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Physico-Mechanical, Aging Properties, and Permeability of Ketones Through Vulcanizates Prepared by Different Mixing Schemes

D. Malomo^a; F. Egharevba^a; A. K. Akinlabi^b; F. E. Okieimen^c; N. A. Oladoja^d

^a Chemistry Department, Ambrose Alli University, PMB Ekpoma, Edo State, Nigeria ^b Chemistry Department, University of Agriculture, Abeokuta, Nigeria ^c Chemistry Department, University of Benin, Benin City, Nigeria ^d Chemistry Department, Ondo State University, Akungba, Nigeria

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Physico-Mechanical, Aging Properties, and Permeability of Ketones Through Vulcanizates Prepared by Different Mixing Schemes

D. Malomo
F. Egharevba

Chemistry Department, Ambrose Alli University, PMB Ekpoma,
Edo State, Nigeria

A. K. Akinlabi

Chemistry Department, University of Agriculture, Abeokuta, Nigeria

F. E. Okieimen

Chemistry Department, University of Benin, Benin City, Nigeria

N. A. Oladoja

Chemistry Department, Ondo State University, Akungba, Nigeria

This article reports on the physico-mechanical properties, chemical resistance, aging properties, sorption, diffusion, and permeability of ketones (cyclohexanone and acetone) through vulcanizates from blends of natural rubber (NR) and epoxidized low molecular weight natural rubber (ELMWNR) compounded by three different mixing schemes. The compounding ingredients were mixed with the two mentioned rubbers using three different mixing schemes by adopting a semi-efficient sulphur vulcanization compounding formulation. In Scheme 1, the natural rubber and ELMWNR were first mixed before adding the compounding ingredients. In Scheme 2, the compounding ingredients were first mixed with the NR before adding the ELMWNR and in Scheme 3, the compounding ingredients were first mixed with the ELMWNR 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 strength of the vulcanizates prepared with mixing Scheme 2 were 4.3 MPa lower than

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Address correspondence to D. Malomo, Chemistry Department, Ambrose Alli University, Ekpoma, Nigeria. E-mail: dosumalomo@yahoo.com

vulcanizates from Scheme 1, whereas Scheme 3 was lower than Scheme 1 with 8.5 MPa. The aging results of the vulcanizates from all the mixing schemes were found impressive. The activation energy and free energy change were highest for Scheme 1 whereas the extent of cyclohexanone and acetone penetrations were the lowest with Scheme 1, signifying well crosslinked and ketone resistant vulcanizates.

Keywords: compounding, diffusion, mixing schemes, natural rubber, vulcanization

INTRODUCTION

Compounding of natural rubber (NR) basically entails the addition of various additives to natural rubber with the expectation of enhancing the properties and processability of the anticipated vulcanisate [1–3]. The additives that are usually added to NR have been found to be mostly from petrochemicals sources [4]. An alternative way of enhancing the processability or improving on some of inherent limitations of natural rubber has been through blending of 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 vulcanizates 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 improved 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 the light of this that Okieimen et al. [9] produced, studied, and reported on the use of epoxidized low molecular weight natural rubber (ELMWNR) 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, like the preparation of rubber blends, 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 between the two rubbers. It is also possible that the blending of two different rubbers results in a vulcanized blend with an uneven distribution of polymer networks, which could be caused by either the higher solubility of sulfur in unsaturated rubbers or uneven affinity of accelerators to more polar rubbers. All these 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.

Okieimen and Akinlabi [3] have documented Low Molecular Weight Natural Rubber (LMWNR) as a plasticizer, having influence in segment packing density of polymers, and base on this, it was believed that epoxidation of LMWNR, which is the formation of oxirane rings (epoxides) by the action of an organic peracid on the carbon-carbon double bonds of the NR, will provide materials with added value that can give improved and desired properties for specific applications. The epoxidized low molecular weight natural rubber (ELMWNR) was also assumed to enhance uniform distribution of compounding ingredients and possibly attract the compounding ingredients more to itself than 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 (NR and ELMWNR) with the compounding ingredients will influence the physico-mechanical properties, crosslinking properties, aging, and resistance of the vulcanizates to cyclohexanone and acetone, because these chemicals often come in contact with rubber. This thought serves 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. 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), low molecular weight rubber (LMWNR), and epoxidized low molecular weight rubber (ELMWNR) were of analytical grade, whereas the rubber compounding chemicals were of commercial grade.

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) [11], and viscosity measurement using Ubbelohde viscometer [3,12]. 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 (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, 33900, 68500, 108000, 293000, 590000, 963000, and 3.0 million (expressed in g/mole). Prior to injection, the solutions were filtered through a porosity of 0.45 μm .

Production and Characterization of ELMWNR

The LMWNR obtained as described earlier was epoxidized using *in situ* method [2,13]. The temperature of the medium was about 5°C. Formic acid (90%) was added to LMWNR over a period of time with gentle stirring. Hydrogen peroxide (30%) was added dropwise while stirring. The reaction was left for a further 3 h before raising the temperature of the medium to about 55°C in order to coagulate the product. The ELMWNR produced was washed with distilled water repeatedly till acid-free and then dried at 70°C. The extent of epoxidation was determined by titrating ELMWNR solutions with a standard hydrogen bromide solution using methyl violet as indicator. This method was found to achieve about 35% level of epoxidation.

Compounding of the Mixes

Recipes used for the four different sulphur vulcanization systems are as shown in Table 1, whereas Tables 2–4 show the mixing sequences. Mixing was carried out using a laboratory two-roll mill in accordance to the method of the American Society for Testing and Materials (ASTM) D 3184-80 and as contained in the Standard Africa Rubber (SAR) Manual No. 2 [14].

Cure Characteristics

The cure characteristics (ODR) of the mixes were measured at 170°C using an Oscillating Disk Rheometer (ALPHA ODR 2000) in accordance to ISO 3417 method and as contained in the Standard Africa Rubber (SAR) Manual No. 2 [14]. The respective cure times as measured by t_{90} , scorch times, torque, and cure rates, were read and recorded as displayed by the rheometer.

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

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
ELMWNR (35% epoxide)	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-efficients vulcanization system (semi-EV).

ELMWNR = Epoxidized low molecular weight natural rubber.

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

CBS = N-cyclohexylbenzothiazole-2-sulphenamide.

TMTM = Tetramethylthiuram monosulphide.

TABLE 2 Showing Mastication Procedures for Scheme 1

Mixing procedures	Time (min)
Mastication of NR and ELMWNR	7
Addition of ZnO and Stearic acid	2
Anti-oxidant	2
Half of the filler	3
The remaining filler	3
Sulphur and MBTS	3
Total	20

TABLE 3 Showing Mastication Procedures for Scheme 2

Mixing procedures	Time (min)
Mastication of NR	8
Addition of ZnO and Stearic acid	2
Anti-oxidant	2
Addition of ELMWNR	4
Half of the filler	3
The remaining filler	2
Sulphur and MBTS	3
Total	24

TABLE 4 Showing Mastication Procedures for Scheme 3

Mixing procedures	Time (min)
Mastication of ELMWNR	4
Addition of ZnO and Stearic acid	2
Anti-oxidant	2
Addition of NR	6
Half of the filler	3
The remaining filler	2
Sulphur and MBTS	3
Total	23

ISO 289 and as contained in the Standard Africa Rubber (SAR) Manual No. 2 [14]. 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 in the Standard Africa Rubber (SAR) Manual No. 2 [14]. 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 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:

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

where t_o = initial thickness and t_r = recovered thickness.

Hardness Test

The hardness test of rubber is the relative resistance of a surface to indentation by an indenter 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 [15]. 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 BS method [16]. 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 was expressed as:

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

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.

Crosslink Density

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

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

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

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

Diffusion Studies

Studies in the sorption, diffusion, and permeability of cyclohexanone and acetone through the vulcanizates were carried out at 30, 40, and 50°C using the gravimetric method. The sorptions was taken as the maximum weight gained. The diffusion coefficient "D" was calculated from this equation [17]:

$$D = \pi \left[\frac{hn}{4M_\infty} \right]^2 \quad (5)$$

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 [17]:

$$P = DS \quad (6)$$

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 [18]:

$$\log D = \log D_0 - E_a \log RT \quad (7)$$

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 entropies, ΔS of the system, the equilibrium adsorption constant "K" was treated with Vant Hoff expression [18]:

$$\log K = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (8)$$

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 to the relation [18]:

$$Kt^n = \frac{M_t}{M_\infty} \quad (9)$$

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 [18]:

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

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

RESULT AND DISCUSSION

Table 5 shows the rheological characteristics of the four vulcanization systems highlighted in Table 1. Generally, in 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, resulting in processing advantages in time gained and

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	0.57	1.36	6.30	5.60	16.47	9.84	20.24
EV ₁	0.52	0.76	5.50	5.95	16.10	9.19	21.09
EV ₂	0.51	0.99	5.70	5.80	13.41	6.91	21.23
Semi-EV	0.55	1.49	4.80	5.70	11.89	5.63	30.21

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: $90(M_H - M_L) + M_L/100$.

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

cost reduction. However, looking at the results in Table 5, it is observed that semi-EV system gave the highest cure rate of 30.21 (%/min) and least cure time of 4.80 min while the conventional sulphur vulcanization system gave the least cure rate of 20.24 (%/min) and highest cure time of 6.30 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 crosslinks and consequently results 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 [19] 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 5.63 Nm was observed in semi-EV system, which was closely followed by the EV₂ system (6.91 Nm) while the CV system gave the highest ODR torque of 9.84 Nm. This observation is very similar to the findings of some previous workers [18–19]. Hence, 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 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 20 min (giving the most efficient time), whereas Schemes 2 and 3 were completed within times of 24 min and 23 min, respectively. During compounding, an initial

mastication of the base polymers was found very essential (breaking of the bonds) before adding the ingredients in order to allow easy penetration and uniform mixing of the ingredients in the rubbers. The mastication time of ELMWNR was faster than that of the NR as can be seen in Tables 3 and 4. This could have resulted from the initial chemical reduction of the starting material, that is, LMWNR. This low molecular weight natural rubber has been documented [3,6,9] as a soft material and usually very sticky on rollers during mixing. Hence, it was thought that epoxidizing the LMWNR will 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 28.2 MPa for Scheme 1 to 18.9 MPa for Scheme 3, which shows a decrease of about 33% in the value of tensile result, signifying Scheme 1 having a 33% tensile strength advantage over Scheme 3. The modulus 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 result of the elongation at break also follows the trend observed in the tensile result. The observed trend in the mechanical properties suggests that during the initial mixing of the NR with EMWNR, there could have been good mixing of the two rubbers, permitting easy incorporation of the ingredients, thereby giving rise to well-crosslinked materials with better tensile and elongation properties. Technologically, the ELMWNR in Scheme 2 and the NR in Scheme 3 might not have been considered as a base polymer because they were added alongside with other additives and this must have led to the poor mechanical properties observed in Schemes 2 and 3 when compared with Scheme 1.

TABLE 6 Physico-Mechanical Properties of the Vulcanizates

Parameters	1	2	3
Tensile strength (MPa)	28.2	25.0	18.9
Modulus at 50% elongation (MPa)	3.2	2.9	2.3
Modulus at 100% elongation (MPa)	8.1	7.3	6.4
Modulus at 200% elongation (MPa)	9.9	8.7	7.9
Elongation at break (%)	962	903	843
Crosslink density ($\times 10^{-4}$)	1.8	1.7	1.5
Hardness (IRHD)	57	54	54
Compression set (%)	45	44	42
Abrasion resistance (%)	66	63	62
Mooney Viscosity ML (1 + 4)100°C	84	79	77

Nevertheless, the mechanical properties of the vulcanizates from Schemes 2 and 3 were still within the accepted range for rubber compounds, which signifies that such vulcanizates will find uses in products where high tensile strength is not of primary importance.

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 throughout the rubber, making the rubber interface rich with high 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 [22], where it was mentioned that uniform distribution and dispersion of compounding ingredients 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 were presented as percentage change in the properties of the vulcanizates, using the following expression:

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

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

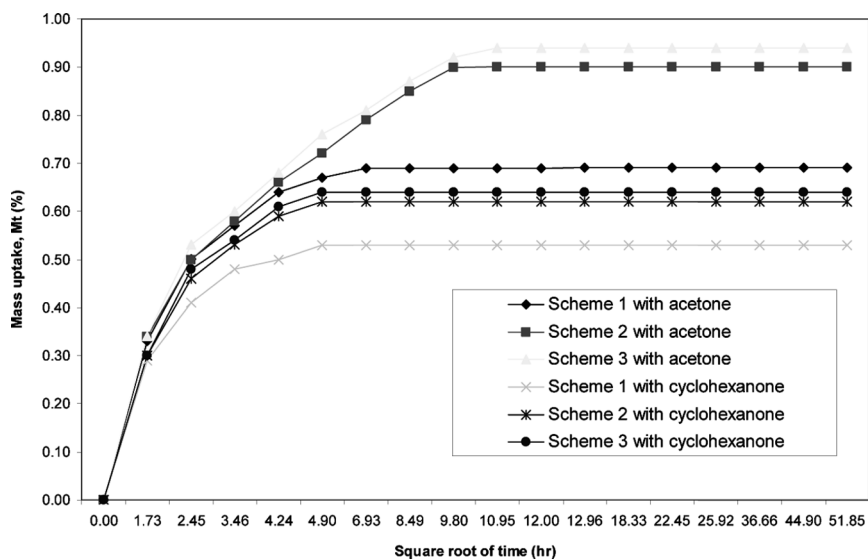
The results of the physico-mechanical properties of the vulcanizates after aging at 70°C for 48h were compared with their unaged results and are as presented in Table 7. The aging results at 30, 40, 50, and 60°C were not discussed because of marginal changes in the values when compared with the unaged. The aging results obtained from all the vulcanizates in terms of the properties measured were not too conspicuously different. It can be inferred that the aging properties of the 3 schemes are nearly the same. This observed phenomenon suggests ELWMNR as having a positive aging influence in rubber vulcanizates, thereby suggesting that ELMWNR can find uses in rubber products where aging properties are of interest and importance. This discovery is an improvement over the aging limitations of natural rubber.

The sorption "S," diffusion "D," and permeability "P" calculations have found uses as a tool for determining the extent of crosslinking and network formation in a rubber matrix [19]. The sorption in this

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

Parameters	A (%)	B (%)	C (%)
Tensile strength (MPa)	9.7	9.1	8.7
Modulus at 50% elongation (MPa)	6.4	6.1	6.1
Modulus at 100% elongation (MPa)	6.6	6.4	6.5
Modulus at 200% elongation (MPa)	6.3	6.2	6.1
Elongation at break (%)	19.8	19.5	19.1
Crosslink density ($\times 10^{-4}$)	3.4	3.3	3.1
Hardness (IRHD)	5.3	5.1	5.1
Compression set (%)	3.6	3.8	3.9
Abrasion resistance (%)	5.7	5.4	5.6
Mooney viscosity ML (1 + 4) at 100°C	6.6	6.8	6.4

experiment was determined as percentage mass gained. The choice of cyclohexanone and acetone was due to their frequent laboratory and industrial usage with the aim of finding the effect of these chemicals. The sorption plot of the vulcanizates in cyclohexanone and acetone at 50°C is shown in Figure 1. The plot appears to show linear relations in the beginning, suggesting this aspect of the plot obeying a Fickian type of transport mechanism. More complex effects became operative after

**FIGURE 1** Sorption plots of the vulcanizates from the mixing schemes in acetone and cyclohexanone at 50°C.

about 11 h of experiment, which 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 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 cyclohexanone and acetone.

The diffusion coefficient “*D*” was calculated from Eq. 5 shown earlier. 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 were having 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

TABLE 8 Showing Sorption (*S*), Diffusion (*D*), and Permeability (*P*) Results of the Vulcanizates from the Mixing Schemes in Cyclohexanone and Acetone

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			
1 with cyclohexanone	21	1.6	33.6
2 with cyclohexanone	24	1.8	43.2
3 with cyclohexanone	27	1.9	51.3
1 with acetone	28	2.2	61.6
2 with acetone	31	2.3	71.3
3 with acetone	36	2.6	93.6
At 40°C			
1 with cyclohexanone	26	2.1	54.6
2 with cyclohexanone	28	2.3	64.4
3 with cyclohexanone	31	2.5	77.5
1 with acetone	34	2.5	85.0
2 with acetone	36	2.7	97.2
3 with acetone	39	3.1	120.9
At 50°C			
1 with cyclohexanone	30	2.3	69.0
2 with cyclohexanone	35	2.6	91.0
3 with cyclohexanone	38	2.8	106.4
1 with acetone	39	2.9	113.1
2 with acetone	41	3.0	123.0
3 with acetone	47	3.4	159.8

organic liquids through elastomers has previously been used by Alfrey et al. [23] to predict the performance 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. 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 from the Eq. 6 earlier. The obtained permeability values of the vulcanizates in the cyclohexanone and acetone are as shown in Table 8. From the permeability values, it is 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 has 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, Eq. 7 earlier. 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 Scheme 1 to mixing Scheme 3. This 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 cross-linking and diffusion results. It was also observed that activation energy of vulcanizates in cyclohexanone were higher than that of vulcanizates in acetone, which shows that activation energy is influenced by solvent's nature and diffusion rate. This observation was found to be in line with the previous report of Uzoma and Isa [24], where it was suggested that activation energy can be influenced by solvents' nature and diffusion rate.

In order to determine the enthalpies, ΔH and entropies, ΔS of the system, the equilibrium adsorption constant " K_s " was treated with Vant Hoff expression, shown earlier as Eq. 8. Plots of $\log K_s$ against $1/T$ for the vulcanizates in Schemes 1–3 are shown in Figure 3. The

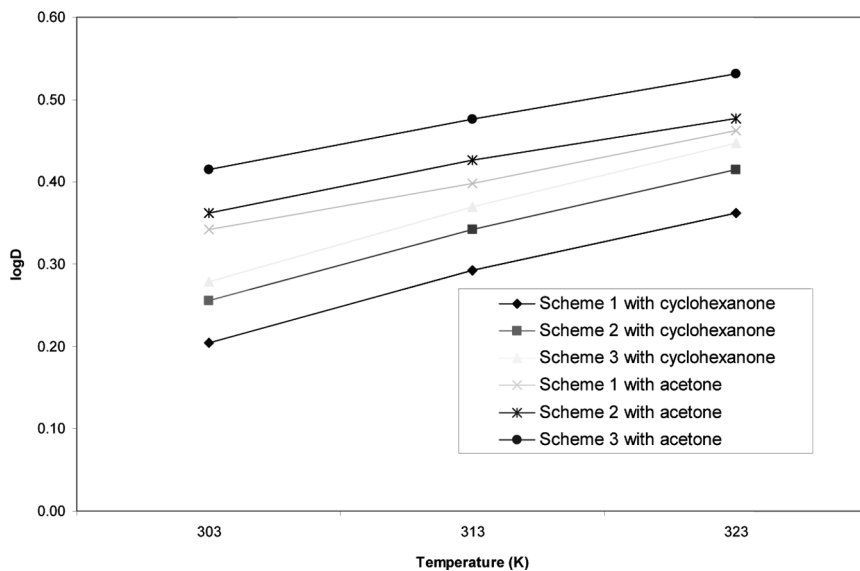


FIGURE 2 Arrhenius plot of the vulcanizates from mixing schemes in cyclohexanone and acetone.

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 9.

The enthalpies, ΔH and entropies, ΔS were also observed to be of varying magnitude. The positive values of enthalpies show that the

TABLE 9 Showing the Results of the Activation Energy (E_a), Enthalpy (ΔH), Entropy (ΔS), and Free Energy (ΔG) of the Vulcanizates from the Different Mixing Schemes in Cyclohexanone and Acetone

Solvents	Absorption energies	Mixing schemes		
		1	2	3
Cyclohexanone	E_a (Jmol^{-1})	842.02	798.50	788.04
	ΔH (Jmol^{-1})	82.24	84.57	86.98
	ΔS (Jmol^{-1})	-0.35	-0.30	-0.27
	ΔG (Jmol^{-1})	187.59	174.43	167.82
Acetone	E_a (Jmol^{-1})	599.88	582.53	576.97
	ΔH (Jmol^{-1})	82.40	86.43	88.57
	ΔS (Jmol^{-1})	-0.33	-0.28	-0.24
	ΔG (Jmol^{-1})	181.96	170.88	160.56

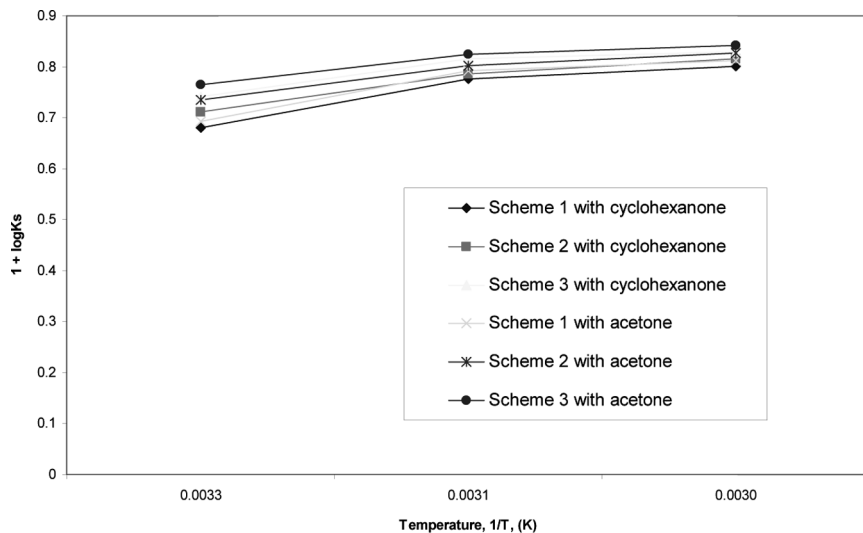


FIGURE 3 Vant Hoff's plot of the vulcanizates from the mixing schemes in cyclohexanone and acetone.

interactions were endothermic. The negative value of enthalpy signified that the interactions 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 earlier as 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 non-spontaneity 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 due to time gained. Hence, this study has proved mixing Scheme 1 having advantages over other mixing schemes and thereby highly recommended for efficient and effective compounding of rubber blends. It was also found that ELMWNR has positive aging influence on rubber compounds. Above all, contacts of

vulcanizates of this type of formulation with ketones should not be encouraged.

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