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# Comparative Analysis of NR/EPDM Ratio and Carbon Black Selection on Mechanical Properties of Vulcanized Pneumatic Fenders

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**Abstract:** In this research, natural rubber RSS1 was formulated with synthetic rubber EPDM and various types of carbon black filler for marine rubber fender products. This study aims to determine the effect of the NR/EPDM ratio and type of carbon black filler on the mechanical properties of rubber compounds. Mechanical properties testing followed the referenced ISO 17357-1:2014. The optimum rubber compound formulation was found in a sample with NR/EPDM ratio of 100/0 and carbon black N220 filler which has superior mechanical properties.

Keywords: Aging, Carbon Black, EPDM, Natural Rubber, Pneumatic Fender.

## 1. Introduction

Pneumatic fenders are a type of rubber fender used in maritime applications to provide cushioning and protection during ship-to-ship or ship-to-dock operations. They are typically cylindrical or cylindrical-shaped rubber structures filled with compressed air. These Fenders are designed to absorb kinetic energy during vessel berthing or mooring, thereby reducing the impact force, and preventing damage to both the vessel and the docking facility<sup>1-2</sup>. The inner and outer parts of the pneumatic fender work together to absorb and distribute the impact energy. When a vessel comes into contact with the fender, the compressed air in the inner bladder compresses and displaces, absorbing the kinetic energy of the impact. The outer part of the fender provides the necessary strength and protection to maintain the integrity of the inner bladder and prevent any damage from the environment, such as: abrasion, ozone and ultraviolet (UV) radiation<sup>3</sup>.

The technical specification of a vulcanized rubber pneumatic fender refers to ISO 17357:2014. To meet these requirements, research was conducted to obtain the best formulation as raw material for a vulcanized rubber pneumatic fender. The rubber must undergo several stages for application, including mixing and vulcanization. During the mixing stage, additives are added to achieve the rubber compound's expected behavior. The rubber is heated with filler, activators, accelerators, and sulfur at 140-160 °C during the vulcanization stage to form cross-links between long-chain rubber molecules that improve

mechanical properties and weather resistance<sup>4</sup>.

Mixing natural rubber (NR) and synthetic rubber (SR) in a rubber compound is a common practice in the rubber industry. The combination of NR and SR offers a balance of properties and allows for customization of the final rubber product. NR has excellent tensile strength, tear resistance, and low-temperature flexibility, while certain Synthetic Rubber, such as Chloroprene Rubber (CR) or EPDM rubber, can offer improved abrasion resistance, chemical resistance, or heat resistance. Selection of the specific types and ratios of NR and SR depends on factors such as the desired properties, processing requirements, and cost considerations for the intended application. EPDM rubber properties are suitable for its weather and heat ozone resistance, which are not found in NR<sup>5-7</sup>. This type of synthetic rubber is primarily used in mechanical work and industrial applications such as automobiles, construction, electronic industries, electricity, and many more.

Carbon black is widely used as a reinforcing filler in rubber compounds and as a pigment in a variety of products. It is produced in large quantities and finds applications in industries such as rubber, plastics, coatings, inks, toners, and batteries. Carbon black greatly enhances the tensile strength, tear resistance, and abrasion resistance of rubber. It acts as a reinforcing filler, improving the overall mechanical properties of the rubber compound. Carbon black particles form a network-like structure within the rubber matrix, providing strength and support. Carbon black can provide some level of UV

protection to rubber compounds. It absorbs and dissipates UV radiation, reducing the degradation caused by sunlight exposure. This property is particularly important for outdoor applications, such as pneumatic fenders.

Carbon black is available in different grades, including N220, N330, and N660. The selection of the appropriate grade of carbon black depends on factors such as the desired properties, performance requirements, and cost considerations for the specific rubber compound. The influences of carbon black variations on natural rubber (NR) compounds were investigated, and 20 phr N220 has superior mechanical and conductivity properties<sup>8</sup>. A high carbon percentage in the compound will improve the composite's viscosity and modulus 300 (M300) due to the strong rubber filler interaction<sup>9</sup>. The interfacial interactions and filler distributions between the rubber matrix and filler particles are essential factors in determining rubber compound properties<sup>10</sup>.

Based on ISO 17357 :2014: Ships and marine technology — Floating pneumatic rubber fender (PF), PF outer layer material is a synthetic rubber. Based on previous research on the use of NR materials mixed with Chloroprene Rubber (CR) type synthetic rubber shows an increase in mechanical properties and can be used as the manufacture of the outer layer of rubber fender products<sup>11</sup>. Some studies also showed that variation in carbon black could also affect the properties of the resulting vulcanization<sup>12</sup>. Therefore, variations in the amount and type of carbon black (CB) were carried out in this study. The biggest concern is that poor interfacial bonding cannot be avoided because fillers have a propensity to aggregate, significantly reducing mechanical and electrical properties. Compared to initial expectations and causes predicting elastic models fail because of incorrect filler/polymer bonding assumptions<sup>13</sup>.

In previous research, the ratio of natural rubber to synthetic rubber was changed to see how it affected the mechanical characteristics of HR (Hard rubber) and SR (Soft Rubber) in vulcanized rubber pneumatic fenders. Given that it showed hardness values that were closest to the required values, a compound with a formulation ratio of 70/30 phr of natural rubber and synthetic rubber was identified to meet the fender rubber requirements for SR and HR<sup>14</sup>. Other research has also been carried out by varying natural rubber (NR) and synthetic rubber (CR) for the rubber pneumatic fender formula, the best formula in this study is shown by the composition of the NR 70%: CR 30% mixture sample which has the best resistance to the aging process. Other studies have been conducted with rubber blending with different blend ratios between natural rubber (SIR10) and synthesized rubber (CR) affecting mechanical properties for rubber pneumatic fender formulations. The addition of CR causes an increase in tensile strength and elongation at break<sup>11</sup>.

Since the cost production for CR is very expensive, this research aims to substitute the synthetic rubber with EPDM which is expected to improve heat resistance,

ozone, and aging properties. In this study, the use of NR mixed with EPDM-type synthetic rubber with a ratio of 100/0, 70/30, and 0/100 was set to achieve the optimum mixing ratio. Variation grade of carbon black N220, N330 and N660 are used in rubber matrix as a filler determined rubber compounds properties to meet requirement. The choice of filler grade can be influenced by the desired balance between cost and performance requirements for the application.

The results of the experiment were tested using the tensile strength, hardness, tear strength and compression set method to determine the mechanical properties of the rubber compound to achieve the objectives set according to ISO 17357 :2014.

## 2. Experimental

### 2.1 Materials

The ratio of Rubber Smoke Sheet (RSS1) as NR from local producer in Indonesia and EPDM Keltan 8570 as synthetic rubber from Lanxess were used as main material. Carbon black is used as an active filler (N330, N330, N660) manufactured by Cabot Indonesia (Table 1). The compound additives were aktiplast 8 (A8), coumarone resin (CoR), stearic acid (SA), Zinc Oxide (ZnO), 2,2,4-trimethyl-12-dihydroquinoline (TMQ), N-Cyclohexyl-2-benzothiazole sulfonamide (CBS), paraffin wax (PW), paraffinic oil (PO) and Sulfur (S) with the same amount for each formulation. The compound with the ratio of RSS/EPDM and carbon black filler variation was formulated (Table 2).

Table 1. Carbon black, average surface area and particle size.

Carbon Black	Average surface area (m <sup>2</sup> /g)	Particle size (nm)
N220	112 - 115	20 - 25
N330	76 - 80	28 - 36
N660	34 - 36	56 - 70

### 2.2 Methods

Table 2 shows the variations in compound formulation. The rubber compounds were blended in an internal mixer with chamber capacity 3 L, fill factor 75 %, temperature of 80 °C and 32 rpm (mixer rotor speed)<sup>5</sup>. The filler and additives were mixed for 4 minutes after mastication of rubber for 2 minutes. Sulphur and CBS were added for 4 minutes. The compound was then shaped into a sheet in a milling machine at 70 °C and stored at room temperature for 24 h before molding in hotpress machine to make specimens testing. The uncured compound was tested for cure time using a rheometer according to ASTM D5289 to obtain ts2, t90 and Curing rate index (CRI).

$$CRI = 100/(tc90 - ts2) \quad (1)$$

Furthermore, the compound is vulcanized using a Dr. Collins model hotpress at a temperature of 140 °C and a pressure of 65 bar with a time adjusted to the rheometer results. The vulcanizates were tested for mechanical properties before and after aging including tensile strength, elongation at break (EaB), shore A hardness, tear strength, compression set and carbon dispersion<sup>15</sup>.

The dispersion measurement process investigates according to ISO 11345 measurements. The vulcanized rubber sample was cut crosswise with a thickness and width of 8 mm and 10 mm, respectively, then placed on the camera system to scan the level of dispersion in the sample. The optical dispersion will be compared with the dispersion classification to show the percentage of dispersion quality (0-100%) of rubber and filler vulcanized samples, based on ISO standard 11345 (Rubber - Assessment of carbon black and carbon black/silica dispersion - Rapid comparative methods).

Table 2. Design compound formulation (phr)

Ingredients	Compound formulation								
	PF1	PF2	PF3	PF4	PF5	PF6	PF7	PF8	PF9
RSS	100	70	0	100	70	0	100	70	0
EPDM	0	30	100	0	30	100	0	30	100
A8	3	3	3	3	3	3	3	3	3
ZnO	6	6	6	6	6	6	6	6	6
SA	3	3	3	3	3	3	3	3	3
CB 220	35	35	35						
CB 330				35	35	35			
CB 660							35	35	35
TMQ	2	2	2	2	2	2	2	2	2
PW	1	1	1	1	1	1	1	1	1
CoR	8	8	8	8	8	8	8	8	8
PO	6	6	6	6	6	6	6	6	6
S	2	2	2	2	2	2	2	2	2
CBS	1	1	1	1	1	1	1	1	1

### 3. Result and Discussion

#### 3.1 Curing Time

The effect of carbon black types and NR/EPDM ratio on the cure characteristics of compounds are illustrated in Fig. 1 for scorch time and optimum cure time. Both scorch time and curing time tended to increase with increasing of EPDM ratio, but the different type of carbon black did not impact significantly to the curing time and scorch time.

The decreased scorch time of the sample, according to Nor & Othman, suggested higher processing capabilities. The total amount of heat history that may be sustained

before the rubber is transformed to a rubber cross link condition determines processing ability<sup>16</sup>. Because scorch time has a positive connection with viscosity, as scorch time (TS2) and curing time (TC90) decreases, so does viscosity. In terms of processability, rubber composite with N220 has a lower scorch time than N330 and N660 at the same NR/EPDM ratio<sup>17</sup>. Based on CRI data shown in Fig. 2, N220 has a higher Curing Rate Index (CRI) compared to N330 and N660 which means that this kind of carbon black accelerates reaction between Sulphur and rubber compounds<sup>18</sup>.

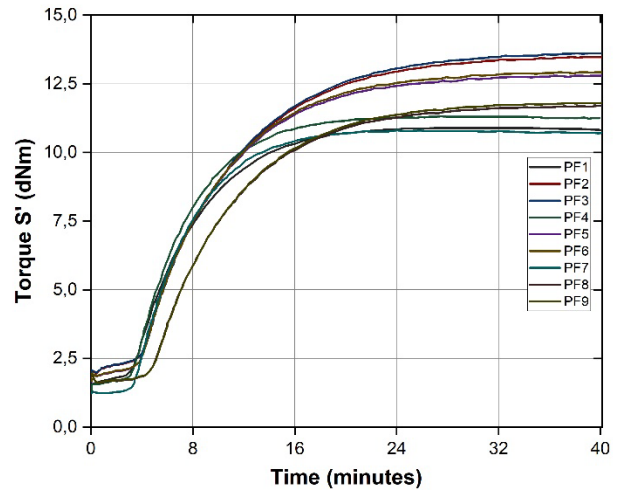


Fig.1: Rheometer data

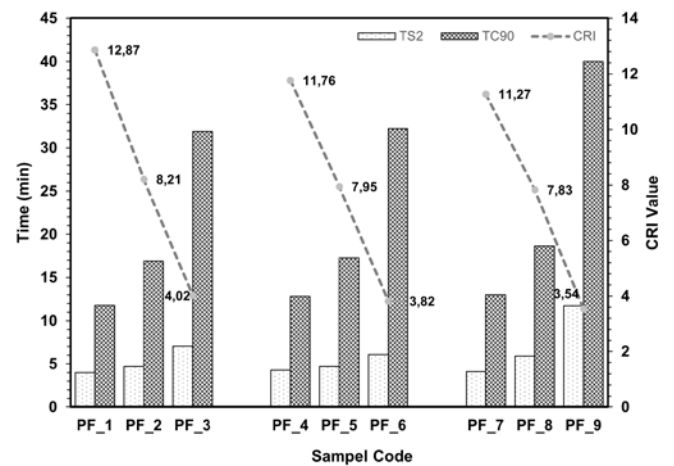


Fig.2: Scorch time and optimum cure time and CRI

#### 3.2 Mechanical properties before aging

Tensile strength testing determines the material's mechanical properties by pulling it and calculating the EaB. Tensile strength is the highest tensile stress a material can tolerate before cracking, fracture, or deformation<sup>19-21</sup>. It is hypothesized that the change in the observed tensile is related to the number of cross-links generated at the filler surface<sup>22,23</sup>.

The rubber compound formulation with NR/EPDM ratio 100/0 and carbon black N220 filler has superior mechanical properties in tensile strength at 27.30 MPa and EaB at 713.89 % due to NR having excellent elasticity and

carbon black surface area. Moreover, the sulfur substance and surface area of carbon black have influenced the cure kinetic and enhanced physical cross-linking of the EPDM/carbon black compound<sup>24</sup>. Changes in molecular structure and properties are unavoidable during the cross-linking phase. Rearrangement of molecules causes interconnected molecules via covalent bonds<sup>25</sup>. Besides that, N220 rubber compound, had higher interaction of rubber/carbon black and improved several desirable characteristics than N330 and N660<sup>26</sup>.

The increase in the tensile strength value was caused by combination of chemical bonding and physical interaction between rubber molecules and carbon black. These changes of mechanical properties are due to high surface energy derived from its unsaturated polyaromatic structure and functional groups of carbon black. Whereas, in the absence of carbon black, rubber vulcanization only has tensile strength that comes from cross-linking by sulfur atoms.

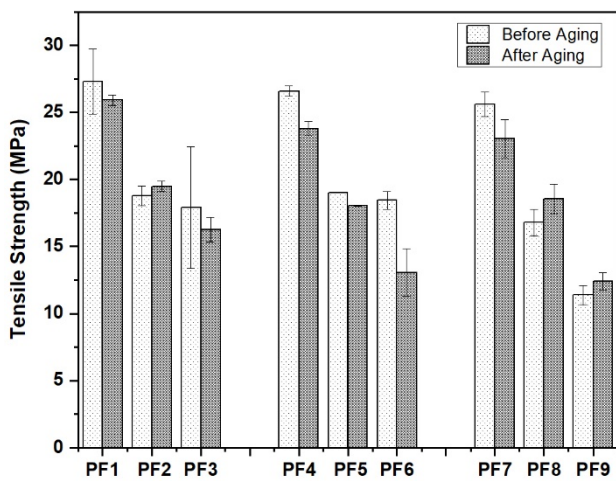


Fig. 3: Tensile strength before and after aging.

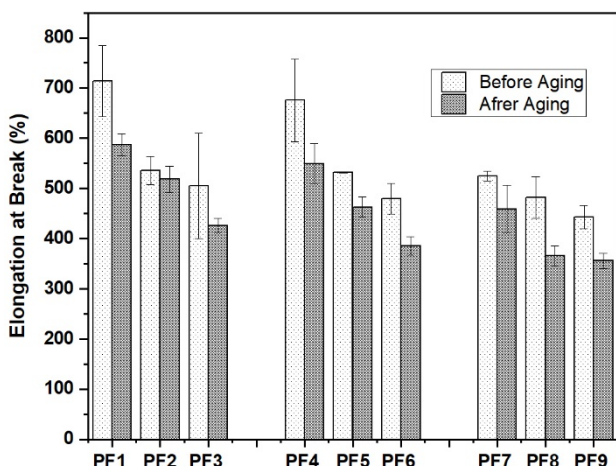


Fig. 4: Elongation at break before and after aging.

In Fig. 3 and Fig. 4, the maximum tensile strength and EaB values were obtained in PF1, the NR sample with the addition of carbon black N220, where there was an increase in the tensile strength and EaB values of 61.996%

against the PF9 sample. The break, which is quite significant, is due to the higher elongation. The filler-polymer interaction becomes more dominant, in contrast to the lower elongation, which is still dominated by the filler's interaction. This is also related to the results of the carbon dispersion test, where PF1 gives the highest dispersion result among others, namely 99.12%.

A hardness test was performed to determine the modulus elasticity of rubber by measuring its resistance to rigid indentation under an applied force. Based on Fig. 5, hardness testing results before aging show that adding EPDM can increase the hardness of the sample in all variations of CB due to EPDM having more cross-links and greater specific gravity, which will increase rubber compound hardness. The hardness value of rubber vulcanizates is influenced by the filler to additive ratio and the density of the material's molecular linkages<sup>27</sup>. The results showed that the use of carbon black N220 provides the highest hardness compared to N330 and N660 since N220 has a smaller particle size, so the interaction between rubber and carbon black becomes higher.

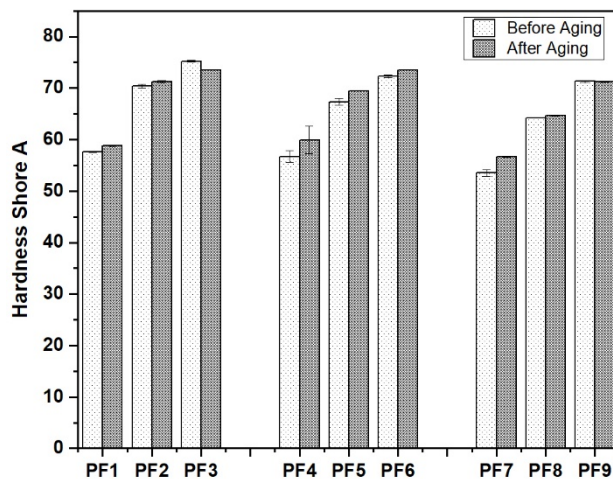


Fig. 5: Hardness shore A before and after aging.

Filler can increase the rubber blend's hardness shore A value<sup>28</sup>. The hardness of shore A value affects the rebound resilience test, where the smaller the hardness value, resulting more excellent rebound resilience value. Temperature increases cause materials to soften, and as a result, their ability to resist compression forces decreases<sup>29</sup>. The test results show in Fig. 6 that PF7, with the ratio of NR/EPDM 100/0 with N660, has the highest rebound resilience value of 68.90%.

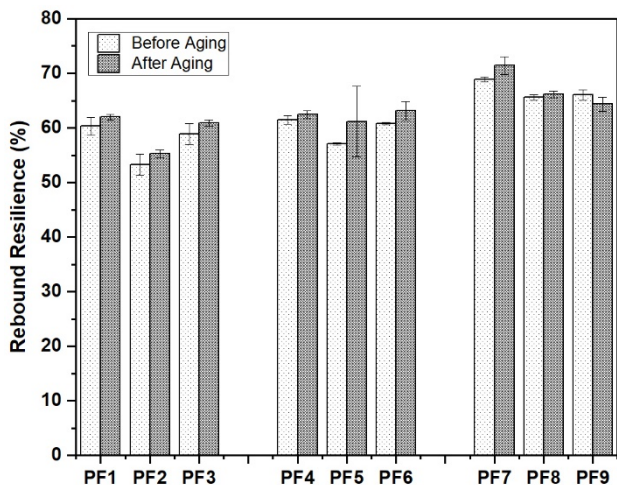


Fig. 6: Rebound resilience before and after aging.

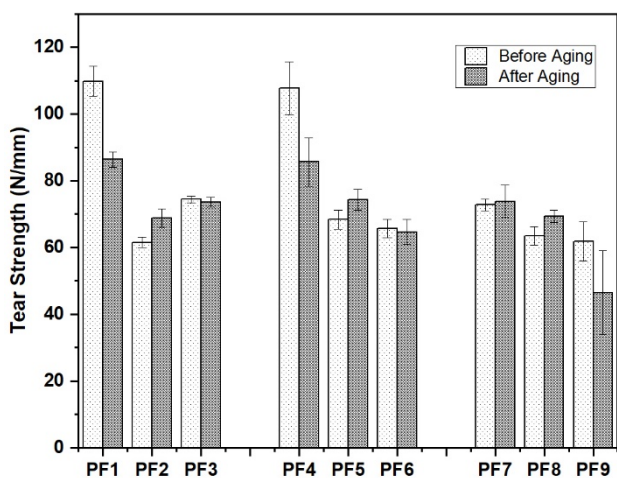


Fig. 7: Tear strength before and after aging.

The tear strength results in Fig. 7 show that the higher NR content sample has a higher tear strength value than the EPDM and NR/EPDM samples because of the excellent elastic properties of NR<sup>30</sup>. The largest tear strength value was in the PF1 sample (NR/EPDM 100/0 with N220), where the occurrence of rubber bonds with carbon black N220, which was stronger, would prevent the tearing process of the resulting vulcanizate.

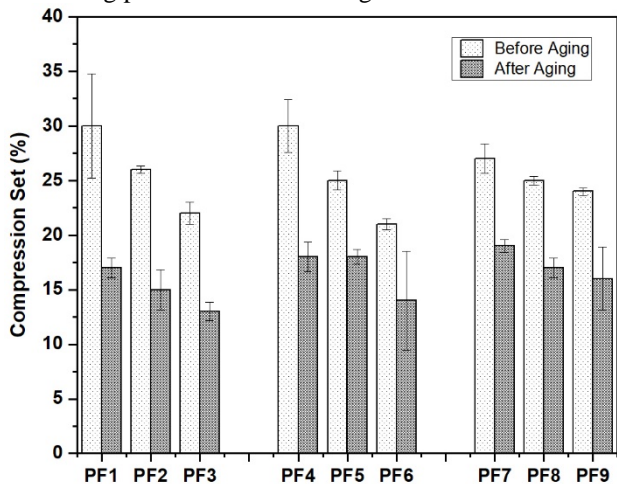


Fig. 8: Compression set before and after aging.

The compression set measured the percentage of initial deflection after a period. The specimens have high compressive strength, and the fiber can withstand the majority of the load, according to a high compressive strength value<sup>27</sup>. 0% means a fully recovered height, and 100% indicates no recovery<sup>14,31</sup>. Fig. 8 depicts the results of numerous compounds' unaged and thermally aged specimens. The data from the compression set test for each variation of carbon black (N220, N330, N660) shows a decrease in the % compression set value for each NR/EPDM ratio. This phenomenon indicates that more addition of EPDM will decrease the elasticity of the sample. The highest % compression set value is shown by PF1, which is 30%. The compression set requirement for rubber fenders is no more than 30%<sup>11</sup>.

### 3.3 Mechanical properties after aging

Environmental factors such as ozone attack, heat, and weather degraded rubber product mechanical properties, such as elasticity and strength. The results from the tensile tests after and before aging are shown in Fig. 3, where the tensile strength after aging has decreased as a result of the aging process. In accordance with the ISO 17357 :2014, the change in tensile strength and EaB after aging is not more than 80%. The highest tensile strength value before aging is PF1 which is 27.304 MPa and after aging, at the value of 25.909 MPa or 94.89%. The highest EaB was shown by PF1 of 713.898% before aging to 587.085% after aging, the decrease was around 82.24%. Ozone test experiment results show there are no encountered cracks as shown in table 4.

The degradation of rubber properties value is quite important in the prediction of their lifespan<sup>32</sup>. Molecular changes happen as the temperature rises, resulting in mechanical properties loss because of the post-treatment effect (resulting in some hardening), cutting of cross-links (causing softening), and breaking of molecular chains<sup>28</sup>. Chemical reactions cause a progressive decrease or increase in modulus and hardness, as well as a loss of elasticity and tensile properties, depending on the elastomer's pressure, temperature, permeability, and exposed surface area.

### 3.5 Carbon dispersion

The dispersion quality is evaluated with vulcanized rubber samples. Fig. 7 and table 3 depict the variety of dispersion qualities obtained using the Disperse tester. Testing the distribution of carbon black using a carbon dispersion tester shows that PF1 has the highest percentage of carbon distribution, which is 99.12% at reference level 8. This result means that carbon black is evenly dispersed in the rubber compound. In the formulation with the same ratio, the dispersion of carbon black N220, N330, and N660 decreased because carbon black N220 has a smaller particle size, so the distribution is more even and easier to interact with rubber polymer chains.

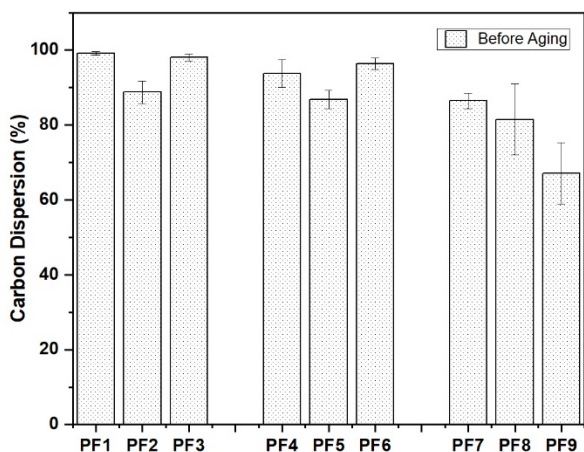


Fig.9: Carbon dispersion before aging.

Table 3. Agglomerate counts

Formulations	Agglomerate (counts)
PF_1	0.59
PF_2	14.54
PF_3	27.44
PF_4	5.67
PF_5	22.40
PF_6	23.62
PF_7	15.72
PF_8	51.90
PF_9	88.15

Mechanical property studies on carbon black filled vulcanizates demonstrate that numerous elements contribute to the filler's reinforcing action. Aside from the hydrodynamic effects, occluded EPDM, chemical cross-links, and the creation of the physical EPDM-carbon black network, the filler-filler interactions contribute significantly to the modulus in the low-strain zone, but they are disrupted at high stresses<sup>7</sup>.

Table 4. Comparison of testing results and standard ISO 17357-1:2014.

Requirement properties	PF								
	1	2	3	4	5	6	7	8	9
<b>Before aging</b>									
Tensile strength (≥ 18 MPA)	+	+	-	+	+	+	+	-	-
Elongation at break (≥ 400 %)	+	+	+	+	+	+	+	+	+
Hardness (60 ± 10 Shore A)	+	+	+	+	+	+	+	+	+
Tear strength (≥ 400 N/mm)	+	+	+	+	+	+	+	+	+
Compression set (≤ 30 %)	+	+	+	+	+	+	+	+	+
<b>After aging</b>									
Tensile strength (Not less than 80% normal tensile)	+	+	+	+	+	-	+	+	+
Elongation at break (Not less than 80% normal elongation)	+	+	+	+	+	+	+	-	+

Hardness (Not more than 8-unit shore A of normal hardness)	+	+	+	+	+	+	+	+	+
Ozone test	No Crack								

\* (+): fulfil requirement  
 (-): not fulfill requirement

### 4. Conclusion

Carbon black and NR/EPDM ratio was considered to define an effect on mechanical properties of rubber compound. From the results of the Comparison of testing results and standard ISO 17357: 2014 (Table 4), there are several before aging and after aging formulations that meet the requirements, namely PF1, PF2, PF4, PF5, and PF7. However, the PF1 sample with NR/EPDM ratio of 100/0 using carbon black N220 before aging had the best results, namely tensile strength 27.304 MPa, EaB 713.898%, 57.6 hardness shore A, tear strength 109.78 (N/mm), and compression set 30%. Ozone test experiment results show there are no encountered cracks.

While the after-aging results show that the PF1 sample gives results in accordance with the requirements. PF1 confirmed to have the best aging strength where the decrease in mechanical properties of tensile strength is up to 94.89%, EaB to 82.24%, and hardness shore A to 58.8 shore A. From the results of this research sample PF1 is recommended as a raw material for the manufacture of pneumatic fender products.

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