

D. MALOMO¹
A. K. AKINLABI²
F. E. OKIEMEN³
F. EGHAREVBA³

¹Chemistry Department, Western
Delta University, Oghara, Nigeria

²Chemistry Department, University
of Agriculture, Abeokuta, Nigeria

³Chemistry Department, University
of Benin, Benin City, Nigeria

SCIENTIFIC PAPER

UDC 678.028:66.02:678

DOI: 10.2298/CICEQ090113001M

INFLUENCE OF MIXING SCHEMES ON AGEING, SWELLING AND PERMEABILITY PROPERTIES OF VULCANIZATES FROM BLENDS OF NATURAL RUBBER AND LOW MOLECULAR WEIGHT NATURAL RUBBER IN PETROLEUM FUELS AND ORGANIC SOLVENTS

Blends of natural rubber (NR) and low molecular weight natural rubber (LMWNR) were compounded using three different mixing schemes by adopting the semi-efficient sulphur vulcanization compounding formulation. In scheme 1, the natural rubber and LMWNR were first mixed before adding the compounding ingredients. In scheme 2, the compounding ingredients were first mixed with the NR before adding the LMWNR and in scheme 3 the compounding ingredients were first mixed with the LMWNR before adding the NR. Properties of the vulcanizates from the three mixing schemes viz-a-viz: chemical resistance, ageing and physico-mechanical properties were investigated and compared. The physico-mechanical results of all the vulcanizates were found to be within the accepted level for NR compounds. The ageing results from all the mixing schemes were found impressive. Vulcanizates from mixing scheme 1 restricted penetration of petroleum fuels and organic solvents best, followed by scheme 2 and the least was scheme 3. The activation energy and free energy change were found to be highest with scheme 1, thereby making mixing scheme 1 being more technologically advantageous than other mixing schemes.

Key words: compounding; diffusion; mixing; natural rubber; permeability; vulcanization.

Several authors [1-4] have documented some of inherent limitations of natural rubber (NR) as factors militating against its wider usage in some polymeric products. The quest of how to improve on the limitation aspects of NR by scientists brought the compounding of NR with the expectation of having a modified rubber that will gain wider commercial interest in usage and acceptability with improved processing characteristics that will enhance more innovations in the rubber technology. Compounding involves the use of additives with NR. Various additives are added to NR to enhance the processability of the vulcanisate and these additives have been found to be mostly from petrochemical sources [5-10]. One way of modifying the limitations of natural rubber is

through the rubber blending strategy, which is relatively simple and commercially attractive as compared to the synthesis of entirely different rubbers. The problems associated with the use of blends of rubbers lies in the preparation of the rubbers for the blends which, if not properly considered and controlled, can lead to blends with unacceptable properties such as: poor interfacial adhesion between phases due to poor compatibility between the two rubbers, a vulcanized rubber blend with an uneven distribution of polymer networks, etc. All these can have more adverse effects on the properties of the blends than optimum. Hence, it is very useful to understand the roles of blending variables on structure-properties of rubber blends before embarking on the choice of polymers to be blended.

Low Molecular Weight Natural Rubber (LMWNR) is a new family of polymers chemically derived from natural rubber by depolymerization of natural rubber latex (NRL) with nitrobenzene [11]. The LMWNR is

Corresponding author: A. K. Akinlabi, Chemistry Department,
University of Agriculture, PMB 2240, Abeokuta, Nigeria.

E-mail: akakinlabi@yahoo.com

Paper received: 13 January, 2009

Paper revised: 20 August, 2009

Paper accepted: 23 September, 2009

akin in some properties to natural rubber e.g. affinity for ingredients during compounding and its chemical behaviour. The LMWNR has been found acting as a plasticizer, hence, it was thought that during blending, LMWNR will enhance a uniform distribution of compounding ingredients and possibly attract the compounding ingredients more to itself than natural rubber since natural rubber is a non-polar hydrocarbon. In addition, we still thought of finding out how sequence of mixing the two rubbers with compounding ingredients will influence the physico-mechanical, ageing, solubility, swelling, sorption, energies of absorption, diffusion and permeability properties of vulcanizates from the blends in petroleum fuels and some organic solvents. All these ideas serve as the basis for this study with an additional belief that some of the limitations suffered by natural rubber might be improved upon, thereby making NR having more novel applications and compete more with the synthetic rubbers.

EXPERIMENTAL

Materials

Natural rubber latex from NIG 903 clone was obtained from the estates of the Rubber Research Institute of Nigeria (RRIN), Iyanomo, Benin City, while the crumb rubber conforming to Technically Specified Rubber (TSR) 10, but usually denoted in Africa as Standard African Rubber (SAR) grade 10, was also obtained from the RRIN. The reagents used in the preparation and characterization of the natural rubber (NR) and low molecular weight rubber (LMWNR) were of analytical grades, while the rubber compounding chemicals were of the commercial grades.

Methods

Production and characterization of LMWNR samples. The method described by Akinlabi *et al.* [11] was adopted with slight modification using nitrobenzene as the depolymerizing agent, the extent of depolymerization was determined by the size exclusion chromatogram (SEC) [12] and viscosity measurement using Ubbelohde viscometer. 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 30cm mixed columns with a porosity of 20 μm . The installation was computer controlled by a special software (baseline). The column temperature was fixed at 55 $^{\circ}\text{C}$. The cyclohexane flow rate was 0.80 ml/min, the injected volume 100 μl (at a concentration of 0.2 mg/ml), for the LMWNR samples, and 25 μl for standard solutions. Calibration was carried out with synthetic poly(cis-isoprene) with molecular weights of 3660, 7000, 33900, 68500, 108000, 293000, 590000, 963000 and 3.0 million (expressed in g/mol). Prior to injection, the solutions were filtered through a porosity of 0.45 μm .

Compounding of the mixes. Recipes used for the four different sulphur vulcanization systems are as shown in Table 1, while Tables 2-4 show the mixing sequences. The mixing was carried out using a laboratory two-roll mill [13] and in accordance to the method described by the American Society for Testing and Materials (ASTM)-D 3184-80 [14].

Cure characteristics. The cure characteristics of the mixes were set at 170 $^{\circ}\text{C}$ and measured at 160 $^{\circ}\text{C}$ using an Oscillating Disk Rheometer (ALPHA ODR 2000) in accordance to ISO 3417 method as contained in the Standard African Rubber (SAR) manual

Table 1. Recipe for the four different vulcanization systems

Compound component	(phr) ^a	(phr) ^b	(phr) ^c	(phr) ^d
Natural rubber	70	70	70	70
LMWNR (50% reduction)	30	30	30	30
Zinc oxide (ZnO)	5.0	2.0	2.0	3.0
Stearic acid	0.7	1.5	1.5	1.0
Carbon black (HAF)	40	40	40	40
Sulphur	2.5	0.4	0.5	1.5
Flectol H(antioxidant)	2.0	2.0	2.0	2.0
Dibenzothiazyl disulphide (MBTS)	-	2.5	-	1.5
CBS	0.5	-	2.5	-
TMTM	-	-	1.0	-

^aConventional vulcanization system (CV); ^befficient vulcanization system 1 (EV₁); ^cefficient vulcanization system 2 (EV₂); ^dsemi-efficient vulcanization system (semi-EV). Flectol H = polymerized 1,2-dihydro-2,2,4-trimethyl quinolene; CBS = *N*-cyclohexylbenzothiazole-2-sulphenamide; TMTM = tetramethylthiuram monosulphide

No. 2 [15]. The respective cure times as measured by t_{90} , scorch times, torque, and cure rates were determined from the rheograph.

Table 2. Showing mastication procedures for scheme 1

Mixing procedure	Time, min
Mastication of NR and LMWNR	5
Addition of ZnO and Stearic acid	2
Anti-oxidant	2
Half of the filler	3
The remaining filler	3
Sulphur and MBTS	3
Total	18

Table 3. Showing mastication procedures for scheme 2

Mixing procedure	Time, min
Mastication of NR	6
Addition of ZnO and Stearic acid	2
Anti-oxidant	2
Addition of LMWNR	3
Half of the filler	3
The remaining filler	2
Sulphur and MBTS	3
Total	21

Table 4. Showing mastication procedures for scheme 3

Mixing procedure	Time, min
Mastication of NR	3
Addition of ZnO and Stearic acid	2
Anti-oxidant	2
Addition of LMWNR	5
Half of the filler	3
The remaining filler	2
Sulphur and MBTS	3
Total	20

Measurement of the Mooney viscosity. The Mooney viscosity of the sample was determined using the shearing disc viscometer model type Wallace MK III, according to ISO 289 as contained in the SAR manual No. 2 [15]. The results were expressed in terms of ML (1+4) at 100 °C.

Mechanical properties. The test specimens were molded in an electrically heated hydraulic press (TECHNO LOIRE) at 160 °C for 5 min as predetermined from the rheograph. Tensile properties of the vulcanisates were measured with a Mosanto Tensile Tester Model (1/M) at a crosshead speed of 500 mm/min using a dumbbell test specimen (Type II) as contained in ASTM D-412-87 (method A) and as in the SAR manual No. 2 [15]. Thereafter, the tensile

strength at break, modulus, and elongation at break were calculated.

Compression set measurement. Wallace compression set machine (Model/Ref. No. C2; 50 Hz) was used. The 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). The difference between the original thickness and the recovered thickness was expressed as a percentage of the original thickness. This was expressed mathematically as:

$$\text{Compression set (\%)} = 100 \frac{(t_0 - t_r)}{t_0} \quad (1)$$

where t_0 is initial thickness and t_r is 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 vulcanisate was determined by adopting the standard dead load method described in BS 903 Part A26 [16]. 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 with the SAR manual No. 2 [15]. The angle between the test specimen and the wheel was adjusted to an angle of 15°. The abrasion was carried out for four 1000 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 1000 revolutions of the abrasive wheel was calculated.

The result was expressed as:

$$\text{Abrasion resistance index} = 100 \frac{[S]}{T} \quad (2)$$

where S is volume loss per 1000 revolutions of the abrasive wheel, calculated from the mean of 5 runs on standard rubber, T is volume loss per 1000 revolutions of the abrasive wheel, calculated from the mean of 5 runs on the sample rubber.

Crosslink density. The chemical crosslinking density ($\rho RTMc$) was calculated from the shear modulus (G), while the molecular mass between crosslinks was calculated using the Flory-Rhener equation [17]:

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

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 the rubber in the swollen sample, Mc is the molecular weight between crosslinking and χ is the polar-solvent interaction parameter given as ($\chi = 0.44 + 0.18V_2$).

Crosslinking densities:

$$\rho / Mc = G / RT \quad (4)$$

Ageing. The ageing was carried out in a thermostated air-circulated oven on the dumbbell shaped specimen at 70 °C for 48 h. The extent of ageing was determined as a change in the physico-mechanical properties of the fresh (unaged) and aged samples.

Swelling and solubility experiments. The resistance of the vulcanizates in toluene, carbon tetrachloride, acetone, ethanol, methanol, *n*-hexane, ammonia, cyclohexane, mineral oil and brake fluid were determined by using the methods described by De and De [18] with a slight modification. In a typical swelling experiment, three different shapes of the cured sample (triangle, square and rhombus) were cut from the 1 mm thickness mould and weighed before submerging each samples in its respective solvent in airtight bottles maintained at the specified various temperature(s) for 72 h. The experiments were carried out in triplicate. At the end of the swelling, the samples were removed from the solvent, carefully blotted to remove the excess liquid on the surface, and the weights immediately taken. Thereafter, the samples were further dried to a constant weight. The percentage increases in weight of the samples were calculated as the swelling while the percentage loss in weight after drying to a constant weight was calculated as the solubility.

$$\% \text{ Swelling} = 100 \left(\frac{W_2 - W_1}{W_2} \right) \quad (5)$$

$$\% \text{ Solubility} = 100 \left(\frac{W_1 - W_3}{W_1} \right) \quad (6)$$

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.

Diffusion studies. Studies in the sorption, diffusion and permeability of petroleum fuels (kerosene, petrol and diesel) through the vulcanizates were carried out at 30, 40 and 50 °C using the gravimetric method. The sorption was taken as the maximum weight gained. The diffusion coefficient, D , was calculated from this Eq. [19]:

$$D = \pi(hn / 4M_\infty)^2 \quad (7)$$

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 which has been estimated by the least-square procedure. The permeability coefficient, P , was calculated from the simple relation [19]:

$$P = DS \quad (8)$$

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 [20]:

$$\log D = \log D_0 - E_a / RT \quad (9)$$

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 entropies, ΔS , of the system, the equilibrium adsorption constant, K , was treated with Van't Hoff expression [20]:

$$\log K = \Delta S / 2.303R - \Delta H / 2.303RT \quad (10)$$

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 this relation [20]:

$$K^t = M_t / M_\infty \quad (11)$$

where n is a 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 [20]:

$$\Delta G = \Delta H - T\Delta S \quad (12)$$

RESULTS AND DISCUSSION

The rheological characteristics of the four vulcanization systems, highlighted in Table 1, are shown in Table 5. Generally, in a natural rubber technology and processing, rubber manufacturers always prefer vulcanization systems that can give low cure time (t_{90}), high scorch time (t_2) and high cure rate as a result of processing advantages in time gained and cost reduction. However, looking at the results in Table 5, it can be observed that semi-EV system gave the highest cure rate of 35.97 %/min and least cure time of 4.03 min while the conventional sulphur vulcanization system gave the least cure rate of 23.75 %/min and highest cure time of 5.26 min. The higher cure time values observed in the conventional vulcanization system could have resulted from the reaction of the sulphur, from the additives (oxidation of sulphides - due to high sulphur level in the recipe), which might have led to ether cross-links and consequently results in the material having high cure time and high ODR

Table 5. Results of the oscillating disc rheometer

Vulcanization systems	t_1 / min	t_2 / min	t_{90} / min	M_L / N m	M_H / N m	ODR / N m	CR / % min ⁻¹
CV	0.52	1.05	5.26	4.30	13.33	12.43	23.75
EV ₁	0.48	0.59	4.46	4.58	13.16	12.30	25.84
EV ₂	0.48	0.81	4.63	4.54	10.93	5.79	26.25
Semi-EV	0.50	1.25	4.03	4.60	7.73	7.42	35.97

t_1 is the time to an increase of 1 unit of torque above M_L ; t_2 is the time to an increase of 2 unit of torque above M_L ; t_{90} is the cure time; M_L is the minimum torque; M_H is the maximum torque; ODR torque is calculated using the formula:

$$\frac{90(M_H - M_L) + M_L}{100}$$

Cure rate (CR) is calculated using the formula $100/(t_{90} - t_2)$

torque. The high cure rate value observed with semi-EV system signifies a well crosslinked system. Morrison [21] had earlier documented that at high vulcanization temperature in a semi-EV system, there is a possibility of having rubber-bound intermediates and their subsequent conversion to cross-links, thereby leading to a high cure rate of the vulcanizates. The least ODR torque of 5.79 N m was observed in EV₂ system, which was closely followed by the semi-EV system (7.42 N m) while the CV system gave the highest ODR torque of 12.43 N m. This observation was very similar to the findings of some previous workers [22,23]. Baker *et al.* [23] earlier suggested that during vulcanization, besides the predominantly polysulphidic cross-links, the high sulphur vulcanizates harden rapidly due to the acidic by-products containing sulphur, resulting in an increase in cure time. Therefore, for this study, the semi-EV sulphur vulcanization formulation was thereafter selected as the vulcanization systems used in the mastication of the three different mixing schemes shown in Tables 2-4, since the semi-EV system gave the best cure time, scorch time and cure rates.

Looking at the mixing procedures in Tables 2-4, it can be observed that scheme 1 was completed within 18 min (giving the most efficient time), while schemes 2 and 3 were completed within times of 21 and 20 min, respectively. During compounding, an initial mastication of the rubber was found very essential (breaking of the bonds) before adding the ingredients in order to allow easy penetration and uniform mixing of the ingredients with the rubbers. The mastication time of LMWNR was faster than that of the NR, because of the initial chemical reduction of the molecular weight of the LMWNR. The low molecular weight natural rubber is as a soft material, found very sticky on rollers during mixing, and was expected to facilitate the incorporation of the compounding ingredients into the rubber matrix within a very short period.

The physico-mechanical properties of the vulcanizates compounded with the recipe in Tables 2-4 is as shown in Table 6. The tensile strength varies from

Table 6. Physico-mechanical properties of the vulcanizate

Parameters	1	2	3
Tensile strength (MPa)	25.5±1.1	22.0±1.2	17.7±1.1
Modulus at 50% elongation (MPa)	2.9±0.17	2.7±0.14	2.4±0.13
Modulus at 100% elongation (MPa)	6.6±0.23	5.4±0.22	4.7±0.20
Modulus at 200% elongation (MPa)	8.7±0.31	6.5±0.28	6.3±0.25
Elongation at break (%)	989±3.2	920±2.9	810±3.1
Cross-link density ×10 ⁻⁴	1.7±0.16	1.5±0.15	1.4±0.15
Hardness (IRHD)	59±1.5	55±1.4	54±1.6
Compression set (%)	44±1.4	42±1.3	42±1.5
Abrasion resistance (%)	63±1.8	59±1.6	60±1.7
Mooney Viscosity ML (1+4), 100 °C	72±1.6	67±1.9	69±1.8

25.5 MPa for scheme 1 to 17.7 MPa for scheme 3, which shows a decrease of about 31% in the value of tensile result, signifying scheme 1 having a 31% tensile strength advantage over scheme 3. The modulus at 50, 100 and 200% elongation were found to be highest with scheme 1, followed by scheme 2 while the least was with scheme 3. The result of the elongation at break also follows the trend observed in the tensile result. The observable trend in the mechanical properties suggests that during the initial mixing of the NR with LMWNR, there could have been synergistic advantages of the two rubbers in permitting easy incorporation of the ingredients, thereby giving rise to a well cross-linked materials with better tensile and elongation properties. In scheme 2, the LMWNR was not acting fully as a base polymer since it was added after the compounding ingredients while similar reason accounts for why NR in scheme 3 was not acting fully as a base polymer. These sequences of mixing might have affected the distribution of the compounding ingredients in the rubber matrix, thereby accounting for the observed low value of tensile strength of the vulcanizates from schemes 2 and 3 when compared with scheme 1. Nevertheless, the mechanical

properties of the vulcanizates from schemes 2 and 3 are still within the accepted range for NR compounds suggesting that such vulcanizates will find uses in some rubber products, where such properties are desired.

The cross-linking density result was calculated from the volume fraction of the rubber in the swollen gel (V_2) by using the Flory-Rhener equation (Eq. (3)) shown above, and it was found to be decreasing from scheme 1 to 3. This presumes that an initial mastication of the two rubbers before the addition of the other compounding ingredients would permit a uniform distribution of the materials across the rubber, making the interface become rich with a higher degree of cross-linking throughout the interfacial region, thereby enhancing the strength of the vulcanizate. The results of the hardness, a compression set, the abrasion resistance and Mooney viscosities of vulcanizates from scheme 1 were found to be the highest giving an indication of a well crosslinked material and supporting the crosslinking results. The effects of a uniform distribution of recipes in natural rubber compounding had been earlier documented by Das [24], where it was mentioned that a uniform distribution and dispersion of compounding ingredients in the rubber matrix will give rise to a well crosslinked material of good physico-mechanical properties. This suggestion of Das could be responsible for the result of the vulcanizates from mixing scheme 1 of this study.

The ageing results were presented as a percentage change in the properties of the vulcanizates, using the expression below:

$$\text{Extent of ageing} = 100 \frac{O - A}{O} \quad (13)$$

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

The results of the physico-mechanical properties of the vulcanizates after ageing at 70 °C for 48 h were compared with their unaged results and are presented in Table 7. The ageing results at 30, 40, 50 and 60 °C were not discussed because of marginal changes in the values when compared with the unaged.

The ageing results obtained do not show a significant difference within the 3 mixing schemes. Thus, it can be inferred that the ageing properties of the 3 schemes are nearly of the same trend. This phenomenon suggests LMWNR having a positive ageing influence in rubber vulcanizates, thereby suggesting that LMWNR can find uses in rubber products where ageing properties is of interest and important. This discovery is an improvement over the ageing limitations of the natural rubber.

Table 7. Aging results of the vulcanizates at 70 °C for 48 h (% of original sample values)

Parameter	1	2	3
Tensile strength (MPa)	10.4±0.35	9.9±0.29	9.7±0.32
Modulus at 50% elongation (MPa)	8.1±0.28	8.0±0.27	7.8±0.27
Modulus at 100% elongation (MPa)	7.3±0.25	7.1±0.25	7.1±0.24
Modulus at 200% elongation (MPa)	6.8±0.25	6.6±0.23	6.5±0.25
Elongation at break (%)	17.2±0.38	17.0±0.35	17.0±0.37
Cross-link density $\times 10^{-4}$	3.9±0.19	3.7±0.19	3.7±0.18
Hardness (IRHD)	5.7±0.32	5.7±0.34	5.6±0.33
Compression set (%)	4.1±0.28	4.2±0.28	4.1±0.26
Abrasion resistance (%)	6.5±0.27	6.4±0.27	6.4±0.26
Mooney viscosity ML (1+4) at 100 °C	8.5±0.25	8.5±0.24	8.4±0.27

The swelling result in Table 8 shows that the vulcanizates from mixing scheme 1 generally showed better resistance to most of the solvents used. The solubility of vulcanizates from mixing scheme 1 was also found to be better than the other mixing schemes. It was also observed that the vulcanizates were generally showing more affinities for toluene, acetone, and carbon tetrachloride than the other solvents. The vulcanizate showed more resistance to brake fluid, mineral oil, and cyclo-hexane. The resistance of the vulcanizates in ammonia, *n*-hexane, methanol and ethanol were nearly of close magnitude and below the observed resistance of carbon tetrachloride but above that of cyclohexane. The resistance of vulcanizates to solvents is usually enhanced by the uniform distribution and dispersion of compounding ingredients in the rubber matrix which leads to a well cross-linked vulcanizate. Swelling of natural rubber has been documented to be influenced by various factors, such as cross-link type and density, amount, nature and type of compounding ingredients and of elastomer [25,26]. The swelling and solubility results shown in Table 8 increase from mixing scheme 1 to mixing scheme 3, suggesting mixing scheme 1 being well cross-linked. When the swelling was prolonged (96 h and longer) in acetone, toluene and carbon tetrachloride the vulcanizates were observed turning into a slurry which could have being due to the penetrating power of those solvents.

The sorption, S , diffusion, D , and permeability, P , are used as a way of determining the extent of cross-linking and network formation in a rubber matrix. Sorption, diffusion and permeability of the vulcanizates in kerosene, petrol and diesel were carried out in anticipation of predicting the likely behavior of the vul-

Table 8. Swelling and solubility results of the vulcanizates from the mixing schemes in different solvents

Solvents	Mixing schemes	W_1	W_2	W_3	% Swelling	% Solubility
Toluene	1	0.3617	0.42543	0.33309	14.98	7.91
	2	0.39214	0.46374	0.36038	15.44	8.1
	3	0.37113	0.4441	0.33792	16.43	8.95
Carbon	1	0.38114	0.44583	0.354879	14.51	6.89
Tetrachloride	2	0.34216	0.403586	0.31749	15.22	7.21
	3	0.36631	0.436968	0.338361	16.17	7.63
Acetone	1	0.36781	0.438966	0.339047	16.21	7.82
	2	0.34412	0.420222	0.31635	18.11	8.07
	3	0.33395	0.415257	0.304195	19.58	8.91
Ethanol	1	0.37645	0.414547	0.359585	9.19	4.48
	2	0.35214	0.389363	0.335237	9.56	4.8
	3	0.38617	0.428079	0.367055	9.79	4.95
Methanol	1	0.35163	0.387685	0.335631	9.3	4.55
	2	0.36721	0.406476	0.349253	9.66	4.89
	3	0.37781	0.41909	0.358693	9.85	5.06
n-Hexane	1	0.34391	0.369359	0.332355	6.89	3.36
	2	0.36972	0.399007	0.355892	7.34	3.74
	3	0.35014	0.379268	0.33652	7.68	3.89
Mineral oil	1	0.38101	0.404942	0.372628	5.91	2.2
	2	0.34692	0.369969	0.337067	6.23	2.84
	3	0.36004	0.385399	0.349275	6.58	2.99
Brake fluid	1	0.37143	0.387068	0.368124	4.04	0.89
	2	0.35028	0.366478	0.346952	4.42	0.95
	3	0.34992	0.367332	0.346071	4.74	1.1
Cyclohexane	1	0.35216	0.37636	0.341842	6.43	2.93
	2	0.3802	0.40794	0.368262	6.8	3.14
	3	0.34968	0.375636	0.337581	6.91	3.46
Ammonia	1	0.35614	0.397256	0.339651	10.35	4.63
	2	0.34869	0.392713	0.331465	11.21	4.94
	3	0.36671	0.414128	0.348081	11.45	5.08

W_1 - is the weight after extraction; W_2 - is the weight after swelling at 25 °C for about 6 h; W_3 - is the weight after drying in a vacuum to a constant mass

canizates if used in automobile products that might come in contact with the chosen fuels. The results of the S , D and P are shown in Table 9. The sorption was determined as the optimum mass gained by the vulcanizate at equilibrium. The sorption plots of the vulcanizates from different mixing schemes in kerosene, petrol and diesel at 50 °C is shown in Figure 1. The fuel uptake by the vulcanizate, which can be seen in Figure 1, was linear at the beginning of the experiments (obeying Fickian type of transport mechanism) but before the system attains equilibrium there was a deviation from the linearity, showing the optimum sorption value attainable by the vulcanizates. The observable trend can be attributed to the fact that when the sorption was initially started, the fuels penetrating power was high but as the experiment progressed, the penetration power of the fuels re-

duced as a result of the relief that was experienced by the fuel uptake power which is represented by the equilibrium part of the sorption experiment. More complex effects became operative after some time (above equilibrium) which brings deviations from linearity as it can be seen in the plots. The sorption results were interpreted as mass increase per unit weight of the vulcanizate and they are presented as percentage increase in Table 9. From the sorption values in Table 9, it is evident that S increases as the reaction temperature increases showing the dependence of S on temperature. S values of vulcanizates from scheme 3 were found having higher values suggesting that the vulcanizates from scheme 3 allow easy penetration of the fuels. It was also noticed that the percentage mass uptake and the time required to attain equilibrium saturation were found to be affected

Table 9. Showing sorption, diffusion and permeability results of the vulcanizates from the different mixing schemes in kerosene, petrol and diesel

Mixing schemes in fuels	$S \times 10^2 / \text{g g}^{-1}$	$D \times 10^5 / \text{mm}^2 \text{min}^{-1}$	$P \times 10^2 / \text{mm}^2 \text{min}^{-1}$
30 °C			
1 in Kerosene	26	2.4	62.4
2 in Kerosene	29	2.5	72.5
3 in Kerosene	33	2.8	92.4
1 in Petrol	25	2.2	55.0
2 in Petrol	27	2.4	64.8
3 in Petrol	31	2.7	83.7
1 in Diesel	19	1.9	36.1
2 in Diesel	22	2.0	44.0
3 in Diesel	25	2.2	55.0
40 °C			
1 in Kerosene	28	2.6	72.8
2 in Kerosene	32	2.8	89.6
3 in Kerosene	37	3.1	114.7
1 in Petrol	26	2.5	65.0
2 in Petrol	30	2.6	78.0
3 in Petrol	35	3.0	105.0
1 in Diesel	21	2.2	46.2
2 in Diesel	23	2.4	55.2
3 in Diesel	27	2.8	75.6
50 °C			
1 in Kerosene	31	2.9	89.9
2 in Kerosene	34	3.1	105.4
3 in Kerosene	39	3.4	132.6
1 in Petrol	29	2.7	78.3
2 in Petrol	32	3.0	96.0
3 in Petrol	38	3.3	125.4
1 in Diesel	24	2.5	60.0
2 in Diesel	27	2.7	72.9
3 in Diesel	32	3.1	99.2

by the mixing schemes. That is, vulcanizates from mixing schemes 3 generally attain equilibrium faster with more mass increase than vulcanizates from scheme 2, which are also faster than the vulcanizates from mixing scheme 1. It was also observed that just before the equilibrium point the mass uptake rate was very slow, which could have resulted from a gradual decreasing penetrating power of the fuels.

The diffusion coefficient was calculated from Eq. (7). The diffusion results obtained were found to be temperature dependent, the diffusion increases as the temperature rises. It was also found that vulcanizates from scheme 3 had the highest value followed by vulcanizates from scheme 2 while vulcanizate from scheme 1 had the lowest. This shows the dependence of diffusion on the mixing schemes. Kerosene

was also found to diffuse faster than petrol and diesel. This could be linked to the molecular masses of the fuels, that is, low molecular mass fuels will diffuse faster than high molecular mass fuels. 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 the transport process is the concentrations difference between the two phases, *i.e.*, the material and the solvent. The molecular transport of organic liquids through elastomers has previously been studied by Alfrey *et al.* [27]. During their molecular transport study Alfrey *et al.* classified the transport phenomena into two cases: case I (Fickian) and case II (non-Fickian). Alfrey *et al.* later showed that when solvent front was sharp and moved at a constant ve-

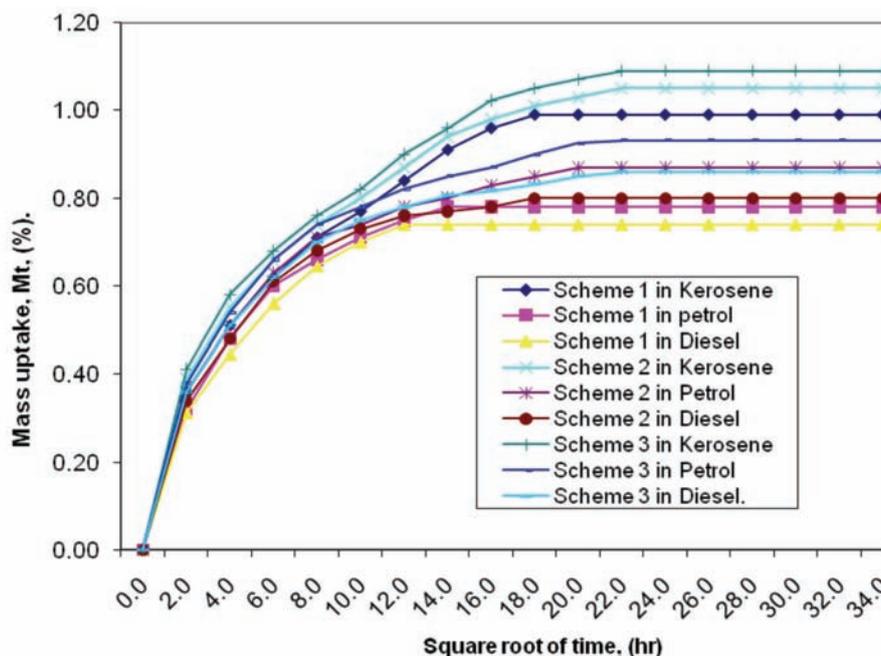


Figure 1. Sorption plots of the vulcanizates from the mixing schemes in various fuels at 50 °C.

locity, the transport dominated the process and both case I and case II mechanism (Fickian and non-Fickian) became operative. These two cases in study of Alfrey *et al.* were represented by the linear and non-linear part of the sorption plot in Figure 1. The linear part of the graph goes with case I while the other non-linear part of the graph goes with the case II.

The permeability coefficient, P , was calculated from the Eq. (8). The obtained permeability values of the vulcanizates in the fuels are shown in Table 9. From the permeability values, it is also evident that permeability increases as the temperature increases. This effect follows the convention that at higher temperatures the increase in the free volume occurs thereby increasing the rate of permeability of solvents. Permeability values of vulcanizates from scheme 1 were observed to be lower than vulcanizates from scheme 2 while vulcanizates from scheme 3 had the highest values. This further confirms the effect of the mixing schemes on the vulcanizate properties, implying that vulcanizates from the mixing scheme 1 were more crosslinked than vulcanizates from mixing schemes 2 and 3. The nature and molecular mass of the fuels accounted for why kerosene generally penetrates more than petrol and diesel.

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). Plots of $\log D$ against T for the vulcanizates in different mixing schemes are shown in Figure 2. The activation energies obtained from the slopes of the curves are

given in Table 10. It was observed that activation energies were influenced by the solvents' nature. On average, activation energies of vulcanizates from scheme 1 were higher followed by vulcanizates from scheme 2 while vulcanizates from scheme 3 were the lowest, that is, the activation energy decreased from mixing scheme 1 to mixing scheme 3. This observation was found to be in line with the previous report of Uzoma and Isa [28], where it was suggested that the activation energy can be influenced by solvents' nature and diffusion rate. Hence, the observed higher activation energy values of vulcanizates from scheme 1 when compared with vulcanizates from schemes 2 and 3 could have been the effect of the mixing schemes on the crosslinking and diffusion results.

In order to determine the enthalpies, ΔH , and entropies, ΔS , of the system, the equilibrium adsorption constant, K_s , was treated with Van't Hoff expression, Eq. (10). Plots of $\log K_s$ against $1/T$ for the vulcanizates in schemes 1-3 are shown in Figure 3. The intercept and slope of the linear plots gave values for the entropy ΔS and enthalpy, ΔH . The ΔS and ΔH values obtained are given in Table 10.

The enthalpies and entropies were also observed to be mixing schemes dependent. The positive values of enthalpies show that the reactions were endothermic. The negative value of enthalpy 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.

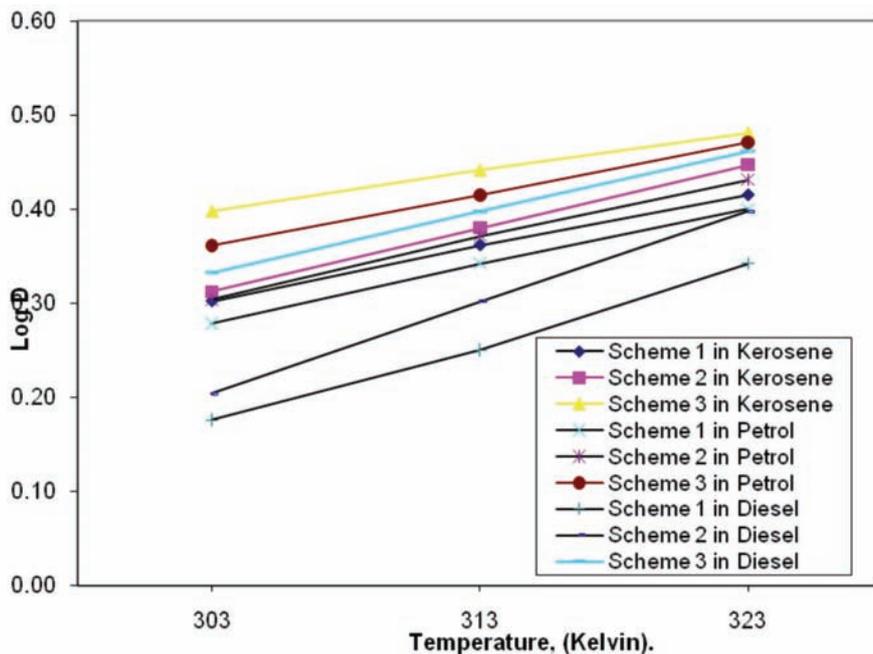


Figure 2. Arrhenius plots of the vulcanizates from the mixing schemes in various fuels.

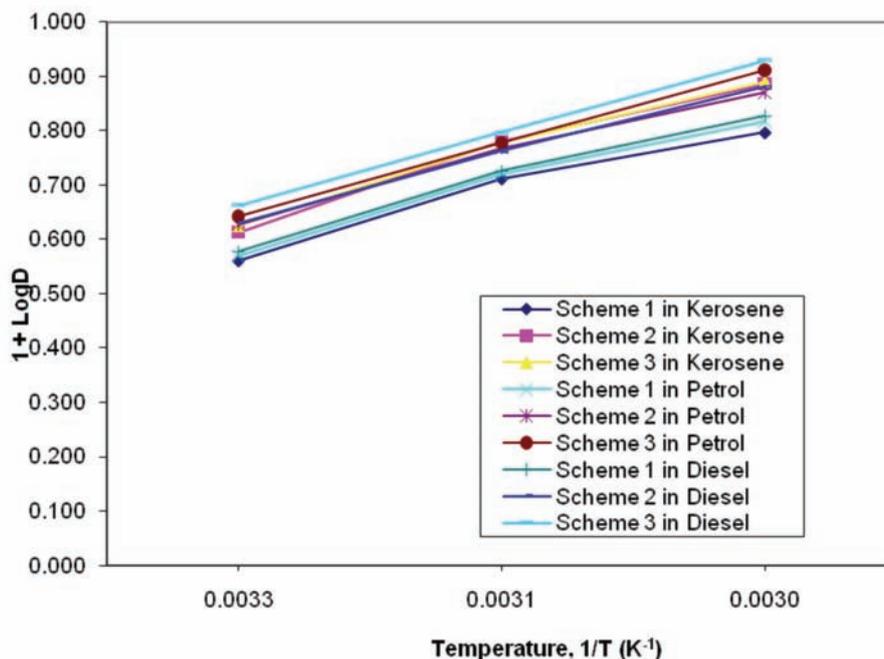


Figure 3. Van't Hoff plot of the vulcanizates from the mixing schemes in various fuels.

The free energy change, ΔG , of the system was obtained by adopting Gibb's thermodynamics expression, Eq. (12). The values of ΔG obtained are given in Table 10. The ΔG was observed to be highest in scheme 1, followed by scheme 2 while scheme 3 has the lowest values. The free energy values were observed to be positive in all cases, indicating non-spontaneity of the process.

CONCLUSIONS

This study revealed that the initial mastication of the rubbers (base polymers) is very essential before adding the compounding ingredients for optimum cross-linking. Vulcanizates from mixing scheme 1 were found to be the best and low molecular weight natural rubber was found to improve the ageing properties of natural rubber. Toluene, acetone and car-

Table 10. The activation energy, enthalpy, entropy and free energy of the vulcanizates from the different mixing schemes in kerosene, petrol and diesel

Parameter	Mixing schemes		
	1	2	3
Kerosene			
$E_a / \text{J mol}^{-1}$	570.143	467.108	421.604
$\Delta H / \text{J mol}^{-1}$	78.656	90.987	84.526
$\Delta S / \text{J mol}^{-1} \text{K}^{-1}$	-0.509	-0.466	-0.435
$\Delta G / \text{J mol}^{-1}$	217.613	218.205	203.281
Petrol			
$E_a / \text{J mol}^{-1}$	535.685	484.550	435.751
$\Delta H / \text{J mol}^{-1}$	76.138	81.013	84.618
$\Delta S / \text{J mol}^{-1} \text{K}^{-1}$	-0.480	-0.422	-0.399
$\Delta G / \text{J mol}^{-1}$	207.178	196.219	193.545
Diesel			
$E_a / \text{J mol}^{-1}$	595.932	534.667	433.047
$\Delta H / \text{J mol}^{-1}$	72.566	79.980	78.633
$\Delta S / \text{J mol}^{-1} \text{K}^{-1}$	-0.424	-0.380	-0.368
$\Delta G / \text{J mol}^{-1}$	188.318	183.720	179.097

bon tetrachloride were found to penetrate all the vulcanizates more and faster than ethanol, methanol, *n*-hexane, ammonia, cyclohexane, mineral oil and brake fluid. Sorption, diffusion and permeability were found to be temperature dependent. The higher the temperature, the faster the diffusion and permeability. Kerosene was found to diffuse more than petrol and more than diesel. The energies of absorption confirmed the reactions as non-spontaneous and in liquid state. Above all, mixing scheme 1 is more advantageous and henceforth recommended for efficient and effective compounding of rubber blends.

Acknowledgement

The authors are grateful to the Executive Director and the management crews of the Rubber Research Institute of Nigeria and Polymer Technology Department of the Federal Polytechnic, Auchi. The appreciation also goes to Dr. Frederic Bonfils of CIRAD and the authorities of the Center de Cooperation Internationale en Recherche Agronomique pour le Development (CIRAD)-CP, Montpellier, France, for putting their laboratory facilities at our disposal.

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D. MALOMO¹
A. K. AKINLABI²
F. E. OKIEMEN³
F. EGHAREVBA³

¹Chemistry Department, Western
Delta University, Oghara, Nigeria

²Chemistry Department, University
of Agriculture, Abeokuta, Nigeria

³Chemistry Department, University
of Benin, Benin City, Nigeria

NAUČNI RAD

UTICAJ PROGRAMA MEŠANJA NA STARENJE, BUBRENJE I PERMEABILNOST VULKANIZATA DOBIJENIH IZ MEŠAVINA PRIRODNE I NISKOMOLEKULARNE GUME U NAFTNIM GORIVIMA I ORGANSKIM RASTVARAČIMA

Mešavine prirodne (NR) i niskomolekularne prirodne (LMWNR) gume su napravljene korišćenjem tri različita programa mešanja i poluefikasnog formulisanja mešavina vulkanizacijom sumporom. U programu 1 prirodna guma je mešana sa LMWNR pre dodavanja komponenti mešavine. U programu 2 komponente mešavine su pomešane sa NR pre dodatka LMWNR, dok je u programu 3 LMWNR prvo pomešana sa komponentama mešavine, a zatim je dodata NR. Ispitana su i međusobno upoređena svojstva vulkanizata dobijenih različitim programima mešanja, kao što su: hemijska otpornost, starenje i fiziko-mehanička svojstva. Rezultati dobijeni ispitivanjem fizičko-mehaničkih svojstava vulkanizata su u okviru očekivanih i prihvatljivih za mešavine NR. Rezultati dobijeni ispitivanjem starenja su više nego zadovoljavajući za sve vulkanizate. Vulkanizati dobijeni programom 1 najbolje sprečavaju prodiranje naftnih goriva i organskih rastvarača, nakon toga vulkanizati dobijeni programom 2 i 3. Aktivaciona energija i promena slobodne energije su najveće kod vulkanizata dobijenih programom 1, zbog čega program mešanja 1 ima više tehnoloških prednosti u odnosu na druga dva programa mešanja.

Ključne reči: umešavanje; difuzija; mešanje; prirodna guma; permeabilnost; vulkanizacija.