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Effect of carbon black fillers on tensile stress of unvulcanized natural rubber compound

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ABSTRACT

This paper presents the effects of carbon black (CB) fillers towards the tensile properties (tensile modulus, tensile stress) and microstructure of natural rubber (NR) compound under the applied force. Two types of the unvulcanized Standard Malaysian Rubber-Constant Viscosity 60 (SMR-CV 60) compound which are the unfilled and the CB-filled compound were used in this study. The tensile tests were conducted on both compounds by using the INSTRON Universal Tensile Machine at room temperature. Based on the results, the higher tensile modulus for CB-filled SMR-CV 60 compound was observed compared to the unfilled compounds which were 2.89 MPa and 1.42 MPa, respectively. However, the CB-filled SMR-CV 60 compound exhibited lower tensile stress value at 0.2535 MPa compared to the unfilled compound with the value of 1.0612 MPa. The increase of the SMR-CV 60 stiffness with the decreasing tensile stress was further proven using the theoretical modelling. Furthermore, the significant changes in the rubber network formation for CB-filled SMR-CV 60 compared to the unfilled SMR-CV 60 were also observed through the microstructure examination. Finally, the condition of permanent set showed slow recovery in the CB compound after it was applied with tension. In conclusion, the use of CB-filled SMR-CV 60 compound was shown able to improve the final tensile modulus property but also reduced the tensile stress compared to the unfilled SMR-CV 60 compound. Based on the findings, further research should be conducted on the effect of CB towards the vulcanized SMR CV-60 in terms of mechanical properties.

Keywords: Natural rubber compound; tensile stress; carbon black

INTRODUCTION

The world rubber production in 2014 was estimated at 28.5 million tonnes with 41% of the production accounted for natural rubber while the other 59% was dominated by synthetic rubber [1]. In Malaysia, the rubber manufacturing industry has shown a remarkable progress, in terms of rubber consumption and export earnings. The indication of the total consumption recorded from 1990 to 2007 has shown a total increase of 209% with natural rubber (NR) as the main ingredients [2]. However, the total consumption of NR started to decline in 2009 before it started to rise up to the present [3-5]. With better infrastructure and research and development (R&D) support from the Malaysian Rubber

Board (MRB) and Tun Abdul Razak Research Centre (TARRC), Malaysia managed to list as the world's seventh largest consumer of NR behind China, India, the USA, Japan, Thailand and Indonesia [1]. The NR has been extensively used in multiple types of applications including the engineering application such as marine, railways, civil, and automotive. The NR was infamously known as an ideal polymer in the application of static and dynamic problem due to its excellent properties such as high elasticity and toughness. It contains about 30-40% of hydrocarbon and 6-8% of the non-rubbery component such as proteins, mineral salt, carbohydrates, organic acids and lipids dispersed in water [6, 7]. These non-rubbery components control the structural changes of the rubber molecule during coagulation as well as affecting the NR compound properties [8-13]. The NR, which is classified in the hydrocarbon group, is composed of polyisoprene arranged in high cis-1,4 configuration. This type of cis-arrangement allows the molecular chain to crystallize spontaneously at low temperature or when subjected to tension [14]. It also allows the elasticity and flexibility features to combine with the crystallization-induced strength and hardness when it was stretched; causing less kinetic energy and reduces heat build-up when subjected to repeated loading or called as resilience.

Besides that, the elasticity properties allow NR to rapidly recover into its original shape and dimension whenever distorted. It makes the NR suitable to be used in dynamic application such as automotive engine isolator and off-road tires for vehicles in the mining site [14, 15]. Moreover, the NR has the ability to withstand the large strains without permanent deformation or fracture in which enable the NR to work in any kind of environment such as oil-rich and high loading environment [16]. Couple with that, it also has an ability to resist most of the corrosive chemicals, which allows it to be used for a long period with minimum maintenance [14]. However, only the cured NR could offer the advantages mentioned above. On the contrary, the uncured NR is unintended for customers use as it is associated with low chemical resistance against heat, oxygen and ozone, low modulus value, and insufficient hardness [17]. Thus, the properties of uncured NR can be enhanced according to the customers' requirement. Several methods are available; one of it is by adding the reinforcing particles or fillers. There are various types of fillers available such as carbon black (CB), silica, clays, and calcium carbonate. Besides that, the current research trends also used plastic such as the Polyvinyl chloride (PVC) polypropylene (PP) and natural fibre as filler to the rubber matrix [18-20]. Among those fillers, CB is the most common filler that has been used in the rubber fabrication industries. This is due to its ability to enhance the compound properties at a lower cost instead of easy to be produced and high availability [17, 21].

The properties of CB compound depend on several factors. However, most of the properties possessed by the CB compound depend on the carbon loading and particle sizes, which involve the influence of particle-particle interactions [22, 23]. The application of these factors is usually related to each other, either using a different carbon loading of fillers with the same particle size or vice versa. One of the purposes of reinforcing the CB into the NR compound is to increase the rubber stiffness. In a study conducted by Arib Rejab et al. in 2013, the mechanical properties of four different types of the elastomeric mount with different percentages of CB loading were investigated [23]. The study showed that the static stiffness for all types of the elastomeric mounted increased with the increasing of CB percentage. Besides that, the addition of CB in the NR compound can highly influence the tensile strength of the rubber compound. Rattanasom and Prasertsri in 2008 studied the partial replacement of clay with various types of CB (N330, N550, and N774) in NR compounds [24]. The researchers found that a compound with N330 carbon gives the highest tensile strength and elongation at break. This is due to the low crosslink density and total filler loading. The reinforcing efficiency in CB plays an important part for the increasing of tensile strength. The reinforcement is usually attainable at 20 nm to 50 nm filler particle size [25, 26]. Their study also showed that the better N330 carbon filler dispersion in NR compound was responsible for highest tensile strength. Other than that, the variation of carbon concentration in the NR compound can effectively affect the rubber modulus properties. The modulus value increases at the higher concentration and rapidly grows to the higher values at smaller particle size [17]. The addition of fillers into the NR compound also exhibits the nonlinear mechanical behaviour such as the Payne's and Mullin's effects [17]. The stress softening was also observed in both filled and unfilled rubbers except for the unfilled non-crystallizing rubbers, respectively [27].

Although there were many studies on the effect of carbon black fillers towards the NR compound, those studies were only limited to the vulcanized rubber and fewer on unvulcanized rubber despite the limited usage of the unvulcanized NR. Still, there was a need to study the properties of the unvulcanized NR either in the compound or raw state as it was important to certain rubber processing operation. Besides that, the difference between the behaviour of the unvulcanized and vulcanized NR compound reinforced with CB filler under various force also become a concern. Thus, the aim of this paper is to study the effect of carbon black reinforcement in the unvulcanized Standard Malaysian rubber with constant viscosity-60 (SMR CV-60) compound in terms of tensile properties. This material is currently used by the Malaysian Rubber Board (MRB) on the development of the SMR CV-60 on the application of the laminated rubber-metal spring [28-30]. The tensile test was performed on two types of unvulcanized NR compound; the unfilled SMR CV-60 and CB-filled SMR CV-60. The tensile stress, permanent set and microstructure analysis of both SMR CV-60 compounds were compared and are discussed in this paper.

MATERIALS AND METHODS

Sample Preparation

In this study, the unvulcanized NR compound called the Standard Malaysian Rubber-Constant Viscosity 60 (SMR-CV 60) was used. It is a conventional normal grade rubber product derived from the natural rubber in Malaysia. It is widely used around the world as it has very low shear and much less time than its bulk modulus value. For the experimental purpose, two types of unvulcanized SMR CV-60 compound were prepared, which are the unfilled SMR CV-60 and CB-filled SMR CV-60. A rectangular shape specimen was cut from an SMR CV-60 sheet with the dimension of 90 mm length, 20 mm width, and 4 mm thickness. The example specimen is shown in Figure 1.

Experimental Setup

In order to investigate the effect of CB fillers on the tensile properties of the unvulcanized SMR CV-60 compound, a simple uniaxial tensile test was performed on the unfilled and CB-filled SMR CV-60 compound. The tensile tests were conducted by following the procedure mentioned in the standard ASTM D6747-10 (Part A). The tensile test was performed by using the INSTRON Universal Tensile Machine (UTM) at room temperature and operated using the Instron Bluehill® 3.0 software. The specimen was tightly placed in the grip of the tensile machine and run on constant rates of separation of moving jaws at 0.8 mm/s until the specimen reached up to 600% of elongation. The experiment was repeated three times and all the data were automatically recorded by the computer connected to the testing machine. In both samples, the before and after tensile tests were used in the microscopic procedure in order to investigate the effect of the tensile stress on the microstructure in scales of 50 µm magnification by using Zeiss LSM 510 Confocal Microscope. For the permanent set analysis, the regular ruler was used to measure the residual extension of the specimens after the experiment. Figure 2(a) shows the tensile machine that used in the tensile test, while Figure 2(b) shows the set up for the tensile test.

Figure 1. Example of SMR CV-60 specimen for tensile test.

(a) (b)

Figure 2. Experimental setup (a) INSTRON 8802 Universal Tensile Machine; (b) Tensile tests.

RESULTS AND DISCUSSION

Tensile Stress

Table 1 shows the experimental results for both the unfilled NR and CB-filled SMR CV-60. Based on the result obtained, the maximum tensile stress recorded by the unfilled SMR CV-60 and CB-filled SMR CV-60 at 600 % of elongation were 1.0612 MPa and 0.2535 MPa, respectively. Besides that, the tensile modulus value for the CB-filled SMR CV-60 was twice of the unfilled SMR CV-60 with the value of 2.89 MPa. The relationship between the tensile stress and percentage of elongation was plotted into a graph shown in Figure 3. Based on the graph, it was showed that the tensile stresses were continuously increased as the percentage of elongation increased for both compounds. Unlike the vulcanized NR where the tensile stress increased as the fillers loading increased, it was found that the tensile stress of the unfilled SMR CV-60 was higher than the CB-filled compound as the elongation increased. The unfilled SMR CV-60 exhibited a good ductility on the strain-stress properties where the stress increased with the increasing strain. While in the CB-filled SMR CV-60, it was found that the materials displayed the small elastic behaviour, where the low-stress level was produced at high strain. On the other hand, it was also found that the CB-filled SMR CV-60 exhibited thicker line rather than the unfilled NR line in which refers to the noise level of the NR compound under the tensile force. The noise level resulted from the effect of molecular interaction between the matrix and fillers particle in respond to the force applied during the tensile test, where the fillers acted as the strain amplifier, which strongly influenced the flow behaviour and its mechanical properties [15, 31].

Table 1. Tensile test result.

Properties	Unfilled NR	Carbon filled NR
Percentage of elongation (%)	600	600
Maximum tensile stress at specified elongation (MPa)	1.0612	0.2535
Tensile modulus (MPa)	1.42	2.89

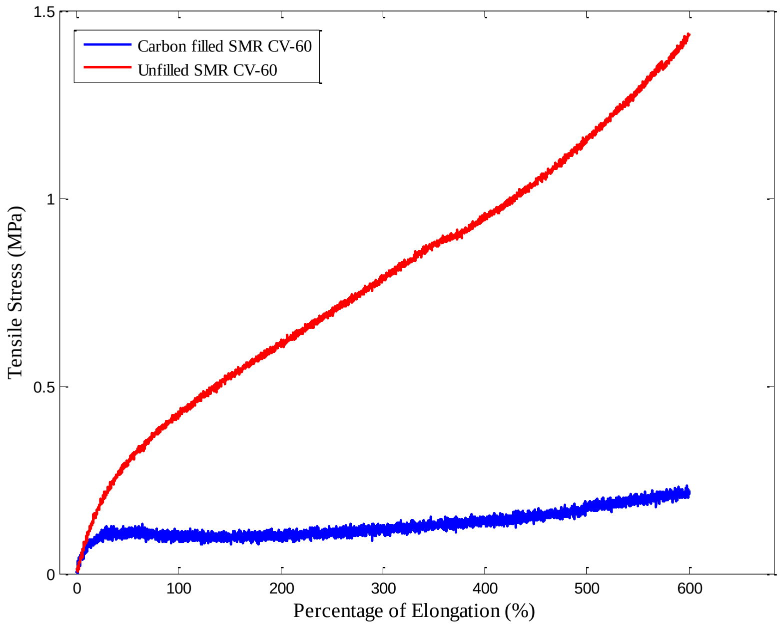


Figure 3. Relationship between the tensile stress and the percentage of elongation for both unfilled and CB-filled SMR CV-60 compound.

Furthermore, the high modulus value exhibited by the CB-filled SMR CV-60 compound showed that the stiffness of the materials increased due to the addition of the CB. It was also theoretically proven that CB fillers were able to enhance the stiffness of the SMR CV-60. By referring to Eq. (1):

$$k = \frac{EA}{L} \tag{1}$$

where, *k* is the stiffness, *E* is the Young's Modulus, *A* is the area, and *L* is the length. On the other hand, tensile stress can be written as Eq. (2):

$$\sigma = \frac{F}{A} \tag{2}$$

where, *F* is the force and *A* is the area.
Eq. (1) is rearranged to obtain Eq. (3) which then inserted into Eq. (2) to form the new Eq. (4).

$$A = \frac{kL}{E} \tag{3}$$

$$\sigma = \frac{FE}{kL} \tag{4}$$

Eq. (4) can also be written as Eq. (5).

$$\sigma \propto k' \left(\frac{FE}{kL} \right) \tag{5}$$

Now, it shows that the stress is directly proportional to force and modulus and inversely proportional to stiffness and length. Eq. (5) is also valid if it is written as Eq. (6):

$$\frac{1}{\sigma} \propto k' \left(\frac{kL}{FE} \right) \tag{6}$$

The equation was simplified by assuming *k'*, *F*, *E*, and *L* as unity to form the Eq. in (7). The equation now shows that the stress is inversely proportional to the stiffness.

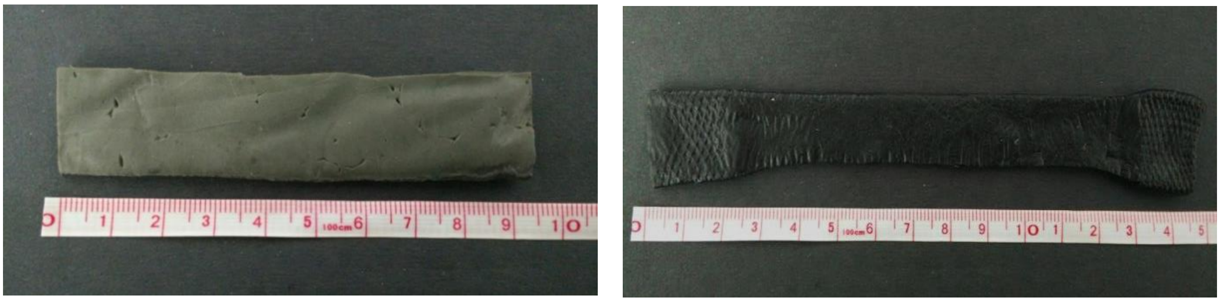
$$\sigma \propto \frac{1}{k} \tag{7}$$

This concedes the problem in the stress versus strain curve whereby the tensile stress decreased since the stiffness increased resulting from the reinforcing effect.

Permanent Set

Figures 4(a) and 4(b) show the comparison of residual extension remained after the tensile test for the unfilled SMR CV-60 and CB-filled SMR CV-60 compound, respectively. Based on the observation of the specimens, after being stretched at the maximum elongation (600%), the unfilled SMR CV-60 residual extension instantaneously reduced to 40% and surprisingly reduced to 6% of residual extension as it passed a day after the test conducted. The unfilled SMR CV-60 specimen showed a rapid recovery after being stretched and almost regained its actual length. Meanwhile, for the CB-filled SMR CV-60, the residual stretch was only reduced to 244% after being released from the tensile gripper and 86% of the residual extension was recorded on the next day. In addition, it was also observed that the CB-filled SMR CV-60 compound remained with the addition of its original length.

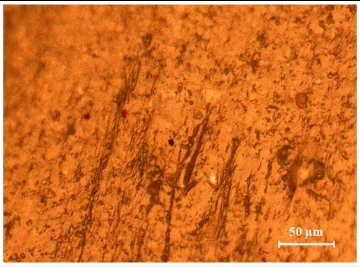
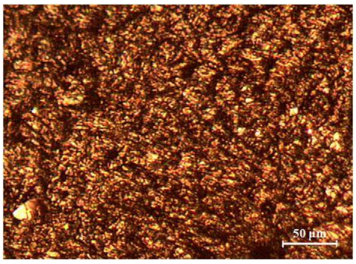
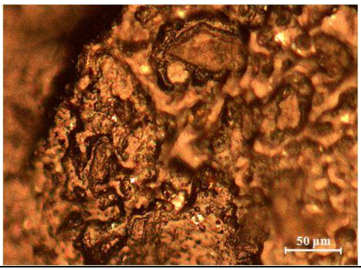
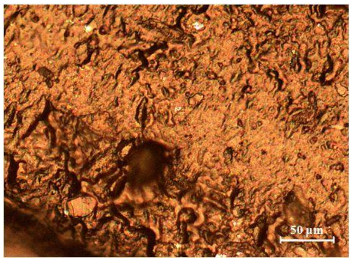
This behaviour was called as a permanent set as explained by Diani in 2009 [27]. Permanent set refers to the extension that remains after being stretched. The researcher observed that the permanent set was not exactly permanent and can be recovered rapidly due to the viscoelasticity of the rubber. The permanent set highly depends on the type and amount of fillers loading in the rubber [32]. However, in this study, the specimen with the carbon content does not regain its original shape as done by the specimen without carbon content. This behaviour may be related to the occurrences of the strain-crystallization which appeared more at the low strain level for the filled NR compound rather than the unfilled NR compound [33, 34].



(a) (b)

Figure 3 Residual extension SMR CV-60 compound (a) Unfilled SMR CV-60; (b) CB-filled SMR CV-60

Table 2. Microscopic view for both compounds before and after testing.

Types of compound	Before testing	After testing
Unfilled SMR CV-60		
Carbon black filled SMR CV-60		

Surface Changes

Table 2 showed the microstructure result for both unfilled SMR CV-60 and CB-filled SMR CV-60 compounds before and after the tensile test. The unfilled SMR CV-60 compound showed significant change on its surface after the deformation load was applied although there were no physical changes observed. On the other hand, there were no changes observed on the CB-filled SMR CV-60 microstructure. Based on the observation, it showed that the interaction between the rubber matrix and the CB fillers was not affected by the tensile stress applied during the experiment. The addition of CB helped to maintain the rubber network, the addition of filler particles that caused the inter-aggregate distance to become smaller, thus increased the probability of the rubber-filler network formation [21].

CONCLUSIONS

In this paper, the study of the effects of the CB fillers on the unvulcanized Standard Malaysian Rubber-Constant Viscosity 60 (SMR-CV 60) compound was carried out. Two types of unvulcanized SMR-CV 60 compounds were used in this study, which is the unfilled and CB-filled SMR-CV 60 compound. The tensile test was performed for both compounds at room temperature and the result was recorded. The experiment showed that the carbon black fillers have increased the tensile modulus of SMR-CV 60 compound at 2.89 MPa from 1.42 MPa which was recorded in the unfilled SMR-CV 60 compound. In the stress-strain curve, the CB-filled compound showed a low tensile stress compared to the unfilled compound with a value of 0.2535 MPa and 1.0612 MPa, respectively. The comparison of microstructure between both SMR-CV 60 compounds before and after the tensile test was also studied in order to describe the rubber-filler particle interaction. The SMR-CV 60 compound filled with CB shows a good interaction between the rubber and filler particle. In the permanent set studies, the CB-filled SMR-CV 60 compound showed a significant change to its length compared to the unfilled SMR-CV 60 compound. By observing all the findings, it was shown that the carbon black fillers influenced the property changes in SMR-CV 60 compound in terms of tensile modulus, tensile stress, stiffness and compound structure. In continuation of this study, further research should be conducted on the effect of CB towards the vulcanized SMR CV-60 in terms of mechanical properties.

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