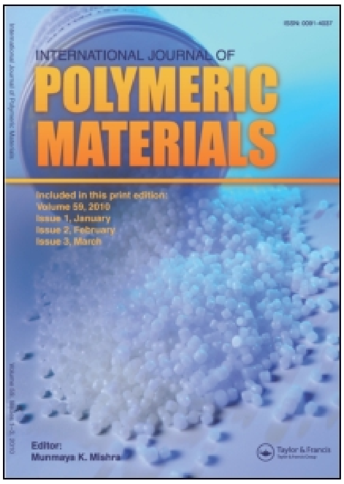

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Thermal Aging Properties and Molecular Transport of Solvents through Vulcanizates Prepared from Thioglycollic Acid Modified Epoxidized Low Molecular Weight Natural Rubber Blends Filled with Admixtures of Carbon Black and Carbonized Rubber Seed Shell

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Physico-mechanical, aging, swelling, solubility, and permeability properties of blends of natural rubber and thioglycollic acid modified epoxidized low molecular weight natural rubber (TGA-ELMWNR) filled with admixtures of carbon black and carbonized rubber seed shell (CRSS) in ketones, alcohols, aldehydes, and petroleum fuels (petrol, kerosene, and diesel) were investigated as a function of different filler composition. The physico-mechanical properties were found reducing as the level of CRSS increases, but were within the accepted level for natural rubber compounds, showing that CRSS can find uses as fillers in materials of low tensile strength. The aging results of all the mixes were nearly of the same magnitude. The swelling and solubility results showed that ketones swell the vulcanizates more and faster than alcohols and than aldehydes. The sorption, diffusion, and

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permeability of the blends as determined by the gravimetric method confirm the better resistance of blends with higher ratio of carbon black. Petrol was found diffusing through the vulcanizates faster than kerosene and faster than diesel. Above all, replacement of carbon black with 15% carbonized rubber seed shell has not shown any serious deleterious effects on the vulcanizates.

Keywords: aging, blends, permeability, properties, resistance, vulcanizates

INTRODUCTION

The quest by scientists, rubber producers, rubber processors, rubber merchants, rubber technologists, and all natural rubber users in developing rubber that can be used and compete favourably with series of synthetic polymers is daily getting stronger and attracting attention all over. It is true that natural rubber (NR) has some outstanding properties like high flexibility, good tensile strength, and so on, which has made it to be widely and commercially acceptable to users [1]. However, it also suffers some limitations in the aspect of poor resistance to organic solvent, oxygen, ozone, high permeability to gases, and so on, which is why synthetic rubbers are finding more uses in the limitation areas of NR. Because NR is a renewable resource and of widely commercial importance, it is very worthy not to let NR be chased out of market, instead ways of improving the limitation areas should be addressed and looked into so that we can develop and have new uses for NR.

Natural rubber is majorly used in tyres, whereas other uses of NR are less than 10% of the total rubber production [2]. Plastics and synthetic rubbers have seriously found uses in the limitation areas of NR, for example in products where low sorption, diffusion, permeability, high solvent, and aging resistance are highly desired, which implies that the need to improve on NR uses is very necessary and essential. NR on its own does not possess the necessary strength, modulus, and so on but the addition of compounding ingredients do impact the needed properties for the NR's demand. Several approaches on NR's modification and improvements have been documented [3–7] in which the two most prominent are: blending of NR with another polymer, and the incorporation of a material that will impact the required properties in the compounding ingredient.

Selection of compounding materials for NR mix is a very technical procedure and has been shown to have pronounced influence on the properties of the vulcanizates. In NR compounding, various additives: accelerators, activators, fillers, vulcanizing agents, anti-degradants, tickeners, softeners, and so on, are added for properties modification. The effect of compounding ingredients on rubber vulcanizate has been widely documented [1,3,6,8]. The choice of compounding ingredients is very selective and needs information about the materials to be added. Fillers are part of compounding ingredients and mostly used in larger quantity (next to the NR) in most rubber formulations. Fillers are added to rubber in order to cheapen the cost of production of a given rubber article; enhance a set of mechanical properties in order to increase longevity of the article in service; and/or to facilitate various shaping processes to which a rubber may be subjected during manufacture [9]. Particulate fillers of which carbon black is a notable example are essentially important and widely used as reinforcing filler in industries. Commercially available carbon blacks are obtained from petroleum products, whereas thermal black from thermal cracking of natural gas and furnace black from incomplete combustion of oil feedstocks [5]. Because petroleum refinery residues are limited and unstable, it is of interest to develop fillers from renewable resources that would serve as viable alternative. The use of agricultural residues as fillers is of interest from both economic and environmental view points. It converts unwanted, low-value agricultural residues to useful, high-value materials. Agricultural residues are low cost materials and readily available in large quantity for use everywhere, of which well over 300 million tons are produced annually [3–6]. The use of carbonized forms of cocoa pod husk and ground nut husk as fillers have been previously documented [4] and it was further thought that the use of carbonized rubber seed shell, an agricultural waste, as filler in thioglycollic acid modified epoxidized low molecular weight natural rubber compounding might be of interest in the development of useful value-added products from locally available renewable resource that are not used in food, in the belief that the agricultural residue will be converted to some useful material in rubber industry. It is on this note that this study was centered on, in the belief that the findings here will serve as entirely new set of information in rubber technology.

EXPERIMENTAL

Materials

Natural rubber latex from NIG 903 clone having a dry rubber content (DRC) of 39.0% and total solid content (TSC) of 44.5% was obtained from the estates of the Rubber Research Institute of Nigeria (RRIN), Iyanomo, Benin City, whereas the crumb rubber conforming to Standard African Rubber (SAR) grade 3 was also obtained from the RRIN.

The reagents used in the preparation and characterization of natural rubber latex (NRL), crumb rubber (NR), low molecular weight natural rubber (LMWNR), epoxidized low molecular weight rubber (ELMWNR), and thioglycollic acid modified epoxidized low molecular weight rubber (TGA-ELMWNR) were of analytical grades, whereas the rubber compounding chemicals were of the commercial grades.

Methods

Production and characterization of LMWNR samples. The method described by Okieimen and Akinlabi [3] was adopted with slight modification using nitrobenzene as the depolymerizing agent, the extent of depolymerization was determined by size exclusion chromatogram (SEC) [10] and viscosity measurement using Ubbelhode viscometer [3]. The SEC used was designed by MILLIPORE consisting of a Waters 717 plus Auto sampler, a Waters 600E system controller, a Waters 510 HPLC pump- an automatic injector, a Waters 486 UV Tunable Absorbance Detector (220 nm), a Waters R1410 refractometer, and two PLGEL 30 cm mixed columns with a porosity of 20 µm. The installation was computer controlled by special software (baseline). The column temperature was fixed at 55°C. The cyclohexane flow rate was 0.8 ml/min, the injected volume 100 µl (at a concentration of 0.2 mg/ml), for the LMWNR samples, and 25 µl for the standard solutions. Calibration was carried out with synthetic poly(cis-isoprene) with molecular weights of 3,660, 7,000, 33,900, 68,500, 108,000, 293,000, 590,000, 963,000, and 3.0 million (expressed in g/mole). Prior to injection, the solutions were filtered (porosity of 0.45 µm).

Production of ELMWNR. The in situ epoxidation method was used with formic acid (90%) and hydrogen peroxide (30%) as a reaction medium at 5°C as described by Akinlabi et al. [11] with slight modification to obtain about 30% level of epoxidation. The extent of epoxidation of LMWNR was determined by titrating ELMWNR solutions with a standard hydrogen bromide solution using methyl violet as indicator.

Production of thioglycollic acid modified epoxidized low molecular weight natural rubber. The method described by Akinlabi et al. [8] was adopted with slight modification. In a typical experiment, thioglycollic acid (0.12 mol. liter^{-1} of solvent) was added to the freshly prepared ELWMNR (15.7 mol% epoxide content) solution at room temperature over 1 h with occasional stirring. The reaction was allowed to proceed for a further 17 h. At the end of this period, the modified material (TGA-ELWMNR adduct) was dried in air for a period of 24 h; The unreacted epoxy groups were estimated by taking the

TABLE 1 Recipes for Compounding Blends of Natural Rubber with Thioglycollic Acid Modified Epoxidized Low Molecular Weight natural Rubber Using Carbonized Rubber Seed Shell and Carbon Black as Fillers

Components (Phr)	Sample								
	A	B	C	D	E	F	G	H	I
Natural rubber	70	70	70	70	70	70	70	70	70
TGA-ELMWNR	30	30	30	30	30	30	30	30	30
Carbon black (HAF)	40	38	36	34	32	30	20	10	—
CRSS	—	2.0	4.0	6.0	8.0	10.0	20.0	30.0	40.0
Zinc oxide (ZnO)	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
MBTS	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Flectol H	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0

TGA-ELMWNR = Thioglycollic acid modified epoxidized low molecular weight natural rubber with 25% thioglycol conversion.

CRSS = Carbonized rubber seed shell and measured as percentages of carbon black that is: 0, 5, 10, 15, 20, 25, 50, 75, and 100% of carbon black.

MBTS = Dibenzothiazyl disulphide.

Flectol H = Polymerized 1,2 dihydro-2,2,4-trimethyl quinolene.

difference between the % epoxide level of the ELMWNR before and after the reaction.

Compounding of the mixes. The semi-efficient vulcanization system recipes recommended by Akinlabi et al. [12] are used. The compounding recipe is as shown in Table 1. Mixings were carried out using a laboratory two-roll mill in accordance with the method described by the American Society for Testing and Materials (ASTM)-D 3184-80 [13].

Cure characteristics. The cure characteristics of the mixes were measured at 170°C using an Oscillating Disk Rheometer (ALPHA ODR 2000) in accordance with the ISO 3417 method [14]. The respective cure times as measured by t_{90}, scorch times, torque, and cure rates were determined from the rheograph.

Measurement of the Mooney viscosity. The Mooney viscosity of the sample was determined using of shearing disc viscometer model type Wallace MK III, according to ISO 289 [15]. The results were expressed in terms of ML $(1+4)$ at 100°C.

Compression set measurement. Wallace compression set machine (Model/Ref. no. C2; Hz 50) was used. Compression set was designed to evaluate the extent by which the specimen fails to return to its original thickness when subjected to standard compression load (1N) for a given period of time (24 h) at a given temperature (100°C) [16].

The difference between the original thickness and the recovered thickness was expressed as a percentage of the original thickness. This is expressed mathematically as:

$$\text{Compression set }(\%) = \frac{(\text{to} - \text{tr})100}{\text{to}} \tag{1}$$

where to = initial thickness and tr = recovered thickness

Hardness test. The hardness test of rubber is the relative resistance of a surface to indentation by an indicator of a specified dimension under a specified load. The hardness of the vulcanizate was determined by adopting the standard dead load method described in BS 903 Part A26 [17]. The standard dead load method of measurement covers rubbers in the range of 30 to 85 International Rubber Hardness Degrees (IRHD).

Abrasion resistance. Wallace Akron abrasion tester was used in accordance to BS method [18]. The angle between the test specimen and the wheel was adjusted to an angle of 15°. The abrasion was carried out for four 1,000 revolutions and the material loss for each run was noted. The specimen was re-weighed between each test run. From the mean of the five runs, the volume of rubber loss per 1,000 revolutions of the abrasive wheel was calculated. The result is expressed as:

$$\text{Abrasion resistance index} = \frac{[\text{s}]100}{\text{T}} \tag{2}$$

where, S = volume loss per 1,000 revolutions of abrasive wheel, calculated from the mean of 5 runs on standard rubber, T = volume loss per 1,000 revolutions of abrasive wheel, calculated from the mean of 5 runs on the sample rubber.

Mechanical properties. The test specimens were molded in an electrically heated hydraulic press (TECHNO LOIRE) at 164°C for 4 min by using the cure time, t_{90} obtained from the rheograph. Tensile properties of the vulcanizates were measured with a Mosanto Tensile Tester Model (1/M) at a crosshead speed of 500 mm/min using a dumbell test specimen (Type II) as contained in ASTM D-412-87 (method A) [19].

Aging properties of the vulcanizates. Air-oven aging testing was carried out in a precision oven with forced circulating air at the required temperature (30, 40, 50, 60, and 70°C) for 48 h in accordance with the procedures described by Allen et al. [20]. Test samples used for tensile-mechanical properties were cut from the dumbbell specimen. Properties measured on the fresh samples were also measured on the aged samples.

Swelling experiments. The resistance of the vulcanizates in toluene, acetone, ethanol, methanol, formaldehyde and acetaldehyde were determined by using the methods described in ASTM D3610 [21] with slight modification. Three different shapes of the cured sample (triangle, square, and rhombus) were cut from the 1 mm thickness mold and weighed before submerging each sample in its respective solvent in air-tight bottles maintained at 25°C for 72 h. Experiments were carried out in triplicate. At the end of the swelling, the sample was removed from the solvent, carefully blotted to remove excess liquid on the surface, and the weights immediately taken. Thereafter, the sample was further dried to a constant weight. The percentage increases in weight of the sample was calculated as the swelling while the percentage loss in weight after drying to a constant weight was calculated as the solubility.

$$\%\ \mathrm{Swelling} = \left(\frac{\mathrm{W}_2 - \mathrm{W}_1}{\mathrm{W}_2}\right) \times 100 \tag{3}$$

$$\%\ \mathrm{Solubility} = \left(\frac{\mathrm{W}_1 - \mathrm{W}_3}{\mathrm{W}_1}\right) \times 100 \tag{4}$$

where W_1 is the initial weight of the sample, W_2 is the weight after swelling, and W_3 is the weight after drying to a constant weight.

Crosslink density. The chemical crosslinking density ($\rho RT/Mc$) was calculated from the shear modulus (G), whereas the molecular mass between crosslinks was calculated using the Flory-Rhener equation [22]:

$$\ln(1 - V_2) + V_2 + \chi V_2^2 + \rho V_1 V_2^{1/3}/Mc = 0 \tag{5}$$

where ρ is the density of the rubber hydrocarbon, V_1 is the molar volume of the solvent, V_2 is the volume fraction of rubber in the swollen sample, Mc is the molecular weight between crosslinking and χ is the polar–solvent interaction parameter given as ($\chi = 0.44 + 0.18V_2$).

$$\text{Crosslinking densities } \left(\frac{\rho}{Mc}\right) = \frac{G}{RT} \tag{6}$$

Diffusion studies. Studies of the sorption, diffusion, and permeability of petroleum fuels (diesel, kerosene, and petrol) through the vulcanizates were carried out at 30,45, and 60°C using the gravimetric method. The sorption was taken as the maximum weight gained. The diffusion coefficient, D, was calculated from the equation [23].

$$\mathrm{D} = \pi[\mathrm{hn}/4\,\mathrm{M}_\infty]^2 \tag{7}$$

where n is the slope of the linear portion of the sorption curve; h, the thickness of the sample; and M_∞, the maximum mass uptake that has been estimated by the least-square procedure. The permeability coefficient, P, is calculated from the simple relation [23] below, where S is the sorption:

$$P = DS \tag{8}$$

Energies of absorption. In order to obtain the activation energy of the system, the data on diffusion coefficient, D, was treated by the Arrhenius type of expression [24]:

$$\log D = \log D_o - E_a \log RT \tag{9}$$

where E_a is the activation energy, R is the gas constant, and T is the absolute temperature. In order to determine the enthalpies, ΔH, and enthropies, ΔS, of the system, the equilibrium adsorption constant, K, was treated with Vant Hoff expression [24]:

$$\log K = \frac{\Delta S}{2.303\,R} - \frac{\Delta H}{2.303\,RT} \tag{10}$$

where K (equilibrium adsorption constant) = mass of polymer/maximum swelling quotient, R is the gas constant, and T is the absolute temperature. K can be calculated in accordance to the relation [24]:

$$Kt^n = \frac{M_t}{M_\infty} \tag{11}$$

where n is system parameter, M_t and M_∞ are the mass uptake values at time t and at equilibrium, respectively. The free energy change, ΔG of the system was calculated by adopting Gibb's thermodynamics expression [24]:

$$\Delta G = \Delta H - T\Delta S \tag{12}$$

where ΔG is the Gibb's free energy, ΔH is the enthalpy, T is the absolute temperature and ΔS is the entropy.

RESULTS AND DISCUSSION

The Physico-mechanical properties of the vulcanizates compounded with the recipes in Table 1 are shown in Table 2. The tensile strength varies from 16.8 MPa for mix A to 8.3 MPa for mix I, which shows a 50.6% decrease in the value of tensile result from 100% CB filled to 100% CRSS filled; that is as the concentration of CRSS in the blend increases, the tensile strength reduces. The modulus at 50% elongation (M50) and modulus at 100% elongation (M100) follow the same

TABLE 2 Physico-Mechanical Properties of the Vulcanizate

Parameters	A	B	C	D	E	F	G	H	I
Tensile strength (Mpa)	16.8	16.2	15.6	14.4	13.5	12.3	10.6	9.7	8.3
Modulus at 50% elongation (MPa)	2.4	2.3	2.2	2.0	1.8	1.7	1.4	1.2	1.2
Modulus at 100% elongation (MPa)	6.5	6.2	6.1	5.8	5.6	5.3	4.9	4.5	4.1
Elongation at break (%)	985	964	955	925	891	876	835	815	801
Crosslink density ($\times 10^{-4}$)	1.8	1.7	1.7	1.5	1.5	1.4	1.4	1.3	1.3
Hardness (IRHD)	58	58	56	54	53	50	45	43	41
Compression set (%)	46	45	45	43	42	42	41	40	40
Abrasion resistance (%)	69	66	64	63	60	57	53	51	48
Mooney viscosity ML $(1+4)$ at 100°C	82	80	77	75	72	68	63	61	57

trend as the tensile result with mix A having the highest alues and mix I having the least values. M50 gave a reduction of 50.0% from mix A to mix I while M100 gave a reduction of 34.0%. The result of the elongation at break gave a reduction of 18.6% from mix A to mix I. The highest value of 985% elongation observed was for mix A while the least value of 801% was observed for mix I, implying that CRSS has not enhanced the elasticity of the vulcanizate.

The crosslinking density result was found reduce by 27.7% as the amount of CRSS in the blends increased. Crosslinking density gives an indication of the network formation in the rubber matrix. Looking at the results here, the percentage reduction was not too pronounced, showing that there are compatibilities within the fillers, which is a characteristic of a well compounded vulcanizate. The result of the compression sets also shows marginal difference of 13.0% from mix A to mix I, which gave an indication of a good recovery vulcanizate after subjecting to heat compression for a minimum period of 12 h. The hardness, abrasion resistance, and Mooney viscosity values of mix A were found to be the highest while mix I is the least. There was a gradual reduction in the values of hardness, abrasion, and Mooney viscosities as the ratio of CRSS in the mix increases, giving an indication that CRSS has not impacted any hardening properties on the vulcanizates, rather, a plasticizing/softening effect. Effects of plasticizers on natural rubber mix have been earlier documented by some workers [25–26], where it was mentioned that plasticizers enhance uniform distribution and dispersion of filler in the rubber martix. This was in line with the crosslink density result, that shows that despite the non-reinforcing characteristics of CRSS, its plasticing characteristics have facilitated the rubber network formation, suggesting CRSS as a good non-reinforcing filler. It should be mentioned that if the fillers were not compatible and the vulcanizate not well compounded, there could be weak polymer network formation, which will give rise to poor physical and mechanical properties. This might in turn decrease the durability and affect the performance characteristics of the product expected, but this was not observed as can be seen in the physico-mechanical properties shown in Table 2. The physico-mechanieal properties of polymer blends are generally controlled by many factors such as the nature of polymer, blend composition, compounding ingredients, nature of crosslinking, and the vulcanization method used [8–12]. It is worth mentioning that the energy requirement for mixes with higher CB loading during rheometric analysis were always higher, signifying the involvement and need of a larger amount of energy in the breaking of highly crooslinked network bonds formed, which shows the reinforcing characteristics of CB.

The aging results are presented as percentage change in the properties of the vulcanizates, using the expression

$$\text{Extent of aging} = \left[\frac{[\mathrm{O} - \mathrm{A}]}{\mathrm{O}}\right] \times 100 \tag{13}$$

where O is the original value for the fresh sample and A is the value after aging.

The results of the physico-mechanical properties of the vulcanizates after aging at 70°C for 48 h were compared with their unaged results and are presented in Table 3. The aging results at 30, 40, 50, and

TABLE 3 Aging Results of the Vulcanizates at 70°C for 48 h (% of Original Sample Values)

Parameters	A (%)	B (%)	C (%)	D (%)	E (%)	F (%)	G (%)	H (%)	I (%)
Tensile strength (Mpa)	7.4	7.5	7.8	7.9	7.6	7.7	7.4	7.7	7.9
Modulus at 50% elongation (MPa)	6.4	6.7	6.6	6.7	6.9	6.5	6.3	6.8	6.9
Modulus at 100% elongation (MPa)	7.9	8.4	8.3	8.5	8.4	8.6	8.1	8.6	8.7
Elongation at break (%)	15.1	14.8	15.3	15.5	15.3	15.4	14.9	15.6	15.6
Crosslink density ($\times 10^{-4}$)	4.7	4.8	5.0	4.9	5.1	5.3	4.8	5.1	5.3
Hardness (IRHD)	5.1	5.3	5.2	5.5	5.5	5.7	5.2	5.6	5.7
Compression set (%)	4.9	5.2	5.2	5.4	5.4	5.6	5.1	5.4	5.7
Abrasion resistance (%)	4.7	4.9	5.1	5.4	5.3	5.4	4.9	5.3	5.5
Mooney viscosity ML (1 + 4) at 100°C	5.6	5.6	5.6	5.7	5.8	6.1	5.6	5.8	5.9

60°C were not discussed because of marginal changes in the values when compared with the unaged.

The aging results shown in Table 3 do not follow any particular ascending or descending trend. It can be inferred that the aging properties of CB with CRSS are nearly the same because, irrespective of the various filler loading compositions, the aging result from all the vulcanizates were observed to be close. This further confirms the compartibility of CB with CRSS and the proper incorporation of the filler admixtures in the rubber matrix. The aging results of mix G (50%CB: 50%CRSS) were in most cases the best, which could possibly been a synergistic aging effect of CB and CRSS. The observed phenomenon suggests CRSS as having a positive aging influence in rubber vulcanizates, thereby suggesting that CRSS can find uses in rubber products where aging properties are of interest and importance. This discovery is an improvement over aging limitations of natural rubber.

The swelling results in Table 4 show that the vulcanizates have more affinities for toluene and acetone followed by ethanol and methanol but are sparingly soluble in formaldehyde and acetaldehyde. This trend indicates that ketones penetrate more than the alcohols and more than the aldehydes. At the initial stage, swelling rate was very high due to a large concentration gradient putting the samples under severe swelling stress, but the stress tends to reduce as swelling continues.

Mix A was observed to swell and solubilize less in all the solvents, the swelling and solubility trend was found to increase as the ratio of CRSS increases from mix A to mix I, suggesting CRSS not to have improved the solvent, swelling or solubility resistant properties of the vulcanizates. Swelling of natural rubber has been documented to be infuenced by various factors, such as crosslink type and density, amount and type of filler, and type of elastomer [2–3,20,25]. The presence of sulphur in the thioglycollic acid was initially thought to increase the crosslinking and reinforcing characteristics of the vulcanizates. So also was the thought that the presence of epoxide in the modified rubber will facilitate the incorporation of the compounding ingredients through the ring-opening of epoxide groups because epoxides are known to be very reactive and can promote reinforcing of the rubber network formed in the rubber matrix [4–6]. Epoxides have been documented to have higher glass transition temperature, good oil resistance, low gas permeability, improved wet grip, and rolling resistance with a high polarity [4–6]. Due to the reinforcing characteristics of CB, it is very likely that CB reacts easily with the sulphur in the thioglycollic acid to form a very strong crosslinked polymer network that hardens the vulcanizates with higher loading of CB and restricts

TABLE 4 Swelling and Solubility Results

Solvents	Mixes	W_1	W_2	W_3	% swelling	% solubility
Toluene	A	0.45674	0.53924	0.42979	15.30	5.90
	B	0.46732	0.55435	0.43928	15.70	6.00
	C	0.42397	0.50593	0.39768	16.20	6.20
	D	0.45896	0.55097	0.43005	16.70	6.30
	E	0.47776	0.57700	0.44671	17.20	6.50
	F	0.45643	0.55459	0.42585	17.70	6.70
	G	0.48816	0.59971	0.45448	18.60	6.90
	H	0.47684	0.58869	0.44298	19.00	7.10
	I	0.45558	0.56524	0.42278	19.40	7.20
Acetone	A	0.48764	0.54730	0.46813	10.90	4.00
	B	0.46591	0.52645	0.44634	11.50	4.20
	C	0.47321	0.53713	0.45286	11.90	4.30
	D	0.44987	0.51296	0.42963	12.30	4.50
	E	0.47862	0.54888	0.45612	12.80	4.70
	F	0.44449	0.51386	0.42315	13.50	4.80
	G	0.47869	0.56053	0.45332	14.60	5.30
	H	0.47115	0.55560	0.44524	15.20	5.50
	I	0.46916	0.55786	0.44195	15.90	5.80
Ethanol	A	0.47739	0.50517	0.46116	5.50	3.40
	B	0.48731	0.51786	0.47025	5.90	3.50
	C	0.48164	0.51457	0.46382	6.40	3.70
	D	0.46668	0.50073	0.44848	6.80	3.90
	E	0.47534	0.51277	0.45633	7.30	4.00
	F	0.45675	0.49539	0.43802	7.80	4.10
	G	0.47384	0.52013	0.45299	8.90	4.40
	H	0.48804	0.53868	0.46608	9.40	4.50
	I	0.45552	0.50557	0.43411	9.90	4.70
Methanol	A	0.49005	0.51207	0.47584	4.30	2.90
	B	0.47804	0.50162	0.46322	4.70	3.10
	C	0.46382	0.48978	0.44898	5.30	3.20
	D	0.47744	0.50738	0.46121	5.90	3.40
	E	0.46599	0.49892	0.44968	6.60	3.50
	F	0.45482	0.49011	0.43845	7.20	3.60
	G	0.43909	0.47779	0.42197	8.10	3.90
	H	0.48815	0.53350	0.46814	8.50	4.10
	I	0.46617	0.51171	0.44612	8.90	4.30
Formaldehyde	A	0.45672	0.47182	0.44530	3.20	2.50
	B	0.48003	0.49796	0.46755	3.60	2.60
	C	0.47745	0.49734	0.46408	4.00	2.80
	D	0.46584	0.48779	0.45140	4.50	3.10
	E	0.47654	0.50109	0.46129	4.90	3.20
	F	0.44991	0.47559	0.43506	5.40	3.30
	G	0.48123	0.51249	0.46391	6.10	3.60

(*Continued*)

TABLE 4 Continued

Solvents	Mixes	W_1	W_2	W_3	% swelling	% solubility
	H	0.46491	0.49670	0.44771	6.40	3.70
	I	0.46541	0.49937	0.44726	6.80	3.90
Acetaldehyde	A	0.45555	0.46867	0.44598	2.80	2.10
	B	0.48713	0.50271	0.47641	3.10	2.20
	C	0.46752	0.48398	0.45630	3.40	2.40
	D	0.47713	0.49598	0.46472	3.80	2.60
	E	0.46663	0.48658	0.45403	4.10	2.70
	F	0.47324	0.49502	0.45999	4.40	2.80
	G	0.48881	0.51454	0.47317	5.00	3.20
	H	0.44999	0.47517	0.43649	5.30	3.40
	I	0.46608	0.49425	0.44930	5.70	3.60

W_1 is the weight after extraction.
W_2 is the weight after swelling at 25°C for about 6 hrs.
W_3 is the wieght after drying in a vacuum to a constant mass.

the solvent penetration. The swelling results has also confirmed that the fillers used were compartible and the vulcanizates well compounded. If it been the other way round, there could have been migration and leaching of compounding materials, which may give rise to poor swelling, poor solubility, poor physical and poor mechanical properties. These properties give information about the durability and the performance characteristics of the product expected from the vulcanizate. Generally, a filler of fine particle size distribution, well-dispersed in good chemically bonded rubber phase should produce vulcanizate having good resistance in solvents. It was initially anticipated that mix G (50%CB: 50%CRSS) will have greater resistance to solvents because of the likely synergistic influence of the fillers but the heterogeneity influence of the fillers dominates over the synergism and this accounts for the observed swelling and solubility results of the vulcanizates.

The sorption results are as presented in Table 5. The sorption results are interpreted as mass increase per unit weight of the vulcanizate and they are presented as percentage increase.

A typical sorption, S, plot of the vulcanizates in petrol is shown in Figure 1. The plot appears to show linear relations in the beginning, suggesting the transport mechanism to be of a Fickian type. However, more complex effects seem to be operative after about 9 h of experiment, which brings deviations from linearity as can be seen in the plot. Similar observations occured in the sorption plots of kerosene and diesel. From the sorption values in Table 5, it is evident that S increases

TABLE 5 Showing Sorption, Diffusion, and Permeability Results

	Sorption × 10^2 (g/g)			Diffusion × 10^5 ($mm^2\ min^{-1}$)			Permeability × 10^2 ($mm^2\ min^{-1}$)		
Mixes	Petrol	Kerosene	Diesel	Petrol	Kerosene	Diesel	Petrol	Kerosene	Diesel
AT 30°C									
A	29	25	21	2.1	1.9	1.7	60.9	47.5	35.7
B	31	28	23	2.3	2.0	1.9	71.3	56.0	43.7
C	32	30	25	2.5	2.2	2.0	80.0	66.0	50.0
D	36	33	28	2.8	2.4	2.2	100.8	79.2	61.6
E	39	36	31	3.0	2.5	2.4	117.0	90.0	74.4
F	41	38	33	3.2	2.8	2.6	131.2	106.4	85.8
G	46	41	36	3.6	3.2	3.0	165.6	131.2	108.0
H	49	43	38	3.8	3.4	3.1	186.2	146.2	117.8
I	51	45	40	3.9	3.6	3.2	198.9	162.0	128.0
AT 45°C									
A	34	30	25	2.4	2.1	1.8	81.6	63.0	45.0
B	36	31	27	2.6	2.2	1.9	93.6	68.2	51.3
C	38	33	28	2.8	2.4	2.1	106.4	79.2	58.8
D	41	36	30	3.1	2.7	2.4	127.1	97.2	72.0
E	43	38	33	3.4	2.9	2.5	146.2	110.2	82.5
F	46	41	37	3.6	3.3	2.7	165.6	135.3	99.9
G	51	46	41	3.9	3.5	3.2	198.9	161.0	131.2
H	54	48	43	4.0	3.7	3.3	216.0	177.6	141.9
I	57	51	45	4.2	3.8	3.5	239.4	193.8	157.5
AT 60°C									
A	38	34	29	2.8	2.4	2.1	106.4	81.6	60.9
B	40	37	31	3.0	2.6	2.3	120.0	96.2	71.3
C	43	40	34	3.2	2.8	2.5	137.6	112.0	85.0
D	45	43	37	3.5	3.1	2.8	157.5	133.3	103.6
E	48	45	40	3.8	3.4	3.0	182.4	153.0	120.0
F	50	48	44	4.0	3.6	3.2	200.0	172.8	140.8
G	55	53	49	4.4	3.9	3.6	242.0	206.7	176.4
H	58	56	52	4.5	4.0	3.8	261.0	224.0	197.6
I	63	60	55	4.7	4.2	3.9	296.1	252.0	214.5

as the reaction temperature increases. S values of blends with higher ratio of CRSS were found having higher values, suggesting that CB restricted the penetration of the solvents, more likely through the enhancement of the CB reinforcing characteristics by the sulphur present in the thioglycolic acid.

The diffusion coefficient "D" was calculated from the Eq. 7 that is:

$$D = \pi[hn/4\ M_\infty]^2$$

where n is the slope of the linear portion of the sorption curve; h the thickness of the sample; and M_∞ the maximum mass uptake, which

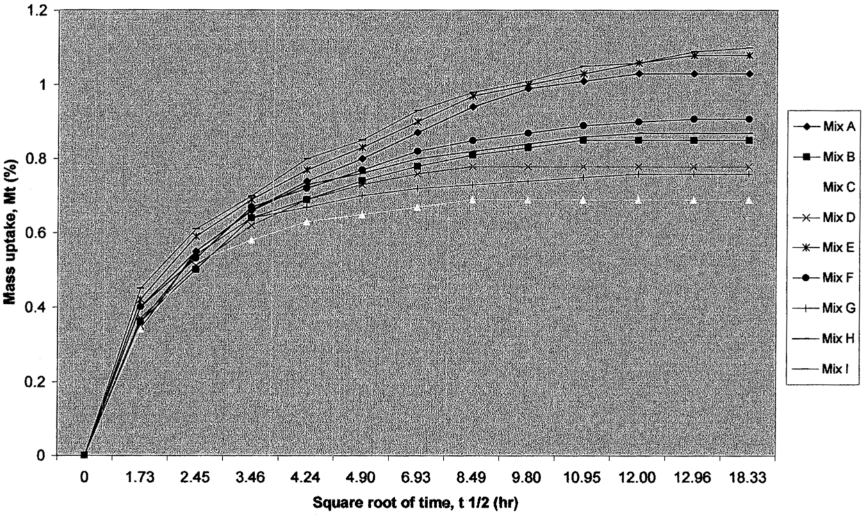

FIGURE 1 Showing a typical sorption plot of mixes A to I petrol at 303 K.

is been estimated by the least-square procedure. The diffusion results obtained were found to be temperature dependent, the diffusion increases as the temperature rises. It was also found that petrol penetrates the vulcanizates more than kerosene and more than diesel, which shows the solvent dependence of diffusion on the vulcanizates and the structural characteristics of the rubber blends. The diffusion in vulcanizates with higher loading of CRSS were observed to be faster when compared with vulcanizates of higher CB loading, signifying that CRSS has not acted as a good solvent resistant. It is true that the diffusion of small molecules through a polymer barrier occurs due to random molecular motion of the molecules. The driving force behind the molecular motion, or transport process, is the concentration difference between the two phases, that is, the material and the solvent. The molecular transport of organic liquids through elastomers can be used to predict the performance of the elastomer in contact with solvents. Alfrey et al. [27] during their molecular transport study classified the transport phenomena into two cases: as case I (Fickian) and case II (non-Fickian). Alfrey et al. later showed that when the solvent front is sharp and moves at a constant velocity, the transport dominates the process and both case I and case II mechanisms (Fickian and non-Fickian) became operative. The sorption plot shown in Figure 1 explains both cases; the linear part of the graph goes with case I whereas the other nonlinear part of the graph goes with the case II, showing that this experiment combined Alfrey et al.'s both cases.

The permeability coefficient, P, was calculated from Eq. 8. The obtained permeability values of the vulcanizates in the petroleum fuels are shown in Table 5. From the permeability values, it is seen that permeability increases as the temperature increases. Permeability values of vulcanizates with higher loading of CB were observed to be slower when compared with the vulcanizates having higher loading of CRSS. This further confirms that CB forms a stronger polymer network bond that restricts the penetration of the fuels through the rubber networks formed. The results of the sorption, diffusion, and permeability were found to correspond with the swelling and solubility results. Chan and Rey [28], in their study, showed that particle size distribution and type of fillers has influence on miscibility, diffusion rate, viscosity, and solvent resistance of vulcanizates. It is very obvious that the results of this study support Chan and Ray's findings in that the effect of the two fillers (CB and CRSS) resulted in the observed variations obtained in this study. The results were also found to be in support of the previous works of Aminabhavi and Naik [29].

In order to obtain the activation energy of the system, the data on diffusion coefficient, D was treated by the Arrhenius type of expression, Eq. 9.

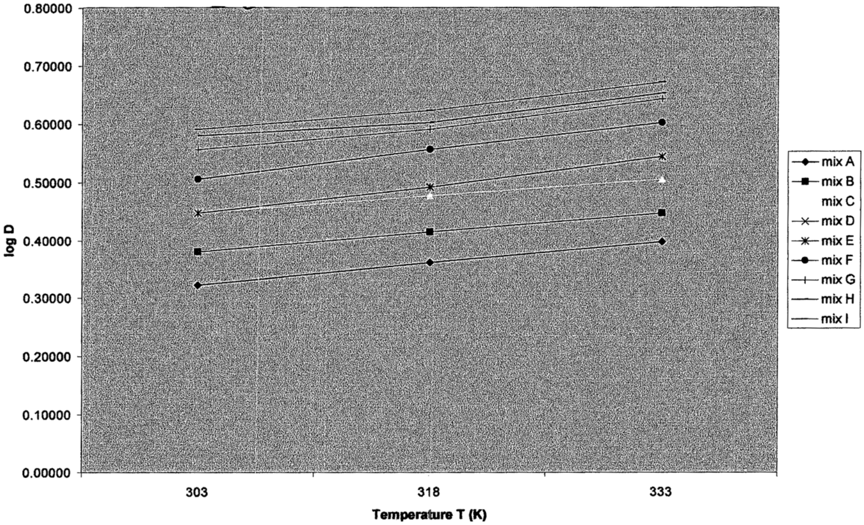

FIGURE 2 A typical Arhennius plot for mixes A to I in petrol.

A typical plot of log D against T for the vulcanizates in petrol is shown in Figure 2.

The activation energies obtained from the slopes of the curves are given in Table 6. It was observed that activation energies vary in the fuels, showing that they are solvent dependent. On the average, activation energies of the mixes in petrol were higher, followed by kerosene, whereas the least is diesel. It was also noticed that activation energy decreases as the ratio of CRSS increases. This observation was found to be in line with the previous report of Uzoma and Isa [24], where it was suggested that activation energy decreases with increases in the molecular mass. Hence, the observed lower activation energy values of vulcanizates in diesel when compared with values of vulcanizates in petrol could have been the effect of the differences in the molecular mass of the two fuels.

In order to determine the enthalpies, ΔH, and enthropies, ΔS, of the system, the equilibrium adsorption constant K_s was treated with Vant Hoff expression, shown as Eq. 10.

$$\log K_s = \frac{\Delta S}{2.303\,R} - \frac{\Delta H}{2.303\,RT}$$

A typical plot of log K_s against 1/T for the vulcanizates in petrol is shown in Figure 3. The intercept and slope of the linear plots gave values for the enthropy ΔS and enthalpy, ΔH. The ΔS and ΔH values obtained are given in Table 6.

The enthalpies, ΔH and enthropies, ΔS were also observed to be solvent dependent. Both the enthaplies and entropies were found to decrease as the ratio of CRSS increases. The positive values of enthalpies show that the reaction is endothermic. The negative value of enthropy signified that the reactions were in a liquid state, which is in agreement with the theory that sorbed solvent molecules remain in the liquid state throughout the reaction.

The free energy change, ΔG of the system was obtained by adopting Gibb's thermodynamics expression, shown as Eq. 12.

$$\Delta G = \Delta H - T\Delta S$$

The values of ΔG obtained are given in Table 6. The ΔG was observed to increase as the ratio of CB in the mix increases. The free energy values were observed to be positive in all cases, indicating non-spontaneity of the process.

TABLE 6 Showing the Activation Energy, Enthalpy, Entrophy, and Free Energy of the Mixes

	Mixes								
Fuels	A	B	C	D	E	F	G	H	I
Kerosene									
E_a(Jmol^{-1})	6533.63	7337.68	6744.70	7157.82	8599.58	7028.64	5532.69	4545.25	4311.21
ΔH(Jmol^{-1})	0.0798	0.1053	0.0798	0.0838	0.0761	0.0832	0.0766	0.0685	0.0619
ΔS(Jmol^{-1})	–0.49	–0.60	–0.72	–0.80	–0.86	–0.93	–0.99	–1.05	–1.10
ΔG(Jmol^{-1})	147.77	181.46	218.70	242.46	260.42	281.08	299.01	319.62	334.49
Petrol									
E_a(Jmol^{-1})	8045.75	7431.06	6904.06	6240.77	6611.21	6240.77	5612.26	4728.64	5218.35
ΔH(Jmol^{-1})	10.53	9.33	8.83	9.11	7.98	7.66	8.83	7.98	7.28
ΔS(Jmol^{-1})	–0.42	–0.60	–0.61	–0.66	–0.80	–0.85	–0.85	–0.88	–0.91
ΔG(Jmol^{-1})	138.19	190.98	192.85	210.42	251 16	265.36	266.99	273.66	282.39
Diesel									
E_a(Jmol^{-1})	5909.79	5343.34	6240.77	6744.70	6240.77	5807.16	5099.08	5694.16	5532.69
ΔH(Jmol^{-1})	0.11	0.12	0.11	0.09	0.08	0.09	0.08	0.08	0.08
ΔS(Jmol^{-1})	–0.63	–0.74	–0.83	–0.93	–1.04	–1.10	–1.20	–1.30	–1.36
ΔG(Jmol^{-1})	191.98	223.90	250.37	281.12	315.66	334.23	363.18	392.54	411.89

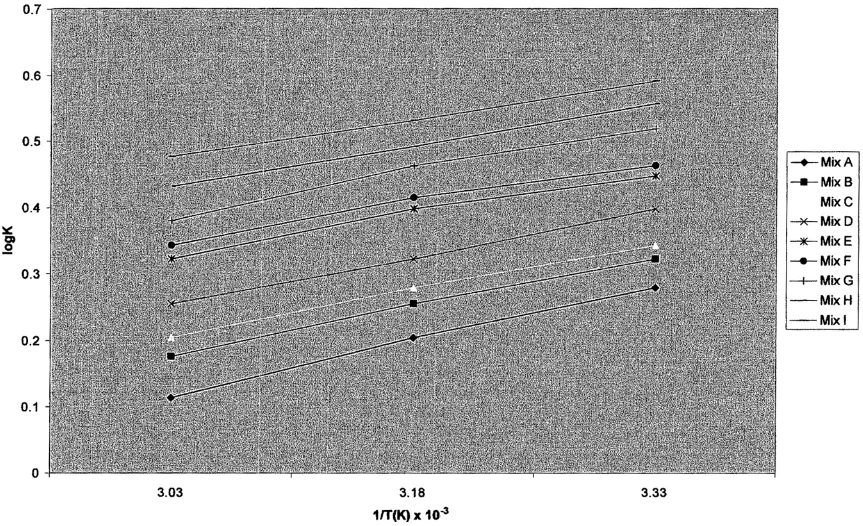

FIGURE 3 Showing a typical Vant Hoof plot of the mixes A to I in petrol.

CONCLUSION

The results of this study have shown the successful usage of admixtures of carbon black and carbonized rubber seed shell as fillers in NR compounding. CB reinforcing properties were found to be enhanced by the sulphur present in the thioglycollic acid. CRSS was found not to cause any significant improvement of the swelling, solubility, sorption, diffusion, and permeabilities of the vulcanizates but have good aging properties. However, the physico-mechanical characteristics of CRSS filled vulcanizate were within the accepted level for NR blends. Above all, 15% replacement of CB with CRSS has not shown any serious deleterious effect on the properties measured. The authors thereby recommend the usage of CRSS, but it should be used in products where tensile strength is not of uptmost important, more so that it has rheological, processing, technological, and cost advantage.

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