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Effect of Modified Molasses Carbon Filler on Mechanical Properties of Natural Rubber Vulcanizates

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Abstract

In this research, a possibility study was carried out on the utilization molasses, inexpensive by-product of the refining of sugarcane into sugar, as alternative filler in rubber. Liquid molasses was converted to powder form under the heating process. Molasses carbon powder (MCP) was finally obtained. As a result of percentage of carbon content in MCP, it was evident that MCP containing 64.5 percent of carbon. Interestingly, the MCP was rich in carbon as well as carbon black (CB) reinforcing filler in rubber. In order to enhance the mechanical properties of MCP filled NR vulcanizates, MCP was modified with a silane coupling agent such asbis (3-triethoxysilylpropyl) tetrasulfide or Si69. Thus, the present work aims to investigate the role of silane coupling agent on properties of NR vulcanizates filled with MCP. Modified and unmodified MCP was incorporated into the NR with loadings of 30 phr (parts per hundred of rubber) and also compared with CB. All of NR filled with carbon fillers were examined in the term of cure characteristics, tensile properties, tear strength and swelling resistance. From the results, it was observed that the cure times were decreased with the incorporation of silane modified MCP. In addition, torque difference, tensile strength, tear strength and swelling resistance of NR vulcanizates were improved.

Keywords: natural rubber, molasses, carbon black, silane coupling agent, filler

1. Introduction

Natural Rubber (NR) is a high molecular weight natural polymer originally derived from latex found in Hevea brasiliensis. NR is a very versatile raw material mainly used as solid rubber and to a lesser extent as latex. Because NR possesses good mechanical properties such as high tensile strength, tear resistance, resilience and abrasion resistance, it is widely used in numerous industries especially in tire industry. Other applications include rubber gloves, anti-vibration mounts, seals, bridge-bearing, conveyor belts, gaskets, rolls, and pharmaceutical goods, for example, urinary drainage catheters [1-5]. Normally, NR is always compounded with additives to satisfy the given applications in terms of properties, cost and processability. Such compounding ingredients include filler, activator, accelerator, antioxidant, processing aids, vulcanizing agents [6-8]. In the case of filler, carbon black (CB) is the most important filler in rubber industry.

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Although CB is still well known among rubber technologists, the use of some other fillers from the natural resources and by-product as alternative reinforcing fillers in NR is an interesting and challenging for rubber industry [9-11].

Molasses is an end product in the sugar industry. Generally, molasses is widely used as raw materials to produce animal feed, ethyl alcohol and a growth medium for yeast production [12]. To add value of the molasses as an efficient low cost carbon source, viscous molasses was converted to powder form under the proper condition. Since the molasses carbon powder was rich in carbon as well as CB filler.

The present work aims to further investigate the improvement of the using carbon powder prepared from molasses by focusing on the modification of molasses carbon powder filler via silane coupling agent. The properties of NR filled with modified molasses carbon powder composites including cure characteristic, tensile properties, tear strength and swelling resistance were studied.

2. Materials and Methods

2.1 Preparation and characterization of molasses carbon powder

Molasses carbon powder (MCP) was prepared from original molasses. Firstly, molasses was dehydrated and carbonized in an electric furnace by setting the temperature at 400 ^oC for 5 hour. The black ash was obtained and was further milled to a powder form. Carbon containing in MCP was analyzed by CHN elemental analyzer. Then, X-ray fluorescence spectrometer (XRF) was used for determination other elements containing in MCP.

In this study, silane treatment used for modifying the MCP surfaces. The MCP was pre-treated by a silane solution. Silanes used in this study is bis (3-triethoxysilylpropyl) tetrasulfide (Si69 or TESPT). The loading of Si69 was varied from 0-6 wt%. The silane solution was prepared with ethanol before wetting on the MCP surfaces. For instance, for a silane content of 2.0 wt%, 2.0 g of the silane was mixed with 100 ml of ethanol, and then stirred for 30 min. The 100g of MCP were then added into the solution with a further 15 min stirring to ensure a uniform distribution of the silane on the MCP surfaces. The treated MCP was then dried at 100 ^oC for 12 h in an oven until a constant weight was reached.

In addition, Fourier Transform Infrared Spectrophotometer (FTIR) was also employed to identify the MCP functional groups. Finally, a scanning electron microscope (SEM) was used to observe the morphology of MCP particles.

2.2 Preparation of rubber composites

The loading of both MCP (with and without silane) and CB filled NR compounds was 30 phr. The formulation of compounds is given in Table 1. All ingredients were mixed with NR in 2- roll mill. The total mixing time was 10 min. Finally, sheets of NR compounds were obtained.

Table 1. Compounding formulation for natural rubber composites

Ingredient (phr)	Formulations	
	no filler	**CB, 0% Si69 MCP, 2% Si69 MCP, 4% Si69 MCP, 6% Si69 MCP**
Natural rubber (STR5L)	100.0	100.0
Zinc oxide	4.0	4.0
Stearic acid	2.0	2.0
6-PPD	4.0	4.0
filler	-	30.0
TBBS	2.25	2.25
Sulfur	0.75	0.75

2.3 Measurement of cure characteristics

Cure time and torque difference of rubber composites were determined at 150 ^{o}C with a moving die rheometer (MDR). The rubber compounds were further vulcanized at 150 ^{o}C with compression molding machine. Finally, vulcanized rubber sheets having a thickness of about 2 mm were obtained.

2.4 Measurement of mechanical properties

Vulcanized rubber sheets were used for tensile and tear testing according to ASTM D412 and D624, respectively. The measurements were carried out using an universal testing machine (Instron Model 3366) with a crosshead speed of 500 mm/min. At least, 5 specimens were tested for these properties and the average values were reported.

2.5 Measurement of swelling resistance

The vulcanizate was cut into rectangular shape with weight about 0.5 g. Then, the sample was immersed in 100 ml toluene for 7 days. The swollen sample was removed from the toluene and the excess toluene was blotted with a paper towel. Then, the swollen sample was accurately weighed. The swelling ratio (Q) was determined using Equation (1). The value of swelling ratio of each vulcanizate was the average of three specimens:

$$Q = (W_S - W_U)/W_U \quad (1)$$

where W_S : weight of swollen sample
W_U : weight of unswollen sample

3. Results and Discussion

3.1 Characterization of molasses carbon powder (MCP)

Determination of some characteristics of MCP and CB used in this study was carried out. Results of percentage of elements and carbon containing in MCP and CB are shown in Tables 2 and 3. It is evident that MCP and CB mainly consist of carbon approximately 64.5% and 98.6%, respectively.

Table 2. Percentage of carbon determined by CHN elemental analyzer of MCP and CB

Filler	MCP	CB
Carbon (%)	64.5	98.6

Table 3. Percentage of elemental containing in MCP and CB analyzed by XRF

Elements (%)	Filler	
	MCP	CB
Carbon, Hydrogen, Oxygen	82.885	98.395
Potassium	7.459	0.006
Calcium	2.527	0.025
Iron	0.102	0.001
Sulfur	2.988	1.430
Phosphorus	-	0.120
Copper	0.003	0.001
Zinc	0.002	-
Manganese	0.015	-
Silicon	0.903	-
Chlorine	3.114	-

Additionally, FTIR spectra of MCP as depicted in Figure 1 shows the strong peaks at 3,500 cm^{-1} and 1,380 cm^{-1} indicating the presence of O-H and C-O bonds, respectively. In addition, MCP filler also presents peak in the region 1,600-1,700 cm^{-1}. The peak can be assigned to the C=O and C=C. The presence of peaks is probably due to hydroxyl groups and some double conjugated bonds with carbonyl group on MCP surface [13, 14]. For modified MCP, FTIR technique was also used to monitor the change in the surface chemistry of MCP before and after the silane treatment. Inaddition, Figure 1 shows the comparison of FTIR results of MCP with and without surface treatment. Upon the treatment with Si69, slightly peaks at wave numbers of 2,900-2,800 cm^{-1} and broad peak at wave numbers 1,400-1,100 cm^{-1} are noticeable which are in the same region of the stretching vibration of the -CH_2, -CH_3 groups and C-O bond [15]. However, slightly peak of the stretching of alkyl group in Si69 silane at 2,900-2,800 cm^{-1} and broad peak of C-O bond at 1,400-1100 cm^{-1} suggests the successful deposition of Si69 on the MCP surfaces. The SEM micrograph illustrated in Figure 2(a). It clearly shows large particle size of MCP when compared with CB as illustrated in Figure 2(b).

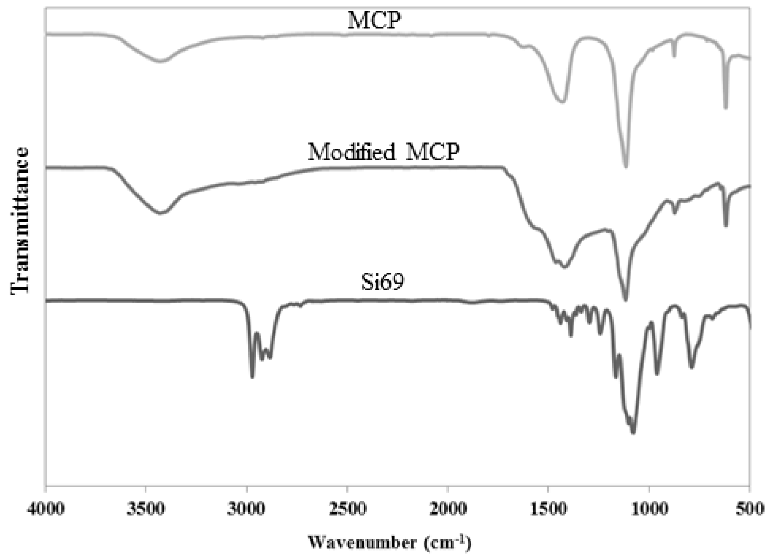

Figure 1. FTIR spectra of molasses carbon powder (MCP), modified molasses carbon powder (Modified MCP) and silane coupling agent (Si69)

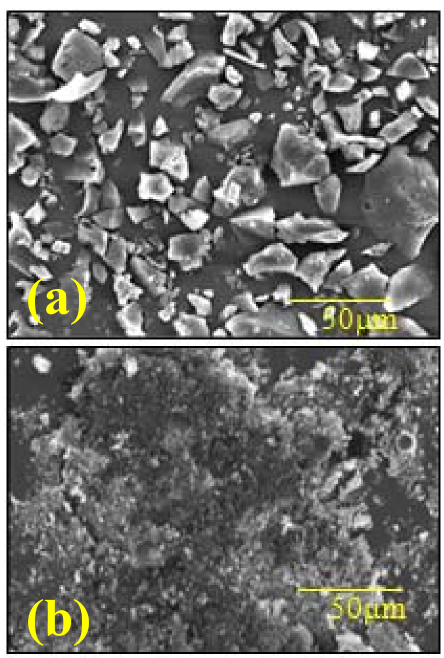

Figure 2. SEM micrographs of (a) molasses carbon powder (MCP) and (b) carbon black (CB)

Some cure characteristics which are cure time and torque difference of MCP, modified MCP and CB filled NR vulcanizates are shown in Figures 3 and 4, respectively. From the result of cure time result, it can be seen that the vulcanizates with the silane treatment MCP obviously show shorter cure times. This is due to the decresing in adsorption of curing agent and accelerator molecules on MCP surface during vulcanization via Si69 tratement suface. For torque difference which is the difference between the maximum and minimum torques of the compound and related to crosslink density of the vulcanizates, it is noticed that the torque difference of the vulcanizates filled with both modified and unmodified MCP are improved when compared with no filler. However, the vulcanizated filled with 6% Si69 modified MCP give maximum torque difference which is similar to CB filler. It appears that the formation of rubber networks is increased when using modified MCP filler. This is due to (i) the reduction in the mobility of rubber chains by the presence of the fillers and (ii) Si69 can participates in sulfur vulcanization reaction giving rise to an increase in crosslink density and hence delta torque [16]. The structure of Si69 are depicted in Figure 5. It can be noticed that Si69 have sulfur which can promotion curing and the rising in crosslink density.

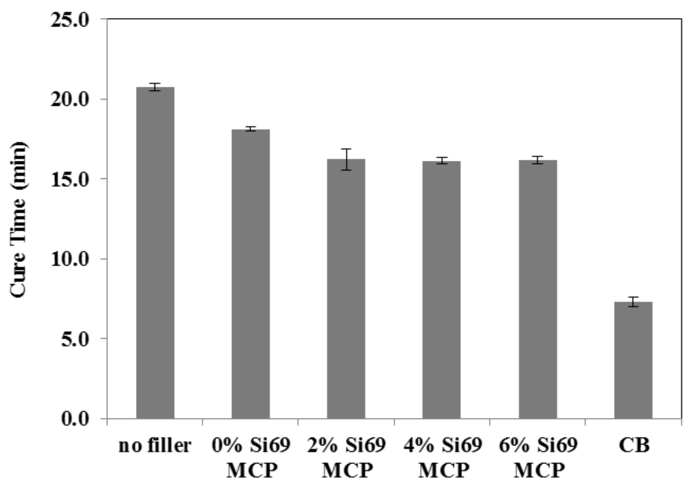

Figure 3. Cure time of unmodified MCP, modified MCP and CB filled NR vulcanizates

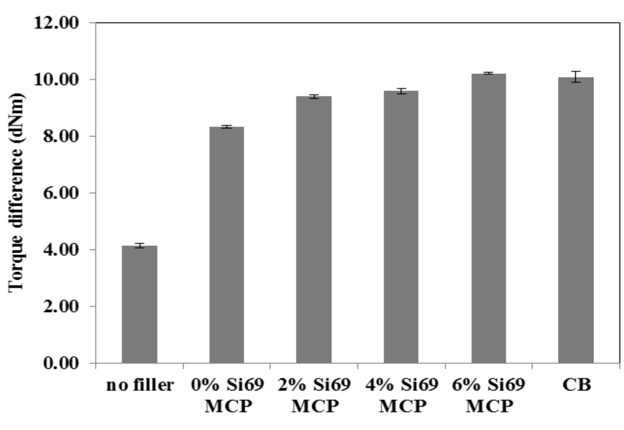

Figure 4. Torque difference of unmodified MCP, modified MCP and CB filled NR vulcanizates

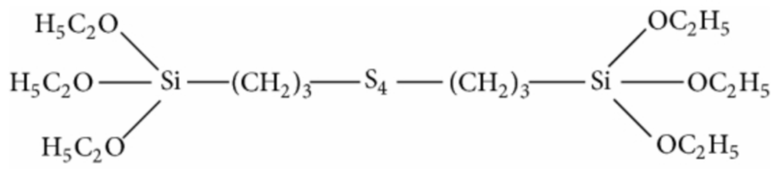

Figure 5. Structures of bis(3-triethoxysilylpropyl) tetrasulfide (Si69 or TESPT) [17]

Figure 6 illustrates tensile strength of the vulcanizates filled with MCP and compares with CB. From the result, it can be seen that the tensile strength of CB filled NR vulcanizated shows higher than those filled with MCP. This is because the large particle size of MCP. In general, the smaller particle size of filler, the greater the tensile strength of the NR vulcanizated. Another explaination is given to the carbon content of fillers. Filler with higher carbon content shows more effective reinforcement than those with lower carbon content, MCP. However, the tensile strength of NR filled with MCP slightly improves with modified MCP with Si69. This behaviour is probably due to the Si69 can improve the filler-rubber interaction leading to enhanced filler dispersion and Si69 can also assist sulfur vulcanization and increase the number of crosslinking [18, 19]. The elongation at break of MCP or CB filled NR vulcanizates are illustrated in Figure 7. It can be observed that the elongation at break of all modifiled MCP filled NR vulcanizates are no significant change when compared with unmodified MCP and CB filler. The modulus at 100 % strain of NR vulcanizates increases with incorporation all of fillers as presented in Figure 8. The enhancement in modulus at 100 % strain clearly displays with increasing silane loading in MCP. It is suggested that Si69 can promote sulfur and then increase in crosslink density. Normally, crosslink density which is related with the torque difference as shown in figure 4 which are chief factors for controlling modulus at 100 % strain [20-22].

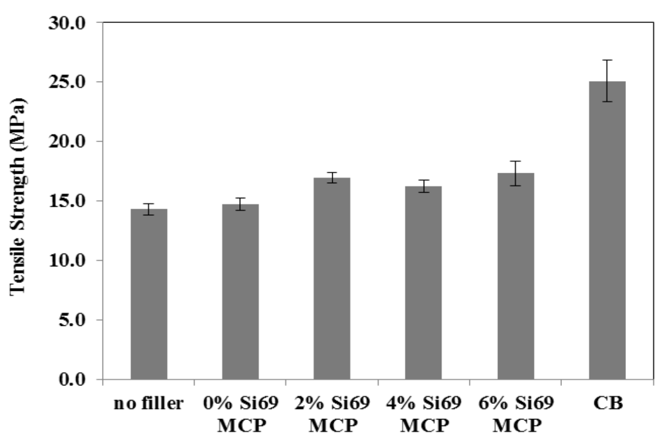

Figure 6. Tensile strength of unmodified MCP, modified MCP and CB filled NR vulcanizates

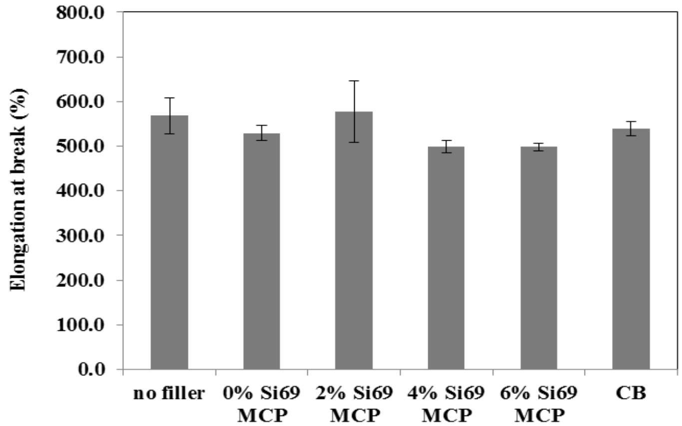

Figure 7. Elongation at break of unmodified MCP, modified MCP and CB filled NR vulcanizates

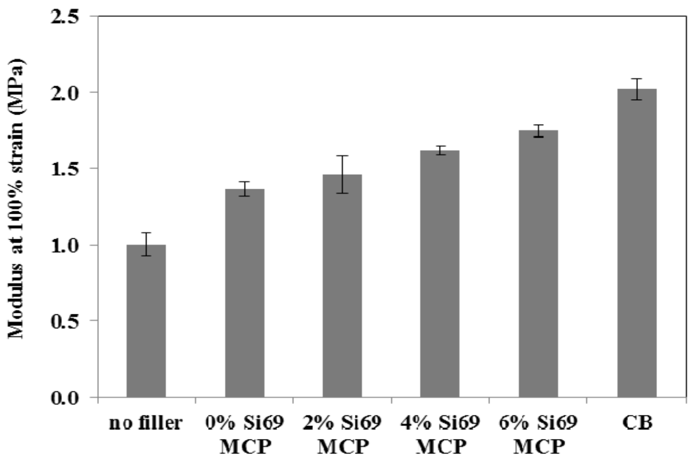

Figure 8. Modulus at 100% strain of unmodified MCP, modified MCP and CB filled NR vulcanizates

As illustrated in Figure 9, the result shows that tear strength increase with incorporation MCP with silane coupling agent. However, it should be noted that tear strength of vulcanizates having modified MCP is clearly lower than those filled with CB. As expected, this is probably because the low reinforcement ablility of MCP as a result of large particle size and carbon content. The results of swelling reisitance of MCP or CB filled NR vulcanizates is illustrated in Figure 10. Swelling resistance of the vulcanizates, which is inversely proportional of swelling ratio. It can be noticed that the swelling ratio decreases or swelling resistance enhances with incorporation all of filler. Compared with unmodified MCP, MCP modified with silane shows improvement in swelling resistance. This is probably due to the Si69 can improve the filler-rubber interaction and the increase in crosslink density. However, swelling resistance of NR filled with CB is still higher than those filled with modified MCP. CB is small particle size and carbon content than MCP [23].

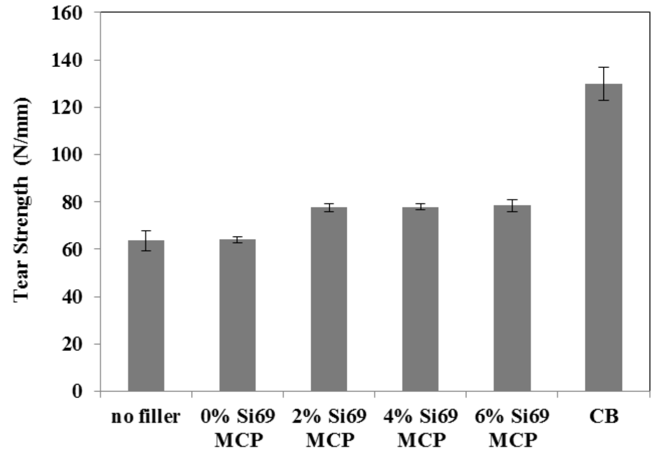

Figure 9. Tear strength of unmodified MCP, modified MCP and CB filled NR vulcanizates

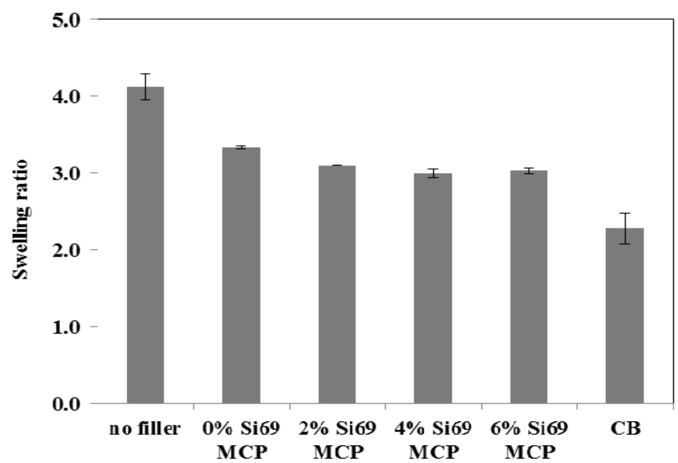

Figure 10. Swelling ratio of unmodified MCP, modified MCP and CB filled NR vulcanizates

4. Conclusions

Molasses which is the by-product can be converted to molasses carbon powder (MCP) under heating process for using as filler in natural rubber. In order to improve the properties of MCP filled NR vulcanizates, MCP was modified with a silane coupling agent namely bis (3-triethoxysilylpropyl) tetrasulfide or Si-69. From the results, it was observed that the cure times were decreased with the incorporation of silane modified MCP. In addition, torque difference, tensile strength, tear strength and swelling resistance of the NR vulcanizates were improved.

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