

## Effect of chemical treatments of wood fibers on the physical strength of polypropylene based composites

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(Received 8 May 2009 • accepted 15 July 2009)

**Abstract**—Wood plastic composites attract great attention in various applications. Chemical modification of the wood fiber with NaOH and various coupling agents was performed for wood fiber composites. Wood fibers treated with NaOH, APTES, TEVS, and BC coupling agents were compounded with PP matrix for measuring physical properties. All those chemical treatments increased physical properties much compared to the untreated case because of the elimination of impurities by NaOH treatment and because of the introduction of compatible molecular structure onto the wood fiber surfaces. Especially, the TEVS case showed the best tensile strength, and it could be attributed to the chain structure having double bond of the molecules for high compatibility with PP matrix. The SEM morphology also demonstrated increased adhesion between wood fibers and PP matrix with chemical treatments. The adhesion between wood fiber and PP matrix would be a key parameter in achieving high physical properties of the composite materials.

Key words: NaOH, Coupling Agents, Wood Fiber, Polypropylene

### INTRODUCTION

Fiber-reinforced plastic composites usually show drastic increase in their mechanical properties compared to those of the base polymer. Glass fiber or carbon fiber-reinforced thermoplastic materials possess good mechanical properties, but they have environmental concerns and are relatively expensive. Bio-fibers have long been considered as a future candidate to replace glass fiber or carbon fiber in thermoplastic composites, and thus help resolve environmental issues and take economic advantage over those artificial fibers.

For many years, bio-fibers have received great attention from many of researchers in fields of bio-composites industries because of its recyclable, environmental friendly, biodegradable, and cheap materials compared to glass fibers [1,2]. Also, bio-fibers give little damage during manufacturing process of bio-composites and are less abrasive than inorganic mineral fillers to molding and mixing equipment [3].

However, the incompatibility of the natural fibers with the polymer matrix sometimes reduces the possibility of bio-fibers to act as fillers and thus limits their usage. In generally all cases of bio-fiber, cellulose is a great stock of constituent [4,5] and it is polymer that is made up of  $\beta$ (1,4)-glucosidic linkages [6-8]. Each of the cellulose's repeating units has three hydroxyl groups and they are able to interact with one another forming intra- and inter-molecular hydrogen bonds [9]. The hydrogen bond gives high bending strength between the units, but it has hydrophilic characteristics on fiber surface. Polypropylene (PP) is widely used in many applications due to its low cost, easy availability, and wide spectrum of properties [10]. However, its relatively low stiffness and hydrophobicity limit

its applications [11]. Therefore, a method to improve compatibility between bio-fibers and polymer matrix would be required to increase physical properties of composite materials.

Extra compatibilizer or modifications with chemical treatments are generally used for final composite applications. Many studies have been reported with polypropylene grafted with maleic anhydride (MA) [12], and with glycidyl methacrylate (GMA) [13] to enhance the mechanical properties of the polymer/wood fiber composites. Also, various surface chemical modifications of wood fibers such as alkali treatment, isocyanate treatment, acrylation, silane treatment, and peroxide treatment have achieved various levels of success in improving fiber strengths and fiber-matrix adhesion in wood fiber composites. Silane modifications [14,15], benzoyl treatment [16,17], and benzyl treatment [18,19] to wood fibers have been reported to improve physical properties of wood fiber composites. These chemical modifications improve overall properties of the composites compared to the cases of no chemical treatment, and it is believed that the adhesion between polymer matrix and the chemically modified wood fiber is significantly increased.

In this study, we performed a sequential approach to modify the wood fibers (Lignocel® C120): first, alkali treatment, and then coupling (silane or benzoyl) agent reaction. Finally, chemically modified wood fibers were compounded with PP resin, and the composites were examined for physical properties and morphology.

### EXPERIMENTAL

#### 1. Materials

PP 5014 ( $M_w=180,000$  g/mol) was supplied from Korea Petrochemical Ind. Co. Lignocel® C120 (Natural wood fiber from JRS, Germany) was used for chemical treatments. Its grain size and bulk density are 70-150  $\mu\text{m}$  and 100-135 g/L, respectively. For alkali treat-

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ment, a reagent grade of NaOH (Ducsan pure chemicals Co. LTD, Korea) bottle was purchased and used without further purification. In silane modification, two types of silanes (3-aminopropyltriethoxysilane (APTES), 99% and triethoxyvinylsilane (TEVS), 97%, both from Aldrich®) were used as received. In addition to silanes, benzoyl chloride (BC, ReagentPlus®, 99% from Aldrich) was also used for benzoyl modification. For all NaOH solution preparation, de-ionized water (resistivity >18 M $\Omega$ ) was used for various weight percent concentrations. In silane reaction with the wood fibers after being treated with NaOH solution, pure ethanol (Ducsan pure chemicals Co. LTD, Korea) was used.

## 2. NaOH Treatment

The wood fibers were immersed in NaOH solutions up to 15.3

wt% of NaOH at 25 °C for 30 minute with vigorous stirring. Solution-to-wood fiber ratio was 15 : 1 (weight percent). The treated wood fibers then washed out thoroughly with the water until the rinsed solution became neutral. The rinsed fibers were then dried at 80 °C in a convection oven for 24 hours.

Generally, alkali treatment affects the swelling of cellulose fibers and the degree of swelling depends on the alkali concentration. Na<sup>+</sup> ion plays a crucial role in widening the pores between the lattice planes and diffuses into those planes, and thus NaOH leads to a high swelling. After removal of excess NaOH, the new form of Na-Cell-I lattice (which has relatively large distance between the cellulose molecules filled with water molecules) is formed. The OH groups in the cellulose fiber are changed into ONa-groups expanding the

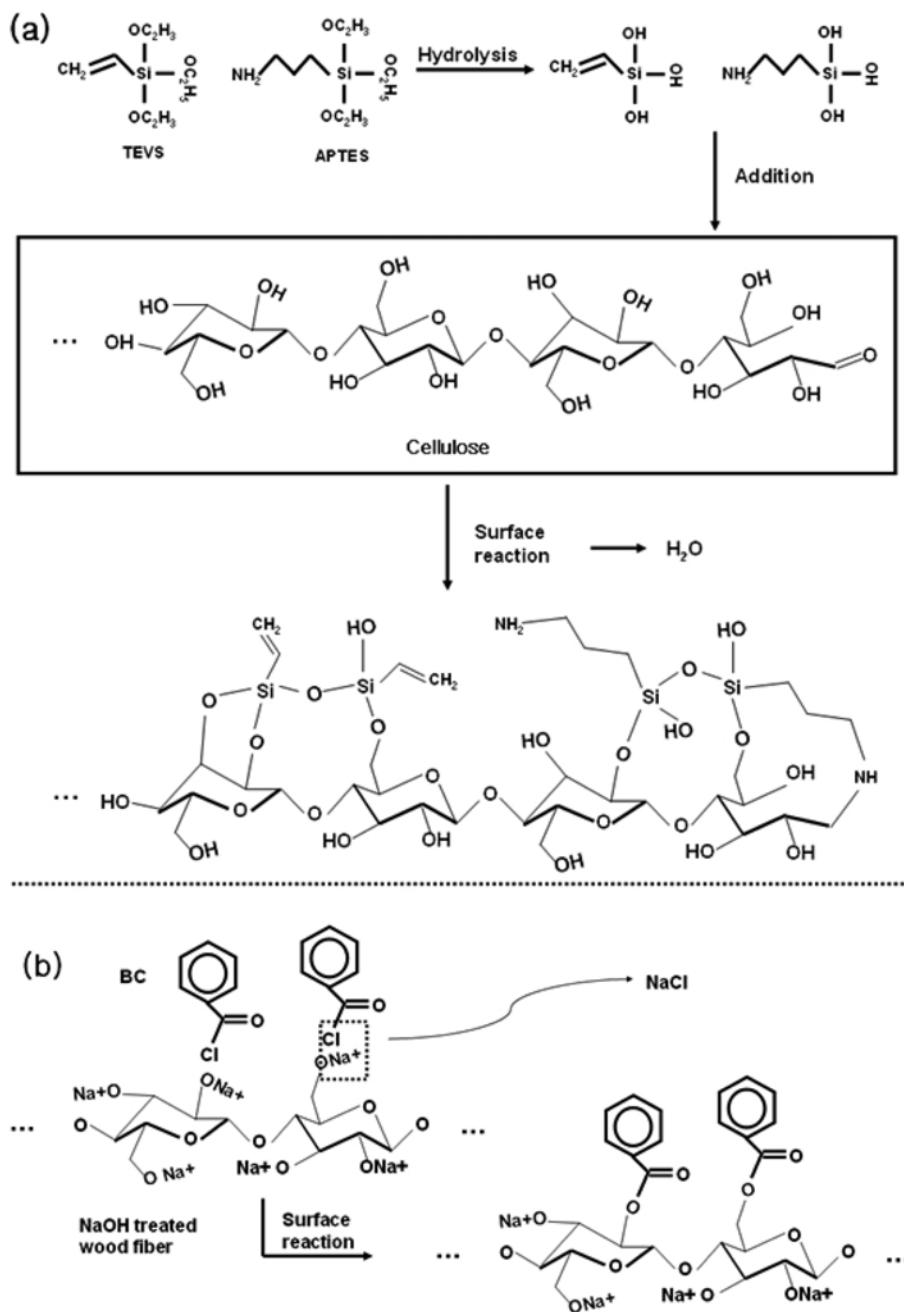


Fig. 1. Schematics of coupling reactions between wood fibers and silane chemicals (a) and benzoyl chloride (b).

molecular dimension. Next, a rinsing step with water removes the linked Na ions and converts the cellulose structure to a new crystalline structure of Cell-II. This new structure (Cell-II) was reported as thermodynamically more stable than Cell-I [20].

### 3. Silane Treatment

Wood fibers treated with various NaOH concentrations were used for 3 wt% (weight percent compared to the fiber) 3-aminopropyltriethoxysilane (APTES) and triethoxyvinylsilane (TEVS) reactions. For the APTES reaction, first the APTES was hydrolyzed for 1 hour in the 95 wt% ethanol solution (containing APTES) at a pH value of 4.5-5, and then the wood fibers were immersed for 2 hours at room temperature for silane coupling with the wood fibers. After the coupling reaction was completed, the fibers were filtered with filter papers and dried at 80 °C in the convection oven for 24 hours. For the TEVS, ethanol solution with 40 wt% water content was used for reaction because it was very difficult to confirm the vinyl silane reaction by FTIR at 95 wt% ethanol solution. The TEVS-treated fibers were also filtered and dried with the same method described above. Fig. 1(a) shows the schematics of the coupling reactions with wood fibers for silane agent. Through silanization, hydrolysis of silane (silanol formation), condensation between silanols, and bond formation between siloxane and wood fibers were consecutively achieved. In addition to the self condensation on the surface of cellulose fiber, amino silane molecules can interact with the OH groups of cellulose via their Brönsted basic amino group [21] and cellulose's end group is combined with APTES's amino group.

### 4. Benzoyl Treatment

Wood fibers pre-treated with NaOH solution were suspended in 10 wt% NaOH solution and mixed well with 3 wt% (weight percent compared to the fiber) benzoyl chloride for 30 minutes. Excess amount of water was used to wash out NaOH solution, and the benzoylated fibers were immersed in ethanol solution for one hour to remove un-reacted benzoyl chloride. Finally, the fibers were washed out with water and dried at 80 °C in a convection oven for 24 hours. Fig. 1(b) shows the schematic of the coupling reaction with wood fibers for benzoyl agent. For benzoylation reaction, Na ions attached to wood fiber by NaOH treatment are further reacted with Cl atoms and NaCl is extracted.

### 5. Preparation of PP Composites

An intermeshing 19mm co-rotating twin-screw extruder (Bau-tek Co., Korea) with 40L/D ratio and a pelletizer (Bau-tek Co., Korea) were used in manufacturing the blends. Chemically modified wood fibers were dried at 80 °C in the convection oven for 24 hours to remove moisture prior to use. The compounding temperature was 170-190 °C with screw speeds in the range of 100-150 rpm. The composites were pelletized and dried for injection molding. All the composites have the same composition (PP/wood fiber=50/50) in weight fraction, and the chemical composition of NaOH and coupling agents is summarized in Table 1.

### 6. Injection Molding and Physical Properties

Test specimens for tensile and flexural properties were molded using an injection molder (Boy 12 M, Dr. Boy GmbH & Co. KG, Germany) at 190 °C. All tests for tensile and flexural properties were performed by applying the ASTM D638 and ASTM D790, respectively.

### 7. FTIR Analysis

Fourier transformed infrared spectra were obtained with the spec-

**Table 1. Chemical composition of NaOH and coupling agents**

NaOH (wt%)	Coupling agents (3 wt%)
0.0	No
2.0	No
	APTES
	TEVS
	BC
5.7	No
	APTES
	TEVS
	BC
10.7	No
	APTES
	TEVS
	BC
15.3	No
	APTES
	TEVS
	BC

trum RXI (PerkinElmer, USA). Samples of the wood fiber (2 mg) were ground and dispersed in a KBr (28 mg) matrix. A pellet was then formed by compression at the pressure of about 200 MPa. Spectra with samples were obtained from 16 scans and a resolution of 4 cm<sup>-1</sup>. During scanning, nitrogen gas was purged for stable operations.

### 8. Scanning Electron Microscopy

Morphology of the fractured surface from tensile tested specimens was taken using Hitachi S-4300 SEM analyzer at the X500 magnification.

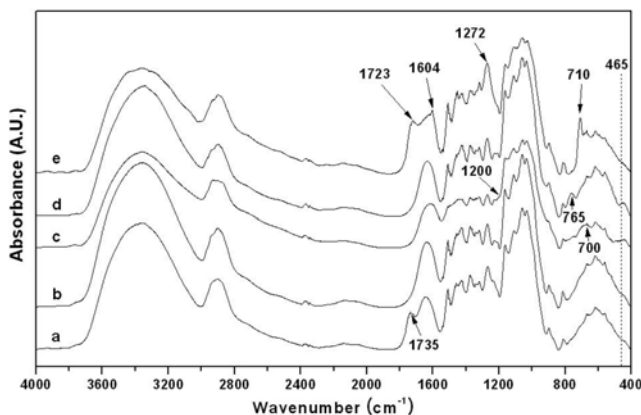
### 9. Chemical Composition Analysis of Lignocel® C120

Holocellulose is the total polysaccharide (cellulose and hemicelluloses) content of wood. Holocellulose determination by removing all of the lignin from wood fiber without disturbing the carbohydrates was performed according to ASTM Standard D 1104. The Klason lignin in the wood fibers is a residue remaining after solubilizing the carbohydrates with 72% H<sub>2</sub>SO<sub>4</sub>. The lignin content was measured according to ASTM Standard D 1106. The alcohol-benzene soluble content of wood is a measure of the waxes, fats, gums, resins, water soluble, and ether-insoluble components. The extractives content of wood fiber was measured according to ASTM D 1107. Every value of the chemical analyses represents the mean of three replicates.

## RESULTS AND DISCUSSION

### 1. Chemical Treatment

Wood fiber mainly consists of cellulose, hemicellulose, lignin, pectins, and waxes [21,22]. There are many hydroxyl groups in wood fiber surface and it causes hydrophilic characteristics on wood fiber surface. In manufacturing of bio-composites, the hydrophilic surface of wood fiber reduces bonding strength between wood fiber and hydrophobic polymer. Therefore, it is necessary to convert the surface properties from hydrophilic to hydrophobic to increase interfacial adhesion. Subsequent chemical modifications for alkali treated



**Fig. 2.** FTIR spectra of the wood fibers treated with coupling agents. Wood fibers with: (a) 0 wt% NaOH (b) 2 wt% NaOH, (c) 2 wt% NaOH+3 wt% APTES, (d) 2 wt% NaOH+3 wt% TEVS, and (e) 2 wt% NaOH+3 wt% benzoyl chloride.

wood fibers with silanes or benzoyl would increase adhesion with polymer matrix in manufacturing bio-composite. In this step, the hydrophilic surface of the wood fibers is transformed to hydrophobic surface by the coupling reaction.

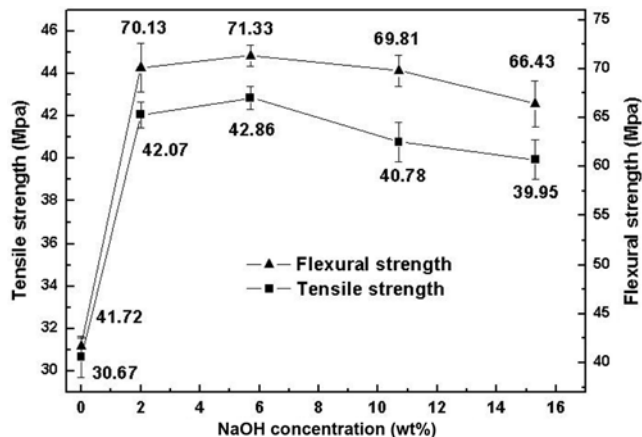
Chemical modification of wood fibers leads changes of molecular interactions, which in turn accompanies wave number shifts in the FTIR spectra. Fig. 2 demonstrates the changes of characteristic peaks representing the chemical reactions including coupling agents. With NaOH treatment, the carbonyl groups in hemicellulose [23] disappeared at  $1,735\text{ cm}^{-1}$  from (a) to (b). In addition, three more curves show peak changes for APTES, TEVS, and BC treatments. Treatments of wood fibers with amino- and vinyl-silanes also showed peak changes at  $1,200\text{ cm}^{-1}$  assigned as Si-O-C band, at  $765\text{ cm}^{-1}$  assigned as Si-C symmetric stretching bond, at  $700\text{ cm}^{-1}$  assigned as Si-O-Si symmetric stretching [24], and at  $465\text{ cm}^{-1}$  assigned as Si-O-C asymmetric bending [25]. Introduction of benzoyl groups resulted in an increase in the carbonyl stretching absorption at  $1,723\text{ cm}^{-1}$ , in band characteristics of aromatic rings ( $1,604\text{ cm}^{-1}$  and  $710\text{ cm}^{-1}$ ), and a strong absorption at  $1,272\text{ cm}^{-1}$  for C-O band associated with an aromatic ring. It demonstrates the clear evidence of benzoyl group attachment to wood fibers. In the following sections, the effect of chemical treatments on the physical properties is given.

## 2. Alkalinization Effect on Physical Properties

The chemical component change of the Lignocel® C120 by alkali treatment was analyzed and it is listed in Table 2. The proportions of holocellulose (cellulose plus hemicellulose), lignin, and extractives are 68.5, 28.1, and 3.0%, respectively. Mean yield of the wood fiber after 2 wt% NaOH treatment is 90.7%. Because cellulose is insoluble in a strong alkaline solution and hemicellulose is extracted with weak aqueous alkaline solution, the reduced proportion of holocellulose is directly due to the extracted hemicellulose after the alkali

**Table 2.** Chemical composition of Lignocel® C120

NaOH (wt%)	Holocellulose (%)	Lignin (%)	Extractives (%)
0	68.5	28.1	3.0
2	63.6	25.9	0.2



**Fig. 3.** Tensile and flexural strengths of the PP composites with NaOH-treated wood fibers.

treatment [26]. As we expected, the proportion of lignin and extractives was also reduced.

In Fig. 3, changes of the tensile and flexural strengths of PP composites with wood fiber treated with NaOH are shown. Alkali-treated wood fibers increased tensile and flexural strengths by about 30% and 70%, respectively, at the NaOH content of 5.7%. By NaOH treatment, the surface roughness and possible reaction sites on the fiber surface are increased [27] and it helps to increase the physical properties of the composite materials. As can be seen in Table 2, the important change of alkali treatment of the wood fibers is reducing the amount of hemicellulose without changing the amount of cellulose. Hemicelluloses are not a form of cellulose at all, and they comprise a group of polysaccharides (excluding pectin) associated with the cellulose [22]. As a result, chemical and physical properties of composite materials are mainly determined by the molecular structure of cellulose, and alkali treatment played an important role in reducing impurities including hemicellulose.

One of alkali (NaOH) treatment's roles in natural fiber is the change of the crystal structure in cellulose from Cell-I to Cell-II. The original crystal structure of the Cell-I is transformed into different type of crystal structure, Cell-II, typically with NaOH concentration higher than 10 wt% [9,28-30]. Fig. 3 shows that tensile and flexural strengths were slightly decreased by alkali treatment above 10 wt%. It is possibly attributed to the transformed Cell-II structure at alkali concentrations of 10.7 wt% and 15.3 wt%. Therefore, it might be explained that mechanical strengths in bio-composites are mainly influenced by removing impurities more than changing crystal structures by alkali treatment. High concentration of NaOH does not necessarily show increases in the tensile and flexural strengths. It can be due to the corrosive interactions between wood fibers in the composites because excess NaOH weakens the wood fiber surface [31]. Therefore, the optimum amount of NaOH should be used for obtaining high physical properties of composite materials.

## 3. Coupling Agent Effect on Physical Properties

Fig. 4 shows the effect of chemical treatment with the TEVS agent on the tensile strength for various NaOH contents. The tensile strength with 3% TEVS treated wood fibers was increased about 50% at 2% NaOH compared to the untreated wood fiber case. It is because hydrophobic shield is formed on the TEVS-treated fiber surface

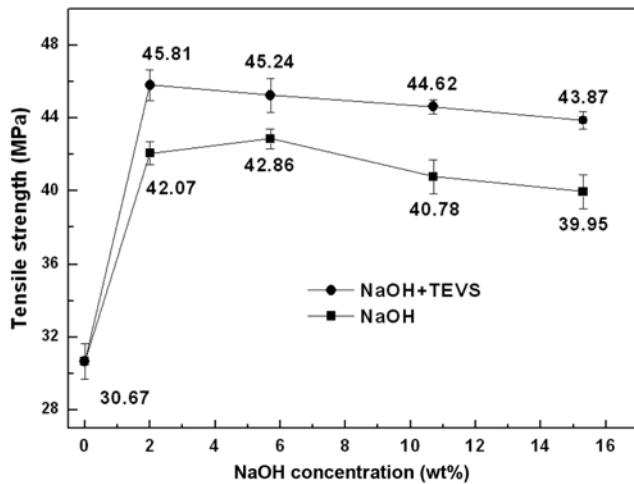


Fig. 4. Tensile strength of the PP composites treated with NaOH only and NaOH+TEVS in various NaOH concentrations.

and so it increases moisture resistance in composites [32]. In contrast to glass fibers, where water adsorption only occurs at the surface, cellulose fibers can interact with water throughout their bulk and sorbed water is considered to decrease the strength of wood fiber/thermoplastic composites due to increasing the incompatibility of the constituents [33]. It is because the coupling agent reduces incompatibility between fibers and PP matrix, and so it increases their interfacial adhesion. For the entire experimental range of NaOH, the tensile strength of the composites with the TEVS coupling agent kept high compared to the strength of the materials with NaOH only. However, the tensile strength was slightly decreased with increased NaOH content, which is likely due to the high content of Cell-II structure in the excess amount of NaOH.

Fig. 5 shows the effect of chemical treatment with the APTES agent on the tensile strength for various NaOH contents. It demonstrated similar trend in the tensile strength with TEVS treatment.

Fig. 6 shows the effect of the BC agent on the tensile strength for various NaOH contents. It demonstrated similar increment in

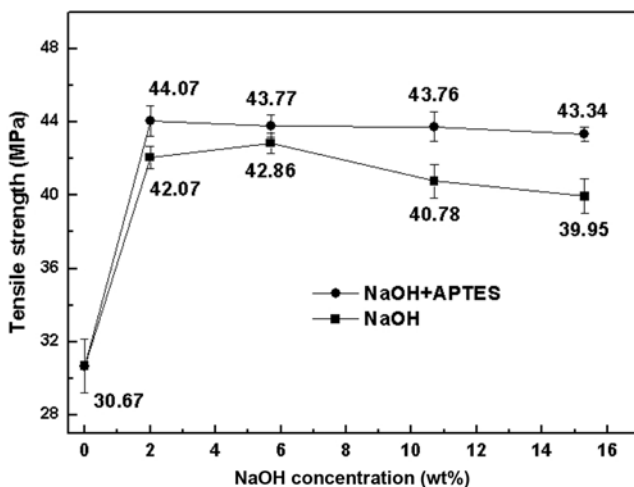


Fig. 5. Tensile strength of the PP composites treated with NaOH only and NaOH/APTES in various NaOH concentrations.

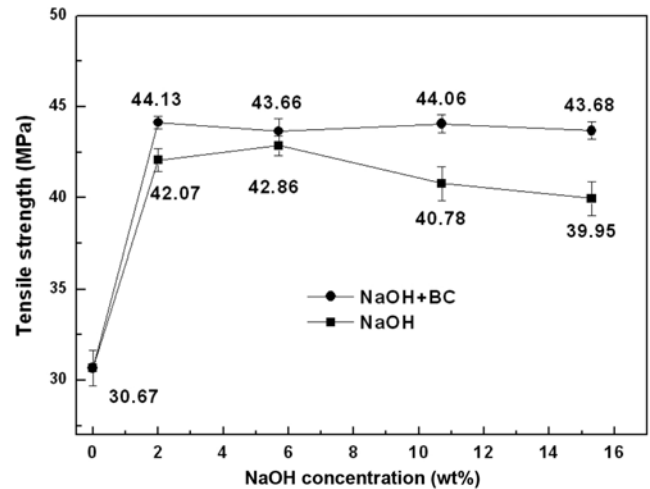


Fig. 6. Tensile strength of the PP composites treated with NaOH only and NaOH+BC in various NaOH concentrations.

the tensile strength with the silane treatment case, and it also would be due to the increased hydrophobicity on the fiber surface and increased compatibility by BC treatment. However, the tensile strength kept similar level for the entire experimental range of NaOH, which might be due to an additional NaOH treatment step before BC attachment.

In Fig. 7, the tensile strength of the composite materials with three coupling agents (APTES, TEVS, and BC) at 2 wt% NaOH was shown. The NaOH treatment itself for the wood fiber increased the tensile strength about 40% compared to the untreated case. Furthermore, all three coupling agents additionally improved the tensile strength about 5-10% to the NaOH treated case. Amongst the coupling agents, the TEVS case showed the highest strength and it could be partly from the molecular structure. The TEVS has double bonds in the chains that they can be broken during extrusion process and this introduces active reaction sites from the double bonds to be compatible with PP radicals also produced in the process. So, the adhesion between wood fiber and PP matrix would be a key

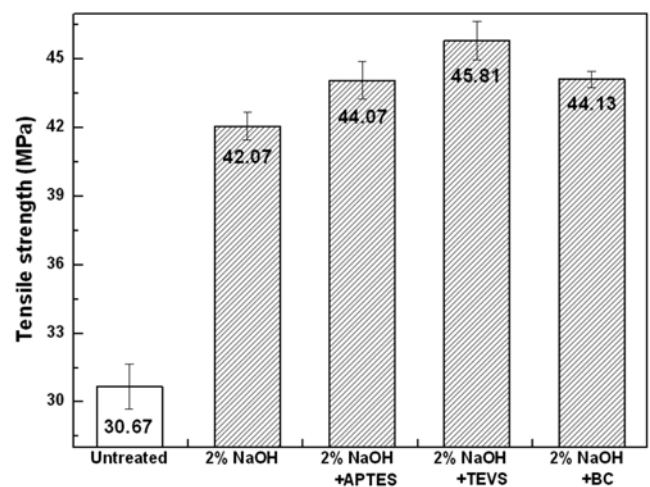
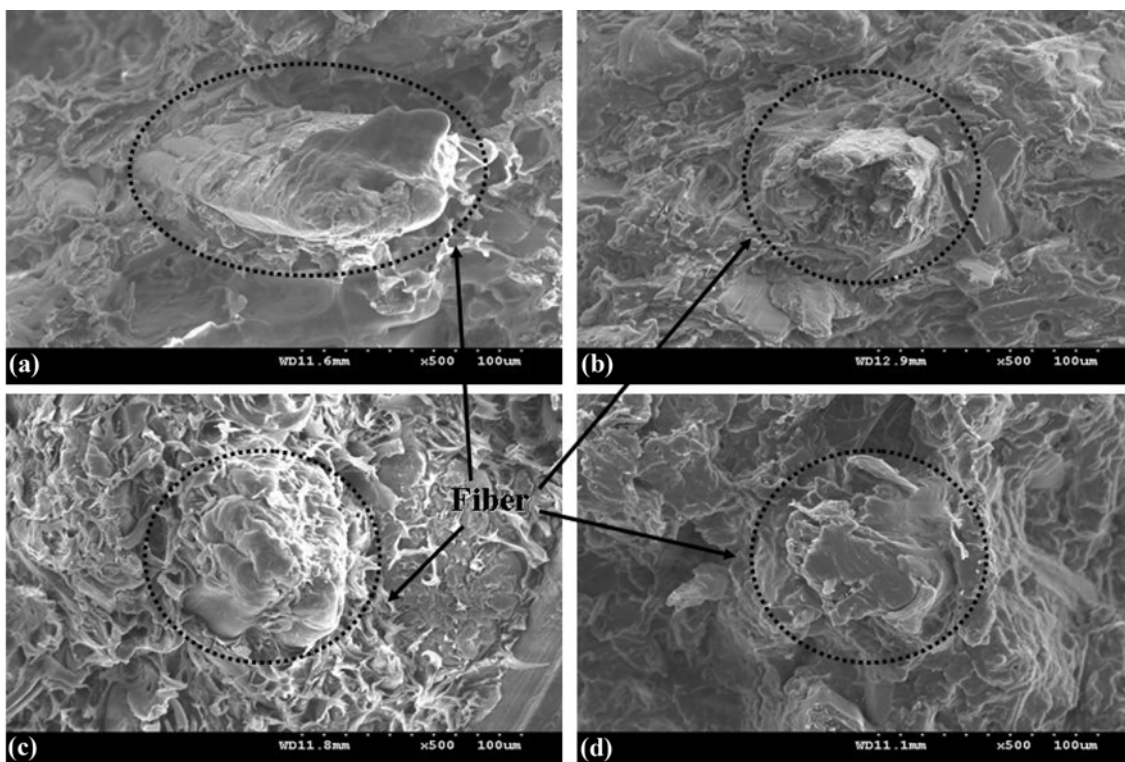


Fig. 7. Tensile strength of the PP composites treated with various coupling agents.



**Fig. 8.** SEM photographs of wood fibers on fractured surfaces in composite matrix. (a) 2 wt% NaOH only, (b) 2 wt% NaOH+APTES 3 wt%, (c) 2 wt% NaOH+TEVS 3 wt%, and (d) 2 wt% NaOH+BC 3 wt%.

parameter in achieving high physical properties of the composite materials.

#### 4. Morphology

Fig. 8 shows SEM photographs of wood fibers on tensile fractured surfaces from composite specimens. From the SEM photos, the TEVS-treated wood fibers in Fig. 8(c) look well contacted in the PP matrix with good adhesive characteristics, which coincides with the result of the tensile strength as shown in Fig. 7. The APTES and BC cases in Fig. 8(b) and (d) also looked better adhesive with PP matrix than the NaOH only case, but no big difference between APTES and BC was observed. These morphological results were also well matched with the physical property results in Fig. 7.

#### CONCLUSIONS

For chemical modification of wood fiber, NaOH and various coupling agents were used. The modified wood fibers were first analyzed with FTIR to confirm the attachment on the fiber surfaces before further uses for composites. Wood fibers treated with NaOH, APTES, TEVS, and BC coupling agents were compounded with PP matrix for measuring physical properties. All those chemical treatments increased physical properties compared to the untreated case because of the elimination of impurities by NaOH treatment and because of the introduction of compatible molecular structure onto the wood fiber surfaces. Especially, the TEVS case showed the best tensile strength, which could be attributed to the chain structure having double bond of the molecules for high compatibility with PP matrix. The SEM morphology also demonstrated the increased adhesion between wood fibers and PP matrix with chemical treat-

ments. The TEVS case looked good compatible with PP matrix, and it coincides with the result of the tensile strength. So, the adhesion between wood fiber and PP matrix would be a key parameter in achieving high physical properties of the composite materials.

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