

INFLUENCE OF CARBONIZED DIKA (*IRVIALGIAGABONENSIS*) NUTSHELL POWDER ON THE VULCANIZATE PROPERTIES OF NATURAL RUBBER/ACRYLONITRILE-BUTADIENE RUBBER BLEND

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ABSTRACT

Vulcanizate properties of rubber blends prepared from natural rubber (SAR) and acrylonitrile-butadiene rubber (NBR), in the presence of carbonized Dika nutshell powder (C-DNS) and carbon black (CB) as fillers were studied. Blend compositions of SAR/NBR : 0/100, 25/75, 50/50, 75/25, and 100/0 wt.%, respectively were reinforced with varying filler ratios of CB/C-DNS : 50/0, 40/10, 30/20, 20/30, 10/40, and 0/50 phr. The influence of C-DNS content and blend ratio on vulcanizate properties, such as stress - extension ratio behavior, tensile strength, elongation at break and crosslinking density were investigated. Carbonization of Dika nutshell powder significantly improved the tensile properties of blend samples. Elongation at break showed a decreasing trend with decreasing C-DNS content. However, a higher elongation at break was shown by SAR and SAR – rich blends mainly because SAR matrix has greater chain mobility than NBR matrix due to the lower T_g of SAR (-72°C) compared to that of NBR (-40°C). An increasing trend in crosslinking density was observed for SAR and SAR – rich blends. This is attributed to the greater chain regularity of SAR over NBR which improves on reinforcement. Marked improvement in all properties tested was obtained at 10 phr C-DNS content. This reveals that at low level of 10 phr, C-DNS proves a potential substitute filler for CB in the rubber industry, especially in the production of low-cost/high volume rubber products where strength is not critical.

Keywords:SAR, NBR, vulcanizate properties, carbonization, Dika nutshell powder, rubber blend

INTRODUCTION

The quest for polymeric materials with desired properties for specific applications has led to the relentless search for polymer blends. Since no one polymer has all the properties required in many application areas, polymers are commonly blended to improve their performance and processing characteristics (Tillekeratine and Scott, 2006). The desired property improvements obtainable through polymer blending include permeability characteristics, processibility, impact strength, solvent resistance, heat distortion temperature and tensile strength, in addition to cost reduction (Findik et al, 2004). Therefore, blending of two or more types of polymers is a very useful technique for the preparation and development of polymeric materials with properties superior to those of individual constituents. Mechanical properties of polymer blends are controlled generally by many factors such as the nature of polymer (George, 1993), blend composition (Valsamis et al, 1988), phase morphology (Findik et al, 2004), and interfacial adhesion (Sathe et al, 1996). The phase morphology depends on processing factors such as type of mixer, blending rate, blending temperature, component rheology, interfacial tension and crosslinking agent (Madani and Badawy, 2005). Natural rubber, an elastomer has been extensively studied because of its wide usage in many engineering applications. Blends of natural rubber have been reported to be compatible with desirable mechanical properties (Sa- Ad Riyajan et al, 2012). Excellent reports exist in the literature on the mechanical properties of elastomer and their blends. Thus mechanical properties studies have been conducted on natural rubber/vinyl alcohol blend (Sa-Ad Riyajan, 2012), natural rubber/ethylene-vinyl acetate rubber blend (Koshy et al, 1992 ;Koshy et al, 1993), natural rubber/epoxidized natural rubber-25 blends (Johnson and Thomas, 1999), natural rubber/linear low-density polyethylene blends (Ahmad et al, 2004), and natural rubber/ultra-low-density polyethylene blend (Tanrattanakul and Udomkichdecha, 2001). Particulate fillers can increase the strength of an amorphous rubber more than 10-fold (Madani and Aly, 2010). A

filler must possess high specific surface area, ie, the particles must be small, less than $1\mu\text{m}$ in size for it to cause significant reinforcement (Madani and Badawy, 2005). Small particles possess large surface area for effective rubber-particle interaction and close particle-to-particle spacing in the rubber. Carbon black is always considered as the most effective reinforcing filler in the rubber industry. Considering its problems such as dark colour and contamination, as well as its high cost and non-renewable nature, researchers are constantly seeking an adequate alternative. Synchronous use of two fillers in the matrix has been investigated in the newest researches (Maiti et al, 2005 ; Bauer et al, 2006 ; Bokobza et al, 2008 ; Cataldo and Angelini, 2001). The synchronous use of carbon black and nanoclay has been reported (Praveen et al, 2010 ; Chattopadhyay and Basuli, 2010). Herrmann et al, 2006 also reported the considerable improvement of mechanical properties for hydrated acrylonitrile-butadiene rubber system containing carbon black and modified nanoclay in comparison with the system reinforced with one type of filler. The synergistic effect between carbon black and organoclay, such as mechanical and dynamic mechanical properties in rubbers (NR, epoxidized NR, styrene-butadiene rubber (SBR), etc.) was also investigated (Praveen et al, 2009). The synergistic mechanism generally explained that the coexistence of clay and carbon black could enhance the clay-carbon black network structure hindering the movement of polymer chains and improving mechanical properties (Chattopadhyay and Basuli, 2010). It has been proved that vulcanized NR containing 20/30 of silica/carbon black gives better overall mechanical properties, compared to those having only 50 phr (parts per hundred parts of rubber) of silica or carbon black (Rattanasom et al, 2007) due to the better filler dispersion. Results of other studies have revealed that a good balance of rubber properties can be achieved when two or more different filler types are added into rubber (Maiti et al, 2005 ; Bauer et al, 2006 ; Bokobza et al, 2008 ; Cataldo and Angelini, 2001). Prevailing economic realities in developing countries like Nigeria with respect to increasing debt burden and low Gross Domestic Product (GDP), is gradually pushing towards reduction on import dependence and the encouragement of locally sourced raw materials. Carbon black used as reinforcing filler in the rubber industry in Nigeria is imported and huge amount of foreign exchange can be saved if part of it is substituted with locally sourced filler. It is therefore thought that fillers sourced from low cost agricultural by-products might be useful in reducing costs in certain natural rubber products. Thus, the use of agricultural by-products to replace part of the carbon black used in rubber reinforcement has attracted significant attention in recent years, particularly for low cost/high volume applications. Nigeria, a Tropical African country is endowed with vast agricultural resources, which are still largely under-utilized. Most agricultural by-products in Nigeria are discarded as waste. Dika is a tropical nut grown in Africa. It has two main varieties distinguished by botanical names, *IrvingiaGabonensis*, which has edible fruit pulp, and *IrvingiaWombolu*, which is bitter and inedible. Nigeria produces about 150,000 tonnes of Dika annually (Imanah and Okieimen, 2004). Other Dika producers in Africa are Senegal, Sudan, Uganda, Democratic Republic of Congo (DRC) and Angola (Ayo et al, 2011). The reinforcement of rubber properties by the incorporation of carbon black is due to the presence of active polar groups such as phenol, carboxyl, quinone and lactones on the carbon black (Wolf et al, 1993 ; Wolf et al, 1994). These polar groups on the carbon black surfaces interact with rubber and the interaction is higher with polar rubbers than hydrocarbon rubbers, which is due to polar-polar interaction (Kraus, 1978). The extent of reinforcement of the filled rubber depend mainly on the filler concentration and principal properties of filler such as particle size, surface area, aggregate structure and its distribution in rubber matrix as well as rubber-filled interaction (El-Tantawy and Dishovsky, 2004). The interaction between hydrocarbon rubber and carbon black can be improved by the introduction of polar groups in the rubber through blending and/or addition of some particular additives (Medalia and Kraus, 1994). In the present paper, blends of non-polar (hydrocarbon) natural rubber and polar acrylonitrile-butadiene rubber (NBR) filled with varying filler loadings of carbon black/carbonized Dika nutshell powder were prepared. Vulcanizate properties of the filled blends were investigated. Carbonized Dika nutshell powder as a filler in rubber blends has not been reported in the scientific literature to my knowledge. However, the effects of carbonization temperature on the filler properties of groundnut shell powder have been reported by Ayo et al, 2011, who determined that the bulk density and percentage loss on ignition decreased with increase in carbonization temperature. The authors also revealed a progressive increase in iodine adsorption number as the carbonization temperature increased, whereas the filler p^H changed from acidity to alkaline with increasing carbonization temperature.

MATERIALS AND METHODS

Materials

The acrylonitrile-butadiene rubber used in this work was purchased from a chemical store in Lagos, Lagos State, Nigeria. Natural rubber conforming to Standard African Rubber (SAR) grade 3 having the characteristics given in Table 1 was kindly provided by Rubber Research Institute of Nigeria (RRIN), Iyanomo, Benin City. Reagents used in the physico-chemical characterization of Dika nutshell powder and its carbonized variety were of analytical grades, while the rubber blend compounding chemicals were of the commercial grades.

Table 1.Characteristics of SAR 3 (Professional Assoc. NR in Africa, 1998)

<i>Parameters</i>	
Dirt content retained on 45 μ m sieve (%)	0.02
Ash content (%)	0.32
Volatile matter	0.40
Nitrogen (%)	0.23
Initial plasticity (p ⁰)	36
Plasticity after aging for 30min @140 ⁰ c (p ³⁰)	24
Plasticity retention index (PRI)	67
Mooney viscosity ML (1+4), 100 ⁰ C	70

Sample preparation

Carbonization and characterization of dika nutshell powder

The Dika nutshells were washed and dried in air to remove sand particles and moisture. Thereafter, portion of the Dika nutshells were milled to fine powder and sieved through a mesh size of 150 μ m. The fine particles that passed through the mesh were collected as unmodified Dika nutshell powder. The remaining portion were weighed and carbonized at a temperature of 800⁰c for 3hours (Ishak and Baker, 1995). The carbonized shells were then milled to a fine powder and sieved through a 150 μ m sieve mesh. The fine powder that passed through the mesh were then collected as carbonized Dika nutshell powder. The unmodified Dika nutshell powder (U-DNS) and the carbonized Dika nutshell powder (C-DNS) were characterized in terms of weight loss on ignition, p^H, surface area, moisture content and oil absorption. The weight loss on ignition was determined gravimetrically, and expressed in terms of percentage according to ASTM 1509. The p^H of the samples were determined by a method described by Ishak and Baker, 1995. Surface area was measured by the iodine adsorption method according to ASTM 1510. Moisture content was determined by drying the sample to a constant weight and the weight loss recorded in percentage as moisture content. The oil absorption was determined by a method described by Hepburn, 1984. The procedures for sample characterization were repeated for carbon black (CB) which was used as a reinforcing filler in this work. The characteristics of U-DNS, C-DNS and CB are given in Table 2.

Table 2.Physical Characteristics of Dika nutshell Powder (U-DNS and C-DNS) and carbon black (CB).

<i>Parameters</i>	<i>U-DNS</i>	<i>C-DNS</i>	<i>CB (N330)</i>
Loss on ignition (%)	40.60	79.80	92.90
P ^H of slurry	5.42	5.98	6.50
Iodine adsorption number (mg/g)	49.50	68.90	79.88
Moisture content (%)	10.40	3.50	2.89
Oil absorption (g/100g)	50.20	52.50	54.0

Compounding Of Blend Compositions

Blend compositions of SAR/NBR used were 0/100, 25/75, 50/50, 75/25, 100/0 wt%, respectively; while CB/C-DNS filler ratios were 0/50, 10/40, 20/30, 30/20, 40/10, and 50/0, phr (parts per hundred parts of rubber), respectively. The formulation used in preparing the blend samples is given in Table 3. Weighed amounts of the compounding ingredients with the exception of vulcanizing agent and accelerators were first introduced into a Banbury mixer already preset at 145-150^oc for the mastication of the ingredients, and the rubber blend produced was later transferred to a two-roll mill which converted it from an irregularly shaped mass to suitable sheets. The temperature of the mill was reduced from 170^oc to 90^oc before the introduction of the vulcanizing agent and accelerators to prevent premature curing of the compound mix. The milled sheets were then cured into sheets of 2mm thick using hot press at 5MPa pressure and heating temperature of 145^oc for 20min.

Table 3. Compounding recipe of SAR/NBR/Filler blend (parts per hundred weight of rubber, (phr) using different CB/DNS blend ratios.

Compounding Ingredients (phr)	Sample				
	A	B	C	D	E
SAR	100	75	50	25	0
NBR	0	25	50	75	100
Zinc Oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
Wax	4	4	4	4	4
MBT	0.5	0.5	0.5	0.5	0.5
TMTD	1	1	1	1	1
Sulphur	3	3	3	3	3
Carbon black (CB) N330	0, 10, 20, 30, 40, 50				
¹ Dika nutshell filler (DNS)	0, 10, 20, 30, 40, 50				

¹DNS: Dika nutshell powder-both unmodified (U-DNS) and carbonized (C-DNS).

MBT: mercaptobenzoylthiazole.

TMTD: tetramethylthiuramdisulphide

Vulcanizate Property Measurement

Determination of tensile properties

Tensile properties were determined on a Monsanto Tensile Tester (Model1/m) with a cross head speed of 500mm/min using a dumbbell test pieces measuring 45mm x 5mm x 2mm according to ASTM D412-87 method A. The recorded value for each tensile parameter is the average of three measurements.

Crosslinking density measurement

The chemical crosslinking density of the blend vulcanizate was determined by following the procedure of equilibrium swelling in toluene (Akinlabi et al, 2000).

Solvent immersion test

The equilibrium swelling of the blend vulcanizates in toluene, petrol and water was conducted at room temperature using the immersion-weight gain method according to ASTM D471.

RESULTS AND DISCUSSION

Tensile Properties

The influence of filler content on the mechanical properties of reinforced-elastomers has been extensively reported in the literature (Ramesan, 2004). In this work, blend compositions of SAR/NBR: 0/100, 25/75, 50/50, 75/25 and 100/0 wt%, respectively were reinforced with CB/C-DNS: 50/0, 40/10, 30/20, 20/30, 10/40 and 0/50 phr, respectively. The degree of reinforcement usually increases with filler loading. The degree of reinforcement will depend on the extent of wetting of filler particles by the polymer matrix (Kurian et al, 1995). The interaction between hydrocarbon rubber and carbon black can be improved by the introduction of polar groups in the rubber through blending and/or addition of some additives (Medalia and Kraus, 1994). The tensile strength of blend composition SAR/NBR:75/25 was studied as a function of filler loading and the results are presented in Fig. 1. The results show that tensile strength of blend increased with filler loading, rising from 10 - 50 phr after showing an initial decrease at 10 phr. The initial decrease in tensile strength is expected since at low filler loading, the fillers tend to act as flaws instead of as reinforcement. This reduces the tensile strength of the filled blend (Onyeagoro, G, 2010). This observation suggests that all the fillers studied are non-reinforcing at lower loadings, although the initial decrease in tensile strength is least pronounced in neat CB-filled blend and most pronounced in neat U-DNS filled blend. However, the degree of reinforcement at low filler loading is found to be highest for carbon black (CB) closely followed by carbonized Dika nutshell filler (C-DNS). The unmodified Dika nutshell filler (U-DNS) showed relatively low degree of reinforcement. This observation is consistent with the measured physical characteristics of U-DNS, C-DNS and CB (Table 2). The results show that weight losses on ignition were 40.60%, 79.80%, and 92.90% for U-DNS, C-DNS and CB, respectively. In physical characterization of fillers, weight loss on ignition is a measure of the carbon content lost during combustion and measures the effectiveness of the filler as a reinforcement. The higher the values the greater the reinforcing potential. The result in Table 2 shows that the order of reinforcement is : CB > C-DNS > U-DNS, which is consistent with the tensile strength result obtained. Again, the iodine adsorption provides an estimate of the surface area of filler. The values obtained (Table 2) indicate that the surface area of U-DNS is markedly lower than that of C-DNS. The higher the value the larger the surface area, and the more reinforcing the filler becomes. The results obtained therefore suggest that the improved surface area of C-DNS over that of U-DNS is due to carbonization of DNS which consequently improved its reinforcement. Thus, the markedly improved tensile strength exhibited by C-DNS is attributed to polar – polar interaction between the cellulosic (polar) DNS and the polar NBR rubber which improved with carbonization of DNS.

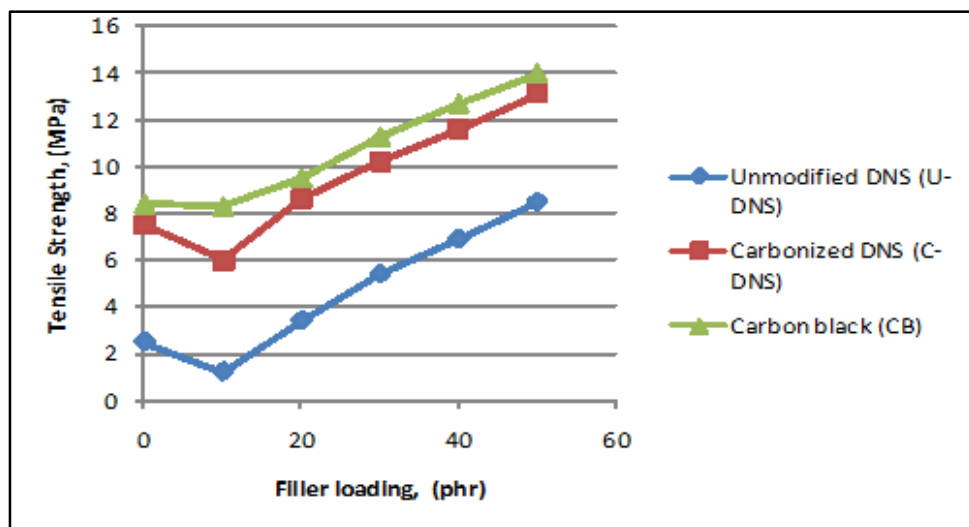


Figure 1. Tensile Strength versus filler loading for SAR/NBR:75/25 blend composition

Normal Stress – Extension ratio behavior

The effects of blend ratio and filler content on mechanical properties of reinforced-elastomers have been extensively reported in the literature (Findik et al, 2004). In this work, different blend ratios of SAR/NBR were reinforced with different filler ratios of CB/C-DNS. The degree of reinforcement will depend on the extent of polymer – filler interaction and the degree of wetting of filler particles by the matrix (Kurian et al, 1995). The normal stress – extension ratio plots of different blend compositions as a function of CB/C-DNS loading are presented in Figures (2 – 6). It can be seen that CB and CB – rich blends withstand stress more.

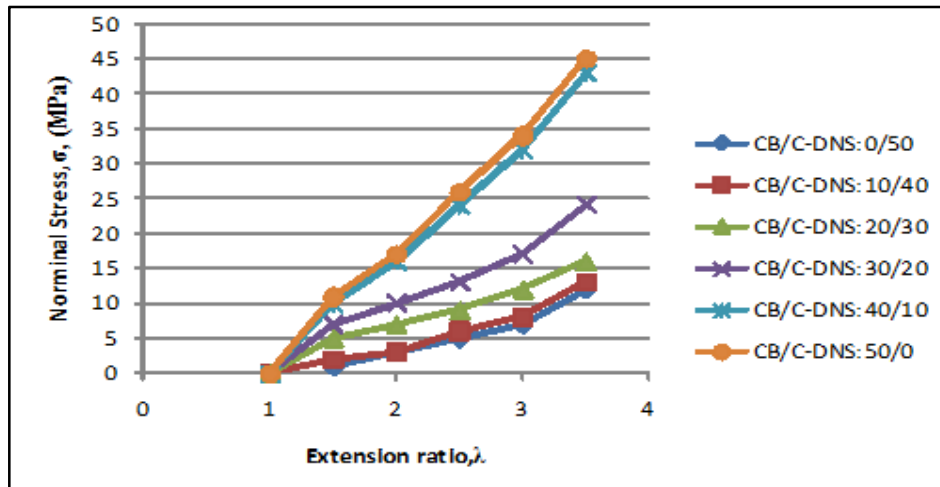


Figure 2. Normal Stress versus Extension ratio for SAR/NBR:100/0 blend

NBR – rich blends showed higher stress – bearing capacity than SAR – rich blends for all CB/C-DNS filler ratios. This observation is consistent with the findings of Kraus, 1978. The author revealed that carbon black surfaces contain active polar groups which interact more with polar rubbers than hydrocarbon rubbers, especially in the presence of non – reinforcing polar fillers. The higher stress – bearing capacity of NBR – rich blends than SAR – rich blends is therefore attributed to better polar – polar interaction. The reinforcement exhibited by CB/C-DNS:40/10 was slightly lower than the highest shown by neat CB, i.e. (CB/C-DNS:50/0), but dropped progressively with further increase in C-DNS content. This is an indication that at low level of 10 phr, C-DNS is a promising substitute filler for carbon black as a reinforcing filler in the rubber industry, especially for low – cost/high volume rubber products where strength is not critical.

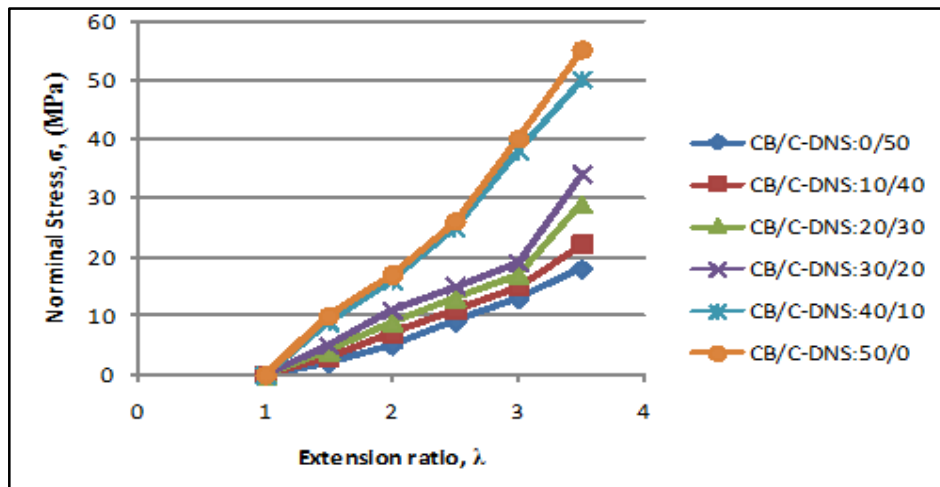


Figure 3. Normal Stress versus Extension ratio for SAR/NBR:75/25 blend

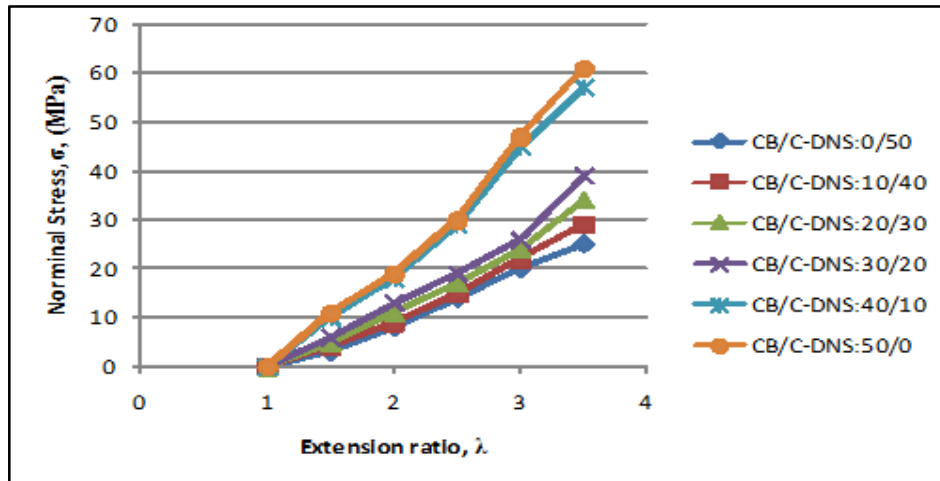


Figure 4. Norminal Stress versus Extension ratio for SAR/NBR:50/50 blend

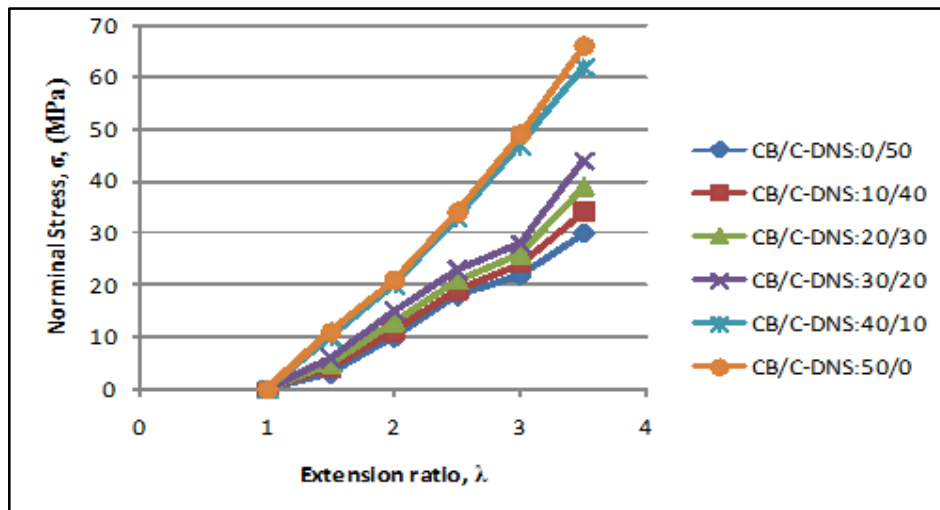


Figure 5. Norminal Stress versus Extension ratio for SAR/NBR:25/75 blend

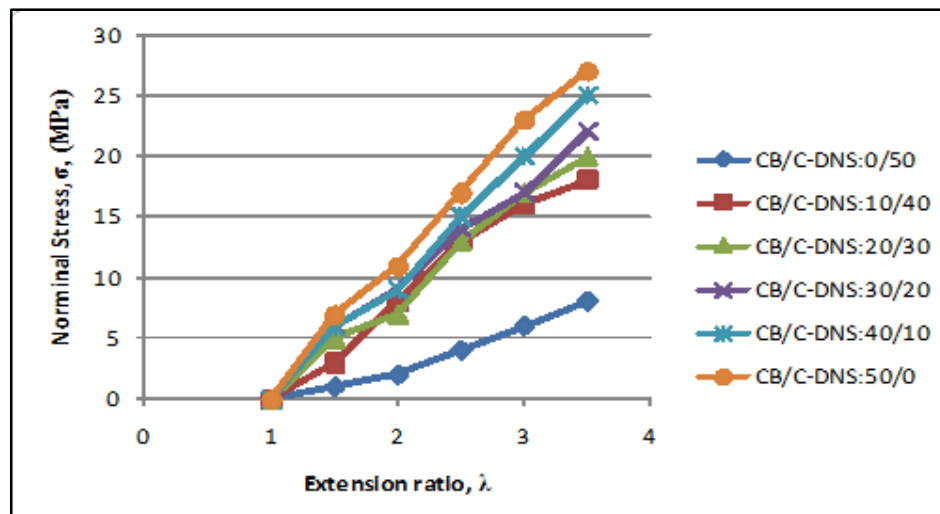


Figure 6. Norminal Stress versus Extension ratio for SAR/NBR:0/100 blend

Effects of Filler and blend ratios on Elongation at break

The effects of filler and blend ratios on elongation at break are presented in Table 4. The elongation at break showed a decreasing behaviour for CB-rich filler for all blend compositions studied. This observation is attributed to the higher reinforcing capacity of CB over C-DNS filler. By increasing CB content, the chain mobility decreased due to the formation of physical bonds between filler particles and polymer chains. Consequently, the elongation at break dropped with increase in CB content. This explains the least value of elongation at break obtained with CB/C-DNS:50/0. For all blend compositions, the reinforcement capacity of CB/C-DNS:40/10 is significant as shown by the slightly higher value of elongation at break when compared with CB/C-DNS:50/0. However, a higher elongation at break was observed for SAR and SAR – rich blends mainly because SAR matrix has greater chain mobility than NBR matrix since the T_g of SAR is -72°C , whereas that of NBR is -40°C (Sau et al, 1997).

Table 4. Effects of Filler and blend ratios on Elongation at break.

Filler (phr)	Elongation at break (%)				
	SAR/NBR	SAR/NBR	SAR/NBR	SAR/NBR	SAR/NBR
	100/0	75/25	50/50	25/75	0/100
CB/C-DNS:0/50	490	426	371	334	305
CB/C-DNS:10/40	435	397	349	316	284
CB/C-DNS:20/30	396	354	327	293	265
CB/C-DNS:30/20	368	335	309	275	242
CB/C-DNS:40/10	314	295	278	246	220
CB/C-DNS:50/0	292	246	213	185	130

Crosslinking density

The crosslinking density of an elastomer can be determined from swelling or mechanical measurements. The crosslinking density values of homopolymers and blends have been calculated by using the following equation (Mark et al, 1986).

$$F = \frac{2 A_0 \rho_p RT [\lambda - (1/\lambda^2)]}{\eta} \quad (1)$$

Where F is the force required to stretch a specimen to an extension ratio (λ), A_0 is the cross-sectional area of the specimen, R is the universal gas constant and T , the absolute temperature and ρ_p is the material density. The changes in crosslinking density of blend samples as a function of C-DNS content in the blend system are shown in Table 5. Although the crosslinking density decreased progressively with

Table 5. Changes in Crosslinking density of blends as a function of blend ratio and C-DNS content in blend system.

Filler (phr)	Crosslinking density, (η), (mol/kg)				
	SAR/NBR	SAR/NBR	SAR/NBR	SAR/NBR	SAR/NBR
	100/0	75/25	50/50	25/75	0/100
CB/C-DNS:0/50	720	535	506	479	410
CB/C-DNS:10/40	945	756	614	495	448
CB/C-DNS:20/30	1250	823	685	523	495
CB/C-DNS:30/20	1485	955	751	582	518
CB/C-DNS:40/10	1748	1228	864	625	542
CB/C-DNS:50/0	1800	1304	972	687	586

increasing C-DNS content in all filler ratios, significant values were obtained with CB/C-DNS:40/10 which compares favourably with the highest values obtained with neat CB, i.e. (CB/C-DNS:50/0). However, crosslinking density showed an increasing trend for SAR and SAR – rich blends, mainly due to greater chain regularity of SAR over NBR which improves on reinforcement.

Solvent Immersion Results – Volume Swell

The volume swell results for the various blends in the three chosen solvents at 25^oc are presented in a bar chart in Figures (7 – 9). Toluene created the highest volume swell for all blends tested, whereas the lowest swells were seen with water. It appears that the volume swell increased as the polar character of the solvent decreased. Even though toluene and petrol (gasoline) are all organic solvents, the lower value of volume swell of petrol over toluene may be due to the presence of anti – knock additive blended with petrol to lower tail pipe emissions (Cackette, T, 2006) which may have impaired its organic character and strength. However, volume swell increased with increase in SAR content, but decreased with increase in C-DNS content in the blends. Volume swell is expected to increase with increase in the hydrocarbon character of blends. This explains the increase in volume swell obtained with increase in SAR (a hydrocarbon rubber) content. Similarly, the higher values of weight loss on ignition and iodine adsorption number of carbon black (CB) over C-DNS (Table 2) is an indication that CB is a better reinforcing filler than C-DNS. This is reflected in the least values of volume swell of neat CB blend, i.e. (CB/C-DNS:50/0 blend). However, volume swells of CB/C-DNS:40/10 are not significantly different from the least values obtained with the neat CB blend. This indicates that blends with low levels of C-DNS (10 phr) are as highly reinforcing as the blends filled with neat CB. This observation shows that the synchronous use of CB and C-DNS fillers at low level of C-DNS (10phr) in rubber blends can produce significant property improvement comparable to blend systems reinforced with only CB. This indicates that at low C-DNS filler loading of 10 phr, C-DNS is a potential substitute filler for CB in the rubber industry, especially in the production of low-cost/high volume rubber products where solvent resistance is not critical.

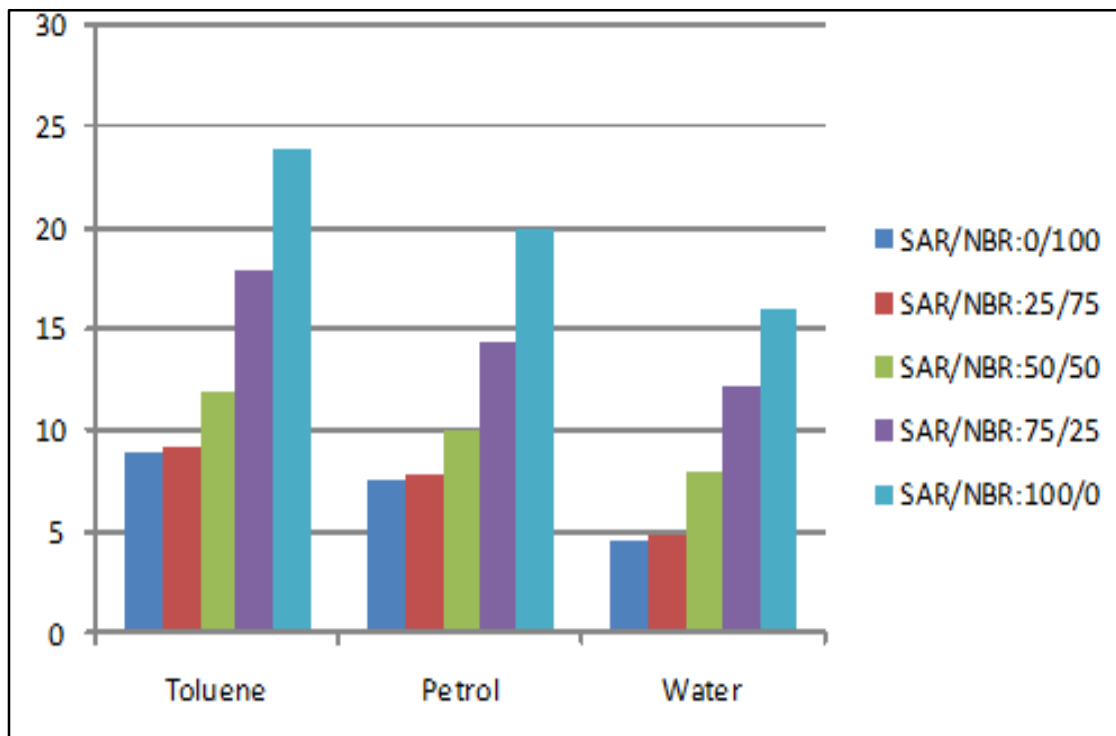


Figure 7. Volume swell versus solvent for CB/C-DNS:50/0 blend composition @ 25^oc.

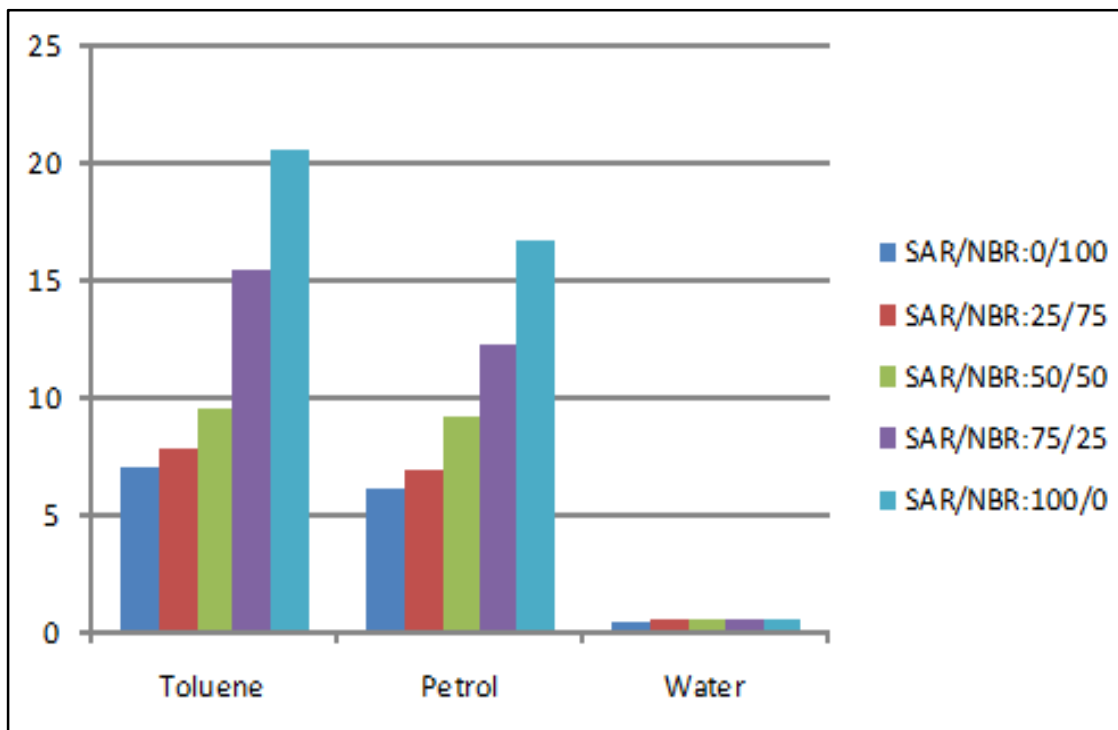


Figure 8. Volume swell versus solvent for CB/C-DNS:40/10 blend composition @ 25°C

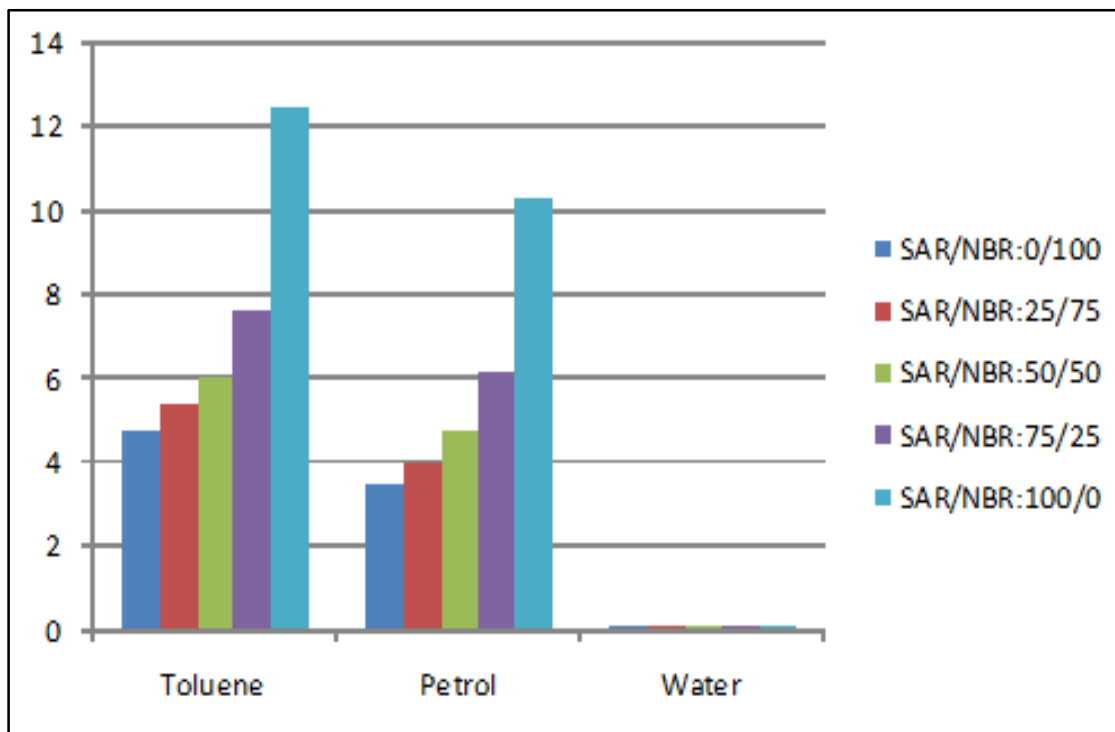


Figure 9. Volume swell versus solvent for CB/C-DNS:0/50 blend composition @ 25°C

CONCLUSION

It has been shown that carbonization of Dika nutshell powder could improve the vulcanization properties of Dika nutshell powder filled – natural rubber/acrylonitrile-butadiene rubber blend. The improvement in vulcanizate properties is supported by data on the increased content of tensile strength in the blend samples.

Synchronous use of carbon black and carbonized Dika nutshell powder as fillers in the blend samples revealed significant improvement in the vulcanizate properties of blends at low carbonized Dika nutshell filler loading of 10 phr comparable to the results obtained with blend samples reinforced with only carbon black. Consequently, carbonized Dika nutshell powder can serve as potential substitute filler for carbon black in the rubber industry, especially in the production of low-cost/high volume rubber products where strength is not critical. Enormous foreign exchange spent on importation of carbon black will be saved with concomitant reduction in the price of rubber products.

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