Cure, physico-mechanical and equilibrium swelling properties of groundnut shell-filled natural rubber

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ABSTRACT

The cure characteristics, physico–mechanical and equilibrium swelling properties of natural rubber vulcanizates filled with groundnut shell (GNS) and commercial grade carbon black, CB (N330) were investigated. The results showed that the scorch and cure times decreased while the maximum torque (Tmax) increased with increasing filler content for both filled vulcanizates. The tensile strength of both GNS and CB (N330) – filled vulcanizates increased to a maximum at 30phr and 40phr filler content respectively before decreasing with increasing filler loading. Properties such as elongation at break and rebound resilience decreased while modulus, specific gravity, hardness and abrasion resistance increased with increasing filler loading for both filled vulcanizates. However, the locally sourced filler, GNS, imparted lower specific gravity and strength (reinforcement) compared with CB (N330) filler. The equilibrium swelling in kerosene, diesel and toluene of the natural rubber vulcanizates decreased steadily with increasing filler loading, although the percentage equilibrium swelling of carbon black (N330)-filled vulcanizates were less than that of groundnut shell-filled vulcanizates probably due to less moisture content and finer particles of the CB(N330) filler.

Key words: Natural rubber, groundnut shell, fillers, reinforcement and swelling.

INTRODUCTION

The development and utilization of reinforcing fillers from renewable natural plant resources in polymer products has been a subject of ardent research in the past few years primarily due to their economic and environmental advantages over the traditional reinforcing materials such as carbon black. Fillers apart from the base polymer are by far the most important of the compounding additives in terms of quantity and their influence on the total property spectrum of the polymer vulcanizates. Documented reports have shown that natural rubber composites reinforced with plant materials have physico-mechanical properties comparable to those reinforced with some grades of carbon black in addition to their enhanced biodegradability, recyclability, low cost, high strength–to–weight ratio, light weight and reduced environmental pollution as well as providing attractive new value–added products[1-13]. Hitherto, carbon black, silica and synthetic fibres such as glass were the only reinforcing fillers in the polymer industry but these are expensive and non-renewable, hence the need to develop prototype low cost and effective reinforcing materials from renewable plant resources as potential substitutes for these synthetic materials. Industrial use of natural plant materials as reinforcing materials have also increased in many sectors of the polymer industry including the automotive, coating, packaging, construction, building and household–wares[14-15]. Among the natural plant materials and agricultural wastes that have been successfully utilized as fillers include rice husks, flax fibre, cocoa pod husk, rubber seed shell, plantain peel, oil palm fibre, mellon seed shell and pineapple leaf fibre[1-9]

The aim of this study is to determine the effect of groundnut shell (GNS) on the cure

characteristics, physico-mechanical and equilibrium swelling (in toluene, kerosene and diesel) properties of natural rubber vulcanizates as part of the on going search for an alternative, low cost, renewable and effective new class of reinforcing materials for polymers. Groundnut (*Arachnis hypogaea*) is a leguminous plant grown in most parts of Nigeria. The seeds may be eaten raw, boiled or fried and they may be processed into cooking oil or cakes. Chemically, groundnut is a lignocellulosic material. In addition, it contains oil, proteins, inorganic minerals, waxes and proteins[16].

EXPERIMENTAL

The materials used for this study include dried groundnuts obtained from local markets at Agbor, Delta state, Nigeria, and Natural rubber, Standard Nigerian Rubber, SNR10 obtained from FAMAD (formerly BATA), Benin City. Industrial grade carbon black (N330), got from Nigerian National Petroleum Corporation (NNPC), Warri, industrial grade compounding additives and rubber test equipment got from the Department of polymer Technology, Auchi Polytechnic, Auchi, Edo state, Nigeria and Dunlop (Nig) Plc, Ikeja, Lagos were used.

Characterization of GNS and SNR10

The groundnuts were shelled manually with hands and the shells were dried to a constant mass in an oven maintained at 120°C and was ground into fine powder with the aid of the corona grinding machine and screened through a sieve of mesh size 200nm. The SNR10 used in this study was characterized in terms of its dirt, ash and nitrogen contents, volatile matter, plasticity retention index (PRI) and Mooney viscosity using standard techniques[10,17]. The sieved powder of GNS was characterized in terms of moisture content, loss on ignition, iodine adsorption number, pH of its aqueous slurry, density and particle size relative to those of carbon black (N330) using standard methods[4,10,18-19].

Compounding and curing of the mixes

The recipe used in the formulation of the natural rubber (SNR10) compounds is given in Table 3. Each of the formulation was masticated and the mixing was carried out using the laboratory two–roll mill of size 160 x 320 mm maintained at 80°C. The compounded natural rubber was cured by compression moulding using the stream press machine with a pressure of 150kg/cm maintained at 140°C. The cure characteristics of the vulcanizates were determined using the Monsanto Rheometer, MDR 2000. The scorch time, cure time and the torque were recorded from the resulting rheometer readings.

Determination of physico-mechanical and equilibrium swelling (S_{eq}) properties of the vulcanizates

The tensile strength, modulus and elongation at break of the vulcanizates were measured with the Monsanto Instron Tensometer, 4301, at a cross-head speed of 500mm/min using the dumb-bell shaped test specimens in accordance with ASTM D412[20]. The Wallace croydon resiliometer 2A was used to determine the rebound resilience while the specific gravity and hardness of the vulcanizates were measured by the Monsanto Densitron 2000 and Monsanto Duratron 2000 respectively, abrasion resistance of the vulcanizates was measured using the Akron Abrader in accordance with the procedure described in BS903 Part A9[21-23].

The equilibrium swelling (s_{eq}) of the natural rubber vulcanizates in solvents (toluene, kerosene and diesel) were determined by gravimetric method[25-26]. The test specimens were cut into square shape of known weights and immersed in air-tight plastic bottles containing the solvents under investigation. The specimens were monitored for 3 days at room temperature (about 30°C) until equilibrium sorption was reached, they were surface dried with blotting paper and reweighed.

The equilibrium swelling (S_{eq}) was calculated using the relation,

$$S_{eq} = \frac{M_{eq} - M_o}{M_o} \times 100$$

where,
M_{eq} = weight of swollen rubber specimen at equilibrium
M_o = weight of rubber specimen before immersion in the solvent.

RESULTS AND DISCUSSION

Physical properties of the natural rubber and filler

Tables 1-2 summarise the properties of the rubbers and filers under investigation. The results of the analyses revealed that the physical properties of the Standard Nigerian Rubber (SNR10) compared favourably with those of other standard natural rubbers such as the Standard African Rubber, SAR[7,23] and Standard Malaysian Rubber, SMR[24], thus indicating a high quality rubber due to its low dirt, ash and nitrogen contents. The high values of PRI and the Mooney viscosity suggest a high resistance of the resulting rubber vulcanizates to ageing and flow respectively[17]. Table 2 shows the physical properties of GNS and CB (N330).The results revealed that GNS has a higher moisture content than CB (N330) at 125^0C. Similar observations have been reported in earlier studies[4,9,27-28]. It has been shown that a high moisture content of a filler often leads to poor filler dispersion into the polymer matrix resulting in a weak interfacial bonding between the filler and polymer matrix[2,9,11,27-28]. The results also showed that the loss on ignition at 1000^0C was higher for CB (N330) than GNS thus suggesting that CB (N330) has a higher content of carbon than GNS. Similar observation has been documented in earlier studies[27-28]. The amount of carbon a filler has is a measure of its reinforcing potential; the higher the carbon content, the greater is its reinforcing power[27]. The results further revealed that CB (N330) has a higher iodine adsorption number and, thus a larger surface area (smaller particle size) than GNS. Further more, the results showed that the aqueous slurry of GNS was more acidic (pH, 5.80) than CB (N330) (pH,6.90). It has been shown that acidic fillers retard cure rates and reduce filler-matrix interactions[1,24]. Thus the filler related parameters such as carbon content, moisture content, surface area, particle size, surface structure determined from oil absorption values and pH of the aqueous slurry of a filler are primary determinants of its reinforcing efficiency. The higher the carbon content and the larger the surface area, the higher are the

Table -1: Characteristics of the SNR10, Standard African Rubber, SAR10 and Standard Malaysian Rubber, SMR5

Parameter	SNR10	SAR10[7]	SMR5[24]
Dirt content (%)	0.01	0.02	0.05
Ash content (%)	0.25	0.32	0.50
Nitrogen content (%)	0.20	0.23	0.70
Volatile matter (%)	0.25	0.40	1.00
Plasticity Retention Index (PRI)	71.01	67.00	-
Mooney viscosity, (1+4) at 100^oC	76.00	70.00	60.00

Table -2: Physical properties of GNS and CB (N330)

Parameter	GNS	CB (N330)
Moisture content at 125^0C (%)	2.25	1.10
Loss on Ignition at 1000^0C(%)	85.50	95.00
Iodine Adsorption number (mglg)	52.60	80.97
Oil absorption(g/100g)	52.50	55.00
pH of aqueous slurry	5.80	6.90
Density (g/cm^3)	1.25	1.80
Particle size range(nm)	20 – 200	30 – 35

possibilities for strong matrix-filler interactions during vulcanizations[1-3,9-11,27-28].

Cure Characteristics of the SNR10 Compounds.

          The cure characteristics of SNR10 vulcanizates filled separately with GNS and CB (N330) at different filler loadings are shown in Tables 4 and 5. The results show that the scorch time and cure time for both GNS and CB (N330)-filled vulcanizates decreased with increasing filler content. Although, the GNS-filled vulcanizates had higher cure times than the CB(N330)-filled vulcanizates probably due to higher acidity (less pH value) of GNS filler than CB(N330) filler (Table 2). Acidic fillers tend to retard cure rate[29].

          The maximum torque (Tmax) for both the GNS and CB (N330) filled systems increased with increasing filler content. This observation is consistent with earlier studies[1,30]. The increase in Tmax with increasing filler content implies that an increasing amount of crosslinks was formed with the addition of fillers. These crosslinks reduced the free mobility of the polymer chains of the natural rubber. However, the GNS-filled vulcanizates had lower Tmax hence fewer crosslink density and thus lower restriction to the molecular mobility of the polymer chains due to poorer filler-rubber matrix interactions probably as a result of the larger particle size and higher moisture content of GNS than CB (N330) filler.

Physico–Mechanical properties of SNR10 vulcanizates

          Tables 6 and 7 summarise the physico-mechanical properties of SNR10 vulcanizates filled separately with CB (N330) and GNS at different filler loadings. The results showed that the tensile strengths of both GNS and CB (N330)–filled SNR10 vulcanizates increased to a maximum level at 30 phr and 40 phr respectively beyond which they decreased with increase in filler content. These observations are consistent with earlier works[1,4,7,9,27-28]. However, GNS–filled vulcanizates exhibited a lower strength than CB (N330)–filled vulcanizates. This implies that GNS has a lower reinforcement power than CB (N330) probably due to its poor dispersion into natural rubber matrix and thus weak polymer matrix-filler interaction as a result of large particle size and high moisture content. It has been shown that the most important factor in determining reinforcement is the particle size of the filler[1,4,7,9,27-31]: the smaller the particle size the more effectively the filler acts to increase the crosslinking sites at the particle-matrix interface. The particle size of the rubber adhesion[1,2,28,32]. The modulus at 100% strain (M100) for both GNS and CB(N330)-filled

Table -3: Recipe for the formulation of SNR10 – GNS Compounds

Ingredient	phr
Natural Rubber (SNR10)	100.0
Zinc oxide	4.0
Stearic acid	2.0
*Filler	0 – 70 **
Processing oil	2.0
CBS	2.0
TMQ	1.5
Sulphur	1.5

*Filler – GNS and CB (N330)
**Filler loading – O,10,20,30,40,50,60 and 70 phr.
CBS=N – Cyclohexyl–2–benzothiazylsulphenamide.
TMQ= 2, 2, 4–trimethyl–1,2–dihydroquinoline

Table-4: Cure Characteristics of SNR10 filled with GNS.

% filler	0	10	20	30	40	50	60	70
Scorch time, ts_2(s)	34.2	33.8	32.3	29.4	28.9	24.0	23.5	23.7
Cure time ,(s) t_{90}	63.8	63.2	62.7	54.0	55.8	56.6	48.0	45.6
Maximum torque (lb–in)	5.80	5.82	6.12	6.70	7.18	7.27	7.55	8.00

Table -5: Cure characteristics of SNR10 filled with CB (N330)

% filler	0	10	20	30	40	50	60	70
Scorch time, ts_2 (s)	34.2	32.4	30.8	28.8	28.4	28.2	26.5	24.0
Cure time, t_{90} (s)	63.8	49.2	46.6	43.8	42.6	41.8	41.2	40.8
Max. torque (1b–in)	5.80	7.57	9.81	11.07	11.18	11.26	12.09	13.18

vulcanizates increased with increasing filler content as shown in Tables 6 and 7. The lower modulus observed in GNS-filled vulcanizates compared with CB (N330)-filled system could be due to poor dispersion of the filler into the rubber matrix as a result of higher moisture content, larger particle size, pH and may be lignin content of GNS compared to CB (N330)[2,4,16].

The results also show that elongation at break for both filled systems decreased with increasing filler content. However, GNS–filled vulcanizates had higher values than CB (N330)– filled vulcanizates probably due to poor interfacial bonding between the filler and rubber matrix thus leading to a lower restriction of the free mobility of the polymer chains of the natural rubber and thus a lower restriction to stretching on the application of strain[10]. The hardness and specific gravity of both filled systems increased with increasing filler content. This can be explained by the fact that with increasing addition of the filler particles into the rubber matrix, the elasticity of the polymer chain is reduced resulting in a more rigid and dense vulcanizates. However, GNS imparted lower hardness and specific gravity than CB (N330).The resilience decreased while the abrasion resistance of both CB (N330) and GNS-filled vulcanizates increased to an optimuam at 50pm with increase in filler loading. Similar observations have been reported in related studies[1,7,30,33]. However, GNS-filled vulcanizates had lower resilience and abrasion resistance than CB(N330) filled system. This may be attributed to the high moisture content, large particle size and pH which could lead to poor wettability and insufficient rubber matrix–filler adhesion resulting in low crosslink density. Thus, the GNS–filled vulcanizates would be expected to be less rigid, lighter weight and less durable than CB(N330) filled vulcanizates.

Equilibrium swelling properties of natural rubber, SNR10 vulcanizates

Equilibrium swelling or sorption (S_{eq}) of natural rubber, SNR10 filled with groundnut shell (GNS) and carbon black (N330) in solvents (toluene, kerosene and diesel) have been shown in Tables 6-7. The equilibrium swelling values of the carbon black (N330) filled vulcanizates were lower than those of the GNS filled vulcanizates. The reason can be attributed to the finer particle size of the carbon black (N330) filler (Table 2). The smaller (finer) the particle size of filler, the better dispersion in the rubber matrix and the higher the crosslinking between filler-elastomer matrix and also the tendency of CB(N330) to form filler aggregates which can lower solvent diffusion into the rubber matrix[34-35]. The equilibrium swelling decreased steadily with increasing filler content. The equilibrium swelling in organic solvents is dependent on the nature of filler and solvent the degree of crosslinking and filler adhesion, dispersion and compatibility with the polymer matrix[35-39].

The higher the crosslinking, the lower the swelling of rubber vulcanizates. According to the work of Lapack *et al* and Quddane, a filler particle acts as obstruction to the diffusion of solvent molecules into an elastomer matrix, thereby reducing the quantity of penetrant liquid into the rubber. So, the higher the filler content, the less quantity of solvent can diffuse or penetrate into the rubber matrix[40-41]. It was observed that the equilibrium swelling was highest in toluene and lowest in diesel. This trend may be attributable to the nature of the solvent involved, its molecular

Table -6: Physico–mechanical and equilibrium swelling properties of SNR10 filled with GNS

% filler (GNS)	0	10	20	30	40	50	60	70
Tensile strength (Mpa)	6.76	6.86	7.92	10.61	8.48	6.98	6.91	6.80
Modulus M100 (Mpa)	0.63	0.48	0.68	0.87	0.98	0.85	1.65	2.28
Elongation at break (%)	805	617	562	495	480	467	351	310
Specific gravity (S.G)	1.001	1.001	1.001	1.002	1.002	1.003	1.012	1.021
Rebound resilience (%)	83.6	62.8	61.6	60.0	63.6	60.6	60.7	54.9
Hardness (IRHD)	38	40	43	45	47	49	51	55
Abrasion resistance index	39	38	39	40	40	41	40	38
S_{eq} T (%)	345.5	332.9	325.7	310.5	296.3	273.3	252.3	246.4
S_{eq} K (%)	329.1	298.3	286.4	274.3	251.1	240.1	236.3	228.9
S_{eq} D (%)	253.2	238.8	219.6	209.9	185.3	176.7	158.8	150.2

Table -7: Physico-mechanical and equilibrium swelling properties of SNR10 filled with CB(N330)

% filler CB(N330)	0	10	20	30	40	50	60	70
Tensile strength (Mpa	6.76	17.74	26.60	31.01	33.02	32.18	30.80	28.48
Modulus M100 (Mpa)	0.63	2.07	2.18	2.49	5.49	5.34	5.51	5.99
Elongation at break (%)	805	558	508	489	411	326	296	220
Specific gravity (S.G.)	1.001	1.001	1.032	1.065	1.091	1.118	1.140	1.178
Rebound resilience (%)	83.6	77.7	72.8	69.9	68.9	68.6	61.7	58.4
Hardness (IRHD)	38	44	48	52	55	67	70	76
Abrasion resistance index	39	40	41	42	43	44	43	41
S_{eq} T (%)	345.5	287.08	251.9	239.30	235.24	217.91	198.64	160.91
S_{eq} K (%)	329.1	269.78	248.57	237.20	225.54	215.33	178.70	159.42
S_{eq} D (%)	253.2	226.95	203.21	160.30	153.16	140.44	120.10	114.98

weight and diffusion coefficient[28,37,42]. The higher the molecular weight of solvent, the slower the diffusion into the rubber matrix. Also, elongated molecules like toluene tend to have higher diffusion coefficient and would diffuse faster than the kerosene and diesel. Diesel is having highest molecular weight and diffused slowest compared to toluene and kerosene.

Conclusion

This research focused on the development and utilization of a local filler from renewable natural plant resources as a potential supliment or diluent for conventional reinforcing materials such as carbon black due to the economic and environmental advantages of the renewable materials. The results showed that the incorporation of groundnut shell (GNS) influenced both the cure characteristics, pyhsico-mechanical and equilibrium swelling properties of natural rubber vulcanizates but its reinforcing efficiency is lower than that of industrial grade carbon black, CB (N330). This has been attributed, to its high moisture content, large particle size and may be pH, all of which probably led to poor dispersion of the filler particles in the rubber matrix and weak filler–matrix interactions. This study suggests that the reinforcing potential of GNS filler could be improved by carbonization and particle size reduction or by chemical pretreatment so as to reduce the moisture content and strengthen the filler–matrix adhesion.

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