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Physico-Mechanical, Solubility and Thermodynamic Studies of Natural Rubber – Neoprene Blends

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ABSTRACT

In this study NR and CR were blended as follows. NR/CR (100/0), NR/CR (80/20), NR/CR (60/40), NR/CR (40/60), NR/CR (20/80) and NR/CR (0/100). The samples were vulcanized before subjecting them to physic-mechanical, swelling and thermodynamic studies. The results of the physico-mechanical tests carried out on the vulcanizates revealed modulus in the range of 3.22MPa to 1.79 MPa from absolute neoprene composition to absolute natural rubber composition, hardness in the range of 16.8 to 14.3 (Shore A) from absolute CR to absolute NR and ultimate tensile strength in the range of 4.17 to 2.83 MPa from absolute CR to absolute NR. The results of swelling revealed that the blends with higher neoprene content showed better resistance to petrol, kerosene and hexane compared to blends with lower neoprene contents. The order of increasing permeability of the solvents regardless of sample composition was; kerosene > hexane > petrol. The results of the thermodynamic studies of three selected blends (samples B, C and F) showed the sensitivity of reaction towards temperature as higher mass uptake values of the blends were recorded as temperature was increased in the order 30 ^{0}C, 50 ^{0}C and 70 ^{0}C. The activation energy of the swelling process was in reverse order of the permeability of the solvents. The solvent with the least permeability (petrol) had the highest activation energies in all the selected blends. The order of increasing activation energies of the solvents in the three blends was; Petrol> hexane> kerosene. The studies showed that solvent resistance of NR can be enhanced by blending with CR in appropriate ratio.

Keywords: *rubber, vulcanizate, vulcanization, compounding, activation energy, thermodynamics.*

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1.0 Introduction

Natural rubber (NR) latex is a natural commodity that has tremendous economic and strategic importance. Among the applications of NR latex is the production of dipped goods, extruded threads, adhesives, carpet-backing and moulded foams.**[1,2]** This is primarily because of the unique characteristics of NR latex, such as high strength, flexibility and elasticity.**[3,4]** Most NR latex products are derived via a sulphur vulcanization system, which achieves the desired physical properties for the product application.Natural rubber (NR) and its blended compounds have been extensively studied because of their superior performance in a wide range of applications, especially in tire application. However, it is prone to deterioration by ozone attack due to its highly unsaturated polymer backbone. This has been a major concern, hence the use of neoprene was investigated with the believe that it will improve the resistance of NR to ozone**[5]**.

The close structural similarities between neoprene and natural rubber are apparent. However, whilst the methyl group (CH_3) activates the double bond in the polyisoprene molecule, the chlorine atom(Cl) exerts opposite effect in neoprene. Thus the polymer is less liable to oxygen and ozone attack. The chlorine atom has two other positive impacts on the polymer properties. Firstly, the polymer shows improved resistance to oil compared with all hydrocarbon rubbers and these rubbers also have a measure of resistance to burning which may further be improved by use of fire retardants.**[6]** These features together with a somewhat better heat resistance than the diene hydrocarbon rubbers have resulted in the extensive use of these rubbers over many years.

2.0 Experimental

2.1 Equipment and Apparatus

The equipment and apparatus used for this investigation include:weighing balance RS232, model WT2203GH, Saumya Two roll mill (DTRM-50) for compounding rubber, Saumya Compression moulding machine 50 TONS (PID528) for vulcanization, Saumya Universal tensile machine (UTM192-2L) for testing tensile properties, Rex durometer (OS-2H) for testing hardness, Din abrasion tester (FE05000) for testing wear resistance, 250ml reagent bottle, Stop Watch: 31305 model, Thermometer .Made in Nigeria.

2.1.2 Materials

The materials used include: natural rubber (ribbed smoked sheet) and, neoprene rubber were obtained from the Rubber Research Institute of Nigeria, Benin. Stearic acid, Zinc oxide, Carbon black, dithiobisbenzothiazole, trimethylquinoline, sulphur were obtained as industrial chemicals from Lagos while petrol, kerosene were purchases from filling station in Ado Ekiti. Hexane was used as an analytical reagent from BDH.

2.2 Methods

General Formulation

The formulation used for the two rubbers are presented in the Table 2.0. All measurements were carried out in parts per hundred of rubber (Phr).

Table 2.0: Formulation for NR and CR

NR formulation	Phr	CR Formulation	Phr
NR	100	CR	100
Carbon black	30	Carbon black	30
Zinc oxide	4.0	Zinc oxide	4.0
Sulphur	2.0	Sulphur	2.0
Stearic acid	1.5	Stearic acid	1.5

MBTS	**1.5**	**MBTS**	**1.5**
TMQ	**2.0**	**TMQ**	**2.0**

2.2.1 Blend Ratio

The blends were prepared using the proportion presented in the Table 2.1

Table 2.1: Blend ratios of NR to CR composition

BLENDS	**NR%**	**CR%**
A	**100**	**0**
B	**80**	**20**
C	**60**	**40**
D	**40**	**60**
E	**20**	**80**
F	**0**	**100**

2.2.2 COMPOUNDING PROCESS

The compounding of the polymers was carried out using the two-roll-mill (DTRM-150) **[7]**.

2.2.3 Vulcanization Process

This was done using the compression moulding machine (PID528) **[8]**.

2.2.4 Characterization of Vulcanizate Properties

The mechanical analysis of the blends was carried out using Saumya universal tensile machine (UTM192-2L model) which determined the stress-strain behavior of the blends. The sample was fixed to the sample holders, one pulling the sample up and the other pulling it down. As the sample was being stretched by the pulling action of the sample holders, the graphical result containing parameters like yield load, elongation at break, tensile strength at yield load, breaking load and so on was shown on the system. A copy was printed for documentation.

2.2.4.1 Young Modulus

This was obtained as the slope of the stress-strain graph of the various samples. The loads were converted to stress by dividing the area (0.6mm^2). The elongations were also converted to strain by subtracting the original length from the elongations and the result divided by the original length (80mm)[7]

2.2.4.2 Ultimate Tensile Strength

The ultimate tensile strength (UTS) was calculated by dividing the maximum load carried by the specimen by the original cross sectional area of the specimen in mm^2[7]

2.2.4.3 Hardness

This was done using a rex durometer (OS-2H). The sample was placed on a metallic base with the indenter pin of the durometer very close to it. The load of the durometer was pressed downward so that the indenter pin could penetrate the sample. The measure of the resistance of the sample to indentation was observed on the display screen and the value was recorded.**[7]** This was done thrice per sample and the average value was taken.

2.5 SWELLING TEST

This was done to know the extent of solvent penetration in the blends. The solvents used were kerosene, petrol and hexane. 1g of each sample was weighed and immersed in kerosene for 2, 4, 6, and 8 hours, the weight of the samples were taken after each time duration. The same procedure was used for petrol and hexane. Results were obtained in triplicates for each sample per solvent used and the average value was taken and recorded**.[8,9]**

2.5.1 Sorption

Three selected vulcanizates; samples B, C and F were immersed in petrol, kerosene and hexane at 30 ^{0}C, 50 ^{0}C and 70 ^{0}C temperatures for 2, 4 and 6 hours and the mass uptake values were taken and recorded. The percentage sorption was calculated using the relation;

Final mass – initial mass / initial mass x 100 **[8]**

Where initial mass= 1g for all the samples.

2.5.2 Activation Energy of Swelling Process

The activation energy is the minimum energy required for a reaction to proceed. In determining the activation energy of the swelling process, three samples, sample B; 80%NR/20%CR, sample C; 60%NR/40%CR and sample F; 0%NR/100%CR were immersed in petrol, kerosene and hexane at 30 ^{0}C,50 ^{0}C and 70 ^{0}C and their mass uptake readings taken. The natural logarithm of percentage sorption was plotted against the reciprocal of temperature for each samples and the slopes of the graphs were fitted into the Arrhenius relation; $K= Ae^{-Ea/RT}$ to determine the activation energy (Ea), where R is molar gas constant, 8.314kJ/mol.**[10]**

3.0 RESULTS AND DISCUSSION

3.1 physico-mechanical properties

Rubber has properties that are drastically different from other engineering materials. Consequently, it has physical testing procedures that are unique .The Young Modulus values for the pure neoprene composition to pure natural rubber composition ranged from 1.79 to 3.22 MPa. The low values obtained when compared with engineering vulcanizates could be due to high CR content.. The hardness values for the pure neoprene composition to pure natural rubber composition ranged from 14.43 to 16.8 (Shore A). The extent to which the blends can be stretched before deformation from pure neoprene composition to pure natural rubber composition varied from 2.83 to 4.17MPa.

3.2 Swelling Test

The sorption in this experiment was determined as mass uptake. The choice of the solvents (hexane, petrol and kerosene) was because they are commonly used hydrocarbon solvents and are readily available. The sorption studies were made in order to determine the rate and amount of solvent uptake and hence determine the resistance of the vulcanizates to different solvents **[11,12]**. The mass uptake results of the blends in petrol, kerosene and hexane carried out at 30^{0}C are shown in Table 3.0. All values are averages of three replicate analysis.

Table 3.0: Mass uptake at 30 ^{0}C by the various blends in petrol, kerosene and hexane at different time intervals.

				Samples NR/CR			
Time(hrs)	**Solvents**	**A 100/0**	**B 80/20**	**C 60/40**	**D 40/60**	**E 20/80**	**F 0/100**
2.0	**Petrol**	**4.43**	**4.22**	**4.12**	**4.02**	**3.70**	**3.42**
	Kerosene	**6.04**	**5.85**	**5.57**	**5.05**	**4.72**	**4.54**
	hexane	**5.95**	**5.73**	**5.41**	**5.24**	**4.73**	**4.35**
4.0	**Petrol**	**4.64**	**4.35**	**4.23**	**4.09**	**3.93**	**3.65**
	Kerosene	**6.35**	**6.04**	**5.65**	**5.24**	**5.12**	**4.73**
	hexane	**6.13**	**5.82**	**5.52**	**5.42**	**4.94**	**4.52**
6.0	**Petrol**	**4.85**	**4.48**	**4.32**	**4.16**	**4.02**	**3.83**
	Kerosene	**6.57**	**6.34**	**5.89**	**5.43**	**5.23**	**5.07**
	hexane	**6.24**	**6.03**	**5.82**	**5.67**	**5.23**	**4.83**
8.0	**Petrol**	**5.03**	**4.63**	**4.42**	**4.21**	**4.10**	**3.98**
	Kerosene	**6.78**	**6.53**	**6.00**	**5.65**	**5.44**	**5.34**
	hexane	**6.42**	**6.21**	**6.03**	**5.75**	**5.41**	**5.03**

The results of mass of solvent uptake presented in Table 3.0 shows that there is a progressive increase in mass uptake from 2hours to 4 hours, 6 hours and 8 hours. For example the mass of sample A increased from 4.43g in petrol to 4.64g,4.85g and 5.03g at 2, 4, 6 and 8 hours respectively. Similar observations were recorded for kerosene and hexane for all the samples irrespective of the percentage composition of the blends. The results equally revealed that the mass uptake in the three solvents studied was in the order kerosene> hexane > petrol. This observation was the same for all the blends and at all times of immersion. Studies show that the permeability of solvent through any polymer or blend is dependent on a number of factors such as nature of solvent, nature of polymer or blend, solvent- polymer interaction (solute- solvent interaction), solute-solute, temperature and time of immersion**[11]**. From these results it was observed that the solvent resistance was in the order petrol > hexane > kerosene. The increase observed from 2 to 8hours might be ascribed to poor cross linking density, molecular weight and polarity.

The results also revealed that irrespective of immersion time of samples in any of the solvents, there was a progressive decrease in the amount of solvent uptake as the %CR increases in the blend. For petrol the order of value decrease after 8 hours was from 5.03g, 4.63g, 4.42g, 4.21g, 4.10g and 3.98g accounting for 20.9% decrease from (NR100%) to (CR100%). The same trend was observed for kerosene, the order of value decrease being 6.78g, 6.53g, 6.00g, 5.65g, 5.44g, 5.24g representing a percentage decrease of 22.7% from 100%NR to 100%CR. Lastly, for hexane the order of value decrease was 6.42,6.21,6.03,5.75,5.41,5.03 conforming to 21.7% reduction from (NR100%) to (CR100%). This may be due to the increasing effect of the polar neoprene polymer which causes the solvent resistance and hence the weight loss. Chloroprene being a polar elastomer with excellent dipole moment is thought to repel the non-polar hydrocarbon fuels of kerosene, petrol and the same reason is adduced for the interaction with normal hexane which is also non-polar.

3.3 Thermodynamics of Sorption Process

The thermodynamic studies of the sorption processes in the three solvents for some selected blend ratios at 30 ^{0}C, 50 ^{0}C and 70 ^{0}C were carried out. The activation energy, Ea of the processes was determined in order to reveal the susceptibility of the solvent uptake process at different times and specified temperatures.

3.3.1 Sorption

In order to know the effect of time and temperature on sorption, studies were carried out on three selected vulcanizates; samples B, C and F each, in petrol, kerosene and hexane at 30^{0}C, 50^{0}C and 70^{0}C. The results at 30^{0}C are presented in Table 3.0 above and those at 50^{0}C and 70^{0}C in Table 3.1.

Table 3.1: Swelling results for sample B, C and F at 30^{0}C, 50^{0}C and 70^{0}C.

Temp (^{0}C)	Sample	Solvent	Time(hr)		
			2	4	6
30	B	Petrol	4.22	4.35	4.48
		Kerosene	5.85	6.04	6.34
		Hexane	5.73	5.82	6.03
	C	Petrol	4.12	4.23	4.32
		Kerosene	5.57	5.65	5.89
		Hexane	5.41	5.52	5.82
	F	Petrol	3.42	3.65	3.83
		Kerosene	4.54	4.73	5.07
		Hexane	4.35	4.52	4.83
50	B	Petrol	6.96	7.38	7.82
		Kerosene	7.42	7.83	8.27
		Hexane	7.24	7.66	8.09
	C	Petrol	7.64	7.88	8.36
		Kerosene	8.09	8.32	8.80
		Hexane	7.92	8.15	8.63
	F	Petrol	6.55	7.15	7.45
		Kerosene	6.99	7.60	7.89
		Hexane	6.81	7.43	7.72
70	B	Petrol	9.14	9.54	9.85
		Kerosene	9.62	10.03	10.35
		Hexane	9.43	9.86	10.17
	C	Petrol	7.76	8.51	8.74
		Kerosene	8.26	8.99	9.23
		Hexane	8.08	8.81	9.06
	F	Petrol	9.89	10.35	10.73
		Kerosene	10.37	10.84	11.22
		Hexane	10.20	10.67	11.05

There was a progressive increase in mass uptake from 2 to 6 hours and also with increasing temperature for the three solvents with kerosene having the highest value of mass uptake.The increase might be due to the fact that an increase in temperature increases the kinetic energy of the molecules and so the rate of diffusion increases **[10]**. The highest sorption value recorded for kerosene might be due to its least viscosity and volatility compared to the other solvents used. Molecular weights and compatibility parameters may also contribute to the observed results.

3.3.2 Activation energy

The activation energy for all the samples B, C and F were determined by determining the rate of sorption at 30 ^{0}C, 50 ^{0}C and 70 ^{0}C.The Arrhenius expression K=Ae^{-Ea}/RT was used to calculate the activation energy values.

Where:

K= rate constant.
A= pre-exponential factor.
Ea= activation energy.
R= Gas constant.
T=temperature.**[10]**
The activation energy of sample B, C and F in petrol, kerosene and hexane after 6 hours are presented in Table 3.2.

Table 3.2: Activation energy of petrol, kerosene and hexane for sample B, C and F after 6 hours.

Sample	**Solvent**	**Activation Energy(KJ/Mol)**
B	**Petrol**	**19.33**
	Kerosene	**11.64**
	Hexane	**12.47**
C	**Petrol**	**17.66**
	Kerosene	**10.60**
	Hexane	**10.81**
F	**Petrol**	**25.57**
	Kerosene	**19.12**
	Hexane	**19.95**

For sample B, the activation energies in petrol, kerosene and hexane were 19.33 kJ/mol, 11.64 kJ/mol and 12.47 kJ/mol respectively. Similar results were observed for sample C and F, the Ea values for petrol, kerosene and hexane being 17.66 kJ/mol, 10.60 kJ/mol and 10.81 kJ/mol respectively for sample C and 25.57 kJ/mol, 19.12 kJ/mol and 19.95 kJ/mol respectively for sample F. The lowest permeability observed for petrol in the three samples as shown in Figures 3.0, 3.1 and 3.2 could be because of its high activation energies making it difficult for the solvent molecules to penetrate the blends and the high permeability observed for kerosene in the three blends might be due to its low activation energies making it possible for the solvent molecules to quickly overcome the energy barrier to penetrating the blends. In other words, the higher the activation energy, the harder it is for solvent permeation and vice versa. This observation is illustrated in figures 3.0, 3.1 and 3.2.

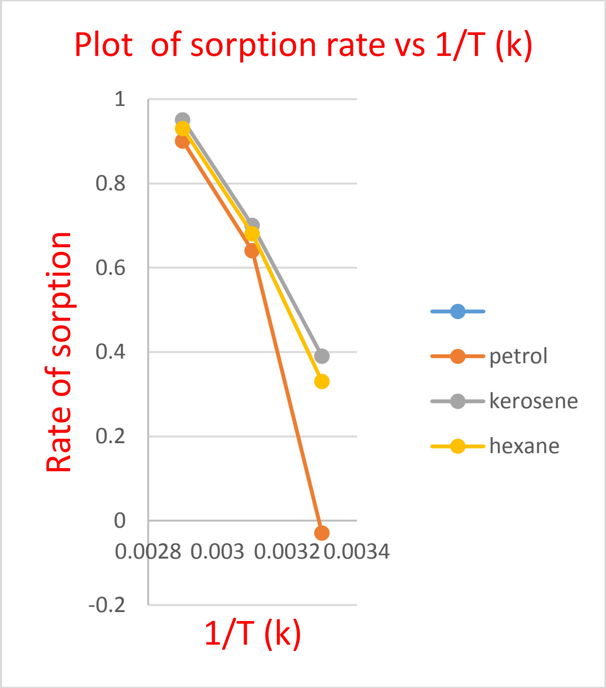

Fig. 3.0: Plot of rate of sorption vs 1/T (k) for sample B.

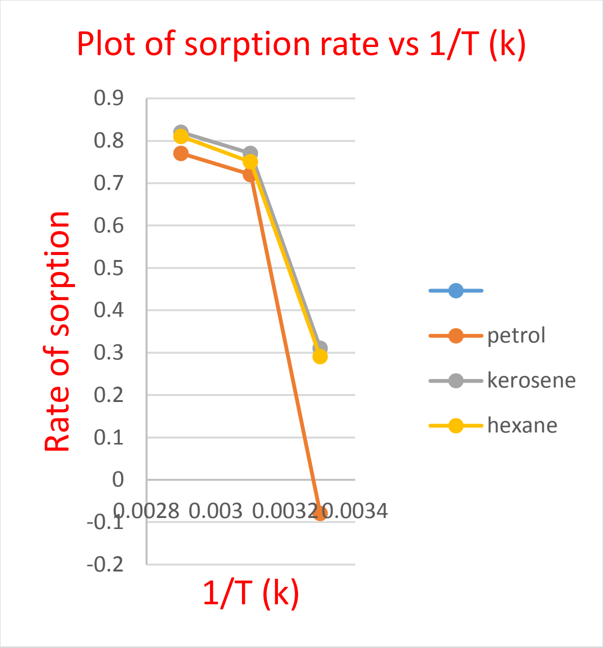

Fig. 3.1: Plot of rate of sorption vs 1/T (k) for sample C.

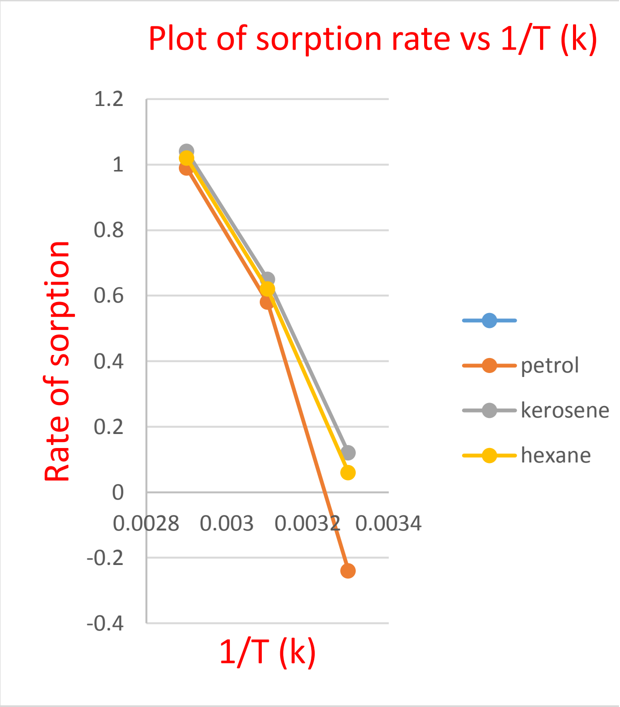

Fig.3.2: Plot of rate sorption vs 1/T (k) for sample F.

4.4 CONCLUSION

The physico-mechanical, solubility and thermodynamics studies of NR/CR blends investigated showed that the addition of compounding ingredients prior to vulcanization helped in producing vulcanizates with improved properties. It was found that blend composition and the nature of the elastomers played a significant role in determining the mass uptake. For absolute natural rubber, the mass uptake was high, nevertheless the results of mass uptake reduced with increasing CR composition in the blends. The results of the physico-mechanical properties obtained were low compared to vulcanizates used for most engineering materials. This could be due to high neoprene content across the blends. The activation energy of the processes was found to influence the permeability of the solvents under investigation. The studies also showed that solvent resistance of NR can be enhanced by blending with CR in appropriate ratio.

4.5 RECOMMENDATION

It is recommended that further research work be carried out on NR/CR blend but at lower CR composition to ascertain if the mechanical properties of engineering vulcanizates can be enhanced beyond those recorded in this study.

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