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A Comparative Study between the Physical properties of Natural Rubber/Carbon Black blend and Natural Rubber/non Carbon Black blend

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Abstract - Natural Rubber has been continuously developed due to its advantages such as good combination of strength and damping property. The addition of Carbon Back (CB) in Natural Rubber is very important to enhance the strength of the natural rubber. We have studied the relative effect of CB on Natural Rubber against a non black rubber, keeping all other parameters constant. This experiment gives us an idea about how reinforced a NR/CB blend can be as compared to a NR/non CB blend.[1]The effects of carbon blacks on vulcanization and mechanical properties of filled and non filled Natural Rubber (NR) are investigated. Curing kinetics is studied by Rheometer and the results indicate that the curing characteristics are influenced by combination of surface area of carbon black and sulphur content on the filler surface, because the former one enhances the physical cross-linking and the latter one introduces the additional chemical cross-linking. Both the degree of cross-linking and cure rate increase with increasing surface area and sulphur content, whereas the optimum cure time and scorch time decrease. The reinforcing nature of the carbon black is assessed from mechanical measurements. It is suggested that the surface area of carbon blacks strongly affects the physical properties of NR/carbon black composites.

Keywords - Natural Rubber, Carbon Black, Physical Properties, Reinforcing, Filler.

I. INTRODUCTION

Natural Rubber produced by *Heva Brasiliensis* whose chemical structure is cis 1, 4- poly isoprene, possesses excellent physical properties of a general purpose rubber. Presently, conventional Carbon Black (N110, N220, N330, etc.) is used because of its outstanding reinforcing filler. NR – CB vulcanizates are characterized by high mechanical stress, remarkable resilience, excellent elasticity, good low heat build up and good dynamic properties.

In this experiment, we have focused on these characteristic phenomenons with respect to a non CB filled natural Rubber. The properties of CB compounds depend on several factors such as carbon loading and the particle sizes, which include the particle-particle interaction.

II. MATERIALS NEEDED

Compound A			**Compound B**		
With CB (with Carbon)			**Without CB (without Carbon)**		
Name		**Phr**	**Name**		**Phr**
1.	Natural Rubber	100	1.	Natural Rubber	100
2	ZnO	5	2.	ZnO	5
3.	Stearic Acid	2	3.	Stearic Acid N110	2
4.	Carbon Black N110	20	4.	Carbon Black	-
5.	Accelerator (MBTS)	1.2	5.	Accelerator (MBTS)	1.2
6.	Sulphur	2.5	6.	Sulphur	2.5
Total		130.7	Total		110.7

a) **Compounding and Processing**
b) **Two Roll Mill**

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Two Roll Mills usually consists of two hollow cast iron rolls, cylindrical in shape, having provisions for passing cold water or steam through the rolls. There are gears attached with the motor which are either of different sizes or of different teeth with some size so s to give a differential speed to the front roll as compared to the back roll. We used the friction ratio of 1.15: 1.00

Other specifications for the mixing mill are provided below:

i) Roll Size (dia X length) = 6 X 12
ii) Approx. batch weight = (0.9 – 1.8) kg
iii) Drive (H.P.) = 7.5
iv) The mixing time for each of the compounds for batch A and batch B are given below:

Compound A			Compound B		
Name		Time (Min)	Name		Time (Min)
1.	Natural Rubber	3	1.	Natural Rubber	3
2.	ZnO	2	2.	ZnO	2
3.	Stearic acid	2	3.	Stearic acid	2
4.	C-Black (N110)	4	4.	C-Black (N110)	-
5.	Accelerator	2	5.	Accelerator	2
6.	Sulphur	2	6.	Sulphur	2
Total		15	Total		11

c) Rheological Test with moving die Rheometer

The moving die Rheometer measures the change in the stiffness of a rubber sample. The sample is compressed betweens two heated plates and by an applied oscillating force. The degree of vulcanization determines the cure characteristics of the sample as it is heated and compressed.

Specifications for the Moving Die Rheometer:

i) Standard – complies with ASTM D 5289
ii) Oscillation frequency : 10 – 300 cpm
iii) Oscillation amplitude : $\pm$ 0.5° ~ 3°
iv) Temperature range : 160° C
v) Torque range : 0 Elasticity S' – 1 – 200 lb-in
vi) Viscosity : S' – 0.3 – 200 lb-in
vii) Power : 1Q, 220 V, $\pm$ 10%, 50 Hz $\pm$ 3 Hz, 10 A

The graph for both the compounds A and B are attached-

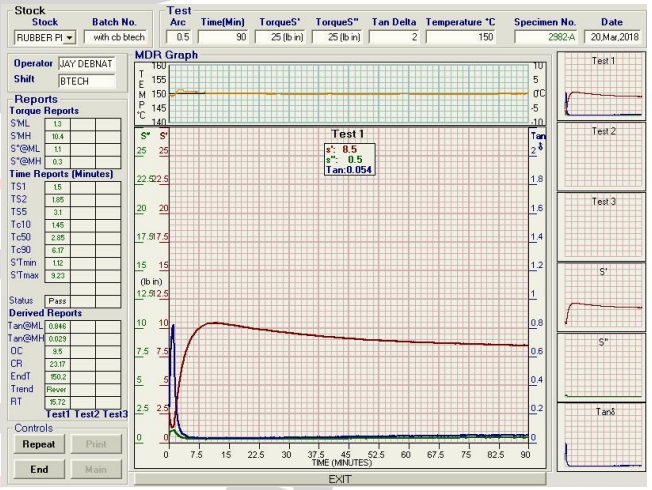

Fig 1- Rheograph for NR CB Blend

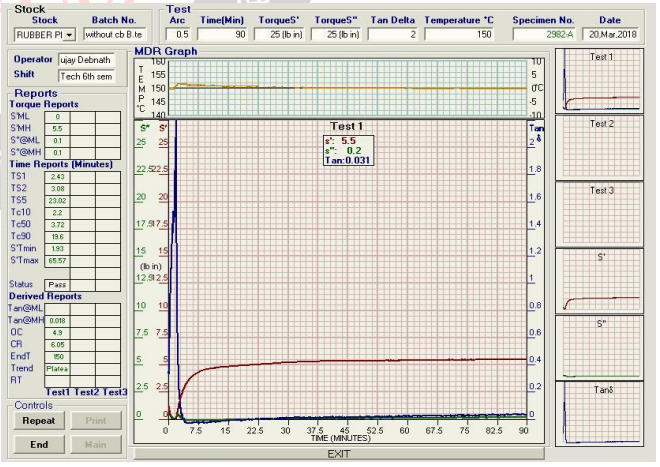

Fig 2- Rheograph for NR/ non CB Blend

The reading from the graph is as follows:

	Parameter	NR/CB blend	NR/Non CB blend
1.	T_c 50	2.85 minutes	3.72 minutes
2.	T_c 90	6.17 minutes	19.60 minutes
3.	S' ML	1.3 lb in	0.0 lb in
4.	S" ML	1.1 lb in	0.1 lb in
5.	S' T^{min}	1.12 minutes	1.93 minutes

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6.	S' T^{min}	9.23 minutes	66.57 minutes

For our compression molding, e had increased a 10°C in the temperature as a result of which the cutting time become half of that being specified by the Rheometer.

For $\Delta T = T_2 - T_1$ (T_2 is the final temperature and T_1 is the initial temperature)
Where $\Delta T = 10$, $T_2 - T_1 = 10$

It follows that the ratio between K_2 (at T_2) and K_1 (at T_1) will equal to 2 owing to doubling of the rate constant.
$K_2/K_1 = 2$

Employing Arrhenius equation,

$K_2/K_1 = \{Ae^{(-Ea/RT_2}\} / \{Ae^{(-Ea/RT_1)} = e^{[-Ea/R(1/T_2 - 1/T_1)]} = 2$

Or, $K_2 / K_1 = \exp(-Ea/R - \Delta 1/T) = 2$
$\therefore \quad \Delta 1/T = (1/T_2 - 1/T_1) = \{(T_1/T_1T2) - (T_2/T_1T2)\} = (-\Delta T/T_1T_2)$

Once we are holding $\Delta 1/T = -10/T_1T_2$

Substituting this into the Arrhenius equation,

$\text{Exp}(-Ea/R -10/ T_1T2) = 2$
Or, $10Ea/R\ T_1T2 = \ln 2$
Or, $T_1T_2 = 10\ Ea/R\ln 2$

Writing in terms T_1,

$T_1 (T_1 + 10) = 10\ Ea/R.lr2$
Or, $T_1^2 + 10T_1 . (10Ea/R.lr2) = 0$
Solving the quadratic equation, we have,
$T_1 = Ea \times 8.3 \times 10^{-3} K$
$T_2 = \{(Ea \times 8.32 \times 10^{-3}) + 10\} K$

$T_1 - T_2 = 10\ K$

d) Compression Molding

The Rubber compression molding process begins with a piece of uncrushed rubber which has been preformed to a control weight and shape. As the mould is closed, the material is compressed between the plates causing the compound to flow to fills the cavity. The material is held in the mould under high pressure and elevated temperature to activate the cure system in the rubber compounds.

III. Property Tests and the Results

i) Rheological Test

The lowest torque value recorded or the graph is called ML. It measures the stiffness of an uncured rubber at a given temperature.

From the graph we see that $ML_{NR/CB} > ML_{NR/nonCB}$

This clearly gives us an indication that the strength of NR/CB blend even at uncured stage is much higher than that of NR/non CB blend

[2] TS_2 is the time from the beginning of the test to the time the torque has increased 2 units above ML value. It is measured in time units and provides information about scorch time or at which point the owing actually starts.

As the curing progresses, the torque increases further. The slope depends on the compound and the system. That is why we see the slope of NR/CB blend is a bit higher than that of NR/Non CB blend. After some time the torque attains a maximum value and plateaus out. The highest torque recorded on the graph, is called the Moment Highest (MH).

Time from the start of the test point to the point where 90% of the MH value is reached is called its T_c90. It is a measure of the curing time of the system.

From our results,

(T_c90 for NR/CB blend) / (T_c90 for NR/non CB blend) = 6.17/19.60 = 1/3 (approx)

The cure time and the cure rate become faster because of the Carbon Black Content. The crosslink density also increases and the reversion resistance is improved in the material as a NR/CB blend. The cure time is faster since it is widely evidenced the CB would automatically perform better as a physical cross linker in the rubber material as a result of the rubber molecules being absorbed into the block surfaces during compounding.

b) Tensile Test

Referring to the chart C1 and both of the compared graphs we got from the Tensile Test, it is evident that the tensile stress of the NR/CB blend was much more higher than that of NR/Non CB blend proving the amount of reinforcement. The tensile strength in MPa recorded for NR/CB blend was 18.41 which that of NR/Non CB blend were 4.462. Beside that there was a great difference in the Young's Modulus that was recorded for both the samples (5.5: 1.0, NR/CB: NR/Non CB)

The relationship between the tensile stress and percentage of elongation was plotted. Based on the graph, it was showed that the tensile stresses were continuously increasing as the percentage of elongation was increased for both the compounds. [3] The stiffness recorded for CB/NR blend was 2769.32 (NM) and that for unfilled NR was 652.352, indicating a great deficiency in the reinforcement. While the CB filled NR, it was found that the materials displayed the small elastic behaviour, where the low stress level was produced at high strain. On the other hand it was

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also found that the CB filled NR exhibited thicker line rather than the unfilled NR line in which refers to the noise level of NR compound under the tensile force. The noise level resulted from the effect of molecular interaction between the mature and filler particles in respond to the force applied during tensile test, where the fillers acted as the strain amplifier, which strongly influenced the flow behaviour and its mechanical properties.

Furthermore, the high modules value exhibited by the CB filled NR compound compressed showed that the stiffness of the material increased due to the addition of the CB.

K = EA/L, where, K is the stiffness,
E is the Young's Modulus
A is the area and
L is the length

The tensile stress

6 = F/A, = Force/Area
Or, A = KL/E (by substituting the value of A)
Or, 6 = FE/KL

Or, $6 \alpha K^{-1}(FE/KL)$
Or, $1/6 \alpha K^{-1}(KL/FE)$

This concedes the problem in the stress versus strain curve whereby the tensile decreased since the stiffness increased resulting from the Reinforcement effect.

c) Shore Hardness

The shore hardness for both the filled and unfilled NR was measured with a SHOR E – A device.
The following data's were observed-
NR/CB blend -63 shore hardness
NR/Non CB blend-58 shore hardness

IV. RESULTS – TENSILE TESTING – C1

CB/NR	Gauge length (mm)	Width (mm)	Thickness (mm)	Total elongation at max. force	Tensile strength (MPa)	Elongation at fracture	Stiffness (Nm)
Proper-ties and their values	25	4.63	2.05	724.97	18.411	181.463	2679.32
	Young's modulus	Load on Break on	Stress at Break (NM)	Extension at break	Strain at break	Ring stiffness	Load at 100% modules
	6.812	0.1744	18.341	181.463	7.251	0.0000262	0.01567
	Stress at 100% modules	Extension at 100% modules					
	1.6541	25					
NR/ Non CB	Gauge length (mm)	Width (mm)	Thickness (mm)	Total elongation at max. force	Tensile strength (MPa)	Elongation at friction	Stiffness (Nm)
Proper-ties and their values	25	4.49	1.93	652.192	4.462	168.088	652.334
	Young's modulus	Load on Break on	Stress at Break (NM)	Extension at break	Strain at break	Ring stiffness (MPa)	Load at 100% modules
	1.396	0.0399	4.415	168.12	6.728	0.000006467	
	Stress at 100% modules	Extension at 100% modules					
	0.7615	0.25					

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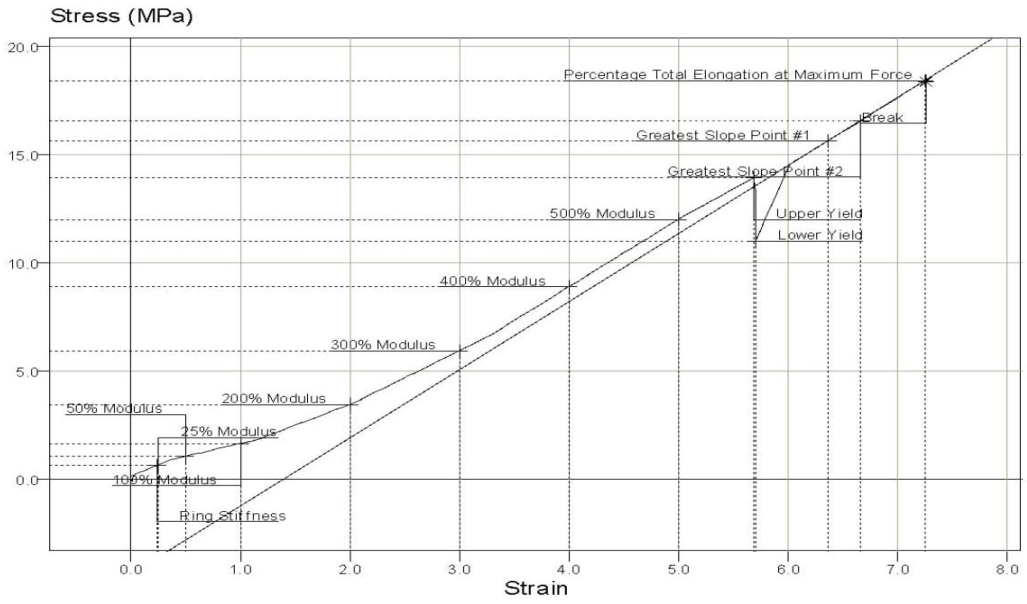

Fig 3- Stress Strain Curve for C Black Filled NR

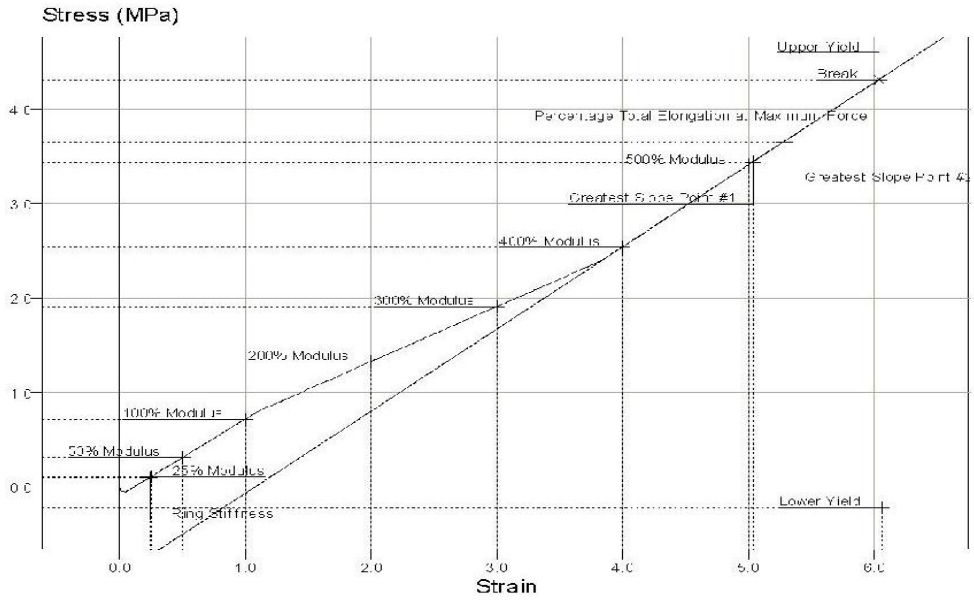

Fig 4- Stress Strain Curve for non C Black Filled NR

During tests of mechanical properties, remarkable modifications of rubbers which are termed as 'reinforcement', both physical and chemical interactions involved. The above table indicates the studied parameters of mechanical properties of NR/carbon black composites used to reflect the different reinforcing abilities among those composites. Hardness, which is one of the most obvious mechanical parameters, varies in a considerable range from 52 to 79 Shore A.

The degree of cross-linking has a great effect on the hardness of the elastomers. The highest surface sulphur content of N110 possibly contributes to the hardness of EPDM filled with N472. The higher degree of chemical cross-linking induced by peroxide and sulphur vulcanization and physical cross linking by entanglement ensures the NR vulcanizates the larger ability to resist deformation. [4]Also, it is reported that the rubber chains are entangled with or permanently locked in carbon black aggregates and form a rigid shell. The amount of shell increases with the increasing surface area of carbon black; thus, the largest area of rigid rubber shell is obtained on the N110 surface since it has the largest external surface area, which is accessible for rubber molecules. The rigid shell causes the enhancement of hardness of total NR composite.

According to the report, it is not surprising that the surface area of a carbon black contributes markedly to the hardness,

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because of the external surface which is accessible to polymer chains and provides a place for them to immobilize. [5] And it is reported that the amount of bound rubber increases with the increasing irregularity of filler surface. This is probably due to that, when the filler loading is the same, the larger surface has more irregularity and hence more bound rubber. Thus, it actually can be expected that larger surface area inevitably rises dramatically the possibility of immobilization of rubber molecules on surface of blacks. Therefore, the whole composite transforms from soft to stiff, owing to the loss of segmental mobility of polymer chains and consequently decreased flexibility of the rubber matrix.[6] Similarly, it is reported that high-structure, that is high external surface area, carbon blacks tend to shorten the elongation at break due to its higher strain amplification degree.

1. Stress Relation

Stress relation experiments, in which a specimen is strain to a fixed level (100% elongation in this case) and the slow decay of stress is monitored, present a simple method of investigating the time dependent modulus of reinforced polymers. In practice stress relaxation influences the residual stress and war page of moulded rubber parts, and is critical in many applications. [7] During the relaxation, the modulus of the material typically decays from an initial value to a stable value. The speed of the process, which has several practical implications, is characterized by relaxation time ל . The time constant is usually defined as the time needed for the modulus to decrease to 1/e of the internal between E_O and E_x.

The relaxation time is a cooperative phenomenon, which means all chains do not relax at the same time. It takes place gradually.

The stress relaxation is usually expressed as

$S/S_o = e^{-t/ל}$ .... i)

Where S = instantaneous stress

S_o = initial stress

t = time

ל = relusation time

Taking ln on both sides of i)

$LnS-lnS_0=-t/ל$

y=mx+c

This gives an equation of the straight line by plotting lnS vs t

We get the slope, inversing which we get the time constant ל.

The ל for NR/CB was forced to be 37.03 sec^{-1} and that fir NR/Non CB was found to be 28.21 sec^{-1}.

We can draw the conclusion from the plot and the experiment that

i) Rate of stress relaxation is a measure of entropic removal of orders of the material, the higher the rate, higher the entropy of the system.

ii) At high strain rate, the rate of stress was low due to the major contribution of elastic components in the system and hence the entropy was small.

iii) At lower strain levels the relaxation mechanism of NR/CB was independent of strain level. [8]But the rate of relaxation increased with the strain level due to its strain induced crystallization.

iv) The rate of relaxation was higher for NR/Non CB as compared to NR/CB blend.

v) The slope of NR/Non CB was high as compared to NR/CB in the lnS vs t plot, which procures the CB acts as reinforcement filler reducing the rate of relaxation.

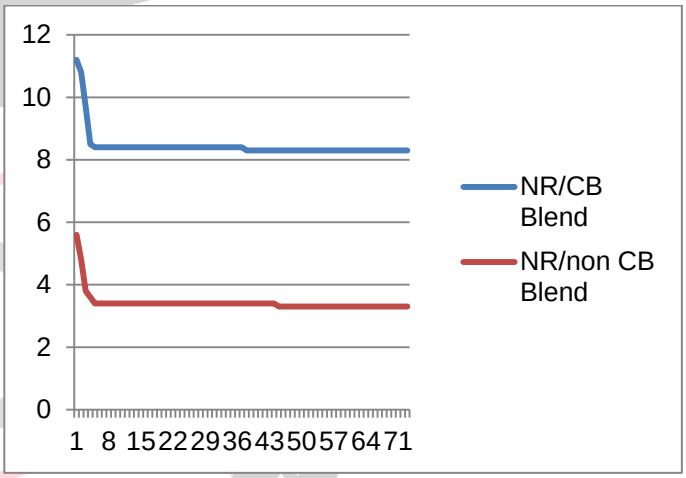

Fig 5- Stress Relaxation Curve for both the blends (Y axis= Stress (N), X axis= Time (in Sec))

2. Swelling Test:

High molecular weight compounds such as rubber can show swelling when immersed in an appropriate solvent.

In this experiment, we have used toluene as the solvent although benzene process to be the best solvent due to carcinogenic effect.

The magnitude of the swelling and the ultimate dissolution depends on the solubility parameter of both the materials. Swelling, as opposed to dissolution occurs when the mobility of the polymer molecules are restricted by the presence of crosslink, entanglements between molecules and the association of the filler with the polymer. [9]In field of elastomers there is a region of immobilised rubber immediately surrounding the filler particles and a region of intermediate mobility where the elastomers segments are less immobilized but constrained in comparison with the pure rubber.

We had taken a sample of both NR/CB blend and NR/Non CB blend compounds. After taking their initial weight, we used the formula.

$S_R = S/S_o$ = Instantaneous weight/Original weight,

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To get the swelling ratio, we plotted S_RVS time to see the differences of the two compounds.

Another interpretation can be carried out using the swelling Index which is given as

$S-S_o/S_o$ X 100% where, S = instantaneous weight

S_o= original weight

SWELLING INDEX					
NR/CB Blend			NR/Non CB Blend		
Initial weight =0.6130 gm after time to time (min)	Increased weight at (gm)	% change	Initial weight =0.5886 gm after time to time (min)	Increased weight at (gm)	% change
20	0.9420	53.5	20	1.1000	86.8
40	1.3550	43.8	40	1.4888	34.5
60	1.5490	14.3	60	1.7670	28.9
80	1.6900	9.1	80	2.0320	18.2
100	1.7500	3.5	100	2.2180	9.15
20 hrs 20 mins	1.9081	2.8	20 hrs 20 mins	2.6878	2.11
22 hrs 55 mins	2.004	2.4	22 hrs 55 mins	2.7520	2.02

We plotted the swelling ratio and have concluded that NR/Non CB blend swells much more than NR/CB blend.

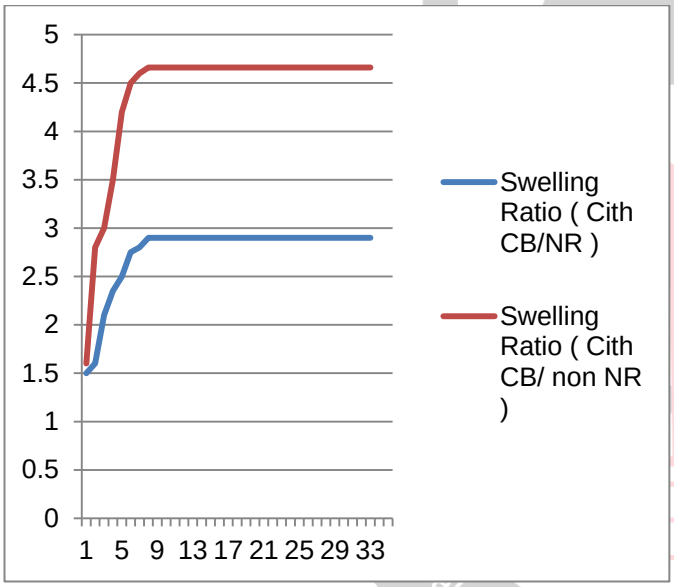

Fig- swelling Index for both the Compounds A and B (X axis indicates swelling Ratio and Y axis indicates time in hours)

3. KRAUS'S Equation for Swelling:

A theory was developed to account for the restricted swelling in solution of cross linked elastomers containing reinforced fillers. [10]Assuming swelling to be completely restricted at the filler rubber interface due to adhesion, the following relation is obtained:

$$V_{ro}/V_r=1-[3C\ (1-V_r^{/3}) + V_{ro}-1]Q/(1-Q)$$

Where,

V_r is the volume fraction of rubber in the swollen rubber phase

V_{ro} is the same quantity referred to or otherwise analogous, unfilled vulcanizates

Q is the volume fraction of filter and

C is a parameter dependent on the filler.

There may be two possible reasons behind this

i) The rubber matrix in the NR/CB blend surrounds around the C black, which is reinforced filler. [11] Thus the rubber points which are generated become immobilized, resulting in the development of additional cross linking sites. Thus a 3D network forms with additional cross linking points.

ii) Now as the solvent enters, because of the more amount of cross linking points, the bounds intends and then contracts too, driving out the solvent away.

This is not in the case of NR/Non CB blend.

iii) As 20 Phr is filler is incorporated into the NR/CB blend, the volume fraction of rubber becomes less. This can be referred from the Kraus's equation.

In contrast to this unfilled rubber has more volume fraction of rubber thus can swell to a greater extent.

V. CONCLUSIONS

In this research, the cure kinetics of NR filled with conductive carbon black and other rubber grade black were investigated. The vulcanization and mechanical properties of the cured NR/carbon black composites were measured. The experimental results show surface area of carbon black as well the sulphur content on the surface of carbon black has influences on the cure kinetics of NR/ carbon black composites. As the surface area of carbon blacks increases, the physical cross-linking is enhanced. In addition, the sulphur on the surface of carbon black also plays an important role in the vulcanization of EPDM/carbon black composites, since it introduce the additional chemical cross linking into the system. Mechanical experimental results demonstrate that the composite with conductive carbon black, comparing with other blacks, has the highest hardness, tensile strength at break, tensile modulus at 300% and permanent set. This is due to the high degree of cross-linking of the EPDM filled with N110. The elongation at

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break of this composite with conductive carbon black is lower than those with other blacks due to the NR molecule firmly absorbed on the N110 surface.

We had studied several physical and chemical properties of NR/CB blended rubber against an unfilled NR. The study reveals the value of CB as reinforcing filler and the mechanical reinforcements it provided.

ABBREVIATIONS USED

1. NR= Natural Rubber
2. CB= Carbon Black
3. C= carbon

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