The effect of modified ijuk fibers to crystallinity of polypropylene composite

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Abstract. Nowadays, plastics becomes concern associated with its degradation and environmental issues. It has led studies to develop an environmental-friendly material. To minimize the impact of those problems, recently the usage of natural fibers as a filler are introduced because of biodegradability and availability. The promising natural fiber is "ijuk" fiber from *Arenga pinnata* plant as a filler and polypropylene (PP) polymer as a matrix. Unfortunately, the natural fibers and polymers have the different properties on which polymers are polar while natural fibers are non-polar so that reducing the compatibility and resulting the poor crystallinity. To enhance the compatibility and crystallinity, ijuk fibers were prepared by multistage treatments including alkalinization with 5 and 10% sodium hydroxide (NaOH), oxidation with 3 and 6% sodium hypochlorite (NaClO) and hydrolysis with 20% sulphuric acid (H_2SO_4) in sequences. The purposes of multistage treatments are to remove the components such as lignin, wax, hemicellulose, to cause an oxidative fragmentation of remaining lignin and to annihilate the amorphous parts respectively. Fourier-Transform Infrared (FTIR) confirms the compatibility meanwhile Differential Scanning Calorimetry (DSC) reveals the crystallinity and Scanning Electron Microscope (SEM) displays surface morphology of polypropylene. The experiments were revealing that the effects of "ijuk" fibers by the multistage treatments of 5 and 10% NaOH resulting the crystallinity of polypropylene around 31.2 and 27.64% respectively compared to the crystallinity before adding the "ijuk" fibers for 16.8%. It indicates that the entire treatments increasing the compatibility and crystallinity of polypropylene. In addition, the use of 5% NaOH offers the better crystallinity than non-treated polypropylene. The experiments conclude that by adding alkalinized "ijuk" fibers of multistage treatments can increase the compatibility and crystallinity of polypropylene.

1. Introduction

Recently, composite materials where plastics as a matrix combined with fibers as a reinforcement are widely used in various applications including military, construction, packaging, household devices and automotive parts. The plastics are used commonly from petro-polymer because of low cost, low density, easily to process, have the mechanical properties compared to metals and ceramics while the fibers usually used carbon and glass fiber offering the high strength and high modulus elasticity [1]. But the problems emerged because the use of non-degradable materials such as plastics and glass or carbon fibers becomes concern regarding to its degradability. It had triggered the

land pollution and had led studies to develop an environmental-friendly materials to reduce the impact of polluted environment. On the other hand, In several decades the use of natural fibers in composites has replaced inorganic materials in some applications due to the ability such as degradation and decomposition. Furthermore, the natural fibers have the properties for instance low cost, low density, and recyclable. They include many types of natural fiber such as flax, hemp, jute, kenaf, sisal, abaca, ramie, coir pineapple leaf fiber, bamboo, rice husk, oil palm and bagasse [2,3]. Another fiber still being developed is ijuk fiber or sugar palm fiber which has the advantages such as corrosion resistance, lower density, lower cost, low processing methods, and also available in the nature. It obtained from Arenga pinnata plant [4]. Bachtiar *et al.*, (2008) also found that ijuk fiber has good mechanical and elongation properties [5]. In some researches, ijuk fiber also merged with polymers such as epoxy and HIPS [6,7]. The problems, however, appear when the ijuk fibers are combined with polymers since they are hydrophobic whereas polymers are hydrophilic [8]. Consequently, the efforts to minimize the impact and to improve the compatibility between ijuk fibers and polymers consist of three different methods namely alkalization, oxidation and hydrolysis. Chalid *et al*., (2015) found that alkalization method can increase the compatibility both in PLA polymers and ijuk fibers [9]. Other experiments involving the immersion of coconout fibers using $NaClO_2$ demonstrated the annihilation of lignin, impurities, wax and fatty substance from its surface [10]. Chalid *et al*., (2015) also conducted the multistage treatments comprising alkalization, oxidation and hydrolysis by utilizing sodium hydroxide (NaOH), sodium hypochlorite (NaClO) and sulfuric acid (H_2SO_4) respectively to improve the compatibility and to enhance the fibrilation. They resulted that the fibers lost the amount of lignin and hemicellulose so the fibers reduced their hydrophobic property and were able to merge with polymers. In addition, the fibers had the high crystallinity as the hydrolysis treatment and it can be a potential candidate to use a nucleating agent while unifying with polymer as a matrix [11]. Another research conducted also by Chalid *et al.*, (2015) found that after ijuk fibers were treat by 0.25% of NaOH during alkalization treatment, the crystallinity of ijuk fibers rose due to exposure of micro-fibril cellulose [12].

Based on the explanations above, this study was performed to investigate the effect of modified ijuk fibers through multistage treatments consisting of alkalization, oxidation, and hydrolysis in sequence, in increasing crystallinity of the polypropylene composite. Furthermore, the experimental was performed to study the effects of alkaline concentration to crystallinity of polypropylene composite. The experimental results were evaluated by measuring FTIR spectra to characterize chemical content in composite, DSC is to measure the crystallinity and SEM to observe the morphological surface within composite material.

2. Materials and Methods

2.1 Materials

The polypropylene was supplied by the Chandra Asri Petrochemical Tbk, Indonesia. The "ijuk" fibers were purchased by the supplier on Tangerang, Indonesia. In addition, NaOH, acetic acid (CH_3COOH) and H_2SO_4 analytical grade were bought from Merck and NaClO analytical grade was obtained from Wako Chemical, Japan.

2.2 Material Preparations

Preparation of ijuk fibers consist of three stages namely, alkalization, oxidation and hydrolysis by NaOH, NaClO and H_2SO_4 in sequence. Alkalization was carried out to remove impurities, wax and dust on the fiber surface. It was carried out to annihilate the amount of lignin and hemicellulose in the fiber. Firstly, the fibers chopped using crusher machine and shieved to obtain uniform size (400-600 μm). Secondly, the fibers immersed into the NaOH solution with its concentration of 5 and 10%. Oxidation is aimed to reduce the amount of lignin and hemicellulose significantly and to make fibrilation of fibers. After alkalization process, the fiber was soaked by using sodium hypochlorite (NaClO) solution with concentration 3 and 6%. Hydrolysis is the process to enhance fibrilation and to increase the crystalline part of the fiber. The process is to immerse the fiber after oxidation process by using 20% of H_2SO_4 and the fibers were washed by distillated water until pH 7 afterwards the fibers were dried at the room temperature for one day. The final step is the hot melt mixing process with fraction volume of fibers and polypropylene is 10 and 90% respectively. The time to blend the materials is about six minutes and the temperature is 165°C. In this research, we compare between method A and B in which method A comprises alkalization 5% of NaOH, then immersing by 3 and 6% of NaClO, then by 20% of H_2SO_4 while B consists of alkalization process using 10% of NaOH, then continuing by 3 and 6% of NaClO, finally by adding 20% of H_2SO_4

2.3 Material Characterizations

2.3.1 Fourier Transmission Infra Red (FTIR)

FTIR spectra were recorded by using a Perkin-Elmer FTIR spectrometer. It was carried out to obtain an infrared spectrum of absorption of a solid, liquid or gas and to collect the resolution of high spectra on a widely range spectra data. It is utilized to characterize lignin, hemicellulose and cellulose fibers with or without multistage treatments and to show the compatibility of polypropylene after adding by the 'ijuk" fibers. Each sample recording comprising 30 scans recorded from 400 to 4000 cm^{-1}

2.3.2 Differential Scanning Calorimetry (DSC)

DSC measurements were recorded by using a Perkin-Elmer 6000. It has range of temperature from 15 to 1000 °C and was carried out to measure the temperature and heat flows regarding transitional phase of materials. This technique conducts the experiment on which the material and reference are heated and chilled on certain condition. DSC also provides the information either quantitative or qualitative data related to the changes chemically and physically in endothermic and exothermic reactions.

2.3.3 Scanning Electron Microscope (SEM)

Surface morphology of polypropylene composite was observed by using Field Emission Scanning Electron Microscope FEI Inspect F50 to image the morphology of polypropylene composite with accelerating voltage of 30 kV, resolution and magnification are 1 nm and 500.000 times respectively. More specifically it was used to clearly investigate the compatibility between matrices and fibers.

3. Results and Discussions

3.1. Compatibility of Polypropylene Composite.

The observation on ijuk fibers shows some spectra either for untreated or for treated ijuk fibers. According to the Figure 1, the spectra on the peak 1.060 and 895 cm^{-1} indicate the specific spectra of lignin based on CO and CH stretch. The increase of intensity on 1.060 cm^{-1} also illustrates the increase of fiber crystallinity, whereas the peaks at 1043 and 1135 cm^{-1} show the decrease of percent transmission of FTIR spectra in which they are proportional with the decrease of amount of lignin components after hydrolysis treatment. Another peak on 1247 cm^{-1} shows the specific spectra of CO stretch describing ijuk fiber itself. Furthermore, the spectra on the peak 1653 and 1736 cm^{-1} represent the amount of hemicellulose. The peaks on range 2900 cm^{-1} and 3500-3300 cm^{-1} exhibit CH and OH stretch respectively [11].

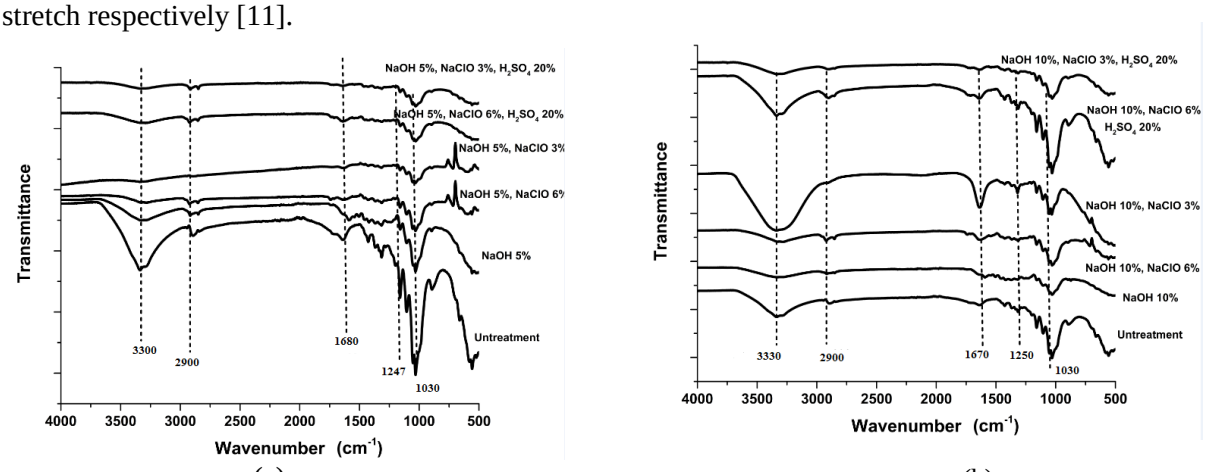


Figure 1. FTIR spectra of ijuk fibers (a) method A and (b) method B using untreated and treated fibers.

Meanwhile, the FTIR spectra of polypropylene are shown in the picture below.

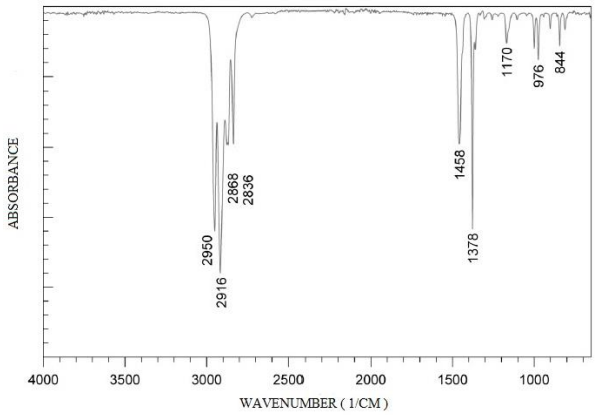


Figure 2. FTIR spectra of polypropylene.

The spectra on 2950, 2918, and 2836 cm^{-1} describe CH stretch while the peak on 1456 and 1376 cm^{-1} are specific spectra of polypropylene containing CH_2 deformation and symmetric CH_3 deformation. Whilst, the spectra on 998. 974 and 842 cm^{-1} show isotactic polypropylene band. Finally, the spectrum on the peak 1167 cm^{-1} indicates the C-C bending which is the backbone of polypropylene itself.

In order to investigate about the compatibility, the polypropylene composite was tested to see clearly whether there are bonds formed after mixing processes. The ijuk fiber itself is hydrophilic and polypropylene is hydrophobic, it will make the composite resulting the poor compatibility due to the moisture content of fibers [13].

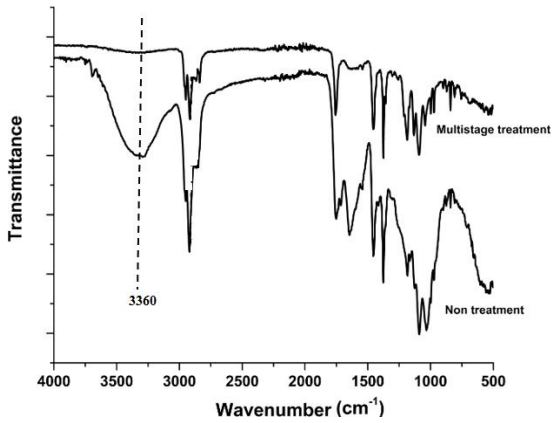
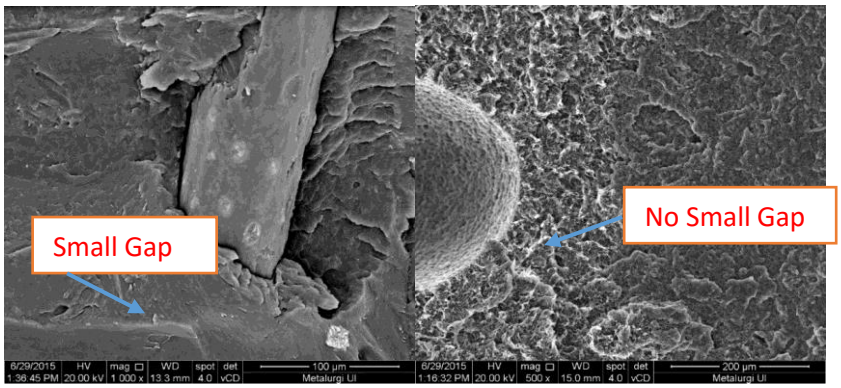


Figure 3. FTIR spectra of polypropylene composite using untreated and treated fibers

Based on the FTIR spectra above, after the mixing process with the ijuk fibers, the FTIR curve shows the new peak related to O-H stretch on 3561 – 3358 cm^{-1} and it also indicates the compatibility between ijuk fibers and polypropylene in composite caused by the bonding formation of

polypropylene composite formed through the interaction between hydroxy alcohol and phenolic. The graph also shows that the number of functional groups has reduced in polypropylene composite with treated ijuk fibers compared with untreated ijuk fibers. Furthermore, it illustrates the compatibility has been achieved after multistage treatments.

Aside from investigating for the new bond formed by FTIR spectra, the compatibility also can be proven by monitoring the surface morphology between polypropylene and ijuk fibers as shown in the pictures below.



(a) (b)

Figure 4. The surface morphology of composite (a) Untreated fibers (b) Treated fibers.

Because ijuk fiber is non-polar meanwhile polypropylene is polar, the incompatibility will be formed after they are combined into composite so that the multistage treatments needed to enhance the compatibility. Multistage treatments can annihilate the hydrophilic component of ijuk fibers such as hemicellulose, lignin, and pectin so they will compatible with polypropylene. The Figure b above reveals that there is no gap between ijuk fiber and polypropylene which indicates good compatibility because the amount of hydrophilic components in fibers has been reduced by the multistage treatments. Meanwhile, The figure a exhibits that there is a small gap between fiber and matrix. It indicates poor compatibility because the fiber and polypropylene cannot wet each other due to the hydrophilic components of fibers [9,11]. Moreover, the untreated ijuk fibers can create the voids and holes when combined with the polypropylene matrix since during the mixing process they can release the volatile substances [14].

3.2. Crystallinity of Polypropylene Composite.

The crystallinity of ijuk fibers after multistage treatments increased compared to the untreated fibers based on the previous research [11]. In this steps, the multistage treatments are expected to remove the amorphous parts in ijuk fibers so the crystalline parts increase after treatments. The increase of crystalline parts is caused by hydronium ions can penetrate amorphous region and cause the hydrolytic

cleavage on glycosidic bonds and sodium ions can dissipate hydrophilic components which are amorphous region within ijuk fibers by forming water vapor [9,15].

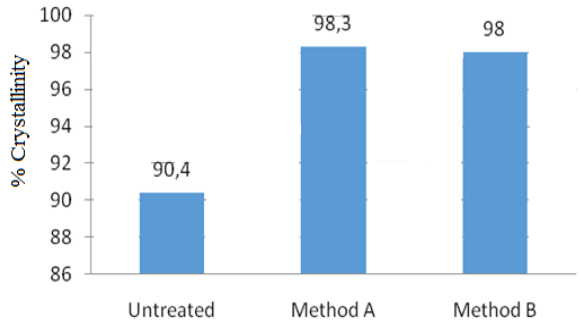


Figure 5. The crystallinity index of ijuk fibers in method A and method B.

As the crystallinity of ijuk fibers increased after multistage treatments, the crystallinity of polypropylene will also increase when combined with ijuk fibers.

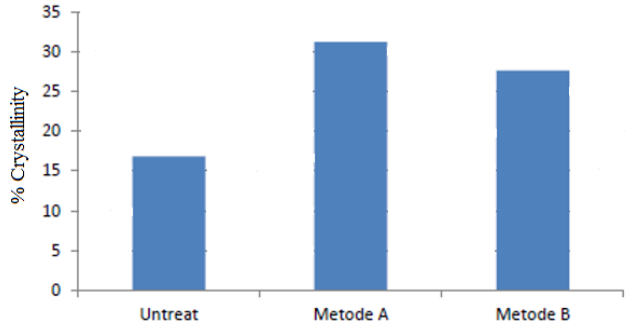


Figure 6. The crystallinity index of polypropylene composite after method A and B treatments.

The crystallinity index (CrI) above defines to examine the effect of the addition of ijuk fibers to polypropylene both in method A and B. The results display that after multistage treatments, ijuk fibers can increase the crystallinity of polypropylene composite compared with polypropylene with the untreated fibers. The crystallinity of polypropylene composite is proportional with the crystallinity of ijuk fibers when untreated ijuk fibers added to the polypropylene the crystallinity index was around 15% , but when using the treated fibers in method A and method B the crystallinity index was rising around 31 and 28% respectively. The crystallinity of polypropylene composite in method A (5% NaOH) is higher than in method B (10% NaOH) caused by there is a minimum concentration of sodium hydroxide used in alkalization treatment, in which the higher concentration causes the damage to the structure of fibers. The damage can reduce the amount of crystalline region so it does not maximize the alkalization treatments [16].

The increase of crystallinity of polypropylene composite also proportional with crystallization time which meant the time needed to crystalize during cooling process. According to DSC results, the increases of crystallization time to method A and B were 0.44 and 12 s obviously faster than polypropylene with untreated fibers which was 2.8 s.

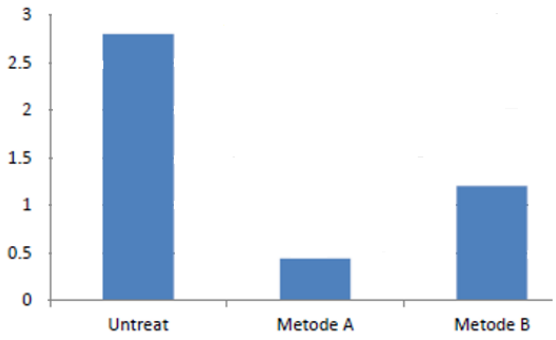


Figure 7. Crystallization time of polypropylene composite after method A and B treatments in seconds.

The crystallization time on method A is faster than on method B influenced by the higher crystallinity of ijuk fibers so it will initiate faster the polypropylene to crystallize vice versa method B results the slower crystallization time influenced also by lower crystallinity of ijuk fibers on method B. The crystallinity of method A (5 % NaOH) is higher because it has the lower concentration of sodium hydroxide whereas method B (10% NaOH) is higher concentration. The higher concentration will cause the damage of structure of ijuk fibers and reduce the crystalline region [12,16]. In other words, the more concentration we used on alkalization, the more crystalline regions are reduced. It will automatically affect crystallization time when the ijuk fibers combined with polypropylene. The ijuk fibers on method A has more crystalline regions than B so its crystallinity is higher than B and it will trigger faster crystallization time when combined with polypropylene.

4. Conclusions

According to our studies, the ijuk fibers prepared by multistage treatments (alkalization, oxidation, and hydrolysis) both in method A and method B reveal that the level of crystallinity increases due to the annihilation of amorphous and hydrophilic parts in fibers, method A can rise the crystallinity of polypropylene composite to 31% while method B rises to 28% more effective compared to untreated ijuk fibers. Aside from the percentage of crystallinity, time needed to crystallize when combined to polypropylene also speeds up which method A and method B can accelerate crystallinity to 0.44 and 1.2 seconds faster. Furthermore, these studies also probed that the good compatibility between ijuk fibers and polypropylene can be achieved by conducting fibers into

multistage treatments and it can be seen from the surface morphology of composite. In accordance with this study, the ijuk fibers were treated by multistage treatments can increase the crystallinity and good compatibility of polypropylene in material composite.

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