IMPROVEMENTS OF INTERFACIAL ADHESION FROM COMPOSITES OF PLA AND ACETYLATED KENAF

T. Chung[1], B. Lee[1], H. Lee[1], H. Kwon[1], H. Kim[1,2]*
[1] *Lab. of Adhesion & Bio-Composites, Program in Environmental Materials Science,*
[2]*Research Team for Biomass-based Bio-Materials, Research Institute for Agriculture and Life Sciences, Seoul National University, Seoul 151-921, Republic of Korea*
* Corresponding author (hjokim@snu.ac.kr, www.adhesion.org)

Keywords: *Acetylation, Extrusion, Compatibilizer*

1 Introduction

In the recent years, the use of biodegradable and renewable materials as filler of polymer-based composites has received more attention because of preferences for environmental favorable materials [1]. Therefore, the composites composed of biodegradable polymers and filler as renewable fibers can be considered a good substitute of petroleum products. For example, biodegradable products can solve disposal problems of products which are composed of the used materials or no more available things. In this study the properties of bio-composites composed of PLA (Polylactic aicd) and acetylated kenaf fibers were prepared and evaluated. It is assumed that acetylated kenaf fibers would show a hydrophobic character and contribute to the improvements in an interfacial adhesion between kenaf fibers and PLA.

2 Materials and Methods

2.1 Materials

The PLA granules composed of average diameter of 81 μm and a density 1.24 g/cm^3 were supplied by Natureworks LLC, USA. The kenaf fibers used were bast fibers and were donated by Sutongsang, Korea. Acetic anhydride was purchased from Junsei Chemical Co., Japan. Pyridine was purchased from Daejung Chemicals & Metal Co., Korea. These chemicals were used for acetylation. The kenaf fibers were acetylated using acetic anhydride.

2.2 Preparing of MAPLA

PLA was dried at 80 ℃ for 12 hours and stored in a polyethylene bag. Those were blended with using a twin-screw extruder after PLA was mixed with maleic anhydride (MA) and benzoyl peroxide (BPO) as a thermal initiator. The extruded materials were cooled with water in a bath and pelletized.

2.3 Extrusion

Materials of the composites were compounded by a twin-screw extruder (BA-19 in Bautek, Korea). The extrusion was carried out 140-185 ^{o}C and the screw speed was maintained at 150 rpm. The output is 5 kg/h and the maximum capacity is 25 kg/h [2]. Figure 1 shows a blending process through an extruder.

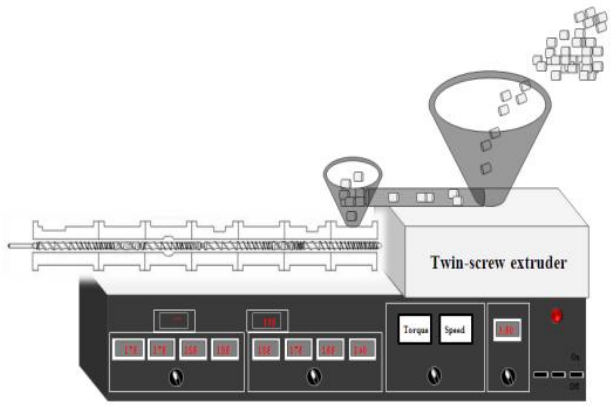

Fig. 1. Schematic picture of the blending process.

2.4 Acetylation of kenaf fibers

Prior to acetylation, the kenaf fibers were stored in polyethylene bags in order to avoid the penetration of water vapor after being dried at 60 ℃. The 10 g oven-dried fibers were placed in a 500 mL round-bottom flask with a magnetic stirrer. 50 mL of acetic anhydride was added to the solution and mixed with kenaf fibers under slow stirring for 30 minutes. Then, an adequate amount of pyridine was added as catalyst. The reaction was carried out for 2 hours while maintaining reflux. Afterward, distilled water was added and the flask was immersed in an ice bath for 10 minutes [3]. This sediment was obtained by adding ethanol followed by filtrating with aspirator. 80 % ethanol was added and the solution was mixed for 30 minutes and filtered in order to get rid of unreacted acetic anhydride and newly formed acetic acid after the reaction. This was repeated twice. The final sample was dried in a vacuum oven at 60 ℃ for 24 hours

2.5 Blending and sample preparation

Dried PLA or MAPLA as a compatibilizer were blended with kenaf fibers or acetylated kenaf fibers by using a twin-screw extruder. The extruded materials were cooled with water in a bath and pelletized. Table 2 shows constituents of samples that were used in this experiment.

Table 1. Composition of samples

Sample	Based materials	Reinforcing materials	Compatibilizer
1	PLA (100 %)	-	-
2	PLA (70 %)	Keanf fibers (30 %)	-
3	PLA (70 %)	Keanf fibers (30 %)	MAPLA (3 phr)
4	PLA (70 %)	Acetylated Keanf fibers (30 %)	MAPLA (3 phr)

3 Measurements

3.1 Tensile strength

The tensile strength test of the composites was carried out according to ASTM D 638-10 with a Universal Testing Machine (Zwick Co.) at a crosshead speed of 100 mm/min and a temperature of 23±2 ˚C. Five measurements were conducted and averaged for the final result.

3.2 FTIR-ATR spectroscopy

Functional groups of the acetylated kenaf fibers and composites with MAPLA were measured with a JASCO 6100 FTIR-ATR spectrophotometer. The samples are analyzed over the range of 4000 – 650 cm^{-1} with a spectrum resolution of 4 cm^{-1}. All spectra were averaged over 30 scans.

3.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was used to observe the interface between those composites using Mini-SEM (Dream Corporation, Korea). Prior to the measurement, the samples were coated with gold to eliminate electron charging.

4. Results and discussion

4.1 Degree of substitution by titration

The way to determine the degree of substitution (DS) suggested by Kim [4] was adopted. First, 1 g of dried kenaf fibers was placed to a 250 mL flask, 40 mL of 75 % EtOH was added and the flasks were heated to 50 – 60 ℃ for 30 minutes. 40 mL of 0.5 N NaOH was added, and then was heated to 50 ℃ for 15 minutes. The mixture kept at room temperature for 48 hours under constant stirring. The excess alkali was titrated with 0.5 N HCl using phenolphthalein as an indicator and DS was calculated. The value of DS was 0.995.

4.2 Acetylation of kenaf fibers

As seen in Figure 2, FTIR-ATR spectroscopy was used to analyze the chemical modification of kenaf fibers before and after acetylation. The hydroxyl stretching band around 3350 cm^{-1} became smaller after acetylation and the symmetric C-H vibration band around 2950 cm^{-1} also was decreased. On the other hand, the carbonyl stretching band around 1740 cm^{-1} in ester bonds and the C-O vibration peaks around 1222 cm^{-1} was intensified [5]. These peaks could confirm acetylation of kenaf fibers. The lowered peaks of O-H stretching band around 3350 cm^{-1} by acetylation indicate a partial modification [6].

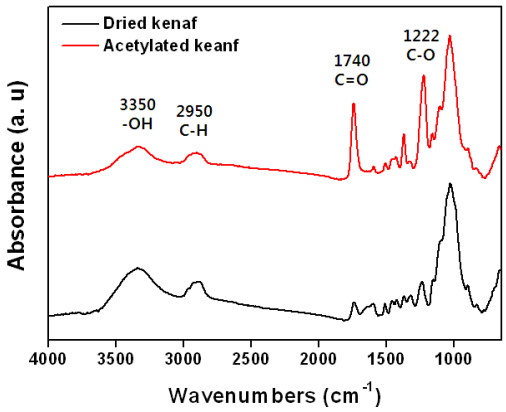

Fig. 2. FTIR spectroscopy of dried and acetylated kenaf.

4.3 Mechanical Properties

4.3.1 Tensile strength

Figure 3 shows the tensile strength of the composites composed of different ratio of filler and compatibilizer with PLA. While comparing the composites with compatibilizer or not, the tensile strength was decreased when the sample did not have a chemical modification. On the other hand, the sample which was modified by acetylation showed a significant increase in the tensile strength.

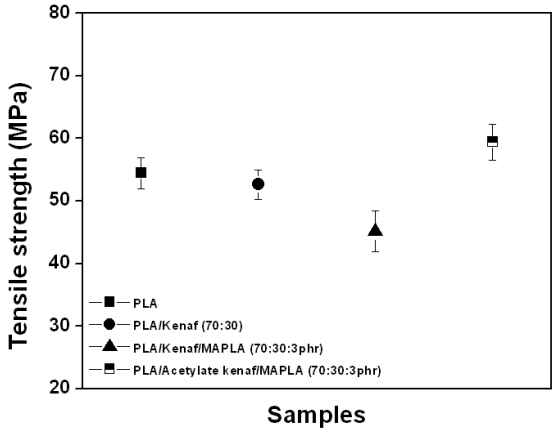

Fig. 3. Tensile strength of the composites composed of different ratio of filler and compatibilizer with PLA.

4.3.2 Stress-strain curve

As seen in Figure 4, when compared to the PLA/kenaf (70:30) sample, the composite composed of PLA and acetylated kenaf and MAPLA showed the value more elongation and a stronger intensity. On the other hand, the composite which was not modified by acetylation indicated more increasing strain than the PLA/kenaf (70:30) sample. But the value of strength showed a lower value.

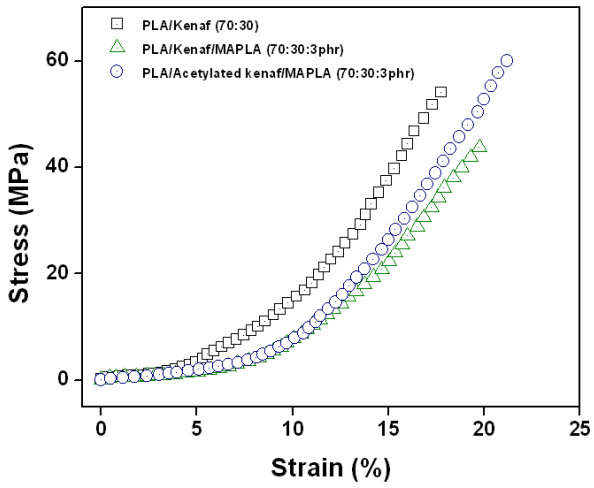

Fig. 4. Stress-strain curve of MAPLA and kenaf fibers-filled PLA composites.

4.4 Morphological characterization

Figure 5 shows SEM images of the tensile fracture surface of untreated and acetylated composite. The unmodified fracture surface (A) indicated the presence of many pores and larger gaps [7]. While the acetylated sample did not show pores. When the figures below (B) and tensile strength were compared, it was found that acetylation improved an interfacial adhesion through an interaction between more hydrophobic kenaf fibers and PLA.

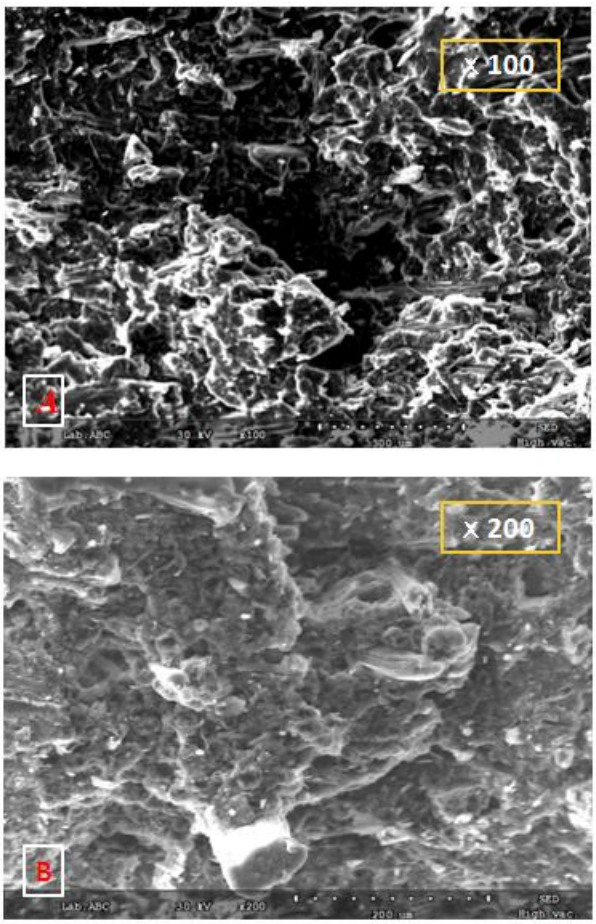

Fig. 5. SEM micrographs of the tensile fracture of PLA/ kenaf/MAPLA (A) and PLA/acetylated kenaf/MAPLA (B)

5 Conclusion

The kenaf fibers were acetylated to make hydrophobic fibers. FTIR results demonstrated the improvement of hydrophobicity as using acetylation from natural fibers.

The composites composed of PLA, acetylated kenaf fibers and MAPLA were prepared and characterized. This approach based on the preparation of acetylated kenaf fibers and addition of a compatibilizer demonstrated that chemical modification improved an interfacial adhesion between hydrophobic PLA and hydrophilic fibers. Also, it was found that the value of tensile strength were more increased though improvements of an interfacial adhesion by acetylation and MAPLA.

References

[1] M. Avella, G. Bogoeva Gaceva, A. Bužarovska, M. Errico, G. Gentile, and A. Grozdanov, "Poly (lactic acid) based biocomposites reinforced with kenaf fibers". *Journal of Applied Polymer Science,* Vol. 108, No. 6, pp. 3542-3551, 2008.

[2] K. Oksman, A. P. Mathew, D. Bondeson, and I. Kvien, "Manufacturing process of cellulose whiskers/polylactic acid nanocomposites". *Composites Science and Technology,* Vol. 66, No. 15, pp. 2776-2784, 2006.

[3] C. Xu, A. Leppänen, P. Eklund, P. Holmlund, R. Sjöholm, K. Sundberg, and S. Willför, "Acetylation and characterization of spruce (Picea abies) galactoglucomannans". *Carbohydrate Research,* Vol. 345, No. 6, pp. 810-816, 2010.

[4] D. Kim, Y. Nishiyama, and S. Kuga, "Surface acetylation of bacterial cellulose". *Cellulose,* Vol. 9, No. 3, pp. 361-367, 2002.

[5] M. Jonoobi, J. Harun, A. P. Mathew, M. Z. B. Hussein, and K. Oksman, "Preparation of cellulose nanofibers with hydrophobic surface characteristics". *Cellulose,* Vol. 17, No. 2, pp. 299-307, 2010.

[6] X. F. Sun, and R. C. Sun, "Comparative study of acetylation of rice straw fiber with or without catalysts". *Wood and Fiber Science,* Vol. 34, No. 2, pp. 306-317, 2002.

[7] H. S. Kim, B. H. Lee, S. Lee, H. J. Kim, and J. Dorgan, "Enhanced interfacial adhesion, mechanical, and thermal properties of natural flour-filled biodegradable polymer bio-composites". *Journal of Thermal Analysis and Calorimetry,* Vol. 104, No. 1, pp. 331-338, 2011.