The Effect of Crosslinking Fibers with Polyvinyl Alcohol Using Citric Acid

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Abstract: This work was aimed at fabricating and characterizing paper manufactured from empty fruit bunch coated with polyvinyl alcohol. The study was conducted by controlling the amount of polyvinyl alcohol coated to the paper. The dimensional changes and morphology of the empty fruit bunch paper coated with polyvinyl alcohol were investigated by Scanning Electron Microscopy and Swelling test. The empty fruit bunch coated paper was characterized using FTIR and TGA analysis. The physical properties of empty fruit bunch paper coated paper were studied by using water absorption test, showed that the increasing amount of polyvinyl alcohol coating reduced the total volume of water absorbed and speed of its absorption.

Keywords: Empty fruit bunch, paper, Polyvinyl alcohol, Dimensional changes

1. Introduction

In Malaysia, a high production in oil palm agriculture had resulted a high amount of empty fruit bunch waste. The oil palm production is about 16 million tons in year 2000 and has potential will be increased to 15.4 million ton during 2016 [1]. Previously EFB has been suggested as an alternative raw material for pulp and paper making[2]. Low in lignin but high cellulose content, plus continuation of supply make EFB fibers attractive as an alternative for paper making[3]. However, the main factor that should be considered when using natural fibers is their hydrophilicity[4]. Paper or composite may experience dimensional changes by swelling and shinkage depending on their condition. Addition of a fillers and crosslinkers was suggested to maintain dimensional stability[5].

Polyvinyl alcohol is a synthetic polymer that is widely used in industrial, commercial, medical and also in food application[6]. PVOH is also capable to be used as a coating material or plastic film[7]. PVOH has good solubility in water at room temperature. To prevent from dilution, PVOH can be crosslinked using curing agents such as citric acid, glutaraldehyde, hex methoxyethyl melamine, maleic acid and others [8]. Therefore, it is necessary to crosslink the PVOH polymer to deal with the wet condition [9]. For past few decades, biodegradable polymers film have been the focus of worldwide attention because their environmental advantages in terms of eco-friendly, recyclability, and reutilization as compared to commercial plastic films. Studies about biodegradable polymer film were mostly related to coating or food packaging [10].

PVOH and natural fibers are compatible as both materials are hydrophilic. Composites made of PVOH reinforced with fibers had good fiber/matrix bonding, as proven by high tensile strength [11]. In the paper industry, PVOH has been used as wet strength additive that protects and reinforces the fiber web[12]. As the result, paper coated with PVOH will possess better mechanical strength during wet conditions[13]. Citric acid widely used in food and drug industry as an excellent crosslinking agent. From previous studies, citric acid was capable to crosslink together with PVOH and cellulose[14-16].

Tissue paper is a type of paper that have good water absorption due to the fiber arrangement as a bulky structure. In order to produce a bulky paper, a suitable drying process has been chosen wisely during the tissue paper formation. Instead of using a hot roller, tissue paper was dried using air during the manufacturing process [17]. Air dry method was able to produce high porosity paper with higher water absorption rate and increase water holding capability [18]. As the void content in the paper web increased, more water could be filled in. Tissue paper had less mechanical strength due to less fiber bonding in the paper fiber network [19].

Most of the commercial paper are coated. The coating material fills in the pores within paper and reduces its porosity. Thus, paper applied with coating will tend to absorb less water. Coating material can reduce dimensional changes in paper due to less amount of moisture adsorbed into the pores when exposed to humid air [20]. In the packaging industry, whey protein coating able to improve the oil resistance and reducing water-vapor permeability of the paper box [18, 21]. The optical properties of paper can be also enhanced by coating with kaolin clay and calcium carbonate [22, 23].
Liquid is able to travel through the porous material by using capillary action. The capillary action is an ability of a fluid to flow in narrow spaces without any external assistance forces like gravity. The capillary action occurred when inter-molecular forces took place between a liquid and its surrounding surfaces. The main factor of capillary action is by cohesion force and adhesion forces. The cohesion forces are the capability of liquid to pull themselves while the adhesion forces are about the ability of the liquid to attach to solid surfaces. The capillary action will be affected by the diameter of the capillary. Capillary with smaller diameter will allow fluid to transfer further due to a huge amount of adhesion and cohesion forces [24, 25].

2. Experimental

2.1 Preparation of crosslinked fiber

In this work, the empty fruit bunches were collected from United Oil Palm Sdn Bhd, Nibong Tebal, Penang (Malaysia). The pulping process was run using 27 % NaOH at 170 °C with 1000 kPa pressure. Pulp was soaked for 1 hr before cooked for 2 hr. The pulp underwent screening and cleaning process to remove the over sized pulp and the remaining lignin. The pulp was formed into hand sheet with grammage 80 gsm. During the hand sheet forming, no pressure was applied to remove remaining water when the pulp was deposited on wire mesh. The hand sheet was dried and conditioned in the conditional room for 24 hours. The polyvinyl alcohol solution was prepared at 1 % concentration and 10% of citric acid was added based on the from amount of polyvinyl alcohol used. The citric acid acted as curing agent. The polyvinyl alcohol solution was applied to the dried hand sheet using a pressurized spray gun. The variable in this experiment was the amount of polyvinyl alcohol solution applied to the hand sheet. For each spray the amount of polyvinyl alcohol solution applied was 10 mL. 5 samples were prepared which were 1 time coating (Sample 1), 2 times coating (Sample 2), 3 times coating (Sample 3), 4 times coating (Sample 4), and without polyvinyl alcohol coating (Sample 0). All samples coated with polyvinyl alcohol solution were crosslinked at 130 °C for 30 minutes and cool down in open air for 24 hours.

2.2 Water absorption and speed of water absorption

All 5 samples were prepared into paper strips of 7 × 1.5 cm. The water absorption test was measured by the maximum amount of water able to be absorbed into the paper strips by immersion in distilled water. For speed of water absorption test, 1 cm of the paper strips was dipped into the distilled water and the time taken for water to reach the opposite side was recorded.

2.3 Swelling test

The swelling test was run by dropping distilled water on the paper’s surface and image were recorded perpendicularly

2.4 Scanning electron microscope (SEM)

The SEM test was run to study the fiber morphology using Leo Supra, 50VP, Carl Zeiss Scanning Electron Micrograph. The sample was mounted to the SEM stub using double-sided tape. The gold coating was applied using Polaron Equipment Limited Model E500 for 10 minutes.

2.5 Fourier transforms infrared spectroscopy

FTIR analysis was conducted with a Perkin Elmer 1600 Infrared spectrometer. The FT-IR will be examined using KBr method with the ratio of 1:100 and made into a pellet. FT-IR spectra of the coated pellet will be recorded by using Nicolet’ AVATAR at 16 scans with a resolution of 2 cm-1. The wave number range is focused on of 3200 to 3600 cm-1 to determine the crosslinking structure in polyvinyl alcohol after curing process. The significant transmittance peak at particular wave numbers will be measured using the “find peak tool” provided by Nicolet OMNIC 5.01 software.

2.6 Thermal gravimetric analysis

TGA analysis will be used to evaluate the thermal stability of hydrophilic polymeric membrane composition. The weight loss of the samples will be measured as a function temperature. In this determination of 10 mg of dried sample will be put into the sample holder and heated at 20 °C/ min in nitrogen flux from room temperature to 600 °C using Parkin Elmer-YGA7 instrument. The thermogram records the percentage of weight loss versus temperature. The mass change of the sample will be recorded continuously over the temperature and time intervals.

3. Result and Discussion

3.1 Water absorption test

Figure 1 indicated that, the higher amount of polyvinyl alcohol applied to the paper, the higher the volume of water absorbed. Sample 1 had the highest amount of water absorbed which was 580 %, followed by Sample 2 (500 %), Sample 3 (480 %),
and Sample 4 (460 %). However, for Sample 0 the total water absorption could not be measured due to disintegration during contact with water. The citric acid in the polyvinyl alcohol solution acted as curing agent which crosslinked polyvinyl alcohol and fibers. The crosslinked structure was insoluble in water, prevented the paper from disintegrating during the test. The crosslinking acted as reinforcement, holding the fiber and polyvinyl alcohol together from separation [12]. Comparing Sample 0 with others, the web formation in paper without polyvinyl alcohol coating was based on hydrogen bonding while in the samples with polyvinyl alcohol coating, they were based on covalent bonding due to crosslinking. Therefore, as the water permeated into the paper, the hydrogen bonding would break, resulting the fiber web to disintegrate [26, 27].

The amount of water absorbed was affected by the porosity of the paper itself. Previous study has shown that the presence of amorphous structure in the empty fruit bunch fiber was about 39%, while the remaining 61% was crystalline. The low percentage of amorphous structure was not the main factor that affected the total water absorption but by its porosity structure. The porosity properties would allow water to penetrate and fill in the voids, leading to high water absorption [18]. Total water absorption decreased with the increasing amount of polyvinyl alcohol coating due to the reduction of voids and porosity in paper [29]. In theory, the increase of polyvinyl alcohol coating should increase the total water absorption due to ubiquitous hydroxyl groups. However, some of the hydroxyl groups might be sacrificed for crosslinking [14].

Capillary action in the paper paper influenced the speed of water absorption. Voids in the paper formed many capillaries. Due to adhesion force between water and cellulose and cohesion force between water itself, the capillary action was able to lift up the water to pass through along the paper strip. Based on the speed of water absorption result (Figure 2), sample with the lowest amount of polyvinyl alcohol applied had the fastest rate of absorption as compared to others due to the plenty of voids. The polyvinyl alcohol coating possibly blocked the capillaries entrances causing the water molecules to slow down traveling along the fiber network [24, 30, 31].

3.2 Speed of water absorption test

Figure 2 had shown that the polyvinyl alcohol coating reduced the speed of water intake. Sample 1 had the fastest rate of water absorption by taking 80 seconds until fully saturation, followed by Sample 2 (88 seconds), Sample 3 (98 seconds) and Sample 4 (120 seconds). However, Sample 0, simply disintegrated during test.

The swelling effect in the SEM image in Figure 3 (a) was due to the moisture adsorption during exposure to open air. The high humidity in the surrounding air

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**Figure 1:** Results of water absorption test (Sample 1) 1 time coating, (Sample 2) 2 times coating, (Sample 3) 3 times coating, (Sample 4) 4 times coating with polyvinyl alcohol.

**Figure 2:** Results of water absorption test and rate of absorption test. (Sample 1) 1 time coating, (Sample 2) 2 times coating, (Sample 3) 3 times coating, (Sample 4) 4 times coated with polyvinyl alcohol.

**Figure 3:** (a) Scanning electron microscope test (SEM)
affected the dimensional stability of the paper\[20\]. SEM image in Figure 3 (b) had no dimensional changes even after exposure to humid condition in open air. Due to the crosslinking between polyvinyl alcohol and fiber by citric acid. The paper was no longer depending on the hydrogen bonding for fiber network formation and did not disintegrate during contact with water or moisture\[32\].

Crosslink also reduced the hydrophilicity of fibers and polyvinyl alcohol itself, due to the sacrifice of hydroxyl groups during the crosslinking (esterification)\[14\]. After crosslinking the paper became less hydrophilic which help to prevent moisture absorption that led to dimensional changes. The crosslinking between polyvinyl alcohol and cellulose by citric acid acted as reinforcement which held the paper structure together during exposure to moisture or humid condition\[12\]. However, after coated with polyvinyl alcohol the paper was still porous. There was no matrix in the fiber web and also no layer formed on the paper surface. It could be concluded that the coating was actually fully coated on the surface of the fibers.

Figure 3: Scanning Electron Microscopy on surface area at cross section side (a) Uncoated Empty Fruit Bunch Paper, (b) Empty Fruit Bunch Paper Coated with Polyvinyl Alcohol Solution

3.4 Swelling test

The swelling test (Figure 4) had shows that the swelling effect on the empty fruit bunch paper after contact with water droplet. Based on the images in Figure 4 (a), the empty fruit bunch paper without polyvinyl alcohol coating swollen after 5 seconds of contact with water droplets, while in Figure 4 (b), the empty fruit bunch paper coated with polyvinyl alcohol was still maintained. Again, the result in Figure 4 (b) was due to the formation of crosslinking between polyvinyl alcohol and fibers. The crosslinking made polyvinyl alcohol insoluble in water while reinforcing the fibers by preventing them from the swell. In the literature, the bonding between fibers was due to the hydrogen bonding \[26, 27\]. During contact with water, the water would penetrate into the paper, breaking the hydrogen bonding \[26\]. As the bonding was no longer occured between the fibers, the fiber web became loosen and disintegrated. Previous work also showed that polyvinyl alcohol had already been used as paper wet-end additive to improve its wet strength properties \[33\]. It was able to protect and reinforced the fiber network in the paper. The paper would not disintegrate in wet condition due to the presence of polyvinyl alcohol that was able to hold the fiber network and prevent from separation by preserve some of the dry strength \[12\].
3.5 Fourier transform infrared spectroscopy

The addition of polyvinyl alcohol coating into empty fruit bunch paper has been characterized using FTIR spectroscopy. The figure 5 shows that four types of spectra which is (A) empty fruit bunch, (B) polyvinyl alcohol, (C) polyvinyl alcohol crosslinked with citric acid, and (D) empty fruit bunch paper coated with polyvinyl alcohol coating. The objective of using the FTIR spectroscopy was to determine of hydroxyl functional group in empty fruit bunch paper before and after coated with the polyvinyl alcohol. The broad peak at region 3500-3600 cm\(^{-1}\) shows that the presence of abundance amount of hydroxyl group in empty fruit bunch and polyvinyl alcohol [34-36]. By having a broad peak in this region, both samples possessed a high hydrophilicity properties making its ability to attract water. However, the reduction of the hydroxyl group occurs in region 3500-3600 cm\(^{-1}\) in polyvinyl alcohol sample after crosslinked using citric acid. This is due to the hydroxyl group in polyvinyl alcohol has been sacrificed in order to form crosslinking with citric acid. This crosslinking reaction has reduced the hydrophilicity properties of polyvinyl alcohol [37, 38]. For coated empty fruit bunch paper shows a reduction of the hydroxyl group in 3500-3600 cm\(^{-1}\) region. This shows that, the curing agent which is citric acid also react with hydroxyl group in cellulose and able to form crosslinking [39]. Since previous studies shows that there are many good interactions between fibers and polyvinyl alcohol has been witness in many micrographs [13].

3.6 Thermal gravimetric analysis

Figure 6 shows the TGA analysis of empty fruit bunch, polyvinyl alcohol, and citric acid. The TGA result shows that the temperature degradation for empty fruit bunch is 346.13 °C with remaining residue 13.63 %, for polyvinyl alcohol is 345.27 °C with remaining residue is 0.93%, and for citric acid is 230.25 °C with remaining residue is 2.78%. Based on the result, the temperature degradation, the polyvinyl alcohol solution is suitable to be used as a coating material to empty fruit bunch paper. This is because, in order to trigger the esterification process, these materials should able to withstand heat at least 130 °C for 30 minutes [14, 39, 40]. While for crosslinked polyvinyl alcohol using citric acid the thermal degradation temperature is 351.98 °C with remaining residue is 5.9 %. It shows that, after crosslinked, the thermal degradation of polyvinyl alcohol has increased. This is because the thermal stability of the polymer has become stable after crosslinking [40]. So, it can be concluded that the empty fruit bunch, polyvinyl alcohol, and citric acid are compatible with each other and become more stable after undergo crosslinking.
4.0 Conclusions

In this work, the empty fruit bunch paper dried by air was used to study about the porosity and bonding between fibers that affected the total water absorption capability and the speed of water absorption. From the results, it could be concluded that by having a higher porosity, the empty fruit bunch paper was able to absorb much more water within short period. The addition of polyvinyl alcohol acted as reinforcement that prevented dimensional changes when in contact with water or moisture. However, excessive polyvinyl alcohol coating was suggested to block the pores, which led to reduction of amount and speed of water absorb. Since, the crosslinking by citric acid had formed an insoluble network between the polyvinyl alcohol and fibers to maintain the paper's integrity. The FTIR and TGA analysis shows that the crosslinked polyvinyl alcohol between fibers able to reduce the hydrophilicity properties and improve thermal stability of empty fruit bunch paper.

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6.0 References