INFLUENCE OF SURFACE LIGNIN CONCENTRATION ON FIBRE SURFACE CHARACTERISTICS AND TENSILE PROPERTIES OF OIL PALM FIBRE/UREA-FORMALDEHYDE RESIN COMPOSITE

G. N. Onyeagoro
Polymer & Textile Engineering Department,
Federal University of Technology,
NIGERIA.
nkemgoddi@yahoo.com

ABSTRACT

Surface lignin plays an essential role in the surface characteristics of fibre and the interfacial behaviour of composites prepared with cellulosic fibres. The influence of surface lignin concentration on fibre surface characteristics and tensile properties of oil palm fibre/urea-formaldehyde resin composite was studied by Scanning Electron Microscope (SEM), tensile testing, and internal bonding strength measurements. Fibre surface lignin was removed by chlorine dioxide ($Cl0_2$) treatment. The results show that surface lignin concentration was 49.5% for the untreated fibre, and then decreased dramatically to 14.1% for the fibre treated with 1.0% $Cl0_2$. Thereafter, it decreased slowly to 9.6% and 7.6% for the fibres treated with 1.5% and 2.0% $Cl0_2$, respectively. While fibre/resin interaction was found to be poor for composites prepared with treated fibres, it decreased progressively with composites made with treated fibres due to reduction in surface lignin as revealed by the tensile properties and internal bonding strength of the composites. The SEM micrographs of the fibres reveal an increase in the surface roughness and specific surface area of fibres with reduction in surface lignin, which is believed to have promoted better fibre/resin interaction. These results indicate that the surface properties of single oil palm fibres can be tailored to improve the fibre/resin interface by chlorine dioxide treatment.

Keywords: Lignin, tensile properties, composite, oil palm fibre, urea-formaldehyde resin, surface characteristics.

INTRODUCTION

Over the years, plant fibres were gradually substituted by newly developed synthetic fibres as reinforcement in composites manufacture because of their higher strength and better performance characteristics. However, with the gradual depletion of petroleum resources in the last decade worldwide, fibres derived from plants have engaged renewed interest and attention of researchers with the possibility of replacing synthetic fibres based on petrochemical sources because of their advantages of renewability, biodegradability, abundance, low cost, and reduced health hazard. Despite their low strength, plant fibres can lead to composites with high specific properties because of their low densities. Plant fibres are comprised of three major chemical components, namely cellulose, lignin, and hemicelluloses. The cellulose forms a skeletal frame that is surrounded and encrusted by the matrix substances (lignin and hemicelluloses) (Reddy and Yang, 2005). Cellulose chains composed of glucose units are organised into the elementary fibrils, which are arranged into micro fibrils with a diameter of 10-50nm in the presence of lignin and hemicelluloses (Paavilainen, 2001). The micro fibrils are subsequently aggregated into larger units called individual plant fibres with a diameter of 10-30μm and further into fibre bundles with a diameter larger than 100μm (Oksman et al, 2009; Mathew et al, 2005). In a study by Le Guen and Newman, 2007, the elastic modulus of natural fibres bundles was reported to be 10GPa while an elastic modulus of up to 40GPa was reported for single cellulosic fibres separated from fibre bundles. On the other hand, micro fibrils separated by hydrolysis followed by mechanical disintegration gave an elastic modulus of 70GPa (Michel, 1989). Van de Oever et al, 1999 have reported that the lateral strength of single flax fibre was higher than that of flax bundle, and the axial tensile strength of single flax fibre approached the strength of glass fibre. Unfortunately, cellulose material is mainly used in the form of fibre bundles in natural fibre-reinforced

composites due to their good dispersibility and also due to the fact that complicated processes are not required (Hepworth et al, 2000). On the other hand, some researchers have investigated the properties of composites reinforced with single plant fibres including wood pulp fibres (Gindl and Jeronimidis, 2004; Awal et al, 2009), thermo mechanical pulp fibre (Rials et al, 2001), and recycled fibre (Rials et al, 2001; Huda et al, 2006). These investigators reported better mechanical properties and fewer flaws and/or weak links (e.g due to lignin or hemicelluloses between fibres) (Andersons et al, 2005; Bullions et al, 2006; Lundquist et al, 2003). Higher aspect ratios and proportion of cell wall contribute to the fibre/matrix interface (Oksman et al, 2009; Sbiai et al, 2008; Stuart et al, 2006; Le Guen and Newman. 2007). These results indicate that single plant fibres exhibit characteristics of a better alternative to conventional fibre bundles, and the surface properties of single plant fibres can be better engineered and will play a more significant role in the interface of composites, mainly due to the much larger specific surface area (Mathew et al, 2005 ; Keener et al, 2004). There are reported studies available in literature on the surface characteristics of single plant fibres from different pulping processes, chemical treatments, or biological treatments (Simola et al, 2000 ; Maximova et al, 2001 ; Koljonen et al, 2003 ; Kangas and Kleen, 2004 ; Risen et al, 2004 ; Koljonen et al, 2004). Report of these investigators show that these treatments greatly affect the surface lignin of fibres and the final application of fibres. However, there is little information available in literature about the influence of surface characteristics of single plant fibre on the interfacial behaviour of composites. In the present study, the surface characteristics of individual oil palm fibres and their influence on the interfacial behaviour of oil palm fibre/urea-formaldehyde resin composites were investigated mainly by characterizing the surface lignin of the single oil palm fibre. Lignin modification by chlorine dioxide treatment was employed to enhance the interfacial adhesion between fibre bundle and urea-formaldehyde resin, while preserving the cellulosic part (Trindale et al, 2004; Hoareau et al, 2004 ; Hoareau et al, 2006 ; Megiatto et al, 2007). The selective oxidation of lignin induced by chlorine dioxide had been found to cause serious degradation of lignin units (Megiatto et al, 2007). This degradation is extremely important for the chlorine dioxide bleaching of pulp fibre in the paper-making industry, of which the main object is to remove as much lignin as practical (Brogdon et al, 2005 ; Svenson et al, 2005,2006). In this work, chlorine dioxide was used to selectively remove lignin from the fibre surface. The surface characteristics of single oil palm fibres and the interfacial behaviour of oil palm fibre/urea-formaldehyde resin composites were investigated by scanning electron microscope (SEM).

MATERIALS AND METHOD

Materials

Oil palm trunk fibre (OPTF) bundles were obtained from Flo Timbre Processing Co Ltd, Sapele, Nigeria, while urea-formaldehyde resin (free formaldehyde $\leq$ 1.5%, gel time 80-90sec at 140^0c) was obtained from a local market in Aba, Nigeria.

Preparation of Oil Palm Single Fibre

Conventional soda pulping process (NaOH and anthraquinone) was used to break the bonds of lignin to separate oil palm trunk fibre bundles into single fibre (Khristova et al, 2002; Rosli et al, 2003). 150g of fibre bundle were pulped with a liquor-t-fibre ratio of 4:1 by weight of a NaOH (BDH) charge of 20% and an anthraquinone charge of 0.1% of the oven dried weight of fibres. The temperature was raised from ambient to 150^0c over 40min and held for a cooking time of 180min in a reactor. The pulp fibre was washed with distilled water until the P^H of the filtrate was approximately 7.0, and then kept wet in polyethylene bags until required.

Chlorine Dioxide Treatment of Fibre

Delignification of fibres was done with chlorine dioxide/water solutions (0%, 0.5%, 1.0%, 1.5%, and 2.0% of the oven-dried weight of fibres) at 75^0c for 80min. The P^H was adjusted to 4 with sulphuric acid. Thereafter, the fibre was washed with distilled water until the P^H of the filtrate was approximately 7.0, and then kept wet in polyethylene bags until required. Lignin content of the fibre was measured with the kappa number method according to the TAPPI standard (T236). The kappa

number is defined as the amount (millilitres) of a 0.1N $KMnO_4$ solution consumed by 1g of moisture-free pulp under standard conditions (Paavilainen, 2001).

Fibre Surface Analysis by SEM

Scanning electron microscopy images of the fibre surface were obtained using an AMRAY 180D (diffusion pump system) operated at 15KV and 200 magnifications.

Preparation of Composites

Oil palm fibres were dispersed in water and stirred for 10min. The water suspension was vacuum filtered using a 200-mesh screen filter to form a fibre mat of 1mm thickness, the fibre mat was oven dried at 80^0c for 10min, cooled at room temperature in a desiccator, and then immersed for 15min in urea-formaldehyde resin (diluted in ethanol and in the presence of 2% hexamethylenetetramine (HMTA)). The dosage of UF resin was kept constant at 40% in all composites. The resin-impregnated mat was taken out and dried at 80^0c to remove ethanol, and the fibre mat was then pressed at 170^0c for 5min at 5MPa pressure. Finally, the fibre mats were dried at 170^0c for 1 hour to obtain the composites.

Mechanical Properties of Composites

Tensile stress-strain measurements were carried out using an Instron Universal Testing Machine according to ASTM D638. The internal bonding strength was measured in an internal bonding testing machine (TMI 80-01-01-0002) according to the Scott bond strength method. The principle behind the method is to measure the strength needed to tear the metal blocks apart (z-directional tensile strength) and tear the metal gauge off the composite sample by de-laminating the composite.

RESULTS AND DISCUSSION

Lignin Content of Fibre

The lignin content of fibre was measured with the kappa number method. The number of fibre which is a measure of the lignin content of the fibre is defined as the amount (millilitre) of a $0.1KMnO_4$ solution consumed by 1g of moisture-free pulp under standard conditions (Paavilainen, 2001). Table 1 shows the kappa numbers of the fibres with and without chlorine dioxide treatment. As shown in Table 1, there is a significant decrease in the kappa number from 12.2 for the fibre without treatment to 8.5 for the fibre treated with 0.5% chlorine dioxide, and then it decreased slowly to 7.3, 6.6, and 6.1 for the fibres treated with 1.0%, 1.5%, and 2.0% chlorine dioxide, respectively.

Table 1: The kappa numbers of fibres

Amount of ClO_2 (%)[1]	0	0.5	1.0	1.5	2.0
Kappa number	12.2	8.5	7.3	6.6	6.1

[1]The amount of ClO_2 based on oven dried fibres

SEM Analysis of Fibre Surface

Soda pulping is a process by which fibre bundles are separated into single fibres by primarily dissolving and removing lignin and hemicelluloses contents of fibres in alkaline solutions at high temperature and pressure. SEM micrographs of the untreated and treated single fibres are presented in Fig. 1. As shown in Fig. 1a, the single fibre was observed to be irregular, exhibiting a non-homogeneous surface that was covered by a thin layer of non-cellulose material, exposing a wrinkled surface. Since the fibre cell wall consists of microfibril aggregates embedded in a matrix of lignin and hemicelluloses, the non-cellulose material mainly corresponds to lignin (Lindstrom, 1979; Sundin and Hartlier, 1998).

During pulping processes, the dissolved lignin would precipitate on the fibre surface again at the final stage of pulping, washing and bleaching, thereby forming a lignin-concentrated surface (Maximova et al, 2001; Koljonen et al, 2004). The observed irregular fibre shapes in Fig. 1 are supposed to produce a larger contact area and stronger mechanical interlocking strength between fibre and resin. For the fibre treated with chlorine dioxide, the wrinkled surface was more visible, forming a progressively rougher

surface for the samples treated with 1.5% and 2.0% chlorine dioxide (Fig. 1c and Fig. 1d). These observations indicate that chlorine dioxide treatment can efficiently remove the residual lignin from the fibre surface.
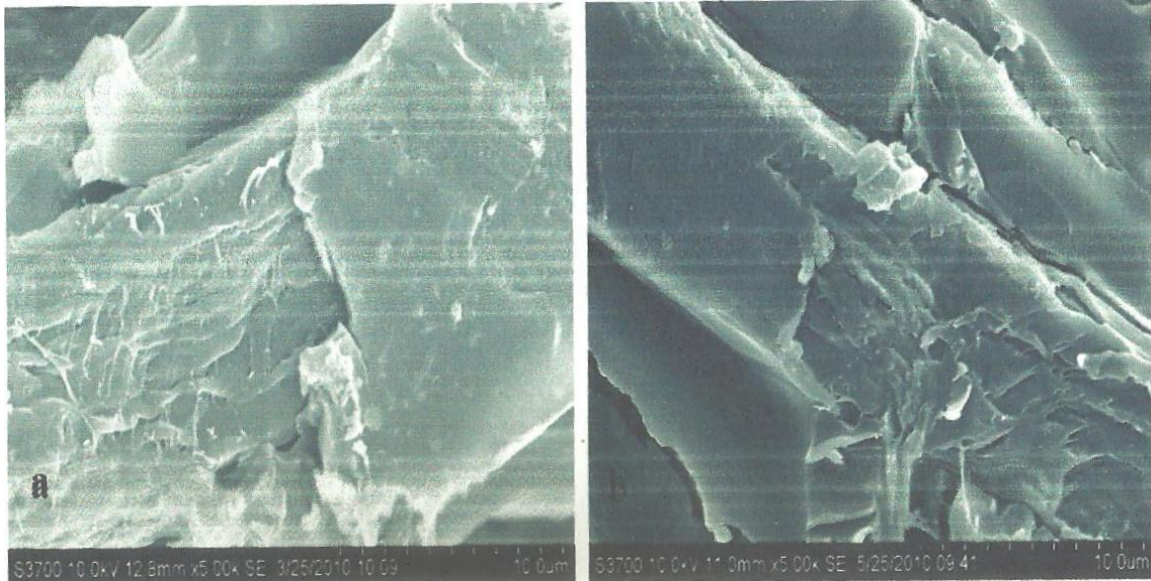

Figure 1: The SEM micrographs of fibres: (a), (b), (c), and (d) represent the fibre samples treated with ClO_2 OF 0%, 1.0%, 1.5%, and 2.0%, respectively

Tensile Properties of Composites

The tensile strengths of the composites are presented in Fig. 2. The tensile stresses at break were $3.8N/mm^2$, $4.6N/mm^2$, $7.6N/mm^2$, and $10.3N/mm^2$ for the composites obtained with untreated fibre, fibres treated with 0.5%, 1.0%, 1.5%, and 2.0% ClO_2, respectively, representing increases by 21%, 26%, 31%, and 36%, indicating significant improvement in the fibre/resin interfacial adhesion.
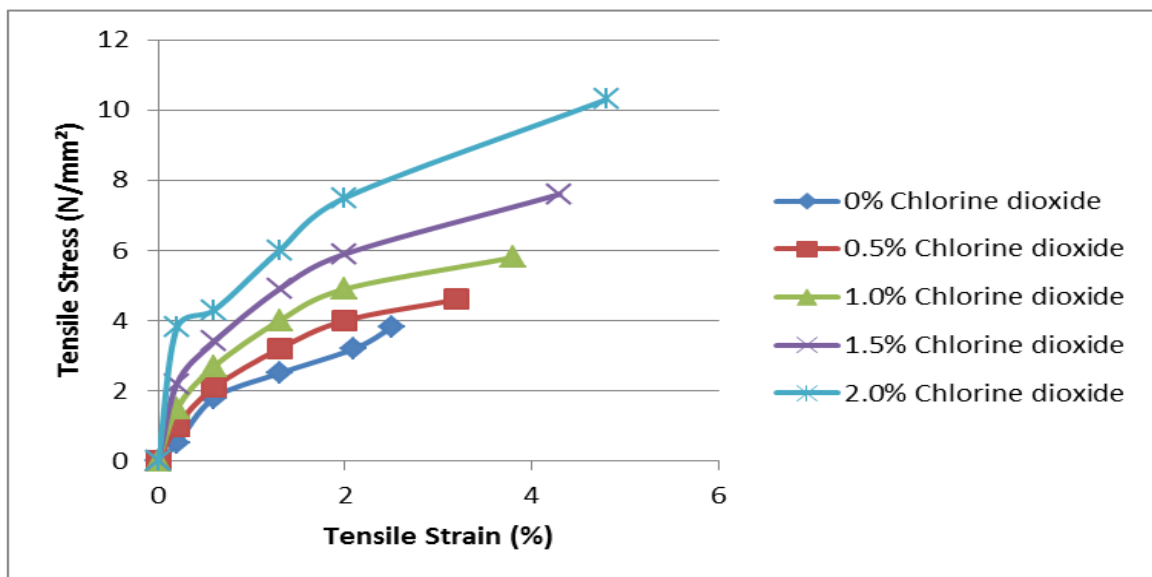

Figure 2: Effect of chlorine dioxide (ClO_2) on the tensile strength of composites

The SEM micrographs presented in Fig. 1 show that the decrease in surface lignin increased the surface roughness and specific surface area, which resulted in larger contact area between fibre and resin, and thus producing a stronger mechanical interlocking strength. This agrees with the earlier report of Le Guen and Newman, 2007 and Bisanda, 2000. In a similar report, Bledzki et al, 2004 pointed out that the rough fibre surface resulting from maceration enhanced the wettability and form fit of the matrix material, thus causing a better fibre/matrix adhesion. Again, the chemical reaction

between plant fibre and UF resin mainly involves the methylol (-CH$_2$OH) groups of resin with cellulosic hydroxyl (-OH) groups (Sreekala et al, 2000). With the removal of lignin from the fibre surface, more hydroxyl groups are exposed because cellulose can provide more hydroxyl groups and thus facilitate the chemical reaction between plant fibre and UF resin, resulting in more efficient stress transfer at the interface. The interface between fibre and resin may involve cellulose micro fibrils, lignin, and UF resin in the presence of surface lignin, contributing to the strength of adhesion at the microfibril/lignin interface, lignin/resin interface, and micro fibril/resin interface. Among these three kinds of interfaces, the micro fibril/surface lignin interface is supposed to be the weakest interface because most of the surface lignin result from the dissolved lignin precipitating on fibre surfaces rather than the original lignin embedded into micro fibrils skeleton (Maximova et al, 2001; Koljonen et al, 2004) forming a relatively weak interfacial adhesion between surface lignin and surface micro fibril of cell wall. This interface may be the source of cracks that lead to composites fracturing when load transfers through the interface. With the removal of more surface lignin, the weak interface between surface lignin and micro fibril becomes less, and larger amounts of UF resin can make direct contact with micro fibrils, resulting in a stronger interface with fewer cracks. The untreated fibre surface as shown in Fig. 1a was relatively smooth and covered by blurry micro fibrils. However, the fracture surface of the fibre (Fig. 3) reveals a clearer wrinkled area after fracturing, which is an indication of a weak fibre/resin interface due to the interference of surface lignin on the fibre/resin interaction. This can provoke cracks development and inefficient load transfer, resulting in the disconnection of the resin from the fibre surface. Fig. 3, however, shows a significant difference in the fracture surface of the treated fibre when compared with the untreated fibre. The wrinkled fibre surface (Fig. 1c), became blurry due to the presence of resin, which indicates stronger interfacial strength between the resin and the outer cell wall of the fibre. In this case, the removal of surface lignin gave rise to stronger physical and chemical interaction between plant fibre and UF resin, as well as stronger adhesion at the interface, resulting in stronger interfacial and tensile strengths.
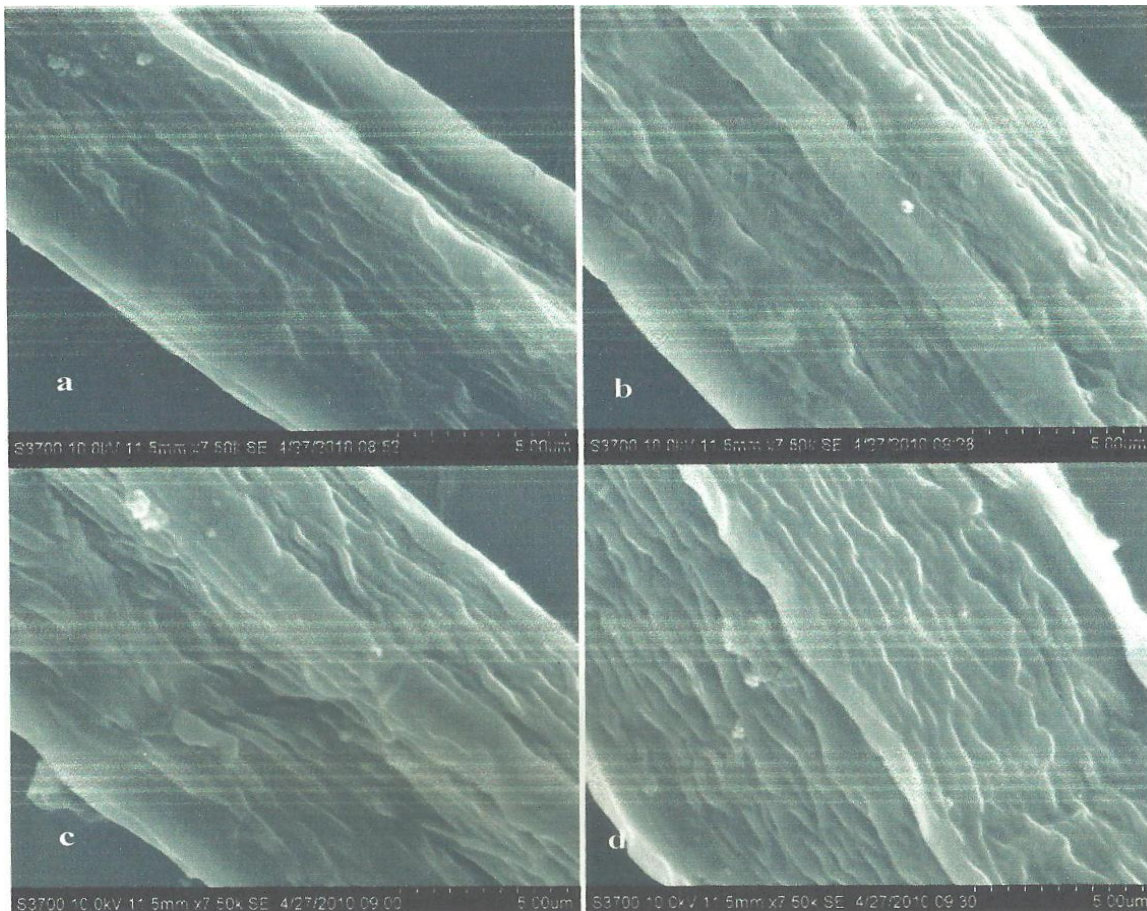

Figure 3: The SEM morphologies of fibres: (a), (b), (c), and (d) represent the samples treated with chlorine dioxide of 0%, 1.0%, 1.5%, and2.0%, respectively

Internal Bonding Strength of Composites

The results of the effect of chlorine dioxide treatment of fibre on the internal bonding strength of the composites are presented in Fig. 4. The internal bonding strength can be defined as the strength in the z-direction, such as at a 90^0 angle to the plane of the fibre mat composites, and is largely dependent on interfacial strength rather than on mechanical properties of fibre. The results show that the internal bonding strength also benefited from chlorine dioxide treatment of fibre. The internal bonding strengths obtained were $225J/m^2$, $255J/m^2$, $275J/m^2$, $285J/m^2$, and $292J/m^2$ for composites obtained with untreated fibre, fibre treated with 0.5%, 1.0%, 1.5%, and 2.0% chlorine dioxide, respectively, representing increases by 13.3%, 22.2%, 26.7%, and 29.8%, indicating significant improvement in the interfacial adhesion between fibre and resin.
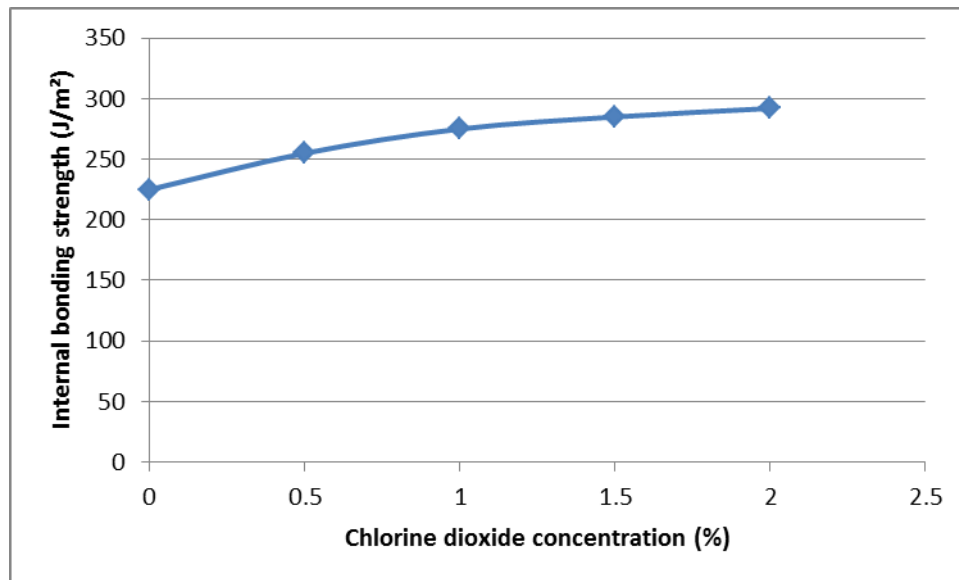

Figure 4: Effect of Chlorine dioxide treatment on the bonding strength of composites

CONCLUSION

Surface lignin is a key player in the surface characteristics of fibre and the interfacial behaviour of composites prepared with cellulosic fibres. Oil palm fibre surface is covered with large amounts of lignin, and relatively few cellulose micro fibrils are exposed. These conditions do not favour effective bonding at the fibre/resin interface.

Significant removal of lignin from the fibre surface can be achieved by chlorine dioxide treatment, thus promoting effective bonding at the fibre/resin interface by increasing the interlocking strength, chemical bonding strength between fibre and resin, and eliminating weak interface.

Surface properties of single oil palm fibres can be tailored to improve the fibre/resin interface. Chlorine dioxide treatment has potential for surface modification oil palm fibre in engineering the interfacial behaviour of composites.

REFERENCES

Anderson, J; Sparnins, E; Joffe, R; and Wallstrom, L. (2005). "Strength distribution of elementary flax fibres." *Compos. Sci. Technol,* 65(3-4), 693-702.

Awal, A; Ghosh, S.B; and Sain, M. (2009). "Development and morphological characterization of wood pulp reinforced biocomposite fibre." *J. Mater. Sci.* 44(11), 2876-2881.

Bisanda, E.T.N. (2000). "The effect of alkali treatment on the adhesion characteristics of sisal fibres." *Appl. Compos. Mater*, 7(5-6), 331-339.

Bledzki, A.K; Fink, H.P; and Specht, K. (2004). "Unidirectional hemp and flax EP- and PP-composites: Influence of defined fibre treatments." *J. Appl. Polym. Sci*. 93(5), 2150-2156.

Brogdon, B.N; Mancosky, D.G ; and Lucia, L.A. (2005). "New insight into lignin modification during chlorine dioxide bleaching sequences(I): Chlorine dioxide delignification." *J. Wood Chem. Technol,* 24(3), 201-219.

Bullions, T.A; Hoffman, D; Gillespie, R.A; Price-O' Brien, J; and Loos, A.C. (2006). "Contributions of feather fibres and various cellulose fibre to the Mechanical properties of polypropylene matrix composites." *Compos. Sci. Technol*, 66(1), 102-114.

Gindl, W; and Jeronimidis, G. (2004). "Wood pulp fibre reinforced melamine-formaldehyde composites," *J. Mater. Sci,* 39(9), 3245-3247.

Hepworth, D.G; Hobson, R.N; Bruce, D.M; and Farrent, J.W. (2000). "The use of unretted hemp fibre in composite manufacture." *Compos. Part A-Appl. S*, 31(11), 1279-1283.

Hoareau, W; Trindale, T.G; Siegnund, B; Castella, A ; and Frollini, E. (2004). "Sugarcane bagasse and curaua lignins oxidized by chlorine dioxide and reacted with furfuryl alcohol: Characterization and Stability," *Polym. Degrad. Stab,* 86(3), 567-576.

Hoareau, W; Oliveira, F.B; Grelier, S; Siegmund, B; Frollini, E; and Castellan, A. (2006). "Fibreboards based on sugarcane bagasse lignin and fibres." *Macromol. Mater. Eng,* 291(7), 829-839.

Huda, M.S; Drzal, L.T; Mohanty, A.K; and Misra, M. (2006). "Chopped glass and recycled newspaper as reinforcement fibres in injection-moulded poly (lactic acid) (PLA) composites: A comparative study." *Compos. Sci Technol,* 6(11-12), 1813-1824.

Kangas, H; and Kleen, M. (2004). "Surface chemical and morphological properties of mechanical pulp fines." *Nord. Pulp Paper Res. J,* 19(2), 191-199.

Keener, T.J; Stuart, R.K; and Brown, T.K (2004). "Maleated coupling agents for natural fibre composites." *Compos. Part A-Appl.S,* 35(3), 357-362.

Khristova, P; Kordsachia, O; Patt, R; Khider, T; and Karrar, I. (2002). "Alkaline pulping with additives of kenaf from Sudan." *Industrial Crops and Products*, 15(3), 229-235.

Koljonen, K; Osterberg, M; Johansson, L.S; and Stenius, P. (2003). "Surface chemistry and morphology of different mechanical pulps determined by ESCA and AFM ." *Colloid Surf,* A 228(1-3), 143-158.

Koljonen, K; Osterberg, M; Kleen, M; Fuhrmann, A; and Stenius, P. (2004). "Precipitation of lignin and extractives on kraft pulp: Effect on surface morphology and paper strength." *Cellulose,* 11(2), 209-224.

Le Guen, M.J; and Newman, R.H. (2007). "Pulped phormium tenax leaf fibres as reinforcement for epoxy composites." *Compos. Part A-Appl. S*, 38(10), 2109-2115.

Lindstrom, T. (1979). "The colloidal behaviour of kraft lignin," Colloid. Polym. Sci. 257(3), 277-285.

Lundquist, L; Marque, B; Hagstrand, P.O; Leterrier, Y; and Manson, J.A.E. (2003). "Novel pulp fibre reinforced thermoplastic composites." *Compos. Sci. Technol*, 63(1), 137-152.

Megiattor Jr. J.D; Hoareau, W; Gardrat, C; Frollini, E; and Castellan, A. (2007). "Sisal fibres: Surface chemical modification using reagent obtained from a renewable source; characterization of hemicelluloses and lignin as model study." *J. Agric. Food. Chem*, 55(2), 8576-8584.

Mathew, A.P; Oksman, K; and Sain, M. (2005). Mechanical properties of biodegradable composites from poly (lactic acid) (PLA) and microcrystalline cellulose (MCC)." *Appl. Polym. Sci*, 97(5), 2014-2025.

Maximova, N ; Osterberg, M ; Koljonen, K ; and Stenius, P. (2001). "Lignin adsorption on cellulose fibre surfaces: Effect on surface chemistry, surface morphology and paper strength." *Cellulose*, 8(2), 113-125.

Michel, A.J. (1989). "Wood cellulose-organic polymer composites," Composite Pacific, Adelaide, Australia, Composites Institute of Australia, Asia Netravali AN, 89,19.

Oksman, K; Mathew, A.P; Langstrom, R; Nystrom, B; and Joseph, K. (2009). "The influence of fibre microstructure on fibre breakage and mechanical properties of natural fibre reinforced polypropylene." *Compos. Sci. Technol*, 69(11-12), 1847-1853.

Paavilainen, L. (2001). Fibre structure: *Handbook of physical Testing of Paper*, R.E.Mark, C.C.J.Habeger, J. Borch, (eds.), New York: Marcel Dekker Inc.

Reddy, N; and Yang, Y. (2005), "Bio fibres from agricultural by-products for industrial applications." *Trends Biotechnol*, 23(1), 22-27.

Rials, T.G; Wolcott, M.P; and Nassar, J.M. (2001). "Interfacial contributions in lignocellulosic fibre-reinforced polyurethane composites." *J. Appl. Polym. Sci,* 80(4), 546-555.

Risen, J; Hulten, A.H; and Paulsson, M. (2004). "Surface characteristics of softwood and hardwood kraft pulp fibres from different stages in a bleaching sequence." *J. Wood Chem. Technol*, 24(4), 307-321.

Rosli, W.D.W; Leh, C.P; Zainuddin, Z; and Tanaka, R. (2003). "Optimization of soda pulping variables for preparation of dissolving pulps from oil palm fibre." *Holzforschung,* 57(1), 106-113.

Sbiai, A ; Kaddami, H ; Fleury, E ; and Maazouz, A. (2008). "Effect of the fibre size physicochemical and mechanical properties of composites on the of epoxy and date palm tree fibre," Macrol. Mater. Eng. 293(8), 684-691.

Simola, J; Malkavaara, P; Alen, R; and Peltonena, J. (2000). "Scanning probe microscopy of pine and birch kraft pulp fibres." *Polym*, 41(6), 2121-2126.

Sreekala, M.S; Kumaran, M.G; Joseph, S; Jacob, M; and Thomas, S. (2000). "Oil palm fibre reinforced phenol-formaldehyde composites: Influence of fibre surface modification on the mechanical performance." *Appl. Compos. Mater*, 7(5-6), 295-329.

Stuart, T; Liu, Q; Hughes, M; McCall, R.D; Sharma, S; and Norton, A. (2006). "Structural bio-composites from flax-Part 1: Effect of bio- technical fibre modification on composite properties." *Compos. Part A-Appl. S*, 37(3),393.

Svenson, D.R; Jameel, H; Chang, H; and Kadla, J.F. (2006). "Inorganic reactions in chlorine dioxide bleaching of softwood kraft pulp." *J. WoodChem. Technol*, 26(3), 201-213.

Tridale, W.G; Hoareau, W; Razera, I.A.T; Ruggiero, R; Frollini, E; and Castella, A. (2004). "Phenolic thermoset matrix reinforced with sugarcane bagasse fibres: Attempt to develop a new fibre surface chemical modification involving formation of quinones followed by reaction with furfuryl alcohol." *Macromol. Mater. Eng*, 289(8), 728-736.

Van den Oever, M.I.A; Bos, H.L; and Molenveld, K. (1999). "Flax fibre physical structure and its effect on composite properties: Impact strength and thermomechanical properties." 2nd International Wood and Natural Fibre Composites Sumposium, Angew. Makromol. Chem. 272, 71-76.