Relaxation behavior of natural rubber composites based on mooney stress relaxation and rheometer data

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Abstract. Studies on relaxation behavior of natural rubber composites were conducted by Mooney stress relaxation coupled with rheometer data. The effect of filler (carbon black N-330) and sulphur loading was monitored on the relaxation behavior. Elasticity of the composites was also determined in term of elongation at break and hardness, as confirmation to the relaxation behavior. The experiments were conducted by varying the N-330 30, 35, 40 and 45 phr with the sulphur baseline of 2 phr. While sulphur loading was varying from 1, 2, 3 and 4 phr with the N-300 baseline of 30 phr. Mooney experiments were carried out at 100 ºC, while rheometer experiments were conducted in a moving die rheometer at 150ºC. Results finding showed that the relaxation rate was reduced with N-330 loading or sulphur loading due to restriction of rubber molecule chain mobility by crosslinking formation. N-330 provided higher effect on stress relaxation rate compared to sulphur. Elongation of the composites was found to decrease upon filler or sulphur loading, while hardness was inversely.

1. Introduction
Rubber is widely used in all aspect life because of its elasticity in nature. Designing a durable rubber based product needs to consider many factors. For load bearing application or when rubber is subjected to any short dynamic loading, it is not enough to define the long term behavior by only determining the mechanical properties, such as tensile strength, elongation, hardness, which are time-independent. Since rubber is viscoelastic material, it is important to take account the viscoelastic time-dependent characteristic such as creep, stress relaxation, dynamic mechanical properties, etc. [1,2]. In general, stress relaxation is observed when a fixed strain applied on rubber to a constant deformation, the stress required to retain the strain is found to decay with the time [1,3]. The time spans for relaxation can be described as transition of the system from one stage to another [4], but typically the rate is strongly related to the molecular mobility involving the elastic and viscous elements [5]. Moreover, the surrounding structure of the rubber chain molecules will also contribute to the rate of rubber relaxation [1]. Chain entanglements and crosslinking could alter the structure of the rubber, and in turn will affect the relaxation rate.

The relaxation behaviour becomes more complicated in filled-vulcanized rubber. During stress relaxation, at least three process could be taken place including physical relaxation due to relocation of rubber chains and the fillers, degradation caused by heat, light or chemicals, and crosslinking breaking or rearrangement of crosslink and/or polymer backbone [4]. Several studies had been conducted to investigate the stress relaxation behaviour in filled rubber. Abu-Abdeen (2010) studied single and double-step stress relaxation in carbon black filled natural rubber [4]. Maria et al. (2014) investigate the
effect of organically modified montmorillonite on stress relaxation of natural rubber/nitrile rubber nanocomposites. It is concluded that the rate relaxation was increased with filler loading due to the decrease of rubber-filler interaction [1]. Mohammadian-Gezaz and Karrabi (2017) conducts a deep study on stress relaxation behaviour of natural rubber filled by nano silicate/carbon black using rubber processing analyzer (RPA). Obaid et al. (2017) investigates the stress relaxation of polymer reinforced by short elastic fiber. They revealed that the presence of short fibers slowed the relaxation rate, and it increases with fiber loading. But, the underlying phenomenon was not well understood because of its complexity [2]. da Rocha et al. (2018) studied the effect of hybrid filler meta-kaolin/carbon black on stress relaxation of nitrile rubber [6]. Most of them studied the stress relaxation behaviour using rubber processing analyzer or monitoring the stress decay in universal testing machine, either in tensile or compressive force. None of them was applying Mooney stress relaxation and rheometer to predict the stress relaxation behaviour.

Vulcanized rubber is composed by two types of crosslink, namely physical and chemical crosslink. Physical crosslinks are resulted from physical interaction between rubber molecule and filler particles (bound rubber formation). Chemical crosslinks are obtained from vulcanization reaction by the formation of the sulphur bridge that linked one rubber molecule chain to another. These crosslinks formation can be monitored through many ways. One of them is by assessing the torque during rheometer experiment. It is generally accepted that the minimum rheometer torque (ML) represents the physical crosslink, while the torque delta (MH-ML) torque indirectly describes the chemical crosslink [7].

In this present study, the stress relaxation behaviour of NR composites was studied by evaluating the effect of filler (carbon black N-330) and sulphur loading on Mooney stress relaxation. Further discussion would be related to the contribution of physical and chemical crosslink to the stress relaxation behavior. Curing characteristics obtained from rheometer experiment were used as additional data. Also, the elasticity of the NR composites was taken account to confirm the relaxation behaviour.

2. Experimental

2.1. Materials
Natural rubber grades Standard Indonesian Rubber (SIR) 10 was supplied by PTPN IX. Carbon black N-330 and N-774 (Ex. OCI, Korea), zinc oxide active (Indoxide), Aflux 42 processing promotor. Paraffinic oil was purchased from CV. Indrasari, Semarang. Antidegradant system consisted of 2,2,4-Trimethyl-1,2-Dihydroquinoline (TMQ) (Kemai) antioxidant, N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) antiozonant (Northeast), and paraffin wax Antilux 654 A (Rhein Chemie). Accelerators N-Cyclohexylbenzothiazole-2-Sulfenamide (CBS) (Northeast) and diphenyl guanidine (DPG) (Shandong Shianxian). Sulphur Midas SP 325 (Miwon) was used as vulcanizing agent. All chemicals were industrial grade.

2.2. Rubber Compound Preparation
The rubber compound formulation was set according to Table 1. Carbon black N-330 and sulphur loading were varied to evaluate the effect of crosslink formed onto the stress relaxation behavior, while another ingredient was incorporated in a fixed amount. The detail of the variable taken in this study was listed on Table 2.

All compounding processes were performed in a two roll mill mixing machine laboratory scale. Rubber was first masticated and then followed by additive incorporation in a sequence. After completed, the rubber compound was soaked in the cold water for 5 minutes to stop the pre-vulcanization which might be proceeded. Then, the compound was allowed to rest for 24 h at 25ºC before testing.
Table 1. Compound formulation.

| Ingredients   | Loading (phr) |
|---------------|---------------|
| SIR 10        | 100.0         |
| ZnO           | 5.0           |
| Aflux 42      | 1.5           |
| N-330         | Varied        |
| N-774         | 30.0          |
| Paraffinic oil| 10.0          |
| TMQ           | 2.0           |
| 6PPD          | 1.0           |
| Paraffin wax  | 0.5           |
| CBS           | 1.9           |
| DPG           | 0.2           |
| Sulphur       | Varied        |

Table 2. Variables of the experiment.

| Variable   | Baseline | Range          |
|------------|----------|----------------|
| N-330      | 30 phr   | 30, 35, 40, 45 phr |
| Sulphur    | 2 phr    | 1, 2, 3, 4 phr  |

2.3. Mooney Viscosity and Mooney Stress Relaxation (MSR) Measurement

Mooney Stress Relaxation (MSR) was a part of Mooney viscosity measurement. This was carried out using Montech Mooney Viscometer MV 3000. Large rotor was applied with the speed of 2 rpm (0.21 rad/sec). The temperature at upper and lower die were maintained at 100±0.03°C. Sample of unvulcanized compounds were prepared using sample cutter, then placed in lower die. Mooney viscosity measurement was performed according to ASTM D-1646. Total testing time for each rubber sample was six minutes, including one minute preheating, four minutes viscosity testing and one minute relaxation testing. Figure 1 depicts the typical Mooney curve obtained from the instrument. The Mooney viscosity, ML1+4, is noted by point D, while Mooney stress relaxation (MSR) is described by curve DE.

The stress relaxation is often described by Power law model as expressed on equation (1),

\[ M = kt^a \]  

where \( M \) is the Mooney torque during the relaxation test, \( k \) is the constant equal to the torque unit 1 s after the rotor has been stopped, \( t \) is the relaxation time and \( a \) is the exponent determines stress relaxation. Taking the log of both sides, equation (1) has transformed equation (2) which is the linear regression form.

\[ \log M = \log k + a \log t \]  

(2)
$a$ is the slope of plot of log $M$ vs log $t$ that represents the relaxation rate. The slope $a$ is obtained from the instrument.

![Typical Mooney curve](image)

**Figure 1.** Typical Mooney curve.

2.4. Rheometer Experiment
Moving die rheometer (MDR) Gotech M3000A was used to characterize the curing characteristic of NR composites. A fixed angle of 3º was employed for all experiments. The tests were performed on unvulcanised rubber compound at 150ºC. The data recorded from rheometer included elastic minimum (ML) and maximum (MH) torques, scorch time ($t_{s2}$), optimum curing time ($t_{90}$). ML roughly represents the physical crosslink, while MH is the highest torque achieved during testing that represents total crosslink density, both physical and chemical crosslinks. The chemical crosslink formed during vulcanization is determined from the delta of maximum (MH) and minimum (ML) torque, MH-ML. The $t_{s2}$ and $t_{90}$ are valuable information regarding vulcanization time. All rheometer tests were performed in triplicate and the average value of each parameter was taken.

2.5. Hardness and Elongation Measurement
Samples were prepared by vulcanizing the rubber compound according to $t_{90}$ obtained from rheometer test. A 2-mm thick slab of elongation test sample and a 12 mm thick round disk of hardness sample were prepared by compression molding in a hydraulic press at 150 kg/cm$^2$ and at temperature of 150ºC. Samples were conditioned for 16 h before testing. Hardness testing was carried out by Shore A durometer. The measurement was performed in three different point of each sample. Elongation testing was conducted in a universal testing machine Tinius Olsen H 50 K. The elongation at which the specimen broken was recorded. All of the samples were tested according to ISO 37. The strain when the sample broken was recorded.

3. Results and Discussion
3.1. Effect of N-330 and Sulphur loading on stress relaxation behavior
Figure 2 and figure 3 depict the torque response after sudden cessation of Mooney rotor for various N-330 and sulphur loading, respectively. All curves exhibit the typical time dependent stress decay of stress relaxation behavior, but with different relaxation degree. The relaxation curves divide into two regions. First region is characterized by rapid drop of Mooney torque (shaded area). This is related to the recovery of elastic motion that takes place at a short time. Second region is noted by irreversibly viscous motion that occurs at longer time, such as chain slippage, disentanglement of rubber molecule chains, breaking down of filler agglomerates or filler-matrix debonding. These govern the flow and
causes gradually reduction to very low amount. The degree of the gradual reduction is depended on final configuration [5].

N-330 loading is greatly affected the rate of relaxation as seen on Figure 2. Increasing N-330 loading tend to prolong the relaxation time, indicating that the presence of N-330 slowed the relaxation rate as shown on Figure 4. This finding was agreed to Obaid et al. (2017) [2]. According to Maria et al. (2014) [1], the rate of the stress relaxation is greatly influenced by the filler and its interaction with rubber molecule chains in the matrix. Filler particles interact with rubber molecule chains through weak physical forces such as van der Waals. This interaction is often called by physical crosslinking, and in rubber, it is related to the bound rubber formation. Crosslink will hinder the mobility of the rubber molecule chains [8], thus lower the relaxation rate. Physical crosslink can be roughly estimated from the minimum rheometer torque (ML). It is clearly seen on Table 3 that ML increases upon N-330 loading. It indicates higher physical crosslink formed as a result of better interaction between filler and rubber. Higher physical crosslink is also confirmed by gradually increase of Mooney viscosity (ML1+4) upon N-330 loading. Increasing rubber-filler interaction is responsible to the increase of composite viscosity as observed in the experiments [9].

Figure 2. Time dependence of Mooney torque decay of NR composites on various N-330 loading.

Figure 3. Time dependence of Mooney torque decay of NR composites on various sulphur loading.
Figure 4. Stress relaxation rate of NR composite on various N-330 loading.

Figure 5. Stress relaxation rate of NR composite on various sulphur loading.

1.1. Sulphur is well-known as crosslinking agent for rubber. When vulcanization reaction proceed, sulphur reacts to the unsaturated sites of rubber molecule chains and forms the chemical crosslink. The density of these crosslinks is proportionally to the sulphur amount in the formula. Chemical crosslinks can be roughly determined by calculating the delta between maximum and minimum elastic rheometer torques (MH-ML) [7]. From Table 3 it is seen that chemical crosslink amount is increased upon sulphur
loading, nevertheless it gives less effect on the rate of relaxation compared to N-330 as depicted on Figure 6.

![Figure 6. Time dependence of Mooney torque decay of NR composites on various N-330 loading.](image)

The rate of relaxation also shows little change upon sulphur loading (Figure 5). In this case, chemical crosslink provides less effect than physical crosslink on rate of relaxation of NR composites.

![Figure 7. The rate of relaxation also shows little change upon sulphur loading (Figure 5). In this case, chemical crosslink provides less effect than physical crosslink on rate of relaxation of NR composites.](image)

Table 3. Curing characteristics and Mooney viscosity of NR composites.

| Loading | ts2 | t90 | MH | ML | ΔM=MH-ML | ML1+4 |
|---------|-----|-----|----|----|-----------|-------|
| N-300   | sec | sec | kgf.cm | kgf.cm | kgf.cm | MU |
| 30 phr  | 23  | 80  | 56.59 | 2.99 | 53.60 | 26.19 |
| 35 phr  | 22  | 84  | 59.88 | 3.92 | 55.96 | 32.82 |
| 40 phr  | 26  | 94  | 62.24 | 3.98 | 58.26 | 35.80 |
| 45 phr  | 22  | 92  | 68.31 | 5.04 | 63.27 | 46.48 |
| Sulphur |     |     |      |     |           |       |
| 1 phr   | 26  | 47  | 41.45 | 3.27 | 38.18 | 28.84 |
| 2 phr   | 23  | 80  | 56.59 | 2.99 | 53.60 | 26.19 |
3.2. Effect of Elasticity of NR Composites on Stress Relaxation

Elastic properties of rubber composite can be represented by its elongation and hardness. These two properties are depended on the rubber crosslink density [10], and are inversely one to another. Figure 8 displays linearly decrease on elongation upon N-330 loading. This reduction is probably caused by polymer chain stiffening through polymer-filler interaction, i.e. physical crosslinking [11]. At higher crosslink density, the length between two crosslink point becomes shorter, thus hinders of molecular mobility of rubber chain. This restriction brings to a slower relaxation rate as exhibited by Figure 4. and Figure 9 increasing crosslink density, either physical or chemical crosslink. At higher crosslink density, the Low crosslink density provides higher elongation due to free movement of the polymer chain. When filler particles amount increased, it is evident that the more physical crosslinks are formed (noted by higher ML) which restricts the mobility of rubber molecule chains. Similar to N-330, the increasing sulphur loading also leads to a linear decrease of elongation as depicted on Figure 9. The more sulphur amount in the formulation, the more chemical crosslink forms that leads to shorten the intercrosslink length and in turn hinder the molecular mobility. Increasing N-330 and sulphur loading causes linear increases of composite’s hardness, as expected. Figure 10 and Figure 11 exhibit increasing of hardness with crosslink density for physical and chemical crosslink, respectively.

| 3 phr | 22  | 97  | 69.26 | 4.10 | 65.16 | 23.44 |
|-------|-----|-----|-------|-----|-------|-------|
| 4 phr | 26  | 134 | 80.42 | 2.60| 77.82 | 17.99 |

Figure 8. Influence of N-330 loading on physical crosslink density and elongation.

Figure 9 Influence of sulphur loading on chemical crosslink density and elongation.
4. Conclusion

Stress relaxation of NR composites has been studied by Mooney stress relaxation coupled with rheometer data. Vulcanized rubber is usually composed by physical and chemical crosslink. Physical crosslink is resulted from rubber-filler particle, while chemical crosslink is formed during vulcanization reaction between rubber and sulphur. The MSR curve showed typical torque decay in which consisted of two regions as a result of elastic recovery and viscous flow. The relaxation rate of the composites, represented by MSR slope, is strongly related to the crosslink densities, i.e. physical and chemical crosslinks. The relaxation rate decreases upon crosslink densities caused by molecular mobility restriction. Physical crosslink density gives markedly effect on the relaxation rate compared to chemical crosslink. Thus, it should be considered when incorporating filler into the rubber matrix. Crosslink densities also affect the elasticity of rubber composite which represented by elongation and hardness. Elongation was linearly decrease with crosslink densities, while hardness was inversely. This confirms lower of relaxation rate of rubber composite.

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