

## Research Article

# Burst Diaphragms Based on Carbon Black/Silica Hybrid Filler Reinforced Nitrile Rubber Compounds

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Received 23 June 2014; Revised 25 August 2014; Accepted 25 August 2014; Published 2 September 2014

Academic Editor: Eri Yoshida

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Nitrile rubber (NBR) based elastomer compounds containing different carbon black/silica composition ratios were prepared using laboratory-scale two roll mill. According to the cure characterization results, addition of the reinforcing filler, either carbon black or silica, shortened the optimum cure time and also scorch time of samples compared to that of pure NBR gum where the optimum cure time and scorch time both decreased with increasing the silica content of hybrid filler. Analysis of mechanical properties showed that burst strength of carbon black-rich NBR compounds was higher compared to the samples containing silica. This is presumably due to the higher elongation at break observed in NBR/silica compounds revealing lower crosslink density. In fact, adsorption of curing agents onto the functional groups present at the silica surface would be responsible for the lower crosslink density. According to the Barlow's formula, despite the higher tensile strength of NBR/silica compounds, higher elongation at break leads to the lower burst strength of NBR/silica/carbon black diaphragms.

## 1. Introduction

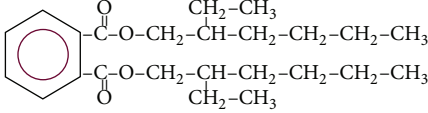
Many industries, such as petrochemical, chemical, pharmaceutical, food processing, and oilfield applications, rely on pressurized equipments and assemblies such as pressure vessels and propellant subsystems. Burst diaphragms, also referred to as bursting discs and rupture discs, as pressure relief devices, sacrificially protect mission-critical systems from predetermined differential pressure, either positive or negative, that is, overpressurization and potentially damaging vacuum conditions. Major advantages of the use of rupture discs compared to pressure relief valves would be leak-tightness, no maintenance and cost.

Burst discs usually have steel or aluminum housings enveloping a one-time-use membrane commonly made of cold-rolled steel, nickel alloys, aluminum, or any other material with yield strength close to its ultimate strength. Nitrile rubber and hydrogenated Nitrile Butadiene Rubber, as a family of unsaturated copolymers of acrylonitrile (ACN), are commonly used to produce such diaphragms operating

up to 120°C. NBR is resistant to aliphatic hydrocarbons, oil, and fuel and hence is selected for this study contemplated for oilfield applications.

The choice of the elastomer compound additives is closely linked to the type of properties to be achieved. Carbon blacks, presenting excellent properties such as heat, chemical, and weathering resistance, lightweight, electroconductivity, and low thermal expansion [1], are commonly used with both polar and nonpolar rubbers to enhance elongation, modulus, tear strength, tensile strength, and resilience. On the other hand, Silica offers a unique combination of tear strength, abrasion resistance, and aging resistance compared to carbon black [2]. Besides, at elevated temperatures, such as those encountered during compound mixing process, the silanol groups present on the surface of silicas may attach to a number of chemical groups present in rubber compounds. It is worth noting that among rubbers (e.g., SBR, NR, BR, EPDM, and IIR), NBR has the strongest interactions with silica surface through hydrogen bonding according to inverse gas chromatography results [3–5]. Accordingly, since both

TABLE 1: Characteristics of the materials used.

Material	Details	Supplier
NBR (Europrene E N 4560)	ML (1 + 4) 100°C = 60 ACN content: 45%	Polimeri Europa
Carbon black	HAF (N-330) Surface area = 75–78 m <sup>2</sup> /g	Pars
DOP		LG chemical, South Korea
Silica (VN3)	Surface area = 175 m <sup>2</sup> /g	Evonik Degussa

carbon black and silica possess their own advantages, the use of hybrid filler or blends of silica and carbon black in rubber compounds would give the benefits from each filler. Therefore, partly substitution of carbon black with silica in the elastomer compound formulation seems to yield positive results.

Rattanasom et al. [7] examined the mechanical properties of natural rubber reinforced with silica/carbon black hybrid filler at various ratios in order to determine the optimum silica/carbon black ratio. They also reported that the use of silica/CB blends enhances the mechanical and dynamic properties of natural rubber vulcanizates as the rubber vulcanizates containing 20 and 30 phr of silica in carbon black/silica hybrid filler exhibit better overall mechanical properties. Wang et al. [8] observed significant improvements in tear and abrasion resistance of SBR/BR (70/30) compounds containing carbon black and silica fillers. Ghoreishy et al. [9] claim that by replacing part of carbon black with equivalent amount of silica in SBR/BR tire compounds, a major increase in fatigue resistance is obtained to the point that 20 phr silica where the best compromise between fatigue properties, rolling resistance, and wet/ice traction can be achieved at 5 to 10 phr silica substitution.

Carbon black/silica hybrid filler is reported to reinforce natural rubber compounds [10], butadiene rubber [3, 11], EPDM [12], Styrene Butadiene Rubber [6], SBR/NBR [13], and SBR/BR [8] but to the best of our knowledge, there is no report on the characterization of silica/carbon black filled NBR compounds. The main aim of this investigation is to study the effect of silica/carbon black hybrid filler on the burst strength of diaphragms made of NBR compounds.

## 2. Experimental

**2.1. Materials.** Detailed characteristics of the materials used to prepare the compounds studied in this work are summarized in Table 1.

**2.2. Preparation.** Table 2 summarizes the detailed composition ratio and nomenclature of the designed samples prepared using laboratory-scale two roll mill (Imanaka Machinery Co., Ltd.) at 50°C according to ASTM D3848. The compounding process was commenced by the mastication of nitrile rubber

TABLE 2: Formulation and nomenclature of NBR/CB/Silica compounds.

Sample code	NBR	Carbon black	Silica
NBR	100	0	0
NC50S0	100	50	0
NC25S25	100	25	25
NC0S50	100	0	50

on the laboratory two-roll mill for two minutes with a 2/1 friction ratio. Then, stearic acid, zinc oxide, sulfur, antioxidant, and other accelerators were added to the compound followed by addition of carbon black and/or silica compounded for 5 minutes. The total amount of hybrid filler in all formulations was kept constant at 50 phr. Therefore, the amount of silica or CB ranged from 0 to 50 phr. Curing was conducted under hot cold double press (Yamatu Scientific Co., Ltd.) according to ASTM D3848.

**2.3. Characterization.** The rheological measurements were performed according to ASTM D2084 using Oscillating Disk Rheometer (Monsanto Rheometer-10) at 80°C.

Tensile properties and abrasion resistance of prepared compounds were measured using Zwick/Roell 2030 (Germany) and Santam—SAT 500 according to ASTM D412 and ASTM D5693, respectively. The microstructure of the nanocomposites was observed by a TESCAN scanning electron microscope.

A set up was developed to measure burst performance of samples equipped to a chamber (with maximum allowable pressure of 50 bar) lid with two flanges, hydraulic test pump, and transducer (see Figure 1). A pressure gauge was devised to monitor the pressure variations with time.

## 3. Results and Discussion

**3.1. Cure Characteristics.** Figure 2 depicts the cure curves for pure NBR, NC50S0, NC25S25, and NC0S50 prepared according to Table 2. Detailed cure characteristics of the elastomer compounds including optimum cure times ( $t_{90}$ ) and torque values ( $\Delta M = M_H - M_L$ ) are compared in Table 3. Comparing to the results revealed that addition of the reinforcing filler, either carbon black or silica, shortened the optimum cure

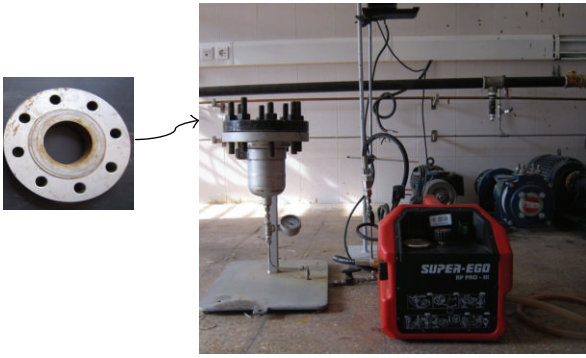


FIGURE 1: Burst strength measurement set up designed for characterizing diaphragm samples.

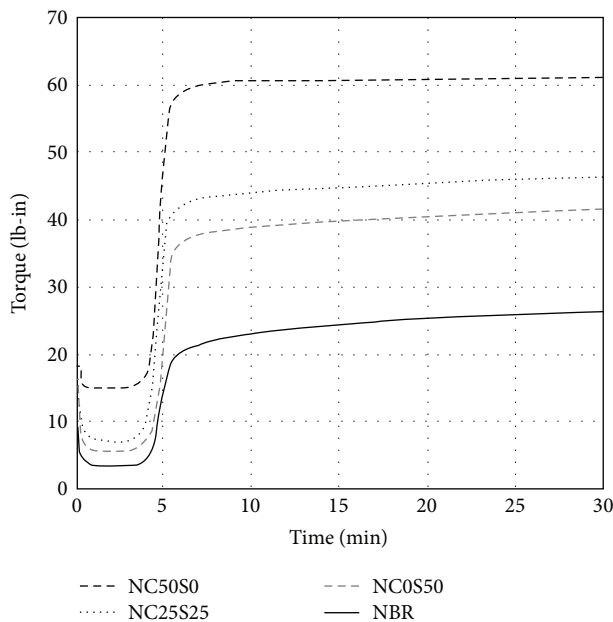


FIGURE 2: Cure curves of NBR/CB/Silica samples.

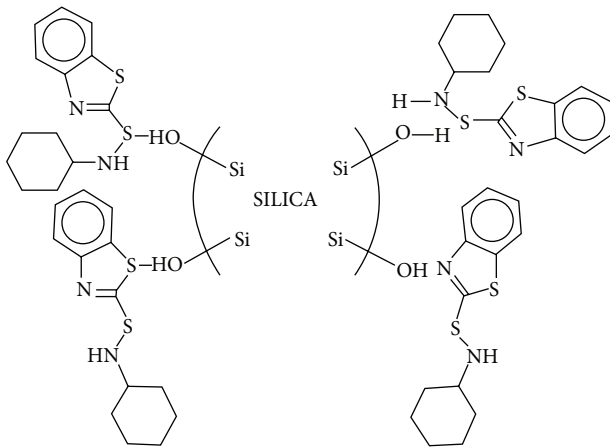


FIGURE 3: Schematic of the interactions between silica surface and N-cyclohexyl-2-benzothiazole sulfonamide (CBS) [6].

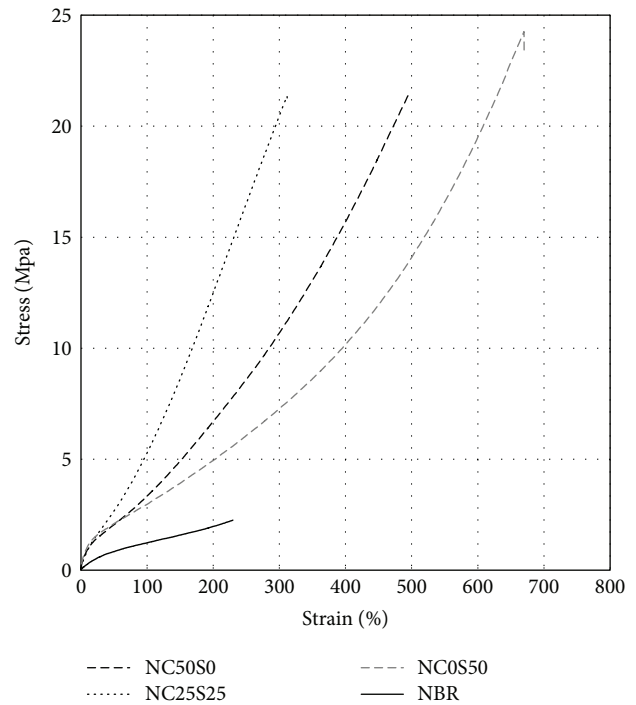


FIGURE 4: Stress-strain curves of NBR/CB/Silica elastomer compounds with different composition ratios.

time and also scorch time of samples compared to that of pure NBR gum. On the other hand, the optimum cure time and scorch time both decrease with increasing the silica content of hybrid filler. In fact, the larger surface area present at higher silica contents might adsorb alkaline components such as N-cyclohexyl-2-benzothiazole sulfonamide (CBS) functioning as the accelerator within the curing formulation consequently prolonging and/or restricting the cure initiation and replete [6]. Figure 3 depicts the probable interactions between silica and the accelerator. Similar effects can result from the reaction of zinc ions with silica filler particles because zinc is involved as an activator in the cure system. Zinc oxide and stearic acid react to produce zinc stearate, an intermediate in the vulcanization mechanism. The active silanols on the silica particle surface will react with zinc stearate. If the reaction is given enough time to progress, it would eventually rob all the zinc leaving none to activate the vulcanization reaction.

Table 3 also compares the torque differences ( $\Delta M = M_H - M_L$ ) measured for the elastomer compound samples. The rising trend of torque differences with addition of filler to the NBR gum could be ascribed to the compound viscosity corresponding to the interactions established between the rubber matrix and the reinforcement. Results show that, at the fixed filler content studied here, the torque differences decrease with increasing the silica substituent indicating the higher affinity of carbon black particles to agglomeration within the compound. In fact, the strong interactions between NBR functionalities and the silanol groups present at the silica surface might be responsible for this behavior. Improved polymer, filler interactions in silica filled NBR

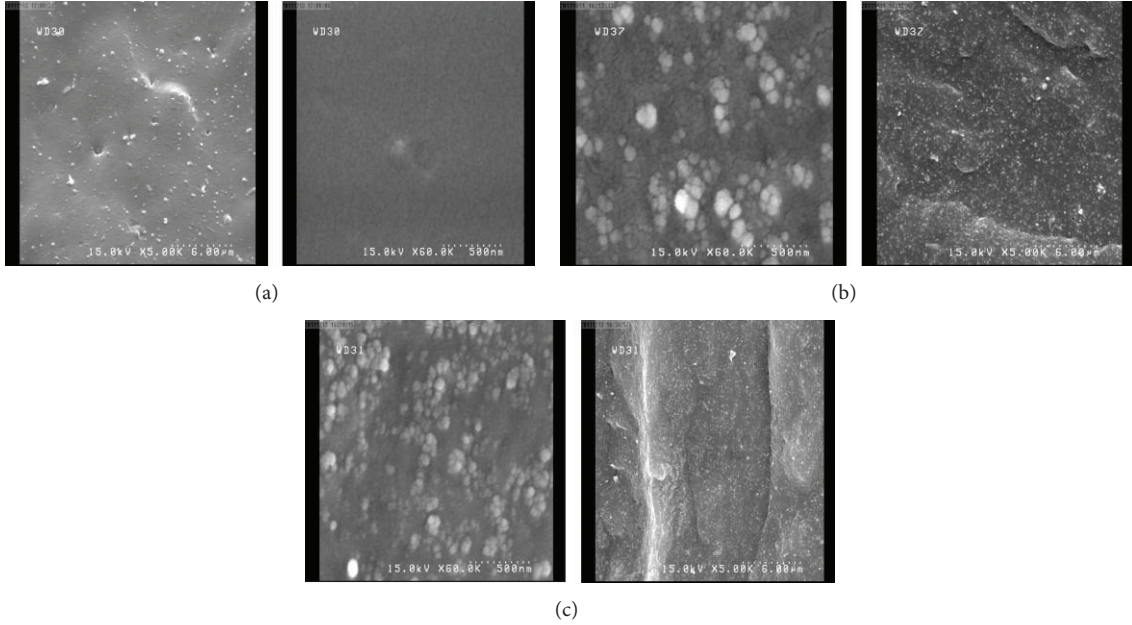


FIGURE 5: SEM micrographs of samples (a) NC50S0, (b) NC25S25, and (c) NC0S50.

TABLE 3: Cure characteristics of NBR/CB/Silica elastomer compounds with different composition ratios.

Sample code	$M_H$	$M_L$	$M_H - M_L$	$t_{90}$
NBR	28.00	5.530	22.47	12
NC50S0	61.64	15.170	46.47	9
NC25S25	47.79	7.739	40.05	7
NC0S50	41.83	6.910	34.92	6

compounds relative to the interactions involved in carbon-black compounds, has been reported elsewhere [14–16].

The reaction of zinc with silanols could also contribute lower viscosity that can be presumed or taken for granted; reasonable as a supposition: presumably by reducing the tendency for silica particles to attach to each other and form a strong silica network. The lower torque undergone by the compound in silica rich compounds can also be ascribed to the lower crosslink density as the result of curing restriction at the presence of silica [6, 11].

**3.2. Mechanical Properties.** Figure 4 depicts the stress-strain behavior of pure NBR, NC50S0, NC25S25, and NC0S50 elastomer compounds containing different composition ratios of CB/silica. As expected, the tensile modulus of compounds increases with the addition of reinforcing fillers, either carbon black or silica. At fixed filler loading investigated here, increased silica content leads to a decrease in the tensile modulus. The different stress-strain responses observed with silica is primarily due to the differences in its surface chemistry compared to carbon black. As formerly discussed, the reactive silica ties up more of the rubber chemicals that are needed for sulfur crosslinking reactions and, thus, yields a compound with lower crosslink density. Therefore, the lower

crosslink density in silica-rich compounds compared to those with higher CB/silica ratios is responsible for this behavior. On the other hand the further agglomeration of carbon black particles would lead to the elastomer chains to be trapped into the filler networks which would consequently increase the effective filler volume [17]. This would yield to higher tensile modulus at low elongations. At higher elongations, the interactions established within the agglomerated filler network would break and the filler-elastomer interactions become dominant [3].

Table 4 summarizes the mechanical properties measured for the elastomer compounds prepared here. Addition of reinforcing filler, due to the higher rigidity compared to the elastomer macromolecules, increased the compound hardness, as expected. However, substitution of carbon black with silica at fixed hybrid filler content would intensify the hardness increment due to the higher filler-matrix interactions.

There is a mathematical formula that calculates the relationship of internal pressure to allowable stress, nominal thickness, and diameter of the sphere. Simply stated, Barlow's formula calculates the pressure containing capabilities of a component. The formula takes into account the sphere diameter ( $D$ ), wall thickness ( $t$ ), and the manufacturer's specified minimum yield strength of the component ( $S$ ):

$$P = \frac{4St}{D}. \quad (1)$$

In elastomers, the component effective thickness depends on the material elongation capability. To modify the formula for the present application,  $\lambda$  is entered as the elongation at break. Finally; we will have

$$P = \frac{400St}{D\lambda}. \quad (2)$$



TABLE 4: Mechanical properties of the prepared samples.

Property	Test method	Dimensions	NBR	NC50S0	NC25S25	NC0S50
Hardness	IRHD	—	50	66	70	76
Modulus 100%	D412	MPa	0.70	6.30	3.32	2.95
Modulus 200%	D412	MPa	1.50	7.60	6.71	4.94
Modulus 300%	D412	MPa	2.70	12.12	10.72	7.27
Tensile strength	D412	MPa	1.80	21.33	22.20	24.21
Elongation at break	D412	%	231.1	319.2	478.2	657.8
Abrasion	D5963	mm <sup>3</sup>	380.0	291.3	279.18	273.05
Burst strength	—	barg	—	21.1	18.3	14.6

According to Table 4, NC50S0 shows higher burst strength compared to NC25S25 and NC0S50. The lower crosslink density between rubber chains in silica-rich samples would lead to higher percentages of elongation. Although sample NC0S50 has a higher tensile strength compared to sample NC25S25 and NC50S0, according to the modified formula suggested above, it shows lower burst strength, as expected.

**3.3. Microstructural Analysis.** Figure 5 shows the SEM observations for prepared samples. The harsh surface of silica-rich samples (NC25S25 and NC0S50) indicates the stronger filler-rubber interactions within the sample. It can be seen that at the fixed hybrid filler content investigated here, with increasing the silica content a better dispersion is obtained which is attributed to the higher affinity of silica particles to the NBR elastomer chains versus carbon black.

## 4. Conclusions

Carbon black/Silica hybrid filler reinforced elastomer compounds based on acrylonitrile butadiene rubber (NBR) were prepared using laboratory-scale two roll mill. The effect of different CB/silica ratio on the properties and behavior of the samples was investigated. According to the cure curves, at the fixed hybrid filler content investigated here, optimum cure time and scorch time of the samples were prolonged with increasing the silica content. Burst strength of NBR/Silica elastomer diaphragms was lower than NBR/Silica/Carbon black due to lower crosslink density arisen from the adsorption of curing agents onto the functional groups at silica surface. In fact, despite the higher tensile strength of NBR/Silica compounds, the higher elongation at break leads to the lower burst strength of NBR/Silica/Carbon black diaphragms, this is confirmed by the suggested formula according to Barlow's.

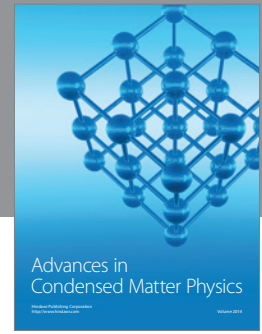
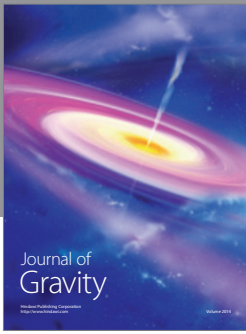
## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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