

The effect of alkali treatment on tensile properties of coir/polypropylene biocomposite

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Abstract. The increase demand for use of natural fiber in biocomposites is due to its inexpensive material, abundantly available and it has reasonable strength. In this study, coir fiber were treated with NaOH solution (3 wt% and 5 wt%) for 2, 4 and 6 hours at room temperature. The treated and untreated coir fiber with size of 160 – 250 µm were extruded with polypropylene (PP) at fiber content of 10 and 30 wt%. The effect of alkali treatment was analyzed for its chemical composition, thermal stability and morphology. The biocomposites were tested for its tensile properties. Results showed that alkali treatment at 5 wt% for 6 hours had higher cellulose composition which was 29% compared to untreated coir. Thermal stability of treated sample increased and had high percentage of residue which showed the improved hydrophobicity of the sample. The surface of treated sample were rough due to removal of impurities and silica bodies. The tensile properties of biocomposite prepared from 5 wt% NaOH treated fiber/PP were higher by 28% compared to untreated coir/PP. This study shows that alkali treated coir fiber had better characteristics compared to untreated coir fiber and lead to the higher tensile properties of the PP-based biocomposite.

1. Introduction

In recent years, there are great interest toward development of natural fiber as reinforcements for polymeric biocomposite. This is because natural fiber reinforced biocomposite have the advantages of low cost, widespread availability, biodegradability, renewability and reasonable mechanical properties. There are various types of natural fibers such as jute, sisal, palm oil biomass, abaca and coir have been studied as reinforcement in biocomposite. Coir fiber is used widely as rope, mat, compost and filler in biocomposite [1]. Coir fiber can be obtained from coconut husk which routinely disposed from coconut plantation.

However, the main drawback of coir fiber is the low thermal stability and compatibility with hydrophobic polymer. The main constituents of coir fibers are 21.5-23.0 wt% hemicellulose, 31-55 wt% cellulose and 15-21 wt% lignin [2]. Coconut fibers has hydrophilic properties due to present of hydroxyl group (-OH) and carboxyl group (-COOH) in hemicellulose and cellulose resulted to incompatibility of coir fibers with hydrophobic polymer. Alkali treatment can be an alternative treatment method for reducing hemicellulose content to make the fibers less hydrophilic and enhance the compatibility of treated fibers with matrix such as polypropylene (PP) [3]. Morphology of alkali



treated fibers is rougher than untreated fibers viewed under SEM which will enhance the physical interaction of fibers and polymer [4].

In this present study, the concentration and treatment time of sodium hydroxide (NaOH) to treat coir fiber were studied. The characteristics of treated fiber were analyzed. Then, the treated fiber were mixed with PP at 10 and 30 wt% fiber content and the tensile strength of the biocomposites were determined. This research aims to utilize the abundant biomass from agricultural industry and to propose a simple treatment method to improve the characteristics of coir fibers.

2. Materials and Methods

2.1. Materials

Coir fiber was collected from coconut factory located in Sabak Bernam, Selangor. NaOH and potassium hydroxide (KOH) were supplied by Merck, Darmstadt, Germany. Sodium chlorite (NaClO_2) was supplied by Acros Organics, Geel, Belgium. Polypropylene is purchased in pellets form from Polypropylene (Malaysia) with code of 606251.

2.2. Alkali treatment

Coir fibers were cut into range of 160 to 250 mm and treated with NaOH solution in different concentration namely 3 wt% and 5 wt% at the room temperature. The treatment time were set at 2, 4, and 6 hours with coir fiber to NaOH solution at ratio of 1:15. After treatment, the fibers were wash with distilled water until neutralize and oven-dried overnight.

2.3. Fabrication of Coir / Polypropylene Biocomposite

The treated coir fibers with size of 160 – 250 μm and PP is dried at 60 °C prior to use. Biocomposites was prepared by twin screw extruder machine (Model: Prism Eurolab 16) at temperature range of 200 – 160 °C and 50 rpm rotor speed. The samples were mixed at 10 wt% and 30 wt% fiber content. Then, the extruded samples were pressed using hot press and cold molding machine (Model: Lotus Scientific-2205) with a pressure of 10 KPa, 160 °C for 10 min to produce 1 mm biocomposite sheet.

2.4 Characterization of Coir Fiber

2.4.1 Chemical Composition Analysis. The analysis was determined according to the procedure described by Iwamoto *et al.* [5]. Firstly, lignin were removed by soaking into 5 wt% of NaClO_2 for 1 hour at 70 °C and wash until pH neutral. The dried sample was weighed. Then, the bleached samples were soaked into 6 wt% of KOH for 24 hours at room temperature. The samples were rinsed and dried. The weight of dried sample was recorded. The final residue of the analysis contain only cellulose component.

2.4.2 Thermogravimetric Analysis (TGA). TGA was conducted on Hitachi STA 7200 Thermal Analysis. The coir weighed 6 to 10 mg was placed on aluminum pan. The sample was heated from 50 to 600 °C at heating rate of 10 °C/min under nitrogen flow of 100 mL/min.

2.4.3 Scanning Electron Microscope (SEM). The surface morphology of the untreated and treated fibers was studied using scanning electron microscopy machine (JEOL-JSM 840). The treated and untreated fibers are mounted on carbon tape and viewed with acceleration voltage of 10 kV [6].

2.5 Tensile Test

Tensile test were determined according to ASTM D638 on dumbbell shape specimens by using a universal tensile testing machine model A6-4. The testing condition used were crosshead speed 10 mm/min and load cell 1 kN. The recorded value are the average of 5 results.

3. Results and Discussion

3.1 Chemical Composition

The chemical composition of treated and untreated fiber are summarize in table 1. Result has shown that the composition of untreated fiber consist of 22.71% lignin, 39.15% hemicellulose and 38.14% cellulose. It was reported the untreated coir has about 21.5-23% hemicellulose, 31-55% cellulose and 15-21% lignin [2]. At longer treatment time the composition of cellulose and lignin were higher while the amount of hemicellulose decreased as the soaking time and NaOH concentration increased.

Table 1. The chemical composition of treated and untreated coir fiber.

Concentration of NaOH (wt%)	Sample	Soaking Time (hours)	Lignin (%)	Hemicellulose (%)	Cellulose (%)
Untreated	1	-	22.71	39.15	38.14
3 wt%	2	2	22.51	31.51	45.98
	3	4	24.29	27.49	48.22
	4	6	24.07	25.47	50.46
5 wt%	5	2	28.72	26.39	44.89
	6	4	28.65	25.12	46.23
	7	6	28.43	22.23	49.34

From table 1, the treatment with 3 wt% and 5 wt% NaOH for 6 hours had increased cellulose content by 32% and 29% respectively. Higher content of cellulose can increased the strength of fiber. As for lignin content, it was increased by 5.9% for 3 wt% and 25% for 5 wt% NaOH at 6 hours treatment. The highest removal of hemicellulose content was found in sample 7 with 43% removal. This result was supported by other studies which had shown that NaOH treatment able to reduce the hemicellulose content in the fiber [7].

Hemicellulose consist of branched and amorphous structure where the hydroxyl group (-OH) is easily broken by alkali treatment, which then react with water molecules (H-OH) and discharged out from the fiber structure. Due to the reaction, the hemicellulose content in the fiber was reduced. The cellulose component has crystalline structure and not easily hydrolyze by chemical treatment, thus the remaining cellulose molecules will formed a chain of fiber-O-Na group between cellulose molecules chain. According to the research conducted by Sun *et al.*, it was found that the treated fiber has a better packing of cellulose chain due to removal of amorphous components and may led to better properties of its biocomposite [8].

3.2 Surface Morphology of Samples (SEM)

The effect of the different concentration treatments on the surface fiber was investigated using the SEM. Figure 1a (i,ii) shows the SEM micrograph of untreated coir fiber. The untreated fiber is covered with a layer of impurities such as wax, pectin, oil and lignin, thus it provide a smooth surface as observed under SEM. The same observation was reported by Carvalho *et al.* whereby it was shown that the surface of coir fiber was covered by a layer of substances such as waxes, lignin and pectin [9]. It can be observed the silica bodies were deposited on the fiber surface.

After alkaline treatment as shown in figure 1b (i,ii) and 1c (i,ii), it can be seen that the fiber had rougher surface due to removal of impurities. Besides that, it can be observed that higher concentration of NaOH can caused more removal of silica bodies. For the 3 wt% NaOH treated fiber, crater can be seen due to removal of silica. While for the 5 wt% NaOH treated fiber, the roughness surface was increased and more crater or pore was revealed indicating more silica was removed. This

result is in agreement with Wong *et al.* which demonstrated that the higher concentration of NaOH will increase the surface roughness of the fiber [10].

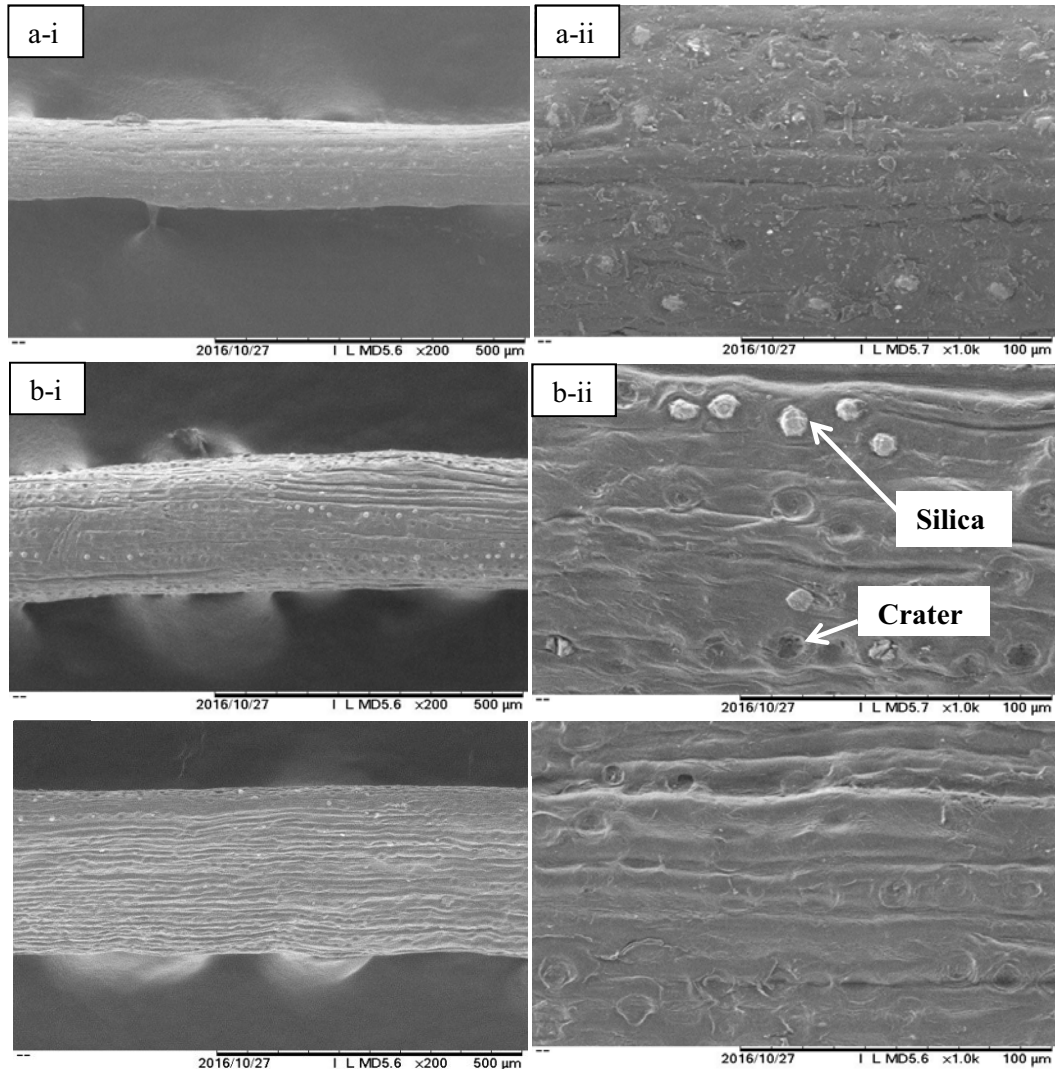


Figure 1. Scanning electron micrographs of (a) untreated fiber, treated fiber with (b) 3wt%, and (c) 5wt% of NaOH treatment for 6 hours.

In addition, the rough surface and dislodging of silica bodies will provide a good anchor for PP which will subsequently improve the physical interaction between fiber and polymer [11].

3.3 Thermal Stability

Figure 2 shows the result of TGA analyses for untreated and coir fiber treated with 3 wt% and 5 wt% NaOH for 6 hours. The thermal composition of coir consists of three decomposition stage. The first stage is the decomposition of moisture content which occurs between 80 and 100 °C. As the fiber is heated, the moisture content from the fiber will evaporated resulting the weight of the material decreased. The moisture content of the untreated coir is the highest and lower for the treated sample as shown in table 2.

The second stage is decomposition of hemicellulose which occurs at 200 to 300 °C. The untreated fibers had higher mass loss compared to the treated fiber. The results is in agreement with study done by Yang *et al.*, reported that hemicellulose degrade within temperature range of 180 to 350 °C [12].

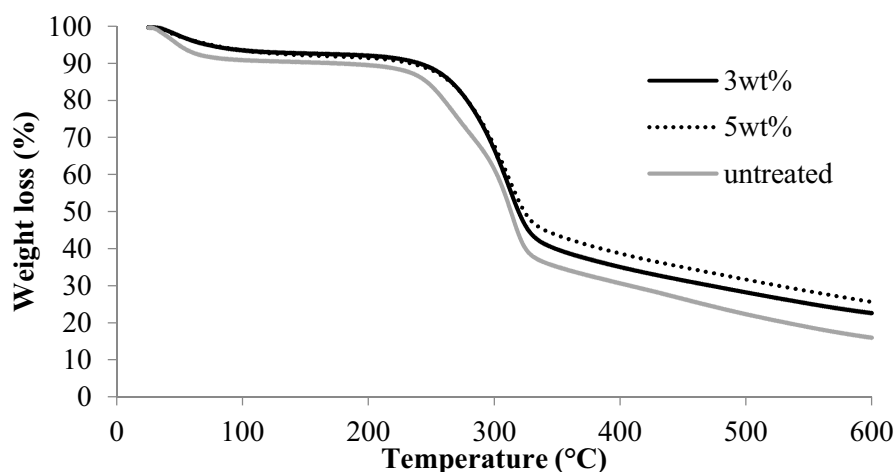


Figure 2. TG analysis for untreated coir fibers.

The third stage of degradation was contributed to lignin degradation. Lignin decomposed at slower rate compare to other components where the degradation temperature start from 190 to 600 °C. According to Yang *et al.*, although the decomposition of lignin could start as early as 160 °C, it decomposed slowly and extended its temperature as high as 900 °C [12]. According to Quajai and Shanks, the decomposition of lignin was occurring in a wider temperature range compared to hemicellulose and cellulose content on the coir [4]. Lignin presents a broad peak throughout the range, degrading between 280 and 500 °C.

Table 2 shows the weight lost and thermal stability of untreated and treated coir fiber. Temperature of fiber at 5% weight loss was increased for treated fiber. At higher concentration of NaOH the fiber had better thermal stability where the 5% and 50% weight loss occurred at higher temperature. This is due to the removal of hemicellulose that have low thermal stability. Based on table 1, untreated coir fiber had the highest composition of hemicellulose, while coir fiber treated with 5 wt% NaOH for 6 hours had the lowest hemicellulose content. The thermal stability result was in agreement with the results shows in table 1. Therefore, the reduction of hemicellulose content in the treated fiber will increased the thermal degradation of the fiber [13]. The residue left at 600 °C mainly containing lignin. Lignin contains polar hydroxyl groups and non-polar hydrocarbon and benzene rings making it less hydrophilic [14]. Thus, the increased residue of alkali treated fiber show the treated fiber had better hydrophobicity compared to untreated fiber. Thus, the compatibility of treated fiber and hydrophobic polymer will increased.

Table 2. Thermal stability of untreated and NaOH treated coir fiber for 6 hours of treatment.

Sample	Weight loss at 100 °C (%)	T _{5%} ^a (°C)	T _{50%} ^b (°C)	Residue at 600 °C (%)
Untreated coir	9.11	49.08	313.17	16.00
Treated fiber (3wt%)	6.47	72.50	319.25	22.62
Treated fiber (5wt%)	6.46	74.83	323.84	25.68

^a Temperature at 5% weight loss.

^b Temperature at 50% weight loss.

3.4 Tensile properties

The fiber content and fiber matrix interfacial adhesion is main factor that can affect the mechanical properties of biocomposite. The tensile properties of untreated coir fiber and alkali treated fiber biocomposite are shown in table 3. It can be observed the tensile strength increased with the fiber loading up to 30% for 3 wt% and 5 wt% NaOH treated fibers. The tensile modulus also increase as the fiber loading increased. The untreated coir/PP biocomposite has the lowest properties while the 5 wt% NaOH (6 hours) treated coir/PP biocomposite had the highest tensile strength. The tensile strength of this biocomposite sample was increased by 28% compared to untreated biocomposite at 10 wt% fiber content. At 30 wt% fiber content, the tensile strength of treated fiber biocomposite also higher compared to untreated biocomposite.

Table 3. Mechanical properties of coir/PP biocomposite.

Sample	10 wt% fiber loading		30 wt% fiber loading	
	Tensile strength (MPa)	Tensile modulus (MPa)	Tensile strength (MPa)	Tensile modulus (MPa)
Untreated coir/PP	21.66	922.27	22.33	1114.88
3 wt% NaOH ^a treated coir/PP	22.48	1122.39	23.79	1226.39
5 wt% NaOH ^a treated coir/PP	27.75	1328.76	28.74	1338.07

^a For 6 hours treatment.

The tensile strength of fiber treated with 5 wt% NaOH was high due to increase cellulose content after alkali treatment. Alkali treatment able to reduce hemicellulose, waxes and silica bodies on the surface of the fiber led to improve the physical interaction between fiber and matrix. According to the study done by Mohanty *et al.*, alkali treatment provides the great fiber matrix adhesion through removal of hydrophilic components in fiber and subsequently enhances the tensile properties of the biocomposite [15].

4. Conclusion

In the present study, it is shown that alkali treatment successfully improved the characteristics of coir fiber to be used as reinforced material in biocomposite production. Coir fiber treated with 5 wt% NaOH for 6 hours gave the significant improvement to the fiber. Alkali treated fiber had low hemicellulose content while having higher percentage of cellulose and lignin. The surface of the fiber was clean and rough which beneficial for physical adhesion with polymer. The removal of low thermal stability components such as hemicellulose had increased the thermal stability of treated fiber. Higher residue at 600 °C of alkali treated coir shows that the treated fiber had better hydrophobicity compared to untreated fiber. Tensile strength of biocomposite prepared from alkali treated fiber is higher than untreated coir biocomposite.

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