn (also known as Maize or *Zea mays*) is a widely cultivated crop around the world. After harvesting of corn, the by-products like corn leaves and stalk are a port of corn stover in the field (Yeng et al. 2013). The main composition of corn stalk (CS) are cellulose, hemicellulose and lignin (Wan et al. 2013). Thus, the CS has potential to be used as filler for composites. The utilization of CS can bring economic benefit and reduced the waste of corn field.

Generally, the use of agricultural by-product as natural filler has many advantages, but they pose a problem as they naturally hydrophilic, which inherently low compatible with hydrophobic thermoplastic matrix. The incompatibility between the natural filler and thermoplastic may cause problems in composite processing and material properties (Chun et al. 2013c). In order to overcome this incompatibility problem, various physical and chemical methods have been employed to modify the natural filler, including use of compatibilizer (Chun et al. 2013d), treatment with silane (Xie et al. 2010), bleaching (Aisaeed et al. 2013), alkali treatment (Jae et al. 2010), esterification with organic acid (Chun et al. 2013b, 2013c) and treatment

with fatty acid and its derivatives (Chun & Husseinsyah 2014a, 2014b; Chun et al. 2013a; Husseinsyah et al. 2014). Coconut oil coupling agent (COCA) is a kind of fatty acid amine, which made from fatty acid of virgin coconut oil. COCA consists of amine groups and fatty acid chains in the structure. Thus, the COCA is reactive to natural filler and it can promote the compatibility between filler and matrix. In our previous studies, the addition of COCA shows a remarkable improvement on the mechanical and thermal properties of coconut shell powder filled polylactic acid composites (Chun & Husseinsyah 2014a) and palm kernel shell filled low density polyethylene (LDPE) composites (Husseinsyah et al. 2014).

In this study, the effect of filler loading and COCA on tensile, thermal and water absorption properties of LDPE/CS composites were investigated.

EXPERIMENTAL DETAILS

MATERIALS

The low density polyethylene grade LDF200YZ was supplied by Titan Chemicals. The CS was collected from corn field located at Kodiang, Kedah. The CS was dried at 80°C for 24 h in the oven. Then, the dried CS was ground and sieved to obtained fine CS powder. The average particle size of CS powder was 30 μm (measured using Malvern Particle Size Analyzer Instrument). The COCA was prepared according to method reported by Chun and Husseinsyah (2014a) and Husseinsyah et al. (2014). Figure 1 shows the schematic reaction of virgin coconut oil fatty acid and ethylene diamine to produced COCA.

PREPARATION OF LDPE/CS COMPOSITES

The LDPE and CS was compounded by using Brabender Plastograph mixer Model EC PLUS at 160°C and rotor speed of 50 rpm. All composites were prepared according to Table 1. First, the LDPE pellets were transferred into compounding chamber for 2 min until it completely melted. Then, the CS powder was added into melted LDPE and compounded for 6 min. For the treated LDPE CS composites, the COCA was incorporated during the addition of CS filler. All the LDPE/CS compounds was moulded into 1 mm thickness sheer using compression moulding machine model GT 714A at 180°C. The compression procedure started with 4 min for the preheating at 160°C then 1 min for compressing and 5 min cooling with 100 kgf/cm² pressure. The LDPE/CS sheets was cut into tensile bar using dumbbell cutter with dimension following to ASTM D638 type IV.

TESTING AND CHARACTERIZATION

Test testing was performed by using an Instron universal testing machine model 5569 and followed by ASTM D 638. The tensile test was performed with a cross head speed of 50 mm/min at 23±2°C. For each composition, five identical samples of tensile properties have been measured and average values of tensile strength, elongation at break and Young's modulus were reported.

Water absorption test on LDPE/CS composites was carried out based on ASTM D570. The specimens (25×20×1 mm) were dried at 80°C for 24 h. Then, the specimens immersed in distilled water at room temperature and water absorption was measured by weighting the specimens at regular intervals with Mettler balance; model AX 200, Shimadzu (Japan, precision of ± 1 mg). The percentage
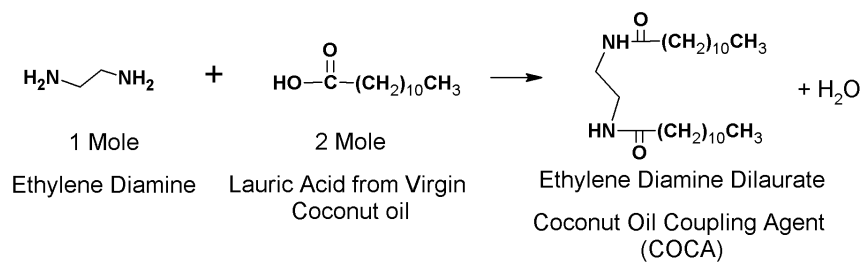

FIGURE 1. Schematic reaction of producing COCA from virgin coconut oil fatty acid and ethylene diamine (Chun & Husseinsyah 2014a; Husseinsyah et al. 2014)

TABLE 1. Formulation of untreated and treated LDPE/CS composites

Materials	LDPE/CS (untreated)	LDPE/CS (treated with COCA)
LDPE (php)	100	100
CS (php)	0, 10, 20, 30, 40	10, 20, 30, 40
COCA (wt. %)*	-	3*

php = part per hundred polymer
* based on weight of filler

of water absorption, M_t was calculated by the following formula:

$$M_t = \frac{W_n - W_d}{W_d} \times 100\%, \qquad (1)$$

where W_d and W_n are the original dried weight and weight after immersion, respectively.

Differential Scanning Calorimetry (DSC) analysis was performance by using DSC Q10, Research Instrument. The LDPE/CS composites (7 ± 2 mg) was placed in close aluminium pan and heated from 30°C to 270°C with a heating rate of 10°C/min under nitrogen atmosphere. The nitrogen gas flow rate was 50 mL/min. The degree of crystallinity of composites (X_c) can be calculated from DSC data by using (2).

$$X_c = (\Delta H_f / \Delta H_f^0) \times 100 \qquad (2)$$

where ΔH_f is the heat fusion of the LDPE composites; and ΔH_f^0 is the heat of fusion for 100% crystalline LDPE (ΔH_{100} = 285 J/g).

The crystallinity of LDPE matrix (X_{LDPE}) was calculated using (3):

$$X_{LDPE} = X_c / W_{f\,LDPE}, \qquad (3)$$

where $W_{f\,LDPE}$ is the weight fraction of LDPE matrix.

Morphological study of LDPE/CS composites was carried out by using a scanning electron microscopy (SEM, model JOEL, JSM-6460LA). The tensile fracture specimens were mounted on aluminium stubs and sputter-coated with a thin layer of palladium for conductive purpose. The SEM analysis performed under an accelerating voltage of 5 kV.

RESULTS AND DISCUSSION

TENSILE PROPERTIES

Figure 2(a) shows the effect of filler loading on tensile strength of untreated and treated LDPE/CS composites. The tensile strength of both composites decreased with increasing of CS loading. Generally, the decrease of tensile strength depend on few factors, such as particulate filler with irregular shape usually act as stress concentrator, which initial the failure of composites under shear stress; filler with low aspect ratio is poor in stress transfer; poor interfacial bonding between hydrophilic natural filler and hydrophobic thermoplastic matrix cause poor stress transfer at interface region; and the presence of filler agglomeration (Chun et al. 2013a, 2013b). Alternatively, the addition of COCA increased the tensile strength of LDPE/CS composites. This is because the COCA reacted with hydroxyl groups on the CS via hydrogen bonding and the fatty acid chains from the COCA was attached on CS surface (Figure 3). The COCA induced an organophilic character on CS surface, which improved the wetting of LDPE matrix on filler surface and enhanced the filler-matrix adhesion
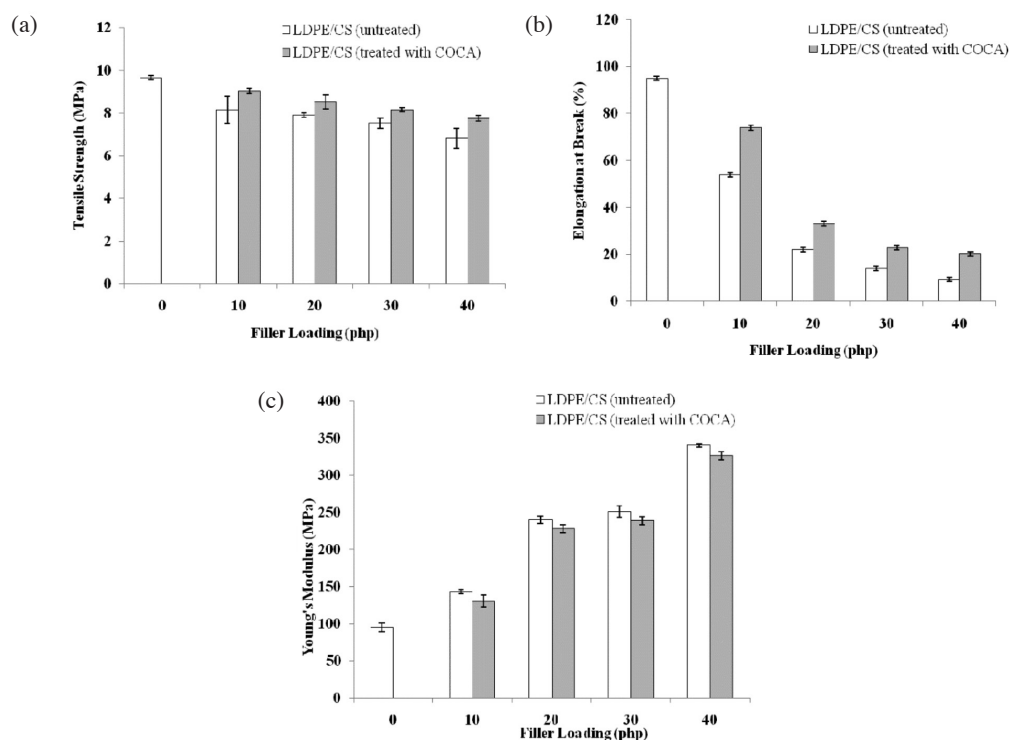

FIGURE 2. Effect of filler loading and COCA on (a) tensile strength, (b) elongation at break and (c) Young's modulus of LDPE/CS composites

(Husseinsyah et al. 2014). As a result, the tensile strength of treated LDPE/CS composites was higher. Amri et al. 2013 and Chun et al. (2013a) also reported the presence of fatty acid chains on filler surface which can improved the adhesion between natural filler and thermoplastic and it contributed to improvement of tensile strength.

The elongation at break of untreated and treated LDPE/CS composites was illustrated in Figure 2(b). The elongation at break of untreated and treated LDPE/CS composites gradually decreased at higher filler loading. The CS is rigid particulate filler and the addition of CS sure decrease the ductility of LDPE matrix. The presence of filler agglomeration (especially at higher filler loading) might act as stress concentrator and it contributed to failure of composites at lower elongation (Zaaba et al. 2013). Thus, filler agglomeration also attributed to decrease of flexibility of LDPE matrix. The similar trend also reported by other researchers (Balakrishna et al. 2012). However, the treated LDPE/CS composites with COCA exhibited higher elongation at break compared to untreated LDPE/CS composites. This probably was due to the presence of COCA that improved the process ability which enhanced the dispersion of filler. As a result, the filler agglomeration reduced and it increased the elongation at break of LDPE/CS composites. Furthermore, the presence of COCA might also contributed to lubricating effect on LDPE/CS composites, which improved the ductility of composites. In our previous study, the addition of COCA to polylactic acid/corn cob composites also showed an increment in elongation at break (Chun & Husseinsyah 2014a).

Figure 2(c) displays the Young's modulus of untreated and treated LDPE/CS composites. The result showed that the Young's modulus of both composites increased with increasing of CS loading. The Young's modulus indicated the relative stiffness of composites. The change of Young's modulus also depends on many factors such as the amount of filler used, the orientation of the fillers, the adhesion between matrix and the ratio filler to the matrix (Shash 1983). Usually, the stiffness of natural filler is higher than thermoplastic (Chun et al. 2015). Thus, the addition of CS will increase the stiffness of LDPE matrix. Besides, the presence of CS also decreased the molecular chain mobility of LDPE matrix. This is also another reason why the composites increase in Young's modulus. However, the addition of COCA decreased the Young's modulus of LDPE/CS composites. This indicates that the presence of COCA has improved the ductility of LDPE/CS composites

and it probably caused the lubricating effect from COCA. Suryadiansyah et al. (2007) also reported that the addition of ethylene diamine dilaurate increased the Young's modulus of polypropylene/waste paper composites due to the lubricating effect.

MORPHOLOGICAL STUDY

Figure 4(a)-4(b) shows the SEM micrograph of tensile fracture surface on untreated LDPE/CS composites at 20 and 40 php of filler loading. The SEM micrographs display the detachment of CS filler on both untreated composites. This indicated lees adhesion between CS and LDPE matrix. Moreover, the filler agglomeration also observed in Figure 4(b) and this indicated the CS has high tendency to form agglomerate at more filler loading. The SEM micrographs of tensile fracture surface for treated LDPE/CS with COCA composites at 20 and 40 php of filler loading are illustrated in Figures 4(c)-4(d). It can be seen that both SEM micrographs exhibited a better filler dispersion CS. The CS also embedded and coated by LDPE matrix. This evidenced the presence of COCA improved the adhesion between CS and LDPE matrix. The SEM micrograph of treated LDPE/CS composites also exhibits the ductile fracture surface, which indicated that addition of COCA also improved the ductility of LDPE/CS composites.

WATER ABSORPTION

Figure 5(a) shows the water absorption versus time curves of neat LDPE, untreated and treated LDPE/CS composites. The neat LDPE exhibited lowest amount of water absorption after 31 days. The equilibrium of water absorption of LDPE/CS composites is illustrated in Figure 5(b). It can be observed that the water absorption of the all composites increased with increasing of filler loading and immersion times. This is because the CS is naturally hydrophilic, which can easily form hydrogen bonding with water molecules. Thus, the presence of CS in composites absorption with certain amount of water and the increases of CS loading also increased the water uptake ability of composites. The similar phenomenal was also observed by other researchers (George et al. 1998; Zhao et al. 2012). Based on Figure 5(b), the treated LDPE/CS composites with COCA show lower water absorption compared to untreated LDPE/CS composites. This is because the addition of COCA that reacted with hydroxyl groups and it provided a hydrophobic
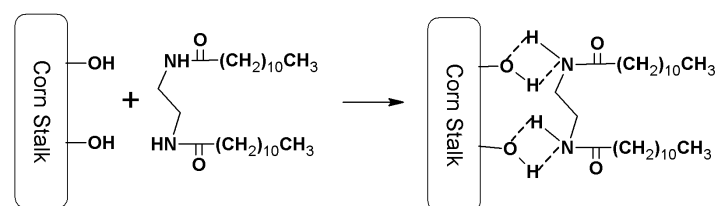

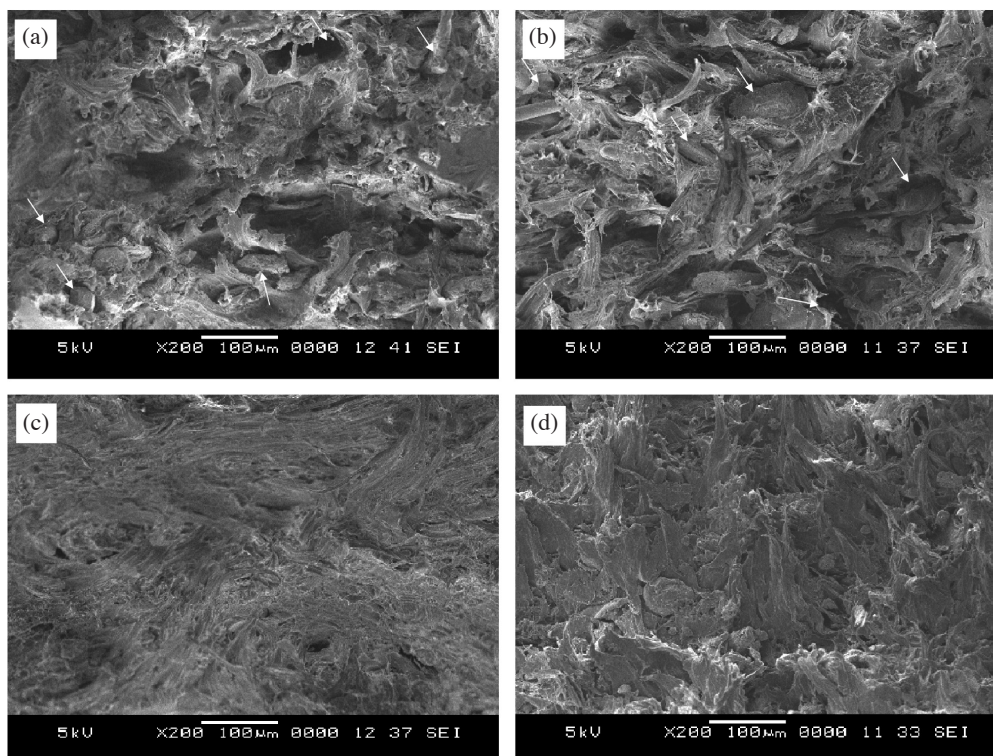
FIGURE 3. Schematic reaction between COCA and corn stalk

FIGURE 4. SEM micrographs of untreated LDPE/CS composites at (a) 20 php and (b) 40 php filler loading; and treated LDPE/CS composites with COCA at (c) 20 php and (d) 40 php filler loading
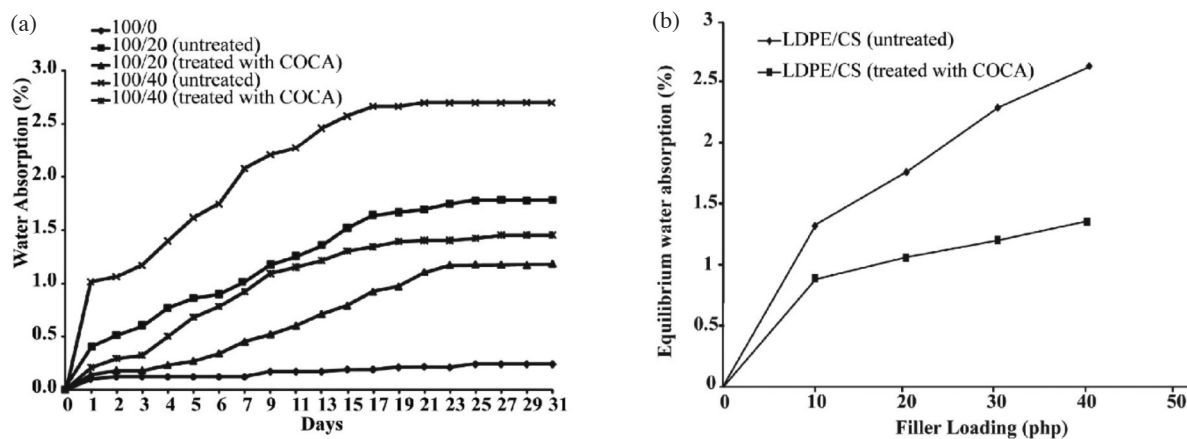

FIGURE 5. (a) Water absorption versus time curves and (b) equilibrium water absorption versus filler loading curves of untreated and treated LDPE/CS composites

fatty acid layer on CS surface. The presence of this fatty acid layer blocked the water molecules from forming hydrogen bonding with CS. Therefore, the water absorption of treated LDPE/CS composites was reduced. Husseinsyah et al. (2014) also reported the addition of COCA also decreased the water absorption of LDPE/palm kernel shell composites.

THERMAL ANALYSIS

Figure 6 displays the DSC thermograms of neat LDPE, untreated and treated LDPE/CS composites. The data

obtained from DSC thermograms is listed in Table 2. The results showed that the ΔH and X_c of both LDPE/CS composites slightly reduced with increasing of filler loading. Taking into account the fraction of matrix, the X_{LDPE} was increased at higher filler loading. This indicates the nucleating effect of CS filler. Many researchers also reported that the natural filler can induced nucleating effect on thermoplastic matrix, which led to increase crystallity of matrix (Chun & Husseinsyah 2014b; Ndiaye & Tidjani 2012). Based on Table 2, the treated LDPE/CS composites with COCA show higher ΔH and X_c then untreated LDPE/
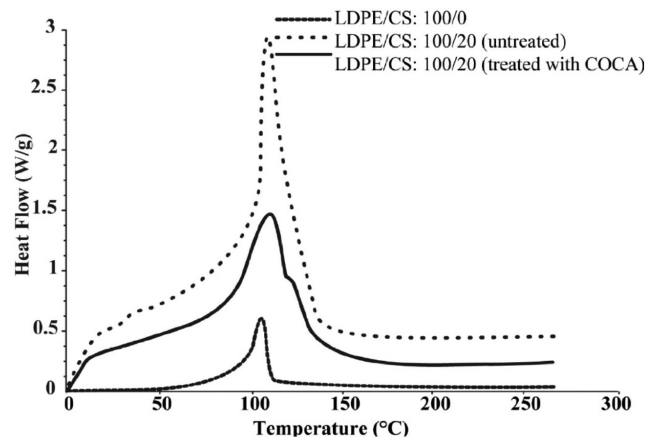
FIGURE 6. DSC thermograms of neat LDPE, untreated and treated LDPE/CS composites

TABLE 2. DSC data of neat LDPE, untreated and treated LDPE/CS composites

Materials	T_m (ºC)	ΔH (J/g)	X_c (%)	X_{LDPE} (%)
Neat LDPE	116.40	78.46	27.50	27.50
LDPE/CS:100/20 (untreated)	116.96	88.15	30.93	37.12
LDPE/CS:100/40 (untreated)	115.84	84.90	29.79	41.71
LDPE/CS:100/20 (treated with COCA)	116.05	100.04	35.10	42.12
LDPE/CS:100/40 (treated with COCA)	117.27	99.15	34.79	48.71

T_m = Melting temperature
X_c = Crystallinity of composites
ΔH = Heat fusion of composites
X_{LDPE} = Crystallinity of LDPE matrix

CS composites. Moreover, X_{LDPE} also increased with the presence of COCA. This is because the addition of COCA has improved the filler-matrix adhesion, which futher enhanced the nucleating effect of filler. As a result, the crystallinity of LDPE has increased. The similar trend was also found in our previous research as well as by other researchers (Amri et al. 2013; Chun et al. 2013a; Ndiaye & Tidjani 2012). However, the T_m of both LDPE/CS composites were not significantly change with the increase of filler loading and addtion of COCA.

CONCLUSION

The increase of CS loading had reduced the tensile strength and elongation at break of LDPE/CS composites, but increased in Young's modulus, water absorption and crystallinity of matrix. The SEM micrographs show a poor dispersion of CS filler and weak adhesion between CS and LDPE matrix. The addition of COCA had significantly increased the tensile strength, elongation at break and crystallinity of LDPE/CS composites. However, the Young's modulus and water absorption of LDPE/CS composites were reduced with the presence of COCA. The addition of COCA improved the filler-matrix adhesion,

which led to improve of properties. The good adhesion between CS and LDPE matrix can be evidenced by SEM micrographs.

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