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Original

Study of rheological characteristics and mechanical strength properties of natural rubber vulcanizates varying the type and content of carbon black

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Abstract: This paper presents a study about the influence of the size and content of two types of carbon black N220 and N550 with loading of 10–100 phr on the properties of the vulcanized natural rubber (NR). The mechanical characteristics such as the tensile strength, the tensile modulus, the elongation at break, the hardness, the abrasion resistance, and rheological properties of NR reinforced with carbon black were investigated. By analyzing the results of an N220 reinforced NR, the reinforcement gives improvement in tensile strengths when fillers are added up to 70 phr. However, and by referring to elongation at break, a fall of product elasticity is observed. The increase of filler loading results a decrease in rheological properties; optimum cure time, scorch time, cure rate index (CRI). Nevertheless, the N220 rubber compound exhibits slightly higher hardness than those registered for the N550 compounds. Regarding the mechanical properties under tensile stress, the engineer's findings are comparative for all the samples of the study. However, the rubber compound filled N220 or N550 gives comparable results on mechanical properties.

Keywords: Natural rubber NR, carbon black CB, N220, N550, cure characteristics, tensile strength

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1. Introduction

Among the materials, elastomers such as rubber play a vital role in industrial fields (Sasikala & Kala, 2018). The use of rubber-like materials in many applications needs the contribution of the rubber compounding science. Compounding ingredients should be thoroughly selected to produce rubber formulation that respects the final product requirement. For instance, the incorporation of fillers improves the toughness and tensile strength of rubber. Consequently, the final products are more durable and have competitive prices (He et al., 2016). The reinforcement of rubbers depends on the interactions between various parameters related to the fillers, including particle size, particles dispersion, surface area, filler structure, particle shape, and the fillers-rubber matrix bonding quality (Imanah & Okieimen, 2003).

Carbon black (CB) is one of the most common reinforcing fillers used to impart relevant characteristics to rubbers. The properties such as tensile strength, elastic modulus, and abrasion resistance of that material are improved. As a result, CB has been widely used in a variety of rubber engineering products (Rattanasom et al., 2007).

Zaeimoedin and Kamal (2014) studied the effect of adding CB particles on the reinforcement of rubber matrix. The authors confirmed that the modification of the mechanical properties of the rubber-product in addition to the ability of CB to control the viscoelastic behavior of the compound properties. When stretched, natural rubbers (NR) have fascinating physical characteristics due to crystallization (Arroyo et al., 2007).

The main characteristics of rubber are frequently improved by combining it with CB of various surface chemistry and aggregate size/aspect ratio to meet the needs of the application (Hu et al., 2013). It has been reported that the smallest particle size of CB imparts marked reinforcing effect resulting in the improvement of the resistance to abrasion of rubber compounds (Hong et al., 2007). However, a simple addition of fillers could not allow reaching the required mechanical properties. Conveniently, improving the mechanical properties of rubber compounds is conditioned by a tedious selection of loading (Sivaselvi et al., 2021).

Li et al. (2019) claimed that the increase of CB content improves gradually the hardness of rubber. Furthermore, they concluded that as CB content is progressively added, the tensile strength will firstly increase and then decrease. The CB content can also affect the abrasive volume and the reversion period time of cure characteristics (Arayapranee, 2012; Dick, 2009).

To optimize a formulation based on NR used to produce different technical parts, samples were prepared in this study to compare the properties of NR and obtain the best suitable size and rate of CB. To this end, rheological and mechanical properties of natural rubber filled with different contents of CB types, labeled N220 and N550, were investigated.

2. Experimental method

2.1. Materials

In this study, commercial polyisoprene rubber (ribbed smoked sheet, RSS3) from Malaysia is used, the carbon black is intermediate super abrasion furnace (N220), and fast extruding furnace black (N550). The primary raw material has been provided by Technoflex company for rubber products (Berraki, Algiers, Algeria). The additives used in the recipe have industrial grades for rubber processing.

2.2. Preparation of samples

In an open two roll mill at room temperature, elastomer gum, CB, paraffinic oil, ZnO (zinc oxide), stearic acid, TMQ (2,2,4-trimethylbutyl-1,2-dihydroquinoline), and IPPD ISO Propylamino Diphenylamine (IPPD) were combined. After that, accelerators were added to rubber compounds by combining CBS (N-cyclohexyl-2- benzothiazole sulfenamide), TMTD (tetramethylthiuram disulfide), and sulfur curing agent, each formulation took 15 minutes to complete mixing. Table 1 lists the quantities of compounds used in each composition. The raw composites must rest for 24 hours before being evaluated for rheological characterization where scorch time, cure time, and minimum torque of the rubber compound were measured. The compression molding of rubber sheet was performed with an electrically heated compression molding press under 14 MPa at 160 °C for 7 min. Mechanical cutting of specimens from vulcanized plaques was used.

Table 1. Compounding formulation of the NR rubber blend reinforced with CB.

Material	Concentration (Phr[1]/NR)	Compound function
NR	100	Rubber
CB N220/ N550 [2]	10/20/30/40/50/ 60/70/80/90/100	Reinforcing agent
Zinc Oxide (ZnO)	5	Activator
Stearic acid	2	
IPPD[3]	1	Antidegradant
TMQ[4]	1	
OIL Plasticizer	5	Processing oil
Sulfur	1.8	Vulcanizing Agent
Cbs[5]	2.1	Accelerators
Tmmt[6]	0.25	

[1] Phr: parts per hundred rubbers (Dick, 2009).

[2] Particle sizes of carbon black N220 and N550, 20–25 nm; and 40-48 nm, respectively.

[3] N-Isopropyl-N′-phenyl-1, 4-phenylenediamine.

[4] 2,2,4-trimethyl-1,2-dihydroquinoline.
[5] N-cyclohexyl-2-benzothiazolsulfenamide.
[6] Tetramethyl-thiurammonosulfide.

2.3. Cure characterization

The cure time data was employed in the molding process. The cure characterizations of minimum torque (M_L), maximum torque (M_H), torque difference (M_H-M_L), scorch time (t_{s2}), and optimal curing time (t_{c90}) were assessed by using an oscillating disc rheometer (ODR) in accordance with ASTM D2084 standard (R100 S). With a 3° arc amplitude for 8 minutes at 160°C, about 10g of unvulcanized rubber was used to define the cure proprieties.

2.4. Abrasion test

Abrasion resistance refers to a material's capacity to withstand mechanical action such as rubbing, scraping, or erosion that acts progressively to remove material from its surface (Arayapranee, 2012). The abrasion resistance is performed by putting a disk-shaped specimen (16 mm in diameter and 6 mm in thickness, see Figure 1a) in a rotary drum abrasion tester (see Figure1b) according to ISO 4649 standard. The rubber test specimen is pressed at a constant force (2.5 N) and a constant speed (0.32 m/s) over a test emery paper of grade 60. The sample was automatically withdrawn from the test emery paper after reaching an abraded distance of 40m.

Relative volume loss (ΔVrel) of the rubber vulcanizates is estimated according to:

$$\Delta V_{rel} = \frac{\Delta_{mt} \times \Delta_{mcont}}{\rho_t \times \Delta_{mr}} \tag{1}$$

where

$P_t$is the density of sample (mg/mm3) that needs to be measured.

$\Delta_{mt}$is the mass loss (mg).

$\Delta_{mconst}$is the value of the mass loss in (mg) of the reference rubber test piece.

$\Delta_{mr}$is the mass loss(mg); of the reference rubber test piece.

Water is used as a reference density.

The density of the rubber vulcanizates was determined using a densimeter as described in ASTM D792.

2.5. Hardness

All samples with flat surface were cut for hardness test and measured using a (shore A) hardness tester (Zwick digital shore hardness tester) as per ASTM D-2240 standard. The test measures the penetration of a specified indenter into the material under specified conditions of force and time (Sisanth et al., 2017). All testing was conducted at room temperature.

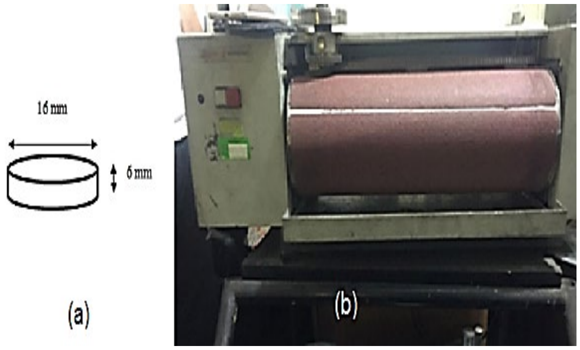

Figure 1. Abrasion test:
(a) dimensions of disk-shaped specimen;
(b) Din Abrader.

2.6. Mechanical testing

Mechanical properties including tensile strength, tensile modulus, and elongation at break of the vulcanizates were determined to study the effect of loading with carbon black on the mechanical properties of NR. The universal testing machine was used to determine tensile strength and modulus of the sample at room temperature according to the procedure described in ASTM D 412 standard at a crosshead speed of 500mm min-1. A dumbbell-shaped specimen (shown in Figure 2) was cut from the rubber sheets. At least five samples were used for the reported values.

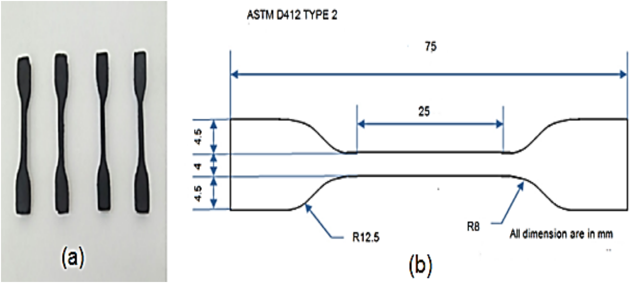

Figure 2. Samples of tensile test: (a) image of Dumbbell-shaped specimens used; (b) Dumbbell-shaped specimen dimensions.

3. Results and discussion

3.1. Unvulcanized rubber cure characteristic

To get the optimum cure characteristics of rubber vulcanizate, rheometric studies were conducted (Arayapranee, 2012). The curing characteristics of loaded NR at different loading rates with N220 and N550 fillers are listed in Tables 2 and 3, respectively. The minimum torque (M_L) is considered as a measure of filler–filler inner aggregate formation for filled vulcanizates and it reflects minimum viscosity of compound

(Al-Nesrawy & Al-Nesrawy, 2021). The maximum torque (M_H) can be expressed as a measure of the vulcanized rubber's stiffness (Surya et al., 2018). The difference between (M_L) and ($M_{H)}$ torque might be expressed as a parameter of crosslink density (Surya et al., 2018). Cure time (t_{c90}) is the time required for the compound to reach 90% of the total state of cure (Savetlana et al., 2017).

The curing rate index (CRI) is a measure of cure reaction. A lower cure time means a higher cure rate (Surya et al., 2018). CRI is calculated as follow (Sivaselvi & Gopal, 2020):

$$CRI = \frac{100}{t_{c90} - t_{s2}} \tag{2}$$

The increasing of CB loading marginally decreases the value of the optimum cure time t_{90} and scorch time t_{s2}, also in the case of curing rate index CRI there is a decrease as shown in Table 2, a higher value of CRI observed in natural rubber filled N220 containing 20 phr (116.28 min^{-1}) while the data in Table 3 shows an increase of CRI in rubber filled N550.

Table 2. The cure characteristics of CB220 reinforced NR.

CB 220 (Phr)	Curing properties					
	M_H (dN.m)	M_L (dN.m)	M_H-M_L (dN.m)	T_{s2} (min)	T_{90} (min)	CRI (min^{-1})
10%	18.75	5.17	13.58	3.2	4.12	108,70
20%	19.94	5.30	14.64	2.90	3.76	116,28
30%	20.72	5.54	15.18	2.76	3.71	105,26
40%	28.97	7.64	21.33	2.40	3.51	90,09
50%	33.82	11.39	22.43	2.17	3.37	83,33
60%	37.79	13.54	24.25	2.10	3.30	83,33
70%	39.79	15.89	23.90	2.07	3.20	88,50
80%	44.26	18.50	25.76	2.00	3.00	100,0
90%	47.40	21.84	25.56	1.82	2.96	87,72
100%	49.40	22.72	26.68	1.38	2.86	67,57

3.2. Abrasion resistance

The results of relative volume loss after an abraded distance (40m) of natural rubber filled with CB N220 and CB N550 with different content are presented in Figure 3. Adding black carbon filler to NR leads to a relative volume decrease up to 70 phr for the N220 composite and 50 phr for N550. This indicates an improvement of the abrasion resistance over these two values, Furthermore, improved results are obtained with the smallest particle size, namely N220 (Sivaselvi & Gopal, 2020).

Table 3. The cure characteristics of CB550 reinforced NR.

CB 550 (Phr)	Curing properties					
	M_H (dN.m)	M_L (dN.m)	M_H-M_L (dN.m)	T_{s2} (min)	T_{90} (min)	CRI (min^{-1})
10%	17.63	3.73	13.90	2.36	4.05	59,17
20%	19.02	3.86	15.16	2.23	3.88	60,61
30%	19.35	3.98	15.37	2.13	3.74	62,11
40%	24.61	6.05	18.56	2.06	3.68	61,73
50%	25.16	10.00	15.16	1.95	3.46	66,23
60%	27.50	11.24	16.26	1.78	3.29	66,23
70%	29.62	13.90	15.72	1.66	2.97	76,34
80%	29.80	14.36	15.44	1.50	2.85	74,07
90%	30.84	15.10	15.74	1.39	2.53	87,72
100%	34.56	16.82	17.74	1.22	2.24	98,04

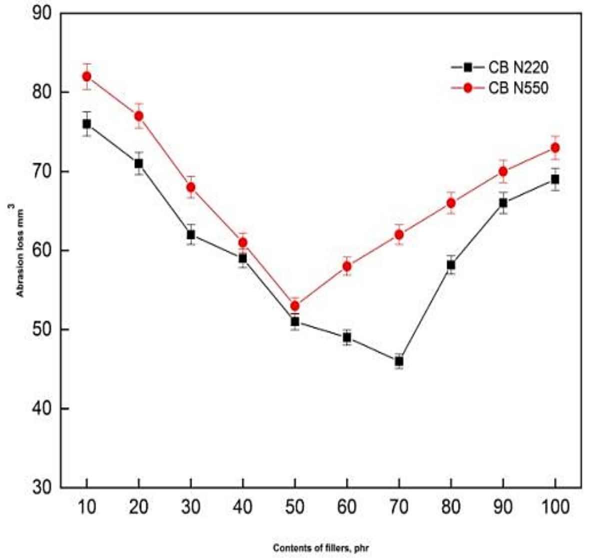

Figure 3. Variation of abrasion resistance of rubber vulcanizates filled with different contents and types of CB.

3.3. Hardness

Figure 4 shows the variation of hardness with the particle size and amount of fillers on target the hardness of NR increases significantly with increasing contents of fillers, as fillers incorporate into the rubber, the elasticity of the rubber chain is reduced, resulting in more rigid vulcanizates (Savetlana et al., 2017). It has been observed that the hardness values showed an improvement for all studied samples regarding the loading rate. However, the N220 composite shows significantly more improvement compared to N550 with variations not exceeding 5% up to 70 phr and then the gap becomes more important up to 8.3% for 90phr. Moreover, this indicates that the more the size of the particles is fine, the more the value of the hardness increases. This can be explained by the correct charge distribution within the matrix according to the work of El-Gamal (2019). It is noteworthy that the hardness level is also improved by the rate of fillers added to the rubber matrix.

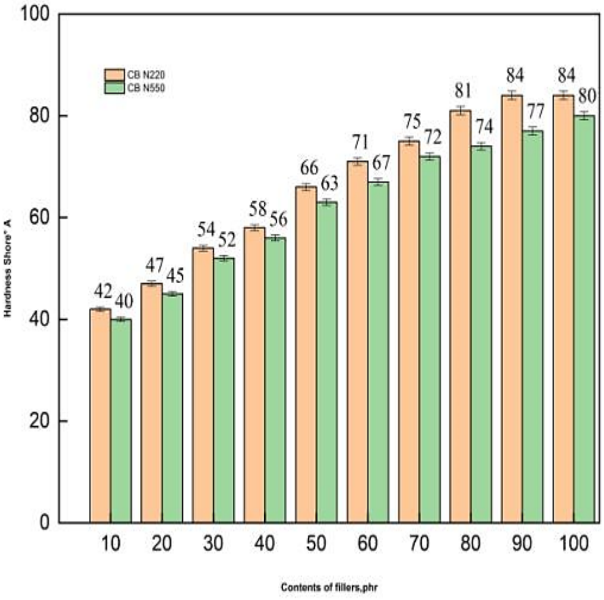

Figure 4. Variation of hardness with different contents and types of CB.

3.4. Mechanical properties

Tensile test

The results of tensile properties such as tensile strength, elongation at break and tensile modulus of all formulations of natural rubber filled carbon black with varied sizes and amounts, are presented in Figures 5, 6 and 7.

The addition of carbon black increases the tensile strength of the vulcanizates. There is a proportional increase in stress with increasing rate of carbon black, reaching an optimum of 19 MPa up to a concentration of 70 phr of N220, and 17 MPa up to a concentration of 50 phr of N550 Figure 5. which confirms the strengthening of the black; the limited amount of agglomeration causes the high tensile strength property (Savetlana et al., 2017), after this increase the tensile strength was reduced at the concentration 80 phr and 60 phr successively. Once the specific surface was saturated, a decrease in stress was observed.

Furthermore, Figure 6 shows a decrease of the elongation at break with increasing rate of CB. This behavior results from an important three-dimensional network with a consequence to get less elasticity and by the fact decreases the elongation. Additionally, this reduction is due to the adherence of the fillers to the polymer phase leading to the stiffening of the polymer chain, and hence, resistance to stretch when strain is applied (El-Gamal, 2019; Sivaselvi et al., 2021).

The two types of CB have identical tensile modulus values up to 40 phr Figure 7.

The modulus continued to rise after that, but the N220 was higher than the N550. As more carbon black is introduced into the rubber matrix, the stiffness of the vulcanizates increases resulting in a higher modulus (Imanah & Okieimen, 2003).

At 80 phr, an unexpected result was reported there was a decline; however, there was a significant increase at 90 phr.

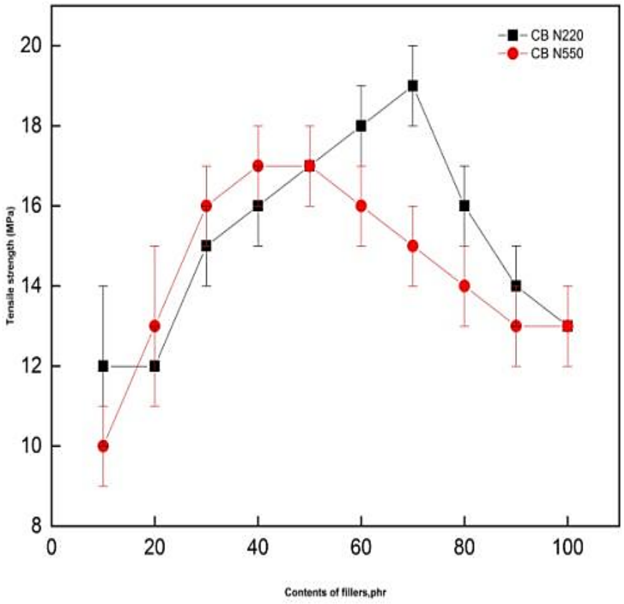

Figure 5. Variation of tensile strength with different contents and types of CB.

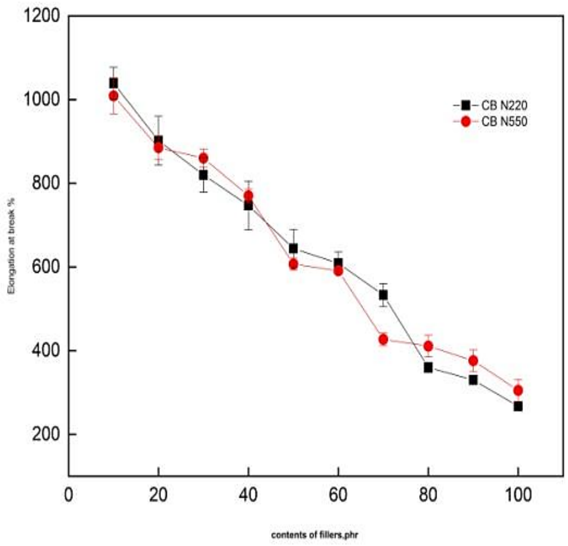

Figure 6. Variation of elongation at break different contents and types of CB.

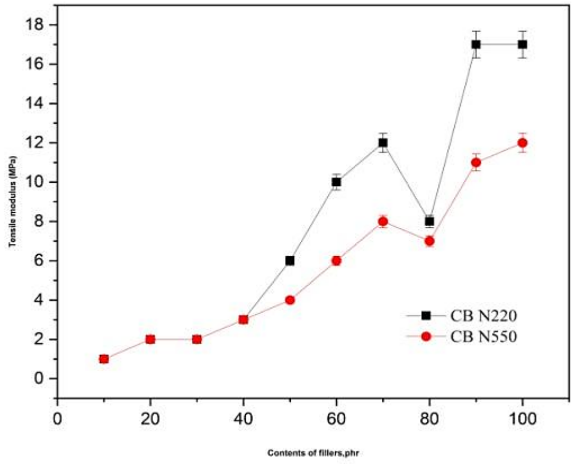

Figure 7. Variation of tensile modulus with different contents and types of CB.

4. Conclusions

Adding fillers like carbon black with several types labeled N220 and N550 to natural rubber strengthens the final product properties.

We remind that, the study was focused on the characterization of two kinds of composites imposed by the company's needs, which did enable to optimize the studied property values of the two composites N220 and N550 to be applied in automotive gaskets, shoe soles and boat dock bumpers. It has been noticed that, with addition of fillers:

The vulcanizates filled CB N220 showed lower abrasion loss than CB N550.

The hardness (shore A) of rubber increased gradually.

Tensile strength firstly increased and then decreased, elongation at break decreases and the tensile modulus increases

As a result of the improved dispersion of carbon black N220 into the rubber compound, it may provide superior mechanical qualities than carbon black N550 due to suitable properties of these blending.

The optimal concentration of filler where the results of abrasion resistance and tensile strength are the best was recorded at 70 phr for the N220 and 50 phr for the N550. As prospects we recommend studying the influence of particle size in depth.

Conflict of interest

The authors have no conflict of interest to declare.

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