Effect of carbon black composition with sludge palm oil on the curing characteristic and mechanical properties of natural rubber/styrene butadiene rubber compound

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Abstract. This study was conducted to investigate the possibility of utilizing sludge palm oil (SPO) as processing oil, with various amount of carbon black as its reinforcing filler, and its effects on the curing characteristics and mechanical properties of natural rubber/styrene butadiene rubber (NR/SBR) compound. Rubber compound with fixed 15 pphr of SPO loading, and different carbon black loading from 20 to 50 pphr, was prepared using two roll mills. The cure characteristics and mechanical tests that have been conducted are the scorch and cure time analysis, tensile strength and tear strength. Scorch time \( t_{50} \) and cure time \( t_90 \) of the compound increases with the increasing carbon black loading. The mechanical properties of NR/SBR compound viz. the tensile strength, modulus at 300% strain and tear strength were also improved by the increasing carbon black loading.

1. Introduction

Rubber and elastomers are some of the most common materials significantly known for its flexibility and their ability to absorb particle like carbon black, silica and clay in enhancing and obtaining the desired properties for specific applications wherever resistance to impact or toughness are desired. Fillers, chemicals, and other reinforcing materials usually are added to enhance the properties of the rubber. Oil is one of these substances which usually are added in the processing phase of the rubber compounding process, and acts as the processing aid in the rubber compounding. Usually the type oil that is used in the rubber compounding process are the highly aromatic (HA) oils. This type of oil was added to the rubber compound with other ingredients to improve the processability and performance of the compounds such as promoting wet grip and wear endurance.

Certain highly aromatic oils as such had been classified as carcinogenic as upon tested according to IP method called IP346,t showed an unhealthy index values exceeding 3% [1]. Numerous other studies had found that aromatic oil addition into rubber compounds, especially oils with high polycyclic aromatic compounds (PAC) content which were identified as suspected carcinogens, might had contributed to increase cancer proliferation [2,3]. HA oils are often not actually bonded chemically to the rubber matrix, where they tend to leach from the mixture and migrate into their surroundings. For certain nations like United States and much of the European Union, the use of these
aromatic oil in rubber compounding had been banned. Besides that, PAC containing aromatic amines such as 2-naphthylamine have long been associated with increased rates of urinary bladder cancer (UBC) in rubber workers [1]. Hence, the environmental problem caused by HA oil use shows the need for natural based processing oil. Studies done by Rahmah et al., (2013) on epoxidised oil (EO) with NR/SBR compound found that EO oil can be an alternative sources to replace the aromatic oil (AO) as a plasticizer and processing aid [4, 5].

For tyre manufacturing, the common elastomers used are the NR/SBR mix. NR are usually mixed with synthetic rubber like SBR, commonly in the 60:40 ratio for rubber tyre and other compounded products. The SBR mixed often imparts suitable properties in meeting the performance needs of passenger car tyre treads [3,6,7]. The reinforcement of rubber properties by the incorporation of carbon black had been extensively studied. Recent studies with carbon black fillers and other fillers had been investigated by Ooi et al., (2013) [8]. In their work, oil palm ash (OPA) as filler was compounded with NR using conventional laboratory-sized two roll mills. For comparison purposes, two commercial fillers (i.e. silica and carbon black (CB)) were also studied. The optimum loading of each type of filler was investigated and compared in terms of curing characteristics, tensile properties, rubber-filler interaction and dynamic mechanical analysis. Results showed that scorch time and cure time of the carbon black filled vulcanizates was the lowest compared to OPA and silica-filled NR vulcanizates, with the OPA compound offers the highest cure rate index. The carbon black filled vulcanizates had the highest tensile strength due to the reinforcement that its filler imparted. Ulfah et al., (2015) had also compounded NR with a blend ration of carbon black and silica fillers. They had found out that carbon black filler of the highest content ratio showed the highest tensile stress at 300% elongation for rubber compound with increasing amount of carbon black filler [9].

Waste cooking oil sludge sourced from waste oil palm cooling oil were used in this study; the waste oil used was collected from the oil trap as grease. The term “trap grease” technically refers only to kitchen waste, rather than septic grease. Sludge oil or trap grease are sometimes collected by rendering companies for purification and are often sold for non-edible applications such as burner fuel [7]. In the present study, sludge from palm oil (SPO) was used as an alternative source for aromatic oil. The effect of SPO loading on the cure characteristic and mechanical properties of NR/SBR compound had been investigated and reported.

2. Materials and Methods

2.1 Materials

NR of grade SMR 10 and SBR of grade Nipol 1502 were supplied by Rubber Research Institute Malaysia (RRIM). Nonox were supplied by Shanghai Rokem Industrial Co., Ltd and High Abrasion
Furnace Carbon black, HAF (N330) were supplied by Black Tiger Carbon Black Co. Ltd. Other chemicals such as zinc oxide and sulphur were supplied by Bayer (M) Sdn. Bhd. The SPO was obtained from Forest Research Institute Malaysia (FRIM) with its chemical compositions has been steam treated and filtered. Table 1 shows the specifications of SPO obtained from FRIM. Nonox was supplied by Shanghai Rokem Industrial Co., Ltd and high abrasion furnace carbon black, HAF (N330) was supplied by Black Tiger Carbon Black Co. Ltd and other chemicals such as zinc oxide and sulphur were supplied by Bayer (M) Sdn. Bhd.

| Specifications                  | Parameters       |
|--------------------------------|------------------|
| Code color                     | Black            |
| Free Fatty Acid (FFA)          | 42.77%           |
| *(Normal crude palm oil: FFA<5%)* |                  |
| Moisture and Impurities (M&I)  | 2.47             |
| Melting Point (2hours)         | 48.7°C           |
| Flash Point                    | 240°C            |
| Total Fatty Matter             | 97.53            |
| Density g/cc @70°              | 0.8615           |
| Calorific Value                | 38.6MJ/kg        |

2.2 Compounding
Compounding of the ingredients as per Table 2 specifications were prepared in a two-step process; preparation of master-batch (sans sulphur and accelerator) was done using Banbury internal mixer (BR1600) at the RRIM under a set temperature of 150°C and mixing speed of 70rpm. The remaining ingredients were later added and mixed using a two-roll mill with 30rpm rolling speed. The sheeted rubber compound was conditioned under room temperature for 24 h. For this study, SPO content are fixed at 15 pphr while the carbon black (HAF N330) were varied to 50pphr (parts per hundred rubber).
2.3 Characterization

According to the ISO 3417:1991 standard, a Monsanto oscillating disc rheometer (ODR) was used to determine the scorch \( t_{s5} \) and optimum cure time \( t_{90} \) at 150°C based on Eq. (1) and Eq. (2) [3].

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t_{s5} = \text{Time to reach 5 unit increase in torque above minimum (at } M_L + 5 \text{ units above it)}
\]

\[

t_{90} = 0.9(M_H - M_L) + M_L
\]

Where, \( M_H = \text{Maximum torque, } M_L = \text{Minimum torque} \)

The tests for the tensile strength and tear strength properties of the rubber compounds were performed using an Instron universal machine (model Testometric MICR0500) at 500mm/min crosshead speed according to the ASTM D412 and ASTM D624 standards respectively.

3. Results and Discussion

3.1 Cure Characteristic

Figure 1 shows the effect of carbon black on both the cure and scorch time with fixed SPO loading (15 pphr). It can be seen that both characteristic increases with the increasing carbon black loading. From the result obtained, the maximum scorch time and cure time was achieved at 45 pphr of carbon black loading, which are 24 min and 65.85 min respectively. Both characteristic then experienced sudden decrease in the time recorded for 50 pphr of carbon black loading. This may due to the carbon black particle aggregating and did neither packed together at certain point nor does it distributed evenly. This process occurs mainly during the compounding (milling) process using the two roll mill machine.

![Figure 1. Effect of carbon black loading on scorch (min) and cure time (min).](image)

The reduction of cure time upon carbon black loading above 45 pphr could be related to the excess carbon black, which indicates a presence of greater number of vulcanisation and crosslink site occurred with the carbon black and waste sludge oil applied onto the NR/SBR compounds. This phenomenon might be explained as the competition for cross-linking agents between the unsaturated
rubber and the excess carbon black, which resulted in the lowering of the vulcanization rate [10]. Other than the cross-linking linkages formation, the process of network formation had been explained by Karak et al., (2000) [11]. As cure time decreases, the vulcanization process can theoretically be explained by the following processes. Both network formation and network degradation occur simultaneously, but the initial network formation rate was much lower than the degradation rate; subsequently, an optimum level can be reached before the rate of network structure degradation finally became much shorter for the NR vulcanizates as cure time decreases.

There were still scarcely enough works on the use and effect of waste or SPO and other vegetables oil forms for tyre tread compound apart from the limited number of works [12,13]. Rahmah et al., (2013) had investigated the effect of AO and EO from vegetables oil on the scorch and curing time. It had shown that an EO addition up to 30pphr had reduced the cure time from 13 to 90% as compared to AO use [5].

### 3.2 Tensile Properties

Figure 2 shows the effect of carbon black (pphr) composition on the tensile strength of rubber compound. Tensile strength was observed to had maintained at values between 14MPa and 15MPa upon incorporation of 20 to 30 pphr of carbon black. The optimum strength was 19.32 MPa at 40 pphr carbon black loading. It shows that there is an interaction; the highest interaction at 40pphr of carbon black loading which occur between the carbon black and the rubber. However, the tensile strength was reduced again by about 10pphr for carbon black in excess of 40pphr. This may due to the overloading of carbon black in the compounding, or the possible use of the two roll mill machine which caused the carbon black particles not to be homogenized completely.

Besides that, the higher amount of carbon black had caused reinforcement between the carbon black particles themselves, fixed SPO and the rubber chains. This finally lead to the interfacial interaction reduction between the rubber chains due to agglomeration of carbon black particles [4]. The carbon black presence induces rigidity to the rubber, in which an increase in carbon black will increase the rigidity of the rubber compound. High rigidity is sometimes needed in rubber compound for tire manufacturing, which provides an improvement in strength.
Figure 2. Effect of carbon black on tensile strength.

Figure 3 shows that there is an interaction between the carbon black and the rubber. The elongation at break reduces as the increase of carbon black between 20 to 45 pphr. This reduction may due to the carbon black reducing the elasticity. The sudden decrease of elongation at break at 50pphr carbon black may due to the uneven distribution of excessive carbon black in the rubber compound.

Figure 3. Effect of carbon black on elongation at break.

Figure 4 shows the 300% elongation results of the modulus at stress. Theoretically, the modulus is inversely proportional to the elongation at break, and it indicates the stiffness and rigidity of the materials tested. The 300% elongation results shows how the tensile modulus consistently increases with the carbon black content. The drop in modulus at 50 pphr may due to the effects of carbon black overloading. This tends to cause the uneven distribution of the carbon black present that tends to agglomerate at certain locations within the material.

Figure 4. Tensile modulus at 300% strain.
3.3 Tear Strength

There are three types of sample for use in the tear tests, which are the trouser, angle or crescent samples. But for this test, the trousers sample was used. The tests were conducted by applying force to the material in a tensile direction, of which a value for the tear strength was calculated. From Figure 5 below, there were some small gradual observable increases in the tear strength when the carbon black content were increased from 20 to 40pphr. Upon reaching 45 pphr and 50pphr of carbon black a drastic increase of about four fold increase in the tear strength were observed.

Carbon black had long been thought to be a reinforcing agent but these higher reinforcing effects were only imparted upon higher amount of carbon black used. The high interaction of carbon black and rubber was apparent through this pronounced reinforcing filler effect.

![Figure 5. Effect of carbon black on tear strength.](image)

This proves that the carbon black had acted as the reinforcing filler, hence caused better resistance to tear for rubber compound. Tear properties were markedly improved with a fourfold increase upon addition of 45pphr of carbon black. Fukahori et al., (2013) stated that, during the tearing of rubber materials, the transition called elastic-viscous transition phenomenon exist; and this transition had occurred due to the crosslink density and visco-elastic energy dissipation [14].

4. Conclusions

In conclusion, the scorch time, cure time, tensile strength, and tear strength shall increase with corresponding increases in the amount of carbon black. Meanwhile, the tensile modulus at 300% strain had showed results that are inversely proportional to the elongation at break which due to the elasticity and stiffness properties of the compounds. An increase of carbon black up to 45pphr results in overloading effect, which causes an uneven distribution of the carbon black in rubber compounding process.
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