Sodium Hydroxide Treatment on Natural Fibers for Better Fiber Morphology: A review

Nor Farhana Jasmi, Nur Farahin Yusoff, Jamaludin Kasim
Centre of Wood Industry, Faculty of Applied Science, Universiti Teknologi Mara Pahang

ABSTRACT

Lignocellulosic fibers seem to be among the best alternative substitution fillers in biocomposite. Among its usages includes as particleboard (PB) and wood polymer composite (WPC) as it is abundantly available and its woody properties offers great usability. However, several problems arise due to the high hygroscopicity of woody materials and less interfacial adhesion between hydrophilic filler with hydrophobic petroleum based polymer. A variety of alkali treatments has been reported in the enhancement of promoting better fiber morphology and thus reduce the water uptake behavior and increase the compatibility. This paper intended to review the alkalization treatment using Sodium Hydroxide (NaOH) on natural fiber surfaces, differentiate treated and untreated fiber surfaces and summarize the effective concentration of NaOH which may be applied on certain wood species. The findings are hoped to be used as a guide throughout future researches.

Keywords: *Wood Polymer Composite, Particleboard, Sodium Hydroxide*

Introduction

Synthetic fibers such as glass fiber and carbon fiber that have actively been used years ago in making composite product are very expensive and hazardous to the environment. Natural fibers including softwood, hardwood and biomass has the potential to be an alternative source of cellulosic materials to replace the synthetic fiber for engineered product development. These natural fibers are abundant in nature that if unutilized will lead to waste disposal problems. This substitution may ensure fully consumption of the biomass and shall reduce the problem of disposing them. The natural fibers have advantages of renewable resources, low cost, strong, light in weight, abundant, non abrasive, and non hazardous (Shinoj, 2011). Despite of giving benefits to the materials sciences field, replacing the synthetic fiber with natural fibers may help people around the world to improve their standard of living. For example, rural jobs opportunities may be provided when lignocellulosic and biomass such as kenaf, jute, and oil palm fibers necessitate extraction process prior to develop reinforcing fillers in many polymers and other products.

However, natural fibers have a disadvantage of highly hydrophilic substance because of hydroxyl group presence in cellulose. Cellulose, hemicelluloses and lignin are major organic compound of lignocellulosic material. The hydroxyl group presence in cellulose is easily attracted to the hydrogen bond of water (H_2O). Thus it makes the engineered product permeable to water. Another problem noticed is the non compatibility between natural fibers and polymer matrix in making wood polymer composite (WPC). Chemical modification technology can greatly improve the properties of lignocellulosic in production of related composite Gu, (2009) and Gwon *et al.*, (2010) . An example of chemical modification that is widely used is alkali treatment using Sodium Hydroxide (NaOH) solution. NaOH treatment is a process of alkalization on natural fibers which may improve the bonding. It is indicated as the best chemical treatment in modifying the surface of natural fibers offering better adhesion with resin polymer (Rosa, 2009, Sawpan, 2011). The natural fiber will be immersed in a solution of NaOH for certain time before it is rinsed and dried and prolong normal process in engineered product manufacturing. Gwon *et al* (2010) stated that natural fiber treated with alkali solution has clearer surface compared to untreated fiber observed under Scanning Eletron Micrograph (SEM). This could be attributed to the part of hemicelluloses, lignin and extractives are removed by alkalization process and may promote better fiber morphology and high compatibility of natural fiber with polymer matrix in WPC. There is a contrast of ideas between researchers on the effect of alkalization towards water uptake by natural fibers (Rahman, 2009 and Ichazo, 2001). This is necessary to be understood in order to produce a high quality engineered biocomposite product with low water uptake. This paper compiles and reviews past studies on NaOH treatment on natural fibers as to make alteration on natural fiber surfaces and fix them into resin. The objectives of this review are: 1) to review the alkalization treatment using Sodium Hydroxide (NaOH) at room temperature on natural fiber surfaces; 2) to differentiate treated and untreated fiber surfaces; and 3) to summarize the effective concentration of NaOH may be applied on certain wood species.

Hygroscopicity of natural fiber

Cellulose contains many hydroxyl groups and it is a very rigid crystalline natural polymer that could avoid any water absorption. Rosa (2009) stated that the impurities in natural fibers have to be removed leaving cellulose alone by chemical treatment to improve their wettability. The impurities included lignin and extractives. However, according to Gwon (2010), water absorption will not occur in lignin and extractives that consist of pectin, wax, ash and volatile materials. This is because even though they are totally amorphous, they have hydrophobic characteristic. This can be seen when the hydrophobic lignin is added externally into the biocomposite, water absorption of the fiber is reduced (Rozman, 2000).

Lignin could reduce water absorption by two possibilities which are bulking and plugging the cell wall lumen. These mechanisms will reduce water to penetrate into the cell wall. Another way to reduce the water uptake in engineered bioproduct and improve the wettability is to remove hemicellulose. This is because hemicellulose has hydrophilic characteristics that tends to absorb water and its dissolution may lead to better fiber dispersion (Cao *et al.*, 2006).

Chemical treatment by alkalization process could lower water absorption tendency and decrease the presence of water sites in biocomposite product. This is due to the decreases in the hydrophilic nature of hemicelluloses that have been dissolved with treatment (Rahman, 2009, Migneault, 2009). This study is also supported by Sinha and Rout (2007). It might be due to the effect of alkaline solubilization of hemicelluloses which are usually ascribed to the destruction and breaking of hydrogen bonds. In particular, all the ester linked substance of the hemicelluloses can be cleaved by alkali except for the cleavage of α-ether bonds between lignin and hemicelluloses. However, these findings contradict the report of Ichazo (2001) who stated that alkaline treatment may increase the permeability of water molecules to particle surfaces. This is because the increment of surface area (due to chemical treatment) has enhanced the hydroxyl (-OH) groups availability on cellulose surface that could absorb water and lead the composite to swell. To avoid this to be happen in developing WPC, coupling agent such as Maleic Anhydride Polypropylene (MAPP) and Maleic Anhydride Polyethylene (MAPE) should be applied.

Alkali treatment

Effect of NaOH concentration

The different concentrations of sodium hydroxide (NaOH) were used in several studies to investigate its effect on tensile and surface of subjected natural fibers. Ndazi *et al.* (2007), Bachtiar *et al.* (2008), and Gu (2009), found that the tensile strength of natural fiber increases with NaOH treatment compared to non treated fibers. The tensile strength was also observed to enhance with the increasing of NaOH concentration. However, Bachtiar *et al* (2008) in the study of alkaline treatment on tensile properties of sugar palm against two different levels NaOH concentration conclude that, higher alkali treatment concentration was not sufficient to enhance the tensile strength because the fiber could damage due to high alkalinity. In general, the reviews of solution concentration affirmed the enhancement of tensile strength due to delignification of lignin, removal of hemicelluloses and some impurities from fiber surface that leave a rougher surface of fiber and offer larger surface area for better contact with matrix increased with the increasing of alkali concentration of up to 10%. "Denser NaOH solution provided more sodium (Na) and hydroxyl (OH) ions to react with the substances on the fiber, causing greater amount of lignin, pectin, fatty acid and cellulose to leach out. This would be detrimental to the fiber surface" (Gu, 2009).

Scanning Electron Micrograph (SEM) may clarify the effect of NaOH treatment on natural fibers. The surfaces of untreated kenaf fibers were observed as porous and rough (Edeerozey, 2007). These appearances indicated that crystalline cellulose is tied up with cementing materials such as hemicelluloses, lignin and other non cellulosic compounds (waxy substance, oil and impurities). Similar results were showed by Beckermann *et al.*, 2008 and Gwon, 2010. Figure 1(a) and (b) showed that the impurities are removed from the treated fiber surface and the filaments are splitting from each other.

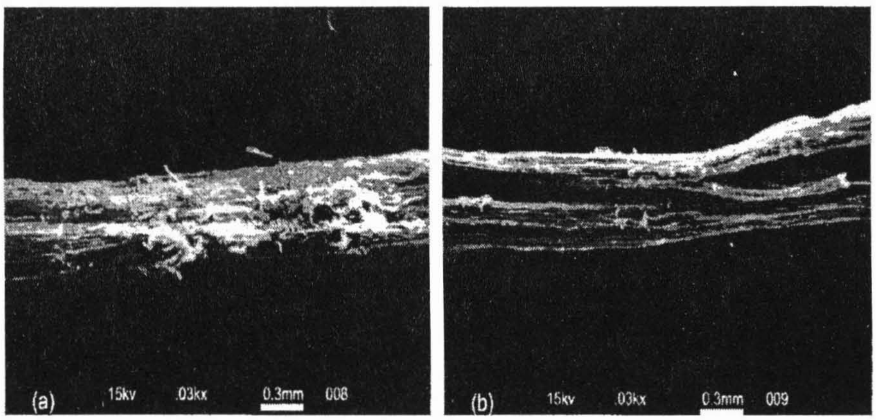

Figure 1. SEM migrograpfs of a bagasse fiber (a) untreated fiber (b) 5% NaOH treated fiber

Mansour Rokbi (2011) observed the changes of treated fiber surfaces in term of color. The SEM micrograph exhibits the color of the Alfa fiber becomes more yellowish with the increment of NaOH concentration. This can be shown in Fig 2(a) and (b). Smoother appearance is observed as compared to the untreated fiber. The dissolution of hemicelluloses and other impurities provide more surface area available for contact with matrix. As the amorphous structure and hydrophilic character of hemicelluloses is been degraded, the water uptake of fiber surfaces can be minimized in the final products (Gwon, 2010).

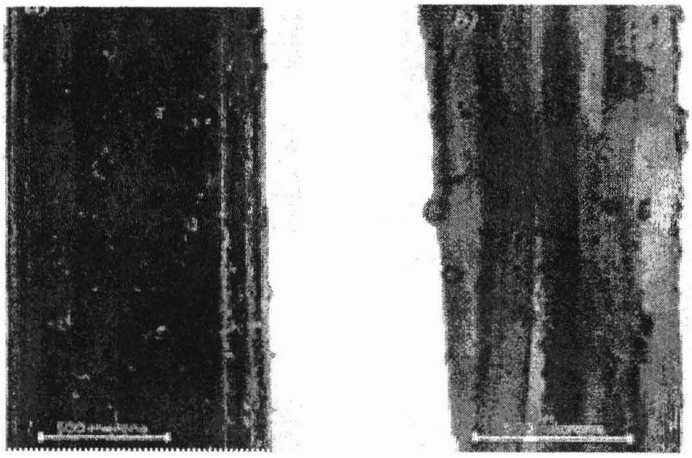

Figure 2.SEM migrograpfs of Alfa fiber (a) untreated fiber (b) NaOH treated fiber

Effects of Temperature

Alkali treatment of fiber was conducted in several conditions such as different concentration of NaOH solution, different soaking time and different level of temperatures. Fiber treatment of NaOH in most research conducted at ambient temperature or in range of 20°C - 30°C. Gu (2009), Brigida *et al.*, (2010) and Trodec *et al.*, (2011) have conducted NaOH treatment at this temperature in different concentration of NaOH solution. The results show similar traits where lignin, hemicelluloses and other impurities composition reduce and lead to rougher surface of fibers. This improves the interfacial area between fibers and matrix for chemical bonding and increase the tensile strength of fiber (Gu, 2009). Saha *et al.*, (2010) meanwhile conducted NaOH treatment on fiber at two different ranges of temperatures, ambient and elevated temperature respectively to investigate the effect of temperature prior to surface and tensile strength of fiber. Both of studies found that, higher or elevated temperature of treatment possess higher tensile strength and rougher surface than fiber used in ambient temperature treatment.

Figure 3 shows the differences fiber surface between treated and untreated fiber and between ambient temperature and elevated temperature of treatment studied by Saha *et al.*, 2010. The surfaces of fiber were examined at different condition. The treated fiber shows rougher surface than untreated one with the elevated temperature treatment possess rougher surface. They conclude that, the fiber separation is excellent at higher temperature with more cementing materials were removed.

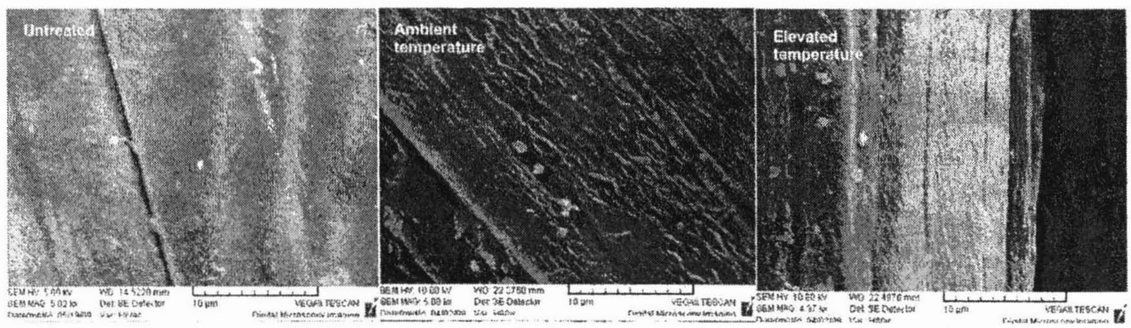

Figure 3. SEM photograph of untreated and alkali treatment at ambient and elevated temperature

Mechanism of Treatment

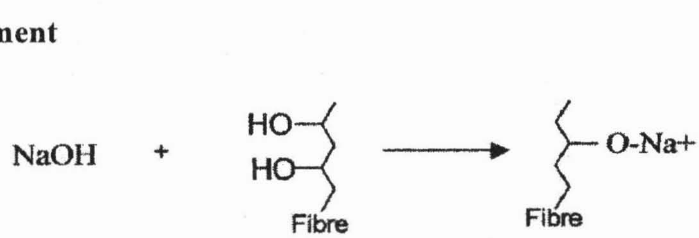

Figure 4.The structure of cellulose after NaOH treatment (Sreekala, 2003).

NaOH treatment tends to remove hydrogen bonding in cellulose structure. Alkali cellulose will be formed when alkali penetrates into cellulose. This penetration may result in removing off hydrogen from the -OH groups of cementing material. Cementing material is a term given to hemicellulose, lignin and other impurities that tied up cellulose fibrils. Figure 4 shows the structure of alkali cellulose after NaOH treatment. The reaction with the –OH groups may cause cellular structure deformation which called as fiber bundle fibrillation. This phenomenon may split up the packed filament and leave a clearer surface on cellulose (Cao, 2006). The treatment may improve particles dispersion and increase the availability of –OH groups on fiber surface. However, this improvement may not increase the bonding between hydrophilic natural fiber and hydrophobic polymer matrix (Beckermann and Pickering, 2008).

The problem of less interfacial bonding between fiber and matrix is called as incompatibility. A coupling agent could be necessary to improve the compatibility and result in better interfacial adhesion as well as its mechanical properties. The coupling agent may create a chemical bridge between fiber and polymer matrix (Bledzki, 1999). For example, the chain of anhydride groups from maleic anhydride polypropylene (MAPP) could interact with –OH groups on fiber surface while the other end of anhydride group may entangle with polypropylene matrix (Xie, 2010). The same thought has been shared by Yang (2006) and Bledzki (2008). This chemical bridge will offer better wettability of both fiber and matrix. Sain *et* al (2005) have emphasized that maleic anhydride will act as binding agent for linear low density polyethylene (LLDPE) and wheat straw. The interaction of cellulose, maleic anhydride and LLDPE is illustrated in Figure 5. Higher NaOH concentration that is applied in treatment may require more coupling agent to saturate the –OH groups available resulted in the treatment (Beckermann and Pickering, 2008).

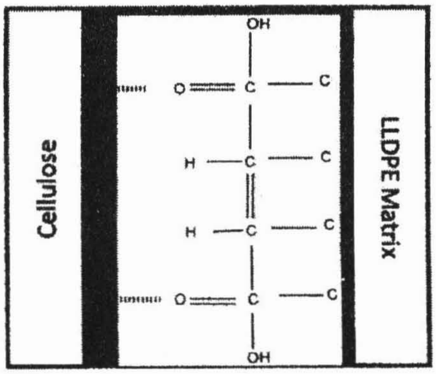

Figure 5. A schematic diagram of the interaction between: cellulose, maleic anhydride, and LDPE matrix (Sain et. Al., 2005)

Effect of Wood Species

Lignocellulosic resources comprise primarily of cellulose, hemicelluloses, lignin and other non-cellulosic materials such as ash and extractive content (Abdul Khalil, 2006). Chemical composition of different lignocellulosic fiber is displayed in Table 1. The plant nature, origin, age and extraction method may influence the properties of cellulosic fibers. Generally, the amounts of holocellulose and lignin are similar to those found in wood and non-wood plants. This statement is also supported by Khiari (2010). These important fractions allow better understandings on similarities between hardwood, softwood and non-wood plant. Concerning now that the chemical composition of those three plants is similar, their properties might be similar as well. Thus, alkalization treatment with NaOH solution on fiber surfaces may be in the range of similar result.

Raw material	Ash content, %	Lignin content, %	Holocellulose, %	Solubility,%			
				Alcohol benzene	1% NaOH	Hot water	Cold water
Oil palm frond [a]	3.41	23.86	75.65	5.68	33.52	12.50	10.23
Kenaf [b]	4.00	21.2	87.70	6.40	n.a	n.a	n.a
Coconut [c]	2.20	32.80	56.30	6.40	n.a	n.a	n.a
Bamboo [d]	1.05-1.39	23.80-26.05	65.61-69.39	2.49-3.60	11.23-25.52	1.11-8.02	2.40-10.19
Hardwood [e]	<1	14-34	71-89	0.1-7.7	n.a	n.a	n.a
Softwood [f]	n.a	26-28	67-69	1-2.6	7.9-10.3	2	n.a

Table 1: Chemical composition of some lignocellulosic plants species

[a] Farhana and Farahin (2011) [b] Abdul Khalil et al (2010) [c] Hashim et al (2011) [d] Jamaludin (2006) [e] Abdul Khalil et al (2006)

[f] Jimenez et al (2008)

Conclusion

Alkali treatment change the fiber morphology by removing cementing material lead to rougher surface and increase the interfacial site for chemical bonding between fiber and matrix. The reaction of treatment is superior at high temperature and high concentration of NaOH solution. But, the concentration and temperature of treatment solution are limited to some condition because extreme treatment might lead to fiber damage. Effective NaOH concentration that can be used to treat natural fiber surface is in the range of 2% - 8% and the optimum result may started at 4% and above. Elevated temperatures at 90±2°c could be an effective temperature in conducting the treatment.

References

Abdul Khalil, H. P. S., Siti Alwani, M., Mohd Omar, A. K., 2006. Chemical composition, anatomy, lignin distribution, and cell wall structure of Malaysian plant waste fibers. "Cell walls of tropical fibers," BioResources 1(2), 220-232

Abdul Khalil, H. P. S., Ireana Yusra, A. F., Bhat, A. H., Jawaid, M., 2010. Cell wall ultrastructure, anatomy, lignin distribution, and chemical composition of Malaysian cultivated kenaf fiber. Industrial Crops and Products 31 (2010) 113-121

Bachtiar, D., Sapuan, M.S., & Hamdan M.M. (2008). The effect of alkaline treatment on tensile properties of sugar palm fiber reinforced epoxy composites. Materials and Design 29 (2008) 1285 – 1290

Beckermann, G.W., & Pickering, K.L. (2008). Engineering and evaluation of hemp fibre reinforced polypropylene composites: fibre treatment and matrix modification. Composites: Part A 39 (2008) 979-988

Bledzki, A.K., & Gassan, J. (1999). Composites reinforced with cellulose based fibres. Prog. Polym. Sci. 24 (1999) 221-274

Bledzki, A.K., Letman, M., Viksne, A., & Rence, L. (2005). A comparison of compounding processes and wood type for wood fibre-pp composites. Composites: Part A 36 (2005) 789-797

Brigida, A.I.S., Calado, V.M.A., Goncalves, L.R.B., & Coelho, M.A.Z. (2010). Effect of chemical treatments on properties of green coconut fiber. Carbohydrate Polymers 79 (2010) 832 -838

Cao, Y., Shibata, S., & Fukumoto, I. (2006). Mechanical properties of biodegradable composites reinforced with bagasse fibre before and after alkali treatments. Composites: Part A 37 (2006) 423-429

Edeerozey, A.M.M., Akil, H.M., Azhar, A.B., & Zainal Ariffin, M.I. (2007) Chemical modification of kenaf fibers. Materials Letters 61 (2007) 2023-2025

Farhana Jasmi, Farahin Yusof, Jamaludin Kasim. (2011). Chemical composition of oil palm frond: Proceedings of Seminar on Wood Science and Furniture Technology: *Sustaining Raw Material Supply for the Future* ISBN 978-983-2607-26-7 held on 11-12th May 2011 at the Universiti Teknologi Mara Cawangan Pahang (pp. 32-37).

Gu, H. (2009). Tensile behaviours of the coir fiber and related composites after NaOH treatment. Materials and design 30 (2009) 3931 – 3934

Gwon, J.G., Lee, S.Y., Chun, S.J., Doh, G.H., & Kim, J.H. (2010). Effects of chemical treatments of hybrid fillers on the physical and thermal properties of wood plastic composites. Composites: Part A 41 (2010) 1491-1497

Hashim, R. et. al., 2011. Characterization of raw materials and manufactured binderless particleboard from oil palm biomass. Materials and Design 32 (2011) 246-254

Ichazo, M.N., Albano, C., Gonzalez, J., Perera, R.,& Candal, M.V. (2001) Polypropylene/wood flour composites: treatments and properties. Composites Structure 54 (2001) 207-214

Jamaludin Kasim, 2006. Properties of particleboard and thermoplasticboard from Buloh Semantan (*Gigantochloa Scortechinii*). University Publication Centre (UPENA), UiTM

Jimenez, L., Rodriguez, A., Perez, A., Moral, A., & Serrano, L. (2008). Alternative raw materials and pulping process using clean technologies. Industrial Crops and Products 28 (2008) 11-16

Khiari, R., Mhenni, M.F., Belgacem, M.N., & Mauret, E. (2010). Chemical composition and pulping of date palm rachis and *posidonia oceanic* – A comparison with other wood and non-wood fibre sources. BioResource Technology 101 (2010) 775-780

Mansour Rokbi, Osmani, H., Imad, A., & Benseddiq, N. (2011). Effect of chemical treatment on flexural properties of natural fiber-reinforced polyester composite. Procedia Engineering 10 (2011) 2092-2097

Migneault, S., Koubaa, A., Erchiqui, F., Chaala, A., Englund, & K., Wolcott, M.P. (2009) Effects of processing method and fiber size on the structure and properties of wood-plastic composites. Composites: Part A 40 (2009) 80-85

Nadzi, B. S., Nyahumwa, C., & Tesha, J., (2007). Chemical treatment stability of rice husks against alkali treatment. BioResource 3(4), 1267-1277

Rahman, M.R., Huque, M.M., Islam, M.N., & Hasan, M. (2009) Mechanical properties of polypropylene composites reinforced with chemically treated abaca. Composites: Part A 40 (2009) 511-517

Rosa, F.M., Chiou, B., Medeiros, E.S., Wood, D.F., Williams, T.G., Mattoso, L.H., *et al.* (2009). Effect of fiber treatments on tensile and thermal properties of starch/ethylene vinyl alcohol copolymers/coir biocomposites. Bioresource Technology 100 (2009) 5196-5202

Rozman, H.D., Tan, K.W., Kumar, R.N., Abubakar, A., Mohd. Ishak, Z.A., & Ismail, H. (2000). The effect of lignin as a compatibilizer on the physical properties of coconut fiber-polypropylene composites. European Polymer Journal 36 (2000) 1483-1494

Saha, P., Manna, S., Chowdhury, S.R., Sen, R., Roy, D., & Adhikari, B. (2010). Enhancement of tensile strength of lignocellulosic jute fibers by alkali steam treatment. Bioresource Technology 101 (2010) 3182 – 3187

Sain, M., Suhara, P., Law, S., & Bouilloux, A. (2005). Interface modification and mechanical properties of natural fiber-polyolefin composite products. Journal of Reinforced Plastic and Composites January 2005 vol. 24 no. 2 121-130

Sawpan, M.A., Pickering, K.L., & Fernyhough, A. (2011). Effect of various chemical treatments on the fibre structure and tensile properties of industrial hemp fibres. Composites: Part A 42 (2011) 888-895

Shinoj, S., Visvanathan, R., Panigrahi, S., & Kochubabu, M. (2011). Oil plam fiber (opf) and its composites: A review. Industrial Crops and Products 33 (2011) 7-22

Sinha, E., & Rout, K. (2007). Influence of fiber surface treatment on structural, thermal and mechanical properties of jute fiber and its composite. Indian Academy of Sciences 32 (2009) 65-76

Sreekala, M.S., Thomas, S. (2003). Effect of fibre surface modification on water-sorption characteristics of oil palm fibres. Composites Science and Technology 63 (2003) 861-869

Troedec, M.L., Rachini, A., Peyratout, C., Rossignol, S., Max, E., Kaftan, O., et al. (2011). Influence of chemical treatments on adhesion properties of hemp fibers. Journal of Colloid and Interface Science 356 (2011) 303 – 310

Xie, Y., Hill, C.A.S., Xiao, Z., Militz, H., & Mai, C. (2010) Silane coupling agents used for natural fiber/polymer composites : A Review. Composites: Part A 41 (2010) 806-819

Yang, H.S., Kim, H.J., Park, H.J., Lee, B.J., & Hwang, T.S. (2006). Water absorption behavior and mechanical properties of lignocellulosic filler-polyolefin bio-composites. Composite Structure 72 (2006) 429-437