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The Effect of Local Materials (Fillers) on the Crosslink Density, Hardness, Resilience and Hysteresis of Natural Rubber

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Abstract. This work reports the influence of local clay, charcoal, silica-sand, limestone and carbon black on the crosslink density, hardness, resilience and hysteresis of the natural rubber compound. The results revealed that all the fillers enhanced the crosslink density and hardness of the gum stock. Charcoal showed higher values of crosslink density, hardness and hysteresis than the other local fillers. At relatively low loading, local fillers showed appreciably higher resilience and slightly lower hysteresis than carbon black charcoal, being the least resilient and most hysteric. The present work suggests that the denser is the crosslink of the composite, the harder, less resilient and the more hysteric the composite becomes.

Keywords: crosslink density, hardness, resilience, hysteresis, carbon black, natural rubber composite

Introduction

Reports show that fillers are used in rubber vulcanization to achieve two purposes, namely: (i) to reinforce the rubber in order to improve the mechanical properties of the resultant composite, and (ii) "beef up" the volume of rubber compounds (Billmeyer, 1984; Maurice, 1981; Studebaker and Beatty, 1978; Garvey, 1970). Reinforcing fillers improve the quality of the final vulcanizate, while inert fillers add little or nothing to the reinforcing characteristics of the final composite. However, these inert fillers are added just to reduce cost and sometimes better processing properties are achieved.

Properties of impregnated natural rubber composites have been investigated extensively (Adu, 1991; Bristow, 1986; Elliot, 1986; Bernard *et al.,* 1985). Our earlier work reported the effect of some agricultural wastes on the mechanical and rheological properties of natural rubber (Adeosun, 2000; Adu *et al.,* 2000). Recently, the characterization of natural rubber impregnated with some locally available materials such as clay, limestone, charcoal and silica-sand was investigated and reported (Adeosun and Olaofe, 2003; 2002). The aim was to examine the reinforcing properties of these local materials when incorporated into natural rubber with a view to finding industrial applications for them.

The thermal and electrical conductivities of natural rubber impregnated separately with local clay, limestone, charcoal and silica-sand have been reported (Adeosun and Olaofe, 2002). In the present work, the crosslink density, hardness, resilience and hysteresis of natural rubber, filled with these local materials, have been determined as a function of filler loading.

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Materials and Methods

Source of materials. Twenty-two conventional accelerator/ sulphur compounds were tested as indicated in Table 1and 2. The natural rubber used was a Nigerian standard rubber grade 10 (NSR10) produced at Michelin plantation, Araromi-Obu, Ondo State, Nigeria. Clay was collected from Afao-Ekiti, limestone from Arimogija, silica-sand from Igbokoda, and wood charcoal was purchased from Erekesan Market in Akure, all in Nigeria.

Elemental analysis of materials. Elemental analysis was done using atomic absorption spectrophotometer (AAS) and colourimeter following the experimental procedures of Vogel (1961) and AOAC (1981).

Table 1. Formulation of the composites examined

Composite	Content in parts per hundred rubber (pphr)
Natural rubber	100
Zinc oxide	5
Stearic acid	3
MBT[a]	1
Sulphur	3
Filler	variable[b]

[a]mercaptobenzothiazole; [b]filler loading in parts per hundred rubber (pphr)

Table 2. Formulated composites as a function of filler loading

Composite code	Filler(pphr)	Filler loading
N1	0	00
NCB1	carbon black	28
NC1	clay	12
NC2	"	28
NC3	"	36
NC4	"	48
NC5	"	72
NL1	limestone	12
NL2	"	28
NL3	"	36
NL4	"	48
NL5	"	72
NCH1	charcoal	12
NCH2	"	28
NCH3	"	36
NCH4	"	48
NCH5	"	72
NS1	silica-sand	12
NS2	"	28
NS3	"	36
NS4	"	48
NS5	"	72

N: gum compound without filler (control); NL: limestone filled composite; NCB: carbon black filled composite; NCH: charcoal filled composite; NC: clay filled composite; NS: silica-sand filled composite; pphr: parts per hundred rubber

Mixing. Mixing was done on a two-roll mill at 70 °C and maximum speed of 24 rpm. The mixing cycle per batch varied between 8-10 min. After milling, the composites were cooled immediately in chilled water and covered with cellophane paper (Adeosun and Olaofe, 2003).

Rheometer test. Milled composite was received, cut and weighed (5.0-5.05 g). The sample was inserted into the rheometer which was operated at 185 °C for complete measurement. The rheometer was connected to a plotter, which produced torque-time plots (rheographs). The rheographs showed maximum torque (M_H) and minimum torque (M_L), the difference of which is a measure of the crosslink density of the composite (Adeosun and Olaofe, 2003).

Hardness measurement. For the measurement of hardness, circular shaped test pieces were cured at 152 °C for 15 min, dropped into chilled water and allowed to cool for 48 h. The test piece was then tested for hardness using rubber hardness tester (BSO, 1975).

Resilience and hysteresis test. Resilience cuboids test piece was cured at 142 °C for 35 min using an electric press. The vulcanizate was allowed to mature for 48 h after being dropped into chilled water. The matured sample was then aged at 50 °C for 2 h. The aged sample was fixed into the Wallace resilience test equipment operated at 30 °C (BSO, 1975). The disc was raised to 45 °C and released. The disc hit the sample and rebound. The maximum angle of rebound was noted and resilience calculated by using equation (1) mentioned below:

$$R = \frac{hr}{hd} \times \frac{100}{1} = \frac{1-\cos\phi}{1-\cos 45} \times \frac{100}{1} \qquad (1)$$

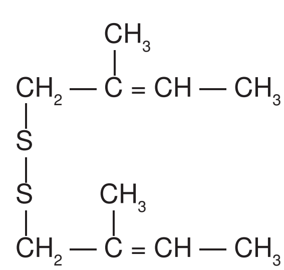
where:
R: resilience
hr: height of rebound
hd: height of release
ϕ: angle of rebound

Hysteresis was calculated as the reciprocal of resilience (i.e., hysteresis = 1/resilience).

Results and Discussion

The unloaded compound has a crosslink density of 7.3 dN-m which increases to 13.35 dN-m on the addition of 12 pphr (parts per hundred rubber) of conventional carbon black filler. The increase in crosslink density on the addition of clay, limestone, silica-sand and charcoal within the concentration range of 12 pphr and 72 pphr was observed to fall, respectively, within 7.99 and 9.65 for clay, 7.64 and 9.64 for limestone, 8.50 and 12.65 for silica-sand, and 11.16 and 19.36 for charcoal. These results suggest that charcoal had better ability to improve crosslinkage than clay, limestone, silica-sand, and even the conventional carbon black.

Noting that even if the entire residue of clay, limestone and silica-sand was carbon (Table 3), charcoal had the highest percentage of carbon. Crosslink in natural rubber vulcanization is of the sort C-S-S-C, as in the structure below:



It is therefore reasonable to infer that high carbon content in the matrix would lead to increased linkage in the presence of

Table 3. Chemical composition of the local materials

Filler	SiO_2	SO_2	Al_2O_3	K_2O	Na_2O	CaO	MgO	Fe_2O_3	CO_2	Residue
Clay	48.83	23.81	10.09	5.91	0.59	1.34	1.02	4.91	nd	3.50
Limestone	4.26	1.49	1.16	6.21	0.70	52.92	10.36	4.02	nd	18.88
Silica-sand	78.13	2.80	1.06	0.24	0.18	0.34	0.02	2.09	nd	15.14
Charcoal	22.44	2.40	0.17	0.34	0.29	0.22	0.09	0.07	51.72	22.29

nd: not determined

sulphur. This explains why charcoal with the highest carbon content shows denser crosslinkage than the other local fillers (clay, limestone and silica-sand). A critical look at Table 3 revealed that charcoal contained sulphur in addition to carbon which could be made available for C-S-S-C linkage. This could be an explanation for charcoal's superior ability over carbon black (which is close to 100% carbon content) to form C-S-S-C linkage. For all the fillers examined, crosslink density increased with increasing filler content (Fig. 1).

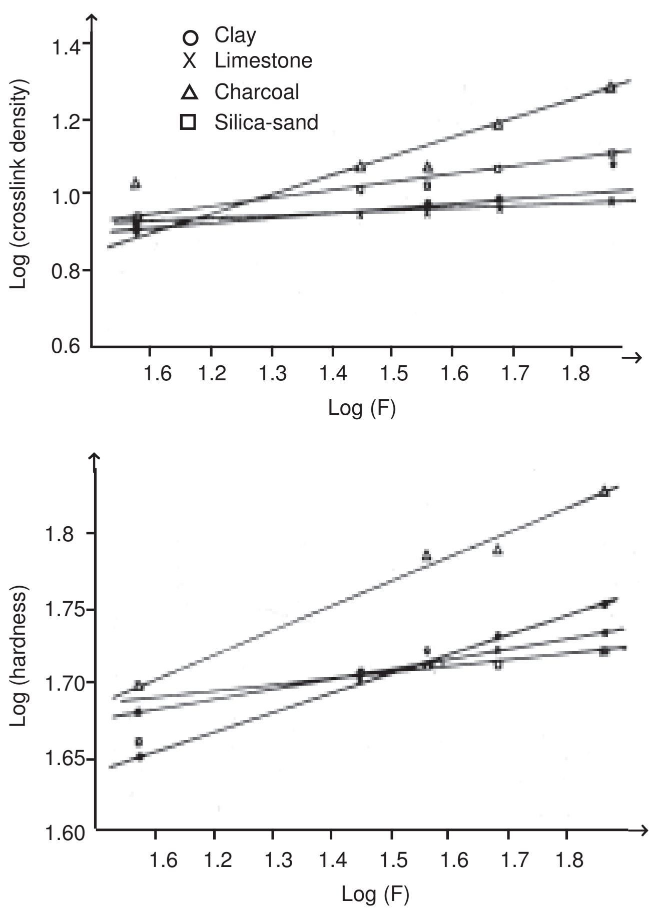


Fig. 1. Log crosslink density and log hardness versus log filler (F) content in the composites.

The unloaded compound had a hardness value of 43.5 IHRD. This value increased to 59.6 IHRD on the addition of 12 pphr of conventional carbon black filler. On the addition of clay, limestone, silica-sand and charcoal, within the concentration range of 12 pphr and 72 pphr, hardness of composites fell within 44.8 and 55.1 for clay, 48.2 and 55.1 for limestone, 46.0 and 52.9 for silica-sand and 50.3 and 66.9 for charcoal. These results indicate that charcoal composites were as hard as the carbon black composites. Also, charcoal composites were harder than the composites of clay, limestone and silica-sand. This trend agrees with the trend observed for crosslink density and the reasons adduced for crosslink density could also be advanced for hardness. The denser the crosslink of the composite, the harder is the composite. Hardness increased with increasing filler loading (Fig. 1). This observed increase in hardness with increasing filler loading agrees with the observation of Parkinson (1946). A similar trend was reported by Adu (1991) for spent paper, wood dust, animal charcoal and coconut fibre.

The unloaded compound showed a resilience of 95.7%, while the resilience of the carbon black composite was observed to be 91.1%. Composites of clay, limestone, silica-sand and charcoal showed maximum resilience values of 94.7%, 95.6%, 94.7% and 93.3%, respectively. These results suggest that clay, limestone and silica-sand composites showed comparable resilience to that of the unloaded compound, which was slightly higher than that of charcoal composite. The carbon black composite was the least resilient out of all the fillers examined. This is the reverse of the trend shown by crosslink density and hardness. The trend of resilience decreasing with increasing filler loading has been reported for carbon black, which agrees with the observed trend in this work (Fig. 2) and with the observations reported for spent paper, wood dust, animal charcoal and coconut fibre (Adu, 1991). This trend is the reverse of the trend observed for crosslink density and hardness. It appears that the denser the crosslink of a composite, the harder and the less resilient the composite becomes.

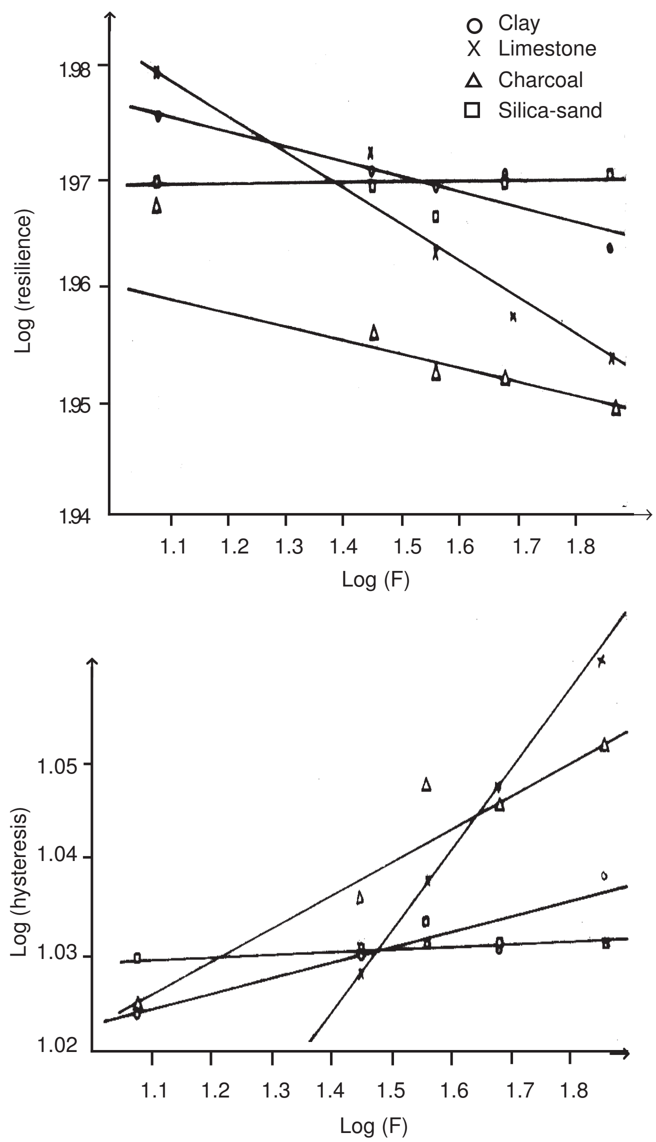


Fig. 2. Log resilience and log hysteresis versus log filler (F) content in the composites.

Hysteresis is a measure of the heat build-up by a composite during usage. All the fillers enhance the value of hysteresis slightly. Hysteresis increased with increasing filler content in the mix (Fig. 2). At relatively low loading (12 pphr), charcoal, clay and limestone showed hysteresis comparable to the gum stock slightly lower than for carbon black. The trend observed for hysteresis agrees with the trend reported for carbon black, wood dust, spent paper, coconut fibre and animal charcoal (Adu *et al.*, 2000; Adu, 1991).

Conclusion

Clay, limestone, silica-sand, charcoal and carbon black enhance the crosslink density of the gum stock. Charcoal shows higher crosslink density than clay, limestone and silica-sand. Hardness was also enhanced by all the fillers examined. The charcoal loaded composites further showed higher hardness values as compared to clay, limestone and silica-sand.

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