Comparison of Mechanical Properties of Natural Rubber Vulcanizates Filled with Hybrid Fillers (Carbon Black/Palm Kernel Shell and Palm Kernel Shell/Sandbox Seed Shell)

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Abstract: **Comparison of mechanical properties of natural rubber vulcanizates filled with hybrid fillers (carbon black/palm kernel shell and palm kernel shell/sandbox seed shell). The compounding was done at varying ratios 0/60, 10/50, 20/40, 30/30, 40/20, 50/10, 60/0phr for the hybrid carbon black/palm kernel shell (CB/PKS) and palm kernel shell/sandbox seed shell (PKS/SSS), using two roll mill. The results showed that incorporation of hybrid CB/PKS and PKS/SSS fillers into the natural rubber vulcanizates generally increased the tensile strength, modulus and hardness at hybrid filler loadings 0/60, 20/40, 30/30, 40/20, 50/10 and 60/0phr of the composites produced, whereas the elongation at break, abrasion resistance and compression set decreased. The hybrid CB/PKS filled natural rubber vulcanizates exhibited higher tensile strength, modulus and hardness than those of the hybrid PKS/SSS filled natural rubber vulcanizates but lower elongation at break, abrasion resistance and compression set than the hybrid PKS/SSS filled natural rubber vulcanizates.**

Key words: **filler; hybrid; modulus; natural rubber; vulcanizates**

I. INTRODUCTION

Composites are materials consisting of two or more chemically distinct constituents, on a macro-scale, having a distinct interface separating them. One or more discontinuous phases are, therefore, embedded in a continuous phase to form a composite (Agarwal and Broutman, 1990). The discontinuous phase is usually harder and stronger than the continuous phase and is called the reinforcement, which provides strength to the composite. Whereas, the continuous phase is termed as the matrix which holds the fibre in desired shape and transfer the load from one fibre to other. For example; polymeric composites normally yield composites which are light yet strong due to filler incooperated. Even-though some materials require a chemical treatment to gain strength. Rubber composites are typical examples since curing is a recipe of chemicals for modification of rubber elasticity and strength. This is dependent on a number of factors including type of vulcanizing agent, accelerator (s), activator (s), reinforcing filler, anti-oxidant, heat retardant, mixing/mastication procedure and processing temperatures (Martins and Ines 2003; Oluwole et al, 2015; Ismail et al, 2008; Mondragog et al, 2009). Generally properties of composite materials are influenced by the two materials involved as well as the method of processing (Ku et al, 2011).

The primary objective in composite formation is to obtain a good orientation of the reinforcement and an efficient interfacial adhesion by combining the matrix and the reinforcing material (Ismail et al, 2002). The reinforcing material provides strength and stiffness and also acts as a load transferring medium. The matrix material acts as an adhesive holding the reinforcing material's particles together. Strong interfacial bond between these two materials is very crucial for superior composite properties. The interest in modern composite materials has increased because of their high strength, low density and ease of manufacturing (Ku et al, 2011). The material properties of composites can be tailored to meet requirements of a specific application. Selecting an appropriate combination of matrix and reinforcement material would permit production of a new material that meets the requirements of a particular application.

Polymer matrix composites made the most largest and diverse use of composites due to ease of manufacturing; low cost; and good properties. Rubber is one of commercially used polymeric matrix mainly due to good energy absorbing properties. It can undergo much more elastic deformations under stress than other materials and still return to its original shape without permanent deformation after the stress is released (Irene et al, 2012). This unique property gives rubber an extensive variety of applications (Khalil et al, 2013).

Natural rubber (NR) is an interesting material with commercial success due to its excellent physical properties, especially high mechanical strength, low heat build-up, excellent flexibility, and resistance to impact and tear, and above all its renewability (Daniel et al, 2009). However, raw dry rubber is seldom used in its original state for any

engineering and domestic application. Consequently, rubber manufacture involves the addition to rubber many ancillary materials called additives to allow the rubber compounds to be satisfactorily processed and vulcanized in order to improve the application properties of the rubber compound. Additives used in rubber manufacture include vulcanizing agents, accelerators, activators and/or retarders, fillers, anti-degradants, among others.

Fillers represent one of the most important additives used in rubber compounding. Fillers are added to rubber formulation in order to optimize properties needed for service application (Sobhy et al, 1997). Due to strong environmental regulations worldwide and increased interest in the proper utilization of renewable natural resources, efforts have been made to find alternative reinforcements that are environmentally friendly while providing the same performance as their synthetic counterparts (Egwaikhide et al, 2007). With their low cost, easy availability, ease of chemical and mechanical modification, and high specific mechanical properties, natural fibres represent a good, renewable and biodegradable alternative to the most common synthetic reinforcement (Lovely et al, 2006). They achieve performance enhancement by forming strong chemical bonds with the rubber, that is, strong filler-elastomer interactions. Carbon black is always considered the most commonly consumed reinforcing filler in the rubber industry. Considering its problems such as its non-renewable petroleum origin, dark color, contamination and pollution, researchers are seeking an adequate alternative (Ismail et al, 1997).

Other different materials have been used to reinforce natural and synthetic rubber such as clay (Kim et al, 2006), organo clay (Arroyo et al, 2003), coal shale-based fillers (Zhao and Xiang 2004), synthetic precipitated amorphous white silica nanofiller (Ansarifar et al, 2006), recycled rubber powder (Ismail et al, 2002), graphite (Yang et al, 2006). Agricultural by-products as fillers has also been investigated, this included banana peel, rice husk, spent mango, bean seed skin and groundnut shell (Adeosun, 2002), cocoa pod and rubber seed shell (Okieimen and Imanah, 2003) and short pine apple leaf fiber (Lopattananon et al, 2006), ash rice husk (Ismail et al 2001), melon shell and sawdust (Amoke et al, 2017), coconut shell and palm fruit fibre (Tenebe et al, 2013). In addition, the processing of these composite materials is flexible, economical, and ecological and it is possible to use the same machinery employed with other traditional fillers.

This research work is aimed at developing filler for rubber compounds which can be an alternative to the commonly used commercial carbon black filler with a consequent reduction in cost. The palm kernel seed shell and sandbox seed shell are agro-wastes in Nigeria which have been applied here as hybrid fillers with commercially used filler (carbon black) for natural rubber.

Objectives

i. To determine the effect of hybrid fillers on the improvement of the mechanical properties of natural rubber vulcanizates.

II. EXPERIMENT

Materials and Methods

The natural rubber (NSR-10) used for the research work was obtained from Rubber Research Institute of Nigeria (RRIN), Iyanomoh Benin-City. Palm Kernel Shell (PKS) were obtained from Auchi Metropolis. Diesel and fuel were obtained from NNPC Omega Filling Station, Auchi Edo State. The rubber compounding chemicals such as processing oil, tetramethyl thiuram disulphate (TMTD), mercaptobenzothiazole disulphate (MBTS), zinc oxide, sulphur and stearic acid were of commercial grades.

Equipments

The equipments involved in this research work are: two roll mill, Manufactured by Bristish Company Limited, England, hydraulic Press, Elektron Technology Series, UK, Monsanto Tensile Tester Model (1/m) Manufactured by Bristish Company Limited, England, Wallace Hardness Tester model C8007/25 for Hardness Test, Elektron Technology Series, UK, Taber Oscillating Abrasion Tester, Model: 6160-F735, Manufactured by Taber Co. Ltd, Canada, was used for the Abrasion Properties, CTM-2P-200-2000KN (200Tons), Manufactured by Interlaken Technologies Co. Ltd Thailand was used for the Compression Set.

Method

Characteristics of Fillers.

The palm kernel shell (PKS) and sandbox seed shell (SSS) were sun dried and ground with automated grounding machine then sieved with a mesh of size 75µm mesh, which was the particle of fillers used for the experiment. The fine particles that passed through were collected and used for compounding of the natural rubber.

Preparation of composites

The rubber was masticated and mixed with an additives using the two roll mill and adopting the standard method specified in the ASTM-D 3184-80 for all the composites. The filler hybrid loadings were varied at ratio of (0/60 – 60/0). The Table 2.1 shows the formulations for the natural rubber composites. The rubber mixes were prepared on a laboratory size two roll mill. It was maintained at 70^0C to avoid cross-linking during mixing after which the rubber composite was stretched out. Mixing follows (ASTMD 3184–80, 1983).

Table 1: Formulations for Reinforced Natural Rubber Composites.

Ingredients	Part per Hundred of Rubber (phr)
NR	100
Zinc oxide	5.0

Stearic acid	2.5
Fillers (CB/PKS and PKS/SSS)	0/60, 10/50, 20/40, 30/30, 40/20, 10/50, 60/0
MBT	1.0
TMTD	1.0
Sulphur	2.5
Processing oil	2.0

Key: CB = Carbon black PKS = Palm Kernel Shell SSS = Sandbox Seed Shell

A batch factor of two (2) was used.

Composite Curing

The curing of test pieces was done in a compression moulding machine at 115^{o}C and 2bar for 5mins.

III. MECHANICAL PROPERTIES OF THE NATURAL RUBBER COMPOSITES

Tensile Properties

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 6mm respectively. Each test piece was clamped into the grips of the tensometer. The stress applied, the load and elongation at break was recorded. The test samples were tested in the machine giving straight tensile pull, without any bending or twisting. The machine measures both the tensile stress and the tensile strain. The tensile stress is the strength of pull in the area between the notch marks; it is based on original cross sectional area. The tensile strain is a measure of how the test sample has been stretched by the pull.

Hardness Test

Test pieces from the moulded spherical rubber pieces were clamped onto a durometer (Instrol Wilson) and the penetration of the indenter measured. The standard dead method of measurement covers rubber in the range of 30 to 85 International Rubbers Hardness Degrees (IRHD). The test was carried out using the Shore "A" Wallace Hardness Tester.

Abrasion Resistance Test

Wallace Akron abrasion tester was used. The angle between the test sample and the wheel was adjusted to an angle of 15^{o}. The abrasion was carried out for 100 revolutions and the material loss for each run was noted. The specimen was re-reweighed between each test run. The mean of the four revolutions of the abrasive wheel was calculated.

$$\text{Abrasion Resistance} = \frac{\text{Weight Loss of the Standard}}{\text{Weight Loss of the Sample}} \times 100 \quad (1)$$

Compression Set Test

The compression set is the difference between the original thickness of the sample and the thickness after the test expressed as a percentage of the original thickness. Compression set evaluate the extent by which the specimen fails to return to its original thickness when subjected to standard compression load for a given period of time at a given temperature. Stress of 2.8MP was used and allowed for 24 hours at 70^{o}C for 30mins.

$$\text{Compression Set (\%)} = \frac{t_o - t_r}{t_o} \times 100 \quad (2)$$

Where: t_o = Initial Thickness and t_r = Recovered thickness of Sample.

IV. RESULTS AND DISCUSSION

Results

Table 2: Mechanical Properties Test Results

Properties	Filler Loadings (phr)						
	F0	F1	F2	F3	F4	F5	F6
	0/60	10/50	20/40	30/30	40/20	50/10	60/0
Tensile Strength (N/mm^2)	(35.15) [31.93]	(28.01) [21.24]	(34.23) [23.05]	(35.88) [26.21]	(37.53) [26.99]	(38.08) [30.00]	(41.24) [35.15]
Tensile Modulus (N/mm^2)	(20.00) [17.96]	(14.26) [9.15]	(18.77) [10.73]	(21.29) [13.52]	(23.16) [13.85]	(23.99) [17.68]	(25.47) [20.00]
Elongation at Break (%)	(425.37) [485.03]	(523.10) [601.21]	(461.78) [582.04]	(420.62) [570.42]	(411.37) [535.12]	(401.76) [502.60]	(378.12) [425.37]
Hardness (Shore A)	(60.30) [54.40]	(47.36) [35.42]	(61.44) [36.85]	(63.26) [39.62]	(65.23) [42.44]	(68.08) [48.93]	(69.35) [60.30]
Abrasion Resistance (Mm^3/rev.)	(16.75) [20.11]	(28.12) [29.33]	(23.28) [29.01]	(20.67) [27.39]	(17.05) [25.03]	(15.80) [20.31]	(13.95) [16.75]
Compression Set (%)	(20.43) [24.59]	(30.94) [34.27]	(25.19) [32.71]	(22.33) [32.06]	(20.39) [30.00]	(18.47) [27.75]	(15.69) [20.43]

Key: CB/PKS = ( ) PKS/SSS = [ ]

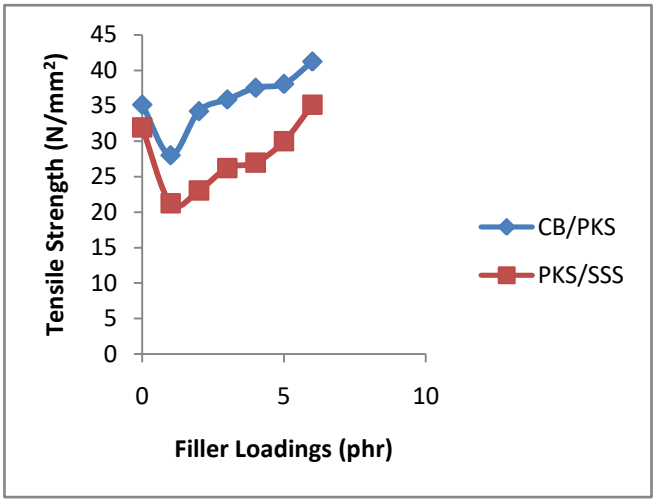

Figure 1: Effect of Filler Loadings on Tensile Strength of Natural Rubber Vulcanizates.

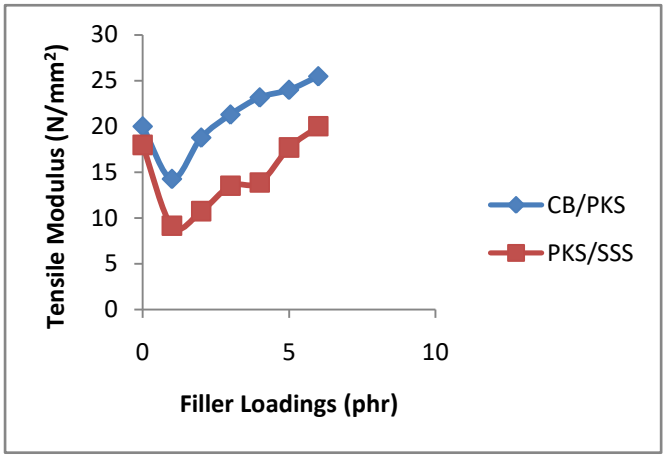

Figure 2: Effect of Filler Loadings on Tensile Modulus of Natural Rubber Vulcanizates

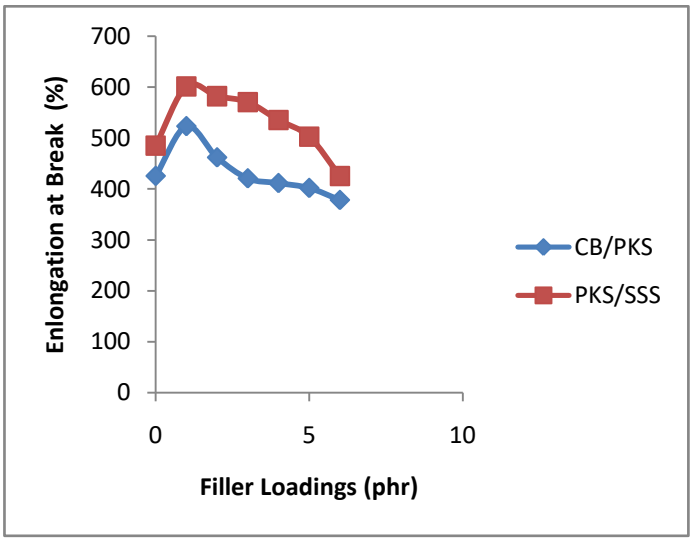

Figure 3: Effect of Filler Loadings on Elongation at break (%) of Natural Rubber Vulcanizates.

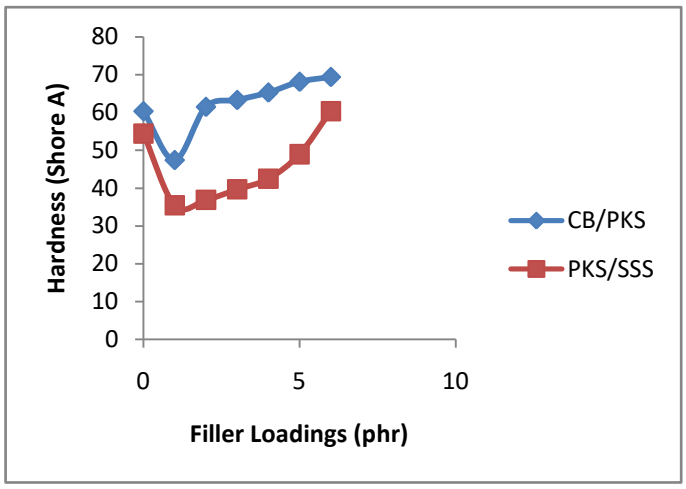

Figure 4: Effect of Filler Loadings on Hardness of Natural Rubber Vulcanizates

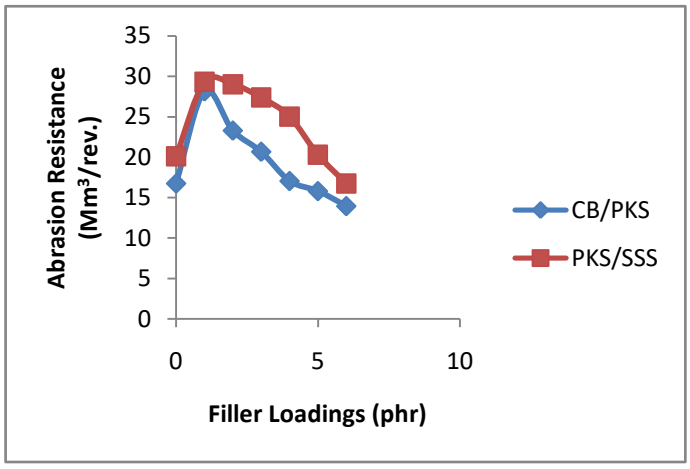

Figure 5: Effect of Filler Loadings on Abrasion Resistance of Natural Rubber Vulcanizates.

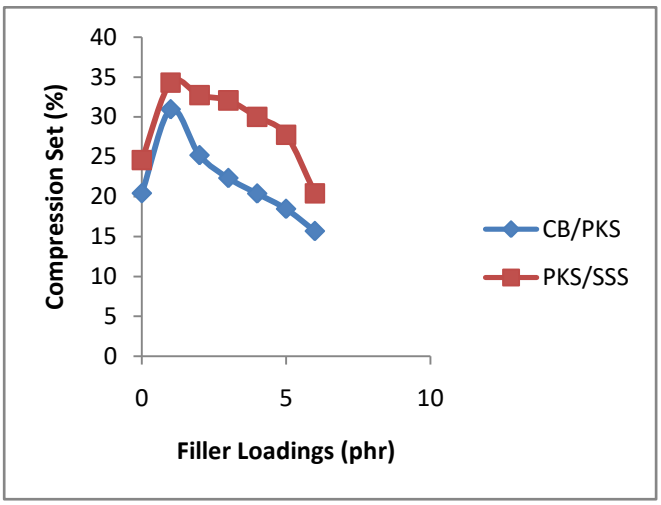

Figure 6: Effect of Filler Loadings on Compression set of Natural Rubber Vulcanizates.

Discussion

Mechanical Properties

The result for tensile strength as presented in Table 2 and Figure 1, at hybrid filler loading 0/60phr for CB/PKS and PKS/SSS showed high tensile strength (35.15N/mm^2 and 31.93N/mm^2 respectively). This shows that PKS has a better reinforcing power than SSS due to better polymer-filler interaction but the tensile strength reduced to 28.01N/mm^2 and 24.24N/mm^2 for both hybrid fillers at 10/50phr. The reason for this reduction in tensile strength might be result of poor blending of the two fillers (CB/PKS and PKS/SSS) and poor dispersion within the rubber matrix. The tensile strength then increased from hybrid filler loadings 20/40phr to 60/0phr for both hybrid fillers. The CB/PKS hybrid natural rubber vulcanizates showed high tensile strength than PKS/SSS hybrid natural rubber vulcanizates, this is as result of increasing level of carbon content in the carbon black. The effectiveness of filler may be measured by its carbon content. High carbon content in fillers, provide greater reinforcement than those with low or no carbon content being that carbon itself is a very good reinforcing filler (Okieimen and Imanah, 2003).

The result for tensile modulus as presented in Table 2 and Figure 2, at hybrid filler loading 0/60phr for CB/PKS and PK/SSS natural rubber vulcanizates showed high tensile modulus (20.00N/mm^2 and 17.96N/mm^2 respectively) showing better reinforcing properties of PKS and SSS in the natural rubber vulcanizates. PKS filled vulcanizates showed high tensile modulus than SSS vulcanizates because of better rubber matrix-filler interaction and good filler dispersion within the rubber matrix as previously mentioned. The tensile modulus then reduced at hybrid filler loading 10/50phr (14.26N/mm^2 and 9.15N/mm^2 for CB/PKS and PKS/SSS respectively) but later increased at 20/40phr to 60/0phr for both hybrid fillers. CB/PKS hybrid filled vulcanizates indicate higher tensile modulus than PKS/SSS hybrid filled vulcanizates. This behaviour can be attributed to the fact that adhesion occurred more between CB/PKS and the rubber matrix, for this reason could lead to the increase in stiffness and rigidity. The reinforcing power of carbon black in the hybrid might also contribute in the high stiffness and rigidity of the filled vulcanizates. Good filler dispersion and rubber interaction, the modulus of the hybrid filled vulcanizates was significantly enhanced.

Table 2 and Figure 3, the result for elongation at break showed an increase from 0/60phr to 10/50phr for both hybrid filled natural rubber vulcanizates but the elongation at break decreased from 20/40phr to 60/0phr for both hybrid filled natural rubber vulcanizates. This behavior may be connected with the sticking of the hybrid fillers to the polymer phase, which results in the stiffening of the rubber chain and exhibited as resistance to stretching under applied strain (Ismail et al, 1997), CB/PKS hybrid filled vulcanizates had lower values of elongation at break than PKS/SSS filled hybrid filled vulcanizates.

The hardness results of the hybrid filled vulcanizates increased for both hybrid fillers as presented in Table 2 and Figure 4. This behavior is expected because as the hybrid fillers get into the rubber, the elasticity of the rubber chain is reduced, therefore creating more rigid vulcanizates and the resilience decreases. The CB/PKS hybrid filled vulcanizates had higher hardness values than PKS/SSS hybrid filled vulcanizates in Table 3.1 and Figure 3.4, showing that CB/PKS is more reinforcing than PKS/SSS.

From Table 2 and Figure 5 showed a decrease in the abrasion resistance for both hybrid fillers. Thus, the abrasion resistance of a solid body is defined as its ability to withstand the progressive removal of the material from its surface as a result of the mechanical action of rubbing, scraping or erosive nature (Arroyo et al. 2003). At hybrid filler loading 10/50phr, there was an increase which is due to poor adhesion of the filler particles to the polymeric matrix. The CB/PKS hybrid showed decreasing values as carbon black increase in the hybrid CB and PKS than PKS/SSS because there was an existence of strong bond between the hybrid filler and the rubber matrix but the PKS/SSS showed higher values, indicating a weak bond between the hybrid filler and the rubber matrix. The weak bond will cause easy detachment of the hybrid filler particles from the rubber matrix leading to wear when subjected to mechanical action (Ojinmah et al, 2017).

Compression set is useful in prediction of the service performance of rubber articles. The level of compression determines the service life and area of application of the rubber composites. The results of compression set in Table 2 and Figure 6 showed that for both hybrid fillers, the compression set of the both vulcanizate decreases. The values obtained for the hybrid CB/PKS filled natural rubber vulcanizates are lower than those obtained by hybrid PKS/SSS natural rubber vulcanizates.

V. CONCLUSION

The hybrid fillers (CB/PKS and PKS/SSS) have demonstrated their potential reinforcing abilities in natural rubber. This research work examined how favourably the mechanical properties of hybrid CB/PKS filled natural rubber vulcanizates compares with those of hybrid PKS/SSS filled vulcanizates. The results obtained showed that mechanical properties of rubber vulcainzates are influenced by hybrid filler loadings. It was observed that the hybrid CB/PKS filled natural rubber vulcanizates exhibited higher tensile strength, modulus and hardness at hybrid filler loadings 0/60, 20/40, 30/30, 40/20, 50/10 and 60/0phr but at these hybrid filler loadings, the elongation at break, abrasion resistance and compression set were lower than those of the hybrid PKS/SSS filled natural rubber vulcanizates. This indicates that the hybrid CB/PKS filled natural rubber vulcanizates would be useful in the production of products requiring higher stress but lower

elongation at break, abrasion resistance and compression set in teir service life while the hybrid PKS/SSS filled natural rubber vulcanizates would be useful in the production of products requiring lower stress but higher elongationat break, abrasion resistance and compression ste in their service life.

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