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# Materials Research Express



## PAPER

# Experimental investigation on chloroprene and acrylonitrile butadiene rubber types reinforced with nano-materials

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## Abstract

In this research, the effects of three different nano-materials (Nano-Carbon Black, Nano-ZnO, and Multi-Walled Carbon Nanotubes (MWNTs)) on two different rubber types (Chloroprene Rubber (CR), and Acrylonitrile Butadiene Rubber (NBR)) were experimentally investigated. In order to achieve this purpose, mechanical tests and detailed aging tests (in air, oil and fuel) were conducted conforming to international standards. Three different nano-materials were added to rubber with different combinations. A good dispersion of MWNTs within the polymer matrix was monitored by using field-emission Scanning Electron Microscopy (FE-SEM). It was observed that nano-materials both have positive and detrimental effects on hardness, tensile strength, ductility and aging tests performance. It was observed that nano-material reinforced rubber composites are thermally more stable than current products. Most significantly, it was seen that compression set value, which is a critical property for rubber grade, decreased with the addition of MWNTs. Therefore, rubber products with higher sealing capacity and longer service life can be obtained by adding MWNTs.

## 1. Introduction

Elastomers are of great industrial importance due to their high and reversible deformability [1]. Incorporation of reinforcements into elastomers is probably one of the most important processes in rubber industry [2]. In order to enhance their mechanical, thermal, and chemical properties, rubber has been reinforced with nano, micro or macro sized ingredients and ancillary substances [3]. In particular, significant changes towards their mechanical and chemical properties can be obtained by changing their sizes from micro to nano scale [4]. These changes generally arise from expanding surface area of these materials due to the dimensional changes that occur at the nano scale.

Polymer/nano-filler composites have received great attention during the past decade due to the unique properties of nanostructures and their potential to create new materials with superior properties [5–8]. Although the positive effects of nano materials are known, it is not completely possible to transfer all of these properties to composite materials. Despite the advancements in composite technology, the dispersion of nano particles in the polymer matrix remains a challenge [2]. If nanoparticles are added at high ratios to the polymer matrix, due to their large surface area and interactions between molecules, agglomeration problem occurs. Therefore, it is a very challenging problem to obtain a homogenous mixture [9]. Due to this reason, the most important point for transferring the nano material's properties to matrix material successfully at a greater extent is using a mixing method to achieve a homogenous mixture [10–12].

Different types of materials are added to rubber to enhance its mechanical, thermal, electrical and chemical properties. Nanocomposites exhibit improvement in their material properties through addition of nanoscale particles. A variety of particles with different size scales or dimensions, including nanosilica [13], nano Fe<sub>3</sub>O<sub>4</sub> [14], nano-alumina [15], nano-clay [16], and graphene [17, 18] were added into rubber matrix by researchers in

order to investigate their effects on the material properties. It was observed that nano silica affects the rate of cross-linking reaction positively [13]. In addition, when  $\text{Fe}_3\text{O}_4$  was added to a rubber grade, tribological properties were improved significantly [14]. Enhancement of thermal conductivity and mechanical properties were observed when nano-alumina was added to a rubber [15]. Addition of nanoclay into rubber enhanced the mechanical properties, such as tensile strength, ductility, and modulus of elasticity [16]. Also, mixing graphene with rubber resulted in remarkable enhancement in tensile strength, storage modulus, and thermal stability [17].

Thanks to the extraordinary mechanical properties of carbon nanotubes and latest technological developments that have led to decreasing costs in synthesizing these materials; carbon nano tubes have become the leading nano-sized materials that have found a wide field of usage in a vast variety of environments and applications. For instance, elastomer/Multi-Walled Carbon Nanotube (MWNT) nanocomposites demonstrate excellent mechanical properties together with high thermal conductivity and low volume resistivity [19]. Carbon Nanotube (CNT)—rubber nanocomposites exhibit higher electrical conductivity [20]. Addition of CNT to rubber significantly enhanced the matrix strength and thermal stability [21]. CNT-dielectric rubber nanocomposites showed superior mechanical and electrical properties [22]. Another study suggested that concentrations of nanofillers (CNTs) can be optimized to achieve the maximum strength and electrical conductivity of composites [18]. Zinc oxide (ZnO) has been generally used as an activator in S-vulcanisation [23], and can be added as a nano material. Rubber with nano ZnO allows higher crosslink density and stronger mechanical properties than those filled with micro ZnO [24]. Another work showed that the mechanical properties of cushion rubber were improved by the addition of ZnO nanograins into rubber [25].

However, in spite of the many research studies on the mechanical, thermal and electrical properties, there are only a limited number of studies focusing on the compression set value and performance comparison after aging tests in air, oil and fuel [24, 26–29]. In these studies, it was observed that after thermal aging, natural rubber (NR) filled with nano ZnO exhibited much more stable chemical and mechanical properties [24]. In addition, Styrene-Butadiene Rubber (SBR)/Carbon Black (CB), SBR/CB/rectorite and SBR/rectorite nanocomposites with the same total filler loading were tested to see the thermal aging properties and it was found that the introduction of nano-dispersed rectorite layers can enhance the thermal aging resistance of the nanocomposites [26]. Moreover, the clay layers, which are added to SBR, can enhance the thermal aging resistance of nanocomposites, significantly [27]. The aging resistance of SBR/CNTs composites was studied by comparing the mechanical properties before and after thermal-oxidative and ozone aging and it was shown that the developed composites performed excellent ozone aging resistance [28]. Carbon black (CB)—Halloysite nanotubes (HNT) hybrid composites based on Acrylonitrile Butadiene rubber (NBR) were prepared, whose results showed that compression set value decreased with addition of HNT [29]. Even though, there are limited number of studies on compression set and detailed aging tests, these tests are very important for rubber-based materials since compression set test value gives data about working life of seal. Accelerated aging tests show the sealing performance of rubber based materials for real working conditions. On the contrary, to the best of the authors' knowledge, compression set test and detailed aging tests of rubber-nanocomposites by using combinations of three different nano materials, have not been conducted, yet.

In this study, two different rubber types were reinforced with MWNTs, nano ZnO and nano size carbon black to investigate their effects on the mechanical and thermal properties of the rubber composites. Carbon black, which has nano-sized particles originally, and ZnO that can be used at nano-scale for rubber compounding were chosen to for proper dispersion at nano-scale. In addition, MWNT filler was chosen due to its superior properties. Two methods were used to disperse nano materials into the rubber grades. These two types of rubber grades (Acrylonitrile Butadiene Rubber-NBR and Chloroprene Rubber-CR) were manufactured by both using conventional materials and nano materials, through which the effects of nano materials on product characteristics were assessed. The dispersion characteristics were investigated by scanning electron microscopy (SEM). Also the effects of nano-materials on thermal stability were analyzed by Thermogravimetric Analysis (TGA). It has been found that reinforcing the rubber matrices with nano fillers both have positive and detrimental effects on the material properties of the composites. By adding nano materials, thermal stability was improved. Most significantly, it has been observed that compression set value of rubber-based materials, which is about sealing capacity and working life of seal [30], decreased when the aforementioned nano materials were added to the rubber grades.

## 2. Methodology

### 2.1. Materials

Two types of rubber were used in the current study. One of them was chloroprene rubber (CR) that has good oxidation resistance [31] and the other one was acrylonitrile butadiene rubber (NBR) that shows fuel and oil

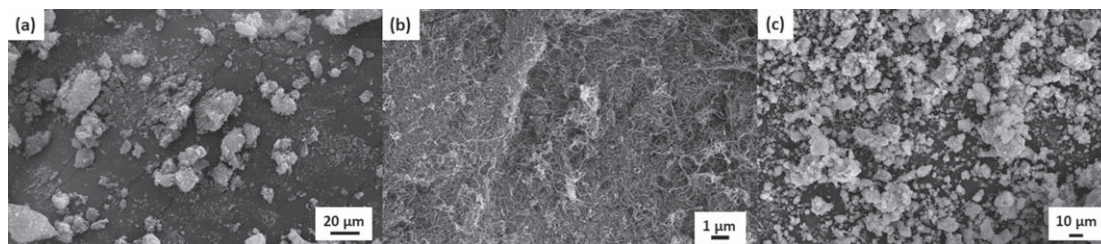


Figure 1. SEM images of rubber nanocomposites containing (a) carbon black, (b) MWNTs, and (c) nano-ZnO.

resistance. Conventional materials, nano carbon black, carbon nanotube and nano zinc oxide were added to these rubber grades with different combinations.

## 2.2. Measurements

The surface characteristics were investigated by using scanning electron microscope (SEM, Zeiss Evo LS 10) and field-emission SEM (Zeiss  $\ll$  GeminiSEM 500  $\gg$  FE-SEM). Particle size distribution was measured by using particle size analyzer (Malvern Zetasizer ZS90). Tensile tests were conducted to determine the tensile strength and ductility of the material by using tensile testing machine (Tensometer T500). Vulcanisation parameters were determined by using rheometer (Rheometer R100S). Thermogravimetric analysis (TGA) was carried out to compare thermal stability of materials by using thermogravimetric analyzer (PerkinElmer Diamond (TG/DTA)). Air and fluid aging tests were conducted in an oven at different time and temperatures. Compression set and volume change tests were conducted according to the American Society for Testing and Materials (ASTM) standards.

## 2.3. Sample preparation

For the preparation of traditional materials; rubber (Baypren B210 for CR and LGChem NBR 6850 for NBR), carbon black, N550 (Prisc Kremenchug), plasticizer, anti-aging material and activators were weighed and put into the open cylinder. After mixing the polymer matrix completely, sulphur (S) for NBR and ethylene thiourea (ETU) for CR were added to the mixture as vulcanizing agents. This mixture was left to stabilize for one day. Then, a sample was taken from this mixture and placed into the rheometer to determine vulcanisation time and temperature. Rubber grade was extruded for pre-shaping and then placed into a 50 ton capacity pressing machine with the molds to obtain vulcanised samples. NBR was vulcanized at 155 °C for 17 min and CR was vulcanized at 155 °C for 21 min. After vulcanising the rubber grade, test parts were produced by using cutting molds. This cutting process was carried out by employing a shearing machine that has 50 ton capacity.

To produce rubber/nano material composites, there was an extra operation to mitigate, and if possible, eliminate agglomeration problems. Before getting started, SEM images of MWNTs, carbon black and zinc oxide were observed to determine the particle size. SEM images for these materials are shown in figure 1. Although these filler materials were nano-sized, the particle sizes were measured in micro- or even milli-scale due to the effects of van der Waals bonds and particle agglomeration [32]. Agglomerated particle size for carbon black (figure 1(a)), MWNT (figure 1(b)), and zinc oxide (figure 1(c)), which is an activator for rubber vulcanisation process [24], were approximately 40  $\mu$ , 20  $\mu$  and 50  $\mu$ .

Ultrasonic mixing process was used to disperse the nano materials. Nano materials (nano-carbon black, MWNT, nano-ZnO) were mixed with polyvinylpyrrolidone (PVP) in ethanol by using high gain probe. PVP is a diffuent, nontoxic reagent that is commonly applied as an assisting reagent [33]. In this work, this reagent was used in order to prevent agglomeration. The particle size distribution was measured by particle size and zeta potential analyzer (Malvern Zetasizer ZS90). The particle size distribution of nano-carbon black is shown in figure 2(a). The average particle size was measured as 332 nm ensuring that all the particle sizes were under micron level (figure 2(a)). Figures 2(b) and (c) shows the average particle size distribution of MWNT and nano-ZnO, respectively. The average particle size of MWNT and nano-ZnO were measured as 840 nm and 426 nm, respectively. The largest size of MWNT has been detected as 7 microns due to MWNT's micron size lengths.

After confirming that all materials were at nano-scale, nano-carbon black colloid was prepared by ultrasonic mixing and added to the rubber grade by using pulverizator. Ethanol was expected to evaporate with the effect of heat due to friction during mixing process.

The rubber grade was vulcanised to prepare test samples. After this process, some surface problems were detected on the resulting rubber grade. These problems may be caused by inadequate evaporation of the solvent.

In order to resolve these problems, it was decided to use the same ultrasonic dispersion method by changing the evaporation procedure. After the colloid was prepared by ultrasonic mixing, it was put into the oven. Nano

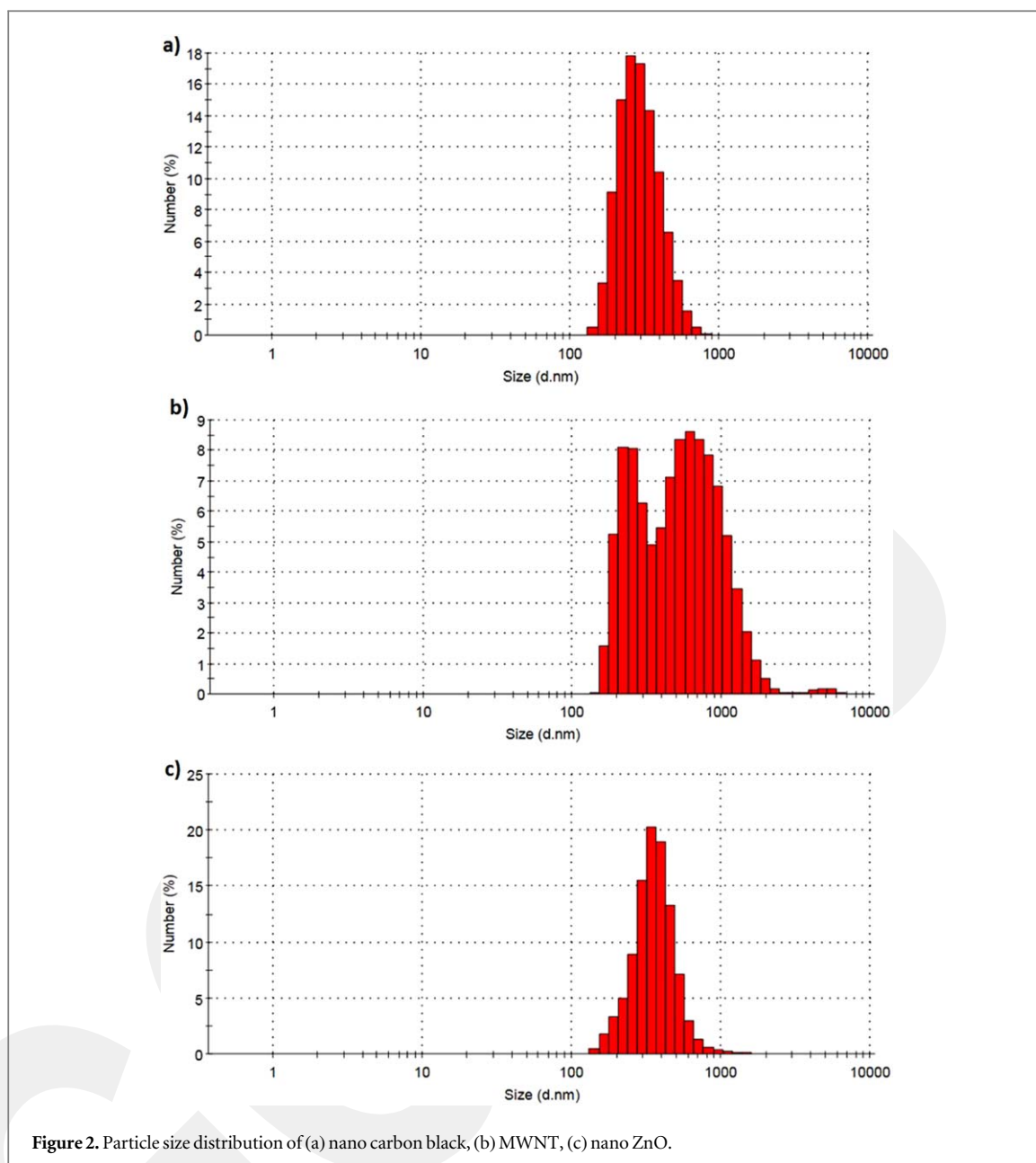


Figure 2. Particle size distribution of (a) nano carbon black, (b) MWNT, (c) nano ZnO.

materials were mixed with the rubber grade in powder form. Following the procedure, vulcanized rubber grade was obtained without surface defects. After that, test samples were prepared. Figure 3(a) shows the defective product whereas the appropriate specimen after changing the evaporation procedure can be seen in figure 3(b).

Nano materials were added to the rubber grade at different ratios, through which it was aimed to see their effects on the material properties. Lowest and highest limits were determined for three nano-materials by taking into consideration the amounts for current recipes and similar previous work in the literature. Within these limits, 'Design Expert 8.0' Software, which is suitable for mixture design, was used to obtain different recipes with different ratios for two rubber composites. Twelve different samples were prepared and tested for both two rubber composites. Four of these contents of the two different types of rubber can be seen in tables 1 and 2.

### 3. Results and discussion

#### 3.1. Structural and thermogravimetric analysis (TGA)

After rubber grades with best overall quality were obtained, FE-SEM technique was employed to observe the structure and dispersion of nanomaterials. ZEISS «GeminiSEM 500» model FE-SEM was utilized to collect the images for two products as can be seen in figure 4. These images belong to Sample 1 of the two rubber types. It can be seen that both of them appear to have homogenous structures devoid of agglomeration problems. Greater surface roughness was observed in CR composites, due to a more ductile fracture of CR.

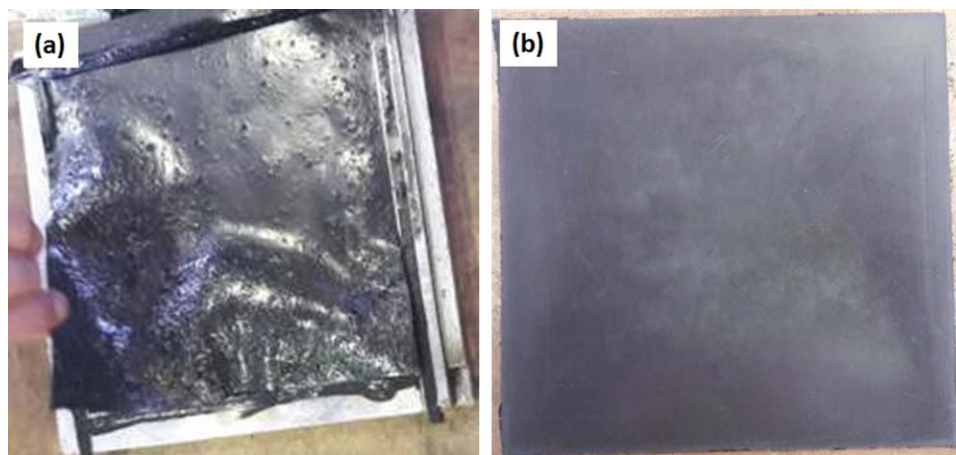


Figure 3. (a) Defective rubber grade, (b) appropriate rubber grade.

Table 1. Nano materials used for CR.

| Materials used for CR(*for 100 gr rubber) | Sample 1 (gr.) | Sample 2 (gr.) | Sample 3 (gr.) | Sample 4 (gr.) |
|---|----------------|----------------|----------------|----------------|
| Nano carbon black (N550)                  | 10.44          | 9.66           | 11.17          | 11.29          |
| MWNT                                      | 3.33           | 2              | 1.47           | 0              |
| Nano zinc oxide                           | 3.33           | 5              | 4.03           | 5              |

Table 2. Nano materials used for NBR.

| Materials used for NBR (*for 100 gr rubber) | Sample 1 (gr.) | Sample 2 (gr.) | Sample 3 (gr.) | Sample 4 (gr.) |
|---|----------------|----------------|----------------|----------------|
| Nano carbon black (N550)                    | 41.6           | 42.7           | 47.88          | 46.77          |
| MWNT  | 13.3           | 8.45           | 0.32           | 0              |
| Nano zinc oxide                             | 3.33           | 5              | 3.33           | 5              |

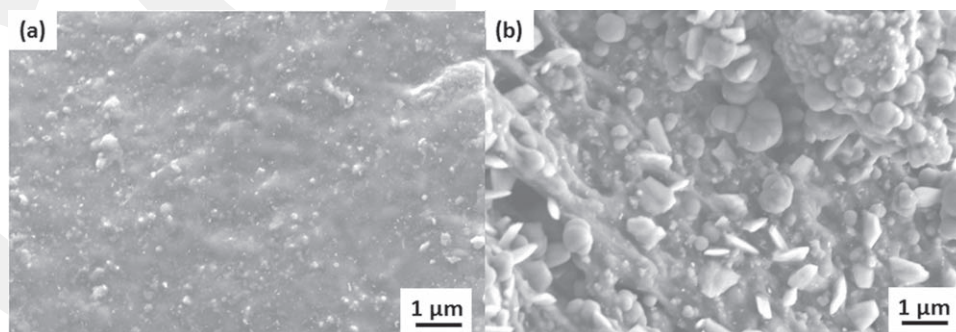
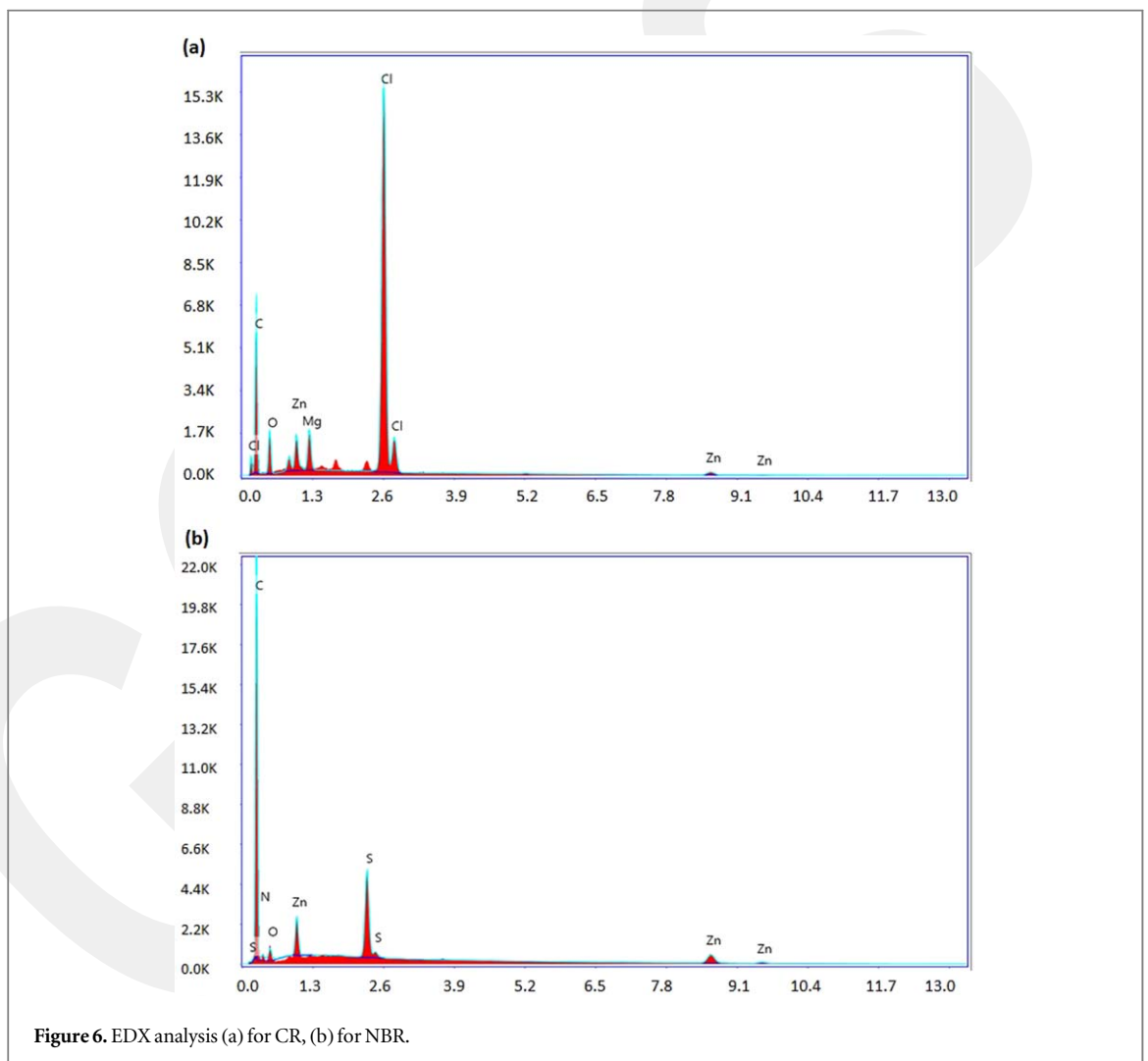
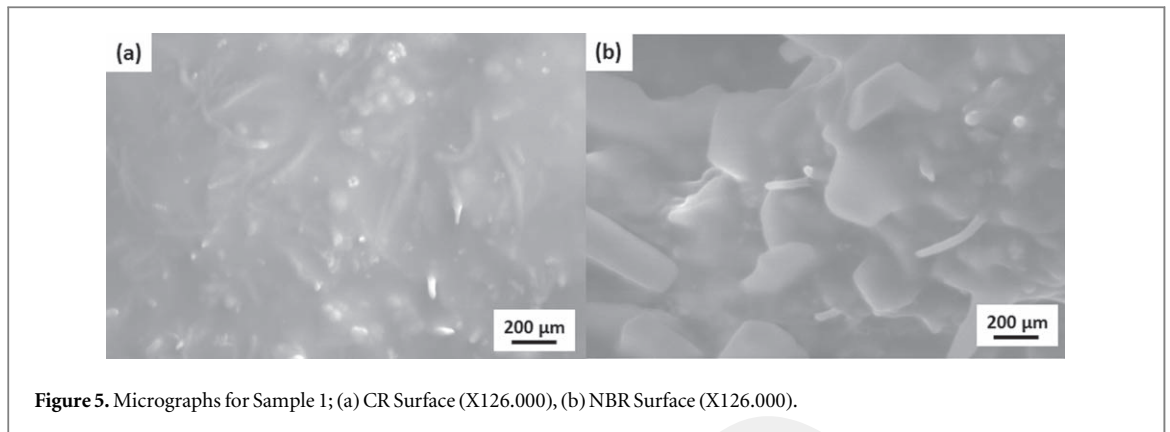


Figure 4. Micrographs for Sample 1; (a) CR Surface (X30,000), (b) NBR Surface (X30,000).

Other images of the two products with higher magnification can be seen in figure 5. Similarly, Sample 1 for both rubber types were used to collect these images. MWNTs with homogenous dispersion within the rubber can be observed in the following figures. In figure 5 (a), MWNTs can be seen within the polymer surface, on the other hand figure 5(b) shows the MWNTs on the polymer surface with the effect of fracture. It was shown that, agglomeration of nano-particles was prevented by using ultrasonic dispersion method. Also, there is no crack initiation observed within the interface.

Energy Dispersive x-ray (EDX) analysis for two samples can be seen in figure 6. With this analysis, chemical compositions of the samples were verified. Cl and Mg are distinctively observed for CR, as CR has Cl in its molecular structure and MgO is used as activator.



With thermogravimetric analysis, it is aimed to investigate whether there is a difference between materials' thermal stability or not. The results of this analysis are provided in figure 7. It is observed that mass loss trends for both current and nano-material reinforced samples are the same. Current products were produced conventionally without using nano-materials. Sample 1 for two rubber types were used as nano-material reinforced samples. Figures 7(a) and (b) reveal that nano material added samples are thermally more stable than current products. It was reported that, MWNTs has the ability to prevent thermal degradation of the matrix material by its good dispersion into the matrix [34]. These results can confirm MWNTs' good dispersion within the polymer matrix.

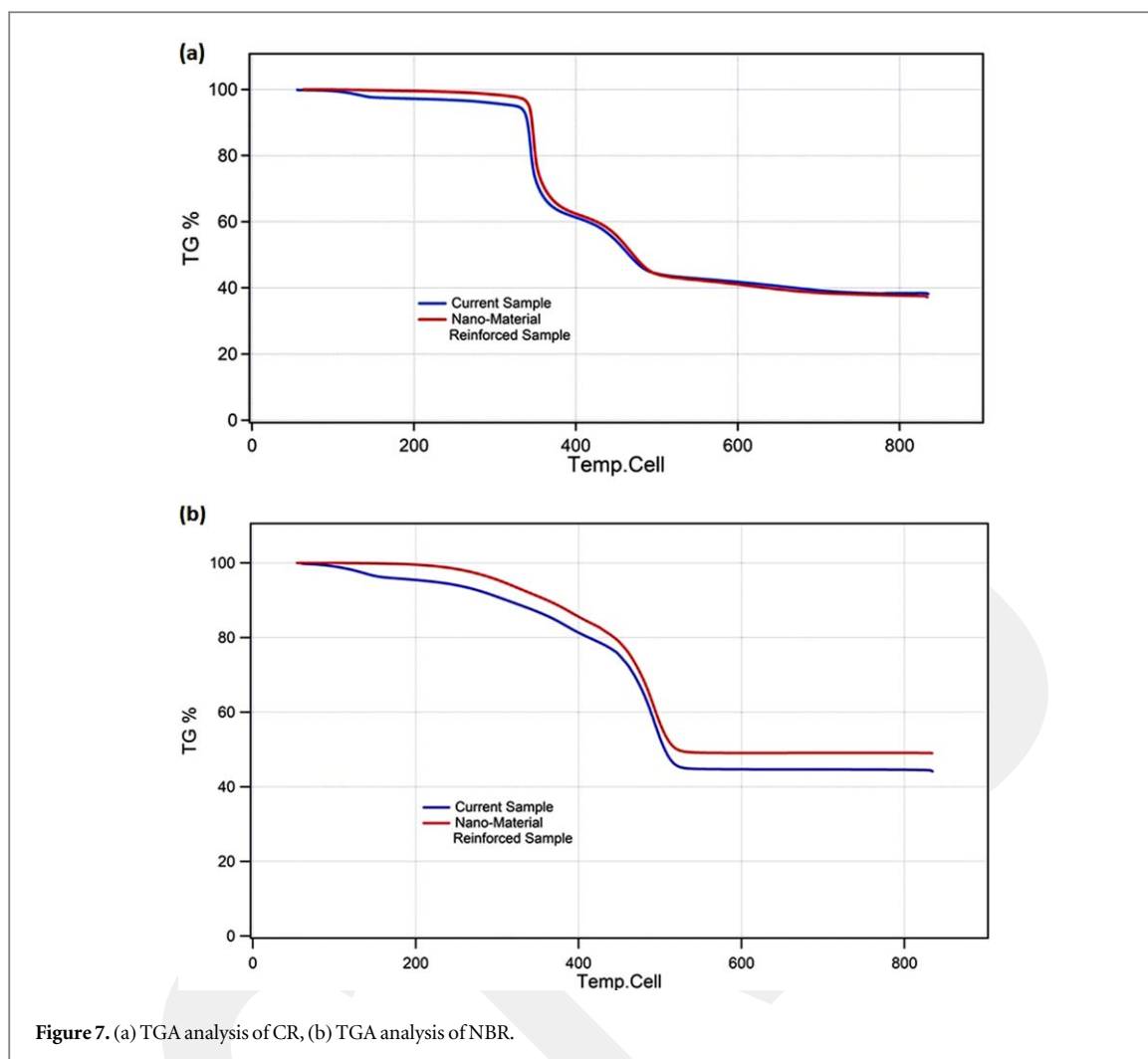


Figure 7. (a) TGA analysis of CR, (b) TGA analysis of NBR.

Table 3. Hardness of the samples.

| Performance criteria    | As is | S1 | S2 | S3 | S4 |
|-------------------------|-------|----|----|----|----|
| Hardness, Durometer 'A' | 50    | 53 | 50 | 53 | 48 |

### 3.2. Performance characteristics

Performance characteristics of CR were also determined by using ASTM test methods and according to AMS 3222, which is an international specification for Synthetic, Hot Oil Resistant, High Swell 45–55 hardness synthetic rubber. Hardness of the samples are shown in table 3. 'As is' means non treated current specimen in the tables. For CR, when sample properties were compared, it can be seen that hardness increased by adding MWNTs since they are ideal candidates for the reinforcement of polymers [22]. When current specimen and Sample 4 are compared, it can be concluded that, using carbon black and ZnO at nano-scale instead of micron-scale decreased the hardness value. This decrease can be attributed to the decrease of cross-link density.

Table 4 shows the tensile strength and elongation value for the samples. Tensile strength and maximum elongation values are affected adversely with the addition of nano materials. Decrease in the maximum elongation and increase in the tensile strength with the addition of Nano-ZnO were reported previously and show good agreement with our results [24]. In this work, three different nano materials were used; therefore, filler-filler and filler-rubber interactions can affect the cross-link density and mechanical properties. The decrease in the aforementioned properties can be attributed to the insufficient formation of a filler network within the rubber.

Table 5 demonstrates the change in hardness, tensile strength, and elongation in the specimens following ageing tests conducted in air. The results in table 5 do not appear to be conclusive. However, noticeable improvements are observed on the performance characteristics for some of the specimens after air-aging, while some others seem to be affected adversely. Adverse effects may be due to the crosslinking of CR macromolecular

**Table 4.** Tensile strength and elongation of the samples.

| Performance criteria  | As is | S1   | S2    | S3    | S4    |
|-----------------------|-------|------|-------|-------|-------|
| Tensile strength, MPa | 22.26 | 9.51 | 15.17 | 14.38 | 13.26 |
| Maximum elongation, % | 712.8 | 303  | 556   | 557   | 432   |

**Table 5.** Results of aging tests in air.

| Performance criteria                           | As is | S1   | S2    | S3    | S4    |
|--|-------|------|-------|-------|-------|
| After aging in air at $100 \pm 3$ °C for 70 h  |       |      |       |       |       |
| Change in hardness, Durometer 'A' <sup>a</sup> | +1    | +2   | +1    | +1    | +2    |
| Change in tensile strength, %                  | -2.2  | +25  | -20.1 | +1.76 | -12.3 |
| Change in maximum elongation, %                | -5.7  | -5.4 | +8.4  | -4.9  | -14.1 |

<sup>a</sup> Change in hardness: the hardness difference between the samples before and after aging test in terms of Shore A.

**Table 6.** Compression set values after aging in air.

| Performance criteria                          | As is | S1   | S2 | S3   | S4 |
|---|-------|------|----|------|----|
| After aging in air at $100 \pm 3$ °C for 70 h |       |      |    |      |    |
| Compression set, %                            | 22.4  | 15.2 | 15 | 16.9 | 21 |

**Table 7.** Aging tests in ASTM Oil No:1.

| Performance criteria                                    | As is | S1   | S2    | S3    | S4    |
|---|-------|------|-------|-------|-------|
| After aging in ASTM oil no:1 at $150 \pm 3$ °C for 24 h |       |      |       |       |       |
| Change in hardness, Durometer 'A'                       | -5    | -5   | -5    | -7    | -2    |
| Change in tensile strength %                            | -19.9 | -3.1 | -12.4 | -23.9 | -30.2 |
| Change in maximum elongation %                          | -19.3 | +4.7 | +11   | -4.35 | -17.4 |

chains that takes place during aging process in air. The higher crosslinking degree makes rubber stiffer and more brittle [26]. MWNT addition appear to have positive effects on the strength of the composite as shown through air aging tests of rubber. Results exhibit that an optimum reinforcement ratio with the best molecular structure possessing efficient filler-filler and filler-rubber interactions, must be chosen to get the best performance for air resistance.

Compression set is a measure of the ability of vulcanized rubber to retain its elastic properties after prolonged compression at constant strain under a specific set of conditions [29]. Table 6 notably shows that compression set values are observed to decrease by adding nano-materials. It was concluded that MWNTs have the most significant effect on compression set value. Compression set value decreased with the addition of MWNTs. This means products with higher sealing capacities and longer service lives can be obtained by adding MWNTs. The better performance of rubber compounds in terms of compression set is attributed to the cross-linked chains forming a permanent network and are unable to relax during the compression stage [29]. The effects of MWNTs on compression set value for CR were not reported so far.

Results for oil-aging tests are given in table 7 below. Comparison of Sample 2 and Sample 4 shows that change in the tensile strength and elongation decreases by adding MWNTs. Therefore, MWNT reinforced samples have more stable cross-link structure against oil.

Performance characteristics of NBR were evaluated by using ASTM test methods according to AMS 7270, which is an international specification for fuel resistant  $70 \pm 5$  hardness nitrile rubbers. Test results for different samples are shown in table 8. It is observed that by adding nano-materials, hardness can be increased. In addition, it was concluded that hardness was affected mostly by higher MWNT addition. MWNTs' positive effect on hardness was also reported before [35].

The tensile strength of the sample with higher MWNT content (S1) appears to be lower than those of other samples as seen in table 9. But adding nano-scale carbon black instead of micron scale carbon black has increased

**Table 8.** Hardness of the samples.

| Performance criteria    | As is | S1 | S2 | S3 | S4 |
|-------------------------|-------|----|----|----|----|
| Hardness, Durometer 'A' | 66    | 80 | 79 | 74 | 73 |

**Table 9.** Tensile strength of the samples.

| Performance criteria   | As is | S1   | S2   | S3    | S4    |
|------------------------|-------|------|------|-------|-------|
| Tensile strength (MPa) | 11.45 | 6.95 | 11.1 | 12.72 | 13.45 |

**Table 10.** Maximum Elongation of the samples.

| Performance criteria  | As is | S1  | S2  | S3  | S4  |
|-----------------------|-------|-----|-----|-----|-----|
| Maximum elongation, % | 245.7 | 241 | 230 | 238 | 251 |

**Table 11.** Results of aging tests in air.

| Performance criteria                          | As is | S1  | S2  | S3  | S4  |
|---|-------|-----|-----|-----|-----|
| After aging in air at $100 \pm 3$ °C for 70 h |       |     |     |     |     |
| Change in hardness, Durometer 'A'             | +5    | +6  | +4  | +2  | +7  |
| Change in tensile strength %                  | +8.5  | +11 | +5  | -13 | -24 |
| Change in maximum elongation %                | -17   | +9  | -10 | -21 | -36 |

**Table 12.** Compression set value of the samples.

| Performance criteria                          | As is | S1 | S2   | S3   | S4   |
|---|-------|----|------|------|------|
| After aging in air at $125 \pm 3$ °C for 70 h |       |    |      |      |      |
| Compression set, %                            | 67.6  | 55 | 58.1 | 57.6 | 60.1 |

the tensile strength. Results indicate that a stronger filler-rubber interaction leads to less sliding deformation for nano-scale carbon black filled NBR and more stress is needed to break the chain entanglement [26]. Adsorption of rubber into the CB surface acts as additional crosslinks, which translates to stronger materials [2].

Maximum elongations of the samples are given in table 10. MWNTs has a negative effect on elongation as it was reported before [36]. Stronger material with lower ductility was manufactured by reinforcing the rubber with MWNTs. It was found that, nano carbon black and nano ZnO have positive effects on elongation by comparing Sample 4 and the base specimen due to sufficient filler-rubber interactions.

Aging in air at  $100 \pm 3$  °C test results are tabulated in table 11. For air resistance, it was confirmed that the optimum ratios must be determined to get the best product with best filler-filler and filler-rubber network. Sample 2 showed better performance in terms of air resistance, due to its 'chain networks' stability against air.

Compression set values after aging in air at  $125 \pm 3$  °C are shown in table 12. Compression set value decreased with the addition of nano-materials. Most significantly, the sample with the highest MWNTs content has the lowest compression set value. This result indicates that sealing capacity can be increased with the addition of MWNTs. Also, it was reported that compression set value decreased with addition of HNT to NBR [29]. The effect of MWNTs and other nano materials on compression set value for NBR was not reported so far.

Table 13 presents the results of aging in ASTM Ref Fuel B at 20 °C–30 °C test. Apart from hardness change, adding MWNTs has improved also the fuel resistivity due to the more stable crosslinks of MWNTs nanocomposites for fuel applications.

The formation of the filler network is not only the result of filler-filler interactions but also of polymer-filler and polymer-polymer interactions [10]. Other factors that influenced the mechanical properties and processability of CR and NBR composites include hydrodynamic effects, particle structure, particle size

**Table 13.** Aging tests in ASTM RefFuel B.

| Performance criteria                                 | As is | S1  | S2  | S3  | S4  |
|--|-------|-----|-----|-----|-----|
| After aging in ASTM Ref fuel B at 20–30 °C for 168 h |       |     |     |     |     |
| Change in hardness, Durometer 'A'                    | –10   | –17 | –17 | –21 | –22 |
| Change in tensile strength %                         | –46   | –9  | –10 | –15 | –52 |
| Change in maximum elongation %                       | –47,7 | –7  | –22 | –29 | –41 |

distribution, filler alkalinity and reactivity with curing chemicals [2]. Differences in rubber structure and composition effect rubber-filler interactions. Since NBR has a more linear chain structure, which allows it to flow more easily into the filler network [2], it showed better performance when compared with CR. These are the reasons why mechanical properties are affected dissimilarly for two different types of rubber.

#### 4. Conclusion

In this research, a method to homogeneously disperse nano materials into rubber grades was introduced. Nano ZnO, Nano Carbon Black and MWNTs were used as nano-materials. These nano-materials were added to two different types of rubber with different ratios. These ratios were determined by using Design Expert Software. CR and NBR were chosen as rubber matrix for their wide application areas. Mechanical tests were conducted for different samples and performance characteristics were compared. Experimental results of this study suggest that reinforcing the rubber matrices with nano fillers both have positive and adverse effects on mechanical properties of the composites. As a significant finding, compression set value appears to decrease through the addition the nano fillers, specifically with MWNTs, which is considered to be a critical property for rubber based materials. This potentially means that, by adding nano-materials, products with higher sealing capacities and longer service lives can be obtained.

Also, detailed aging tests were conducted conforming to international standards. The results reveal that other performance characteristics can also be improved by changing nano-material content according to the application type such as usages in air, fuel, or oil environments.

In addition to performance tests, via FE-SEM (Field Emission Scanning Electron Microscope) imaging of the samples, micro structure and dispersion characteristics were evaluated. Homogeneous dispersion of MWNTs in the rubber matrix was observed. TGA (Termogravimetric Analysis) analyses of products that are produced with conventional methods and with the suggested methods introduced in this study show materials' thermal stability. Nano material reinforced samples appear to be more thermally stable than current products.

Although there are many factors affecting rubber based materials' mechanical and thermal performance, this research shows how to improve these properties by adding nano-materials. Products, that are produced by conventional method and a new method with nano materials, were compared in terms of their performance by thermal, mechanical and detailed aging tests. Overall, this study shed light on how to obtain better sealing capacity by decreasing the compression set value and get better performance in aging tests of rubber-nanocomposites by using combinations of three different nano materials.

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