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Preparation and Characterization of CarbonBlack Reinforced Natural Rubber Composite Materials

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Abstract: The properties of polymers are enhanced by addition of filler/additive. The former part of present research dwells upon discussion on carbon black (CB) powder and then its application in rubber technology. The three industrial grades of carbon black (CB) namely N405, N375 and N509 were selected to inspect the suitability and application of these grades that are of commercial interest. The particle size, surface area and structure are the three fundamental characteristics of CB powder that determine their process ability and application as filler in preparing rubber compounds. These CB powder grades were primarily characterized for their physical properties prior to mixing them in natural rubber (NR) matrix. The powders were characterized for their structure using dibutyl phthalate absorption (DBPA), particle size via laser particle size analyzer, surface area by nitrogen adsorption method, pellet hardness by means of pellet hardness tester. The CB powders were also characterized by X-ray diffraction (XRD) and fourier transform infrared spectroscopy (FTIR). These grades were mixed with NR matrix along with other constituents via two roll mill; and CB reinforced with natural rubber (CBNR) composites were synthesized.

Keywords: Carbon, Rubber, Composite materials.

1. Introduction

Elastomers are cross-linked polymers possessing low modulus and high deformation reversibility, affirming their utility in wide range of applications [1-2]. The CB is used as a principal reinforcing filler for NR because it enhances the physical and chemical adsorption of elastomer molecules on its surface. This was due to the presence of CB specific structure and organic functional group (mainly, –OH). The three main contributions responsible for this reinforcement are: (i) hydrodynamic effect related to the gain in strength by dispersion of inclusion in a rubber matrix, (ii) polymer-filler interconnection responsible for modified rubber layer, and (iii) percolating point associated with agglomerated framework [3-4]. The significant role of CB as active filler in elastomers for tyre technology has been known for more than a century [5]. This reinforcement of elastomer with CB increases their mechanical properties such as tensile strength, resilience, elastic modulus and hysteresis that find application in anti-vibrating operations of industries. Thus, it is agreeablyrecognized that CB filled rubber composites having multiphase system, dependent on the mobility of rubber molecules, impacts the reinforcement of the composites. The viscosity of NR is reduced by mixing it with peptizers and subjecting it to a shearing process. The service span and mechanical efficiency can be notably improved by mixing fillers in elastomer matrix.

Park et. al. investigated the interrelation of mechanical properties with the surface energy of CB and had established that the specific surface area increases non-polar characteristics. This further increases mechanical properties and improves vulcanization reactions of the composites. Moreover, previous researchers had examined the key function of networking fillers on the properties of elastomer composites. They had elucidated that the filler- filler interaction play an integral role in influencing reinforcement mechanism in composites. The chemical and physical synergy between polymer matrix and CB affect the mechanical and curing characteristics had also been previously examined. There had been continuous interest towards studies on dependence of size, structure and surface activity of CB on the properties of CB composites but few investigations have been reported on studies of different grades of CB[6].

The effects of three different grades of CB on the curing and mechanical properties of the CBNR composites have been investigated. Additionally, the variation in properties of CBNR composites due to particle size and surface chemistry were ofimportance, as done previously. The three industrial grades (N375, N405 and N509) were chosen to examine the differences that are of commercial interest between N405 with that of N375 and N509. These grades of CB powder were initially characterized for their physical characteristics before mixing it with NR. The standard procedures were followed for synthesis and vulcanization of different rubber composites. And the ASTM standards were adhered to, for testing characteristics, in order to gain insight into the influence of different grades of CB on CBNR composites [7-8].

2. Studies on CBNR Composites

The NR, is an elastic polymeric material with monomer unit Isoprene (2 methyl butadiene), acquired from the latex of trees sap (particularly trees belonging to the genera of Ficus and Hevea) that are vulcanized and finished for different useful applications. The prime parameters related to vulcanization process can be determined using rheometer, with 1.7 Hz oscillation frequency and 145 °C die temperature, for assessing the rate of cross- linking and curing due to the CB-rubber interactions. The vulcanization curves of CBNR composites, associated with various grades of CB are displayed in Figure 1 and 2. The cure characteristics: M_L (minimum torque), M_H (maximum torque), T_{c90} (optimum cure time), T_{s2} (scorch time) of CBNR composites with three different grades of CB such as N375, N405 and N509 were determined from the curve as shown in Table.1.

The CRI values calculated for CBNR composites using N375, N405 and N509 were0.090, 0.105 and 0.093 s^{-1}, respectively. Thus, it was observed that the fastest cure rate and optimum cure time resulted in highest CRI for N405 composite. The decreased cross-linking speed due to the existence of quinolic group caused lowest CRI for N375 composite [11].

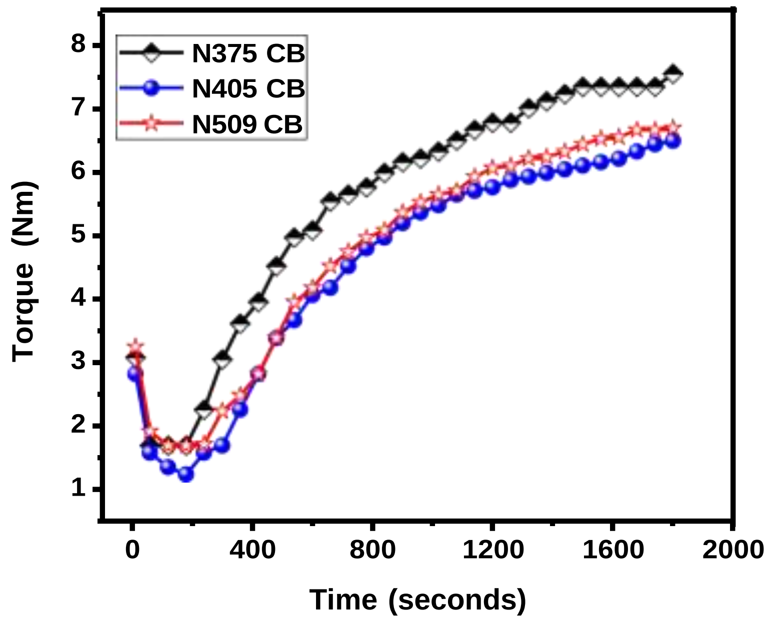

Figure .1: Vulcanization curves between torque versus time of CBNR composites at 145°C,associated with various grades of CB (N375, N405 and N509).

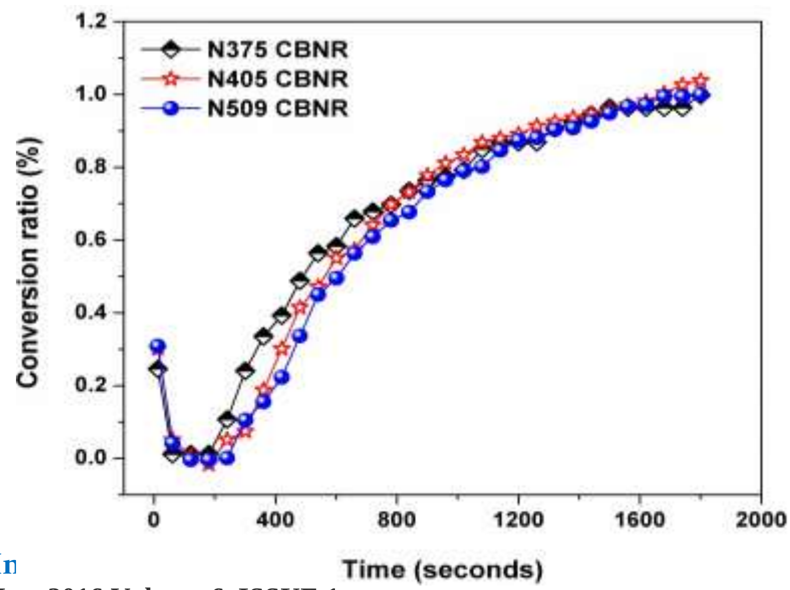

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Figure 2: Conversion ratio of CBNR composites for N375, N405 and N509grades of CB as a function of cure time

Table 1: Rheometric data comprising of maximum torque M_H (Nm), minimum torque M_L (Nm), $M_H - M_L$ (Nm), scorch time T_{s2} (sec), optimum cure time T_{c90} (sec), cure rate index (CRI) for CBNR composites with different grades of CB.

CBNR composites of different grades	M_H (Nm)	M_L (Nm)	$M_H - M_L$ [a] (Nm)	T_{s2} [b] (sec)	T_{c90} [c] (sec)	CRI [d] (sec^{-1})
N375	7.56	1.62	5.93	194.4	1309.2	0.090
N405	6.30	1.32	4.98	256.8	1212.0	0.105
N509	6.69	1.71	4.98	260.4	1332.6	0.093

[a] Difference between maximum and minimum torque.

[b] Scorch time, time at which the vulcanization begins (derived from the measurement done on Monsanto Rheometer).

[c] Optimum cure time, time needed for curing of rubber samples (derived from the measurement done on Monsanto Rheometer).

[d] Cure rate index determined from rheological testing using Equation (1).

The difference ΔM (= M_H - M_L), the characteristic of cured rubber, provides the information on degree of chemical cross-linking which occurs during the process of vulcanization. The property that varies with the surface area of different CB is modulus at 300% elongation along with M_L. The surface area of CB plays a significant role in the physical cross-linking of CBNR composites. The increase in the number of rubber chains entangled with CB aggregate enhances with the CB surface area. This entanglement of polymer chains with CB further enhances the torque, and thus CB serves as physical cross link in CBNR composite. Therefore, it can be noticed that N509 grade CB having highest NSA showed largest value of M_L out of the three different grades of CB. This was due to the decrease in the number of mobilized rubber chains on CB surface [12-13].

The flat rubber composite sheets were made, according to the ASTM standard D2084, by using hydraulic press that was heated electrically to vulcanize compounds at 145 °C and for cure times, T_{c90}. The conversion rate of vulcanization χ_T for a given time had been

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evaluated from the rheocurves using Equation (2), and is depicted in Figure 2.

$$\chi_T = \frac{M_T - M_L}{M_H - M_L}$$

Here, M_T denotes the torque at a given time T; while M_L and M_H are the minimum and maximum torques, respectively. The Figure 2 shows the conversion ratio of composites of CBNR for various grades of CB as a function of time of cure. Thus, the conversion rate of vulcanization for CBNR composites at these specified conditions show the order as N375 > N405 > N509. Here, in order to complete 50% conversion, N375 CBNR takes 491 s, N405 CBNR takes 561 s and N509 CBNR takes 609 s. This confirms that all the vulcanization characteristics vary proportionately with the increase in surface area. The rheological test, exhibited lowest CRI for N375 rubber composite having highest RSF, which is illustrated in Figure.3.

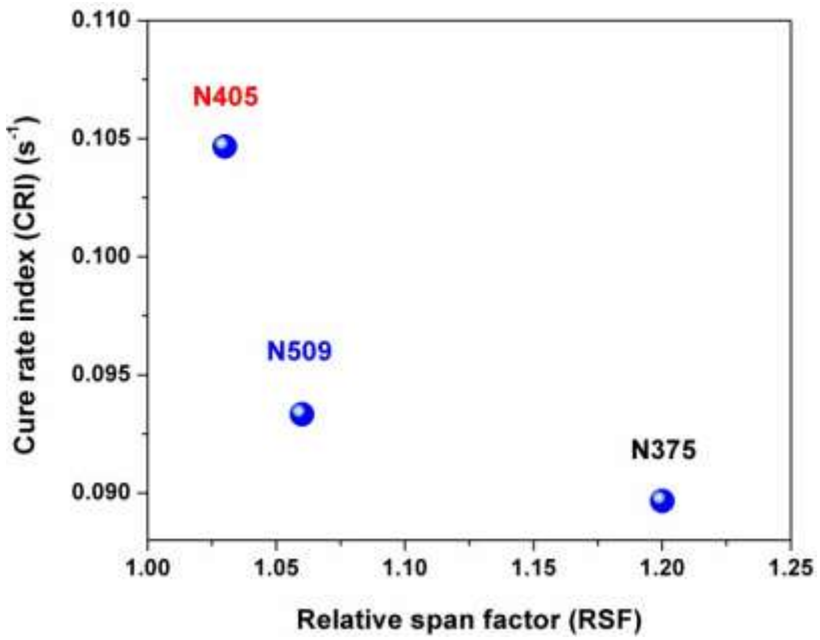

Figure .3: CRI of CBNR composites as a function of RSF of CB powders.

3. Mechanical Testing

The mechanical properties of CBNR composites made by furnace CB were inspected by employing universal electric tensile testing (Zwick 1435) machine. Here, dumbbell sections of 25 x 10^{-3} m width, 130 x 10^{-3} m length and 2 x 10^{-3} m thickness were cut with the help of die cutting machine. The tensile strength and elongation at break; as well as modulus at 200% and 300% elongation were determined according to ASTM method D412-06a at 5 kN load and test speed of 0.008 ms^{-1}. The stress-strain profile for different CBNR composites

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are shown in Figure.4, whereas tensile strengths and modulus at 300% elongation along with their respective errors are illustrated as histogram in Figure.5. Here, Table.2 depicts the different reinforcing abilities of the composites by listing mechanical properties such as tensile strength, elongation at break, modulus at 200% elongation and modulus at 300% elongation of CBNR composites. The factors that affect the modulus at 300% elongation are shape of the particles and surface activity including surface treatment. It was observed that the tensile strength of CBNR composites increase with increasing surface area of CB powder. N509 rubber composite, having largest surface area showed highest tensile strength among all grades of CB. Further, RSF was found to have correlation with elongation at break. N405 possessing lowest RSF showed maximum elongation at break. Thus the extent of formation of weak bonds, by physical adsorption on filler surfaces to affix polymer chains, is influenced by the surface area[14-15].

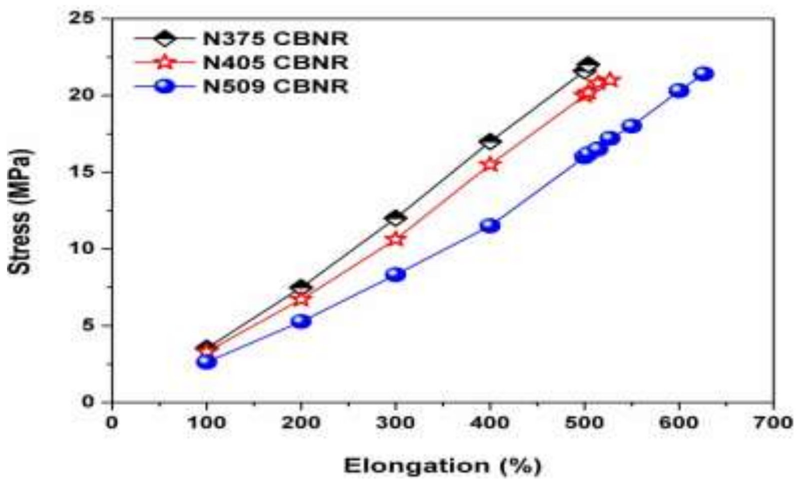
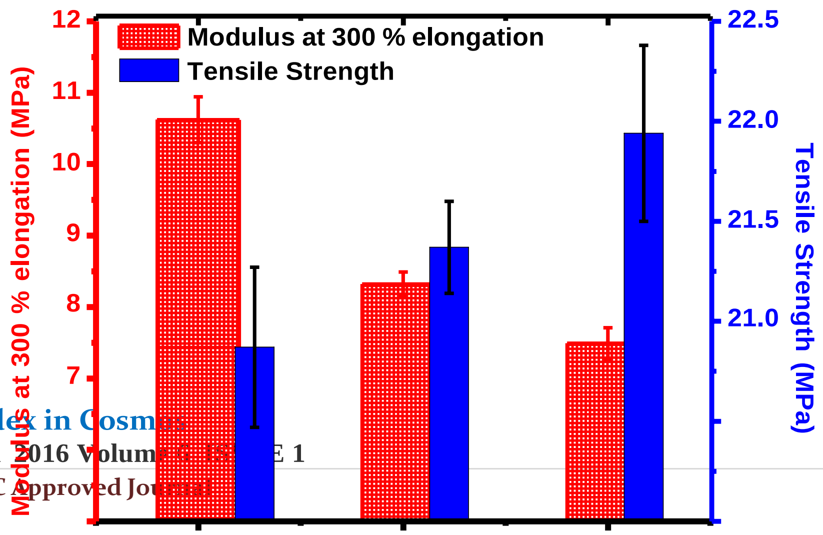


Figure 4: Stress-Strain curve of N375, N405 and N509 grades of CB obtained from tensile testing machine Zwick 1435.



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20.5
6
5
20.0
N375 N405 N509

Figure 5: Histogram for modulus at 300 % elongation and tensile strength of CBNR composites.

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Table .2: Reinforcing abilities of the composites using N375, N405 and N509 grades of CB having tensile strength (MPa), elongation at break (%), modulus at 200 % elongation and modulus at 300 % elongation.

CBNR composites	Tensile Strength (MPa)	Elongation at break (%)	Modulus at 200% elongation (MPa)	Modulus at 300% elongation (MPa)
N375	20.87±0.40	527±14	6.71±0.25	10.62±0.32
N405	21.37±0.23	626±5	5.27±0.09	8.32±0.17
N509	21.94±0.44	504±9	3.53±0.21	7.49±0.22

4. Hardness and Resilience Testing

The Durometer is a standard device that is used to assess the hardness of rubber, polymers or rubber-like materials. It measures the hardness by the penetration of an indenter into the material and is expressed as a number value. Here, Shore hardness was measured before and after curing (Figure 6 and Figure 7) of rubber samples as outlined in Table .4. The hardness increased with the increasing surface area as N375 < N405 < N509 for cured CBNR composites, similar to Litvinov's report. The highest NSA and STSA depicted by N509 CB powder had highest hardness of its CBNR composite. This implies that surface area is a vital criterion in determining the hardness behaviour of CBNR composites [16].

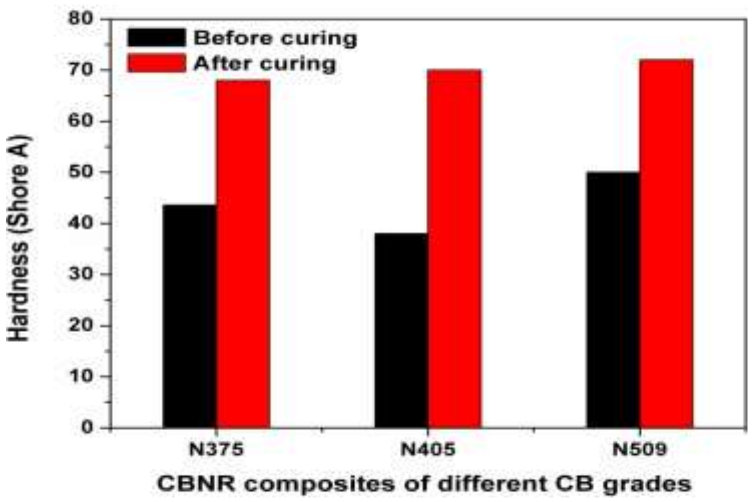

Figure .6: Histogram illustrating Shore Hardness of CBNR composites before and after curing.

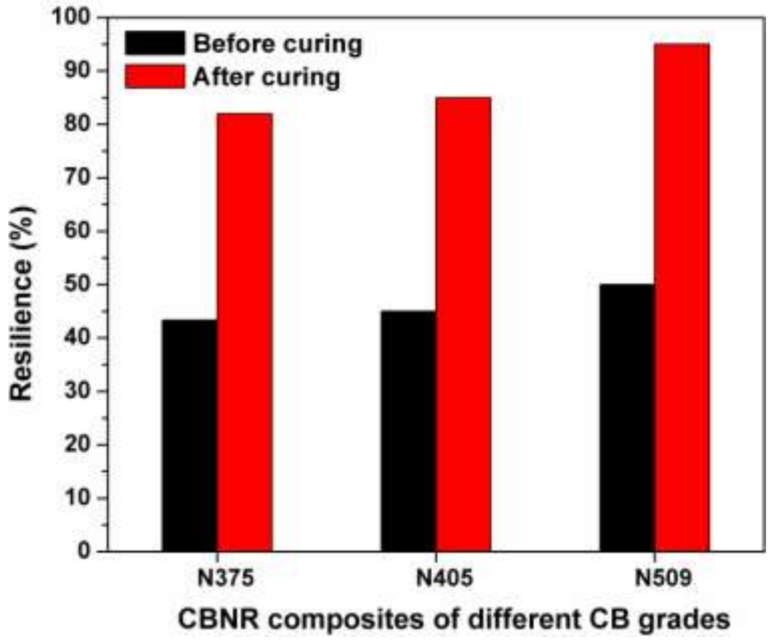

Figure 7: Histogram depicting Resilience of CBNR composites before and after curing.

Table .3: Hardness and Resilience for CBNR composites with different grades of CB (N375, N405, and N509) before and after curing.

Mechanical Property	N375 CBNR	N405 CBNR	N509 CBNR
Hardness (Shore A) before Curing	43.6	38.0	50.0
Hardness (Shore A) after Curing	68.0	70.0	72.0
Resilience (%) before Curing	43.3	45.0	50.0
Resilience (%) after Curing	82.0	85.0	95.0

5. Swelling Studies

Swelling behaviour of the rubber composites was determined by the change in mass by means of method used by Ahmed et. al. The test pieces of known weight (W_b) of vulcanized CBNR composites were immersed in toluene solvent in diffusion test bottles and kept at room temperature for five days. After five days the test rubber samples were removed from the bottles and the wet surfaces were instantly cleaned of liquid via tissue paper swab and re-weighed (W_a). The test rubber samples of the CBNR composites were further evaporated in an oven at 60°C for 24 hours, cooled in a desiccator and immediately weighed (W_c). Figure .9 illustrates the flow chart of the method used in this study [17-18].

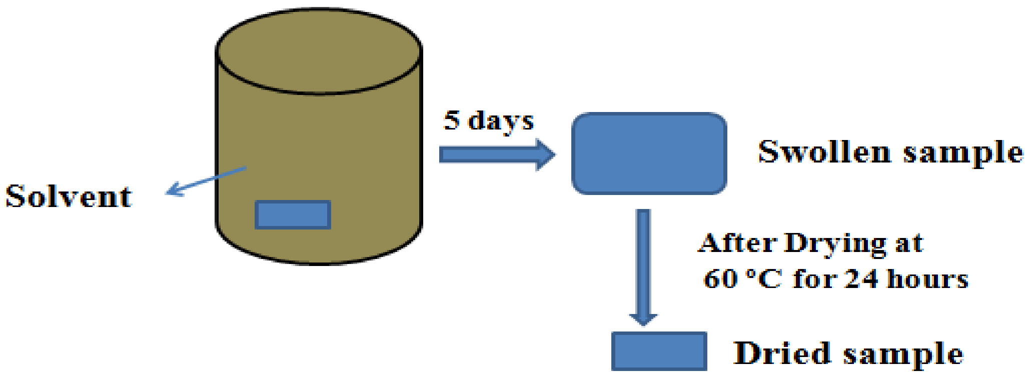

Figure 8: Optical image of swelling studies.

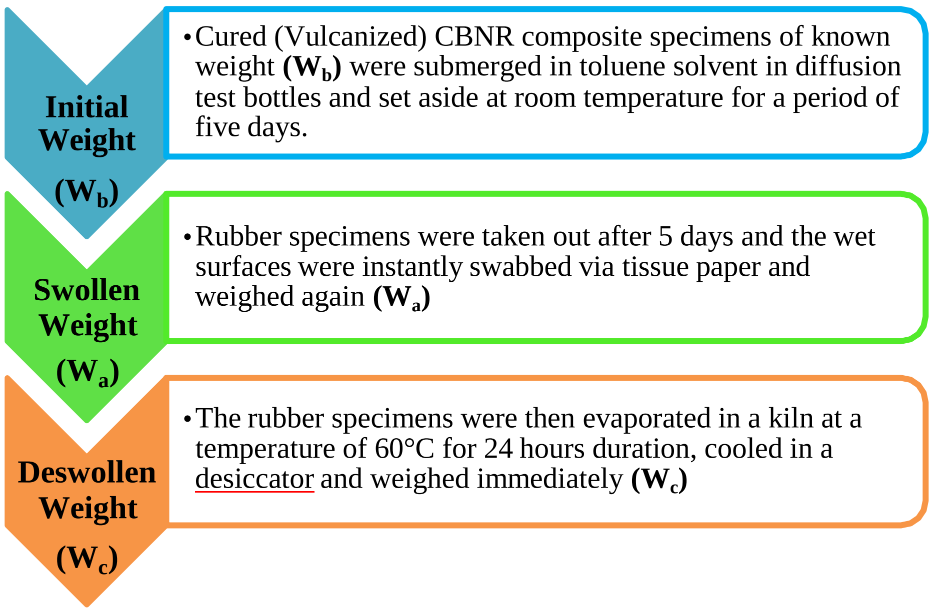

Figure 9: Flow chart depicting the procedure of swelling studies.

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The swelling parameters of the CBNR composites were computed by the subsequent swelling data and the results are tabulated in Table 4.

i) Swelling index (SI)

Swelling index (SI) was computed by the equation

$$SI\,\% = \frac{Wa - Wb}{W_b} \times 100$$

ii) Solubility %

Soluble fraction (SF %) was determined by the following relation.

$$SF\ \% = \frac{Wb - Wc}{W_b} \times 100$$

where:

W_a = Swollen Weight;

W_b = Initial Weight/dry weight;

W_c = De-swollen Weight;

Table 4: Swelling parameters of CBNR composites.

CBNR composite	SI (%)	SF (%)
N375	206.25	4.37
N405	198.34	3.87
N509	195.00	3.50

From the swelling studies, it is seen that N509 showed minimum swelling index and swelling fraction, which indicates maximum cross-linking occurred in N509 CBNR composite among all the three rubber composites (N375, N405 and N509).

6. Morphological and Chemical Composition Analysis

The three prepared CBNR composites were characterized by SEM in order to see the morphology of the rubber composite. SEM results (Figure 10) showed that CB mainly exists as the aggregates in the rubber matrix. Almost all types of carbon black (N375, N405, and N509) aggregates were observed to be distributed uniformly in the matrix of NR. However, carbon black aggregates size varies with the type of carbon black grade. The filler N509 with large surface area has a small size. It was

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clearly seen from the SEM micrographs that there is cross-linking occurring in N509 grade CB which justifies its mechanical properties.

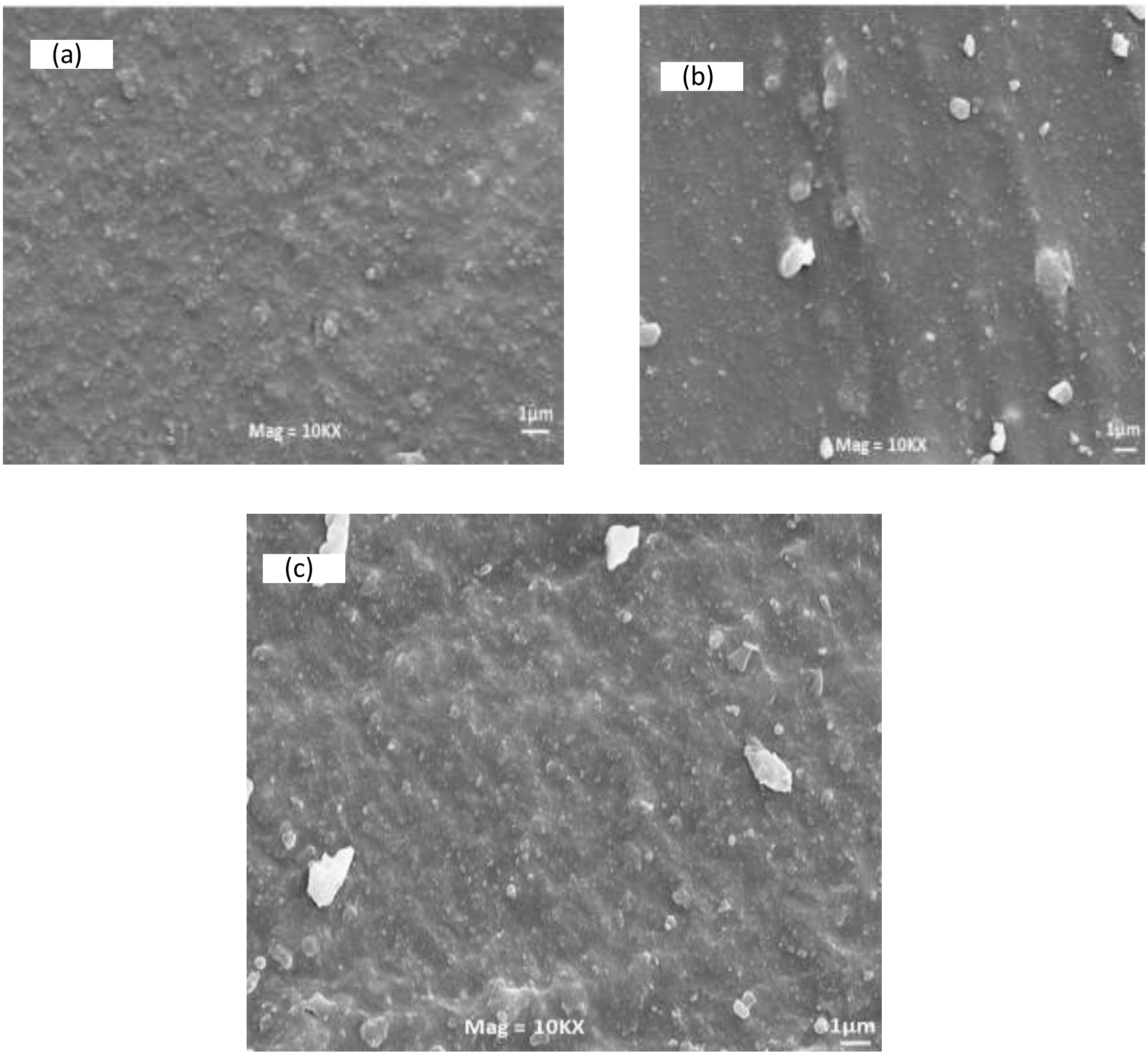
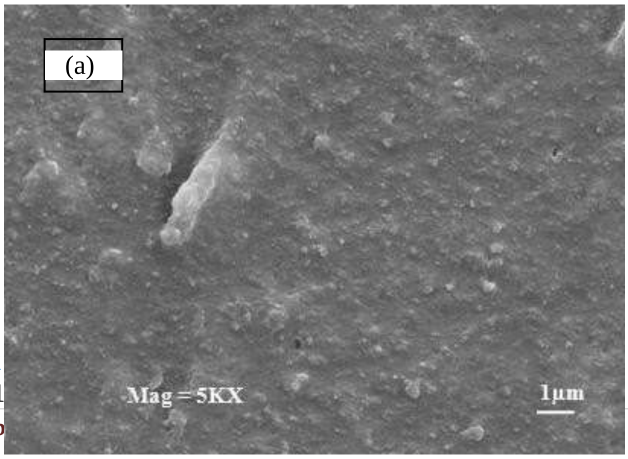


Figure 10 (i): Secondary electron SEM micrographs of (a) N375 CBNR, (b) N405 CBNR, (c) N509 CBNR composite at 10KX magnification.



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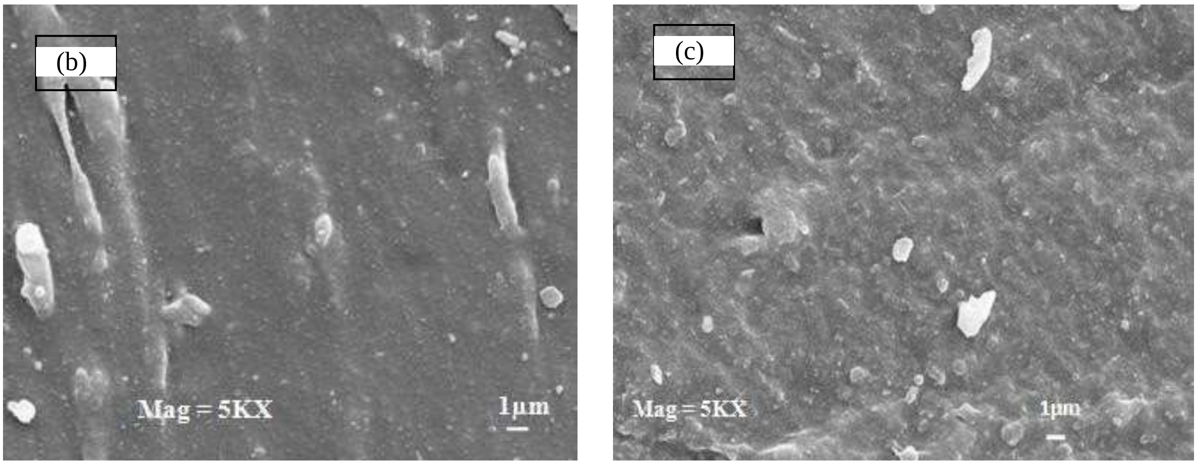

Figure 10 (ii): Secondary electron SEM micrographs of (a) N375 CBNR, (b) N405 CBNR, (c) N509 CBNR composite at 5KX magnification

7. EDS Analysis of CBNR Composites

The three prepared CBNR composites were characterized by EDS to observe the chemical composition of the constituents present in the rubber composites. The EDS spectrums of the composites are illustrated in Figure.11 and the results of chemical composition of the constituents present in the rubber composites are tabulated in Table .5 and Table.6. It is observed that the content of the cross linking agent Sulfur is found to be maximum in N509 compared to N375 and N405 CBNR composites.

Table .5: Weight % of different elements present in CBNR composites.

Element	(N375) Weight %	(N405) Weight %	(N509) Weight %
C	87.37	90.08	91.61
O	7.97	3.94	_
Si	0.22	0.69	1.62
S	1.96	2.34	4.39
Zn	2.49	2.33	2.39
Ca	_	0.61	0.61

Total	100	100	100

Table.6: Atomic % of different elements present in CBNR composites.

Element	(N375) Atomic %	(N405) Atomic %	(N509) Atomic %
C	92.32	95.00	96.78
O	6.32	3.12	_
Si	0.10	0.31	0.73
S	0.77	0.93	1.74
Zn	0.48	0.45	0.76
Ca	_	0.19	0.19
Total	100	100	100

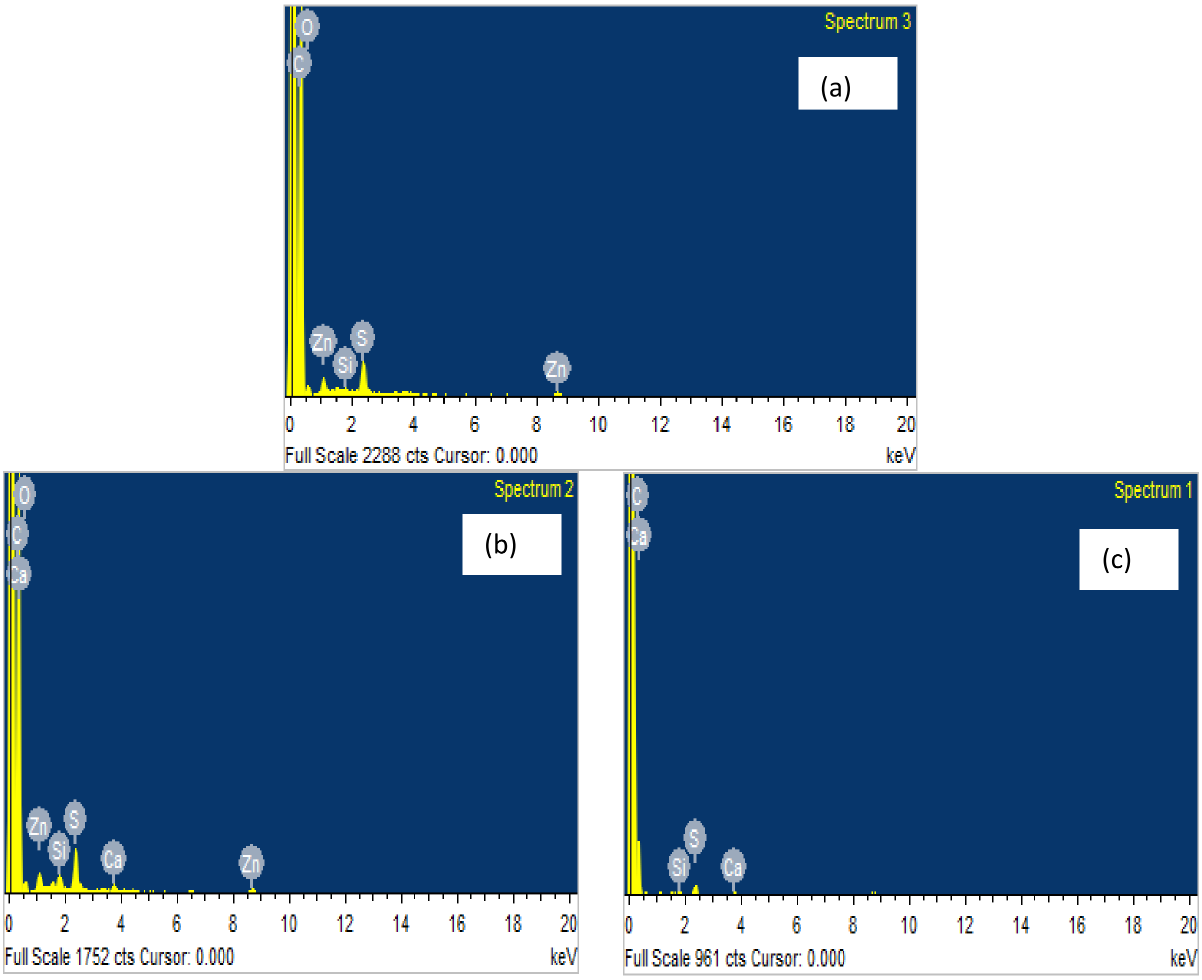

Figure .11: EDS spectrum of **(a)** N375 CBNR composite **(b)** N405 CBNR, **(c)** N509 CBNR composite.

Conclusion

The present studies confirmed the significant dependence of mechanical and rheological characteristics of rubber composites on the morphological factors of CB such as surface area, particle size and pellet hardness. These experiments showed a likely direct correlation of tensile strength, resilience and hardness of CBNR composite with the surface area of CB. The decrease in particle size of CB powder additionally reduced modulus of CBNR composite at 200% and 300% elongation. Further, the interconnection of calculated RSF value of CB powders with that of CRI and elongation at break of CBNR composites could be employed to predict the feasibility of different grades of CB for manufacturing CBNR composites. Among the three grades under investigation N509 grade CBNR composite showed highest hardness, resilience, tensile strength which is justified by maximum cross linking of N509 CBNR composite suggested by the SEM and EDS studies.

1. Shenderova O. A. and Gruen D. M., Ultrananocrystalline diamond: synthesis, properties and applications: William Andrew, 2012.

2. Kartsova L. A. and Makarov A. A., "Properties of Carbon Materials and Their Use in Chromatography", Russian Journal of Applied Chemistry, vol. 75, pp. 1725-1731, 2002.

3. Donnet J.-B., Bansal R. C., and Wang M.-J., Carbon black : science and technology. New York: Dekker, 1993.

4. Zhang W., Blackburn R., and Dehghani-Sanij A., "Effect of carbon black concentration on electrical conductivity of epoxy resin–carbon black–silica nanocomposites", J Mater Sci, vol. 42, pp. 7861-7865, 2007.

5. Starý Z., "Electrical conductivity and rheology of carbon black composites under elongation", AIP Conference Proceedings, vol. 1662, p. 040001, 2015.

6. Sahoo B. P., Naskar K., and Tripathy D. K., "Electrical Properties of Ethylene Acrylic Elastomer (AEM) Loaded With Conducting Carbon Black", AIP Conference Proceedings, vol. 1349, pp. 190-191, 2011.

7. El-Tantawy F., Kamada K., and Ohnabe H., "Electrical properties and stability of epoxy reinforced carbon black composites", Materials Letters, vol. 57, pp. 242-251, 2002.

8. Azim S. S., Satheesh A., Ramu K. K., Ramu S., and Venkatachari G., "Studies on graphite based conductive paint coatings", Prog Org Coat, vol. 55, pp. 1-4, 2006.

9. Moteki N., Kondo Y., and Nakamura S.-i., "Method to measure refractive indices of small nonspherical particles: Application to black carbon particles", Journal of Aerosol Science, vol. 41, pp. 513-521, 2010.

10. Rattanasom N. and Prasertsri S., "Relationship among mechanical properties, heat ageing resistance, cut growth behaviour and morphology in natural rubber: Partial replacement of clay with various types of carbon black at similar hardness level", Polymer Testing, vol. 28, pp. 270-276, 2009.

11. Coran A. Y., "Chemistry of the vulcanization and protection of elastomers: A review of the achievements", Journal of Applied Polymer Science, vol. 87, pp. 24-30, 2003.

12. Ponnamma D., Maria H., Chandra A., and Thomas S., "Rubber Nanocomposites: Latest Trends and Concepts," in Advances in Elastomers II. vol. 12, P. M. Visakh, S. Thomas, A. K. Chandra, and A. P. Mathew, Eds., ed: Springer Berlin Heidelberg, 2013, pp. 69-107.

13. Donnet J. B., "Nano and microcomposites of polymers elastomers and their reinforcement", Composites Science and Technology, vol. 63, pp. 1085-1088, 2003.

14. Vilgis T. A., "Time scales in the reinforcement of elastomers", Polymer, vol. 46, pp. 4223-4229, 2005. [91] Kohls D. J. and Beaucage G., "Rational design of reinforced rubber", Current Opinion in Solid State and Materials Science, vol. 6, pp. 183-194, 2002.

15. Heinrich G., Klüppel M., and Vilgis T. A., "Reinforcement of elastomers", Current Opinion in Solid State and Materials Science, vol. 6, pp. 195-203, 2002.

16. Bhattacharya M. and Bhowmick A., "Synergy in carbon black-filled natural rubber nanocomposites. Part I: Mechanical, dynamic mechanical properties, and morphology", J Mater Sci, vol. 45, pp. 6126-6138, 2010.

17. Edwards D. C., "Polymer-filler interactions in rubber reinforcement", J Mater Sci, vol. 25, pp. 4175-4185, 1990.

18. Litvinov V. M. and Steeman P. A. M., "EPDM−Carbon Black Interactions and the Reinforcement Mechanisms, As Studied by Low-Resolution 1H NMR", Macromolecules, vol. 32, pp. 8476-8490, 1999.