Crosslinking Density Characteristics of a Nanocomposite Elastomer

N. A. Habib1*, Ahmed S Jabbar1, F. L. Hassan2 and N. I. Intan3

1Applied Sciences Department – University of Technology-Baghdad, Iraq
2Department of Mathematics - College of Education – University of Basra, Iraq
3Malaysian Rubber Board, Stesen Penyelidikan RRIM, 47000 SG Buloh, Selangor, Malaysia.
* Corresponding: N. A. Habib 100365@uotechnology.edu.iq

Abstract. Nanocomposites elastomers are being developed in the field of nanomaterials as it has low weight and high properties compared to the conventional rubbers. Acrylonitrile butadiene rubber (NBR) is used in automobile parts due to its ability to resist oil. In this research, Carbon Black nanoparticles (CBnp) type FEF N550 was used to reinforce this rubber to reduce the swelling ratio. Therefore, physicochemical characteristics were investigated for five different samples of vulcanized CBnp/NBR nanocomposites with 0, 0.2, 0.6, 1.2 and 2.4 phr of CBnp using the solution mixing method. The homogeneity of these nanocomposites was evaluated by Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD). Furthermore, the influence of different contents of CBnp on the tensile strength was analyzed. The results showed that the crosslinking densities in the CBnp/NBR nanocomposites structure have been improved compared with the neat vulcanized NBR and the mechanical properties as well. It’s an essential result which can employ it to prepare washers (rubber rings) resist against oils for several applications.

1. Introduction

NBR vulcanized a synthesis rubber has high physicomechanical properties such as tensile and wear resistance. Also, it has great resistance to oils, that it is being used for special applications in automobiles parts. This is attributed to the group of Carbon-Nitrogen (CN) in acrylonitrile of NBR chains which forms an essential factor in raising the physical properties. The higher content of acrylonitrile makes NBR the strongest against the oil and chemicals. NBR is used in environments with temperature ranges of ~ -25°C to 120°C, though; the rubber life is shortened when the temperature exceeds 100 °C. On the other hand, the elastomeric characteristics of this rubber elasticity are provided by vulcanization and the formation of compounds with several fillers [1-3]. The vulcanization process converts rubber into a more durable material, in which one of the additives “Sulfur” is forms cross-links between the rubber molecular chains and results in increasing rigidity. However, the second essential additives are Zinc oxide where it shows as an activator in rubbers many physicochemical characteristics such as strength, heat resistance, abrasion, ultraviolet degradation. Moreover, it is a protectant for anti-ageing, plasticizers to increase flexibility to ease processing [4-6]. Generally, fillers are incorporated to improve mechanical and thermal properties or modifying them in enhancing the processibility and cost reduction. Among such substances used in rubber compounding, Carbon black (CB) is unique in its ability to significantly enhance the properties of NBR elastomer. It is produced from the incomplete burning of petroleum fuels. Moreover, it is used in various formulations with different rubber types to customize the performance properties such as abrasion resistance, thermal stability, fuel resistance and hysteresis [7-8]. CB possesses a high thermal insulation capacity and is mainly used with elastomers. The particle size yield to the optimization of the process for getting Nanoparticles of 40-48 nm (ASTM, 1765) and a surface area of ~49 m²/g. It is
insoluble in water, alkali in type, with average absorption of about 114 ml/100g, and a density of 345 kg/m$^3$ (ASTM D1513). Therefore, CBnp-N550 is used currently for getting high physical characteristics [9-10]. NBR requires the additives for enhanced its properties for useful applications. The common additive that is added into NBR is silica in addition to CB, and now a day they are used in nanoscale such as carbon black nanoparticles (CBnp). This is to improve the cross-linking in the NBR molecular chains to enhance the mechanical and thermal properties. Mixing and processing of NBR was generally carried out commercially using an internal mixer and extruder or two roll mill mixing. There are several chemical groups on the surface of CBnp such as carboxyl, hydroquinone, quinine, and lactone [11]. In a study conducted by Arib Rejab et al., the mechanical properties of four different types of an elastomeric mount of NR with different percentages of CB loading were investigated [12]. The study showed that the static stiffness for all types of elastomeric mounted increased with the increase of CB percentage. Besides that, the addition of CB in the NR compound can highly influence the tensile strength of the rubber compound. When a polymer is placed in an active solvent, it absorbs a percentage of the solvent which makes it swell. The extent of the elastomer’s size represents the opposition between two forces: $\Delta f_{el}$ the swelling deformation force and $\Delta f_{ee}$ the elastic force in opposite reactions. These forces are generated by the polymer chains. The volumetric swelling attains a steady state when the forces are in equilibrium with each other (Flory, 1950) [13].

$$\Delta f_{el} = kT [n_1 \ln u_1 + X_1 n_1 u_2]$$  \hspace{1cm} (1)

where $k$ is the material constant, $T$ is the temperature, $n_1$ is the molecule number of the solvent, $X_1$ is the Flory interaction parameter of the polymer-solvent, and $n_1$ and $u_2$ are the volume fractions of the solvent and elastomer respectively.

The free energy of the elastic component, $\Delta f_{ee}$, is associated with the change in the entropy as the network is deformed, so it can be written as below:

$$\Delta f_{ee} = [kT \nu_e / 2] \cdot [3Q^2 - 3 - \ln Q^3]$$  \hspace{1cm} (2)

where $\nu_e$ is the number of chains in the crosslinks net, $y$ is the swelling ratio between a composite to a polymeric matrix (neat), i.e $Q = (Q_e/Q_0)$, which is the ratio between the swelling reduction of the rubber composite with the filler ($Q_e$) to the same parameter without filler ($Q_0$). Also, it is equal to $1/u_2$.

Since $\Delta f_{el} = \Delta f_{ee}$ at the equilibrium state, the chemical potential of the solvent in the polymer will be equal to the pure solvent. Therefore, equation (1) is equal to equation (2). Also, after re-arrangement, the final expression for finding the crosslink density ($D$) is given according to the standard of the swelling test. The rate became stable at the final equilibrium after 48h [14]. The saturation limit of solvent absorption might be attributed to the degree of the crosslinking of the NBR chains which are explained in terms of density. Also, it is called the cross-link density (D) which is calculated by using the Flory–Rehner equation and the formula became as below:

$$D = U_m \cdot \frac{\left[u_2^{1/3} - \frac{1}{2} u_2\right]}{-[ln(1-u_2) + u_2 + Xu_2^2]}$$  \hspace{1cm} (3)

where $u_2$ is the volume fraction given by ($u_2 = 1/Q_e$), $U_m$ is the molar volume of toluene which is equal to (106.3 mL/mole) and $X$ is equal to 0.35 [15-17].

In this work, the nanoparticles of carbon black (CBnp) were used to improve elastomer-filler interactions. Moreover, combining two techniques for preparation (CBnp/NBR) rubber nanocomposite
(Brabender and two rolls mill) was the novelty in the mixing and processing stages. Achieving completed grafting of CBnp on NBR micro molecules chains in addition to the functional groups was investigated via the enhancement in mechanical properties. The excellent nanocomposite characteristics of CBnp/NBR can assist to study the reduction of swelling in rubber and improving oil resistance. The best application that could be wanted is manufacturing O rings for oil seals in machines and automobiles rubber parts.

2. Experimental work

2.1. Materials
The elastomeric matrix that has been used as a type of dry rubber called acrylonitrile-butadiene rubber (NBR). The commercial name is Bona Krynac® 3345F- LANXESS was obtained from Malaysia rubber board, Mooney viscosity ML(1+4) 100°C and 45 ± 5 MU, and acrylonitrile content of 33 wt%, ISO 289.
Carbon black nanoparticles (CBnp) type Fast Extruding Furnace black (FEF) N550. It is a powder with an average particle size of 40-48 nm (ASTM, 1765) and a surface area of 49 m²/g. It is insoluble in water, and a pour density of 345 kg/m³ (ASTM D1513), used in composites samples with different loading.
The compound formulation and vulcanizing additives used for NBR rubber vulcanization treatment were Zinc oxide (Mw=81.37 g/mole), Stearic acid (Mw=284.48 g/mole, M.P. 68°C), Sulfur (Mw=32.06 g/mole, M.p 115°C), N-Cyclohexyl-2-benzothiazole sulfonamide (CBS) as an accelerator and N-Isopropyl-N-phenyl-P-phenylenediamine 4010NA (IPPD) as an oxidant agent, and were purchased from Rongcheng Chemical Co. Ltd. The procedures were performed according to ASTM D3187.
Some solvents were used for the dissolution of the rubber NBR and dispersion CBnp in it. These were Toluene and distilled water, they were purchased from Evergreen Co. which is supplied by R&M Chemical Marketing.

2.2. Preparation of CBnp/NBR nanocomposite
The solution mixing method was used to dissolve NBR, and the direct mixing technique of CBnp was used by an internal poly-drive mixer for preparing vulcanized CBnp/NBR nanocomposite. Due to the efficiency of this mixer, other vulcanization additives were mixed with the mixture to achieve a high homogenous rubber composite. The formulation and ratios of additives are listed in Table 1. Characteristics of CBnp enable it to use high shear forces for mixing the composite when the process keeps avoiding the aggregation of the particles due to the agglomeration and humidity. The cure characteristics were determined by the rheometer and the moulding of the standard samples was also performed based on the rheological data of the torque-time and temperature. The novelty of this work is dispersing the CBnp into the NBR solution is suitable and compatible solvents separately and then mixing them both mechanically after drying. This process provided an easy methodology and excellent results for the mechanical properties later [18]. The proper liquidity of an elastomeric matrix with low viscosity allows the nanoparticles, such as carbon black, to cover a large volume in the prepared composite. The main side effect of this method (for the rubber composite’s properties) is when the solvent does not evaporate completely. The homogeneity of the filler’s distribution into the rubber matrix should be fully completed before the coagulation state. This is to avoid some agglomerations that may appear through the mixing process.
Forty grams of NBR were used with CBnp contents which were prepared by volume fractions and composites were expressed by part per hundred part rubber (phr) which were 0.2, 0.6, 1.2 and 2.4 as shown in Table 1.
Table 1. Formulation of CBnp/NBR nanocomposites

| NBR 100 g | CBnp   | CBnp at 40g NBR | CBnp (40g)*100/1.76 | Vulcanization | Phr |
|-----------|--------|-----------------|----------------------|---------------|-----|
|           | Phr    | wt%             | Vol. 40%             | Additives     |     |
| 0.2       | 0.08   | 4.545           |                      | Zinc oxide    | 4   |
| 0.6       | 0.24   | 13.636          |                      | Steric acid   | 1.5 |
| 1.2       | 0.48   | 27.273          |                      | Sulphur       | 2   |
| 2.4       | 0.96   | 54.545          |                      | CBS           | 0.5 |
| Total     | 4.4    | 1.76            | 100                  | IPPD          | 1   |

NBR was cut into small pieces then added to 300 mL of Toluene. This mixture was stirred by a magnetic stirrer at 70°C until the rubber was dissolved completely. CBnp then was added gradually and mixed for 3 hrs. The process of vulcanization was done through the addition of the materials using the phr scale. A homogeneous phase was observed in the mixture colour and the coagulant of the CBnp/NBR nanocomposite was dried completely in a vacuum oven at 70°C.

3. Characterization and Results

3.1. Morphology Analysis
It is essential to verify the structure of the prepared (CBnp/NBR) nanocomposite and other characteristics. Therefore, the degree of dispersion CBnp into NBR molecular chains attached functional groups, and the surface topography of the elastomeric nanocomposites was analyzed to support the other properties.

XRD tests were carried out to characterize CBnp, NBR, and CBnp/NBR nanocomposites at different content of CBnp. The conditions of the XRD test were applied with Cu K-alpha radiation and a wavelength of 0.154 nm. As the d-spacing of the atomic levels can indicate to CB particles, Bragg’s equation ($n\lambda = 2d \sin\theta$) was used for that; the diffraction pattern appears at the angle $2\theta = 24.6^\circ$ corresponding to a d-spacing of 0.36 nm. The broadened peak of CBnp as shown in Figure 1 refers to the amorphous structure of the CB’s agglomerated particles.

![Figure 1 XRD patterns of the neat NBR, CBnp and CBnp/NBR nanocomposites at low 0.2 (phr) and optimal 1.2 contents of CBnp.](image-url)
FTIR test performed on the same samples using Nicolet 6700 over the wavenumbers range from 400 to 4000 cm\(^{-1}\) spectral. This technique used to determine the functional groups of composite contents by detecting their molecule characteristics through distinct vibrational frequencies.

![FTIR Spectra](image)

**Figure 2** FTIR spectra of CBnp, NBR, and vulcanized CBnp/NBR nanocomposites at low and optimal contents of CBnp.

CBnp/NBR nanocomposites have a similar FTIR spectrum to the neat NBR as shown in Figure 2, except some molecular structures are affected by the main groups of CBnp and NBR. Both have an amorphous molecular structure as the most common chemical groups on the surface of CBnp are hydroquinone and lactone groups. These groups are insufficient to create a high interfacial interaction with the polymers. However, polar elastomers such as NBR can bond strongly via the radical initiators with the CB nanoparticles’ surfaces. The performance of non-functionalized CBnp in the rubber composites has been developed by using coupling agents and modifiers [19].

Further characterization, to study the surface morphology of CBnp, has been performed in this study and was carried out using Scanning Electron Microscopy (SEM). A general overview of a sample of CBnp FEF-N550 nanoparticles indicates that this filler mainly consists of agglomerates of carbon particles (at 10μm scale and 1000x magnification). Some aggregates of CBnp have been noted at the 500nm scale as shown in Figure 3.
3.2. Mechanical characteristics

The vulcanized samples of NBR and CBnp/NBR nanocomposites were characterized and carried out by the rheometer MDR-2000 (Monsanto) according to ISO 289-2. It is used to determine the optimum cure conditions, which torque required to rotate the disc of the rheometer as a function of initial time (scorch time $T_{s2}$) and time to 90% cure ($T_{90}$). Torques have gotten from the torque-time curves were $\tau_L$ the minimum and $\tau_H$ the maximum torque. ($T_{s2}$) is the early vulcanization time of the rubber at $\tau_L$ but the time to reach 90% of the torque increment as shown in equation (4) [20]. CBnp/NBR nanocomposites with different contents of CBnp were tested and verified from the rheological cure curves at temperature 160°C and 30 min.

The $\tau_H$ increased to 23.4% in the CBnp/NBR nanocomposite, which was more than in the neat NBR at 1.2 phr of CBnp. This is probably attributed to the degree of the crosslinking resulting from the interaction between the CBnp and the rubber chains. Also, this is due to the low oxidization of the carbonyl group on the CB particles’ surfaces, and the lower surface area and distribution level of the particle.

On the other hand, the scorch time ($T_{s2}$) showed an increment when the CBnp contents were increased in the CBnp/NBR nanocomposites until the percolation limit at 1.2 phr was reached, as shown in Table 2. Moreover, as the vulcanization process reached the end, $T_{90}$ was observed to decrease with the increase of the CBnp contents up to 1.2 phr in their nanocomposites. This occurred due to the sample reaching 90% of the cure.

In the same context, the cure rate index (CRI) increased with CBnp increasing. This demonstrated the effective dispersion of the nanofiller within the NBR matrix at different values depending on the percentage of $\Delta \tau$. Also, this increment might have introduced an additional network system within the rubber nanocomposite until reaching the percolation threshold of the fillers. CBnp declined at 2.4 phr.

Figure 3 Carbon Black – CBnp FEF N550
Table 2 Cure characteristics of vulcanized CBnp/NBR nano composites

| CBnp (phr) (g) | $\tau_H$ (dN.m) | $\tau_L$ (dN.m) | $\Delta\tau$ (dN.m) | $T_{92}$ (min) | $T_{90}$ (min) | CRI at $T_{90}$ |
|----------------|-----------------|-----------------|------------------|--------------|--------------|----------------|
| NBR (neat)     | 9.39            | 0.51            | 8.88             | 1.47         | 5.97         | 22.22          |
| 0.2            | 10.85           | 0.41            | 10.44            | 1.37         | 4.73         | 29.76          |
| 0.6            | 11.15           | 0.49            | 10.66            | 1.4          | 3.44         | 49.02          |
| 1.2            | 11.48           | 0.27            | 11.21            | 0.93         | 5.85         | 20.33          |
| 2.4            | 11.77           | 0.44            | 11.33            | 1.35         | 5.81         | 22.42          |

Tensile strength properties of the vulcanized NBR and CBnp/NBR nanocomposites were investigated as per the ISO 37: 2011 standards on a Universal Testing Machine (UTM) using (Testometric M350-1). Dumbbell shaped samples with a gauge length of 20mm and thickness of 2 mm were used at a testing crosshead speed of 500 mm/min with the cell load machine with 10 kN. Five samples of CBnp/NBR nanocomposites were tested, four of which were reinforced by CBnp to compare them with neat NBR (pure). In which, five samples were tested for each content of CBnp in the nanocomposites under the ambient condition to measure the elastic modulus, ultimate tensile strength and elongation at break of the rubber (the used material in this research).
It observed that the increase in the CBnp content in the rubber nanocomposite sample led to an increase in the value of the stress and a decrease in the elongation value (strain). This means that the role of the CB particles acts to restrict the movement of the NBR chains, where the tensile strength of the composites was increased as shown in Table 3.

Figure 4 stress-strain curves of (CBnp/NBR) nanocomposites

The curves in Figure 4 show that the strain was decreased as the contents of CBnp increased in the rubber nanocomposites, where, CBnp particles worked on limiting the movements of the chains and
increase the rigidity of the samples until the maximum load. Based on that, the modulus increased as well according to the proportional relation with the stress as shown in Table 3.

**Table 3. Tensile tests parameters of CBnp/NBR nanocomposites compared to NBR**

| CBnp (phr) (g) | Tensile stress (MPa) | Elongation (%) | Modulus(M100) (MPa) |
|----------------|----------------------|----------------|---------------------|
| NBR (neat)     | 1.45 ± 0.11          | 477 ± 21       | 0.76 ± 0.03         |
| 0.2            | 2.57 ± 0.14          | 452 ± 23       | 0.89 ± 0.01         |
| 0.6            | 2.81 ± 0.16          | 447 ± 24       | 0.94 ± 0.02         |
| 1.2            | 2.98 ± 0.20          | 425 ± 46       | 0.97 ± 0.04         |
| 2.4            | 3.12 ± 0.43          | 420 ± 76       | 1.12 ± 0.06         |

The surface morphology of the fractured samples gained from tensile tests was characterized using Scanning Electron Microscopy (SEM). They were coated by sputtering with gold and then observed and analyzed by several SEM micrographs images viewed at various magnification degrees, as shown in Figure 5.

The reinforcing efficiency in CBnp plays an important part in the increase of tensile strength. The results agree with other works as the variation of carbon concentration in other types of rubber such as NR compound which can affect the rubber modulus properties. The modulus value increases at a higher concentration and rapidly grows to higher values at smaller particle sizes [21].

**Figure 5.** SEM images for NBR and CBnp/NBR nano composites; (a)- NBR (neat) with 50µm magnification. (b)- NBR (neat) with 10µm magnification. (c)- CBnp/NBR at 100µm , (d)- CBnp/NBR at 2µm.
3.3. Swelling and crosslinking characterization

Characterization of the crosslinking density using a swelling test was performed for five samples; neat NBR and 4 of CBnp/NBR nanocomposites samples with various content of CBnp as shown in Table 4. The test was achieved by equilibrating the samples (immersion in toluene) for 48 hours. The samples were weighed before and after insertion them into this solvent at ambient temperature. The swelling reduction ratio ($Q_r$) is calculated by the gravimetric method as given by equation (5), [22].

$$Q_r = \frac{(M_s - M_i)}{M_{dr}}$$  

(5)

Where, $M_s$ is the weight of the sample after 48 hours immersion in toluene as in Figure 6, $M_i$ is the initial weight before the test and $M_{dr}$ is the weight after drying at 70°C (until no further change occurred in the weight). The high swelling percentage indicates that the composite has a low crosslinking density of the elastomer chains which reduces the solvent resistance.

It is noted at 1.2 phr of CBnp content; there is an improvement in the network structure of the rubber composites due to increasing the adhesion between NBR chains and the carbon nanoparticles in the rubber nanocomposite. This led to reduce the solvent diffusion in the rubber matrix and improve rubber resistance against oil.

![Figure 6. Immersion of samples in the toluene](image)

| CBnp (phr) | Composites weights | $Q_r$ ratio | $Q_r/Q_o$ ratio | (D) x10^{-3} (mole/cm^3) |
|------------|---------------------|-------------|-----------------|-------------------------|
| NBR (neat) | 0.352 0.862 0.342   | 1.491       | 1.000           | 9.847                   |
| 0.2        | 0.332 0.821 0.333   | 1.470       | 0.985           | 10.075                  |
| 0.6        | 0.361 0.784 0.307   | 1.380       | 0.924           | 11.108                  |
| 1.2        | 0.345 0.801 0.365   | 1.250       | 0.838           | 13.101                  |
| 2.4        | 0.338 0.821 0.357   | 1.350       | 0.907           | 11.436                  |
There are several indications related to particle size and particle distribution in the matrix. This helps to find the type of adhesion or fail could happen due to the defects or the external forces. The images in Figure 5 showed that NBR (pure) with 50µm magnification has a phase of rubber with some vulcanization additives. Also, more details on the surface feature with 10µm magnification were appeared, as shown in Figure 5 (a and b). The CBnp/NBR nanocomposites with 1.2 phr of CBnp, at 100µm magnification, CBnp particles were shown clearly in a homogeneous pattern of CBnp particles folded by NBR chains as appeared in Figure 5 (c and d) at 2µm magnification. The distributions of CBnp particles reflect the degree of crosslinking of the network of rubber nanocomposites. As the crosslinking density increases the swelling ratio reduces and mechanical properties improve.

Conclusions

From the results, it is possible to conclude that CBnp is a compatible filler with NBR to prepare rubber nanocomposite. Few contents of CBnp in CBnp/NBR nanocomposite showed a clear effect on the mechanical properties via the improvement in the tensile strength. Therefore, CBnp is used to reinforce NBR to increase rubber stiffness. However, most of the properties possessed by the CBnp are depend on the CBnp loading and particle sizes. This is attributed to the role of grain size and its boundaries to increase the surface area of filler-matrix interfacial adhesion. The reduction in the swelling in rubber could improve by adding CBnp within the range 0.2-1.2 phr to the rubber matrix to increase the rubber resistance against oils diffusion in the hoses or other parts, especially in the automobile.

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