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The effect of bacterial cellulose on the mechanical and thermal expansion properties of kenaf/polylactic acid composites

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Abstract. The reinforcement of PLA matrix with natural fibers aims to generate the sustainable biocomposites. Kenaf fiber (KF) and bacterial cellulose (BC) were employed to reinforce and diminish the usage of PLA matrix. Particularly, BC is nano-cellulose which was anticipated to increased interfacial area and therefore low volume fractions of additives. That was consequently to attain mechanical property improvement. Thus, the incorporation of KF and BC reinforced PLA composites was investigated. The extrusion method was utilized and materials were mixed outside prior to adding. The specimens were examined mechanical testing, Dynamic Mechanical Analysis (DMA), Differential Scanning Calorimetry (DSC), Thermo Gravimetric Analysis (TGA) and Scanning Electron Microscopes (SEM). The mechanical study revealed that the increment of elastic modulus increased concomitantly with the augmentation of KF content. Interestingly, PLA/KF/BC sample at ratio of 60/39/1 wt.% was efficiently to maintain tensile and flexural strength comparing to 50% reduction of without BC sample with equal fiber volume. Therefore, it could recognize that mechanical properties was improved by using low amount of nano-cellulose. This would be a high aspect ratio of BC that capable to connect between PLA matrix and KF which enhanced a large contact surface and therefore excellent coherence. The temperature dependence of storage, loss and tan delta was determined by DMA. A decrease of storage modulus was consistent with increasing of temperature, result from softening of the composites. Loss modulus was increased approximately at T_g which related to storage modulus cause. In addition, the tan delta peaks of PLA and composites were around 60°C and it did not significantly shift when emerged of fiber. DSC of both composites indicated an influence of fiber on the crystallization and enthalpy. On the other hand, glass transition and melting temperature did not significantly affect. The composites exhibited a small reduction of thermal stability when examined by TGA analysis. Notwithstanding, BC showed an improvement of thermal stability of PLA/KF/BC sample at 40 wt.% total fiber content. The linkage of BC between PLA matrix and KF was monitored by SEM.

Introduction

Recently, the use of biodegradable plant-based lignocellulosic fibers has been investigated by abundant research groups which aimed to replace the glass fiber utilization. This cognitive receiving would be due to the advantages of plant fibers such as biodegradability, renewability, low density, high specific strength, low cost, and carbon dioxide sequestration [1,2]. Therefore, a number of natural plant fibers for instance jute, kenaf, hemp, flax, pineapple leaf, bamboo and sisal were employed to strengthen both renewable and nonrenewable resources to create the biodegradable composites [3]. Presently, PLA is the most outstanding biodegradable polymers. Due to it derives from renewable resources by fermentation using carbohydrate materials such as corn and tapioca starches [4]. Furthermore, it has good mechanical properties and easily degrades by microorganisms

in control conditions [5]. However, the cost of PLA is a limitation which is relatively higher than petroleum based plastics. Therefore, this would be a reasonable utilization plant fibers as filler which can be directly reduced the production cost. Moreover, plant fibers are also expected to improve the mechanical properties. Kenaf fiber (KF) has been using long time ago by our ancestors such as rope, canvas and sacking [6]. Recently, KF usage is get along with various industries which provide highly valuable products such as paper, textiles and automotive parts. However, KF with other natural fibers have inevitable bottleneck that is multiple hydroxyl groups on the linear chain of glucose moieties which is fully exhibited hydrophilic property. Therefore, this would be an obstacle for compatibility of hydrophilic natural fibers and aliphatic polyesters. The poor interfacial adhesion between two components results weak mechanical properties which is due to inefficiency of stress transfer between matrix and filler. To overcome this subject, researchers have been modified fiber surface to promote hydrophobicity which supposed to enhance surface interaction to the matrix. Chemical modifications to natural fibers such as silanization [7], coupling by lysine and methylene diisocyanate [8,9] have been studied. However, due to global environmental awareness, researchers aim to create environmentally friendly composites, which avoidance of chemical usage.

It extensively knew that reinforcement of PLA using plant fibers remarkably increase the Young's modulus with an increase of fiber content. On the other hand, a tensile strength was decreased [10]. To step over this hurdle, reinforcement with nano-cellulose has been widely studied. Cellulose nanowhiskers can be produced from plant based materials but the utilization of chemical treatment in production process is not sustainable approach. Bacterial cellulose (BC) is biopolymer which generally produces by *Acetobacter xylinum.* This biopolymer has been used in several applications such as acoustic diaphragms, paper, wound dressings, artificial skin, and reinforced composites. It was resulting from unique properties for instance; high crystalinity, high purity, high Young's modulus, biodegradability, large water holding capacity etc. [11]. The aim of this work was to investigate the physico-mechanical properties of PLA based-composites with combination of KF and BC. We supposed that the connecting of nano-sized of BC between KF and PLA matrix would have some property benefits to these green composites.

Materials and Methods

Materials. Poly(lactic acid) (PLA) was purchased from Huvis Ltd., (South Korea). The kenaf fibers (KF) were kindly given by Sutongsang (South Korea) which an average size 850 μm. Bacterial cellulose (BC) was produced by *Acetobacter xylinum* which purchased from Institute of Food Research and Product Development, Kasetsart University, Thailand. Brown coconut water was used as the medium in terms of production cost reduction. The cultivation was carried out for 7 days. BC was purified within 0.1 N NaOH in order to remove cells and other impurities from the inner BC sheet. Freeze drying was used to dry wet BC and ground by rotor mill with an average size 750 μm. All materials were mixed prior to feeding in to twin screw extruders. Various compositions of materials were exhibited in Table 1.

Mechanical testing. The tensile and flexural properties were examined by means of Universal Testing Machine (Zwick Co.) according to ASTM standards D638 and D790, respectively. The crosshead speed of tensile testing was 5 mm min^{-1} with the gage length of 63 mm of dumbbells shape. All tests were performed for at least five specimens and the data was taken into account of the average values.

Fracture surface analysis. Surface characterization was monitored by using a scanning electron microscopes (SNE-3000M, Dream Corp., Korea). The samples were attached to the aluminum stubs with carbon tape and dried at 80°C for 2 hours. The specimen surfaces were coated with gold to abstain from charging prior to the image analysis.

Dynamic mechanical analysis (DMA). TA instruments dynamic mechanical analyzer (DMA Q800, TA Instruments) was utilized for the storage modulus, loss modulus and loss factor (tan δ) determination. The samples were performed at a frequency of 1 Hz, a heating rate of 2˚C/min and temperature range between -20˚C and 140˚C.

Differential scanning calorimetry (DSC). Thermal properties together with glass transition temperature (Tg), melting temperature (Tm) and melting enthalpy (ΔHm) were investigated by using a TA Instrument DSC Q 1000 at a heating rate of 10 ˚C/min, and sample weight was approximately 10 mg.

Thermogravimetric analysis (TGA). Thermal stability of biocomposites was monitored by using TGA Q500 with a heating rate of 10˚C/min. The temperature range was started from ambient temperature to 500˚C and fully fumigated with N_2.

Table 1. Compositions of different materials.

Materials	PLA matrix (wt.%)	KF (wt.%)	BC (wt.%)
PLA	100	-	-
PLA/KF	90	10	-
PLA/KF	80	20	-
PLA/KF	70	30	-
PLA/KF	60	40	-
PLA/KF/BC	90	9	1
PLA/KF/BC	80	19	1
PLA/KF/BC	70	29	1
PLA/KF/BC	60	39	1

Results and discussion

Mechanical properties. Figure 1 (a) and (b) are exhibited the tensile properties of PLA biocomposites. The elastic modulus was increased which corresponded to the augmentation of fiber contents. This phenomenon could be described from the effect of hydrogen bonding of entangle cellulose that was dispersed in the PLA matrix [12]. However, the decrease can be recognized when the fiber content was 40 wt.%. The PLA/KF specimen showed 17% decrease comparing to 11% reduction of PLA/KF/BC sample. The reduction of elastic modulus at high fiber content could be ascribed to the insufficient filling of PLA matrix. The outstanding effect of composite containing BC was remarkably presented to tensile strength. At the highest percentage of fiber, a sharp decrease of tensile strength of PLA/KF was demonstrated. This can be described that 40 wt.% KF had less PLA matrix which created low interfacial interaction between PLA and fiber. Therefore, the applied stress was not transfered to the rigid filler particles. On the other hand, perfect stabilization was shown to PLA/KF/BC sample at the same total fiber volume. The explanation would be due to the good connection of BC between matrix and KF. The intermolecular forces between BC and PLA matrix may promote the tensile strength of the PLA-based composites [13]. This resulted to the remaining of tensile strength at high amount of fiber. Figure 2 showed the flexural strength of PLA-based composites. According to the results, 40 wt.% fiber content of PLA/KF sample showed approximately 40% decrease of flexural strength. This would be the result of poor dispersion of fiber in the matrix [14]. However, the efficient stress transfer between PLA matrix and KF was clearly seen when it presented of BC. Therefore, this would be a great interest phenomenon that we can create PLA-based composites with high fiber content and stabilize preference mechanical properties. Moreover, it can be seen that nano-filler have the potential for significant reinforcement in composite materials at small loading.

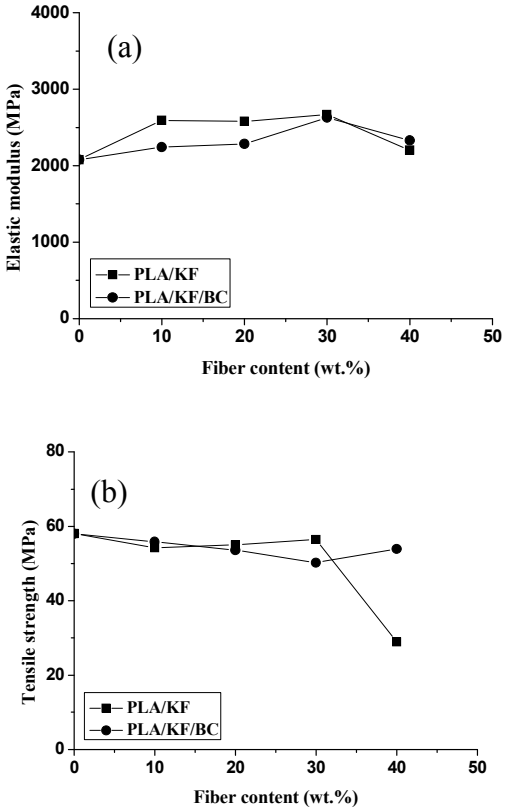

Fig.1 Effect of kenaf fiber content and the combination with BC on the elastic modulus (a) and tensile strength (b) of PLA biocomposites.

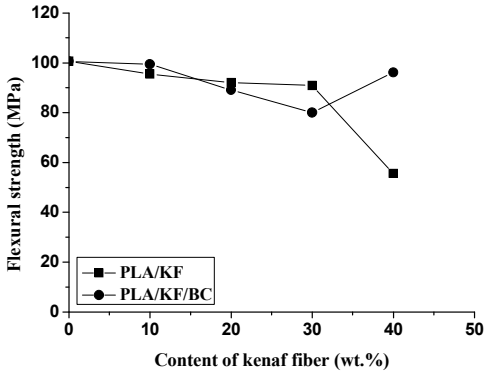

Fig.2 Flexural strength of neat PLA and PLA-based composites.

Crystallization and melting property. The thermal properties were exhibited in Table 2 which composed of glass transition temperature (T_g), melting temperature (T_m), melting enthalpy (ΔH_m) and degree of crystallinity (χ). The neat PLA showed a 58% degree of crystallinity which determined from the assumption that PLA is merely crystalline. The percentage of crystallinity calculated by using the following formula, $\chi = \Delta H_m / \Delta H^0_m \text{ X } 100$, where ΔH_m is obtained from the DSC study and ΔH^0_m is the pure crystalline matrix of PLA (93.7 J/g). The reduction of percentage of crystallinity with the addition of fibers is probably the presence of the polar groups which is an obstruct of crystallinity forming [15]. In addition, the reduction of melting enthalpy also displayed with loading of fiber samples which is indicated that less energy was needed to melt the composites. This circumstance described that thermal degradation of composites containing KF became easier [16]. T_g and T_m of PLA with addition of KF did not significantly change. The same results can be found with PLA/KF/BC composites.

Table 2. Thermal properties of neat PLA and PLA-based composites.

Fiber content (wt%)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	χ (%)
Neat PLA	60	153	54.3	58
10	57*/58*	156/156	22.1/24	23.6/25.6
20	57/57	155/155	25.4/21.8	27.1/23.3
30	56/55	152/153	17.8/17.6	19/18.8
40	54/57	151/155	21/23.7	22.4/25.3

X*/Y*; where X is the sample of PLA/KF, Y is the sample of PLA/KF/BC.

Dynamic mechanical properties. The result of thermal analysis of PLA/KF and PLA/KF/BC samples was displayed in Figure 3 and 4, respectively, which composed of storage modulus (a), loss modulus (b) and tan delta (c). Generally, DMA was employed to determined how disclosing of the microcomposites to elevated temperatures influence to the stiffness of the composites [15]. The storage modulus represents the stiffness of the composites which obviously seen in Fig. 3(a) and 4(a) that the increment of storage modulus was shown with fiber content raise. This was remarkably the reinforcing affect by the fiber to pure matrix. The feasible explanation of this phenomenon is bonding between the molecules and stringent skeletal structure of cellulose molecule [17]. A decrease in the storage modulus was notably recognized with the increasing of temperature due to the softening of the composites. A reduction was dramatically observed between 50-70°C which was consistent with the glass transition temperature. Figure 3(b) and 4(b) showed the loss modulus of composites which represents the dissipation of energy into heat when a material is deformed. The loss modulus decreased around the T_g in composites, corresponding to the storage modulus. However, T_g of composites was not significant shift from neat PLA which was contrast to [18]. The loss factor or tan delta is the ratio of loss modulus to storage modulus which indicated in Fig. 3(c) and 4(c). Generally, the peak of tan delta was frequently used as the T_g and the peak of PLA was approximately 60°C, corresponding to DSC result. The reduction in intensity of tan delta was consistent with the rising of fiber contents. This can be ascribed that the addition of fibers prevented the mobility of PLA matrix [19].

Thermogravimetry. Figure 5 showed the result of thermal stability and degradation profiles which investigated by thermogravimetric analysis. The thermal stability was slightly reduced comparing with increase of fiber content. This circumstance has been observed with other natural fibers such as wood flour [16] or protein based fiber, silk [20]. The weight loss of KF and BC (data not shown) began to reduce at around 270°C consistent with degradation temperature. While, 380°C corresponded to accomplish temperature degradation [21]. PLA/KF sample showed the lowest thermal stability, particularly, sample at 40 wt.% fiber content presented much lower than PLA/KF/BC. The addition of low amount of BC to the composites, resulted in the thermal stability of the composites. Remarkably, 40 wt.% fiber of PLA/KF/BC sample demonstrated approximately 10°C improvement comparing with PLA/KF specimen. This can be explained by that BC created the ultra fine network even at low filler content of 1 wt.% that was sufficiently to restrain composites deformation. Moreover, it is noteworthy that awesome compatibility between two fibers is also enhanced the thermal stability.

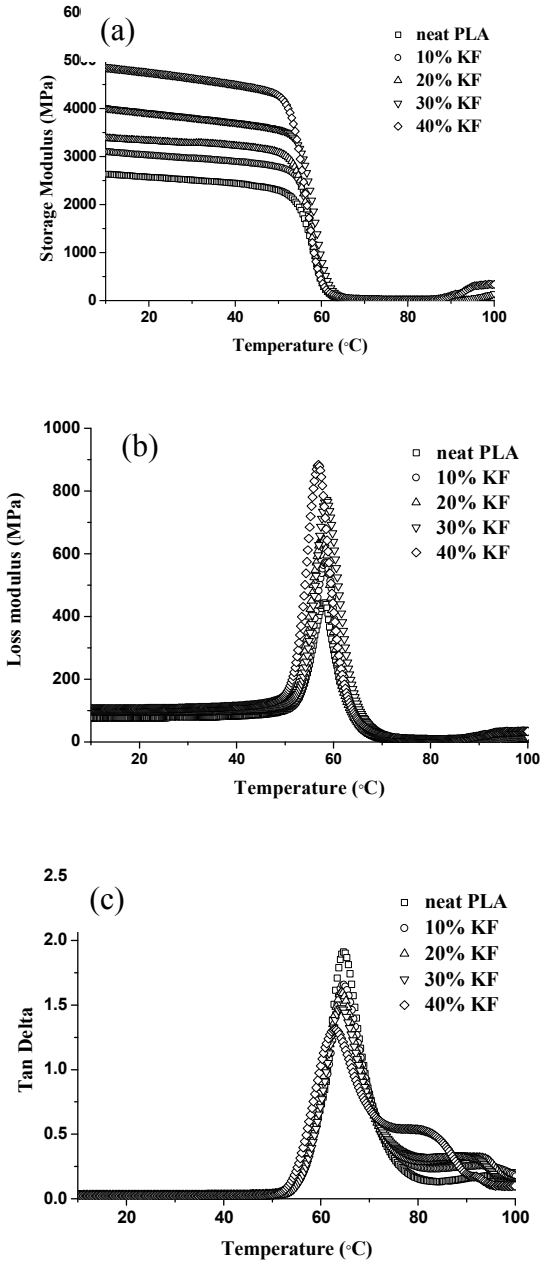

Fig. 3 Temperature dependent of storage modulus (a), loss modulus (b) and tan delta (c) of PLA and PLA/KF composites.

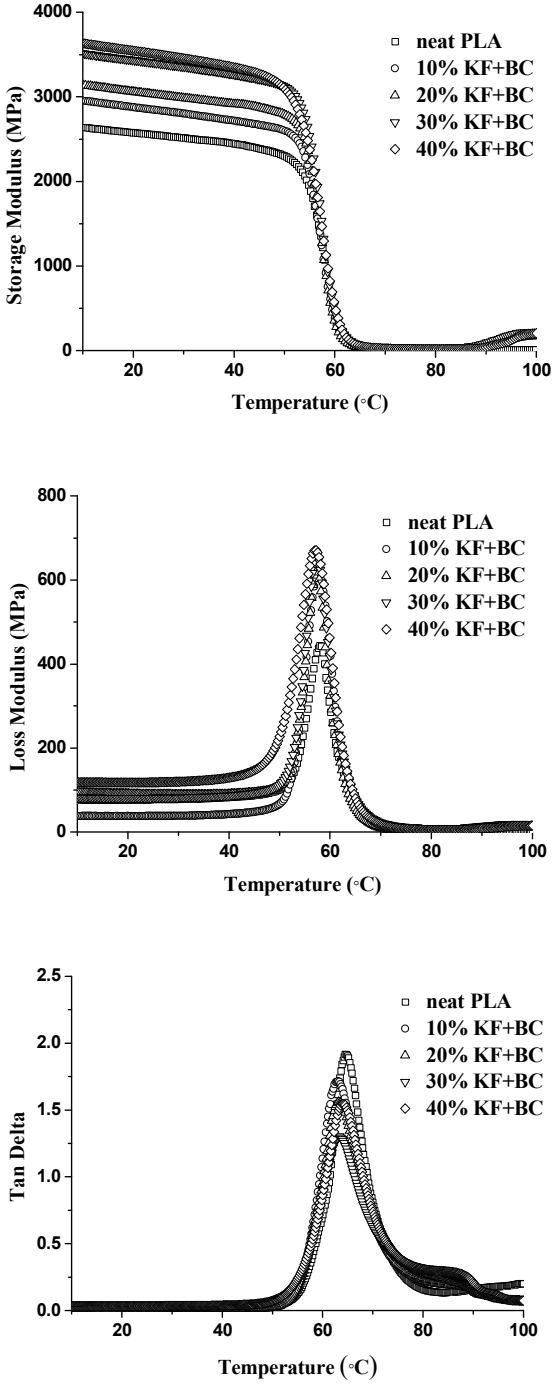

Fig. 4 Temperature dependent of storage modulus (a), loss modulus (b) and tan delta (c) of PLA and PLA/KF/BC composites.

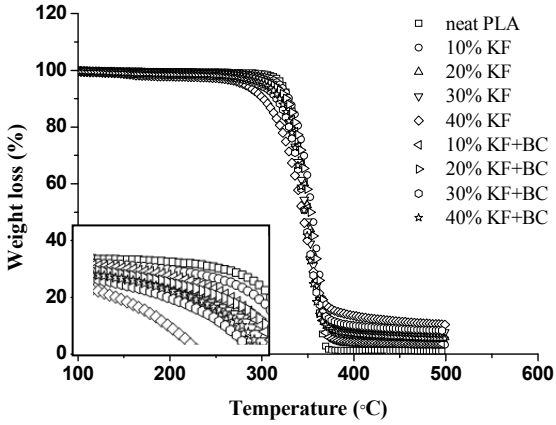

Fig. 5 Thermogravimetric curves of PLA and PLA composites

Fracture surface analysis. Figure 6 exhibited the fracture surface of the PLA composites. It can be seen that pulled-out of fibers was displayed and void was surrounding it (Fig. 6a). This would be ascribed the poor surface adhesion between fiber and PLA matrix. However, If we considered to the results of tensile strength test, PLA/KF/BC at 40 wt.% fiber had much higher than without BC at the same fiber volume. This would be resulted from BC web that exhibited a substantial capability to fortify of biocomposites. The small dimensions of BC capable to connect between PLA matrix and KF which increased a large contact surface and therefore excellent coherence. Bridging of BC networks between matrix and KF is shown in Fig. 6b.

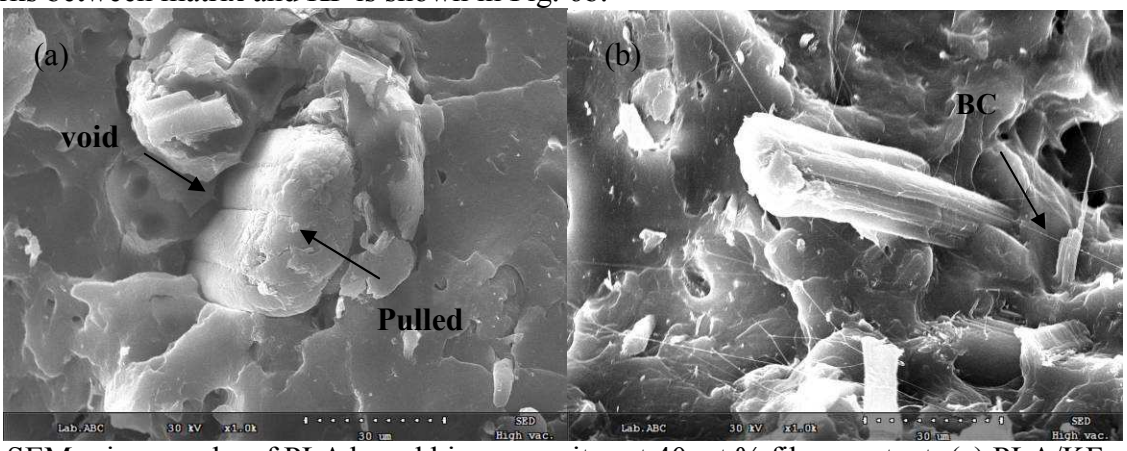

Fig. 6 SEM micrographs of PLA based biocomposites at 40 wt.% fiber content; (a) PLA/KF and (b) PLA/KF/BC.

Summary

A low content of BC was added to the PLA-based composites which is a remarkable influence to tensile properties and thermal stability. These improvements would be due to the combination of BC that provided excellent interfacial adhesion to PLA matrix and great hydrogen bonding to KF. Therefore, this will be one approach to create biocomposites at high fiber content and still preserve of physico-mechanical properties. Furthermore, nano-fillers have the potential for significant reinforcement in composite materials at small loading.

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