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Comparative Study of Acetylated Sawdust Powder as Filler in Natural Rubber Compounding

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Abstract

A comparative study of the filler's reinforcing potentials of acetylated sawdust, non- acetylated sawdust and those filled with the conventional N330 carbon black was investigated. The sawdust was sourced and characterized in terms of moisture content, bulk density, pH, ash content and iodine adsorption number, using prescribed methods. Natural rubber samples were compounded with 50% acetylated sawdust powder, non- acetylated sawdust powder and with that of the N330 carbon black at filler loading levels of 10phr, 20phr, 30phr, 40phr and 50phr respectively. Standard formulation with efficient vulcanization system was used. The physico mechanical properties of the acetylated sawdust powder filled vulcanizates were compared with those filled with untreated Sawdust and N330 carbon black. The result obtained show that the acetylated sawdust filled vulcanizates present better tensile strength than the untreated sawdust. N330 carbon black had the highest value for tensile test which shows from the result obtained that N330 carbon black is more effective as reinforcing filler than the acetylated sawdust filled and non- acetylated sawdust filled vulcanizates

1. Introduction

In the raw state, rubber has virtually no engineering application. It becomes necessary to incorporate additive into the polymer in order to ensure easy processing characteristics, desired cure properties in the finished products, cost of products and enhancement of service performance [1]. Recent research has proved that more than 65% of chemist, scientist, engineers and nearly all physicists are involved with research or developmental work with polymers [2]. Fillers are one and the most frequently used additives in the processing of polymers. In the rubber industries, apart from reducing cost, fillers help to enhance mechanical properties such as tensile strength, abrasion resistance and improve processing characteristics. Carbon black (CB) is one of the most important conventional reinforcing fillers especially for the rubber industry and carbon black is a petroleum oil derived product and it is very expensive. Carbon black unceasing accessibility could be a threat due to depletion.

Natural fibres and locally sourced agricultural by – products have been discovered as potential alternative fillers over the years as a result of investigation. However, natural fibres exhibit a high degree of hydrophilicity due to attraction or interaction between hydroxyl groups of the structure consisting mainly of fibre components and other non-fibrous components [3]. The high moisture content of sensitivity of natural fibres causes dimensional instability and limits the use of fibres as reinforcement in composite material [4].

Chemical treatment of the natural or cellulosic fibres by acetylation process involves the pretreatment of fibres with acetylating agents in order to produce high quality moisture resisting fibres. It involves the substitution of the hydroxyl groups of the fibre with the acetyl groups thereby making it hydrophobic [5]. Acetylation leads to the development of rough topography that results in better fibre matrix interface adhesion and increase in mechanical properties [6,7].

Sawdust a by – product of wood processing is often referred to as a waste. In developing country like Nigeria, proper utilization of sawmills waste has not been fully harnessed. The sawmills often are faced with the challenge of disposing the waste material, thus constituting environmental problem and therefore land pollution.

The main objective of this work is to assess and compare the performance level of acetylated saw-dust powder, non-acetylated sawdust. The conventional carbon black was used as the control in this study.

2. Methodology

2.1 Materials

Natural rubber (SAR3) was obtained from the Rubber Research Institute Iyanomoh, Benin City, Nigeria. Sawdust was obtained from wood workshop in Auchi, Edo State. The other reagents and ingredients (zinc oxide, stearic acid, trimethyl quinoline, (TMQ), processing oil etc.) were obtained from commercial sources and used as received.

Sawdust was thoroughly washed to remove sand and possible impurities. It was milled and sieved using 75µm screen gauze and stored for further analysis.

Acetylation Process: the saw dust was immersed in 5 % NaOH solution for 1 hr at room temperature; the alkaline-treated saw dust was soaked in glacial acetic acid for 1 hr at room temperature; it was decanted and soaked in 10 % acetic anhydride containing one drop of concentrated H_2SO_4 for 5 min.

$$\text{Fiber} - \text{OH} + \text{CH}_3\text{CO}^- \rightarrow \text{Fiber} - \text{OOCCH}_3 + \text{H}^+$$

2.2 Characterization of the Saw Dust

Moisture content was determined for the untreated and treated samples in an oven, maintained at temperature of 125°C for an hour (ASTMD 1509). The p^H of the slurry of the untreated and mercerized sawdust was determined as described by Ishak [8]. The bulk density of the various samples was determined by the tapping procedure as described by Ishak [8]. The ash content of the untreated and treated sawdust was determined; using gravimetric method.

The FTIR was determined to ascertain the changes in the functional groups of the sawdust after treatment.

2.3 Preparation of the Vulcanizates

The formulation of the mixes was based on ASTM 3184 [9] as shown in Table 1:

Table 1: Formulation for Compounding Natural Rubber at varying Loading

Ingredients	**Part per Hundred (Phr)**
Natural Rubber	100
Filler (TSD)	10/20/30/40/50
Filler (USD)	10/20/30/40/50
Filler (CB)	10/20/30/40/50
Zine oxide	5.0
Stearic acid	2.5
Sulphur	1.5
MBTS	1.5
Processing Oil	5.0

A batch factor of four was used to multiply weight of the ingredients in phr
(TSD)- Treated sawdust powder. (USD)- Untreated sawdust powder. (CB) - Carbon black

The compounding was carried out on a two-roll mill after pre-heating the rolls up to a controlled temperature of 80^{o}C to avoid cross linking during the mixing. The efficient vulcanization system was adopted in designing the formulation.

2.4 Determination of the Properties of the Vulcanizates

The curing of the test pieces was done using compression moulding machine. The curing was carried out at 130^{o}C for 25 minutes. The tensile strength, modulus and elongation at break were measured using a Monsanto Instron Tensometer in accordance with ASTMD412-87 method A [10]. Dumbbell test pieces of dimension (4552mm) were used.
The hardness of the vulcanizates was measured with a Wallace hardness taster model
C8007/25 in accordance with ASTM 1415, [11], abrasion resistance measurement was based on DIN to 1504646 Akron to B5 905 part 49 method [12]. Compression set test measurement was based on ASTM 385 [13].

3. Results and Discussion

3.1 Results of the Characteristics of the acetylated and untreated sawdust and N330 carbon black

The physical properties of the treated and the untreated sawdust powder and that of carbon black are shown in Table 2. The result indicated that the p^{H} of the treated and the untreated sawdust are 6.60 and 6.93 respectively which are relatively close to the P^{H} values of N330 carbon black as shown in Table 2, this is an indication that the treated and untreated sawdust powder are slightly acidic, therefore when used as fillers in compounding, the rate of cure of vulcanizate will be expected to be high and enhance less time of cure and little amount of accelerators may be needed [14]. The percentage weight loss and the moisture content of the treated and untreated sawdust are 3.20% and 5.83% respectively with the treated sawdust lower which is as a result of the chemical treatment or modification these values indicate low level of moisture contents even though higher than that of carbon black which is 2.41%. The result however shows that the effect of moisture at this level on the properties of the vulcanizate will be negligible and discountenanced.
Weight loss on ignition is a measure of the carbon content lost during combustion and measures the effectiveness of the filler and its reinforcement potentials. The result in Table 2 shows that weight loss on ignition for the treated sawdust is greater than that of untreated sawdust but lesser

than N330 carbon black. The higher the values the greater the reinforcing potentials [15]. This is an indication that treated sawdust is more reinforcing than the untreated sawdust but less reinforcing than the carbon black.

Table 2: Characteristics of Fillers Test Results

PARAMETERS	TREATED SAWDUST	UNTREATED SAWDUST	CARBONBLACK
pH values	6.60	6.93	6.50
Moisture content (%)	3.20	5.83	2.41
Ash content (%)	9.38	25.20	7.12
Bulk Density g/em^3	0.28	0.86	6.35
Iodine adsorption number (mg/gwt.)	385.5	154.8	547.3
Loss on ignition (%) at125^0 C	90.62	75.20	92.80

The bulk density of the treated and untreated sawdust is 0.28g/cm^3 and 0.86g/cm^3 respectively. The bulk density is mainly influenced by the particle size and structure of the fiber and the lower the particle size, the lower the bulk density and therefore the better the interaction between the polymer matrix and the reinforcing fiber [16]. The bulk density of the treated sawdust is lower than the untreated sawdust which means that the treated sawdust has a better reinforcing potential. However, compared to that of the carbon; the carbon has a far better reinforcement properties as shown in Table 2. This shows that the compounded material could be used for foot mat and shoe sole, unlike the carbon black that is used for tire production. The results obtained for the iodine adsorption number from Table 2 indicate that the value for the treated sawdust is significantly higher than that of the untreated sawdust but less than N330 carbon black. The higher the value, the larger the surface area and the more reinforcing the filler becomes hence it can be postulated that the treated sawdust powder could be more reinforcing than the untreated sawdust but not as reinforcing as carbon black.

3.2 FTIR Analysis

The FTIR spectral of the untreated and treated sawdust is shown in Figure 1, however, the untreated absorption bands in the region of 3380 cm^{-1}, 2968 cm^{-1} and 1663 cm^{-1} are as a result of the O-H stretch, C-H stretch, and C=C stretch, respectively; representing the hydroxyl group in the cellulose, carbonyl group in the hemicellulose, and carbonyl aldehyde in the lignin. The treated sawdust absorption band show that O-H slightly shifted towards 3380cm^{-1} and at C-H stretch absorbance shifted towards 2951 cm^{-1} respectively. It can be deduced that, the carbonyl peak C=C at 1663 cm^{-1} was slightly shifted towards 1682 cm^{-1} in the spectra of treated sawdust because the carbonyl bonds in the hemicellulose was broken as a result of the chemical treatment. The C-N stretch at 1059cm^{-1} representing an alkene also shifted to 1061 and 626cm^{-1} C-H bend which is an alkyne group shifted to 641cm^{-1}.

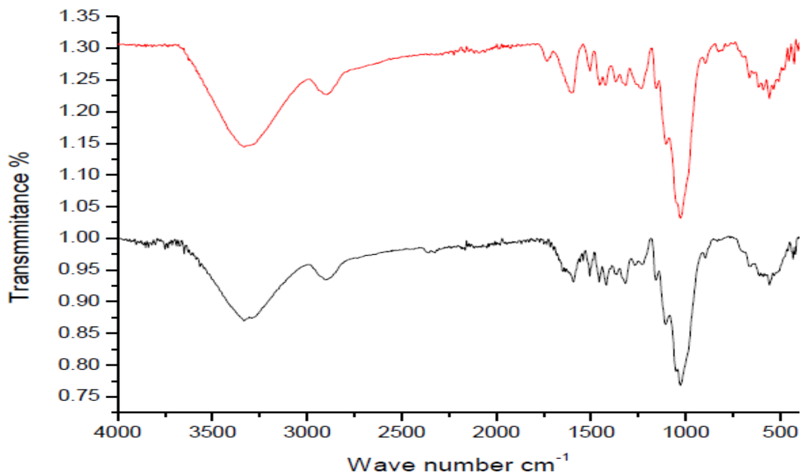

Figure 1: FTIR of untreated and treated sawdust (Red – untreated, Black - treated

3.3 Results of the Physico Mechanical Properties of the Untreated, Treated Sawdust and Carbon Black filled Natural Rubber Vulcanizates

Table 3: Properties of the Untreated, Treated Sawdust and Carbon Black filled Natural Rubber Vulcanizates

	USD					TSD					CD				
Filler loading level	10	20	30	40	50	10	20	30	40	50	10	20	30	40	50
Tensile strength (Mpa)	7.52	10.10	12.74	15.30	20.10	10.21	14.36	26.95	25.10	32.42	18.30	27.40	31.32	35.20	43.50
Modulus at (100%)	1.72	1.79	1.83	1.98	2.08	2.90	3.36	5.92	7.10	10.12	3.12	5.50	7.65	10.96	13.20
Elongation at Break %	275	251	234	211	192	398	374	350	340	285	431	413	400	377	300
Compression Set %	25.40	21.60	20.00	18.25	17.00	16.52	18.33	15.30	10.98	9.98	14.40	12.30	11.04	9.40	8.60
Hardness (IRHD)	24.62	25.56	26.30	27.20	32.61	38.10	40.00	44.32	44.96	45.20	59.20	61.30	63.20	66.90	67.00
Abrasion Resistance	17.71	20.45	23.41	25.30	29.10	30 50	34.30	37.10	39.33	41.30	44.20	50.54	57.54	61.24	61.34

The physico-mechanical properties of the natural rubber filled with treated sawdust powder, the untreated sawdust powder and that of the carbon black are shown in Table 3. The results show that there is an improvement in the tensile properties of the treated sample over the untreated vulcanizates.

The tensile strength and modulus at 100% obtained were less for untreated sawdust compared to the treated sawdust and the carbon black. This indicates that treated sawdust had effect on the vulcanizates. In all filled systems, the tensile strength and modulus at 100% increase with increasing filler content until a maximum level is reached as shown in Table 3. A further loading reduces this property. The marked increase in tensile strength with increasing filler loading for the treated and the carbon black filers could be as a result of the superior surface area and loss on the ignition of the treated sawdust and the carbon black fillers over the untreated sawdust .The results indicate that the tensile strength for the treated sawdust is stronger than the untreated. This suggests a better surface area, surface reactivity and a better polymer filler interaction.

The results in Table 3 also show the value of elongation at break as a function of filler loading for the treated /untreated sawdust and the carbon black. The values of elongation at break at break (EAB) decrease with increase in filler content or the mixes for all the fillers. The decrease in elongation at break with the increasing filler loading may be due to the adherence of the filler to the polymer phase or matrix leading to stiffening or the polymer chain and hence resistance to stretch when a strain is applied [17].
The result for elongation at break (EAB) in Table 3 for the treated sawdust filled vulcanizates approached that of N330 carbon black than the untreated sawdust showing a superior service performance.

The compression set results in Table 3 show that as the filler type and loading increase the compression set decreases for both treated, untreated sawdust and carbon black filled vulcanizates.

However, the vulcanizates filled with carbon black has the lowest compression set followed by treated sawdust. The observation may not be unconnected with the amount of filler incorporated into the matrix, the degree of dispersion of the filler and its particle size. As the filler loading increases, it should be expected that more and more filler particles and aggregates not be dispersed and wetted sufficiently by the rubber matrix [18]. The results for the hardness in Table 3 indicate that hardness values increase with increasing filler loading. This is an expected trend because as more fillers get into the rubber, the elasticity of the rubber chain is reduced resulting in a more rigid, vulcanizates, the hardness result for carbon black is the highest followed by treated sawdust and then untreated sawdust, this indicates that the reinforcing potential has more towards carbon black followed by treated sawdust powder.

Abrasion resistance of a solid body is defined as its ability to withstand the progressive removal of the material from its surface resulting from mechanical action of rubbing, scraping or erosive nature. Abrasion resistance increases marginally with increasing filler loading or concentration for all the all the samples as shown in Table 3. This may be due to the fact as the filler loading increases the strength of adhesion between the polymer matrix and the filler become very strong. The results also indicated that abrasion resistance of vulcanizate filled with treated sawdust has a better resistance of surface scratch than the untreated sawdust however N330 CB performs better.

4. Conclusion

The ultimate aim of this research is an attempt at assessing and comparing the filler properties in natural rubber filled with treated and untreated sawdust powder with that of carbon black. The results from this study shows that in comparing the physico mechanical properties of the vulcanizates which serve as a function of reinforcing properties of fillers used at different loading levels, treated sawdust filler was found to be comparable to N330 carbon black than the untreated sawdust. These results predict that the reinforcing potentials of treated sawdust as low cost filler is better than the untreated sawdust and is more comparable to N330 carbon black in some measured properties.

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