Maize Stalk As Reinforcement In Natural Rubber Composites

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Abstract: Maize stalk fibres can be used as fillers in natural rubber composites replacing expensive and non-biodegradable inorganic fillers. Maize stalk fibres were chemically modified with acetic anhydride (acetylation) to enhance their compatibility with the hydrophobic rubber polymer matrix. The fibre was characterised using FTIR showing a spectrum with a well defined peak at 1742 cm^{-1} (attributed to the carbonyl groups –C=O), indicating that new acetyl groups were introduced to cellulose. The curing and physico–mechanical properties of the composite as a function of filler loading was determined and compared with the values obtained using commercial grade hydrated silica. The natural rubber-maize stalk filled composites showed good processing safety in terms of torques and scorch. Compared with untreated maize-natural rubber composites, the acetylated composites exhibited higher mechanical properties, reduced moisture absorption and higher resistant to hydrothermal aging. Based on mechanical properties and statistical treatment of data, composites filled with 20 phr treated maize stalk had the optimum set of mechanical properties (tensile strength of 22.4 MPa, elongation at break 404 % and hardness Shore A of 55) that were closely comparable with commercial hydrated silica filled composites. Maize stalk has therefore demonstrated its potential to be used to reinforce natural rubber for shoe sole production.

Index Terms: Fillers, composite, natural rubber, fibre, matrix, maize stalk, reinforcement, vulcanisation, compounding

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1 INTRODUCTION

Composite materials are a combination of two or more different components which generate a substance with overall performance characteristics exceeding those of individual components [1]. In polymer matrix composites, fibrous materials that are either synthetic or natural are added as fillers or as reinforcements that provide strength and stiffness to the structure, while the polymer acts as the load transferring medium and serves as the adhesive holding the fibres in place [2], synthetic fibres such as glass, carbon, talc and aramid are widely used as fillers in polymer composites because of their high stiffness and strength [3]. However, these fibres have serious drawbacks such as non-biodegradability, high initial processing cost, non-recyclability, high energy consumption, machine abrasion and health hazards [4]. Adverse environmental impact of synthetic materials has shifted attention to the use of natural fibres. Natural fibresfulfill all the requirements to replace inorganic fillers in natural rubber composites. The natural fibres are inexpensive, renewable, recyclable, biodegradable, low density and have favourable mechanical properties compared to inorganic fillers [5], [6]. However, the poor compatibility between the hydrophilic fibresand the hydrophobic polymer matrix leads to a weak interface, which results in poor mechanical properties, high moisture sensitivity which leads to the loss of properties, swelling and dimensional instability [7]. To enhance the effective interfacial bonding between fibre and matrix, the fibre surface needs to be chemically modified [8].

Chemical treatment makes the natural fibre more hydrophobic [9] and hence improves polymer compatibility with the matrix. Chemical modification directly influences the fibres structures and changes their compositions. As a result, moisture absorption tendency by the fibre is reduced facilitating better bonding with the matrix materials. Different methods offibre modification such as acetylation [7], [10], [11], [12], [13], alkaline treatment [12], [14], [15] and silane hydrolysis [16] have been cited in literature. Various authors [17], [18] have reported the use of natural fibres particularly in the area of plastic reinforcement. However, less attention has been paid to the incorporation of natural fillers to elastomeric substances. Agro wastes that have been used as fillers for natural rubber include rice husk [19], [20] and cherry seed shells [21]. Egwaikide et al. [22] investigated the effect of coconut fibre filler on the rheological, physico-mechanical and swelling properties of natural rubber vulcanisates. Hussain et al. [7] reported the effect of incorporating modified linen fibre waste on physico-mechanical properties of polar and non-polar rubber. It was observed that the use of modified sisal fibre in natural rubber composites resulted in superior mechanical properties [23]. This study focuses on the use of maize stalk as filler in natural rubber. Maize stalk is one widely available underutilised agro-waste product and to the best of our knowledge there seems to be no evidence in literature on its use as filler in rubber processing. Hassan et al. [24] investigated the microstructure and the mechanical properties of maize stalk ash particles reinforced polyester composites with the aim of producing a composite material showing enhanced properties for engineering purposes. The tensile strength, tensile modulus and compressive strength value increased as the maize stalk ash content increases but there was a gradual decrease in impact strength. These results showed that maize stalk ash could be used to improve the strength of polymer matrix composites. Maize stalk contains cellulose (38-40%), hemicelullose (28%), lignin (7-21%) and ash (3-7%) [25]. Maize stalk has proven to be one of the most interesting candidates for polymer reinforcement due to its high specific strength and modulus, low density, renewability, and no health risk.

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2 METHOD

2.1 Sample Preparation
Dry maize stalks were ground into a powder. The powder was screened using a 180 μm mesh. The fibre was oven dried before use for 24 h at 105ºC.

2.2 Characterisation of Maize Stalk Powder

2.2.1 Lignin
2 g of the powdered sample were placed in a flask containing 15 mL of 72% sulphuric acid. The mixture was continuously stirred for 2.5 h at 25ºC. This was followed by addition of distilled water (200 mL) and boiling the mixture for 2 h before cooling. After 24 h the mixture was filtered and the residue acidic lignin was transferred to the crucible and washed with hot water repeatedly until it was neutral. The lignin was dried at 105ºC and cooled in a desiccator before weighing. The drying and weighing were repeated until constant weight [8], [26].

2.2.2 Holocellulose
Air dried samples (3 g) were placed in an Erlenmeyer flask followed by successive addition of distilled water (160 mL), glacial acetic acid (0.5 mL) and 1.5 g of sodium chloride. The flask was heated in a water bath for 1 h maintaining a temperature of 75ºC. Additional amounts of glacial acetic acid (0.5 mL) and 1.5 g of sodium chloride were added to the mixture twice in 1 h. The mixture was cooled in an ice bath to a temperature below 10ºC, filtered and the residue holocellulose washed with 10 mL each of acetone, ethanol and water respectively. The holocellulose was dried in an oven at 105ºC before weighing [8], [26].

2.2.3 Cellulose
2 g of holocellulose were soaked under continuous stirring in a beaker containing 10 mL of sodium hydroxide solution (17.5 wt.%). Sodium hydroxide solution (10 mL) was added to the mixture periodically (once every 5 min) for half an hour and the temperature of the mixture was maintained at 20ºC. This was followed by addition of 33 mL of distilled water to the mixture and allowing it to stand for 1 h. The mixture was filtered and the residue holocellulose was transferred to a crucible followed by successive washing with 100 mL of sodium hydroxide (8.3 wt.%), 200 mL of distilled water, 15 mL of acetic acid (10%) and distilled water (200 mL). The cellulose in the crucible were dried and weighed [8], [26]. Hemicellulose content was determined by subtracting cellulose content from holocellulose content.

2.3 Acetylation of Maize Stalk
Maize stalk powder (50 g) was first activated for 5 min by heating with acetic acid (500 mL) at 80ºC. The mixture was filtered followed by addition of catalytic mixture of 0.1% perchloric acid (10 mL) and acetic acid (80 mL) to the residue. The mixture was filtered after 1 min. The maize stalk (10 g) was then acetylated at 20ºC in a solvent mixture containing acetic anhydride (30 mL) and acetic acid (70 mL) for 45 min. The acetylated sample was then washed with distilled water until neutral. The acetylated raw material was stabilised by treatment with hot distilled water (100 mL). The acetylated raw material was then air dried, and the acetyl content was determined according to the method described by Hussain et al. [7]. The unmodified and acetylated maize fibres were characterised using FTIR (2000 Diglab Merlin).

2.4 Compounding
The ingredients were mixed thoroughly on a mixing roll mill to produce a thin sheet of compounded rubber ready for vulcanisation in steam-heated presses. A standard method adopted by the American Society for Testing Materials (ASTMD 3184-80) was used to formulate rubber as shown in Table 1.

TABLE 1
FORMULATION OF RUBBER COMPOUNDS

Ingredients	Parts per hundred
Natural rubber	100.0
Stearic Acid	4.0
Zinc Oxide	6.0
Sulphur	1.6
Mercaptabenzthiazole	2.4
D.P.G	1.0
Filler	Variable (0-30)

2.5 Vulcanisation
The compounded rubber was cut into dimensions slightly smaller than those of cavities. Pressure (3.5 bar) was applied for 12 min to the moulds. The moulds were immediately removed and cooled in a large cold water tank for 10 min. The sheets were wiped dry and retained for 24 h before testing.

2.6 Cure characteristics of Natural rubber compounds
The cure characteristics were measured using the Rheometer (1005 Monsato). A 2 g sample of compounded rubber was cut and placed in the die cavity of the rheometer. The rheometer was closed and set at a temperature of 150ºC and pressure (3.5 bars) applied for 3 min. The graph of curing characteristics was recorded. The cure times predicted by the rheographs were used as guidelines to obtain vulcanisates for the test specimens [21], [27].

2.7 Mechanical characterisation

2.7.1 Tensile Strength and Elongation at Break
The test specimens were cut from the moulded dump-bell rubber sheets along the grain direction. The thickness and width of each test piece at the middle was maintained at 2.5 and 6 mm respectively. Each test piece was clamped into the grips of the tensometer (Lhormagy). The stress applied, the load and elongation at break was recorded [20].

2.7.2 Hardness (shore A)
Test pieces from the moulded spherical rubber pieces were clamped onto a durometer (Instrol Wilson) and the penetration of the indenter measured.

2.8 Mechanical characterisation
About 19 mm diameter and approximately 2 mm thickness were punched out from composite sheets. The dried coupon was weighed. The samples were then immersed in 20 mL of water at room temperature. The coupons were periodically removed from the liquid, towel dried of any surface liquid and weighed. Samples were initially weighed hourly followed by once a day and eventually after a couple of days [28]. Weighing was continued until equilibrium swelling was reached.

3 RESULTS AND DISCUSSION

3.1 Chemical Properties

3.1.1 Chemical Composition of Modified and Unmodified Maize Stalk

Table 2 shows a comparative study of the chemical components in maize stalk. Differences in percentage compositions are attributed to different geographic locations, ages, climate and soil conditions in which maize plants were grown. Since cellulose is the component present in largest amount its characteristics will have the greatest impact on the composite's physical properties. The mean acetic acid and acetyl content of the acetylated maize are 30.1 and 21.6% respectively.

TABLE 2
COMPARATIVE CHEMICAL COMPOSITION OF
COMPONENTS IN MAIZE STALK

| Component	Composition (%)	Reference
Cellulose	30-40	[29]
	28	[25]
	33-37	Current study
lignin	28	[29]
	16	[25]
	20-23	Current study
Hemicelluloses	17-21	[29]
	17-21	[25]
	15-23	Current study

3.1.2 FTIR Studies

Fig.1 shows that there is a difference in chemical structures of FTIR spectra for the unmodified and modified maize stalks due to chemical modification. Comparison of the two spectra shows that there is emergence of new absorption peaks upon acetylation. The main difference between the spectra is the presence of a clear and well defined peak at 1742 cm^{-1}. This peak is attributed to the carbonyl groups (–C=O) stretch, confirming formation of new acetyl groups in cellulose. This peak is due to an esterification reaction that results in an increased stretching vibration of C=O group of the ester linkage [30]. The absorption in this region is attributed to both the C=O groups in the acid and ester groups attached to maize stalk. If the –COCH$_3$ groups were in the form of acetic acid, then the stretching of C=O should have appeared below 1720cm^{-1} in the case of diacids and at about 1760cm^{-1} in the case of monoacids. The appearance of a new peak at 1244 cm^{-1}, attributed to C-O stretching of the ester linkage further confirms that an esterification reaction occurred. The spectrum of unmodified cellulose shows an absorption peak at 1375 cm^{-1} attributed to the –CH- bond vibration. After esterification, the added contribution of the acetyl (-C-CH$_3$) stretching vibration produces a more intense absorption peak [31]. A reduction in the broadening of the peak ranging from 3300 to 3800 cm^{-1} due to hydrogen bonded -OH vibrations of the cellulose structures of maize stalk powder upon chemical modification also confirms esterification. The absence of a peak in the region 1840-1790 cm^{-1} of the spectrum of acetylated maize stalk sample is indicative of the fact that the acetylated product was free of unreacted acetic anhydride [31]. Absence of a peak at 1700 cm^{-1} for a carboxylic group in the spectra of acetylated samples also indicates that the acetylated product is free of the acetic acid by-product.
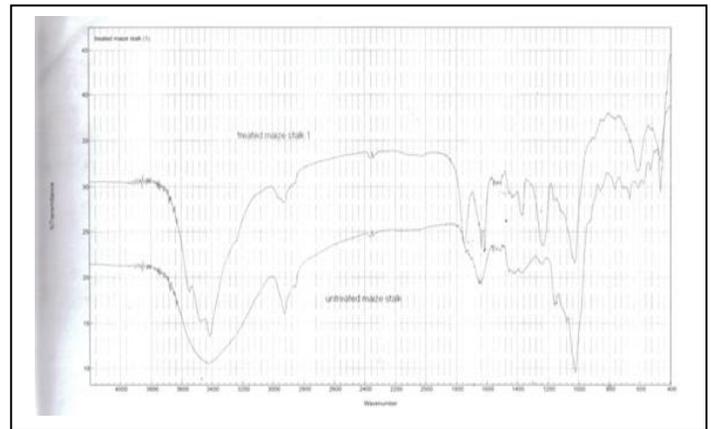
Fig.1. FTIR spectra of untreated and treated maize stalk powder.

3.1.3 Cure Characteristics

Fig. 2 shows rheographs of unfilled natural rubber and rubber composites filled with three different types of fillers at 30 parts per hundred (phr) filler loading. The maximum torque (M$_H$) gives an idea about the crosslink density and the degree of reinforcement of the filler in the matrix. M$_H$ has been found to be higher for the filled samples compared to unfilled natural rubber. The increase in M$_H$ value is due to increased restriction to polymer chain mobility and viscosity of the mixes caused by filler reinforcement [32]. The maximum torque for untreated maize-rubber composite is lower that the treated one. This could be explained in terms of introduction of the carbonyl groups during acetylation which improves the compatibility between maize fibre and the rubber matrix. M$_H$ of hydrated silica (commercial) rubber composite is higher than that of chemically modified maize. This is attributed to the highest reactivity of commercial filler among all the used fillers giving the maximum reinforcement in the matrix and hence the highest M$_H$.
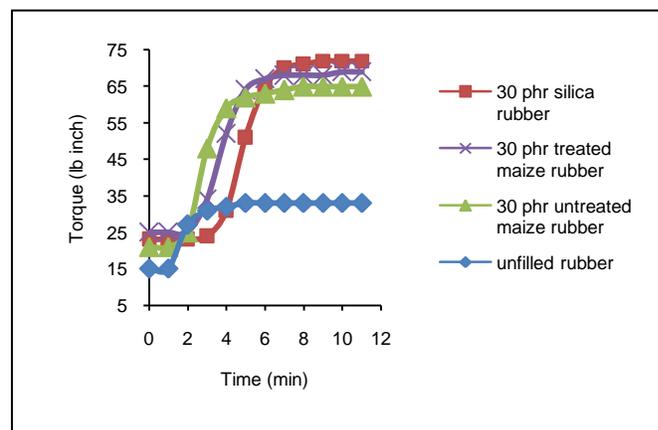
Fig.2. Torque as a function of time for natural rubber and rubber composites filled with 30 phr of different fillers.

Fig. 3 shows the maximum torque as a function of filler loading deduced from the rheographs. At any given filler loading, the commercial filler rubber composite shows the highest M$_H$ value while the untreated maize stalk filled rubber composites show the least M$_H$ values. For all composites, the torque value increases with increase in filler loading. The increase in torque values with increasing filler content indicates that as more and

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more filler gets reinforced into the matrix, the mobility of macromolecular chains of natural rubber becomes reduced resulting in more rigid vulcanisates [22]. These observed trends are in agreement with results reported by Hussain et al. [7] using isorafibre as a filler for polar and nonpolar rubber. The increase in torque with increasing filler loading is attributed to the increase of the crosslink density.
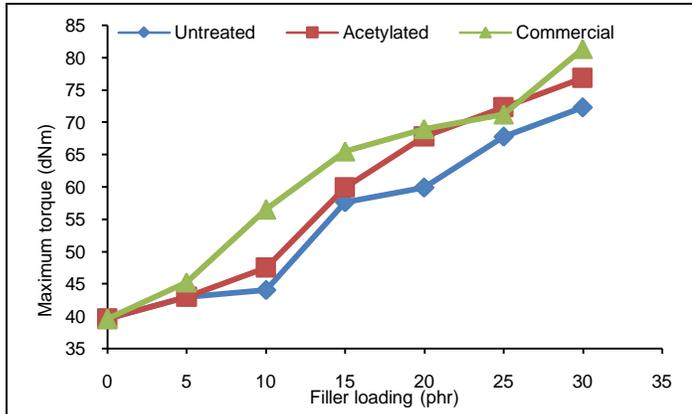
Fig.3. Effect of filler loading on maximum torque of different natural rubber composites (filled with untreated, treated maize stalk powder and commercial filler).

3.1.4. Scotch Time
Fig. 4 shows the scotch time as a function of filler loading for different rubber composites. There was a decrease in scotch time with increasing filler loading. Lopattananon et al. [33] also reported similar results using bamboo and pineapple leaffibres as fillers for natural rubber. The decrease in scotch time for all the formulations was due to the restriction of mobility and deformation of the matrix with the introduction of mechanical restraints [7]. The formulation with modified maize stalk and commercial filler had higher scotch time than the unmodified maize stalk due to good dispersibility of the modified and commercial filler in the rubber matrix. Chemical modification of the maize stalk renders the fibre surface more hydrophobic, enhancing its compatibility with the hydrophobic rubber matrix [30].
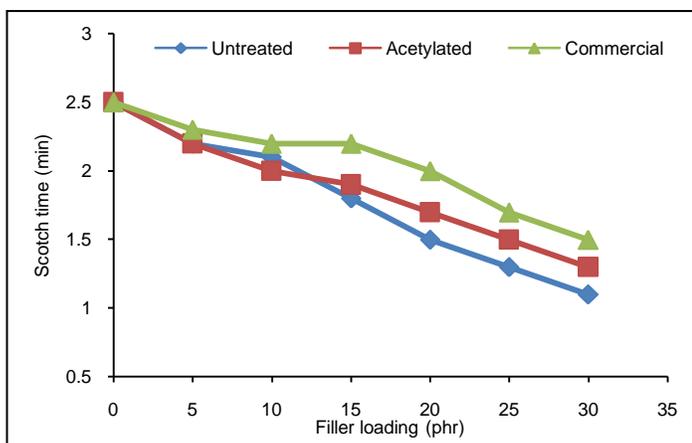
Fig.4. Effect of filler loading on scotch time of natural rubber composites filled with untreated, acetylated maize stalk fibre and commercial filler.

3.1.5 Cure Time
Curing refers to heat treatment which changes the physical properties of a substance due to a chemical process, resulting in the formation of a more durable product. Cure time of natural rubber composites decreased with increasing filler loading as shown in Fig. 5. The reduction in cure time of the filled vulcanisates was attributed to the higher time the rubber compounds remain in the mill during mixing. As the filler loading increases, the time of incorporation also increases and consequently generates more heat due to friction. Cure time of acetylated maize stalk fibre filled natural rubber is higher than that of the untreated maize fibre filled composites. In general, a faster cure time is obtained with fillers having high moisture content. It was reported that cure rate is directly related to humidity and water content of the rubber compound. The higher the moisture content, the faster the cure time [21]. Chemical modification with acetic anhydride (CH_3-C(=O)-O-C(=O)-CH_3) substitutes the polymer hydroxyl groups of the cell wall with acetyl groups, modifying the properties of these polymers so that they become hydrophobic. Lignocellulosicfibres esterified with acetic anhydride and used to prepare composites present reduced moisture absorption of both the fibres and the resulting composites in comparison with untreated systems [30].
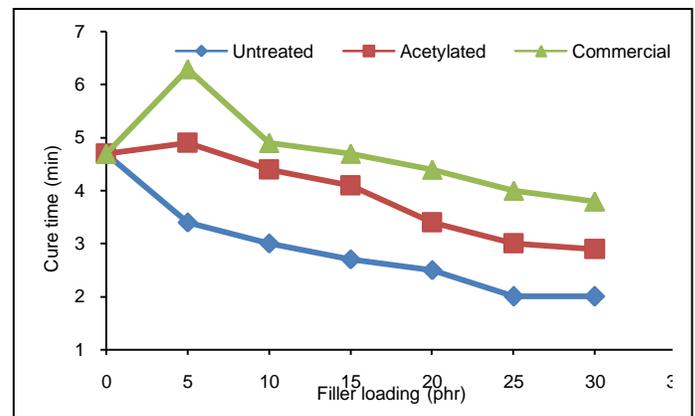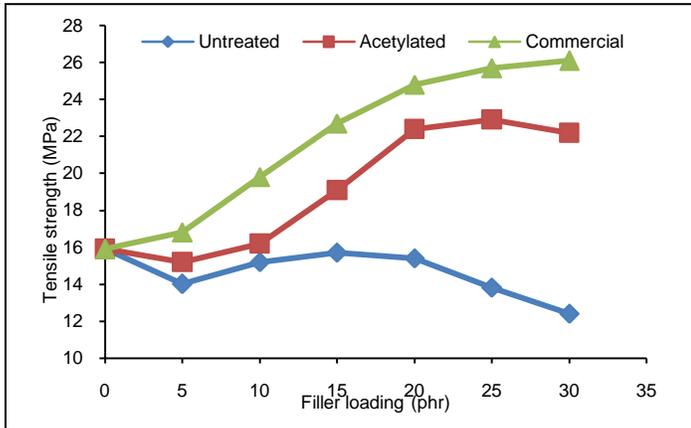

Fig.5. Effect of filler loading on cure time of natural rubber composites filled with untreated, acetylated maize stalk powder and commercial filler.

3.2 Chemical Properties

3.2.1 Tensile Properties
Tensile strength of natural rubber composites as a function of filler loading is shown in Fig. 6. The tensile strength of unfilled natural rubber is 16 MPa. Introduction of unmodified maize fibre produces a rubber composite with lower tensile strength compared to the natural rubber. At loadings below 10phr, the maize treated rubber composite has a lower tensile strength than the natural rubber. Natural rubber inherently has high tensile strength owing to strain-induced crystallization [34]. On incorporating the fibres into the matrix, the regular arrangement of rubber molecules is disrupted resulting in loss of strain-induced crystallisation. The tensile strength of natural rubber increases with increase in filler loading using the commercial filler. However, the tensile strength of treated maize-rubber composites increases from 10 to 25 phr. The decrease in tensile strength above 25 phr is due to high fibre population leading to fibre agglomeration resulting in difficult

stress transmission from matrix to fibre and disturbance of the continuity of the matrix phase. The decrease in tensile strength indicate the loading at which the filler bears more of the stress and it somehow shows the limiting loading levels. A similar trend was reported by Mathew and Joseph [35] using isorafibre-natural rubber composites.
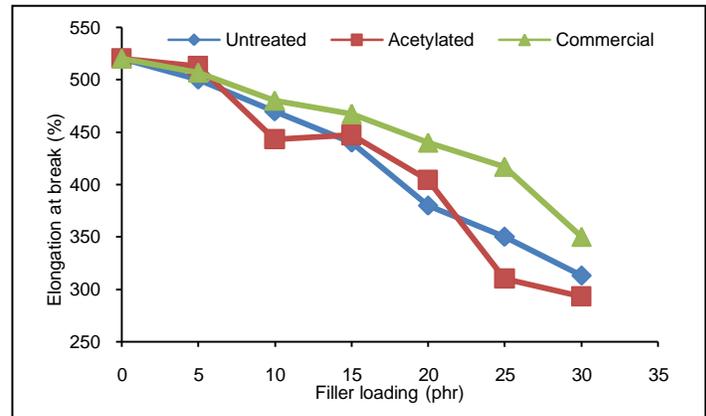

Fig.6. Effect of filler loading on tensile strength of natural rubber composites filled with untreated, acetylated maize stalk powder and commercial filler.

The acetylated maize-rubber composite always exhibited a higher tensile strength than the untreated maize rubber composite. It has been reported [7] that the acetylation treatment increases the dispersibility of the fibre in the natural rubber matrix which enhances the mechanical properties. More so, acetylation leads to fibre fibrillation i.e., breaking down of fibre bundles into smaller fibres, which increases the effective surface area available for contact with the matrix. It results in improvement in the interfacial bonding by giving rise to additional sites of mechanical interlocking, thereby promoting more resin fibre interpenetration at the surface. According to Bledzki et al. [26], when fibres are acetylated, the increase in tensile strength could be also due to the removal of lignin and extractible, slight increase in cellulose content and a little portion of hemicellulose converting to acetylated hemicelluloses. Acetylation of maize stalk fibre removed waxy material from fibre surface, increased fibre-matrix interfacial strength and increased surface free energy which are favourable for better properties of composites. The stress transfer ability at fibre-matrix interface of the composites subjected to a given tensile loading was efficiently improved. Bledzki et al. [26] also observed similar results on acetylated flax fibre polypropylene natural rubber composites.

3.2.2 Elongation at Break
The effect of the filler loading on the elongation at break is shown in Fig. 7. The values of elongation at break (EB) decrease with the increase in loading for all the fillers. A decrease in elongation at break is explained in terms of adherence of the filler to the rubber polymer matrix leading to the stiffening of the polymer chain and hence resistance to stretch when the strain is applied [36].


Fig.7. Effect of filler loading on elongation at break of natural rubber composites filled with untreated, treated maize stalk fibre and commercial filler.
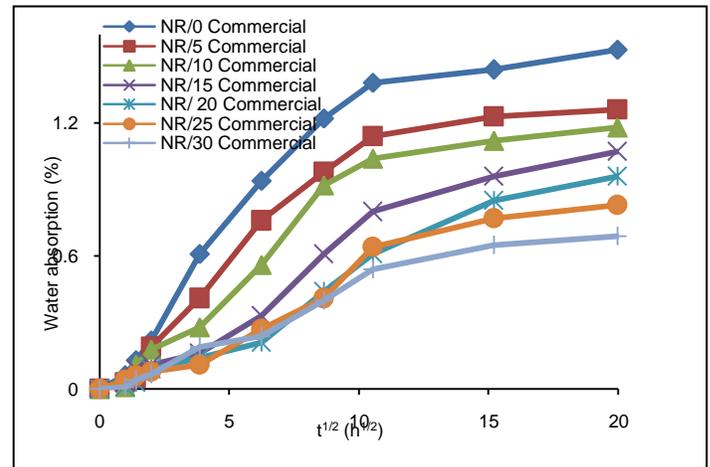
3.3 Water Absorption Kinetics
Liquid swelling experiments were performed on rubber composites to monitor their performance in water and to study the characteristics of rubber-fibreinterface. Figs. 9 and 10 show the percentage moisture uptake of untreated and treated maize stalk reinforced composites as a function of square root of time at different filler loadings. The time axis on the plot was plotted as square root of time in order to conform to Fick's law. Moisture content was determined using Equation 1.

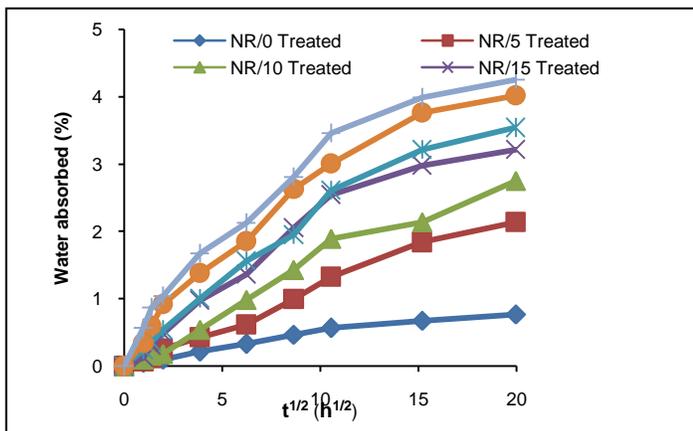$$M_t = 100 \times \left(\frac{w_t - w_o}{w_o} \right) \qquad (1)$$

Where: M_t is the amount of water absorbed at time t, w_o is the initial sample weight and w_t is the sample weight after absorbing water for a time t [15], [20]. It can be seen that composites with higher fibre loadings show greater moisture absorption capacity at any given time. This is because of the hydrophilic nature of natural fibres that make them absorb a lot of water. At any given filler loading, untreated rubber composites absorb more water than acetylated maize rubber composites. This is due to decreased hydrophilicity of maize stalk fibres as a result of acetylation and the enhanced interfacial bonding between the fibre and matrix that prevent the fibre from absorbing water. An increase in fibre content in the rubber composite increases the volume of the interfacial region, where the water molecules can be easily absorbed.
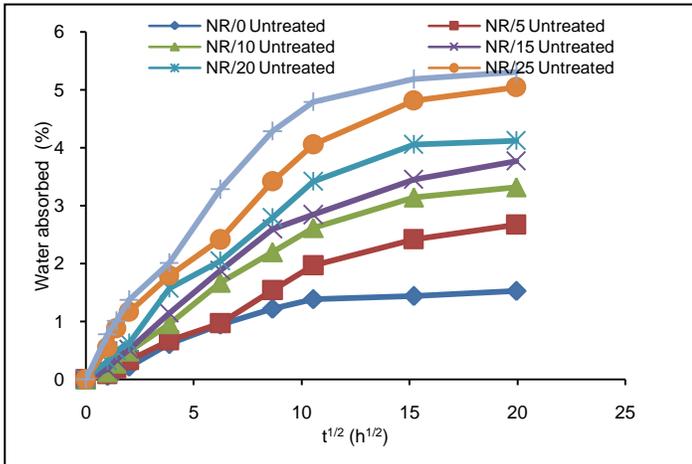
Fig.9. Water absorption of untreated maize-natural rubber (NR) composites against $t^{1/2}$ at different filler loadings.

Fig.10. Water absorption of the treated natural rubber (NR) composites against $t^{1/2}$ at different maize stalk filler loadings.

Fig. 11 shows the sorption curves of hydrated silica (commercial) rubber composites. Compared to maize-rubber composites, hydrated silica-rubber composites absorb less moisture. This is due to lower hydrophilicity of silica. Vulcanization restrains the long-range movements of the polymer molecules but leaves their local segmental mobility high. Reinforcement restricts these local freedoms of movement and thereby improves water resistance. Dasan et al. [37] investigated the solvent transport through carbon black filled poly(ethylene-co-vinyl acetate) composites and obtained similar results. They concluded that the fillers form chemical as well as physical crosslinks with the polymer chains experiencing a certain level of immobilization. This complex crosslink clusters prevent the rearrangement of the polymer chains during solvent ingression and reduces the free volume in the composite, thereby causing resistance to the path of penetrants [38].

Fig.11. Water absorption of hydrated silica (commercial) rubber composites against $t^{1/2}$.

3.3.1 Mode of Transport
The movement of liquids through rubber compounds follows different mechanisms depending upon various factors such as chemical nature of rubber and vulcanizing agents, dimension and shape of the filler, rubber-filler compatibility, and interfacial adhesion between the filler and matrix. The liquid diffusion can be Fickian, non-Fickian, or anomalous [20]. Different diffusion cases can be distinguished from the shape of the curve provided by Equation 2.

$$\frac{M_t}{M_m} = kt^n \qquad (2)$$

Where: M_m is the maximum moisture content and k and n are constants. In this analysis, the experimental data were fitted to the logarithmic expression (Equation 3) with the slope determining the diffusion case.

$$\log\left(\frac{M_t}{M_m}\right) = \log k + n \log t \qquad (3)$$

Typical plots of the fitting of the experimental data to Equation 3 for treated and untreated maize natural rubber composites are shown in Figs. 12 and 13.
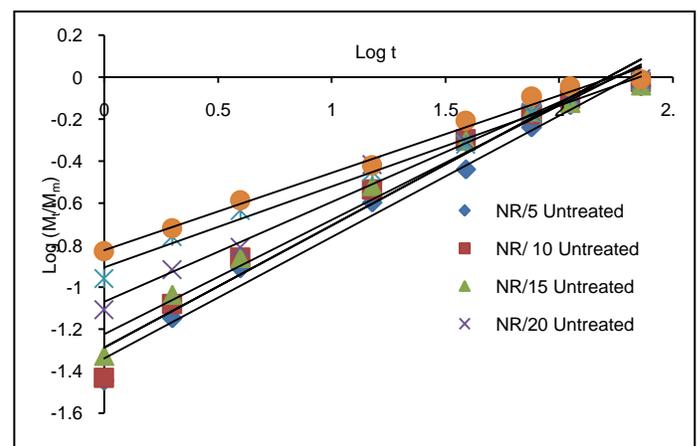
Fig.12. Diffusion case fitting plot for untreated maize stalk-natural rubber (NR) composites immersed in water.

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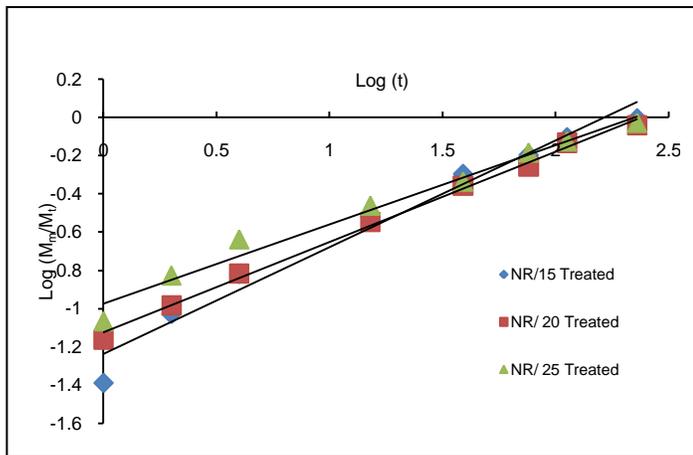
Fig.13. Diffusion case fitting plot for treated maize stalk-natural rubber (NR) composites immersed in water.

The values of the parameters n and k calculated from the fitting of the experimental data to Equation 3 are shown in Table 3. It can be concluded that the diffusional behaviour approaches the Fickian case, since all n values are close to 0.5, a representative for Fickian diffusion. The factor k is a constant that varies with the structure of rubber and provides an idea about the interaction between the rubber compound and water. It can be observed that the value of k is lower for the unfilled natural than for the composites. This is due to lower interaction and sorption of non-polar natural rubber in polar water [37]. The value of k increases with an increase in filler loading indicating the increase in the interaction of the composites with water as fibre loading increases. This is explained by the increase in hydroxyl groups (hydrophilicity) of the system at higher fibre loading [39]. This results in enhanced hydrogen bonding between maize stalk fibre and water molecules.

TABLE 3
CALCULATED VALUES OF n AND k FOR MAIZE RUBBER COMPOSITES

Rubber composite	Maize filler loading (%)	n	k
Chemically modified	0	0.5861	0.0378
	5	0.5720	0.0400
	10	0.5955	0.0540
	15	0.5586	0.0578
	20	0.4782	0.0749
	25	0.4138	0.1060
	30	0.3485	0.1480
Unmodified	5	0.5784	0.0458
	10	0.5819	0.0515
	15	0.5445	0.0598
	20	0.4759	0.0852
	25	0.3849	0.1242
	30	0.3682	0.1504

4   CONCLUSION

Maize stalk has demonstrated its potential to be used as filler in natural rubber. FTIR results confirm acetylation of maize fibres indicated by appearance of a new peak at 1742 cm^{-1} (attributed to the carbonyl groups –C=O). Chemical modification results in enhancement of interfacial adhesion between the fibre and natural rubber matrix. Acetylated maize fibrenatural rubber composites show better physico-mechanical properties than untreated maize fiber natural rubber composites at all fibre loadings.

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