NR/precipitated silica/dodecanol composites: Torque, hardness and morphology behaviors

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Abstract. The effects of dodecanol (DDC) incorporations on torque, hardness and morphology behaviors/properties of natural rubber (NR)/precipitated silica (PSi) composites were studied using a typical Semi EV. The NR was loaded with the PSi at a settled dose, thirty phr. The DDC is one type of fatty alcohols that is produced based on the oil of palm kernel. The DDC was incorporated toward the PSi-loaded NR systems/compounds with various doses from one to four 4.0 phr. Because of its roles as a co-curing and internal plasticizer, it was revealed that the DDC affected the torque, hardness and morphology properties of PSi-loaded NR systems. The DDC exhibited the enhancements in torque change and hardness, especially till a three phr of DDC dose. The study on morphology behavior confirmed that the three phr of DDC was the optimum dose in which the cracked surface of PSi-loaded NR system with a three phr of DDC displayed the tremendous line of matrix fracture and surface breaking. Based on the overall results, the DDC incorporations caused the PSi-loaded NR systems in a less hardness but a higher torque change.

1. Introduction
Silica reinforcement on natural rubber (NR) is the enhancement of some properties include tensile strength and moduli, resistances to abrasion and tear of vulcanizates of NR because of the incorporation of precipitated silica (PSi) filler [1]. Reinforcing fillers include carbon black (CB) and PSi affects the NR systems/vulcanizates properties significantly [2, 3].

Whenever compare the reinforcement effect CB to that of PSi and the fillers with comparable particles sizes; the reinforcement effect of PSi is usually inferior to that of CB [4, 5]. It is because of the PSi surfaces cause some difficulties in applying it in NR reinforcement. The surfaces are very hydrophilic and polar and as a consequence, they are incompatible with NR. Therefore, the rubber to filler interactions are weak but filler to filler interactions are strong; the results are the forming of some agglomerates with large volumes and a poor filler dispersion.

So many experiments have been done to enhancing the PSi reactivity on NR. One of the experiments was the silane-treated PSi, which showed more significant enhancement in reinforcement effect than that of the basic form of PSi. Based on some results, the silane-treated PSi promises as an alternative reinforcing filler to the lower reinforcement affectation of CB. Anyhow, in factual utilization the achievement of the silane-treated PSi has not been interpreted apparently. Maybe, the expensive price of the silane was the problem.

One optional approach to clarify the problem of the PSi was the use of dodecanol (DDC) in PSi reinforcement on NR. The DDC is an ingredient that can be produced from palm oil kernel. Since it comes from oil material and hence, ingredient oil is a variety of plasticizing agents [2, 3]; it has the
potential to be used as a plasticizing agent to helping better dispersion of the PSi filler. Therefore, the study investigated the effect of DDC incorporations on torque, hardness and morphology properties of the PSi-loaded NR systems.

2. Experiment

2.1. NR and Rubber Ingredients
The SIR 3L-type of NR, IPPD, stearic acid, sulfur, ZnO, MBTS and PSi were prepared by P.T. Industri Karet Deli, Medan-Indonesia. The DDC \((\text{CH}_3\text{CH}_2_{11}\text{CH}_2\text{OH})\) was given by P.T. Ecogreen of Batam Branch, Indonesia.

2.2. Making NR Compounds
Typical sulfur accelerated vulcanization system was used in making NR composites on an XK-160 Model of 2-roll mill. All the compounding procedures were executed based on ASTM D 3184-80. Table 1 shows the NR/PSi composites.

| Table 1. The NR/PSi composites |
|-------------------------------|
| **NR/Ingredients**            | **Phr** |
| SIR                           | 100.0   |
| Stearic acid                  | 2.0     |
| ZnO                           | 5.0     |
| MBTS                          | 1.5     |
| IPPD                          | 2.0     |
| Sulfur                        | 1.5     |
| Precipitated silica           | 30.0    |
| DDC                           | 0.0; 1.0; 2.0; 3.0; 4.0|

2.3. Torque Behavior
The torque behavior of the systems of NR was determined by the MDR 2000 - Rheometer include minimal torque and maximal torques, torque difference based on ISO 3417. The NR compounds were heated at 150 °C.

2.4. Hardness Behavior
The hardness behavior of the NR composites was determined by using a Shore A type manual durometer (based on ISO 7691-1).

2.5. Morphological Behavior
The cracked surfaces of NR/PSi plus DDC composites were tested applying a Zeiss Supra-35VP scanning electron microscope/SEM to achieve the data relating to the availability of some micro-defects. The cracked samples were covered with a gold layer to minimize electrostatic charge build-up as long as the testing.

3. Results and discussion

3.1. Torque Behavior
The torque behavior of the NR/PSi composites in the presence of DDC is shown in Table 2. As shown, the DDC incorporation at 1.0 phr reduced minimal torque \( (M_N) \) of the control compound. The \( M_N \) is believed as the rubber compound viscosity \([7-9]\). The bigger \( M_N \) means a higher value of viscosity. The DDC reduced the viscosity of the NR/PSi composites, it was connected to the role of DDC as an internal plasticizing ingredient that softened, diminished the viscosity, respectively. A bigger DDC dose made a lower viscosity.
Table 2. The torque behavior of the NR/PSi composites at different DDC doses

| NR/PSi composites | DDC (phr) | 0.0 | 1.0 | 2.0 | 3.0 | 4.0 |
|-------------------|-----------|-----|-----|-----|-----|-----|
| MX in dN.m        |           | 11.4| 10.4| 10.6| 11.3| 9.7 |
| MN in dN.m        |           | 2.7 | 2.3 | 2.2 | 2.2 | 2.0 |
| Torque change in dN.m |       | 8.7 | 8.1 | 8.4 | 9.1 | 7.7 |

The DDC incorporation at 1.0 phr raised torque change (MX – MN) of the control compound. The torque change was further raised with the DDC incorporations up to three phr and initiated to decrease after the three phr. The torque change is believed as the rubber compound level of crosslinks [10-13]. The lower the value, the fewer is the crosslinks. The level up of torque change or crosslinks level till an optimum concentration of DDC (at three phr) was because of chemical & physical behaviors of DDC. Its hydroxyl groups might activate strongly both NR and sulfur constituent in the time of vulcanization. With others ingredients, hydroxyl groups provided some complexes that tied some usable sulfur to NR chains more effective [2,14] and hence, leading to a higher curing degree.

Since the DDC is an oily ingredient, it has the role of an internal plasticizing ingredient. As discussed previously, DDC diminished viscosity of systems of NR/PSi and hence, raised the homogeneity of PSi dispersion, rubber to filler interactions/bonds, jointly. The NR to PSi bond is physical crosslinks [15], together plus sulfide crosslinks mean the overall crosslinks [16,17].

The decline in torque changes, above the optimum concentration of DDC, was connected to dilution affection of the excessive amounts of DDC that created several oily layers and hence, absorbed PSi and other ingredients. By this step, the crosslinks were reduced.

3.2. Swelling Behavior

The swelling percentage (SP) of NR/PSi composites with/no DDC is visualized in Fig. 1. The SP is the crosslinks level of a composite system [18], a more toluene penetration into compounds indicating fewer crosslinks.

Figure 1. The swelling percentage of NR/PSi composites at different DDC doses

The DDC incorporation at one phr reduced swelling percentage (SP) of control compound. Increases in DDC doses until a three phr caused a farther reducing in SP. Beyond the three phr DDC concentration, the SP started to raise. The increases in crosslinks were due to the role of DDC as an internal plasticizing ingredient.
ingredient [19,20] which plasticized and reduced the filled NR. A relatively lower viscosity makes easier the operation of PSi dispersion, and enhanced NR to PSi interaction, jointly. The NR to PSi type of interaction is the extra physical crosslinks and, together plus sulfide crosslinks are the overall crosslinks [7-9].

3.3. The Hardness Behavior
The effect of DDC incorporations on hardness behavior of NR/PSi composites is presented in Table 3. The DDC reduced the hardness or stiffness of the NR/PSi composites. The bigger the DDC dose, the less was the hardness. The hardness is believed as the stiffness of a rubber vulcanizate [1, 5] and hence, the DDC incorporations produced softer NR/PSi composites. It was connected to the role of DDC as an internal plasticizing ingredient.

| Table 3. Hardness behavior of NR/PSi composites at different DDC doses |
|-----------------------|-------|-------|-------|-------|
| NR/PSi composites      | 0.0   | 1.0   | 2.0   | 3.0   | 4.0   |
| Hardness, Shore A      | 35.0  | 34.5  | 34.0  | 33.0  | 32.0  |

3.4. Morphology Behavior
Figure 2 shows SEM images (at magnification 340 X) of the cracked surfaces of the NR/PSi composites with/without no DDC. As observed, the NR/PSi images with DDC (Figures 2B and 2C) displayed a greater surface breaking and tremendous lines of matrix fracture than that of the NR/PSi system with no DDC (Figure 2A). The surface-breaking of a rubber vulcanizate announces that the matrix breaking that relates to the level of filler dispersion [21,22]. As observed, the rougher surfaces also announced a stronger synergy of rubber to filler and the images of the tensile cracked surfaces matched with the natures of torque change (Table 2) and swelling property (Fig. 1).

An improvement in fracture energy indicates a stronger synergy of rubber to the filler that correlated to the breaking and matrix tearing line of cracked surface. The 2B micrograph of NR/PSi composite with three phr of DDC displayed the greatest surface breaking and matrix fracture. It correlates to the highest level of crosslinks which changed the interactions of NR to PSi into the strongest one and hence, causing an increase in the degree of filler dispersion.

The images of the tensile cracked surfaces agreed with the results received by others workers who published that an enhancement in filler dispersion could be indicated by the breaking and degree of matrix fracture lines of cracked samples [21,22].
Surface breaking and matrix fracture

Greatest surface breaking and matrix fracture

(a) A

(b) B
4. Conclusions
The dodecanol role as a curative ingredient for natural rubber/precipitated silica composites. It was a co-curing and internal plasticizing ingredient. The dodecanol diminished the minimal torque and hardness but raised the degree or level of precipitated silica homogeneity. The dodecanol increased the torque change and crosslinks of natural rubber/precipitated silica composites. The three parts per hundred rubber of dodecanol was the optimum dose. The dodecanol incorporations yielded natural rubber/precipitated silica composites with less hardness behavior.

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