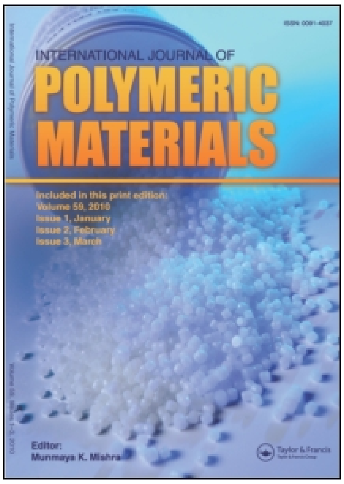

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Effect of Mixing Schemes on Physico-Mechanical, Aging Properties, and Permeability of Aldehydes through Blends of Natural Rubber and Low Molecular Weight Natural Rubber

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Effect of Mixing Schemes on Physico-Mechanical, Aging Properties, and Permeability of Aldehydes through Blends of Natural Rubber and Low Molecular Weight Natural Rubber

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This article reports on the physico-mechanical properties, chemical resistance, aging properties, sorption, diffusion, and permeability of aldehydes (acetaldehyde and formaldehyde) through vulcanizates from blends of natural rubber (NR) and low molecular weight natural rubber (LMWNR) compounded by three different mixing schemes. The compounding ingredients were mixed with the two mentioned rubbers 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 LWMNR and in scheme 3, the compounding ingredients were first mixed with the LMWNR before adding the NR. The physico-mechanical results of the vulcanizates showed that changes in the mixing schemes significantly influence the tensile properties of the vulcanizates. The tensile strengths of the vulcanizates prepared with mixing scheme 2 were 3.5 MPa lower than vulcanizates from scheme 1, whereas scheme 3 was lower than scheme 1 by 7.8 MPa. The aging result of the vulcanizates from all the mixing schemes were

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found to be similar. The activation energy and free energy change were highest with scheme 1 whereas the extent of acetaldehyde and formaldehyde penetrations were lowest with scheme 1, signifying a well crosslinked and aldehyde-resistant vulcanizate.

Keywords: aldehydes, mixing, natural rubber, physico-mechanical properties, vulcanization

INTRODUCTION

Natural Rubber (NR) compounding is as old as the history of natural rubber itself. Compounding of NR entails the addition of various additives to enhance the properties and processability of the expected vulcanizate [1–3]. These additives have been found to be mostly from petrochemicals sources [4]. Another very important and alternative method of enhancing the processability or improving on some of inherent limitations of natural rubber is by blending NR with different rubbers [3,5–6]. These developments about blending of rubbers have gained commercial interest and wider acceptability from the rubber users by having rubber vulcanizate that can combine improved processing characteristics with modifications in the limitation areas of NR. For example, some of the limitations suffered by natural rubber in areas like poor resistance to oxygen and ozone, high permeability to gases, and so on, were found to be improving after blending NR with some new generic family of polymers of lesser solubility problems and good processing characteristics as reported by Perera et al. [7–8]. It was in light of this that Okieimen and Akinlabi [3] produced, studied, and reported the use of Liquid Natural Rubber (LNR) as a co-polymer with natural rubber.

The rubber blending strategy 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 have to be considered and controlled to obtain a blend with acceptable properties. These might include poor interfacial adhesion between phases due to poor compatibility; it is also possible that the blending of two different rubbers results in a vulcanized rubber blend with an uneven distribution of polymer networks. This could be caused by either the higher solubility of sulfur in unsaturated rubbers or uneven affinity of accelerators by more polar rubbers. Either can have adverse effects on the properties of the blends. 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.

Akinlabi et al. [9] have documented Low Molecular Weight Natural Rubber (LMWNR) as a plasticizer, having influence on segment packing density of polymers, and based on this, it was believed that LMWNR will enhance uniform distribution of compounding ingredients and possibly attract the compounding ingredients more to itself, than to natural rubber because natural rubber is a non-polar hydrocarbon. In this regard, it was further thought that it will be of interest to find out how the sequence of mixing the two rubbers and the compounding ingredients will influence the physico-mechanical properties, crosslinking properties, aging, and resistance of the vulcanizates to acetaldehyde and formaldehyde, because these chemicals occur freely in nature (although in minute quantity) and are frequently used in the laboratory. These thoughts serve as the basis for this study.

EXPERIMENTAL

Materials

Natural rubber latex from NIG 901 clone was obtained from the estates of the Rubber Research Institute of Nigeria (RRIN), Iyanomo, Benin City, whereas 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, 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 [3,11]. 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 0.80 ml/min, the injected volume 100 μl

TABLE 1 Recipes 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	—

[a] Conventional vulcanization system (CV).
[b] Efficient vulcanization system 1 (EV_1).
[c] Efficient vulcanization system 2 (EV_2).
[d] Semi-efficients vulcanization system (semi-EV).
Flectol H = Polymerized 1,2 dihydro-2,2,4-trimethyl quinolene.
CBS = N-cyclohexylbenzothiazole-2-sulphenamide.
TMTM = Tetramethylthiuram monosulphide.

(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 3660, 7000, 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 through a porosity of 0.45 µm.

Compounding of the Mixes

Recipes used for the four different sulphur vulcanization systems are shown in Table 1, whereas Tables 2–4 show the mixing sequences. Mixing was carried out using a laboratory two-roll mill in accordance

TABLE 2 Mastication Procedures for Scheme 1

Mixing procedures	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 Mastication Procedures for Scheme 2

Mixing procedures	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**

to the method described by the American Society for Testing and Materials (ASTM)-D 3184-80.

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. The respective cure times as measured by t_{90}, scorch times, torque, and cure rates, were determined from the rheograph.

Measurement of Mooney Viscosity

The Mooney viscosity of the sample was determined using a shearing disc viscometer model type Wallace MK III, according to ISO 289. 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

TABLE 4 Mastication Procedures for Scheme 3

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

rheographs. 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 dumbbell test specimen (Type II) as contained in ASTM D-412-87 (method A). Thereafter, the tensile strength at break, modulus, and elongation at break were calculated.

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 (1 N) for a given period of time (24 hr) 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:

$$\text{Compression set } (\%) = \frac{(\text{t0} - \text{tr})100}{\text{t0}} \tag{1}$$

where t0 = 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 [12]. The hardness of the vulcanizate was determined by adopting the standard dead load method described in BS 903 Part A26. The standard dead load method of measurement covers rubbers in the range of 30 to 85 International Rubber Hardness Degrees (IRHD).

Abrasion Resistance

A Wallace Akron abrasion tester was used in accordance to BS method [13]. 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 results was 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 and T = volume loss per 1000 revolutions of abrasive wheel, calculated from the mean of 5 runs on the sample rubber.

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 [14]:

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

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

$$\text{Crosslinking densities } (\rho/Mc) = G/RT \tag{4}$$

Diffusion Studies

Studies of the sorption, diffusion, and permeability of acetaldehyde and formaldehyde 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 equation [15]:

$$\mathrm{D} = \pi[\mathrm{hn}/4\mathrm{M}_\infty]^2 \tag{5}$$

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 [15]:

$$\mathrm{P} = \mathrm{DS} \tag{6}$$

where S is sorption.

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 [16]:

$$\log \mathrm{D} = \log \mathrm{D}_0 - \mathrm{E}_\mathrm{a} \log \mathrm{RT} \tag{7}$$

where E_a is the activation energy, R is the gas constant, and T is the absolute temperature in Kelvin. In order to determine the enthalpies, ΔH and enthropies, ΔS of the system, the equilibrium adsorption constant "K" was treated with the Vant Hoff expression [16]:

$$\log \mathrm{K} = \Delta\mathrm{S}/2.303\mathrm{R} - \Delta\mathrm{H}/2.303\mathrm{RT} \tag{8}$$

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 with the relation [16]:

$$Kt^n = M_t/M_\infty \tag{9}$$

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 [16]:

$$\Delta G = \Delta H - T\Delta S \tag{10}$$

where ΔG is the Gibb's free energy, ΔH is the enthalpy, T is the temperature in Kelvin, and ΔS is the enthropy.

RESULT AND DISCUSSION

The rheological characteristics of the four vulcanization systems highlighted in Table 1 are shown in Table 5. Generally, in natural rubber technology and processing, rubber manufacturers always prefer a 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 will be observed that semi-EV system gave the highest cure rate of 35.97 (%/min) and least cure time of 4.03 min whereas 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

TABLE 5 Results of the Oscillating Disc Rheometer

Vulcanization systems	t_1 (m)	t_2 (m)	t_{90} (m)	M_L,Nm	M_H,Nm	ODR,Nm	CR (%/min)
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 in minute to an increase of 1 unit of torque above M_L.
t_2 is the time in minute to an increase of 2 unit of torque above M_L.
t_{90} is the cure time in minutes.
M_L is the minimum torque, Nm.
M_H is the maximum torque, Nm.
ODR torque is calculated using the formula: $\frac{90(M_H - M_L) + M_L}{100}$.
Cure rate is calculated using the formula $100/(t_{90} - t_2)$ (%/min).

of sulphides—due to high sulphur level in the recipe), which might have led to ether crosslinks and consequently result in the material having high cure time and high ODR torque. The high cure rate value observed with semi-EV system signifies a well crosslinked system. Morison [17] had earlier documented that at high vulcanization temperature in a semi-EV system, there is possibility of having rubber-bound intermediates and their subsequent conversion to crosslinks, thereby leading to a high cure rate of the vulcanizates. The least ODR torque of 5.79 Nm was observed in EV_2 system, which was closely followed by the semi-EV system (7.42 Nm) whereas the CV system gave the highest ODR torque of 12.43 Nm. This observation is very similar to the findings of some previous workers [18–19]. Baker et al. [18] earlier suggested that during vulcanization, besides the predominantly polysulphidic crosslinks, 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 selected as the vulcanization system used in the mastication of the three different mixing schemes shown in Tables 2–4 because the semi-EV system gave the best cure time, scorch time, and cure rates.

Looking at the mixing procedures in Tables 2–4, it will be observed that scheme 1 was completed within 18 min (giving the most efficient time), whereas schemes 2 and 3 were completed within 21 min 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, usually 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 as shown in Table 6. The tensile strength varies from 25.5 MPa for scheme 1 to 17.3 MPa for scheme 3, signifying that scheme 1 has a 31% tensile strength advantage over scheme 3. The moduli at 50% elongation, 100% elongation, and 200% elongation were found to be highest with scheme 1, followed by scheme 2 whereas the least was with scheme 3. The results of the elongation at break also follow 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

TABLE 6 Physico-Mechanical Properties of the Vulcanizates

Parameters	1	2	3
Tensile strength (MPa)	25.5	22.0	17.7
Modulus at 50% elongation (MPa)	2.9	2.7	2.4
Modulus at 100% elongation (MPa)	6.6	5.4	4.7
Modulus at 200% elongation (MPa)	8.7	6.5	6.3
Elongation at break (%)	989	920	810
Crosslink density ($\times 10^{-4}$)	1.7	1.5	1.4
Hardness (IRHD)	59	55	54
Compression set (%)	44	42	42
Abrasion resistance (%)	63	59	60
Mooney Viscosity ML (1 + 4) at 100°C	72	67	69

advantages of the two rubbers in permitting easy incorporation of the ingredients, thereby giving rise to a well crosslinked material with better tensile and elongation properties. However, in scheme 2, the LMWNR could not be considered as a base polymer because it was added after the compounding ingredients whereas similar reason accounts for why NR in scheme 3 could not be considered a base polymer. These sequences of mixing might have affected the distribution of the compounding ingredients in the rubber matrix, thereby accounting for the low strength of the vulcanizates from schemes 2 and 3 when compared with scheme 1. Surprisingly, the mechanical properties of the vulcanizates from schemes 2 and 3 were still within the accepted range as a result of the fact that because of its softness the LMWNR on itself, is soft compared to NR and would have possibly acted as a plasticizer here, thereby gaining easy incorporation into the rubber matrix, even after the addition of the ingredients.

The crosslinking density result was calculated from the volume fraction of the rubber in the swollen gel (V_2) by using the Flory-Rhener equation (Eq. 4) shown earlier, and it was found to be decreasing from scheme 1 to scheme 3. This presumes that an initial mastication of the two rubbers before the addition of the other compounding ingredients would permit uniform distribution of the materials across the rubber, making the interface rich with a higher degree of crosslinking throughout the interfacial region, thereby enhancing the strength of the vulcanizate. The results of the hardness, compression set, abrasion resistance, and Mooney viscosities of vulcanizates from scheme 1 were found to be the highest, giving an indication of a well crosslinked material. Effects of uniform distribution of recipes in natural rubber compounding were earlier documented by Das [20], who mentioned that uniform distribution and dispersion of fillers in the rubber matrix will give rise to a well crosslinked material of good physico-mechanical properties. This finding of Das was similarly observed in scheme 1 of this study.

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

$$\text{Extent of aging} = \left[\frac{[\mathrm{O}-\mathrm{A}]}{\mathrm{O}}\right] \times 100 \qquad (11)$$

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 7. The aging results at 30, 40, 50, and 60°C were not discussed because of marginal changes in the values when compared with the unaged.

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

Sorption "S," diffusion "D," and permeability "P" have found uses as a way of determing the extent of crosslinking and network formation in a rubber matrix. The sorption was determined as percentage mass gained. The sorption plot of the vulcanizates in acetaldehyde and formaldehyde at 50°C is shown in Figure 1. The plot appears to show linear relations in the beginning, suggesting this part of the plot obeying a Fickian type of transport mechanism. More complex effects

TABLE 7 Aging Results of the Vulcanizates at 70°C for 48 h (% of Original Sample Values)

Parameters	A (%)	B (%)	C (%)
Tensile strength (MPa)	10.4	9.9	9.7
Modulus at 50% elongation (MPa)	8.1	8.0	7.8
Modulus at 100% elongation (MPa)	7.3	7.1	7.1
Modulus at 200% elongation (MPa)	6.8	6.6	6.5
Elongation at break (%)	17.2	17.0	17.0
Crosslink density ($\times 10^{-4}$)	3.9	3.7	3.7
Hardness (IRHD)	5.7	5.7	5.6
Compression set (%)	4.1	4.2	4.1
Abrasion resistance (%)	6.5	6.4	6.4
Mooney viscosity ML (1 + 4) at 100°C	8.5	8.5	8.4

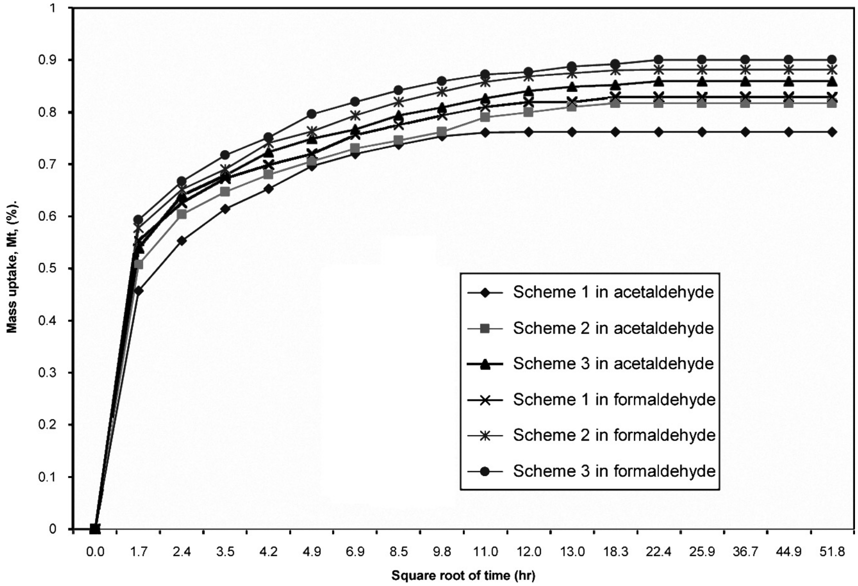

FIGURE 1 Sorption plots of the mixing schemes in acetaldehyde and formaldehyde at 50°C.

became operative after about 9 h of experiment that brings deviations from linearity as can be seen in the plots. The sorption results were interpreted as mass increase per unit weight of the vulcanizate and they were presented as percentage increase in Table 8. From the sorption values in Table 8, it is evident that S increases as the reaction temperature increases. S values of scheme 3 were found to have higher values, suggesting that the vulcanizate from scheme 3 allows easy penetration of the acetaldehyde and formaldehyde.

The diffusion coefficient "D" was calculated in Eq. 5. The diffusion results obtained were found to be temperature dependent; the diffusion increases as temperature rises. It was also found that vulcanizates from scheme 3 had the highest value, followed by vulcanizates from scheme 2 whereas vulcanizate from scheme 1 has the least. This shows the dependence of diffusion on the mixing schemes. 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 has previously been used by Alfrey et al. [21] to predict the performance

TABLE 8 Sorption, Diffusion and Permeability Results

Mixing schemes	$S \times 10^2$ (g/g)	$D \times 10^5$ ($mm^2 min^{-1}$)	$P \times 10^2$ ($mm^2 min^{-1}$)
At 30°C			
MS1 with acetaldehyde	22	1.7	37.4
MS2 with acetaldehyde	24	1.8	43.2
MS3 with acetaldehyde	27	2.0	54.0
MS1 with formaldehyde	31	2.3	71.3
MS2 with formaldehyde	34	2.6	88.4
MS3 with formaldehyde	37	2.9	107.3
At 40°C			
MS1 with acetaldehyde	27	2.1	56.7
MS2 with acetaldehyde	30	2.3	69.0
MS3 with acetaldehyde	32	2.4	76.8
MS1 with formaldehyde	38	2.9	110.2
MS2 with formaldehyde	42	3.3	138.6
MS3 with formaldehyde	43	3.4	146.2
At 50°C			
MS1 with acetaldehyde	32	2.3	73.6
MS2 with acetaldehyde	35	2.5	87.5
MS3 with acetaldehyde	37	2.7	99.9
MS1 with formaldehyde	42	3.2	134.4
MS2 with formaldehyde	47	3.6	169.2
MS3 with formaldehyde	50	3.8	190.0

of the elastomer in contact with solvents. Alfrey et al. [21] during their molecular transport study classified the transport phenomena into two cases; as case I (Fickian) and case II (non-Fickian). Alfrey et al. also showed that when 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 both Alfrey et al's cases.

The permeability coefficient, P, was calculated in Eq. 6. The obtained permeability values of the vulcanizates in the acetaldehyde and formaldehyde are shown in Table 8. From the permeability values, it is also evident that permeability increases as the temperature increases. Permeability values of vulcanizates from scheme 1 were observed to be lower than vulcanizates from scheme 2 whereas vulcanizates from scheme 3 have the highest values. This further confirms the effect of the mixing schemes on the vulcanizate properties.

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

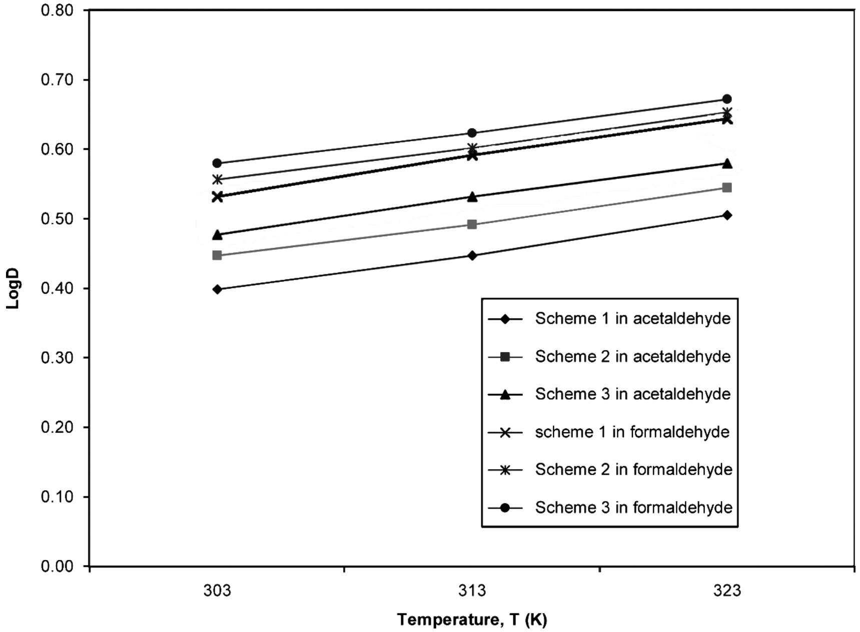

FIGURE 2 Showing Arhennius plots of the mixing schemes in acetaldehyde and formaldehyde.

Eq. 7. Plots of log D against T for the vulcanizates in the different mixing schemes are shown in Figure 2.

The activation energies obtained from the slopes of the curves are given in Table 9. It was observed that activation energies were influenced by the solvents' nature. On the average, activation energies of vulcanizates from scheme 1 were higher, followed by vulcanizates from scheme 2, whereas vulcanizates from scheme 3 were the least, that is, activation energy decreases from mixing sceme 1 to mixing scheme 3. This observation was found to be in line with the previous report of Uzoma and Isa [22], where it was suggested that 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 enthropies, ΔS of the system, the equilibrium adsorption constant K_s was treated with Vant Hoff expression, shown in Eq. 8. Plots of log K_s against 1/T for the vulcanizates in schemes 1–3 are shown in Figure 3. The

TABLE 9 Activation Energy, Enthalpy, Entrophy, and Free Energy of the Vulcanizates from the Different Mixing Schemes in Acetaldehyde and Formaldehyde

	Mixing schemes		
Solvents	1	2	3
Acetaldehyde			
Ea ($Jmol^{-1}$)	536.05	484.55	513.31
ΔH ($Jmol^{-1}$)	86.36	87.93	75.33
ΔS ($Jmol^{-1}$)	–0.7	–0.68	–0.61
ΔG ($Jmol^{-1}$)	226.11	219.65	197.04
Formaldehyde			
Ea ($Jmol^{-1}$)	435.75	367.14	405.17
ΔH ($Jmol^{-1}$)	65.94	70.31	65.38
ΔS ($Jmol^{-1}$)	–0.54	–0.50	–0.47
ΔG ($Jmol^{-1}$)	174.43	161.51	151.82

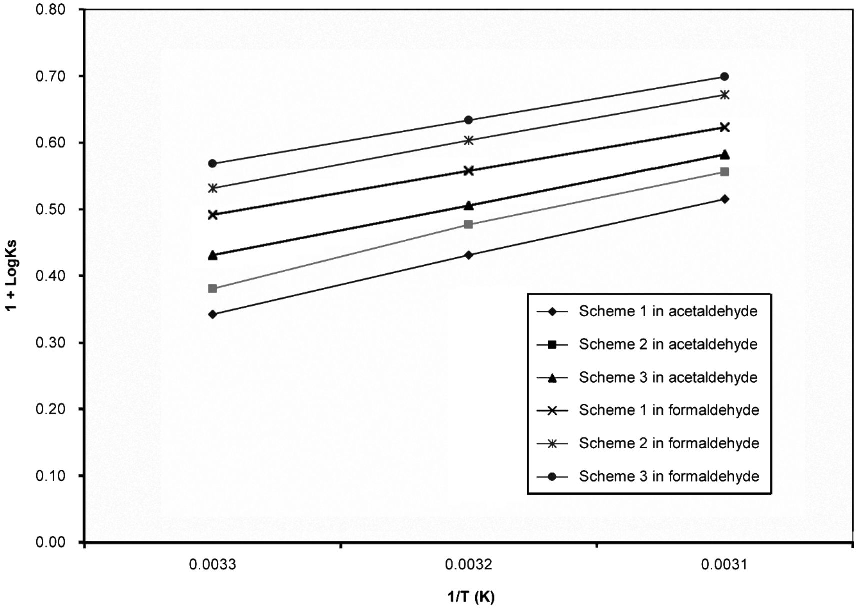

FIGURE 3 Vant Hoff plot of the mixing schemes in acetaldehyde and formaldehyde.

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 9.

The enthalpies, ΔH and enthropies, ΔS were also observed to be mixing schemes dependent. The positive values of enthalpies show that the reactions were endothermic. The negative value of enthrophy 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 in Eq. 10. The values of ΔG obtained are given in Table 9. The ΔG was observed to be highest in scheme 1, followed by scheme 2, whereas scheme 3 has the least values. The free energy values were observed to be positive in all the cases, indicating nonspontaneity of the process.

CONCLUSION

This study has found that an initial mixing of the base polymer (rubbers), before the addition of any other ingredients is highly desirable and a prerequisite for vulcanizates of better technological advantage in terms of physico-mechanical properties, aging, permeability resistance, and cost effectiveness with respect to time gained. Hence, this study has proved mixing scheme 1 having better advantages over other mixing schemes and thereby highly recommended for efficient and effective compounding of rubber blends.

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