Natural Rubber Based Industrial Compounds:
Study of Carbon Black and Plasticizer Types
on the Properties

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ABSTRACT: *The effects of two types of CBs (N330 and N550) and also two kinds of plasticizer, paraffinic and aromatic oils (PO and AO), on the ultimate characteristics of Natural Rubber (NR) were comparatively studied. The comparative study was performed using rheometric behavior, fatigue life (in tensile mode), aging behavior (168 hours at 70 °C), and compression set analyses. Obtained results showed that there is an optimum ratio of CBN330/CBN550 fillers and also an optimum ratio of PO/AO plasticizers which have the best influence on the properties, especially on the fatigue life. It is found out that synergistic effects of the CBN330 and CBN550 fillers, and also PO and AO plasticizers, due to better dispersion and chain mobility of rubber chains, are the main reason for enhanced outcomes. Another point is that to achieve more superior behavior for this kind of compound, the starting point could be the consequences of this paper. The main goal of this work is to develop an enhanced formula for a NR-based industrial compound.*

KEYWORDS: *NR; CB filler; paraffinic oil; aromatic oil; fatigue life; aging.*

INTRODUCTION

Attributed to their outstanding and distinguished properties, elastomers such as polyisoprene (NR), Poly(styrene-co-butadiene) rubber (SBR), polybutadiene (BR), silicon rubber, etc., are mostly applied where their products are subjected to dynamic or cyclic loads. Under these dynamic loads, the elastomeric products may fail because of the creation and subsequent growth of cracks. Like all materials, the fatigue resistance of elastomeric materials

under time-depending or cyclic loads is an important and critical issue. Some important parameters affecting fatigue behavior are product formulation, environmental factors, loading conditions, and processing conditions of the compound. To design a formulation or compare the products, a dynamic mechanical testing instrument (in tensile mode) is often used to evaluate fatigue behavior [1-11].

Carbon Black (CB), an important reinforcing additive for elastomers, is used to improve the structural, UV resistance, thermal and mechanical properties of rubbers especially NR. When an elastomeric filled compound is under loading, the polymer matrix around CB is strained more than the rest which is defined as stress concentration. If a higher or dynamic force is applied, CB particles are separated from the polymer matrix and microcrack nucleation has occurred. Other sources of microcracks in the matrix are voids or contaminants, mold lubricants, inappropriately dispersed ingredients, and surface defects which can promote nucleation of microcracks. Upon higher or continuous loading, coalescing of the microcracks causes to a significant crack and may consequently lead to failure. So, exploring the characteristics of CB is one of the important parameters to predict or figure out the behavior of CB-filled elastomeric compounds [12-18].

Another additive can affect the behavior of rubber compound (*e.g.* fatigue resistance) is a plasticizer. Plasticizer molecules can easily penetrate into the rubber matrix, place between the chain segments, decrease the cohesive forces between the polymeric chains, subsequently facile the segmental motion of chains and consequently reduce the glass transition temperature and enhance fatigue resistance of the product. Moreover, some plasticizers such as aromatic-based oils cause better processability of compounds, and some of them like chlorinated paraffinic oils or hydrocarbons are usually used as flame retardants [19-26].

In this work, the effects of two types of CBs (N330 and N550) and also two kinds of plasticizers (paraffinic and aromatic oils) on the ultimate properties of NR were comparatively investigated. In many aspects, the laboratory conditions for the production and characterization of samples often deviate from industrial applications. In our work, the characterization conditions are very close to industrial measurement ones by a specific product. The materials used are industrial elastomer blends which were developed for these specimens. Only the samples geometry differs from the geometry of products and the maximum strain is higher in order to avoid extra analysis times. During the fatigue life investigations, the specimens are not cooled since the industrial products are also not cooled in industrial applications.

EXPERIMENTAL SECTION
MAterials

Ribbed Smoked Sheet natural rubber (RSS1) was supplied from Saksham Gati Co., Singapore. Zinc Oxide 99.7% and paraffin wax (Rangineh Pars Co., Iran), aromatic 290 and paraffinic 840 oils (Behran Co., Iran), sulfur and carbon blacks (CBN330 and CBN550) (Pars Co., Iran), colophony and coumarone (CM-C190) resins (Mahnoor Kimia Co., Iran), and stearic acid (rubber grade, Universal Streams Co., Malaysia) were used as received. Pre-vulcanization inhibitor n-cyclohexy(thio)phthalmide (PVI), antioxidants; 2,2,4-trimethy-1,2-dihydroquinoline (TMQ) and n-isopropyl-n′-phenyl-1,4-phenylenediamine (IPPD), accelerators; n-cyclohexylbenzothiazole-2-sulphenamide (CBS) and tetramethylthiuram disulfide (TMTD) were all purchased from Richon Chem Co., China and used as received.

Sample preparation

The compound was prepared using a Banbury blade HAAKE internal mixer (SYS 90, USA). In a typical compound, natural rubber (NR) was firstly fed into the chamber and after 3 minutes, the CB and CBS were added to them. The compounding process continued for 4 minutes at 90±5 °C for proper dispersion. The other ingredients were added and mixed using a Polymix 200L two-roll mill instrument (Schwabenthan Co., Germany) with a friction ratio of 1:1.6 and rotor speed of 15 rpm for 15 minutes at room temperature. Table 1 shows the details of nine different formulae prepared in this research. The amounts of ZnO, paraffin wax, sulfur, colophony, coumarone, stearic acid, PVI, TMQ, IPPD, CBS, and TMTD are kept constant at 5, 2, 1.8, 2, 1, 1.5, 0.4, 1, 1.5, 1.5 and 0.4 respectively, for each formula. The vulcanization process (semi-efficient type) of the specimens was carried out with a WCH202 compression molding instrument (Toyo Seiki Kogyo Co., Japan) at 155 °C for 5 minutes with the pressure of 160 bars.

Table 1: Details of nine different formulae prepared in this research.

Sample code	NR (g)	Oil 290 (phr)	Oil 840 (phr)	CB N330 (phr)	CB N550 (phr)
CNR0	100	0	12	0	60
CNR1	100	0	12	40	20
CNR2	100	0	12	25	35
CNR3	100	0	12	10	50
CNR4	100	0	12	20	40
CNR5	100	12	0	10	50
CNR6	100	6	6	10	50
CNR7	100	4	8	10	50
CNR8	100	8	4	10	50

Measurements

Rheological analysis was performed using a 4308 rheometry (Zwick Co., Germany) considering ASTM D2084. Fatigue behavior or fatigue life of samples was investigated according to ASTM D4482-11. This standard describes the analysis method for the Fatigue to Failure (FTF) test.

Specimen undergoes tensile strain cycles with a frequency of 1.667 Hz (100 cycles/min) and an extension ratio of 2.5 (150 % elongation) until sample failure occurs in a HT8021 DeMattia Flex Fatigue Tester (Qualitest Co., USA).

The aging behavior of samples was evaluated according to ASTM D573-04 in an oven equipped with a fan. Tensile and hardness analyses were performed after aging (168 hours at 70 °C); a 6025 tensile tester machine (Instron Co., UK) were applied to measure mechanical properties of samples according to ASTM D412 and to determine the Shore A hardness of the cured specimens (with 30 mm diameter and 6 mm thickness), a 3114 hardness tester (Zwick Co., Germany) was used considering ASTM D 2240-05.

The compression set analysis was performed under constant deflection according to ASTM D395 B. At first, the thickness of the sample was accurately measured (12.5 mm). The specimen was then placed in a compression device and compressed to 25% of its primary thickness using spacers to measure the compression. After 2h of assembly, the test device was placed in an oven at 70°C for 22h. Finally, the sample was allowed to cool (30 minutes at ambient temperature) before determining the final thickness. The compression set was calculated using this equation:

$$Compression\ Set = \frac{L_2 - L_1}{L_1} \times 100 \tag{1}$$

Where, L_1 and L_2 are the thickness of the sample before and after compression, respectively.

MiniTab 15 software was used to investigate and compare the obtained results from the viewpoint of statistical analyses. The statistical significance of the obtained values was assessed by a single factor analysis of variance (ANOVA). When the calculated p-value was less than 5%, differences between values were considered statistically remarkable.

RESULTS AND DISCUSSION
Cure characteristics

Generally, a rheometer is applied to determine the crosslinking properties of elastomeric compounds. These characteristics for all formulae were summarized in Table 2. The ts_2 is the time to attain 2 points increase in torque from minimum torque values (M_L) and can be considered as approximate scorch time. The t_{95} stands for the time consumed to reach 95% of the total torque difference from M_L and can be considered as optimum cure time. The M_H is the maximum torque value and the Cure Rate Index (CRI) was calculated as $100/(t_{95}-ts_2)$ [27].

At first, we decide to interpret the effects of CBN330 and CBN550 in CNR0 to CNR4 samples. Table 2 indicates that with an increase in CBN330 content to 40 phr or decrease in CBN550 content to 20 phr for CNR1 in comparison with CNR0 sample, the M_L value has significantly decreased from 24.14 to 19.23 lbf.in. Again, with an increase in CBN550 contents from 20 to 50 phr for CNR2, CNR3

Table 2: Cure characteristics of samples.

Sample code	M_L (lbf.in)	ts_2 (min)	t_{95} (min)	M_H (lbf.in)	t_{MH} (min)	CRI (min^{-1})
CNR0	24.14	2.52	4.68	115.7	8.75	46.29
CNR1	19.23	2.72	4.45	106.6	6.69	57.80
CNR2	21.33	2.95	4.70	107.8	7.64	57.14
CNR3	22.70	2.99	4.79	109.1	8.31	55.56
CNR4	21.51	2.97	4.73	108.0	7.68	56.82
CNR5	23.12	3.09	5.33	123.1	8.98	44.64
CNR6	22.59	3.03	4.92	120.5	8.51	52.91
CNR7	22.13	2.99	4.78	118.2	8.14	55.87
CNR8	22.81	3.08	5.12	121.9	8.39	49.02

and CNR4 specimens, the M_L values have increased ($p < 5\%$) while the CNR1 has the lowest and the CNR0 has the highest M_L. It depicts that CB with a larger particle size deteriorates the processability of the elastomeric compound. This phenomenon can be explained by how the polymer chains and CB fillers interact. Generated free radicals of NR, from the mechanical milling process, can attack and attach to the CB surfaces and form the elastomeric compound. The quantity of attached rubber is directly proportional to the external surface area of CB. Attributed to the smaller specific surface area or lower aspect ratio of larger particle size of CBN550, less elastomer chain can be grafted to its surface. So, the higher particle size of CB induces relatively bad processability to NR compound [28]. This trend was also seen for the M_H values and corresponding times to reach M_H (t_{MH}).

Although both ts_2 and t_{95} show maximum points of 2.99 and 4.79 min, respectively for CNR3 including CBN330/CBN550 ratio of 1:5, the CRI values show different trends. In another word, the CBN330 has remarkably increased the CRI values ($p < 5\%$). This phenomenon may attribute to the better mobility of polymer chains or better processability of rubber compounds in presence of CBN330. By increasing in CBN550 content crosslinking rate decreases and the lowest CRI belongs to the CNR3 sample which contains CBN330/CBN550 ratio of 1:5 (with the exception of CNR0).

To study the influences of plasticizer type on cure characteristics, the CBN330/CBN550 ratio was kept at 1:5 and, along with the paraffinic oil 840 (PO), the aromatic oil 290 (AO) was also added. As seen in table 2, the CNR5 sample which contains 12 phr of AO has the highest M_L and M_H values between samples CNR5 to CNR8 ($p < 5\%$). Another point is that each NR compound that contains a higher amount of AO has higher M_L and M_H values. These findings may attribute to the fact that; the PO has a dramatic effect on reducing the interaction between the rubber macromolecules themselves, and also rubber chains and CB molecules, resulting in better mobility of the polymer segments. From the viewpoint of physical chemistry, the interaction between two materials (*e. g.* NR and processing oil) is reciprocally proportional to the square of the difference of their solubility parameters, $\Delta\delta^2$. This value for NR and PO, in comparison with NR and AO, is significantly greater, and the attractive interaction between NR and PO is thus much stronger than that for the AO. In other words, PO is more miscible with NR and consequently, the mobility of the NR segments in presence of PO became easier than those in presence of AO [29]. Also, the restricted mobility of rubbery chain segments in presence of the AO causes higher ts_2, t_{95}, and t_{MH} and consequently lower values of CRI. Additionally, in comparison to POs, better heat absorption property of aromatic structures[30] prevents perfect heat transferring throughout the rubber compounds and subsequently causes to lower decrease in viscosity, larger ts_2, and t_{95}, and also lower curing rate [31].

Fatigue behavior

The main goal of this research is to achieve a formula with the highest fatigue resistance. Fatigue life is known as the number of loading cycles of a determined test that a material can sustain before failure. This property drastically depends on crack initiation and subsequent

crack propagation. Fatigue crack initiation usually occurs between two or more separated phases throughout the rubber matrix where the maximum stress concentration is usually existed [32].

The comparison of fatigue life for all samples is illustrated in Fig. 1. As shown in this figure, there is an optimum value of CBN550/CBN330 concentration ratio that causes the best fatigue resistance between the samples CNR1 to CNR4 *i.e.* the 5/1 ratio in the sample CNR3. Also, the differences between the fatigue values especially between CNR3 and other samples *i.e.* the CNR1 to CNR4Also, are statistically significant ($p < 5\%$). The synergistic effects of CBN550 and CBN330 are the main reason for this phenomenon. On one hand, the presence of the CBN550 with a larger particle size leads to better processability of rubber compound, and consequently, appropriate dispersion of ingredients within these rubber matrices is obtained. On the other hand, well-dispersed CBN330 with a smaller size can reduce stress concentration between phases which means can decrease crack nucleation. Thus, the formation of fewer crack nuclei results in lower crack initiations and subsequently lower crack propagation [32-34]. It can be concluded from this part that the best ratio of CBN550/CBN330 should be determined more than the ratios of 5/1.

Effects of the AO on fatigue behaviors of the vulcanized samples (CNR5 to CNR8) are also displayed in Fig. 1. As illustrated in this figure, the sample CNR5 containing 12 phr of AO has a better fatigue life than sample CNR0 containing 12 phr of PO ($p<0.05$ for these two samples). This phenomenon can be due to the better resistance of the AOs, especially their thermal resistance [30]. Another point is that the AOs usually contain a few heteroatoms which have a good ability to neutralize the free radicals generated during cyclic or dynamic tests or applications[29] within the rubber matrix and prevent further chain scission. But, the addition of PO has a positive influence or synergistic effect on the fatigue resistance of the compound while the best ratio of PO/AO is 8/4. It means that, on one hand, enhanced mobility of rubber chains, better processability, and appropriate dispersion of ingredients throughout the polymer matrix in the presence of the PO have a great effect on the efficiency of the crosslinking process in the rubber compounds [29]. On the other hand, the presence of a small amount of the heteroatoms (in the AO) can play an effective role in significantly
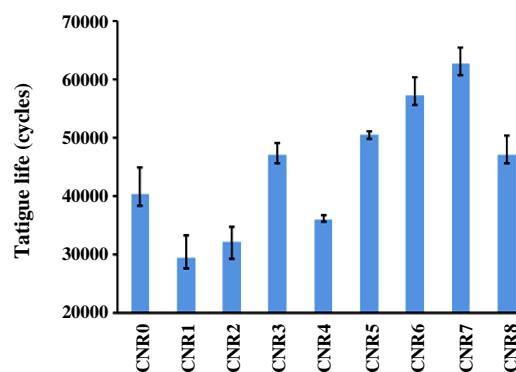

*Fig. 1: Comparison of fatigue life for crosslinked samples.*

reducing chains scission process. It is notable that both paraffinic and aromatic oils can act as an internal plasticizer between rubber chains and carbon black particles to prevent fatigue failure during the cyclic analysis. The friction between the filler (CB) particles in the elastomer matrix would create micro and macrocracks in the rubber bulk or surface leading to catastrophic failure [27]. Statistical analyses show significant differences between the fatigue value of CNR7 and other samples *i.e.* the CNR1 to CNR8 ($p<0.05$). It can be concluded from Fig. 1 that the optimum ratio of PO/AO should be determined between 8/4 and 6/6.

Aging behavior

Aging can be determined as the entirety of the physical and chemical time-dependent transformations which result in a change in properties such as mechanical properties which can affect the duration of useful life for a product [35]. Aging processes can therefore cause physical and/or irreversible chemical changes such as polymer chain scission, breaking and recombination of covalent bonds, or crosslinking. The stiffness, strength, toughness, and hardness of rubbers can be significantly influenced by these changes. In sulfur-vulcanized rubbers, aging behavior can generally lead to the change of polysulphide bridges to di- and/or monosulfide sulfur ones [35,36] and consequently, inappropriate properties are obtained. Table 3 and Fig. 2 illustrate tensile and hardness properties of the CNR0 (control) and CNR7 (which have the best fatigue life) specimens before and after aging for 168h at 70 °C, respectively. It is clear that an increase in young's modulus and hardness values has occurred for both samples.

Table 3: Tensile properties of samples before and after aging.

Property	CNR0		CNR7	
	Unaged	Aged	Unaged	Aged
Modulus (MPa)	4.96±0.20	5.01±0.15	4.28±0.13	4.55±0.17
TS (MPa)	18.17±0.28	16.77±30	18.20±0.31	18.93±0.24
EB (%)	298±15	259±10	357±12	355±16
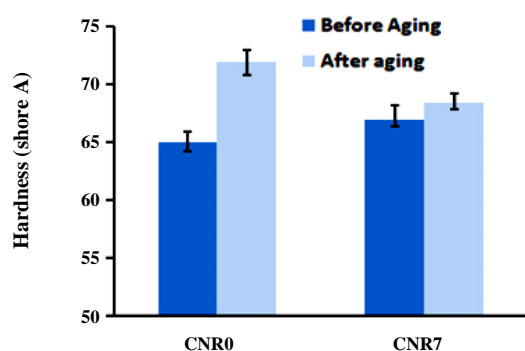
Fig. 2: Hardness property of CNR0 and CNR7 samples after and before aging.

As mentioned before, attributed to the scission of the polysulfide linkages and creation of monosulfide ones (apparently increasing in crosslinking density), modulus and hardness values are increased. But, different results were obtained for TS and EB values in these cases. During thermo-oxidative or thermal aging, the scission of the rubber chains is significantly higher, which in turn reduces the EB and ultimately the TS value (see supplementary material). Similar results were reported in the literature [35-37]. Also, in the viewpoint of statistical analyses, because the calculated *p*-value is less than 5 %, there are remarkable differences between the modulus, TS, EB, and shore A values of CNR7 and CNR0 after aging.

Mainly, the dispersion quality of CB fillers in an elastomer matrix is one of the acute parameters that can affect the fatigue and fracture behavior, and mechanical characteristics of the elastomer compound. Homogeneous and appropriate dispersion of the CBN330 and CBN550 in presence of each other in an optimum ratio (with synergistic effect) [32] in one hand, and internal plasticizing effect of oils (in an optimum ratio) between CB particles and rubber chains, and prevention of phase separation of CBs and rubber matrix, on the other hand, can ensure only slight changes in properties for CNR7 in

compare with significant changes for CNR0 after and before aging. In other words, the CNR7 formulation has an appropriate resistance against aging (Table 3 and Fig. 2).

Compression set

Compression Set (CS) is the ratio of the elastic/viscous components of an elastomer response to a given deformation. A material with the lowest CS value shows the highest level of elastic behavior and therefore, the lowest viscous characteristic. CS analysis is applied to ascertain the ability of rubbers to preserve their elastic behavior after long-term compressive loading or stress [38]. This analysis is especially helpful for applications that rubbers would be in a constant pressure/release condition. The CS values for the samples CNR0 and CNR7 are compared in Fig. 2 (five repetitions of measurement for each specimen). As illustrated in this figure the sample CNR7 has significantly a better CS value than the sample CNR0. Statistical analyses reveal considerable differences between the CS values of CNR7 and CNR0 ($p < 5\%$). This enhancement is drastically attributed to the type of CB *i.e.* N330 which has a specific surface area of about 73-83 m^2/g according to its characteristics obtained from the manufacturer (Pars Co.). Similar results were reported in the literature which confirms that the CB with a specific surface area of about 78 m^2/g can significantly decrease the CS of the NR-based elastomeric compound[39]. On the other hand, the presence of CB with lower particle size can appreciably preserve the elastic property of the rubber compound [40].

CONCLUSIONS

Various natural rubber-based compounds with two kinds of CB *i.e.* N330 and N550 and two kinds of oils *i.e.* paraffinic and aromatic oils (PO and AO) were prepared. Obtained results firstly showed that the addition of CBN330 with small particle size and also the presence of the AO cause unpleasant processability or compound. Secondly,
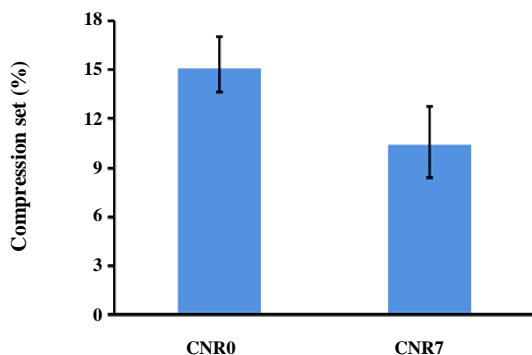
Fig. 3: Compression set analysis for CNR0 and CNR7.

to gain the best fatigue life, the main goal of this research, the ratio of N550/N330 CBs of 5/1 and the ratio of PO/AO of 8/4 applied for the sample CNR7 are the best ratios. In other words, synergistic effects of CBs and oils play an effective role to improve fatigue life. Finally, the formula of sample CNR7 has an acceptable aging resistance and compression set. It means that the starting point to achieve a NR-based compound with more desirable industrial properties can start from this formula. Further study on this formula can lead to great and significant results.

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