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Improved Strength Of Sugarcane Bagasse Fibers-Polypropylene Composite Using Alkali Treated Fibres

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Abstract: Sugarcane is one of the main agricultural products in Indonesia after palm oil, coconut, and rubber. Bagasse fibres are produced from the milled sugarcane stalks. These fibres are considered as byproduct and has little value. These natural fibres are strong, lightweight, and offer benefits in reductions in cost, CO₂, less reliance on oil sources and recyclability. They have been investigated and identified as potential reinforcement to replace synthetic fibres such as glass and carbon fibres. In this present work, bagasse composites using polypropylene (PP) matrix were developed. Alkali treatment using 14% v/v Ca(OH)₂ was applied on bagasse fibres and the strength of the composites produced was evaluated as the effects of the soaking time during alkali treatment, fiber length, and the quantity of bagasse fibres used. Alkali treatment for 2, 4, and hours gave a composite strength in the range of 3.36-9.07 MPa, 4,84-11.3 MPa, and 7.0-14.72, respectively. The strength of composites which used untreated fibers in original length was in the range of 7.22-11.38 MPa with the highest strength obtained in the composites with 20/80 wt. % ratio of bagasse/PP. Those strength data means that treated bagasse fibers with Ca(OH)₂ was not effective in increasing strength of composite when duration of alkali treatment was up to 4 hours. Two hours soaking time gave the lowest strength of the composite. Adding the treated bagasse fibers to 25 wt. % to PP increased the strength of the composite and increase the fiber content up to 30 wt. % reduced the composite strength. Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were performed to study the structural change on the fiber surface after alkali treatment. SEM was also used to evaluate the fracture surface of the composite after tensile testing.

Keywords: sugarcane bagasse, alkali treatment, calcium hydroxide, polypropylene.

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1. Introduction

Biocomposites made from polymers reinforced with natural fibers have been developed and manufactured. Automotive sector is one of the growing market for components made from biocomposites. Those components produced are mainly used for door panels, trunk lining, headliner panel, seat backs, rear parcel shelf (package trays), and noise insulation panels. They offer weight reduction about 10%, energy saving in production of 80%, and cost reduction of 5%.^[1] The increase of consumers with green awareness to use natural fiber composites will also grow the natural fiber composites market. The global natural fiber composites market has reached US\$ 298,3 million in 2010 with compound annual growth rate (CAGR) of 15% from 2005. By 2016 the market is predicted to reach US\$ 531,3 million with CAGR of 11% from 2010.^[2] European countries is the top continent for consumption of natural fiber composites and makes it the largest region for automotive applications. While North America is the biggest consumers for building and construction applications made from wood fibers. The increasing demand for natural fiber composites in China and India will make Asia as one emerging big market for those biocomposites.^[3]

Natural fibers used for manufacturing components in the automotive sector are non-wood fibers, such as flax, kenaf, hemp, jute, and sisal. Research done by a team at Baylor University led by Prof. Walter Bradley has used coir from the outer husks of coconuts to make trunk liners, floorboards, and car-door interior to replace polyester fibers that commonly used in the automotive application.^[4] Using similar approach of finding natural fibers for biocomposites application, in this research work the potentials of bagasse fibers which are renewable resources and grow in Indonesia were studied. Bagasse fibers is the fibrous residue which are obtained from milled sugarcane stalks that are harvested from grass family plant named *saccharum officinarum*. The sugar production results in large amounts of bagasse which is about 30-32% of the total cane weight.^[5] It consists of fibres (48% including ash), water (50% moisture), and relatively small amount of soluble solids (2%) - mostly sugar.^[6] The fibre as similar with other lignocellulosic materials consists mainly of cellulose (42,3%), pentosans (25,1%), lignin (24,7%), acetyl groups (3,7%), and ash (3,5%).^[7] To prepare and enable wide-scale acceptance and confidence of the commercial communities, a thorough and fundamental of some major technical considerations must be addressed. Some of the limitations of natural fibers as reinforcement for composites are related to the low strength properties, low interfacial adhesion between fibers surface and matrix, low moisture repellance, limited processing temperature ($\pm 200^{\circ}\text{C}$), and flame-retardant properties. To overcome the

limitations, various treatments can be applied to modify the fibers surface in order to improve the adhesion between fibers and matrix which can result in improvement of mechanical properties of the end products. One of the treatments is mercerization (alkaline treatment). Strong alkaline solution of NaOH is a common alkaline solution used in the treatment. However, NaOH is reactive and hazardous solution to handle. Other works have used different solution in the pretreatment stage to prepare the bagasse fibers. Cerqueira, *et al.* reported an increase of 16% in tensile strength of composite (22.3-23 MPa) compared to the strength of polypropylene when adding 5, 10, and 20% treated bagasse fibers. The solution and the treatment steps used were pretreatment using 10% H₂S solution followed by delignification with 1% NaOH solution.^[8] Leite *et al.* used Ca(OH)₂ solution to neutralise sugarcane pulp before drying, grinding, and forming the composite using phenolic resin. Highest tensile strength was found in the composite with 29% fibers with a size of 80-170 mesh.^[9] In this present study, calcium hydroxide or Ca(OH)₂ was used as an alternative alkaline solution to NaOH as it is less corrosive and less hazardous.^[10] Soaking time during alkali treatment was varied from 2, 4, and 6 hours. The bagasse fibers were provided in various length, i.e. 3 cm, 5 cm, and as their original length. Composites were prepared using wt. % ratios of bagasse fibers to PP fibers of 20/80, 25/75, and 30/70. The strength property of the composites was evaluated by studying the effect of fiber length, alkali treatment, and the wt. % ratio. Structural characterisations using SEM, EDAX analysis and FTIR both on the fiber surface and the fracture surface of composite were performed.

2. Experimental

2.1. Materials Preparation

Bagasse fibers obtained was first neutralised using 70% ethanol for 1 hour. A ratio of bagasse weight (kg) to volume of ethanol (litre) of 1:2,5 was used. The aim of neutralisation process was to prevent bagasse fermentation due to the presence of bacteria which could cause fiber degradation and released unpleasant smell. The neutralised bagasse was then oven dried at a temperature of 200°C for 30 seconds. After drying, the bagasse were soaked in alkaline solution of calcium hydroxide, Ca(OH)₂ 14 v/v % for 2 hours, 4 hours, and 6 hours at temperature of 60° - 70°C. The alkali treatment applied used a ratio of dried bagasse weight (g) to volume of Ca(OH)₂ 14 v/v% (ml) of 1:15 g/ml. After treatment, fibers were then rinsed with distilled water. To ensure the fibers were already clean, pH of rinsed water was monitored. Rinsing ended when pH of rinsed water reached pH=7. Oven drying at a temperature of 200°C for 30 seconds was done to remove absorbed water. Those steps were repeated to prepare bagasse fibers at various length of 3 cm, 5 cm, and as their original length.

PP fibers were available from a local carpet industry as waste with a length of ± 20 cm. To ensure a homogeneous mixture with bagasse fibers, these PP fibers were cut into short fibers of 1 cm long.

2.2. Making Composite Samples

Table 1 shows the amount of bagasse and PP fibers prepared to make composite samples (60 g per sample) with ratios bagasse fibers/PP in wt.%: 20/80, 25/75, and 30/70. Both fibers were mixed for ± 3 minutes in a mixing machine using centrifugal blower. The mixture was formed into a sheet by a hot press machine using a pressure of 9,8 kPa at temperature of 175°C for 3 minutes. Table 2 shows sample coding to identify condition of bagasse fibers used and composition of each sample.

2.3. Tensile Test

Tensile test specimens were prepared from hot pressed composite sheet with specimen dimension conformed with ASTM D 638M-03. Tensile test was performed using Instron DX model with an extension rate of 10 mm min⁻¹.

2.4. Structural Characterisation

Structural characterisation using SEM (Scanning Electron Microscopy) was performed not only on fracture surface of tensile tested samples but also on fiber surface after alkali treatment at various soaking time. Obtaining the information about the structure change on fiber surface due to various duration of alkali treatment can help to understand the tensile properties together with the observation on the fracture surface on tensile tested samples. SEM machine used was FEI type Inspect S50 which was equipped with EDAX analysis. Characterisation on the fibers in isolation was also done using FTIR (Thermo Scientific Nicolet model) to study the effect of calcium hydroxide treatment on the chemical structure of the bagasse fibers.

Table 1 Volume fraction and weight % ratio of bagasse/PP

Table 2 Sample identification

Volume Fraction (%)	Weight % Ratio of Bagasse/PP	Weight of Bagasse Fibers (g)	Weight of Polypropylene (g)
12,7	20/80	12	48
16,3	25/75	15	45
18,4	30/70	18	42

Sample Code	Weight % Ratio of Bagasse/PP	Length of Bagasse Fiber (cm)	Alkali Treatment Soaking Time (hours)
Aix	20/80	3	2
Aiy	25/75		
Aiz	30/70		
Ajx	20/80	5	
Ajy	25/75		
Ajz	30/70		
Akx	20/80	original length	
Aky	25/75		
Akz	30/70		
Bix	20/80	3	4
Biy	25/75		
Biz	30/70		
Bjx	20/80	5	
Bjy	25/75		
Bjz	30/70		
Bkx	20/80	original length	
Bky	25/75		
Bkz	30/70		
Cix	20/80	3	6
Ciy	25/75		
Ciz	30/70		
Cjx	20/80	5	
Cjy	25/75		
Cjz	30/70		
Ckx	20/80	original length	
Cky	25/75		
Ckz	30/70		

3. Results and discussion

3.1. Thickness

Composite thickness was measured from tensile test samples using micrometer before test was performed. Thickness data were collected to understand the effect of pressure used during hotpressing on different conditions of bagasse fibers mixed with PP. Fig.1 shows composite thickness from all samples. The range of thickness data obtained was from 2,17-3,31 mm. The sample thickness increases with the increase of wt. % bagasse fibers in the composite. Composites which contained 25 wt. % bagasse fibers (code 'Y') were thicker than composites contained 20 wt. % bagasse fibers (code 'X'). That thickness increment can be found in composites contained fibers treated for 2 and 4 hours. However, loading the composites up to 30 wt. % bagasse fibers which treated for 6 hours (code 'Z') results in thickness reduction. Bagasse fibers in the composite provide a rigid architecture in the composite structure therefore when the amount of bagasse fibers added to PP increases, thickness will be added. However, when soaking time during alkali treatment was added up to 6 hours, the cleaning action on the fiber surface occurred in longer time leading to a decrease in fiber diameter, increasing the aspect ratio and wetting area of PP on fiber surface which resulted in reduction of thickness of the composites. Similar trend was found in previous work using NaOH solution to treat bagasse fibers. [11]

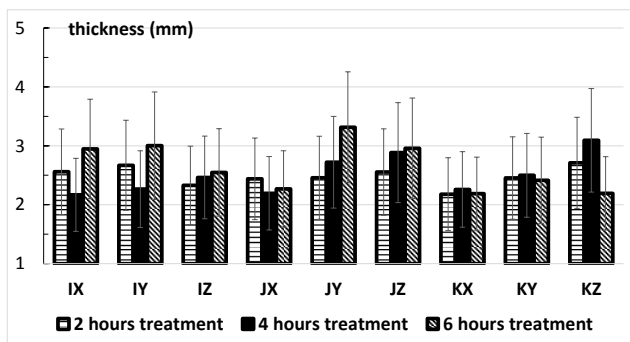


Fig. 1 Thickness of composite resulted from various weight % ratio of bagasse/PP, length of bagasse fibers, and soaking time

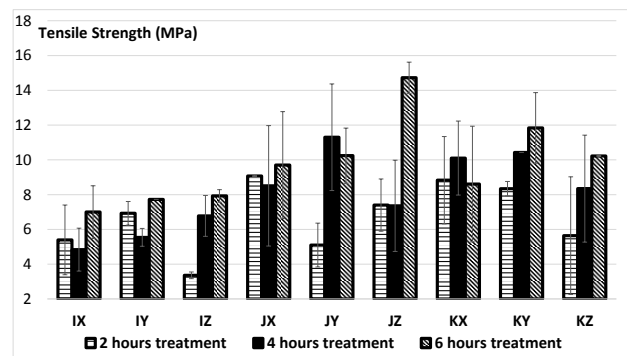


Fig. 2 Tensile strength of composite resulted from various weight % ratio of bagasse/PP, length of bagasse fibers, and soaking time

3.2. Tensile Properties

Bagasse fiber provides a rigid architecture for the composite. During hotpressing at temperature 200°C, melted PP fibers fill in the spaces available between the bagasse structure and wet the bagasse fibers and hence improving composite strength. Looking at the chart in Fig. 2, most of the data show that the presence of bagasse in the composite increases its strength up to 25 wt. % bagasse. The strength data obtained for composites with 25 wt. % fibers are 5.54-7.73 MPa (3 cm fibers), 5.1-11.3 MPa (5 cm fibers), and 8.3-11.84 MPa (original length fibers). Meanwhile the composites with 20 wt. % bagasse fibers had data strength of 4.84-7.0 MPa (3 cm fibers), 8.51-9.7 MPa (5 cm fibers), and 8.61-10.1 MPa (original length fibers). Loading the bagasse of original length up to 30 wt. %, the tensile strength decreased (5.6-10.22 MPa) due to lacking PP to wet the bagasse. However, composites contained short bagasse fibers (3-5 cm) which were treated for 6 hours show an increase in their strength when loaded up to 30 wt. %. Short fibers could be easily wetted by PP then longer fibers when they were added up to 30 wt. %. The length of fibers from original length group was measured. Their length was in the range of 3-24 cm with the majority of fibers present had a length of 12-21 cm (70%).

Tensile strength of the composites was also affected by the duration of alkali treatment using $\text{Ca}(\text{OH})_2$. The strength data range obtained for composites using fibers which were treated for 2 hours were 3.36-9.07 MPa. Their strength were the lowest strength compared to composites using 4-hour treated (4.84-11.3 MPa) and 6-hour treated fibers (7-14.72 MPa). The strength of composites using untreated bagasse fibers of original length was also evaluated and their strength values obtained were 11.38 MPa, 7.38 MPa, and 7.22 MPa for a wt. % ratio of bagasse/PP 20/80, 25/75, and 30/70 respectively. These values show that treating the original length of bagasse fibers using $\text{Ca}(\text{OH})_2$ for 2-6 hours (sample code KX, KY, KZ) did not give significant change to the composite strength (the highest strength was 11.48 MPa).

3.3. Structural Study on Fibers Surface

Structural study on the fibers surface is important to get a better understanding of structural change due to alkali treatment on the fibers surface. The structural change on the surface determines the surface adhesive bonding of the fibers which can improve the strength of the composites produced. Alkali treatment on the fibers caused weight loss due to removal of wax, lignin, and hemicellulose from fiber surface. The weight loss calculated after completion of neutralisation process in 70% ethanol was 15%. Fig. 3 shows the weight loss data in various soaking time during alkali treatment. The data were calculated from the weight difference of oven dried fibers after neutralisation process (before alkali treatment) and after alkali treatment. Though the weight loss increases with the addition of soaking time, however in the first 2 hours of treatment, the fibers experienced a significant loss (25%) compared to the weight loss of the same length of time from 2 hours to 4 hours (11%) and from 4 hours to 6 hours (10%). This was understood that effective cleaning of fiber surface took place in the first 2 hours. FTIR tests in Fig. 4 and SEM images in Fig. 5 could help to explain the findings.

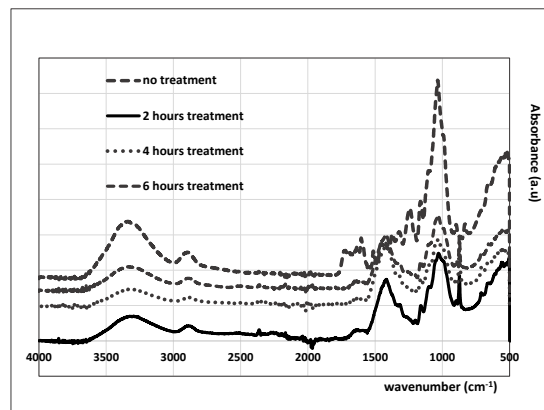
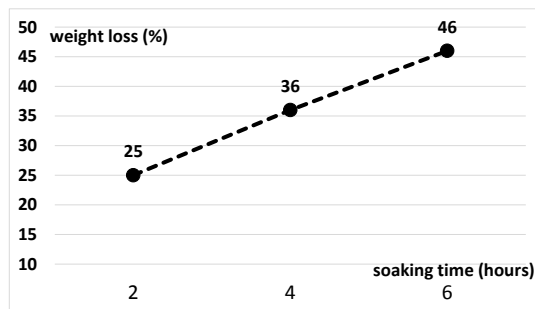


Fig. 3 Weight loss data obtained in different soaking time during alkali treatment

Fig. 4 FTIR Spectra of untreated and treated bagasse fibers

All treated fibers which soaked in different time were tested with FTIR to study the surface chemical structure. The spectra was shown in Fig. 4 and they were compared with the FTIR spectra of untreated bagasse fibers for comparison. As it is known that the components of bagasse include cellulose, hemicellulose, lignin, ash, and other components. The cellulose and hemicellulose are hydrophilic, while lignin is hydrophobic.^[12] The amount of each component varies depending on the climate, soil condition, and the age of the crop. Comparing the spectra of treated and untreated fibers, there were several absorption bands were not observed in treated fibers within the region from 2000 to 700 cm^{-1} . The CH stretch at 2893 cm^{-1} is identified in all fibers both untreated and treated. This band refers to polysaccharide which is component of cellulose.^[13] The band 1730 cm^{-1} indicates the C=O stretching of the acetyl groups of hemicellulose^[14,15] and was only noted in untreated fibers. This band was not observed in all treated fibers which indicating the removal of hemicellulose even in the 2 hours of treatment. The absorption band at 1250 cm^{-1} which is a lignin spectrum was not appeared in treated bagasse fibers. Lignin is an amorphous phenolic macromolecule and has the least water sorption of the natural fiber components.^[16] The removal of lignin during treatment was favorable to improve interfacial bonding

between fibers and matrix. There were found absorption bands in the range of 1500-1400 and 872 cm^{-1} in spectrum of treated fibers. Those bands indicated the presence of carbonate peaks on the fiber surface after treatment. SEM images on the fiber surface after treatment observed the presence of bright particles deposited on the surface (Fig. 5 b)-d)). Surface of untreated fiber in Fig. 5 a show no such particle. Those particles were from the $\text{Ca}(\text{OH})_2$ solution which contained CaCO_3 as indicated by XRD test. Cleaning of sugar cane fiber from lignin and hemicellulose is the main goal of alkali treatment to improve the wetting ability of PP on the surface of sugarcane fiber.

Fig. 5 shows the effect of alkali treatment on bagasse fibers. They show a significant different on SEM images between untreated and treated fibers. The untreated fiber was observed without fibrillation (Fig. 5 a) compared to the surface structure of the treated ones. As lignins are the cementing components that bond cellulose fibers together, therefore as they were removed during the treatment causing fibrillation of the fiber bundle to take place. The increase of soaking time during the treatment causing the fibrillation more obvious (Fig. 5 c).

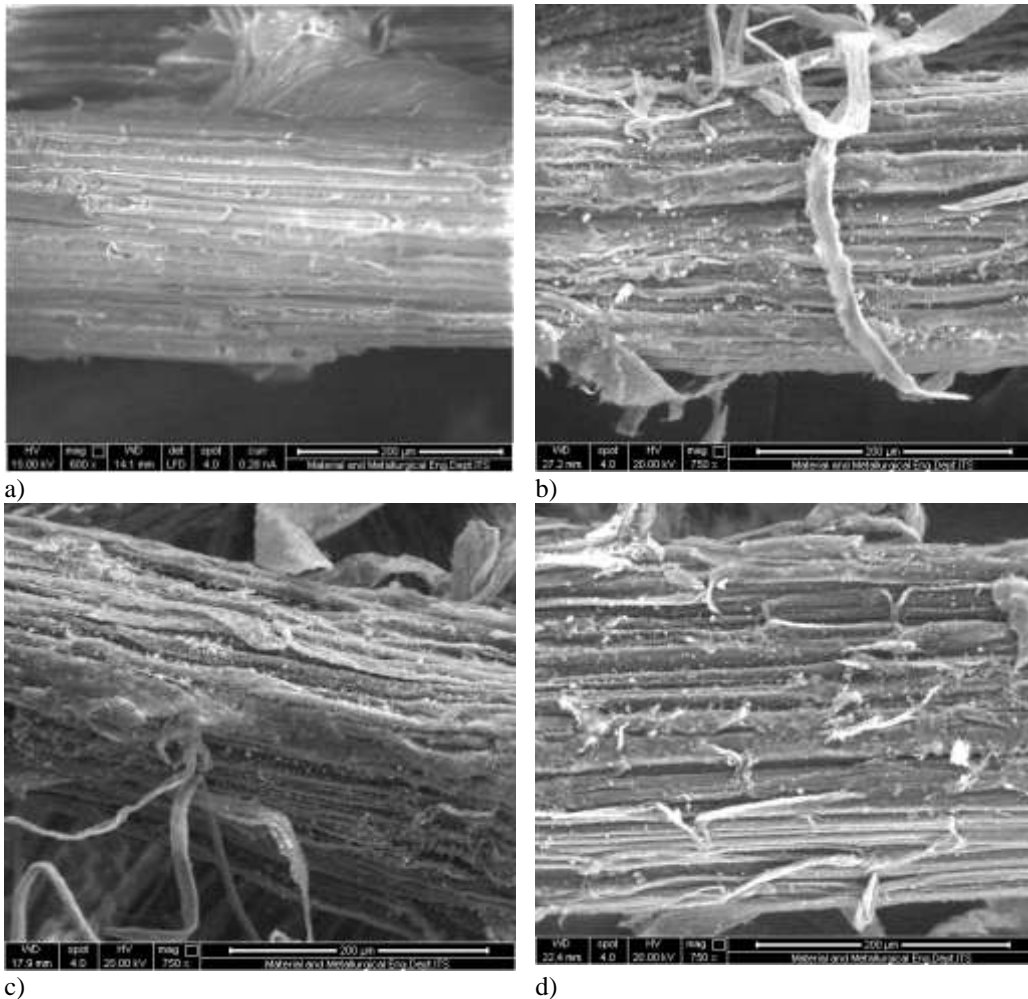
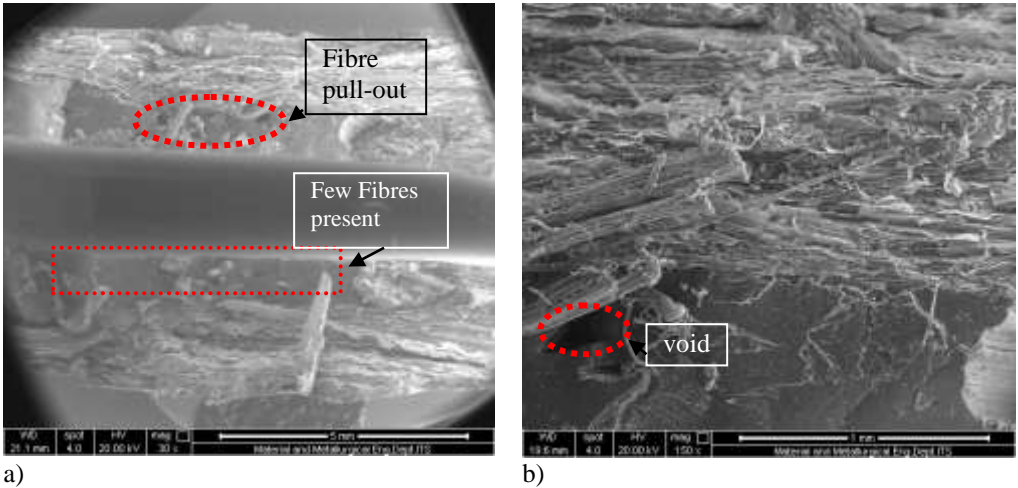


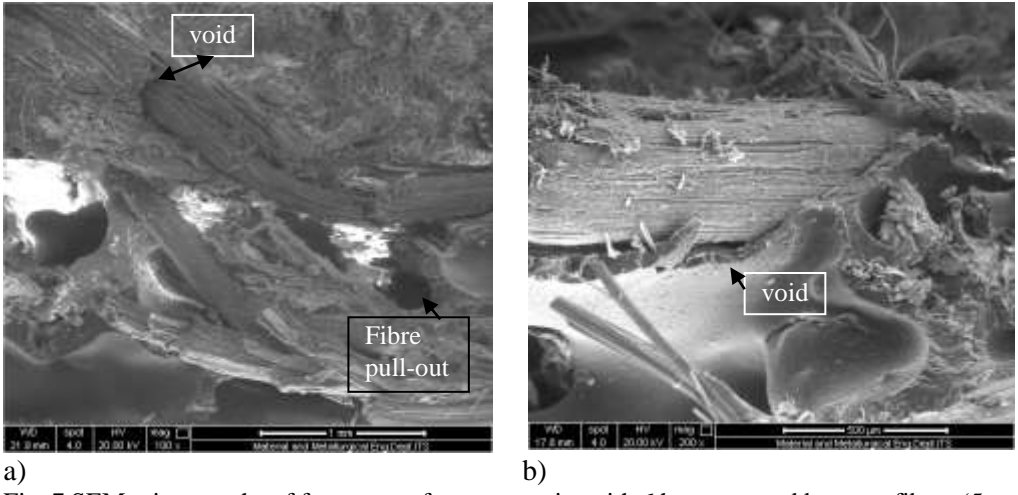
Fig. 5 SEM micrographs of bagasse fibers in different treatment a) untreated, b) 2 hours treatment, c) 4 hours treatment, and d) 6 hours treatment.

3.4. Structural Study on Fracture Surface of Composite

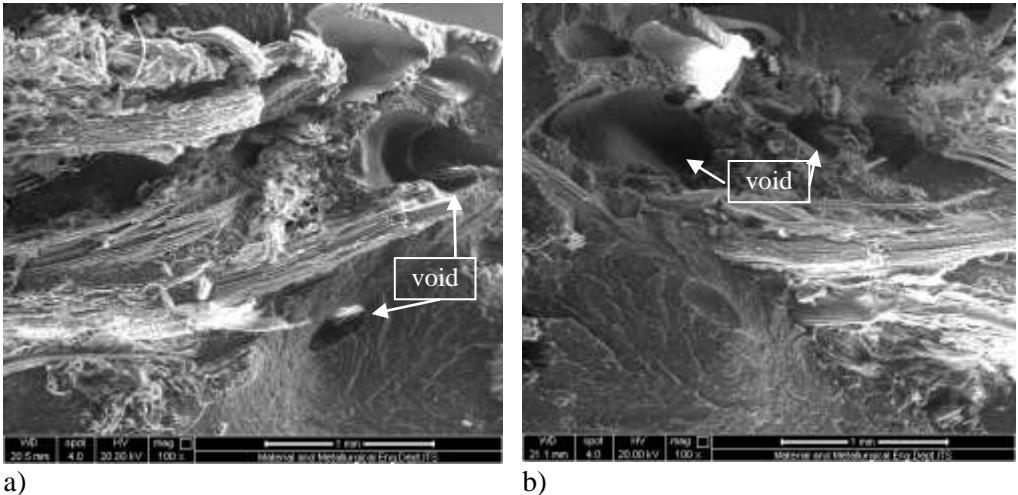
Fracture surface of the composite samples after tensile test was characterised by SEM to study the fibers/matrix bonding mechanism, fibers orientation and distribution, as well as fracture mechanism. Fig. 6 a) and b) are the SEM images of the fracture surface of composite sample contained 20 wt. % of 5 cm length of 4 hours treated bagasse fibers. Fig. 6 a) shows an area about $1 \times 6,25 \text{ mm}^2$ in the cross sectional surface has very few fibers in the PP matrix. This observation shows that the fibers in that sample were not homogeneously distributed across the sample thickness. Small void was also identified in the cross sectional area in Fig. 6 b). Most fibers in the PP matrix were in transversal direction to the tensile stress. Fiber pull-out was observed in another sample using same length and amount of bagasse fibers (Fig. 7 a). The fibers used were experiencing 6 hours soaking in $\text{Ca}(\text{OH})_2$ solution. Void in the interfacial region between fiber and PP matrix was evidenced in Fig. 7b). The strength obtained for this composite (JX 4 hours treatment) as shown in Fig. 2 was 9,7 MPa. The work of Cerqueira *et al.* (2011) using bagasse fibers pretreated with 10% H_2S solution followed by delignification with 1% NaOH solution mixed with PP resulted in composite strength of 22.3 MPa. ^[8] The carbonate deposit remained on the fibers surface after rinsing could be one of the obstacle for wetting thus prevent to have good adhesion. Fig. 8 a) and b) show fibers splitting and presence of voids in the structure.



a) b)
 Fig. 6 SEM micrographs of fracture surface composite with 4 hours treated bagasse fibers (5 cm length and wt. % ratio bagasse/PP 20/80)



a) b)
 Fig. 7 SEM micrographs of fracture surface composite with 6 hours treated bagasse fibers (5 cm length and wt. % ratio bagasse/PP 20/80)



a) b)
 Fig. 8 SEM micrographs of fracture surface composite with 6 hours treated bagasse fibers (3 cm length and wt. % ratio bagasse/PP 25/75)

4. Conclusion

Bagasse fibers which were alkali treated using $\text{Ca}(\text{OH})_2$ solution experienced a significant change on their surface structure. Lignin and hemicellulose were removed from the fibers surface as evidenced by FTIR and fibrillation of cellulose fibers was obvious with the increase of soaking time. Tensile strength of the composites produced from these treated fibers reinforced PP using short fibers of 3 cm was lower than the strength obtained in the composites using untreated original length fibers.

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