Rubber mixing process and its relationship with bound rubber and crosslink density

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Abstract. This research studied the relationship between bound rubber and crosslink density based on rubber mixing process. Bound rubber was obtained after natural rubber was masticated and mixed with rubber chemicals and filler while crosslink density was collected after rubber compound was vulcanized. Four methods are used and each method refers to four ways of incorporating carbon black during mixing. The first method, after rubber was masticated for 5 minutes, the addition of rubber chemicals and filler was done simultaneously. Rubber was masticated for 1 minute and continued mixing of rubber chemicals and filler where mixing was different from first method. This was the second method. The third method was the same as the second method but the filler used N 660 while in the second method N 330. The last method is not the same as the first and second, the rubber is only masticated for 3 minutes and then mixed with filler and followed by rubber chemicals sequentially. The results showed that bound rubber and crosslink density were influenced by mixing and mastication process. Bound rubber dropped and crosslink density was relatively stable in the first three mixing methods for increasing carbon black at the beginning of the mixing process. Bound rubber and crosslink density stated opposite results in the fourth mixing method. The higher the bound rubber the lower the crosslink density. Without regard to mixing methods, there is a non-linear relationship between bound rubber formation and crosslink density determination.

1. Introduction

Rubber mixing process (RMP) is one of the determinations of physical and chemical properties of vulcanized rubber. RMP starts from rubber mastication and then followed by rubber chemicals and/or filler mixing into rubber. Rubber compound as a RMP product forms bound rubber and its vulcanizate contains crosslink density. Bound rubber is reinforcement level in rubber vulcanized which is formed from physical bonding of filler and rubber molecules. Bound rubber is predisposed by filler content [1], the type of filler [2], storage time [3] and the mixing time [4]. Crosslink density is the level of vulcanization of rubber backbone and sulfur as vulcanizing agent or reactant [5-8]. Crosslink density is worked on structure and carbon black’s surface chemistry [9-10] while the type and content of filler affect cure characteristics [9-12]. Bound rubber and crosslink density greatly affect physical and chemical behaviors of vulcanized rubber. To produce rubber with the specific physical and chemical properties, requires a certain RMP anyway. The order of mixing rubber chemicals and fillers can affect the physical properties such as abrasion resistance of vulcanized rubber. RMP was studied by carbon black addition into rubber in the first footpace and then oil was put into rubber after the carbon black fused, abrasion was significantly bigger compared with that of the compound prepared by...
adding oil together with carbon black in rubber [13]. The change in abrasion resistance is more due to the increase of bound rubber than that of the crosslink density. The extent to which the relationship between the bound rubber and crosslink density is not widely studied. Wang (1998) states that if the active center of carbon black is littered with rubber chemicals, especially the type of antioxidants such as amine it is very difficult to be replaced by rubber molecules [4]. This means that the bound rubber being dropped. This fact can be considered analogous to that of affairs between the bound rubber and crosslink density. When bound rubber up on the other way the crosslink density to be down. Choi (2007) studied bound rubber based on carbon black reinforced rubber compounds and crosslink density came from rubber vulcanizates, but in this study the relation of bound rubber and crosslink density did not discuss [14]. It is therefore in this study not only studied the effect of RMP upon bound rubber formation and crosslink density analysis but also its relation both.

2. Experimental

2.1. Rubber formula
Natural rubber RSS-1 as Indonesian’s product and carbon black type N 330 and 660 from Cobot Indonesia were main raw materials in the investigation as well as sulfur, TBBS, TMQ, ZnO, C_{18}H_{36}O_{2}, and softener as rubber chemicals. Together with bound rubber level was determined by toluene. All ingredients were commercial commodities and non-treated materials.

| Table 1. Natural Rubber Formula. |
|----------------------------------|
| No | Ingredients                  | phr |
|----|-------------------------------|-----|
| 1  | RSS-1                         | 100 |
| 2  | ZnO                           | 5   |
| 3  | C_{18}H_{36}O_{2}             | 2   |
| 4  | Carbon Black type N 330/660   | 50  |
| 5  | Softener                      | 5   |
| 6  | TMQ                           | 2   |
| 7  | TBBS                          | 0.5 |
| 8  | Sulfur                        | 2.5 |

| Table 2. Mixing process consecution of A. |
|------------------------------------------|
| No | Ingredients | Time, minutes |
|----|-------------|---------------|
| 1  | RSS-1       | 5             |
| 2  | ZnO         | 2             |
| 3  | C_{18}H_{36}O_{2} | 1           |
| 4  | TMQ         | 2             |
| 5  | CB_1        | 2             |
| 6  | CB_2 + oil  | 4             |
| 7  | TBBS        | 1             |
| 8  | Sulfur      | 1             |

2.2. Equipment
Equipment used in this research were open two roll mill, hot press apparatus and glassware for determination of bound rubber and crosslink density

2.3. Mastication and milling process
Rubber and ingredients listed in Table 1 were masticated and milled on mixing temperature of 60°C. This milled rubber formula followed the mixing procedure stated on Table 2. These rubber samples were called A. The addition sequence of carbon black followed consecution on Table 5 code 1, so this sample called A1. Rubber was masticated about 5 minutes, continued by putting into practice of ZnO and C_{18}H_{36}O_{2} and milled for 2 minutes. Then TMQ was added into the mix and milled for 1 minute. Carbon black at amount of 10 phr was farthered into the mix and milled for 2 minutes. This process is called CB_1. The rest of carbon black about 40 phr was combined into the mix together with oil and milled about 4 minutes. It is regarded as CB_2+oil. Then TBBS and sulfur addition needed 1 minute for milling time each.

The formula based on Table 1, a mixing process was also conducted in relation to the consecution and the time each consecution needed, as shown in Table 3. The sample produced was called B. Rubber was masticated for 1 minute, followed by C_{18}H_{36}O_{2} addition and milled for 1 minute. Then sulfur and ZnO were added into the mix and milled for 2 minutes. The amount of carbon black 10 phr
was added into the mix and milled for 3 minutes. This process is called CB_1. The rest of carbon black about 40 phr was added into the mix together with oil and milled for 7 minutes. It is regarded as CB_2+oil. Then TBBS addition into the mix was milled for 6 minutes and TMQ was needed 1 minute for milling time. Carbon black addition process into the rubber was applied using the method performed to the consecution of Table 5. The samples were designated as B1, B2, B3 and B4.

| Table 3. Mixing process consecution of B. | Table 4. Mixing process consecution of D. |
|----------------------------------------|----------------------------------------|
| No | Ingredients  | Time, minutes | No | Ingredients  | Time, minutes |
|----|--------------|---------------|----|--------------|---------------|
| 1  | RSS-1        | 1             | 1  | RSS-1        | 3             |
| 2  | C_{18}H_{36}O_{2} | 1             | 2  | CB_1         | 2             |
| 3  | Sulfur       | 2             | 3  | CB_2 + oil   | 5             |
| 4  | ZnO          | 3             | 4  | ZnO          | 2             |
| 5  | CB_1         | 4             | 5  | C_{18}H_{36}O_{2} | 2             |
| 6  | CB_2 + oil   | 6             | 6  | TMQ          | 1             |
| 7  | TBBS         | 7             | 7  | TBBS         | 1             |
| 8  | TMQ          | 8             | 8  | Sulfur       | 1             |

Formula on Table 1 was used to mixing process too following mixing process such listed on Table 4. Rubber was masticated for 3 minutes. Carbon black was added after that and milled for 7 minutes. Carbon black was affixed into in the amount of 10 phr out of the total amount of 50 phr. Such process was called CB_1 and needed 2 minutes for milling. The rest of 40 phr was affixed into the rubber afterwards together with oil. It was regarded as CB_2+oil and needed 5 minutes for milling. ZnO and C_{18}H_{36}O_{2} was added after that and milled for 2 minutes, followed by TMQ addition, sulfur and TBBS milled for 1 minute each. This sample was called D1. After mastication and mixing process, bound rubber determined and rubber compound then were vulcanized on temperature of 150°C and followed analysis of crosslink density.

Bound rubber testing using rubber compound 1 gram was rendered in 50 ml toluene solvent for 4 days. Dissolution performed at room temperature. After dilution, the rubber compound was then dried at a temperature of 110°C to constant weight under vacuum. Initial sample and sample after dissolution were then weighed. Bound rubber is calculated in a way that used by Choi [2], Choi et al. [3], Choi [4], Qian et al. [15], Wang et al. [16], and Wolf [17] as follows:

\[
\text{Bound rubber} = \frac{W_{fg} - W_{f}}{m_{p}} \times 100 \%
\]

(1)

Where \(W\) is initial sample weight, \(W_{fg}\) carbon black load and gel, \(m_{f}\) filler mass in the compound, dan \(m_{p}\) the polymer mass in the compound.

Testing of crosslink density used swelling technique. Vulcanized rubber about 1 gram was soaked in the toluene solvent for 24 hours at room temperature, then weighed weight of vulcanized rubber in an expanding after a surface residual solvent removed using tissue paper. Vulcanized rubber was dried for 24 hours at a temperature of about 110°C under vacuum conditions. After that, vulcanized rubber was left at room temperature for 24 hours, and then weighed weight in the dry state. Crosslink density is calculated using the equation Parks [18] the following:

\[
Q = \frac{(\text{swelling weight} - \text{dried weight})}{(\text{original weight} \times 100)} \quad \text{(2a)}
\]

Crosslink density \(= \frac{1}{Q} \quad \text{(2b)}\)
Table 5. The Carbon Black Enlargement into Mixing Process.

| Code | CB_1   | CB_2+oil |
|------|--------|----------|
| 1    | 10 phr | 40 phr+oil |
| 2    | 20 phr | 30 phr+oil |
| 3    | 30 phr | 20 phr+oil |
| 4    | 40 phr | 10 phr+oil |

3. Results and discussion

The bound rubber samples A, B, C, D, and D4 as well as crosslink density are shown in Figure 1-6. Figure 1 shows that the bound rubber down significantly as well as crosslink density is almost stable from A1 to A4. The trend is almost the same as the curve in Figure 1 occurs also in the curves in Figure 2. RMP of A and B are not significant impact on crosslink density and even tend to be stable, otherwise bound rubber to be down sharply.

In the RMP for samples A and B illustrated in Figure 1 and 2, ingredients mixing were simultaneously performed, this can cause the surface of carbon black tainted by rubber chemicals so it does not provide the increase of bound rubber. Here, carbon black also can not properly serve as a catalyst, so that the reaction of sulfur with rubber backbone is not so influenced by the RMP. Thus crosslink density showed no significant change despite initial mixing of more carbon black in the RMP. Bound rubber B is greater than that of A. It is caused by mastication time B for 1 min less than that of A for 3 min. Low rubber mastication time results high shearing force of rubber. High shearing force can solve aggregate into fine particles of carbon black that is better than low rubber shearing force. Bound rubber B is greater than that of C (see Figure 3). This is caused by the difference in size of the carbon black particles used. Compound B employs carbon black with a small particle size and C uses carbon black particle greater than that of B. The smaller the particle size the easier carbon black dispersed in rubber, so that the bound rubber bigger.

![Figure 1. Effect of RMP upon formed bound rubber and determined crosslink density of A. Milling temperature of 60°C.](image-url)
RMP influences of bound rubber formation and crosslink density determination on sample D shown in Figure 4. Bound rubber has a tendency down and instead crosslink density rises from D1 until D4. RMP on sample D mixing process of carbon black conducted in advance than that of rubber chemicals so that carbon black surface is not stained by rubber chemicals yet. Rubber molecules adsorption on carbon black surface get better until the bound rubber formation rises. Therefore the bound rubber D somewhat larger than those of A and B. Increase bound rubber from D1 until D4 caused disturbed vulcanization reaction so that crosslink density goes down from D1 until D4. The increase of rubber bound was due to the more and more carbon black is mixed in early RMP. Here, high shearing force causes carbon black aggregates break down into finer particle size until particles are easily dispersed into the rubber. In consequence, more rubber backbone was adsorbed on carbon black surface as well as bound rubber risen from D1 until D4.

**Figure 2.** Effect of RMP upon formed bound rubber and determined crosslink density of B. Milling temperature of 60°C.

**Figure 3.** Effect of RMP upon formed bound rubber and determined crosslink density of C. Milling temperature of 60°C.

Bound rubber formation and crosslink density analysis were contradictory as based on Figure 4, the experiment was then carried out to study how phr carbon black rubber compound and phr sulfur in
vulcanized rubber influenced bound rubber and crosslink density formation (Figure 5-6). From Figure 5, the contradiction of bound rubber and crosslink density (Figure 4) could be described. Figure 5 gives information that innumerable of carbon black (phr) into the rubber causes high comfortable bound rubber and it shows crosslink density decreased. High phr of carbon black into rubber compound causes high surface area and it results in high bound rubber. High bound rubber can decrease active center of carbon black and causes the reaction of rubber backbone and sulfur is stained. In this matter, the crosslink density becomes low.

**Figure 4.** Effect of RMP upon formed bound rubber and determined crosslink density of D. Milling temperature of 60°C.

Figure 6 gives an information how phr of sulfur into rubber compound affects crosslink density and bound rubber formation contradictively. The main reason why the contradiction exists is the same as like described on Figure 5. High phr of sulfur into rubber compound causes high reaction rate and decreases the active center of carbon black. This fact results the decrease of bound rubber prior to the increase of crosslink density. The facts stated on Figure 4-6 give the relation crosslink density and bound rubber. Bound rubber becomes low in contras crosslink density is gained.

**Figure 5.** Effect of carbon black content against bound rubber and crosslink density of D4. Milling temperature of 60°C.
Regardless how to process the rubber compound A, B, C or D, and refer to the facts illustrated on Figure 4-6, the curve that relate crosslink density/bound rubber and bound rubber were existed such illustrated us on Figure 7.

**Figure 6.** Effect of sulfur content against bound rubber and crosslink density of D4. Milling temperature of 60°C.

Figure 7 gives the information that there is a non linear relation between crosslink density with bound rubber. Plot result shows the relation between crosslink densities with bound rubber that follows following equation:

\[ y = -1.128 \ln(x) + 0.1856 \]  \hspace{1cm} (3)

\( y \) is crosslink density/bound rubber and \( x \) bound rubber.

It can be concluded that the crosslink density is more formed when bound rubber formation is low, in the other words at a certain rubber bound, crosslink density becomes constant. According to Lorenz dan Parks [19], the filler may affect the properties of vulcanizate either through the interaction between the filler and the vulcanizing agent as well as reciprocal action between filler and rubber. When the reciprocal action between filler and curing agent occurs, a number of curing agents or accelerators cannot react with rubber. Kraus [20] stated that softener and oils can reduce the amount of crosslinking or reduce the efficiency of sulfur reaction. This also shows that there is an interaction between softener and oil with vulcanizing agent. From both of these facts it is stated that crosslink density is decreasing and otherwise the bound rubber rises.
According to Lorenz and Parks [19], the filler can affect the properties of vulcanized rubber through interactions between the filler and a curing agent or interaction between filler with rubber. When interaction between filler and curing agent case, a part of curing agent or accelerator can not cause a reaction with the rubber. Kraus [20] stated that the softener and oil can reduce the amount of crosslinking or decrease the efficiency of the use of sulfur. This matter shows that there is an interaction between softener and oil with curing agent. From these facts indicate that the crosslink density rubber down and instead bound up.

4. Conclusion
RMP affected bound rubber formation. More carbon black is added at the initiation of RMP resulted in the decrease of bound rubber on sample of A and B. These were caused by sequence of rubber mixing and rubber chemicals as well as carbon black simultaneously. If carbon black was mixed at the beginning of RMP followed by rubber chemicals mixing into rubber, such as on sample of D, so the formation of bound rubber increased as well as the increase of large amount of carbon black mixed at the beginning of RMP. RMP also influenced the crosslink density on sample of D but it had small effect upon sample of A and B. Without regard to mixing methods, there is a non-linear relationship between bound rubber and crosslink density.

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Figure 7. Relationship between bound rubber and crosslink density.
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