THE INTERNATIONAL JOURNAL OF
SCIENCE & TECHNOLEDGE

Synthesis of Trimethylol Urea Composite from Alkali Treated Tea Waste Fiber: Thermal Behaviour

Fidelis Timothy Tizhe
Student, Department of Chemistry, Modibbo Adama University of Technology, Yola, Adamawa State, Nigeria
Louis Hitler Muzong
Student, Department of Chemistry, Modibbo Adama University of Technology, Yola, Adamawa State, Nigeria
Barminas Jeffery Tsware
Professor, Department of Chemistry, Modibbo Adama University of Technology, Yola, Adamawa State, Nigeria
Bisong Asu Emmanuel
Student, Department of Pure and Applied Chemistry, University of Calabar, Calabar, Cross River State, Nigeria
Bassey E. Ansa
Assistant Lecturer, Department of Pure and Applied Chemistry, University of Calabar, Calabar, Cross River State, Nigeria
Akakuru Ozioma Udochukwu
Assistant Lecturer, Department of Pure and Applied Chemistry, University of Calabar, Calabar, Cross River State, Nigeria
Philip Monday
Student, Department of Chemistry, Modibbo Adama University of Technology, Yola, Adamawa State, Nigeria

Abstract:
Composite of tea waste fiber from untreated and treated tea waste (UTWF and TTWF) using different fiber weights (2g, 3g, and 4g) with trimethylol urea (TMU) were prepared and the weight loss was studied. Result indicated that, for UTWF composite 2g show maximum weight loss by 43% at 60oC for 90min and 4g UTWF show maximum weight loss by 29% at 60oC for 90min compared to 3g UTWF that show it maximum weight loss by 39% at 60oC for 90min. While TTWF composite, 4g show maximum weight loss by 31% at 40 oC for 90min and 3g TTWF show maximum weight loss by 8% at 40 oC for 90min compared to 2g that show it maximum weight loss by 19% at 40oC. For (TMU), show weight loss by 27% at 70 oC for 90min. This study gives us the idea of disintegration of material from natural fiber reinforced trimethylol urea composite when subjected to temperature above 30 oC. Ash and moisture content of the untreated and treated tea waste fiber (UTWF and TTWF) was determined as well. The ash content of UTWF was higher than that of TTWF. While the moisture content of the UTWF was also higher than that of TTWF.

Keywords: *Tea waste, trimethylol urea, composite, weight loss*

1. Introduction

Tea is one of the major drinks in the world. Consumption of ready-made tea, which packed into cans and bottles, has been increasing remarkably in recent years. Beverage companies manufacturing various tea drinks produce various tons of tea leaf waste annually. On world scale, Nigeria is a medium producer of tea crop, being flavored by the humid condition in the southern Nigeria. They produce large quantities of chaff, which are burnt. Some literature have shown that, these tea waste may be considered as a valuable protein source consisting of 22~35% of crude protein (CP) [8]. While tea waste contains high CP, it is known to contain a high proportion of tannins (Kondo *et al.*, 2004). The by-product from tea leaf (TL), otherwise known as spent tea leaf (STL) may be used as an alternative feed resources for ruminant animals. The by-product may be utilized by ruminants, which are capable of converting fibrous feed into human edible food as milk and meat. Although, the gas production from the *in vitro* fermentation is a nutritional waste, it remains one of the reliable means to measure quality of feeds (Fievez *et al.*, 2005).Apart from losing the economic value of the waste through burning, a huge amount of capital is expended in disposing it. In some places, the waste constitutes environmental hazards through indiscriminate dumping and incineration and some youths within the domain of the company used it as intoxicant (smoking as cigarette). Having considered the above negative impact of the waste, not only on the environment, but also on human, this waste tea was converted into a valuable industrial. The objective of this research was to evaluate how this tea waste was transformed in a natural fiber composite followed by weight loss and water uptake determination of the composite. Natural fiber composites are emerging as realistic alternatives to glass and carbon-reinforced composites in many applications. Shortcomings associated with natural fibres have to be overcome before using them in polymer composites. The most serious concern with natural fibres is their hydrophilic nature due to the presence of pendant hydroxyl and polar groups in various constituents, which can lead to poor adhesion between fibres and hydrophobic matrix polymers (Rong *et al.*, 2001, Bledzki & Gassan *et al.*, 1996). The hydrophilic nature of the fibre surface lead also to high moisture up take for the natural fibres which can seriously lower the mechanical properties of the fibres themselves.Lack of good interfacial adhesion, low degradation temperature, and poor resistance towards moisture make the use of natural fibre reinforced composites less attractive than

Synthetic fibre (glass, carbon, aramid, etc.) that have been up to now the only choice forreinforcing polymeric composites, due to their superior mechanical properties. However,the production of composites reinforced with synthetic fibres and matrices requires a large amount of energy which is only partially recovered with incineration of fibre reinforced composites. This has once again drawn the attention towards natural fibres due to their environmental advantages. It has been demonstrated that the energy needed for productionof natural fibres is, on average, more than half of the amount needed for synthetic fibres Thus, the renewed interest in the natural fibers, due to their lightweight, nonabrasive, non-irritating,combustible,nontoxic,biodegradable properties (Saheb & Jog,1999), low energy consumption for production, budget zero CO_2 emissions if burned, low cost, main availability and renewability compared to synthetic fibres, has resultedin a large number of applications to bring it at par and even superior to synthetic fibers.Because of such properties natural fibers are fast emerging as a viable choice as reinforcingmaterial in composites (kalia et al., 2009).Even if natural fibre has very low energy consumption for production compared to othersynthetic fibre, such as glass or carbon, careful environmental impact evaluation must be taken in consideration in order to make the right choice. In fact, the validity of “green” casefor substitution of synthetic fibre by natural ones is dependent on the type of reinforcementand related production processes.

2. Experimental

2.1. Materials

Urea, formaldehyde, sodium dihydrogen phosphate, sulphuric acid and sodium hydroxide pellets were reagent grade products from the British Drug House (BDH). The waste tea fiber also known as spent tea leaf (STL) was collected from a tea making company, located in Taraba State of Nigeria. All materials were used as received.

2.2. Treatment of Tea Waste Fiber

The fiber was treated with alkaline solution and this treatment is also known as mercerization, NaOH concentration of 3% was used as it has been reported improve the tensile strength and the flexural strength of the fibres (Rout J *et al.*, 2001). The waste tea fibre was soaked in 3% of NaOH for 24 hours at room temperature as shown on the reaction. After that, the waste tea fibre were rinsed and dried under the sun. Therefore fibres were randomly spread within the matrix.

$\text{FIBER-OH} + \text{NaOH} \rightarrow \text{FIBER-O-Na}^+ + H_2O$.

2.3. Proximate Analysis of Both the UTWF and TTWF

2.3.1. Determination of Ash Content

The method reported by National agency for food and drug administration and control (NAFDAC) for the analysis of food samples was adopted for the determination of the ash content. In brief, a dry crucible dish (w_1), was weighed and 1g of the waste tea fiber was spread into the dish and weighed (w_2). Then it was transfered into a muffle furnace at 1000°C until fully ash (colour changes to gray) was obtained and weighed (w_3). Triplicate determinations were made for each sample (UTWF and TTWF) and the average value recorded.

$$\% \text{ Ash} = \frac{(W3\text{-}W1)}{(W2\text{-}W1)} \times 100$$

2.3.2. Determination of Moisture Content

The method reported by National agency for food and drug administration and control (NAFDAC) for the analysis of food samples was adopted for the determination of the moistures content. In brief, a dry crucible dish (w_1), was weighed and 1g of the waste tea fiber was spread into the dish and weighed (w_2). Then the dish and its content was transfered into an oven at 105°C to dry for 3 hours. The dish was removed and weighed (w_3). Triplicate samples (UTWF and TTWF) were used and average value taken.

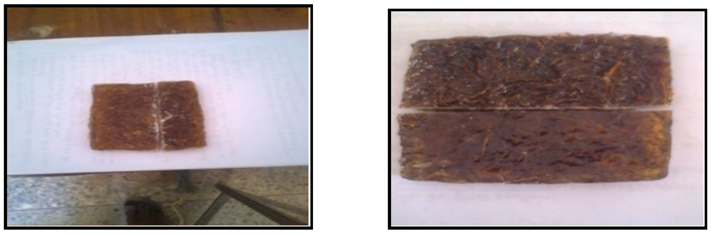
$$\% \text{ Moisture} = \frac{(W2\text{-}W3)}{(W2\text{-}W1)} \times 100$$

2.4. Synthesis of Trimethylol urea

Trimethylol urea was prepared by the method described by Barminas and Osemeahon, (2006). One mole (6.0 g) of urea was reacted with three moles (24.3 ml) of 37% (w/v) formaldehyde using 0.2 g of sodium dihydrogen phosphate as catalyst. The pH of the solution was adjusted to 6 by using 0.5 M H_2SO_4 and 1.0 M NaOH solutions. The solution was then heated in a thermostatically controlled water bath at 70°C. The reaction was allowed to proceed for 2 h after which the sample was removed and kept at room temperature (30°C). The UF samples used in this experiment were obtained by removing 125ml of resin from the synthesized UF resin and was mixed with the tea waste using different weights (2g, 3g, and 4g) both the untreated and the treated tea waste fiber (UTWF and TTWF).

2.5. Preparation of Composite

The fiber was reinforced with Tirmethylol urea (TMU) resin after the mercerization process, the TMU resin serve as the matrix. The TMU resin helps to bind the individual component together. But this requires series of chemical treatment for this bonding between the matrix and waste tea fiber to be effective, because natural fibres are inherently incompatible with nonpolar-hydrophobic thermoplastics, such as polyolefins. Moreover, difficulty in mixing because of poor wetting of the fibreswith the matrix is another problem that leads to composites with weak interface (John &Anandjiwala, 2008). The fiber in form of mats were randomly oriented in a mould using different fiber weights (2g, 3g, and 4g) both the (UTWF and TTWF) and pressed into a mat of different thickness (10, 20, and 30mm). The thickness observed in treated tea waste fiber (TTWF) tends to be higher than the untreated tea waste fiber (UTWF). TMU resin, which served as a matrix medium, was mixed with the tea waste fiber and poured into a square plastic container of 10cmx10cm in dimension which served as a mould. After being cured for 48 hours, the CFRP composites were removed from the mould for characterisation as seen in Fig 1.



A: Treated tea waste composite B: Untreated tea waste composite

Figure 1: Treated (A) and unreated (B) tea waste composite

2.6. Characterization of Composite

2.6.1. Determination of Weight Loss

The weight loss method reported by (Mumtahenah*et al.,* 2014.) was adopted, where loss in weight was determined after degradation, in this case we used an oven (thermal degradation). For the weight loss determination for both UTWF, TTWF and TMU with zero fiber.The composite were cut into 40×20 mm rectangular specimens. Weight loss test was carried out at different time (30min, 60min, and 90min) and temperature (30^{o}C, 40^{o}C, 50^{o}C, 60^{o}C, and 70^{o}C). The composite was placed in a crucible and kept in an oven and monitoring the time and temperature difference for each composite (2g, 3g, 4g) both the UTWF and TTWF composite and TMU. The composite was removed out of the oven after the time and temperature difference had elapsed for each composite respectively. Then it was weighed again with analytical balance. Weight loss was determined by measuring loss in weight of the composites. Thepercentage weight loss (wt) can be measured as:

$$\%\text{wt loss} = \frac{Wo-W(t)}{Wo} \text{x}100$$

Here W(t) is the total weight after time t, W_o is the reference dry weight of the specimen before oven.

3. Results and Discussion

3.1. Proximate Analysis of both the UTWF and TTWF

3.1.1. Determination of Ash Content

The ash content obtained from UTWF is higher than that of the TTWF due to loss of inorganic components during processing of the raw material used in making the tea. The difference between the value of ash content obtained from both the UTWF and TTWF is (0.08%). This can be seen on (Table 1).

Fiber	Ash Content	Temperature (^{O}c)
UTWF	2.22±0.01	1000
TTWF	2.15±0.01	1000

Table 1: The ash content for both UTWF and TTWF at a temperature of 1000^{o}C

3.1.2. Determination of Moisture Content

In Table 2, the moisture content obtained from UTWF is higher than TTWF. This may be due to the pendants hydrophilic hydroxyl groups present in the cellulose of the UTWF than TTWF. Perhaps, the hydrophilic hydroxyl groups present in the cellulose of the TTWF had been reduced during the chemical treatment thereby increasing fibers moisture resistance property (John and Anandjiwala, 2008).

$\text{FIBER-OH} + \text{NaOH} \rightarrow \text{FIBER-O-Na}^+ + H_2O$.

Scheme 1: Mercerization of the tea waste fiber

Furthermore, the chemical treatment of the fibers as illustrated by scheme 1 lead to the formation of pores on the fiber surface, increases the number of reactive sites and allowing better wetting property between the matrix and fiber.The difference between the value of moisture content obtained from both the UTWF and TTWF is (0.02%).

Fiber	**Moisture Content**	**Temperature (°c)**
UTWF	0.14±0.01	105
TTWF	0.12±0.01	105

Table 2: The moisture content for both UTWF and TTWF at a temperature of 105°C

3.2. Characterization of Composite

3.2.1. Determination of Weight loss

A gradual increased in weight loss was observed up to 30min in the entire composites prepared from both the UTWF and TTWF (2g, 3g, and 4g) and TMU with zero fiber respectively at all the temperatures as seen in Figs 2, 3, 4, 5, 6, 7 and 8.

A fig 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, and 3.7 shows the weight loss profile of UTWF, TTWF and TMU. At 30°C, the weight loss increases up to 30min. This is because of low cross linking density and high molecular pore sites within the composites which cause smaller molecular species that are trapped within the matrix to diffuse out rapidly. As the escaping of the trapped molecular species increases, the cross linking density and dimensional stability of the composites increases (compacted). At 30°C, the composites is said to have attained it maximum thermal stability. Furthermore, at this point, there are few or no molecular trapped species reduced molecular pore sites and improved mechanical interlocking of fiber and matrix. After 30min the weight loss begins to decreases as a result of the phenomenon explained above. This means that at room temperature the composite is curing gradually until it reaches a maximum curing time. And at this time, there is strong chemical interlock of fiber with matrix which leads to high cross linking density. But as the temperature increases to 40°C, the weight loss increases up to 30min, even though at this point, the weight loss is less than that of 30°C as shown in Figures 3.2, 3.4, 3.6 and 3.7. The increased in weight loss at a temperature 40°C above 30min is as a result of decreased in the cross linking density because at this point, the cross linking sites begins to loss due to high temperature. Therefore, with increasing time above 30min, the weight loss increases for all the temperatures (40°C, 50°C, 60°C, and 70°C). The increased in weight loss above 30°C and after 30min is because the cross linking density at this point begins to lose it chemical integrity. This leading to decreased in cross linking density after 30min, meaning that the composite at this point is no longer compacted (i.e. the molecular orientation of the fiber chains begins to disentangle within the matrix) as it was initially. The loss of cross linking density means that disintegration was taking place which result to thermal degradation of the composites. This behavior occurs at a temperature range of 40°C, 50°C, 60°C, and 70°C respectively, where the composite was heated from 2hr to 4hrs.

Generally, the cross linking density decreases up to 30min for all the temperatures (30°C, 40°C, 50°C, 60°C, and 70°C) with the exception of TMU which is acting as the standard and showed high decreased in cross linking after 60min for 30°C as shown in Fig 3.7. This may be due to the absence of reinforcement (tea waste fiber).

Figs 2, 4 and 6 show the weight loss profile for the UTWF. A gradual increased in weight loss was observed up to 30min. However, above 30min the weight loss continues to increase due to higher molecular pore size, high trapped molecular species and lesser cross linking of composites. It is assume that, the UTWF is less compactable with the polymer matrix relative to the TTWF as shown in Figures 3, 5 and 7. The loss in weight was so pronounced in 2g UTWF compared to 3g and 4g UTWF as shown on the Figs 1. This is as a result of the low fiber content within the polymer matrix even though the same volume (125ml) of matrix was used during the fabrication process of the composite. The orientation of the fiber within the polymer matrix was random; this will tend to expose the polymer matrix to degradation due to sparsely dispersion of 2g fiber within the matrix compare to 3g and 4g fiber. However for the TTWF composite, maximum weight loss was observed at a temperature of 40°C at 90min for (2g, 3g and 4g) composite as shown in the Figs 3, 5 and 7.

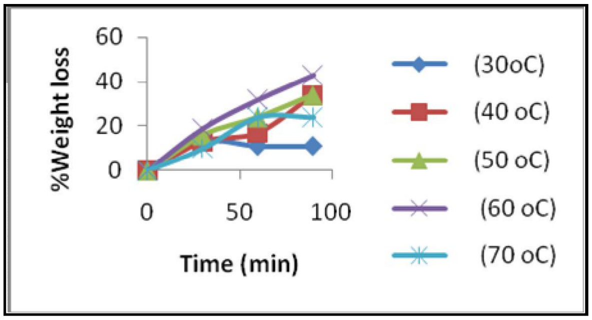


Figure 2: Show change in %weight loss for 2g UTWF composite at different temperature

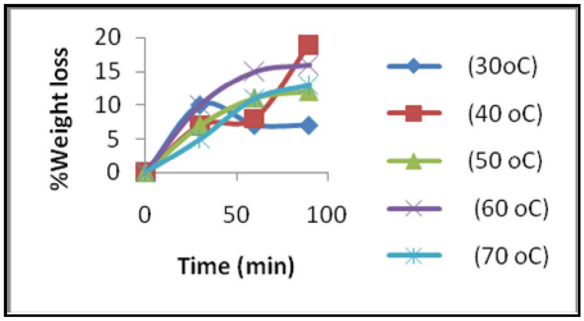


Figure 3: Show change in %weight loss for 2gTTWF composite at different temperature

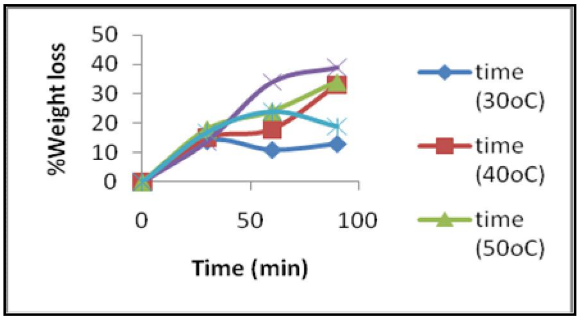


Figure 4: Show change in %weight loss for 3g UTWF composite at different temperature

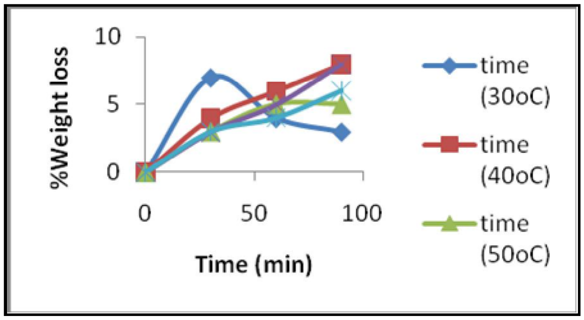


Figure 5: Show change in %weight loss for 3g TTWF composite at different temperature

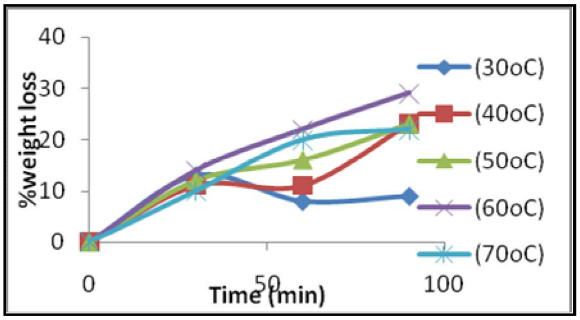


Figure 6: Show change in %weight loss for 4g UTWF composite at different temperature

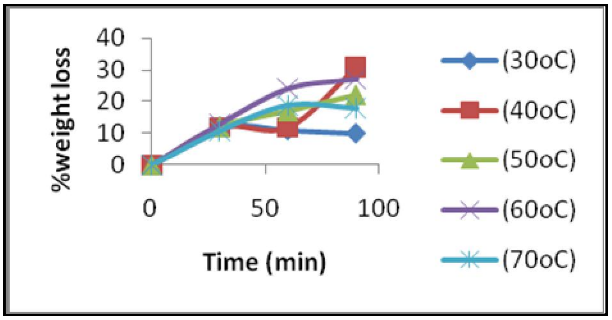


Figure 7: Show change in %weight loss for 4g TTWF composite at different temperature

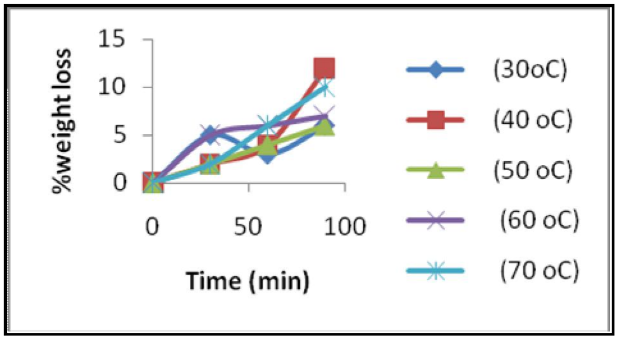


Figure 8: Show change in %weight loss for TMU with zero at different temperature

4. Conclusion

Tea waste fiber reinforced trimethylol urea composites was successfully synthesized. A lot of research has been done on natural fiber reinforced polymer composites but research on tea waste fiber polymer composites is very rare. Against this background, the present work has been undertaken, with an objective to explore the potential of the above said fiber polymer composites in which the weight loss was studied at different temperatures and time as well as water uptake determination of different fiber weights (2g, 3g, and 4g) used in producing the composites and also TMU with zero fiber. Proximate analysis such as moisture content and ash content was determined as well for both the UTWF and TTWF. The synthesized composite material can be used to make indoor furniture's like table and the temperature of exposure should not exceed 40^{o}C, even though other parameters unique to the composite are yet to be characterized.

5. Acknowledgement

The author wishes to sincerely acknowledge the support and contributions of Egr. (Mrs.) Ansa E. Bassey of the Department of Pure and Applied Chemistry, University of Clabar, Calabar, Cross River State, Nigeria.

6. References

i. Babayemi, O.J., D. Demeyer and V. Fievez, 2004a. Nutritive value and qualitative assessment of secondary compounds in seeds of eight tropical browse, shrub and pulse legumes. Comm. Appl. Biol. Sci. Ghent University, 69/1: 103-110.

ii. Babayemi, O.J., D. Demeyer and V. Fievez, 2004b. In vitro fermentation of tropical browse seeds inrelation to their content of secondary metabolites. J.Anim. Feed Sci., 13 Suppl. 1: 31-34.

iii. Barminas J.T and S.A Osemeahon ,(2005).development of sodium alginate and Konkoli gum-grafted polyacrylamide blend membrane. Science forum .j. pure applied science 8; 70-79.

iv. Bledzki AK & Gassan J. (1996), Natural fiber reinforced plastics. Kassel, Germany: University of Kassel; 1996.

v. Fievez, V., O.J. Babayemi and D. Demeyer, 2005. Estimation of direct and indirect gas production in syringes: a tool to estimate short chain fatty acid production requiring minimal laboratory facilities. Anim. Feed Sci. Tec.

vi. John M.J. & Anandjiwala R.D. (2008), Chemical modification of flax reinforced polypropylene composites, Polym. Compos., 29, 187.

vii. Kalia S., Kaith B.S. & Kaura I. (2009), Pretreatments of Natural Fibers and their Application as Reinforcing Material in Polymer Composites – A Review. Polymer Engineering and Science, 49, 1253-1272

viii. Kondo, M., Kita, K and Yokota, H. (2004). Effects of tea leaf waste of green tea, oolong tea, and black tea addition on sudangrass silage quality and in vitro gas production. J. Sci: food Agric., 84: 721-727.

ix. Lu J.Z., Wu, Q., and McNabb, H.S. (2000). "Studies on the water absorption properties of short hemp-glass fiber hybrid polypropylene composites," Journal if composite materials 41(15), 1871-1883.

x. Mumtahenah Siddiquee Kh, Md. Maksud Helali, Md. Abdul Gafur, Soma Chakraborty. (2014), Investigation of an Optimum Method of Biodegradation Process for Jute Polymer Composites, American Journal of Engineering Research (AJER)e-ISSN : 2320-0847 p-ISSN : 2320-0936 Volume-03, Issue-01, pp-200-206

xi. National agency for food and drug administration and control (NAFDAC) (1982). Manual of chemical methods of food analysis. Prepared by : food and drugs administration and laboratory services, federal ministry of health Lagos Nigeria.

xii. Panthapulakkal, S., Sain, M. (2007). "Chemical coupling in wood fiber and polymer composites: A review of coupling agents and treatment" Wood and fiber science 32(1), 88-104.

xiii. Rong. M.Z., Zhang M.Q., Liu Y., Yang G.C. & Zeng H.M. (2001), The effect of fiber treatment on the mechanical properties of sisal-reinforced epoxy composites. Compos.Sci.Technolo., 61, 1437.

xiv. Rout J, Misra M, Tripathy SS, Nayak SK, Mohanty AK. The influence of fibre treatment on the performance of coir-polyester composites. Comp Sci Tech 2001; 61(9): 1303-1310

xv. Saheb DN & Jog JP. (1999) Natural fiber polymer composites: A review. Adv Polym. Technol., 18, 351–63.

xvi. Sanadi, A.R., Caulfield, D.F., and Jacobson, R.E. (2007). "Agro-fiber/thermoplastic composites," in paper and composite from Agro-based Resources, CRC Lewis publishers, 377-401.

xvii. Stokke, D.D., and Gardner, D.J. (2003). ''Fundamental aspects of wood as a component of thermoplastic composites," Journal of Vinyl and Additive Technology 9, 96-104

xviii. Var, A.A., and Oktem, E. (1999). "Reduction by natural resin of water uptake in various wood species," Turk, Agricultural forest 23, 413-418