Relaxation Behavior of Natural Rubber Composites Through Recovery Measurement after Tension and Compression Set

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Abstract. Relaxation behavior of natural rubber (NR) composites in term of the recovery after tension and compression set had been successfully studied. The effect of crosslink density, either physical or chemical, on the recovery percentage was evaluated. Filler carbon black N-330 and sulfur crosslinking agent were varied for this purpose. N-330 loading ranging from 30, 35, 40 and 45 phr with baseline of 2 phr sulfur. Meanwhile, sulfur loading ranging from 1, 2, 3 and 4 phr with the baseline of 30 phr N-330. Tension set was performed on constant elongation with 25, 50 and 100% strain. The measurements were performed at 100ºC for 72 h. While compression set was carried out in constant deflection 25% of initial thickness, carried out both at room temperature and 100ºC for 72 h. The results findings showed that the tension set was independent to crosslink densities, but greatly depended on the strain level. Low strain level provided higher recovery percentage. The filler increment markedly increased the compression set, but sulfur tended to improve it. Compression set was higher at elevated temperature since the deterioration not only generated by physical process but also by chemical oxidative thermal process.

Keywords: relaxation, natural rubber, tension set, compression set, crosslink

1. Introduction
Rubber is versatile engineering materials due to its elasticity and durability [1]. It can be formulated to obtain wide range of mechanical properties for many applications. Designing rubber product should consider many factors. It is not enough to characterized rubber product by its mechanical properties because they only describe the short term behavior. Consideration should have to be taken involving the long term behavior such as creep, stress relaxation and dynamic properties.

In the application, rubber is exposed to various forces whether as a stress, strain or shear either in static or dynamic loading. If definite forces are worked on the system, then all parts of the system are involved in the effort resisting the force. When these forces are removed out from the system, the molecule chains relax until achieves new equilibrium. Thus, relaxation is rate related to the how fast the transition of the system from one stage of equilibrium to another [2]. The relaxation process can be physical or chemical. Physical relaxation is occurred mostly by rearrangement of rubber molecule chains and the filler when subjected to deformation. Chemical relaxation is more prominent at higher temperature and longer time exposure involving the oxidative thermal aging which results in chain scission, crosslink breaking or even crosslink formation [3]. Chains scission and crosslink breaking
evidently slower the rate of relaxation. These could be a permanent deformation known as set properties. Set is correlated to the measurement of the recovery after removal of an applied forces. In practice, set is a convenient way to describe the relaxation phenomenon of a material. Moreover, it is quite simple method and relatively fast measurement, that makes it very useful to adopt in industry. Set properties can be measured under either tension or compression force.

Many efforts have been attempted by researchers in studying relaxation behavior of rubber to dates. However, to date only few of them discussed relaxation in term of recovery. Ayoub et al. [4] modeled permanent set in terms of a visco-hyperelastic damage. Maiti et al. [5] applied Tobolsky model to interpret the radiation effect of silicone rubber on the permanent set. Rosszainily et al. [6] measured permanent set of unvulcanized natural rubber filled by carbon black through tensile stress experiment. High percentage recovery was given by low carbon black loading as a result of strain induced crystallization. Mohaved et al. [7] studied the effect of efficient vulcanization (EV) curing system on compression set of nitrile rubber filled by various carbon black. Kömmling et al. [8] revealed the effect of chain scission of EPDM rubber during aging through relaxation and recovery experiments under compression force. Dai et al. [9] studied recovery after compression of γ-ray irradiation vulcanized HNBR. Compression set was decreased with increasing adsorbed γ-ray dose, which means improved crosslink density. Vishvanthperumal and Gopalakannan [10] investigated the effect of nano-clay loading and curing systems on compression set of EPDM nanocomposite. Compression set was found to increase incrementally with increasing nano clay loading, while sulfur vulcanization also showed the highest compression set among mixed- and peroxide curing.

In this present work, relaxation behavior of NR composite is investigated in term of the recovery after deformations, either in tension or compression. For these purposes, filler (carbon black N-330) or sulfur loading is varied to evaluate physical or chemical crosslink formed within the matrix. Bound rubber (BdR) has measured to identify the physical crosslinking, whilst total crosslink density is determined by equilibrium swelling. Tension set is carried out in constant elongation with various strain level, while compression set is done with constant deflection both in room and elevated temperature.

2. Experimental method

2.1 Materials
Natural rubber grades Standard Indonesian Rubber (SIR) 10 was supplied by local estate PTPN IX. Carbon black N-330 and N-774 (Ex. OCI, Korea), zinc oxide active (Indioxide), 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). Sulfur Midas SP 325 (Miwon) was used as vulcanizing agent. All chemicals were industrial grade.

2.2 Rubber compound preparation
The rubber compound was prepared according to the formulation as seen on Table 1. Carbon black filler (N-330) and sulfur loading were varied to evaluate the effect of crosslink formed onto the recovery percentage after tension or compression set, while another ingredient was incorporated in a fixed amount. The detail of the variable taken in this study was listed on Table 2.

Mixing process were performed in a two roll mill 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. The rubber compound was then allowed to rest for 24 h at 25°C before testing.
Table 1. Rubber Compound formulation

| Ingredients    | Concentration (phr) |
|----------------|---------------------|
| SIR            | 10.0                |
| 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. Testing samples preparation

The rubber samples for both tests were prepared by compression molding. Uncured rubber compounds were cured in a hydraulic press with hot platen in both sides (upper and lower) according to the dimension requirements for each test. The pressure applied was 150 kg/cm² and at temperature of 150 ºC. The curing time was determined from curing test that performed in a Moving Die Rheometer (MDR) Gotech M3000A at the same temperature. Curing was performed corresponding to t₉₀ obtained from MDR.

2.4. Bound rubber (BdR) and crosslink density measurement

Bound rubber (BdR) was essentially measured by swelling method of uncured rubber compound. The sample was cut in small pieces and placed in the wire basket, then immersed in toluene for 72 h at room temperature. After completion immersion period, the sample was taken out from the solvent. Rubber sample was then carefully removed from the wire basket and dried in air-circulated oven until achieving constant weight. The weight of the sample before and after swelling were taken, and BdR was calculated using Equation (1),

\[
BdR (\%) = 100 \left( \frac{w_i - \left( \frac{CPD}{100} \right) w_f}{w_i} \right)
\]

where \(w_i\) is the initial weight of the sample before immersion (in grams), \(w_f\) is the final weight after immersion and dried (in grams), and CPD is the total filler in the formulation (in phr).

Crosslink density was determined by equilibrium swelling. The swelling experiment was carried out by immersing the rubber sample in toluene at ambient temperature for 72 h. Swelling test was carried out for both samples, before and after compression of sample was taken before immersion. After completion swelling period, the sample was taken out and blotted with tissue paper to remove excess solvent. The mass of the sample, initial (\(w_0\)) and final (\(w_f\)), were weighed using analytical balance with 0.0001 g accuracy. The crosslink density was determined according to Flory-Rehner as expressed on Equation (2),

\[
M_c = \frac{-\rho_p V_s V_r^\frac{1}{2}}{\ln(1-V_r)+V_r+XV_r^2}
\]

where \(\rho_p\) is the density of polymer, \(V_s\) is the volume fraction occupied by solvent, \(V_r\) is the volume fraction occupied by rubber, and \(X\) is the mixing parameter.
where $M_c$ is the number average molecular weight of the rubber chains between crosslink; $\rho_p$ is density of the polymer; $V_s$ is molar volume of the solvent (for toluene $V_s=106.2 \text{ cm}^3 \text{ mol}^{-1}$), $V_r$ is molar volume of rubber, $X$ is polymer-solvent interaction parameter (for NR-toluene=0.42). The term $V_r$ was calculated by using the relation as expressed on Equation (3).

$$V_r = \frac{w_1 \rho_1}{(w_1 \rho_1 + w_2 \rho_2)}$$  \hspace{1cm} (3)

$w_1$, $\rho_1$ are the weight and density of rubber, while $w_2$, $\rho_2$ are the weight and density of solvent. The swelling experiment was performed on original and compressed samples. Flory-Rehner equation calculates total crosslink density of the composites, included physical and chemical crosslinks. Thus, chemical crosslink is then obtained by subtracting the total and physical crosslink. In this calculation, physical crosslink is determined from the intercept of the extrapolated curve (N-330 or sulfur loading vs crosslink density) as illustrated on Figure 1.

![Figure 1. illustration of physical crosslink determination based on Flory-Rehner Equation.](image)

2.5. **Tension and compression set tests**

Tension set measurements were performed at constant load according to ISO 2285:2013. A bar-type sample with 2-mm thickness was used. A fixed strain was applied to each sample and aged for 72 h at 100 °C in dry-air circulated oven. Three different strains were employed, i.e. 25, 50 and 100% of initial length. The detail of tension set testing is presented on Figure 2. The final length was ($L_f$) measured 30 minutes after the sample was removed from the test device using electronic digital Mitutoyo calliper with 0.01 mm accuracy. Tension set is expressed in percentage of recovery after strained, calculated according to Equation (4), where $L_0$ denotes for initial length (before strained), while $L_f$ is the final length after being strained.

$$tension\set = \frac{L_0-L_f}{L_0} \times 100\%$$  \hspace{1cm} (4)
Compression set testing was carried out in accordance to ISO 815-1:2014. The test was performed both on ambient and elevated temperature using assembled device as depicted on Figure 3. A cylindrical disc standard sample was employed for each test. The samples were placed between the space bars. The distance of the samples was adjusted to accommodate sufficient clearance for bulging when the rubber samples were compressed. Each bolt shall be tightened in order to get the uniform drawn throughout the compression area. The compressive stress was taken 25% of initial thickness \(h_0\). For elevated temperature testing, the assembled device was aged in the dry-air circulated oven for 24 h at 100 \(^\circ\)C. After completion of compression, the samples were removed from the device and placed in non-heat conductive material, such as wooden bar. The samples were allowed to recover for 30 minutes, then the final thickness was measured using electronic digital Mitutoyo caliper with 0.01 mm accuracy. Compression set is expressed as the recovery percentage of rubber sample respect to compress thickness. It is calculated using Equation (5),

\[
\text{compression set} = \frac{h_0 - h_f}{h_0 - h_s} \times 100\%
\]  

where \(h_0\) is the initial thickness, \(h_f\) is the final thickness after testing and \(h_s\) is the height of the spacer. Compression set tests at ambient temperature were conducted in similar way to the elevated temperature test, but without aging. The assembled device was placed in dry room with controlled-ambient temperature of 25 \(^\circ\)C. The effect of compression on rubber samples were monitored by crosslink densities measurement of the original and compressed samples.

3. Results and discussion

3.1. Crosslink densities of NR composites

Rubber composites are usually composed by two types of crosslinking, e.g. physical and chemical crosslink. Physical crosslink is a result of filler-rubber chain interaction or chain entanglement. Carbon black has surface activities resulted from active functional groups that can provide strong interaction with rubber chains. A thin layer of rubber covers single filler particle or agglomerates which is stabilized by physical bonds such as van der Waals forces as well as chemical bond. This phenomenon is well-known as bound rubber (BdR). It is solvent-resistant interphase that often used to characterized the physical crosslink [11]. The BdR is reduced by increasing N-330 amount (Figure 4), indicating filler agglomeration occurred within the rubber matrix. It should be noticed because it will bring negative effect to the composite when certain deformation forces work on it. Meanwhile, BdR tends to unchanged by increasing sulfur loading (Figure 5) attributed to constant filler loading employed in these composites.
Figure 4. Bound rubber of NR composites on various N-330 loading.

Figure 5. Bound rubber of NR composites on various sulfur loading.

Chemical crosslinks are formed during curing as a result of reaction between sulfur and rubber chain. Their formation can be determined by monitoring the torque changes over the time during curing test, or by equilibrium swelling method of vulcanized rubber. Increasing N-330 loading does not change the chemical crosslink density significantly since the sulfur used in the formulation is in the same level. In the other side, chemical crosslink rises markedly by increasing sulfur amount as expected. Sulfur reacts with unsaturation sites of NR backbone resulting in crosslinked chains through sulfur bridge. Thus, the more sulfur amount theoretically will result in the higher crosslink density.

Table 3. Crosslink density determination using Flory-Rehner equation.

| Loading   | Crosslink Density ($x10^{-4}$ mole/cm$^3$) | Total$^1$ | Physical$^2$ | Chemical |
|-----------|-------------------------------------------|-----------|--------------|----------|
| N-330     |                                            |           |              |          |
| 30 phr    | 2.222                                     | 1.004     | 1.218        |
| 35 phr    | 2.306                                     | 1.004     | 1.302        |
| 40 phr    | 2.580                                     | 1.004     | 1.576        |
| 45 phr    | 2.783                                     | 1.004     | 1.780        |
| Sulfur    |                                            |           |              |          |
| 1 phr     | 1.482                                     | 0.831     | 0.652        |
| 2 phr     | 2.222                                     | 0.831     | 1.391        |
| 3 phr     | 3.234                                     | 0.831     | 2.403        |
| 4 phr     | 3.525                                     | 0.831     | 2.694        |

$^1$Flory-Rehner
$^2$intercept of extrapolated curve

3.2. Effect of N-330 and sulfur loading on tension set

Tension set characterizes the ability of rubber to recover after being stretched. It is dealing with the residual strain that is generated as a result of new equilibrium state of molecular network after stress is removed. Upon stretching small chains reach their extensibility limit and brake, and free chains are in their relaxed configuration. Thus, the molecular network is more organized and causes reduction of entropy compared to virgin network. Tension set is depended on strain level and the composition of rubber, i.e. filler [3-5].
Figure 6. The tension set of NR composites on various N-330 loading.

Figure 7. The tension set of NR composites on various sulfur loading.

Figure 6 and Figure 7 clearly depict that tension set of NR composites is remain unchanged upon increasing either N-330 or sulfur loading. But, the level of strains markedly increases the tension set. Many crosslinked chains are probably broken during stretching resulting more free chains that is in relaxed configuration. Since the experiments were performed at elevated temperature, the chain breaking of crosslinked network could be due to stretching and heat aging. Heat aging may be caused chain scission that produces short-free chain. This lowers the entropy and hence increases the residual strain. Therefore, the recovery ability of NR composites after stretched is reduced.

3.3. Effect of N-300 and sulfur loading on compression set

Similar to tension set, compression set also measures the ability of rubber to recover after deformation force is removed. The difference is relied on the deformation force acted on the rubber. In compression set, the deformation force is compressive. In general, low compression set is better. In this study, compression set is carried out at ambient and elevated temperature. Ambient temperature compression set only describes the set phenomena caused by physical changes, whilst testing on elevated temperature will provide set description attributed by physical and chemical changes. Figure 8 depicts the compression set of NR composites on various N-330. Compression set tends to increase gradually with the increment of N-330. It is probably attributed by poor interaction between rubber and filler within the matrix, or agglomerates of filler are presented in large amount at higher loading of filler. Consequently, the physical crosslinking is decreased indicated by lower BdR content (Figure 4). Interaction between filler particles in agglomerate is weaker than of filler-rubber chain. It makes the agglomerates of filler is easier to break down by applied stress. Thus, better filler particle dispersion will result in a low compression set. Meanwhile breaking agglomeration of filler under compressive stress tends to increase compression set [13]. High filler loading also induces an increase of stiffness so that increases the compression set [10].

In the other sides, increasing sulfur amount rises compression set as seen on Figure 9. During compression, enormous crosslinks are involved in resisting the forces indicated by an increase of stress in the rubber network. This resistance may cause some crosslinks to break down. Then, the number of crosslinks responsible for the strain recovery are less than the number of crosslinks responsible to resist the compression [14]. These breakdown crosslinks may be categorized as permanent set that cause reduction of recovery percentage (lower than 100%). At low sulfur loading (1 phr), the total crosslink density is somewhat lower (Table 3). Of course the number of crosslinks involved in resisting compressive force are much lower than those of composite with high loading sulfur. Surprisingly, compression set deviates when 4 phr sulfur is employed. In this formulation, sulfur amount is much higher than of accelerator (high sulfur to accelerator ratio) that possible to form polysulfide crosslink
(C-Sx-C, with x>2), with longer S-S bond. The S-S bond has low bonding energy that is easily broken out. Thus, the longer S-S bond in crosslink probably the more chance of chain breaking that lead to a reduction on compression set. The occurrence of crosslink breaking is confirmed through crosslink density measurement as showed on Figure 10 and Figure 11.

![Graph](image1)

**Figure 8.** The compression set of NR composites on various N-330 loading.

![Graph](image2)

**Figure 9.** The compression set of NR composites on various sulfur loading.

In general, compression set results in lower value at ambient temperature compared to those at elevated temperature (in this case 100°C). At low temperature, the chain breaking is mainly due to the physical deterioration, such as resisting the compressive force. The effect becomes more severe at elevated temperature because thermal degradation is taken account. Degradation at elevated temperature is mainly oxidative aging that may cause chain scission, crosslinking or even modify the filler-rubber interface [5]. Chain scission may dominate resulting in lower crosslinking. Thus, the number of broken crosslink is the sum of physical deterioration and thermal degradation. This explains the reduction of compression set at elevated temperature. A marked reduction on crosslink density is observed at 4 phr sulfur. This confirms the existence polysulfidic linkage at higher sulfur loading. This linkage is unstable at elevated temperature.

![Graph](image3)

**Figure 10.** Crosslink density before and after compression set on various N-330 loading

![Graph](image4)

**Figure 11.** Crosslink density before and after compression set on various sulfur loading
4. Conclusion
Studies on relaxation behavior of NR composites has been successfully done through comprehensive studies on the tension and compression set. Tension and compression set represented the recovery of the rubber after certain forces worked on it. In this study, Carbon black N-330 and sulfur loading were varied to evaluate their effect on recovery of the composites. Tension set was carried out at constant elongation, i.e. 25, 50 and 100% strain of initial length, whilst compression set was conducted at constant deflection of 25% of initial height. Physical crosslinks were observed to reduce by increment of carbon black, but it stayed constantly on various sulfur loading. Meanwhile, the total crosslink density was found to increase upon sulfur loading, but it tended to steady on N-330 loading. Tension set was greatly affected by the level of strain instead of crosslink density. The set properties rose by increasing strain, either for N-330 or sulfur loading. Consequently, the recovery was decreased. Compression set was conducted both at room temperature and elevated temperature (100 ºC). Compression set increased with the increment of N-330 that meant decreasing recovery percentage. Bound rubber measurement has confirmed this finding. Increasing sulfur loading improved the compression set. But deviation was found at higher sulfur loading (4 phr). High sulfur to accelerator ratio resulted in polysulfidic linkage that unstable to either stress or heat. High temperature imparted negative impact on compression set correlated to heat aging effect on rubber network. Chain scission could be majorly occured that increase the chain breaking possibility during compression.

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