



Thermal and Water Absorption Characteristics of Rubber Composites Reinforced with different Plant Biomass

J.O. Oboh¹, J.O. Okafor², A.S. Kovo³, A.S. and Abdulrahman⁴

¹Department of Polymer Technology,
Nigerian Institute of Leather and Science Technology, Zaria, Nigeria.

^{2&3}Department of Chemical Engineering,
Federal University of Technology Minna, Nigeria.

⁴Department of Material and Metallurgical Engineering,
Federal University of Technology, Minna, Nigeria.

ABSTRACT

The use of plant biomass as sources of cellulosic material for the reinforcement of polymer matrix is taking up a lot of research space due to their specific strength and stiffness, availability, renewability, sustainability and environmental friendliness. However their tendency to absorb water, low thermal stability and poor compatibility with hydrophobic polymer matrix still hamper their use on industrial scale. In this study, cellulosic nanoparticles were obtained from some selected plant biomass namely coconut husk, bamboo and cotton linter for the preparation of natural rubber composites. The resultant composites were compared with rubber composite reinforced with commercially purchased N330 carbon black in terms of thermal stability and thermo-molecular decomposition using Thermogravimetric Analyser (TGA) and Differential Scanning Calorimeter (DSC) respectively. The effect of varying filler volume fraction and period of water immersion on % water absorption of composite samples were also studied. DSC results showed that cold crystallization and crystalline melting temperatures of rubber reinforced with 25 pphr of coconut husk, bamboo, cotton linters nanoparticles and carbon black occurred at temperatures of 67 & 358, 70.3 & 361.5, 70.5 & 365 and 70.4 & 365 °C respectively while that of reference neat rubber was 65.9 & 354 °C. Results also showed that there was no water uptake by any of samples within the first 4 days, however equilibrium swelling was obtained at about the sixteenth day of immersion. The highest amount of water uptake was 5.68 % for cotton linter based composites at 30 pphr filler content.

ARTICLE INFO

Article History

Received: June, 2019
Received in revised form: July, 2019
Accepted: August, 2019
Published online: November, 2019

KEYWORDS

Water absorption, Nanoparticles, DSC, TGA

INTRODUCTION

Water absorption test is a technique used to determine the amount water absorbed by a material under specific set of conditions. The percentage water absorption of a polymer composite is usually affected by the nature of the polymer matrix, reinforcing material, other additives/ modifiers present in the polymer composites, testing temperature and duration of exposure to water (Rao and Hussain, 2013, Munoz and Manrique, 2015). Water absorption test is basically used to determine the performance of materials under water and humid environments. The water absorption of a composite material under specific set of environmental conditions does not only depends on its hydrophobicity (ability of the material to repel water), but also on the porosity

and the characteristics nature of the pores present in the material microstructure. For instance, a material microstructure with open and connected tiny pores has higher tendency for water absorption. Conversely, if the micro-pores are closed, it becomes relatively difficult for water to be absorbed. Hence, the water absorption capacity vary from one material to another because of the difference in micro-structural configuration of different materials, for example, the percentage water absorption of hydrophobic materials such polymer matrices can vary from 0 to 5 % , while hydrophilic materials such as wood and other cellulosic materials can absorb over 100 % of water on mass basis. The presence of excess water in materials can lead to material expansion (swelling), increase in electrical and thermal conductivity and decrease in strength and

durability of materials (Jafar *et al.*, 2011). The thermal properties of polymers are as important as its mechanical properties, unlike metals; polymers are extremely sensitive to changes in temperature. In fact, the mechanical properties of polymeric materials are dependent on the thermal properties at which their values were obtained hence the temperature at which they are measured are always required to be specified (Anil, 2005). On the other hand, the molecular weight and chain crystallinity in addition to molecular orientation of polymers dictates their thermal properties. Hence, the melt flow orientation tends to decrease the dimensional stability of the polymer structure at higher temperatures; also, molecular weight affects low-temperature flexibility and the impact strength of polymers (Premamoy, 2006). Polymers are processed and used over a wide range of temperatures, hence the effects of temperature and loads over a period of service time on its properties must be established before polymer products can be specified or recommended for service applications (Anil, 2005). In the processing of polymer materials, knowledge of their thermal properties such as glass transition temperature, melting temperature, decomposition temperature amongst others are very important. Various thermal analytical methods such as Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA), and Dynamic Mechanical Analysis (DMA) amongst others are usually employed. The objective of this study is to investigate the water absorption and thermal properties of rubber composites reinforced with cellulosic materials.

EXPERIMENTAL PROCEDURE

Materials

Dry natural rubber crumb, Carbon black, Stearic acid, Mercaptobenzothiazole disulfide (MBTS), Trimethylquinolone (TMQ), and Zinc oxide were supplied by Tony West rubber factory, Lagos Nigeria. The specifications of the dry rubber according to the supplier were $\leq 0.05\%$ dirt content, $\leq 1.00\%$ volatile content, $\leq 0.7\%$ nitrogen content, $\leq 0.6\%$ ash content, minimum of 30 initial plasticity, minimum of 60 plasticity retention index (PRI) and blackish brown in colour. The Carbon black was of N330 grade and was manufactured by Warri refinery and petrochemical a subsidiary of Nigerian National Petroleum Corporation (NNPC) with particle size distribution of 50 to 500 nm. Other compounding

ingredients were of rubber processing commercial grade and were used as received.

Sample Preparation

The cellulosic nanoparticles obtained from bamboo, coconut husk and cotton linter with respective particle size distributions of 32 - 175, 68 - 311 and 620 to 5408 nm were used as reinforcing fillers (nanoreinforcement phase) in natural rubber matrix. The composites samples of bamboo, coconut husk and cotton linter were coded NR-BNC, NR-CHNC and NR-CLNC respectively while commercially purchased carbon black based composite was coded NR-CB. The various particles from lignocelluloses biomass (coconut husk, bamboo and cotton lints) were obtained through defibrillation (fibre extraction), alkaline-peroxide treatment and particle size reduction procedure. The detailed procedure for particle preparation and sizing as well as the composites formation have been reported in our previous work (Oboh *et al.*, 2017)

Water Absorption test

The water absorption test was carried out according to ASTM D570 in which samples of equal dimensions (2 x 2 x 0.5 cm) were dried in an oven at 105 °C for 2 h and then cooled in desiccators. The cooled samples were weighed and then immersed in water at ambient temperature (25 - 30 °C) for period of 21 days. The percentage change in mass of test sample was recorded on daily bases, such that the samples were removed from the water medium, patted with a dry clean lint free cloth and reweighed. The percentage of water absorption was calculated using equation 1 (Alamri and Low, 2012).

$$\% W \quad A \quad = \frac{M_2 - M_1}{M_1} \quad 1$$

where M_1 is the mass of dry sample and M_2 is the mass of the wet sample

Thermal Study

Thermogravimetry analysis (TGA) experiments were carried out in air using TGA 4000. In these experiments, about 40 mg of neat NR and rubber composites filled with 25 pphr of bamboo (NR-BNC₂₅), coconut husk (NR-CHNC₂₅), cotton linter (NR-CLNC₂₅) and carbon black (NR-CB₂₅) were separately heated from 27 - 800 °C at a heating rate of 10 °Cmin⁻¹. In each case, the temperature for different percentages of weight loss, onset and complete degradation temperatures were obtained. On other hand, the thermo-molecular behaviour of

the respective samples were analysed using METTLER TOLEDO STAR SW 13.00 Differential Scanning Calorimeter (DSC) in power compensation mode, such that 5 mg of a composite sample was heated in an aluminium pan from 60 to 400 °C at controlled heating rate of 10 °C/min alongside an inert reference material while measuring the corresponding differential heat input to the sample and reference inert material required to keep them at exactly the same temperature (South, 2001).

RESULTS AND DISCUSSION

Water Absorption of Composites

The percentage water absorption is a measure of the quantity of water uptake or water

absorbed over a period of time at a defined temperature on mass basis. It is of immense importance in the handling of hydrophilic materials such as cellulosic materials. Figures 1, 2, 3 and 4 showed the effect of CHNC, BNC, CLNC and CB loadings (0, 5, 10, 15, 20, 25 and 30 pphr) and time (7, 14 and 21 days) of water immersion on the percentage of water absorbed by respective composites samples based on initial mass of sample while Figure 5 presented the combined effect of loading, filler types and time (7, 14 and 21 days) on the percentage water absorption of composites at ambient temperature (25 – 30 °C).

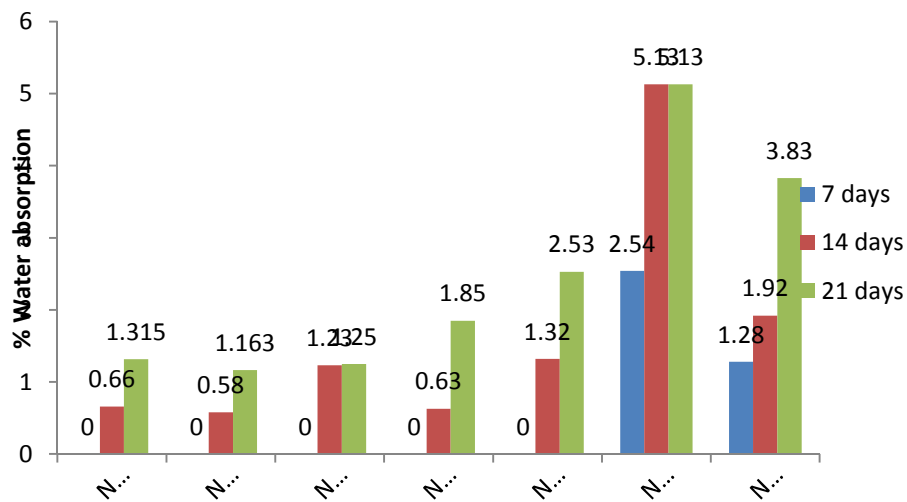


Figure 1: Effect of CHNC loading and Time on Water Absorption

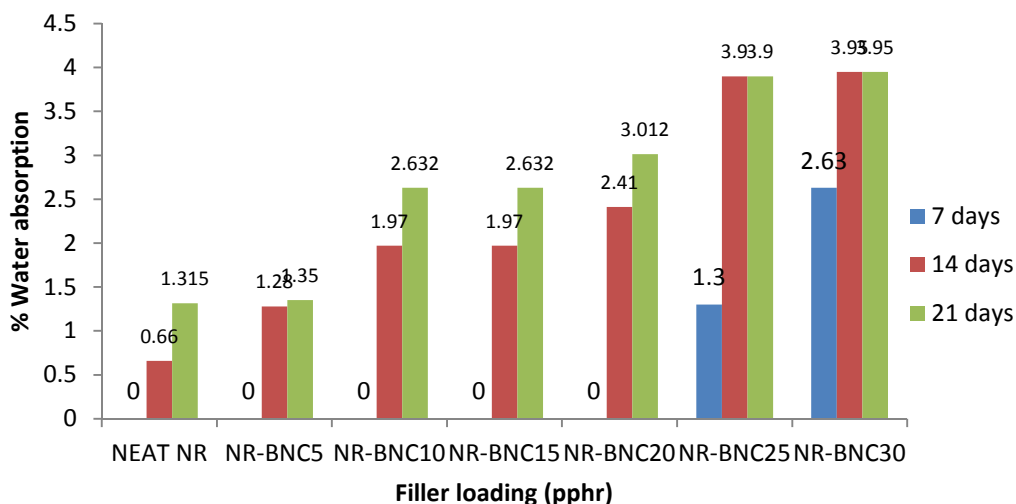


Figure 2: Effect of BNC loading and Time on Water Absorption

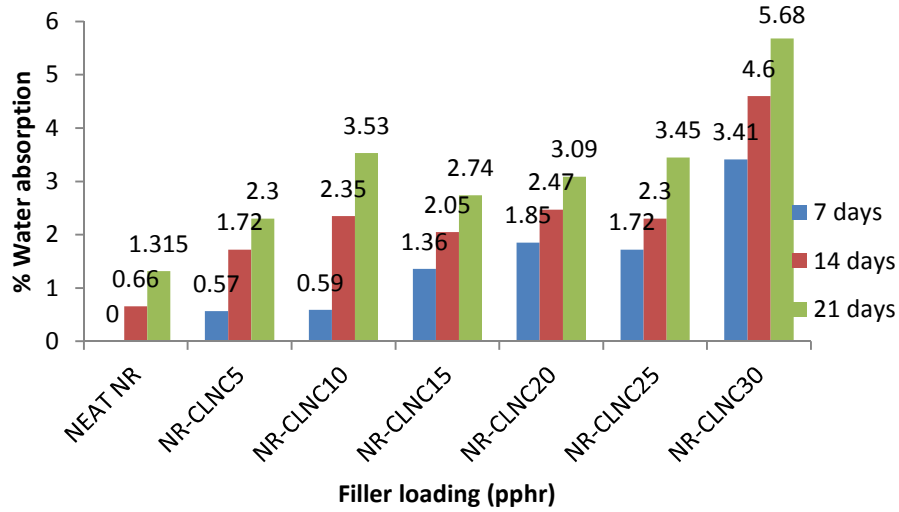


Figure 3: Effect of CLNC loading and Time on Water Absorption

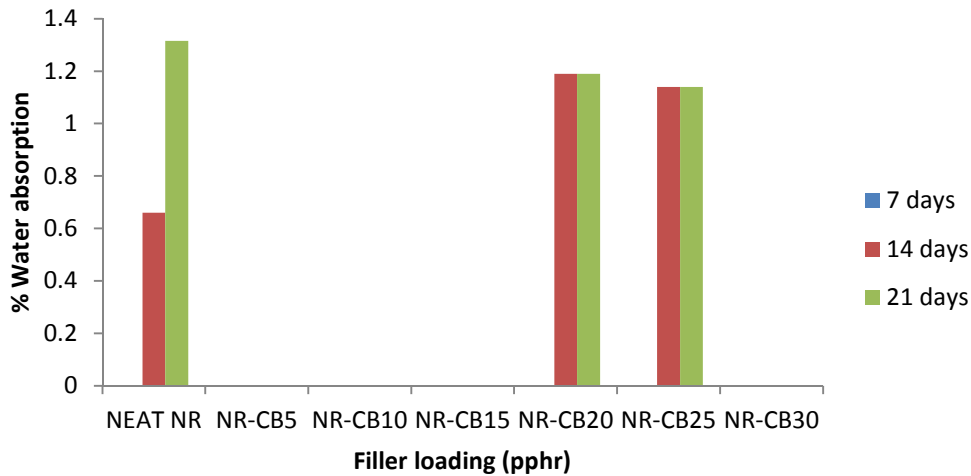


Figure 4: Effect of CB loading and Time on Water Absorption

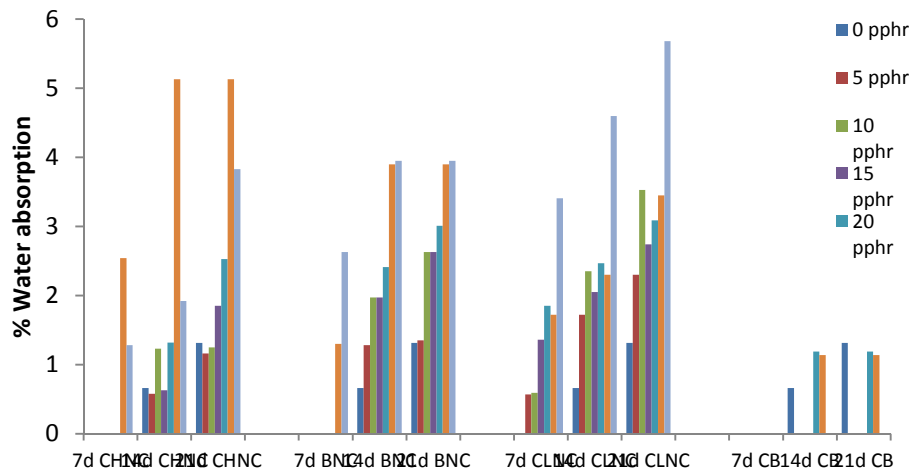


Figure 5: Effect of Time, Filler Type and Loading on water absorption



Results revealed increase in amount of water absorbed by samples as the time of immersion was increased, however composites filled with 0 – 20 pphr of CHNC and BNC did not absorb water for the first seven days of immersion (Fig. 1 and 2) while composites with 5, 10, 15 and 30 pphr of CB (Fig.5) did not uptake water for the entire 21 days of immersion. Virtually all samples were observed to reach their equilibrium swelling on the sixteenth day of immersion (that is, no increase in mass of sample was observed after this period). Overall, after 21 days of samples immersion in water, percentages of water absorption were found to increase from 1.3 to 5.13, 1.3 to 3.95, 1.3 to 5.68 % as loading of CHNC, BNC and CLNC respectively were increased from 0 to 30 pphr (see Fig.5). The composites of CB as shown in Figure 5 demonstrated lower potential to absorb water when compared to other cellulosic based composites because of the hydrophilic characteristics of cellulose (kuburi *et al*, 2017, Trakuldee and Boonkerd, 2016). Usually, the absorption of water by materials requires the presence of micro-pores or permeable channel in their microstructure in form of quasi-open cells to create path way for passage (Eldho *et al.*, 2013). These micro-pores can either be active in water absorption through osmotic and non-osmotic absorption or passive absorption such that the pores do not participate in the water absorption process. About 96 % of the total amount of water absorbed by cellulosic and other hydrophilic materials is by passive water absorption while the remaining 4 % is by active water absorption whereas hydrophobic materials water uptake are predominantly active water absorption, hence the presence and nature of micro-pores becomes the determinant factor. The relative low water absorption observed with CB composites could be due to either presence of little or no open cells in the composite microstructure or predominantly closed cells making the microstructure difficult to be absorbing water. On the other hand, the likely most preferred theory for the relative high water absorption of cellulosic fillers based composites (CHNC, BNC and CLNC) especially at higher filler loading is due to the possibility of the active hydroxyl groups present in cellulosic material to react with water molecules leading to the formation of hydrogen bond or linkage between the cellulosic particles and water molecules. This newly formed linkage will subsequently give rise to a hydrophilic network for further water uptake until a

saturation point is reached (kuburi *et al*, 2017, Trakuldee and Boonkerd, 2016).

Thermal Properties

The thermal decomposition pattern and crystallinity studied with DSC are presented in Figure 6 and Table 1 respectively. Plots of heat flux (Mw) versus temperature (°C) curves were obtained from the DSC experiments to determine thermo-molecular events such as crystallization and melting or decomposition temperatures of the various composites. The negative region of the differential heat input (y-axis) in the graph represents an exothermic event such as crystallization, while the positive region of the graph is endothermic event such as melting or thermal decomposition. Conventionally, the first thermal event (usually depicted by peaks) in the DSC trace or curve is the glass-rubber transition temperature (T_g), above which the polymer chains have high degree of mobility and eventually reach a temperature called cold crystallization temperature (T_{cc}) at which polymer chains are able to organize into crystals, the process of crystallization is exothermic, hence differential heat input will be negative. From the results obtained, the cold crystallization temperatures (T_{cc}) for the various samples were found to 65.9, 67, 70.3, 70.5 and 70 °C for neat NR, NR-CHNC₂₅, NR-BNC₂₅, NR-CLNC₂₅ and NR-CB₂₅ respectively. On completion of crystallization, a new baseline which relates to the specific heat capacity of the polymer samples will be established. As temperature is further, increased, there will be little or no change in differential heat input until the crystallization melting or degradation temperature (T_m) is reached, at this point the polymer crystals either begin to melt or get destroyed. This process is endothermic and is signified by a positive change in differential heat input. The crystallization melting or decomposition temperatures (T_m) were found to be 354.4, 358, 361.5, 365, and 365 for neat NR, NR-CHNC₂₅, NR-BNC₂₅, NR-CLNC₂₅ and NR-CB₂₅ respectively. From the results, the cold crystallization and decomposition temperatures for all samples were close due to the restriction in chain mobility already imposed by sulphur vulcanization (Visakh *et al.*, 2012). In this experiment, only two of such DSC trace events (as indicated by two arrows on Figure 6) corresponding to cold crystallization temperature (T_{cc}) and crystalline melting temperature (T_m) were obtained since the testing temperature range (ambient to 400 °C) was far

above glass transition temperature (T_g) of vulcanized rubber compounds which is usually in the neighbourhood of -55 to -45 °C (South, 2006, Visakh *et al.*, 2012, Oboh *et al.*, 2018). In addition to T_{cc} and T_m , the degree of crystallinity of the neat rubber and composite samples were calculated using equation 2 (Olatunji and Richard, 2016)

$$X_c = \frac{\Delta H_m - \Delta H_c}{(1-f)\Delta H_M} * 100\% \quad 2$$

where X_c is the degree of crystallinity of composites, H_{cc} and H_m are crystallization and melting enthalpies respectively and were obtained from DSC curves, f is the weight fraction of the fillers (25 pphr or 20%), and H_M is the melting enthalpy of pure natural rubber usually obtained from literatures as 16.7 J/g. Table 1 showed the crystallinity (X_c) of samples and other thermal characteristics obtained from DSC study.

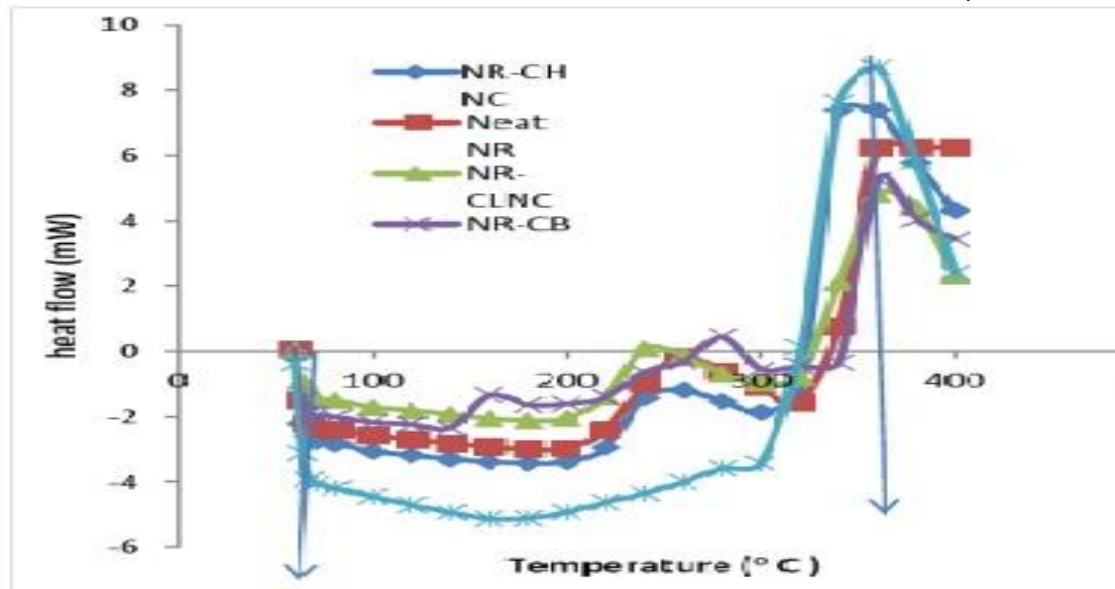


Figure 6: Effect of filler types on DSC curves of Composites

Table 1: Crystallinity and melting characteristics of samples

Samples	H_{cc} (J/g)	H_m (J/g)	F	T_{cc} (°C)	T_m (°C)	X_c (%)
Neat NR	-3.908	0.298	0	65.9	354.4	21.62
NR-CHNC ₂₅	-2.692	8.111	0.20	67	358	43.26
NR-BNC ₂₅	-4.056	8.595	0.20	70.3	361.5	36.24
NR-CLNC ₂₅	-1.432	4.811	0.20	70.5	365	26.97
NR-CB ₂₅	-1.947	5.77	0.20	70.4	365	30

Thermo gravimetric analysis (TGA) of composites sample was studied to determine thermal stability by measuring the change in the weight of the composite samples when heated in air.

The results of thermal stability comprising thermo-gravimetric (TGA) curves for neat NR, NR-CHNC₂₅, NR-BNC₂₅, NR-CLNC₂₅ and NR-CB₂₅ are shown in Figure 8 and Table 2.

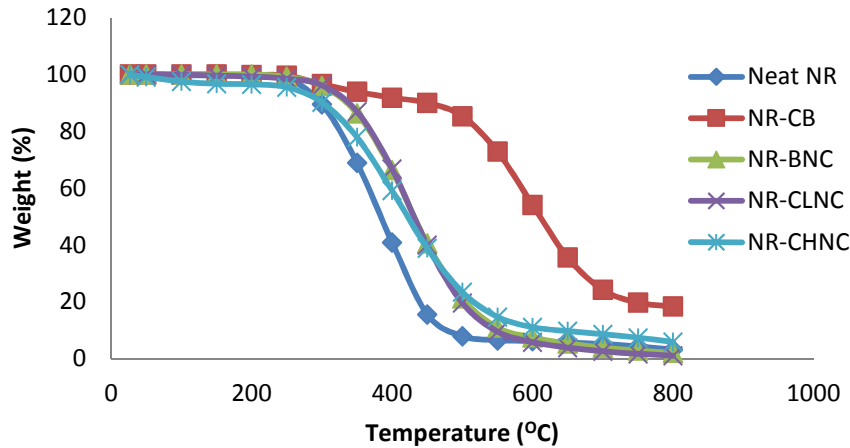


Figure 8: Effect of filler type on TGA curves of composites

Table 2: Thermal Degradation Characteristics

Sample	Thermal degradation properties			
	T _{onset} (°C)	T _{50%} (°C)	T _{degradation} (°C)	% Residues at 600 °C
Neat NR	270	383	380	6
NR-CHNC ₂₅	258	422	408	11
NR-BNC ₂₅	307	431	425	7.5
NR-CLNC ₂₅	309	431	420	6.0
NR-CB ₂₅	328	610	600	54

Three broad thermal regions/stages are usually associated with TGA, such that first, second and third stages correspond to drying/ evaporation, onset decomposition /devolatilization and complete degradation respectively (Bernard *et al.*, 2017). The first region is used to determine the onset of thermal degradation temperature which is defined as the temperature at which sample losses not more than 5 % of its initial mass. This onset temperature of degradation can also be used to determine the maximum operating temperature of a sample, and they correspond to 273, 258, 307, 309 and 328 for neat NR, NR-CHNC₂₅, NR-BNC₂₅, NR-CLNC₂₅ and NR-CB₂₅ respectively. Other important parameters that can be obtained from the TGA curves such as T_{50%} (temperature at which the sample losses 50% of its initial mass), T_{max} (temperature at which maximum rate of degradation obtainable from DTG curves) and percentage inorganic residues are shown in table 2. Usually, when rubber compound/composites are heated at lower temperature, moisture and other volatile components will get evaporated first, further heating of the rubber compound will get part of it degraded and converted into gaseous products with corresponding weight loss which is reflected in TGA curves (South, 2006, Visakh *et al.*, 2012), subsequent heating will remove all organic matter leaving

behind inorganic components. This happens at complete degradation temperature.

CONCLUSION

The percentage water absorption of all cellulosic particle based composite samples was found to increase with time (until equilibrium swelling was reached) and loading. The range of percentage water absorption after 21 days of water immersion was approximately 1.16 – 5.65 % as against 1.315 % for unfilled rubber matrix. The presence of BNC and CLNC in the rubber was observed to slightly increase the thermal stability of composites. The influence of the fillers on the vulcanized rubber matrix was negligible.

Acknowledgment

The authors gratefully acknowledge the financial support of TETFUND under Project No. TETFUND/FUTMINNA/2016-2017/6th BRP/22

REFERENCES

Alamri, H., & Low, I.M. (2012). Mechanical properties and water absorption behaviour of recycled cellulose fibre reinforced epoxy composites. *Journal of polymer testing*, 31 (5), 6220-6228.



- Anil, K.B. (2005). *Mechanical properties of polymers*. Kharagpor, India, materials science and engineering publishers
- Bernard, E., Jimoh, A., Yahya, D.M., & Auta, M. (2017). Application of surface response methodology for the preparation of activated carbon from melon husk. *Proceedings of International Engineering conference*, 2, 262 - 271
- Eldho, A., Merin, S.T., Cijo, J., Pothan, L.A., Shoseyou, O. & Thomas, S. (2013). Green nanocomposite of natural rubber/celluloses: Membrane transport, rheological and thermal characteristics. *Industrial crops and product*, 51, 415-424.
- Jafar, H.I., Husaen, S.I. & Ajaj, E.A. (2011). Effect of water absorption on some electrical and dielectrical properties of epoxy resin reinforced with chopped carbon fibre. *Journal of Al-Nahrain university*, 14 (4), 87-94.
- Munoz, E., & Manrique, J.A.G.(2015). Water absorption behaviour and its effect on the mechanical properties of flax fibre-reinforced Bioepoxy composites. *International journal of polymer science*, 2015 (2015), 1-10.
- Oboh^a, J.O., Okafor, J.O., Kovo, A.S. & Abdulrahman, A.S. (2017). Investigation of eco-friendly cellulosic nanoparticles potentials as reinforcement agents in the production of natural rubber composites. *Nigerian journal of technology*, 36 (4), 1078-1087.
- Oboh^a, J.O., Okafor, J.O., Kovo, A.S. & Abdulrahman, A.S. (2018). Dynamic mechanical properties of crosslinked natural rubber composites reinforced with cellulosic nanoparticles. *Nigerian journal of Technology*, 37 (3), 668-673.
- Olatunji, O., & Richard, O. (2016). *Processing and characterization of natural polymers*. Switzerland: Springer international publishing.
- Premamoy, G. (2006). *Thermal transitions in polymers*. Kolkata, India: Tata McGraw-Hill publisher
- Rao, P. S. & Hussain, M.M. (2013). Hydrothermal ageing effects on flexural properties of GFRP composite laminates. *Indian journal of engineering and material science*, 20 (2013), 415-424.
- South, J. T. (2001). Mechanical properties and durability of natural rubber. *Ph.D Thesis*, 34-60.
- Visakh, P.M., Sabu, T., Kristiina, O., & Aji P. M. (2012). Crosslinked natural rubber nanocomposites reinforced with cellulosewhiskers isolated from bamboo waste: Processing and mechanical/thermal properties. *Composites part A. Applied Science and Manufacturing*, 43, 735-741.