STUDY OF SURFACE TREATMENT OF PINEAPPLE LEAF FIBER (PALF) ON PERFORMANCE OF PALF/ABS COMPOSITES

P. Threepopnatkul[1,*], T. Krachang [1], W. Teerawattananon[1], K. Suriyaphaparkorn[1], C. Kulsetthanchalee[2,*]

[1]*Department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000, Thailand*
[2]*Faculty of Science and Technology, Suan Dusit Rajabhat University, Bangkok 10300, Thailand*
**e-mail address of the corresponding author: poonsubt@yahoo.com, chanink@gmail.com*

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Abstract

This research is to study the influence of surface treatment for pineapple leaf fiber (PALF) on the mechanical properties of PALF reinforced ABS composites (ABS/PALF). PALF was pre-treated with sodium hydroxide (PALF/NaOH), cellulase enzyme treatment and modified with N-2(aminoethyl) 3-aminopropyl trimethoxysilane (PALF/silane) to improve interfacial strength of the composites. PALF with different surface treatment methods were characterized using Fourier Transform Infrared and Scanning Electron Microscopy technique. The composites were tested mechanical properties by Universal Testing machine. The results show that the modified PALF composites lead to the enhancement of mechanical properties such as young's modulus. Young's modulus is the highest for PALF/NaOH/Cellulase composites. PALF/silane composites possessed the highest tensile strength and impact strength among all the treated system.

1. Introduction

Acrylonitrile-butadiene-styrene terpolymer (ABS) plastics possess several prominent properties such as strength, rigidity, and toughness. In addition, it has resistance to chemicals and endurance provision for wide ranges of temperature usage. Each component of terpolymer provided different effects on the properties of ABS. Acrylonitrile contributes to heat and chemical resistance. Butadiene provides impact properties due to its rubbery phase. Styrene has its function on processability and surface properties. Therefore, outstanding properties of ABS plastics could be tailored-made by adjusting the proportion of its components. Research and development of ABS composites with natural fibers and the study of their properties have been found very little in literature, mostly been carried out using wood sawdust as reinforcements [1-2].

Nowadays, natural fiber reinforced composites had been in great interests due to the cost saving, productivity enhancement and mechanical properties improvement of the final product. Among various natural fibers, PALFs exhibit excellent mechanical properties due to its high cellulose content of more than 70% [3]. However, a critical problem of using fiber as reinforcement in plastic is poor adhesion between natural fiber and polymer matrix [4]. Thus, the improved interface quality of composites is commonly achieved by treating surfaces of the fibers with suitable methods such as chemical modifier, coupling agent and compatibilizer agent [5-7]. The use of enzyme technology has been increased substantially in the natural fiber processing. A major reason for embracing this technology is the fact that application of enzyme is regard as environmental friendly and the catalytic reactions are very specific with focused performance as a consequence [8]. Cellulases are commonly used as industrial enzymes for bio scouring which is able to remove unwanted elements from fiber surface [8]. However, waxes and other non-cellulosic compounds can be a barrier to these enzymes [9]. In order to achieve good results, these enzyme treatments have been pre-treated by alkaline treatments, for example, sodium hydroxide.

This study is a continual research that focuses on the use of PALFs as reinforcement to improve mechanical properties of ABS composites. This research also aims at the preparation of green composites by surface modification of PALF with NaOH and/or cellulase enzyme and/or N-2(aminoethyl) 3-aminopropyl trimethoxysilane (as know as KBM603).

2. Experimental

2.1. Materials

PALFs were used as reinforcement for composites. ABS (ABS GA300) obtained from IRPC Public Co., Ltd., Rayong, Thailand, was used as the matrix. Sodium hydroxide (NaOH) was purchased from Ajax Finechem, Australia. Cellulase (VZ221448) was purchased from Dystar Thai Ltd. Bangkok Thailand. Acetic acid, methanol and acetone Laventin, a wetting agent and detergent were supplied by BASF SE Ludwigshafen, Germany. Silane coupling agents, N-2(aminoethyl) 3-aminopropyl trimethoxysilane (KBM603) whose chemical structure is shown in Figure 1. This coupling agent was supplied by Sigma-aldrich, Inc. Germany.

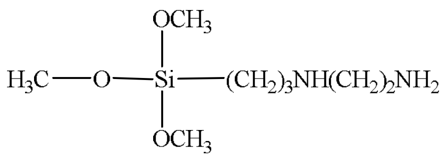


Figure 1. The chemical structure of N-2(aminoethyl) 3-aminopropyl trimethoxysilane.

2.2 Fiber surface modification

Alkaline pre-treatment - PALFs were cut into 5-10 mm in lengths. The fibers were washed and immersed in water at 50 °C for 10 min. Then fibers were immersed in a bath containing water (liquor ratio 1:25), 2% on weight fabric (owf) NaOH solution and 1% owf of wetting agent (laventin type) at 60 °C for 30 min. Next, the fibers were washed with distilled water until all NaOH was eliminated. After washing, the fibers were kept in open air for 3 days following by drying in an oven at 80 °C for 24 h.

Enzyme treatment - PALFs were immersed in bath containing water (liquor ratio 1:40), cellulase enzyme (0.5 g/l) and 1% owf of wetting agent (laventin type) at 55 °C for 4 h. The pH of the solution was adjusted to 6-7.5 with acetic acid. Next, the fibers were washed with distilled water at 75 °C for 10 min. followed by rinsed by twice distilled water. Finally, the fibers were dried in open air for 3 days following by drying in an oven at 80 °C for 24 h.

Silane treatment - 0.5% w/w N-2(aminoethyl) 3-aminopropyl trimethoxysilane (KBM603) (weight percentage compared to the fiber) was dissolved for hydrolysis in methanol solution. The pH of the solution was adjusted to 3.5 with acetic acid and stirred continuously for 10 min. Next, the fibers were soaked in the solution for 6 h and dried in oven at 100 °C for 24 h. following by drying in air for 3 days.

Alkali and silane treatment - First, the fibers were treated by 2 wt. % sodium hydroxide solution as described in the alkali treatment step. Next, the fibers were treated by KBM603 as describe in silane treatment step.

Alkali and enzyme treatment - First, the fibers were treated by 2 wt.% sodium hydroxide solution as described in the alkali treatment step. Next, the fibers were treated by cellulase enzyme as describe in enzyme treatment step.

2.3 Composites compounding and processing

10 wt. % of the modified PALF were compounded with ABS using diisononyl phthalate 1% w/w (weight percentage compared to the ABS) as plasticizer in a co-rotating twin screw extruder, Enmach SHJ-25. The blending temperature profiles on the extruder were 175 - 190 ^{o}C from hopper to die zones. The screw rotating speed was 80 rpm. An injection molding machine, Battenfeld 40 tons, was used to prepare the specimens for mechanical tests. The barrel temperature profiles on the injection molding machine were 180 – 190 ^{o}C from hopper to nozzle zone.

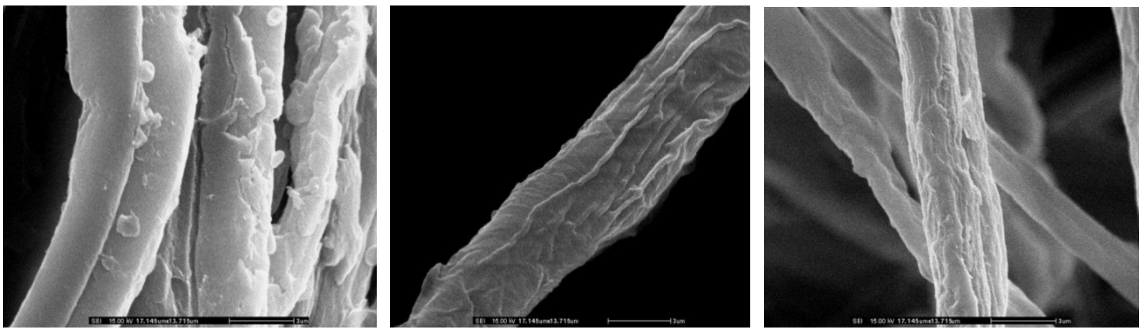
2.4 Characterization and testing

The modified fiber was identified using a Fourier transform infrared spectroscopy (FTIR, Nicolet impact 410). A universal testing machine (LLOYD Instruments Corp. LR 50K) was used for tensile properties measurements, according to ISO 527-2 at a cross-head speed of 5 mm/min. Izod impact tests, following ASTM D256, were performed on a Zwick impact tester (B102.202) with the notched side facing the pendulum. The interfacial PALF/ABS adhesions and PALF surface were investigated using a scanning electron microscopy (SEM), Cam Scan, MX 2000 operated at 15 keV. The composite fracture surfaces for examination were obtained by the specimen immersion in liquid nitrogen.

3 Results and discussion

3.1 Characterization of treated PALF by SEM and FTIR

From SEM, these cells are surrounded by thin walled tissues. Residual cell fragments remain on the surface of the fiber bundles as seen in Figure 2a. Most of the waxy layer at the surface and other noncellulosic substances were removed by NaOH as depicted in Figure 2b. Cellulase catalyzes the hydrolysis of both primary and secondary cell walls. The hydrolysis effect is shown in Figure 2c where the outer layer of the fiber is loosened and started to fall apart.



(a) (b) (c)

Figure 2.SEM micrographs of (a) Untreated PALF, (b) 2% NaOH treated PALF, (c) 2% NaOH + cellulase treated PALF

The FTIR spectrum of untreated and surface treated PALF were presented in Figure 3. The peak around 1664 cm^{-1} can be attributed to the presence of the carboxylic ester in the pectin and wax. The two bottom lines showed a significant reduction for NaOH and NaOH + cellulase treated fibers when compared to untreated fibers indicating the removal of pectin and wax. Characteristic peak of silane was revealed at around 1749 cm^{-1} corresponds to the $-NH_2$ stretching. All of untreated and treated PALF revealed broad peaks at around 3300-3600 cm^{-1} which could be contributed to -OH. As for silane treated PALF spectra, characteristic peak of silane at around 1749 cm^{-1} corresponded to the $-NH_2$ stretching which reassured the silane reactions with pineapple leaf fibers. Such reactions occurred via direct condensation reactions between the hydrolyzed silane and hydroxyl groups of the cellulose in pineapple leaves as shown in Figure 4.

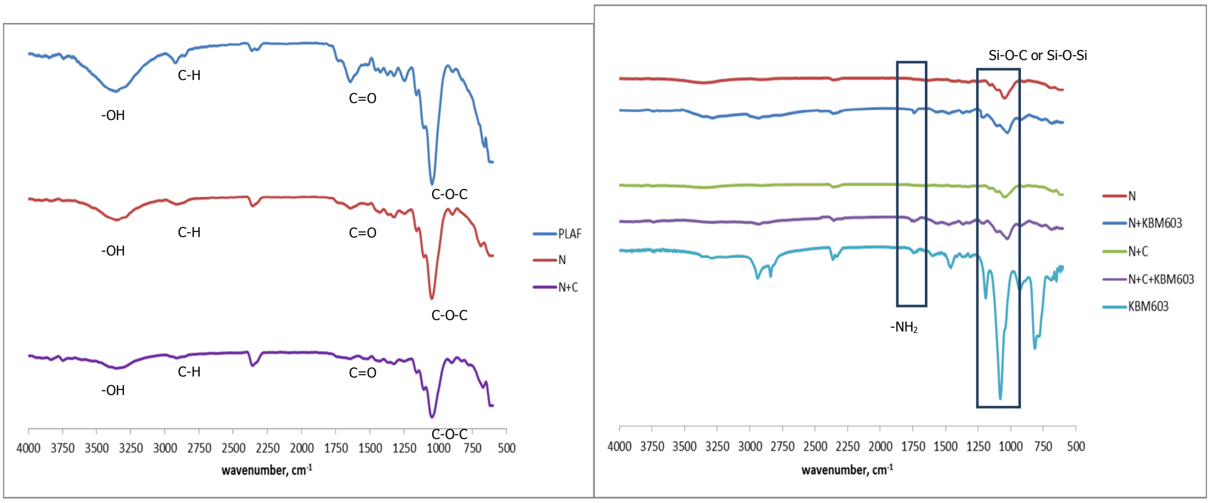


Figure 3.FTIR spectrum of untreated PALF (PALF), NaOH treated PALF (N), NaOH+cellulase treated PALF (N+C), NaOH+silane treated (N+KBM603), NaOH+cellulase+silanetreated PALF (N+C+KMB603), KBM603

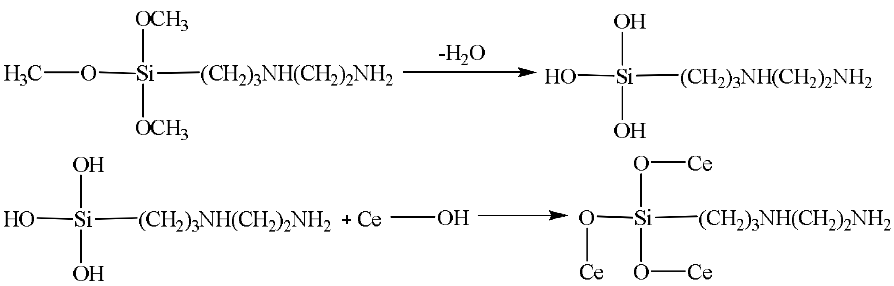


Figure 4. Reaction between pineapple leaf fibers and N-2(aminoethyl) 3-aminopropyl trimethoxysilane.

3.2. Effect of surface treatment on mechanical properties of PALF/ABS composites

3.2.1 Tensile properties

The ductile behavior of PALF/ABS composites was changed to brittle as seen from figure 5. Tensile modulus, tensile strength, percentage elongation at break of neat ABS and PALF/ABS composites are shown in Table 1.

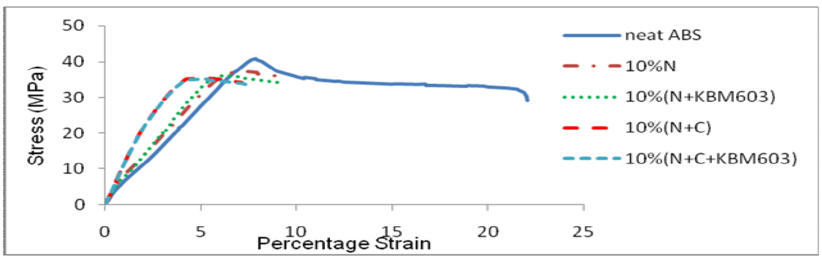


Figure 5. Stress-strain curve of tensile test

From Table 1, the addition of PALF could significantly increase the modulus according to the rule of mixture at which the stronger portion of PALF was blended in. Due to the main cellulosic component of PALF, once they were mixed together would enable the composites to become somewhat higher in modulus. ABS/PALF treated with NaOH and cellulase enzymes (N+C) composites were stronger than treated with only NaOH (N). The treatments with cellulase enzyme would degrade amorphous cellulose. The fiber would have more crystalline cellulose and thus the system N + C treated fibers are stronger. Therefore, the Young's Modulus of ABS/PALF treated with N + C system would be higher than the ABS/PALF treated with N. Addition of silane (N+KBM603) would reduce the modulus because of polysiloxanes formed by silane. The reaction scheme is shown in Figure 6.

Sample	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Impact strength (kJ/m^2)
Neat ABS	763.45 ± 22.02	41.55 ± 0.50	30.47 ± 8.61	33.22 ± 1.02
NaOH treated PALF/ABS	1092.33 ± 80.14	36.52 ± 0.21	8.43 ± 0.94	3.30 ± 0.69
NaOH + silane treated PALF/ABS	955.77 ± 62.86	36.56 ± 0.35	9.08 ± 0.61	3.62 ± 0.36
NaOH + cellulase treated PALF/ABS	1193.54 ± 9.77	35.50 ± 0.09	6.90 ± 0.13	4.88 ± 0.32
NaOH + cellulase + silane treated PALF/ABS	1168.71 ± 30.89	35.57 ± 0.33	7.06 ± 0.40	5.08 ± 0.35

Table 1. Effect of surface treatment on mechanical properties of PALF/ABS composites.

For the tensile strength of all treated PALF composites, the values dropped down when compared to neat ABS. Thus, introducing the fibers at this fraction could act as the flaws and thus the fibers were not perfectly aligned with matrix and causing the inconsistency of the force transmission.

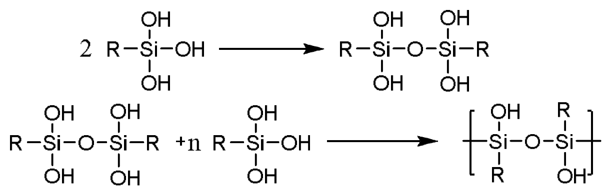
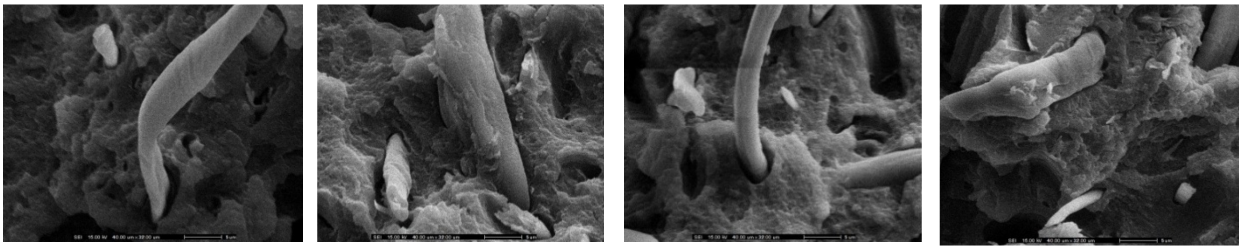


Figure 6. Polymerization reaction of coupling agent

Percentage elongation at break of neat ABS was reported at 30.47 in this study as shown in Table 1. And the percentage elongation at break of PALF/ABS composites decreased significantly in comparison with neat ABS. Those fibers could obstruct the chain mobility of polymer matrix. NaOH treated PALF composites possessed the percentage elongation at break lower than the one of the NaOH + silane treated PALF composites. This might be the result from a formation of flexible polysiloxane from self-condensation reaction of silane which act as plasticizer. For the following two systems i.e.; NaOH + enzyme cellulase treated PALF composites and NaOH + enzyme cellulase + silane treated PALF composites, they showed the percentage elongation at break was further reduced due to the defect of entanglement of fiber as shown in Figure 7. The fibers also impeded the mobility of polymer chains and therefore caused even more brittle materials as witnessed from the lower numbers of percentage elongation at break.

3.2.2 Impact properties

Table 1 showed that impact strength of composites were decreased dramatically in comparison with the neat ABS. This could be the fibers which were added into polymer matrix causing flaws in the polymer matrix. Once the external force was exerted into polymer material, the ability to absorb energy was then reduced. The following ABS composites were put in order from the most to the least value of impact strength starting with the one of PALF treated with NaOH + enzyme cellulose + silane; the one with NaOH + cellulose; the one with NaOH + silane and lastly the one with NaOH respectively. Sodium hydroxide and enzyme were believed to be the one which were responsible for physical interfacial area. And for chemical interfacial bonding, silane coupling agent would improve the surface between the polymer phase and fibers. The non-cellulosic parts would be removed to roughen up the fiber surface and enable the physical-interlocking between the fiber surface and polymers matrix once were treated with NaOH and enzyme cellulase. Lastly, the fibers would be treated by silane, the impact strength would be slightly increased due to the silane effect between surface of fibers and polymer matrix. Result could be cross-checked by the image of SEM as shown in Figure 7d.



(a) NaOH treated (b) N + silane treated (c) N + C treated (d) N+C+silane treated

Figure 7. SEM micrograph of impact specimens with different modifed PALF/ABS composites

Conclusions

The modified PALF composites would enhance mechanical properties especially young's modulus. Young's modulus is the highest for PALF/NaOH/Cellulase composites. PALF/silane composites possessed the highest tensile strength and impact strength among all the treated system.

References

[1] Chotirat L., Chaochanchaikul K., Sombatsompop N. On adhesion mechanisms and interfacial strength in acrylonitrile-butadiene-styrene/wood sawdust composite. *International Journal of Adhesion & Adhesives*, **27**, pp. 669-678 (2007).

[2] Threepopnatkul P., Teppinta W., Sombatsompop N. Effect of co-monomer ratio in ABS and wood content on processing and properties in wood/ABS composites., *Fibers and Polymers*, **12**, pp. 1007-1013, (2011).

[3] Arib R.M.N., Sapuan S.M., Ahmad M.M.H.M., Paridah M.T., Khairul Zaman H.M.D. Mechanical properties of pineapple leaf fibre reinforced polypropylene composites. *Materials and Design*, **27**, pp. 391–396 (2006).

[4] Threepopnatkul P., Kaerkitcha N., Athipongarporn N. Effect of surface treatment on performance of pineapple leaf fiber-polycarbonate composites. *Composites Part B*, **40**, pp. 628-632 (2009).

[5] Payae Y., Lopattananon N.: Adhesion of pineapple-leaf fiber to epoxy matrix: The role of surface treatments. *Songklanakarin J. Sci. Technol*, **31**(2), pp. 189-194, (2009).

[6] Huda M. S., Drzal L. T., Mohanty A. K., Misra M. Effect of fiber surface-treatments on the properties of laminated biocomposites from poly(lactic acid) (PLA) and kenaf fibers. *Composites Science and Technology*, **68**, pp. 424–432 (2008).

[7] Yu T., Ren J., Li S., Yuan H., Li Y. Effect of fiber surface-treatments on the properties of poly(lactic acid)/ramie composites. *Composites: Part A*, **41**(4), pp. 499-505 (2010).
[8] Bledzki A. K., Mamun A. A., Jaszkiewicz A., Erdmann K. Polypropylene composites with enzyme modified abaca fibre. *Composites Science and Technology*, **70**(5), pp. 854-860 (2010).
[9] Li Y., Pickering K.L.: Hemp fibre reinforced composites using chelator and enzyme treatments. *Composites Science and Technology*, **68**, pp. 3293–3298 (2008).