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Swelling behaviour of natural rubber filled with carbon black and plant wastes

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Abstract

Natural rubber (NR) is used in many applications; ranging from automobile through health to food industry. However, unfilled NR has poor properties. The purpose of this study was to evaluate the effects of carbon black (CB), carbonized and un carbonized plant wastes on the swelling behavior of NR. The plant wastes used were corn cob husk (CC), cocoa pod husk (CPH) and empty palm fruit bunch (EPFB). NR vulcanisates with carbon black and different organic wastes fillers were prepared by a two-roll mill. The swelling behavior was studied by immersion in toluene for 72 h. Carbon black and carbonised plant wastes filled NR vulcanisates had better swelling resistance than uncarbonised plant wastes filled NR vulcanisates.

Keywords: Natural Rubber; Fillers; Plant Wastes; Carbonised

1. Introduction

Natural rubber (NR) obtained commercially from Hevea brasiliensis is used in many applications [1, 2]. In its unfilled state, it has very few applications. The properties of raw rubber are usually improved by incorporating additives such as fillers [3]. Over the years, carbon black has been the major filler used in the rubber industry. Carbon black is not a renewable material therefore there is need to evaluate locally available and renewable materials to replace carbon black. Studies on the use of agricultural by- products, such as rice husk, groundnut shell, rubber seed shell, cocoa pod husk, corncob, palm kernel fibre, jute fibre etc. [4,5] as fillers for NR have been carried out. According to [6, 7] the use of organic materials as fillers offer the following advantages; renewable, environmental friendly, low cost, biocompatible, and bio-degradable. Amongst the renewable and locally available agricultural wastes products with little or no use are: cocoa pod husk, corncob and empty palm fruit bunches [8,9]. In order for these materials to be used as fillers for natural rubber, the properties of NR filled these materials such as swelling ratio needs to be evaluated. Plant based fillers have poor resistance to moisture absorption and this causes swelling and quality variation in plant filler-based composites [10].

The swelling behavior of composites is quite important for their applications in products like pipes that will be in contact with solvents. A reviewed study by Habeeb *et al.,* 2021 [11] showed that the swelling properties played a substantial role in decreasing the efficiency of the elastomer compounds as a result of immersing or contacting these compounds with organic solvents. Therefore, it is very important to determine the efficiency of these compounds for resistance to uptake of organic solvent. This study was carried out as a first step to evaluate the swelling behavior of natural rubber vulcanisates filled with carbonised and uncarbonised agricultural waste materials (cocoa pod husk, corncob and empty palm fruit bunch) in comparison with carbon black filled vulcanisates.

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2. Material and methods

2.1. Materials

The Cameroon Standard Rubber Grade L (CNR3L) was used for this study. The vulcanizing ingredients such as stearic acid, zinc oxide, sulphur, tetramethylthiuram disulphide (TMTD), trimethyl quinine (TMQ), and carbon black (N330) were of standard laboratory grades obtained from Sigma. Carbonised and uncarbonised corncob (CC), carbonized and uncarbonised cocoa pod husk (CPH) and carbonised and uncarbonised empty palm fruit bunch (EPFB) powders were used as fillers in the preparation of natural rubber (NR) vulcanisates. The corncob, cocoa pod husk and empty palm fruit bunch were sourced locally around IRAD Ekona research farms and they are among the waste produced from the production of maize, cocoa bean and palm oil respectively.

The CC, CPH and EPFB were individually washed to remove dirt particles, sun dried to maximum of 10% water content. The low moisture content, ensures a lesser degree of a defect arising from shrinkage during the curing process at elevated temperatures [12]. The dried samples were milled to fine powders of less the 0.35mm diameter (uncarbonised fillers). Part of the dried CC, CPH and EPFB were carbonized to produce carbonized fillers. The carbonized materials were also milled into fine powder. These fillers as well as carbon black (N330) were filtered with a 0.35mm sieve. The sieved fine powders were then collected and used for vulcanisates preparation.

2.2. Preparation of Natural Rubber Vulcanisates

The ingredients used in compounding natural rubber are presented in Table 1. The ingredients are arranged in the order in which they were used during the compounding process. A two-roll mill was used in the compounding process with the temperature maintained at 70°C to avoid cross linking during mixing [13]. After compounding, samples were obtained, coded accordingly, and processed further by curing.

2.2.1. The curing process

Each rubber vulcanisate produced was cured by placing in a rectangular shaped mould and introducing it into a compression moulding machine for 5 min at 150°C, and pressure of 1800 psi to produce a rectangular sheet. After curing, samples were cut from the sheets for property testing.

Table 1 Compounding formulation used in the study

Ingredient	Amount (phr)
Natural Rubber	100
ZnO	5
Stearic acid	2.5
Tetramethylthiuram disulphide (TMTD)	1
Sulfur	2.5
Mecaptobenzothiazole (MBT)	1
Fillers	10

phr = parts per hundred rubbers

2.3. Determination of swelling ratio

Determination of the swelling ratio (SI) of rubber vulcanisates was by the free swelling method and calculated in terms of percentage swelling. A 0.1 g of dry sample was immersed in Toluene at room temperature for 72 hours to reach swelling equilibrium. Each swollen sample was taken out, dried between folds of filter paper (blotting method) and weighed. After weighing the swollen samples, the equilibrium swelling ratio was calculated using equation. (1)

$$\% \text{ Swelling } = \frac{W_1 - W_0}{W_0} \text{ x } 100 \ldots\ldots\ldots\ldots\ldots\ldots.(1)$$

% Swelling is the equilibrium swelling ratio of sample which were the averages of three measurements. W_0 and W_1 were the weight of the dry and toluene swollen samples respectively.

3. Results and discussion

The swelling ratio is a direct measurement of the degree of cross-linking where the smaller the ratio is, the higher the degree of cross-linking obtained [14]. A swelling test is performed to observe the filler-rubber matrix interaction. The swelling ratio can also be described as the quantity of solvent uptake per weight of rubber [14]. The swelling percentage of the vulcanisates with incorporated carbon black and plant wastes are presented in Figure 1. The uncarbonised empty palm fruit bunch (EPFBuc) filled vulacisates presented the highest swelling ratio. This indicates that this vulcanisate had the lowest degree of cross linking. In a whole, vulcanisates filled with uncarbonised plant wastes namely; un carbonized corn cob (CCuc), uncarbonised cocoa pod husk (CPHuc) and un carbonized empty palm fruit bunch (EPFBuc) presented the highest swelling ratio compared to carbon black and carbonized plant wastes; carbonized corn cob (CCc), carbonised cocoa pod husk (CPHc) and carbonized empty palm fruit bunch (EPFBc) filled vulcanisates.

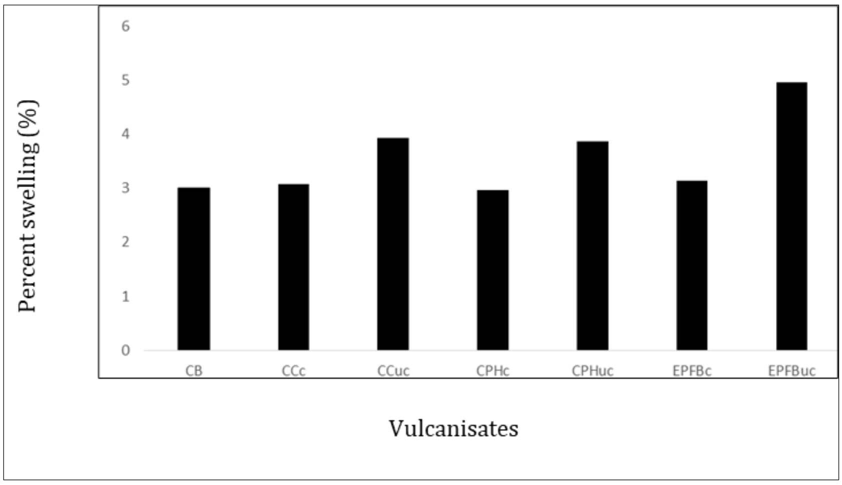

Figure 1 Swelling behaviour of carbon black (CB) and plant wastes filled natural rubber vulcanisates (un carbonized corn cob (CCuc), uncarbonised cocoa pod husk (CPHuc) un carbonized empty palm fruit bunch (EPFBuc), carbonized corn cob (CCc), carbonised cocoa pod husk (CPHc) and carbonized empty palm fruit bunch (EPFBc))

The results of this study show that uncarbonised fillers absorbed more solvent than the carbonized fillers and carbon black. Carbonising plant wastes has been known to reduce the particle size [15]. The smaller particle size fillers from carbonized plant wastes did not offer spaces for water absorption hence the low swelling ratio obtained. In addition, CB and carbonized plant wastes have smaller particle sizes, which means the larger surface area so that the physical crosslink climbs up. Fillers with higher surface area provide a higher reinforcing effect on rubber [16]. Swelling occurs because there are the free volume to facilitate the mass transfer of solvent [17)]. The presence of CB and carbonized plant wastes provide better interfacial interaction in natural rubber (NR) composites. The enhancement of interaction between NR and filler increases the formation of more crosslinks. CB and carbonized plant wastes make higher rubber network, the polymer chain is trapped or entangled in the microstructure and the porosity of CB and carbonized fillers. Thus, the rubber chains become highly immobilized.

4. Conclusion

Vulcanisates filled with uncarbonised plant wastes gave higher swelling percentages compared to those filled by carbon black and carbonized plant wastes. CB and carbonized plant wastes make had better interactions with rubber thus reinforcing the composites. The lower particle sizes of CB and carbonized plant wastes compared to uncarbonised plant wastes ensures better filler interaction with NR. This information is valuable as a step in getting low cost and environmentally friendly fillers for natural rubber composites preparation.

Compliance with ethical standards

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Disclosure of conflict of interest

There is no conflict of interest.

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