PREPARATION AND PROPERTIES OF JUTE / POLY(LACTIC ACID) / ACETYLATED KRAFT LIGNIN BASED THERMOPLASTIC POLYURETHANE BIOCOMPOSITES

Jongshin Park* and Hyun-gyoo Roh

Department of Biosystems and Biomaterials Science & Engineering, Seoul National University, Seoul 08826, Korea
* Corresponding author: jongshin@snu.ac.kr

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ABSTRACT

Poly(lactic acid) (PLA) is a popular one and used for bioplastics and biomedical applications. However, its brittleness and low thermal resistance restrict its application as bioplastics in spite of its comparable strength to general purpose plastics. Lignin, complex aromatic heteropolymer from woody plants, was studied in many ways for high-value utilization. Jute, a kind of lignocellulosic fibers with low density and high specific modulus, is applied as reinforcement of biocomposites in many studies.

In this study, alkali-treated jute (AJ) / poly(lactic acid) (PLA) / acetylated softwood kraft lignin based thermoplastic polyurethane (ASKLTPU) biocomposites were prepared as bioplastics with high content of natural resources and biodegradability. ASKLTPU was prepared by solution casting method as thermoplastic polyurethanes (TPU) with relatively high lignin content (up to 60 weight % of ASKL), and applied for improving brittleness of PLA. AJ was used for further reinforcement

PLA/ASKLTPU blends and alkali-treated jute (AJ) / poly(lactic acid) (PLA) / acetylated softwood kraft lignin based thermoplastic polyurethane (ASKLTPU) biocomposites were prepared by melt blending and hot press method. Mechanical properties, thermal properties, and water absorbancy of ASKLTPU, PLA / ASKLTPU, and AJ / PLA / ASKLTPU biocomposites are investigated. Especially, TPU60 (ASKLTPU with 60 wt. % content of ASKL) shows significant increase of Young's modulus. After introduction of 15 wt.% of AJ to PLA/ASKLTPU blend(80/20, w/w), tensile strength and Young's modulus increases significantly. Thermal properties of PLA / ASKLTPU blends and AJ / PLA / ASKLTPU biocomposites are investigated by differential scanning calorimetry (DSC). The blends are partially miscible, and shows clearer thermal transition as PLA content increases. Consequently, prepared novel biocomposites has a potential of alternative to commercial plastics

1 INTRODUCTION

Bio-based and/or biodegradable plastics and natural fibers as polymer composite reinforcement were studied for alternatives to general-purpose plastics in order to cope with global regulations for environmental issues. [1, 2] Among the bio-based or biodegradable plastics, poly(lactic acid) (PLA) is a popular bio-based polymer used for bioplastics and biomedical applications. However, its brittleness and low thermal resistance restrict its application as bioplastics in spite of its comparable strength to general purpose plastics. [1,3] Lignin is a kind of complex aromatic heteropolymer from woody plants. [4] Lignin is usually obtained as a form of industrial lignin, including kraft lignin from by-product of kraft pulping process. For high-value application, lignin was studied in many fields such as polyurethane chemistry, epoxies, adhesives, polymer blends, and others. [5, 6] Jute is a kind of natural fibers with low density and high specific modulus, and is applied as reinforcement of biocomposites in many studies. [1, 2]

As one of the methods enhancing brittleness of PLA, PLA/TPU blends were studied before. [7,8] In this study, alkali-treated jute (AJ) / poly(lactic acid) (PLA) / acetylated softwood kraft lignin based thermoplastic polyurethane (ASKLTPU) biocomposites were prepared as bioplastics with high content of natural resources and biodegradability. ASKLTPU was prepared as thermoplastic polyurethanes

(TPU) with relatively high lignin content (up to 60 weight % of ASKL), and applied for improving brittleness of PLA

2 EXPERIMENTAL

2.1 Materials

PLA (Ingeo 2002D®, NatureWorks, USA), Softwood kraft lignin (SKL) (Indulin AT®, MeadWestvaco, Charleston, USA), Jute fiber (Bangladesh Jute Institute, Bangladesh), Acetic anhydride, Polyethylene glycol (PEG; MW = 1000 g/mol), Hexamethylene diisocyanate (HDI) (Wako chemical, USA), Tetrahydrofuran (THF), Sodium hydroxide (Duksan Pure Chemical, Korea), Acetic acid (Showa Chemical, Japan)

2.2 Acetylation of SKL

SKL is acetylated by the procedure of our previous studies. [9,10] 100 g of SKL, dried under vacuum at 105°C, was reacted with 300 mL of acetic anhydride at 80°C for 40 minutes. Then the reactants were quenched by ethanol/water mixture (1:1 v/v). The resultant solid was washed by deionized water, followed by vacuum drying at 105 °C for 24 hours. The resultant, ASKL, was conditioned at RT. The degree of acetylation of ASKL was 90%.

2.3 Alkali treatment of jute fiber

Jute fibers were chopped to about 50 mm in length. Chopped jute fibers were soaked in a 5% NaOH solution. The fibers were kept immersed in the alkali solution for 4 hours, then washed with fresh water to remove NaOH repeatedly. The washed fibers were neutralized with acetic acid, and washed again with distilled water repeatedly. A final pH of 7 was maintained. The fibers were then dried at room temperature for 48 hours followed by oven drying at 100℃ for 6 hours. Resultant fibers (AJ) were conditioned at RT.

2.4 Preparation of ASKLTPU

ASKLTPU, which ASKL content is 40, 50, 60 wt. %, is prepared by solution casting method below, modified from our previous stuedies.s [9, 10] About 50 g of THF was added to the polyol mixture, which consists of certain amounts of vacuum dried ASKL and PEG. The polyol mixture solution was stirred for 20 minutes, followed by adding certain amount of HDI. The mixture was reacted for 5 - 20 minutes until the reactant becomes fairly thick. The reacting solution was casted onto a PTFE dish coated with a urethane mold release. The casted sheet was placed into a vacuum oven and degassed at 90°C for 1-4 hours, followed by curing at 90 °C for 48 hours. Finally, the resultant ASKLTPU were conditioned at RT. The –NCO/-OH ratio of ASKLTPU was 1.05. The composition of ASKLTPU samples was listed in Table 1

Sample	ASKL content (wt. %)	Hard segment content (wt. %)	ASKL (g)	PEG (g)	HDI (g)
TPU40	40	50.6	14	17.29	3.71
TPU50	50	59.5	17.5	14.17	3.33
TPU60	60	68.4	21	11.06	2.94

Table 1: The composition of ASKLTPU

2.5 Preparation of PLA/ASKLTPU blends and AJ/PLA/ASKLTPU biocomposites

PLA / ASKLTPU blends and AJ / PLA / ASKLTPU biocomposites were prepared by hot press method. TPU60 was selected as TPU component for blend preparation. AJ, PLA, and TPU60 were vacuum dried before use. For PLA/ASKLTPU blends, PLA and TPU60, which ratios were 20/80, 50/50, 80/20 (w/w), were mixed by table type kneader at 160 ℃, followed by hot-press method using

two post manual hydraulic presses at 160 ℃. For comparison, 100% PLA were processed by same procedure. For AJ/PLA/ASKLTPU biocomposites, AJ, PLA, and TPU60, which ratios were 5/76/19, 10/72/18, 15/68/17 (w/w), were prepared by same procedure.

2.6 Characterizations

Mechanical properties of ASKLTPU, PLA/ASKLTPU blends, AJ/PLA/ASKLTPU biocomposites were characterized by tensile tests using universal testing machines (UTM) (LRXPlus, LLOYD Instruments, UK). The tensile test was performed according to ASTM D 638-10 guidelines with ASTM type V specimens, but some settings were changed due to characteristics of samples. Gage length, strain rate, and preload were wet as 10.0 mm, 50 mm/min, 0.1 N, respectively.

Thermal properties were characterized by differential scanning calorimetry (DSC). DSC was performed from −50 to 200 ℃. The heating and cooling rate was 10 °C/min.

Water absorbency was characterized by water immersion method. The samples were immersed in deionized water and water absorbency was calculated as Eq. 1

$$\textit{Water absorbency (\%)} = \frac{W-W0}{W0} \times 100\,(\%) \quad (1)$$

w is immersed weight of the samples at the certain time while w_0 is original weight of samples.

3 RESULTS AND DISCUSSION

3.2 Mechanical properties of ASKLTPU, PLA/ASKLTPU blends, and AJ/PLA/ASKLTPU biocomposites

Mechanical properties of ASKLTPU with different ASKL contents were shown in Figure 1. As ASKL content increased, tensile strength and Young's modulus increased while strain at break decreased. Especially, TPU60 showed significant increase of Young's modulus. ASKL was functioned as hard segment of TPU in ASKLTPU. As ASKL content increased, hard segment of ASKLTPU increased. Then, hard segment domain of TPU, which act as physical crosslinks, also increased, resulting in increase of strength(tensile strength) and Young's modulus. In contrast, increase of hard segment domain also resulted in decrease of flexibility, so strain at break decreased as ASKL content increased.

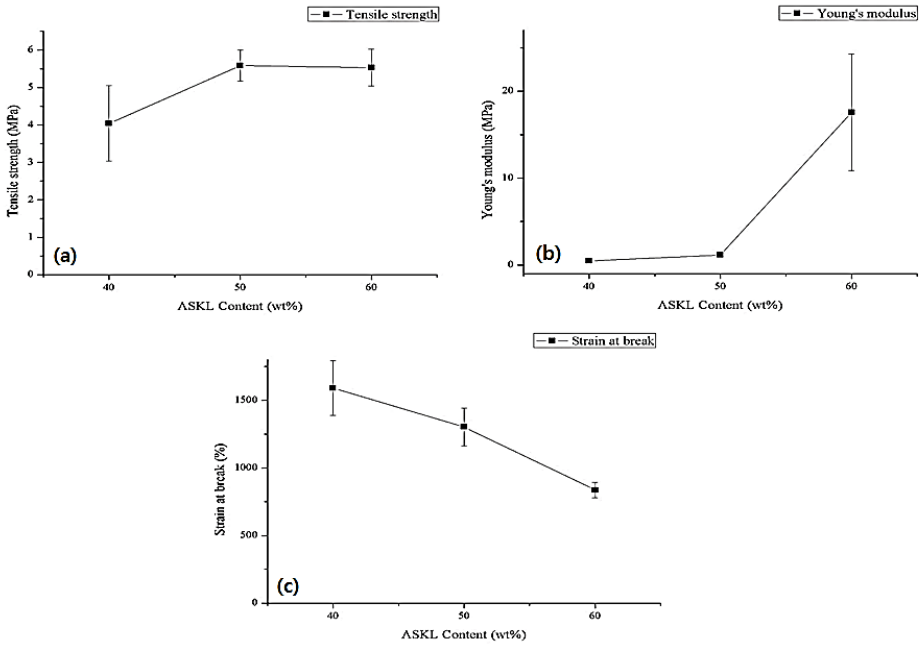

Figure 1: Mechanical properties of ASKLTPU with different ASKL contents
(a) Tensile strength (b) Young's modulus (c) Strain at break

Mechanical properties of PLA/ASKLTPU blends with different TPU contents were shown in Figure 2. Among ASKLTPUs, TPU60 was selected as TPU component for blend preparation. As TPU content increased, tensile strength and Young's modulus decreased while strain at break increased. After introduction of 20 wt.% of TPU to PLA, tensile strength and young's modulus of the blend significantly decreased. Generally, mechanical properties of blends were dependent on its composition. The higher TPU content, the mechanical properties became more similar to flexible TPU, so strength and stiffness decreased while flexibility increased. Especially, tensile strength, Young's modulus, and strain at break of PLA/TPU 80/20 blend (the matrix of biocomposites below) were 24.1 MPa, 404 MPa, and 7.6 %, respectively.

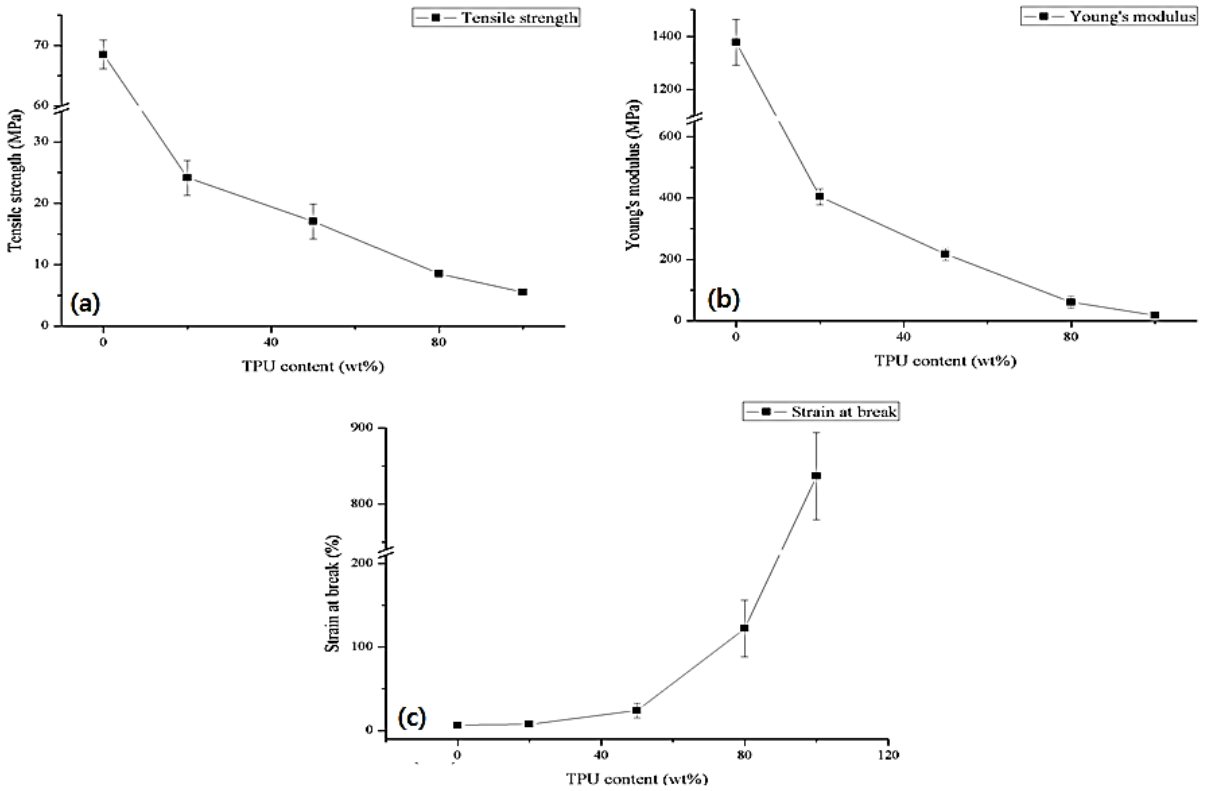

Figure 2: Mechanical properties of PLA/TPU60 blends with differentASKLTPU contents
(a) Tensile strength (b)Young's modulus (c) Strain at break

Mechanical properties of AJ / PLA / ASKLTPU with different ASKL contents were shown in Figure 3. Among PLA/ASKLTPU blends, PLA/TPU60 20/80 was selected as the matrix for preparation of biocomposites. As fiber content increased, tensile strength and Young's modulus increased. After introduction of 15 wt.% of AJ, tensile strength increased by 48% (reached 35.7 MPa) and Young's modulus increased by 51% (reached 611 MPa). The increase of mechanical properties was due to effect of fiber reinforcement though the fiber orientation might be random for isotropic properties. Interestingly, strain at break remained in spite of fiber reinforcement, even it seemed to be little increase of strain at break. It could be discussed in further studies. Especially, tensile strength of AJ/PLA/ASKLTPU 15/68/17 (35.7 MPa) was comparable to that of polypropylene, which showed the potential of alternatives to commercial plastics.

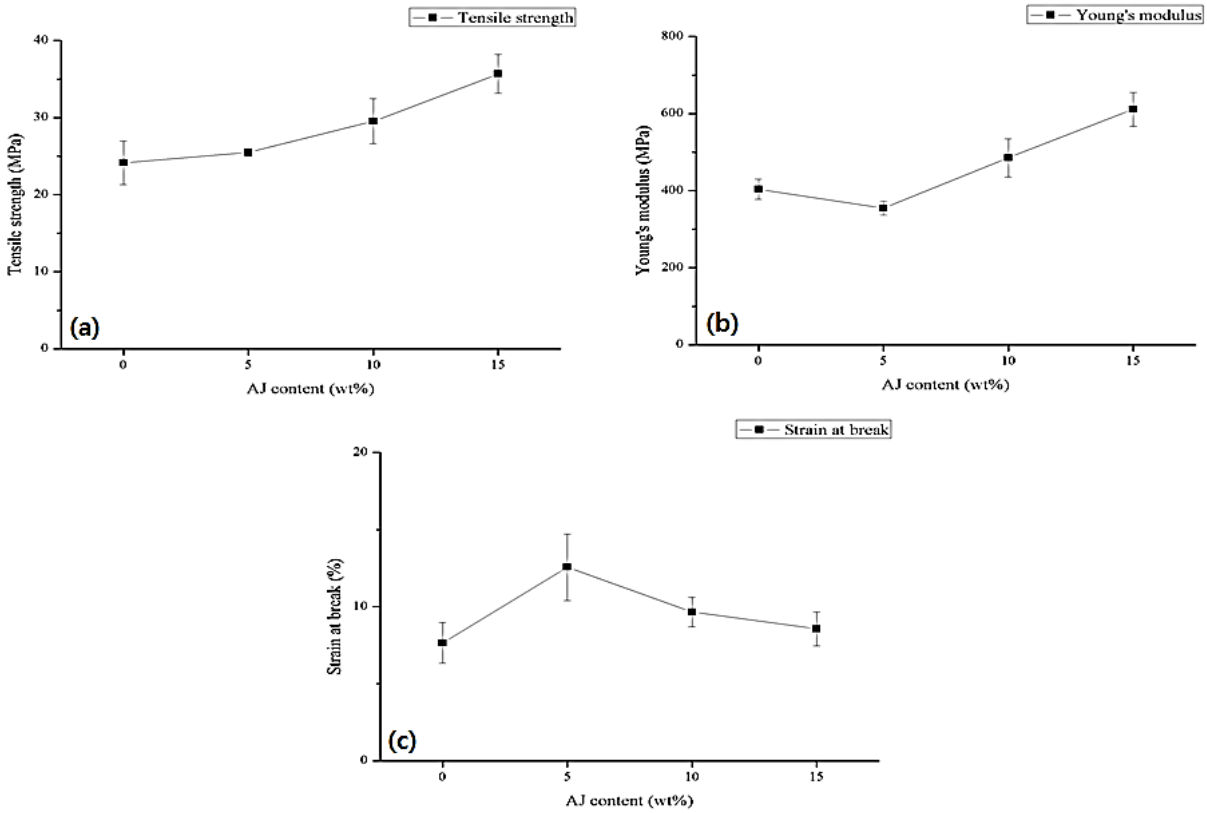

Figure 3: Mechanical properties of AJ / PLA/ASKLTPU biocomposites with different fiber contents (a) Tensile strength (b)Young'smodulus (c) Strain at break

3.3 Thermal properties of PLA / ASKLTPU blends and AJ / PLA / ASKLTPU biocomposites

Thermal properties of PLA/ASKLTPU blends and AJ/PLA/ASKLTPU biocomposites were investigated by differential scanning calorimetry (DSC) and shown in Figure 4 and Table 2. The blends were partially miscible, and showed clearer thermal transition as PLA content increased. In case of heat of fusion, it was estimated that crystallinity of the blends decreased as TPU content increased. It might be explained that amorphous ASKLTPU interrupted crystallization of PLA. Similar effect by AJ was showed in DSC curves of the composites.

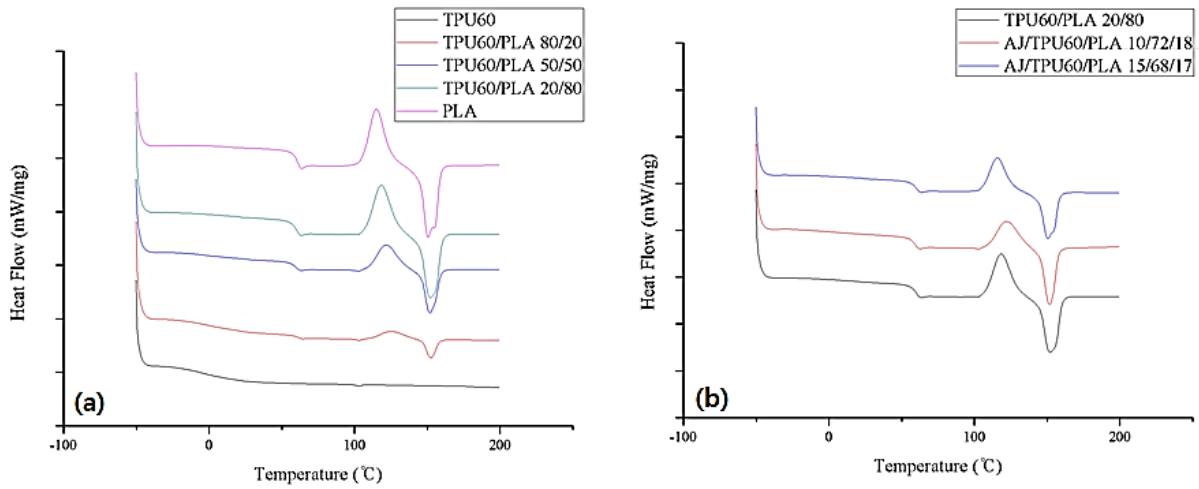

Figure 4: DSC curves of (a) PLA/ ASKLTPU blends and (b)AJ / PLA/ASKLTPU biocomposites

Samples	Tg (℃)	Tc (℃)	Tm (℃)	Δ Cp (J/g-K)	Δ Hc (J/g)	Δ Hf (J/g)
TPU60	-5.5	-	-	0.202	-	-
TPU60/PLA 80/20	0.2	124.4	152.4	0.189	4.679	-4.571
	60.3			0.088		
TPU60/PLA 50/50	58.5	121.8	151.8	0.252	14.2	-13.39
TPU60/PLA 20/80	58.9	118.3	152.2	0.434	24.45	-24.45
PLA	59.5	115.0	154.7	0.485	26.37	-26.36
AJ/TPU60/PLA 10/18/72	58.2	122.3	151.7	0.374	18.55	-18.46
AJ/TPU60/PLA 15/17/68	58.9	115.7	150.4	0.354	18.65	-18.63

Table 2: Thermal properties of PLA/ASKLTPU blends and AJ/PLA/ASKLTPU biocomposites (Tg: glass transtion, Tc: crystallization temperature, Tm: melting temperature, ΔCp : heat capacity, ΔHc: heat of crystallization, ΔHf: heat of fusion)

3.4 Water absorbency of PLA/ASKLTPU and AJ/PLA/ASKLTPU biocomposites

Water absorbency of PLA/ASKLTPU blends and AJ/PLA/ASKLTPU biocomposites were shown in Figure 5. Water absorbency of PLA/ASKLTPU blends increases rapidly over the first 48 hours, then gradually increases, and after 72 hours there is little change. Water absorbency of TPU60 absorbed reached at 53.24% in final equilibrium state, but the water absorbency tended to decrease with increasing PLA content. As with the PLA/ASKLTPU results, AJ/PLA/ASKLTPU composites showed an increase in water uptake over time but showed little change. The higher the AJ content, the higher water abosrbancy was investigated due to the increased content of hydrophilic nature of AJ. However, in earlier stage, the introduction of AJ lowers the water absorbancy. It might be due to the hindrance of penetration of water by fiber reinforcement.

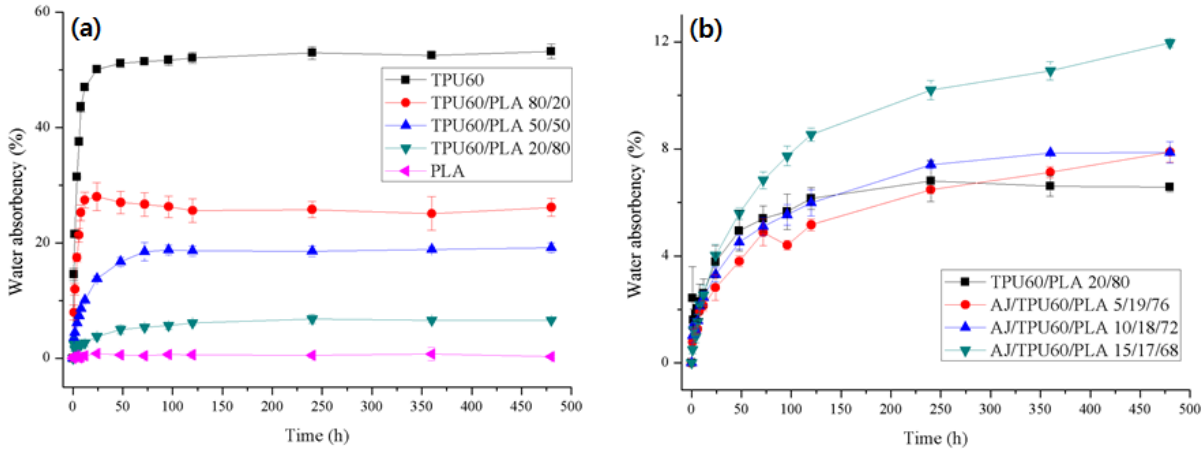

Figure 5: Water absorbency of (a) PLA/ASKLTPU blends and (b) AJ/PLA/ASKLTPU biocomposites

4 CONCLUSIONS

Alkali-treated jute (AJ) / acetylated softwood kraft lignin based thermoplastic polyurethane (ASKLTPU) / poly(lactic acid) (PLA) biocomposites were prepared and characterized. ASKLTPU was prepared as thermoplastic polyurethanes (TPU) with relatively high lignin content(up to 60 weight % of ASKL), and applied for improving brittleness of PLA. As ASKL content increased, tensile strength and Young's modulus of ASKLTPU increased while strain at break decreased. As TPU content increased, tensile strength and Young's modulus of PLA/ASKLTPU blends decreased while strain at break increased. Strength and stiffness were enhanced by AJ fiber reinforcement. In thermal

properties, the blends were partially miscible, and showed clearer thermal transition as PLA content increased. As PLA content increases, water absorbency of the biocomposites decreased and is expected to be stable against water or moisture content. As a result, new prepared biocomposites had a potential of alternative to commercial plastics.

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