Utilization of chitin powder as a filler in natural rubber vulcanizates: In comparison with carbon black filler

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ABSTRACT

Natural rubber (NR) vulcanizates were prepared from natural rubber and chitin using a two-roll mill. The chitin was extracted from crab shell waste obtained from a local market in Oron, Akwa Ibom State, Nigeria using the chemical extraction method. The effects of the chitin at different contents (0–40 phr) on the mechanical properties of the NR/Chitin vulcanizates with carbon black as reference filler have been investigated. The tensile strength of the chitin filled natural rubber (NCH), and the carbon black filled natural rubber (NCB) vulcanizates were found to increase with an increase in filler content to reach optimum at 30 phr after which it decreased. The hardness, impact and abrasion resistance properties of the NCH and NCB vulcanizates increased as filler content increases. The tensile strength and abrasion resistance of the vulcanizates containing blends of varying percentages of carbon black to chitin (CBCH) increased as more carbon black (CB) is introduced while the hardness and impact strength increased with increase in chitin content. However, carbon black filled vulcanizates showed better property enhancement than the chitin filler.

KEYWORDS

natural rubber, chitin, carbon black, vulcanizate, mechanical properties

1. INTRODUCTION

Elastomeric materials have a wide range of applications due to their inherent reversible deformation characteristics. Natural rubber is a prototype of an elastomer. Due to the high structural regularity of natural rubber, it tends to crystallize spontaneously at low temperatures or when stretched [1]. Natural rubber in its natural state has virtually no engineering applications. Natural rubber is therefore vulcanized to make it less sticky and have superior mechanical properties. However, there is a limit to the mechanical properties of rubber that can be achieved by mere vulcanization [2].

The introduction of fillers to natural rubber improves its properties such as high stiffness, compression strength, hardness and other physical properties, at the same time it reduces the cost of rubber products [3]. Fillers are grouped according to their sources, colour, properties and morphology [4]. These fillers can be classified based on their properties into reinforcing and non-reinforcing fillers. The reinforcing fillers are those which when introduced into rubber matrix will improve the tensile strength, tear strength, abrasion resistance and other mechanical properties of the rubber vulcanizate, whereas non-reinforcing fillers are added to increase the volume and reduce the cost of elastomeric products [4]. Reinforcement of rubber can be achieved using conventional fillers such as clay, calcium silicate, calcium carbonate and petroleum-based fillers such as carbon black [5]. However, these fillers have limitations which include non-biodegradability, non-recyclability, machine abrasion, high initial processing cost and health hazard [6]. Carbon black causes pollution and gives black colour due
to its origin [7]. The increasing societal desire for environmentally friendly products has led researchers and manufacturers to explore the use of renewable materials as alternatives to the non-renewable conventional fillers [8]. The use of green materials provides an alternative way to solve the problem associated with agricultural residues [9]. The disposal of agricultural residues from plants and animals is inappropriately managed. These wastes pollute our environment. Sibi et al. [10] reported that about 40–50% of the total weight of crustaceans goes as waste while processing human food and the slow degradation of crustacean shell waste has become the major concern in sea food processing industries. Different agro-based fillers have been explored in the reinforcement of natural/synthetic rubber. Igwe and Ejim [11] studied the mechanical and end-use properties of natural rubber filled with snail shell powder. He reported that the introduction of the snail shell powder did not enhance the tensile strength, modulus and elongation at break. Rather, the specific gravity of the rubber vulcanizates increased with increase in snail shell content.

Imanah and Okieimen [12] investigated the rheological and mechanical properties of natural rubber reinforced with agricultural byproduct. It was found that vulcanizates with 40–50% filler loading showed a maximum tensile strength of 8.4 MPa for Cocoa pod powder and 9.5 Mpa for Carbonized Cocoa pod powder. He also reported that the hardness of the vulcanizates increased with increasing filler loading. Egwai-khide et al. [4] did comparative studies of the rheological, physico-mechanical properties of natural rubber compounds, reinforced with carbon black (N330) and blends of raw coconut fibre and carbon black. The result indicated that the addition of filler blends into natural rubber improved the hardness but decreased the tensile strength. Ogbeifun et al. [8] investigated the physico-mechanical properties of natural rubber vulcanizates filled with carbonized agricultural residues. In their study, hardness, abrasion resistance and compression set of the rubber vulcanizates were increased with the addition of carbonized rice shell. Saquoi et al. [13] studied the use of rice husk as filler in natural rubber vulcanizates, in comparison with other commercial fillers. He reported that the mechanical properties of the vulcanizates filled with rice husk ash were comparable to those filled with inert fillers. The influence of fibre length and concentration on the physical properties of wheat husk fibre rubber composite was investigated by Sobhy and Tamman [14]. The result showed that the tensile strength decreased as the filler increased, however, the elongation at break increased with increased filler content. In this present work, chitin extracted from crab shell waste used as reinforcing filler in natural rubber vulcanizate is reported. The filler was sieved to 43 μm and chitin content of 0–40 phr was used with carbon black as the reference filler. Blends of varying percentages of chitin and carbon black at 40 phr basis were also investigated. Crab shell is considered a domestic waste and currently has little or no industrial application in our locality. Chitin is a naturally occurring renewable and biodegradable polysaccharide. Therefore, by combining natural rubber with chitin makes the resultant product biodegradable and environmentally friendly.

2. MATERIALS AND METHODS

Rubber Research Institute of Nigeria supplied Nigeria Standard Rubber Grade 10 (NSR10). Crab shell waste was obtained locally from a local market in Oron, Akwa Ibom State, Nigeria. Analytical grade HCl, NaOH, stearic acid, zinc oxide, Mercapto Benzyl Thiazole (MBT), 2,2,4-Tri-methyl-1,2-dihydroquinoline (TMQ) and sulphur were supplied by Campal Scientific and Technological Company, Bridge Head Market, Onitsha, Nigeria. All mixing ingredients were used as received.

2.1. Preparation of the filler

The shells were separated from the crab, washed thoroughly with distilled water and dried for 6 h at 80 °C. The shells were pulverized to powder form and sieved to 43 μm particle size. The demineralization of the crab shell powder was done using HCl (4% v/v) at a ratio of 1:15 for 24 h at room temperature to remove mineral residues such as calcium carbonate from the shell. The treatment was accompanied by periodic stirring of the mixture followed by continuous rinsing with distilled water until a neutral pH was obtained. The demineralized chitin was deproteinized by boiling with NaOH (2% v/v) at a ratio of 1:10 at 80 °C for 2 h. The process was repeated until a clear colour was obtained indicating the removal of residual protein from the chitin. The flow process for the chitin preparation is shown in Fig. 1.

2.2. Preparation of the rubber compounds

The natural rubber was masticated and mixed with the additives using the two roll mill and adopting the standard method specified in the ASTM D 3184-80 for all the vulcanizates in accordance to the mixing formulation shown in Table 1. Three different batches of natural rubber (NR)/Chitin vulcanizates were prepared. The first batch comprises NR compounded with Chitin (CH) at different filler loadings of 10, 20, 30 and 40 phr labelled NCH10 to NCH40. The second batch comprises NR compounded with Carbon Black (CB) at different filler loadings 10, 20, 30, 40 phr and labelled NCB10 to NCB40. The third batch comprises three sets of formulations of NR compounded with varying blends of Carbon Black/Chitin filler at 40g filler loading basis. The first set consists of 40% Carbon Black (CB) and 60% Chitin (CH). The second set comprises 50% CB and 50% CH. The third set consisted of 60% CB and 40% CH. The batches were labelled CBCH40/60, CBCH50/50 and CBCH60/40, respectively.

2.3. Characteristics of the NS rubber grade 10 (NSR 10) sample

Table 2 shows the characteristics of the Nigeria Standard Rubber Grade 10 (NSR 10) used in this work.
2.4. Testing of the rubber compounds

The mechanical properties of the natural rubber vulcanizates filled with chitin filler with carbon black as reference filler were tested. In accordance with the test standards, the following tests were carried out on the rubber vulcanizates: tensile properties, hardness, abrasion resistance, impact strength. The tensile properties were determined on an Instron Testing Machine as described in ASTM D 638M; the hardness was determined using a Durometer Hardness Shore A according to ASTM D2240. The abrasion resistance was determined on a Wallace Akron Abrasion Tester by ASTM 105, and the impact properties were determined using a RESIL Impactor as described in ASTM D 0256. The FTIR spectra of the filler and the vulcanizate samples were taken by placing a minimal amount of the samples on a Cary 630 Fourier Transform Infrared Spectroscopy. The spectrum from each of the vulcanizate samples showing the functionalities present was then obtained.

3. RESULTS AND DISCUSSION

3.1. Characterization of chitin filler

Table 3 shows some characteristics of the chitin filler extracted from crab shell waste in comparison with that of carbon black which served as the reference filler for this work. The pH of the chitin filler is slightly alkaline at 8.05. This alkaline pH of the chitin filler might be attributed to the method of extraction, as it can be recalled that the shell was treated with sodium hydroxide during the deproteinization process.

The moisture content of the chitin filler is low at 6.56 but higher than that of carbon black at 2.72 as shown in Table 3. This low value is an indication that the chitin filler lost a small amount of moisture on heating whereas carbon black lost the least amount of moisture. The lower the moisture content, the lesser the degree of a defect arising from shrinkage during the curing process at elevated temperatures [4].
The chitin filler has significant iodine adsorption number which is an indication of slightly high surface area whereas carbon black showed a much higher iodine adsorption number (Table 3) indicating that the carbon black has higher surface area than the chitin filler used. The higher the iodine adsorption number of a material, the greater the surface area of that material and the reinforcing potential of the filler [15]. The loss on ignition of the chitin filler is high at 82.9%, which is an indication of the reinforcing potential of the material. The weight loss on ignition is a measure of the carbon content lost during combustion and equally an indication of the effectiveness of the material. The higher the value, the greater the reinforcing potential [15].

| Parameter                  | Chitin  | Carbon black |
|----------------------------|---------|--------------|
| pH of Slurry at 28 °C      | 8.05    | 6.80         |
| Moisture content (%)       | 6.56    | 2.72         |
| Iodine adsorption number (mg/g) | 52.40  | 88.60        |
| Loss on ignition (%)       | 82.90   | 92.00        |

### 3.2. Properties of the natural rubber vulcanizates

The effect of filler loading on the tensile strength of chitin (NCH) and carbon black (NCB) filled natural rubber vulcanizates are shown in Fig. 2. The tensile strength of NCH showed an initial decrease at 10 phr and then increased with increase in chitin content to a maximum tensile strength of 2.11 MPa at 30 phr, after which further increase in chitin content showed a decrease in the tensile strength of NCH. The reference filler NCB showed a steady increase to an optimum tensile strength of 3.75 MPa at 30 phr, after which it decreased with further increase in carbon black. The initial decrease in tensile strength is also reported by Onyeagoro [16] and Arumagam et al. [17].

The initial decrease in tensile strength can be attributed to the inability of the filler to support stresses transferred by the polymer matrix at low filler content and the subsequent increase in tensile strength as filler content increases suggest the ability of the filler to support the stresses transferred by the polymer matrix. This behaviour is in agreement with the study carried out by Hanafi et al. [18]. The decrease in tensile strength after the optimum filler ratio as shown in the figure suggests that as the reinforcement of a material increases, the tensile strength of the material also increases to a point where further reinforcement leads to decrease in tensile strength of the material. A similar result is reported by Jacob et al. [19].

Figure 3 shows the tensile strength of vulcanizates comprising blends of varying percentages of CB and CH at 40 phr filler loading. The result indicates that the tensile strength of the vulcanizates with blends of different proportions of CB and CH increases as the carbon black content of the vulcanizates increases in the order NCH40 < CBCH40/60 < CBCH50/50 < CBCH60/40 < NCB40. The behaviour can be attributed to the higher carbon content and higher surface activity of carbon black than that of chitin. The higher the carbon content, the higher the reinforcing potential. Furthermore, the vulcanizate with 100% chitin at 40 phr (NCH40) has the least tensile strength. As the chitin content is substituted with carbon black, the tensile strength of the vulcanizates increases gradually, with NCB40 as the highest tensile strength. This behaviour makes it evident that chitin filler has poor tensile strength when compared to carbon black. However, the high surface activity of carbon black is an indication of higher filler-matrix interaction of the rubber and carbon black than that between the chitin and natural rubber. The scenario is also evidence of the adsorptive bond between natural rubber and carbon black [20]. Igwe and Ejim [11] reported the similar result of the poor tensile strength of snail shell filled rubber vulcanizates.

Figure 4 shows the effect of filler content on the hardness property of NCH and NCB. The result showed that there is a steady increase in hardness of NCH with an increase in chitin content. The introduction of chitin filler to natural rubber remarkably improved the hardness property of the rubber vulcanizate and can be comparable with that of NCB. It is expected because as filler particles are added to rubber matrix, there is a corresponding reduction in the elasticity of...
the rubber thereby resulting in more rigid rubber vulcanizes. In the case of NCB, it is observed that there is a rapid increase in hardness at 10 phr after which it maintained a steady increase with an increase in carbon black content. The increase in hardness with an increase in filler content is in agreement with the results obtained by Hanafi et al. [18].

The result obtained from blends of varying percentages of CB and CH at 40 phr filler content is shown in Fig. 5. The result indicates that the vulcanize with 60% chitin content (CBCH40/60) has the highest hardness property. As the percentage chitin content is substituted with carbon black, the hardness of the vulcanizes decreased in the order CBCH40/60 > CBCH50/50 > CBCH60/40. It is obvious that the chitin filler gave good hardness property when introduced to rubber.

Figure 6 shows the abrasion resistance property of NCH and NCB. It is seen that there is an increase in abrasion resistance of both the chitin and carbon black filled vulcanizes with increasing filler content up to 30 phr filler content, after which the abrasion resistance decreases as further filler is introduced to the rubber. The carbon black filled rubber vulcanize NCB shows a higher abrasion resistance than that of the chitin filled vulcanize NCH. The increase in abrasion resistance with increasing filler content for both composites is evidence of the fillers’ potentials to withstand or hinder the progressive removal of materials from the surface of the vulcanizes.

As shown in Fig. 7, it is evident that further introduction of filler after the optimum filler ratio of 30 phr, there is a reduction in the abrasion resistance of the composites, which might be as a result of reduced cohesion between the polymer matrix and the filler brought about by excessive filler content in the vulcanizes.

The abrasion resistance of vulcanizes at 40 phr filler content is presented in Fig. 6. It can be seen that the vulcanize with 100% carbon black (NCB40) at 40 phr filler content has the highest abrasion resistance value. The substitution of carbon black with chitin filler in the blends, however, showed a decrease in abrasion resistance of the vulcanizes. The increase in abrasion resistance of the blends with an increase in carbon black content can be attributed to the higher surface activity of carbon black. From Fig. 6, it is evident that vulcanizes reinforced with carbon black filler have more abrasion resistance than those reinforced with chitin filler.
Figure 8 shows the effect of filler loading on the impact resistance of NCH and NCB. It is seen that there is an increase in impact resistance of NCH vulcanizates with increasing filler content with a slight decrease at 30 phr and maximum impact resistance at 40 phr. The increase in impact resistance with an increase in filler content suggests the ability of the filler to support the impact stresses transferred by the polymer matrix. The impact resistance of chitin filled vulcanizate NCH is higher than that of the reference filler NCB. It is evident that the chitin filler improves the impact resistance of natural rubber and this property improves with an increase in chitin content.

The result obtained from the impact resistance of vulcanizates with filler blends of varying percentages of CB and CH at 40 phr filler content is shown in Fig. 9. From the result obtained, it can be seen that the vulcanizate with 100% chitin filler (NCH40) has the highest impact resistance. It is observed that as more of the chitin filler is substituted with carbon black, the impact resistance of the vulcanizates decreases in the order NCH40 > CBCH40/60 > CBCH20/20 > CBCH60/40 > NCB40. This result suggests that the introduction of chitin into natural rubber matrix improved the impact resistance of the natural rubber.

3.3. FTIR spectra analysis

The IR spectra obtained from chitin filler, pure NR vulcanizate and the vulcanizates (NCH, NCB and CBCH) are shown in Figs 10–14. From Fig. 10, the FTIR spectrum of the chitin filler shows the characteristic medium broad absorption bands at 3,257.7 cm⁻¹ showing the presence of O–H stretching present in the chitin chemical structure. It also shows weak absorption band at 3738 cm⁻¹, 1,621.4 cm⁻¹, 3,101 cm⁻¹, the medium band at 1,412.7 cm⁻¹ and a strong peak at 1,025 cm⁻¹ showing the presence of N–H stretching, C=O stretching, C–H stretching, O–H bending and C–O bending functional groups, respectively. From Fig. 13, it can be seen that there are two peaks of strong absorptions bands at 2,918 cm⁻¹ and 2,851.4 cm⁻¹ showing the presence of C–H stretching. From Fig. 13 also, the weak band at 3,749.7 cm⁻¹ shows the presence of N–H stretch of the chitin in

Figure 8. Effect of filler content on the impact resistance of NCH and NCB vulcanizates

Figure 9. Effect of varying percentage of CB and CH filler blends on impact resistance of vulcanizates at 40 phr filler content

Figure 10. FTIR spectrum of chitin
Figure 11. FTIR spectrum of NR vulcanizate

Figure 12. FTIR spectrum of NCB10 vulcanizate

Figure 13. FTIR analysis of NCH 10 vulcanizate
natural rubber. It can be seen that the strong absorption band at 1,595.3 cm$^{-1}$ showing the presence of C═C bonding shown in Fig. 11 has been shifted to 1,654.9 cm$^{-1}$ as shown in Fig. 13 upon incorporation of the chitin filler. The weak band at 1774.2 cm$^{-1}$ confirms the presence of C═O bonding present in the chitin filler as shown in Fig. 14.

4. CONCLUSION

The use of chitin extracted from crab shell waste as filler in natural rubber vulcanizate has been studied. Blends of varying percentages of carbon black and chitin as filler in natural rubber have equally been studied. The tensile strength of chitin filled (NCH) and carbon black filled (NCB) natural rubber vulcanizates were found to increase with an increase in filler content with optimum tensile strengths at 30 phr. Further increase in filler content after 30phr resulted in the decrease in tensile strength of NCH and NCB. The hardness properties, abrasion resistance and impact resistance of NCH and NCB were found to increase with an increase in filler content. The tensile strength and the abrasion resistance of the vulcanizates with blends of varying percentages of CB to CH fillers were found to increase with increasing carbon black filler. However, the hardness and impact resistance of the vulcanizates increased as more carbon black filler was substituted with the chitin filler.

Conflict of interest: Authors declare no conflict of interest regarding the publication.

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