Effect of acrylonitrile butadiene rubber on the properties of silica-reinforced natural rubber

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Abstract. The effect of acrylonitrile butadiene rubber (NBR) as a compatibilizer in silica-reinforced natural rubber (NR) is studied. NBR, Emulcril 3380 with 32-34%, was various at 5, 10, 15, 20 and 25 part per hundred parts of rubber (phr) to be used as a compatibilizer for silica-filled NR. The use of NBR as a compatibilizer can improve cure time (T₉₀), cure rate index (CRI), and Mooney viscosity of silica-filled NR compounds, but the re-agglomeration of filler still observes. The use of NBR does not show significantly effect on bound rubber contents. However, tensile strength, reinforcement index and tear strength are increased with increasing amount of NBR contents due to a presence of some rubber-filler interaction through acrylonitrile groups of NBR and silanol groups on the silica surface. It leads to observe more surface roughness on tensile fractured surfaces.

1. Introduction
Silica is widely used as a reinforcing filler for white applications. In tire industry, silica has been used as a filler to provide saving energy tires because the use of silica can improve a rolling resistance and wet grip, while wear resistance is still remained. However, silica basically shows a poor dispersion and a low filler-rubber interaction because of a high surface polarity. Silane coupling agent is required to use in the silica-filled rubber compound to improve silica-rubber interaction such as bis-(triethoxysilylpropyl) tetrasulfide (TESPT)[1] and bis-(triethoxysilylpropyl) disulfide (TESPD).[2] Mixing condition of silica and silane coupling agent has been considered to obtain a good silanization reaction during mixing.

Surface polarity of silica tends to from silica agglomerates and shows low interaction with non-polar rubbers. Silica-filled NR shows very poor silica dispersion and silica-rubber interaction, leading to low physical and dynamic mechanical properties. On the other hand, the mixing of silica with a polar rubber can provided some interaction through their functional groups. Chloroprene rubber (CR) can generate a silica-rubber interaction via polarity of chlorine atom and silanol groups on the silica surface.[3] Epoxidized natural rubber (ENR) shows a good improvement of dynamic mechanical properties because epoxy groups in ENR structure can generate some interaction with silanol groups which become a strong bonding at high temperature.[4] For silica-filled NBR compounds, the interaction between silica and NBR is observed though hydrogen bond and the interaction increases with amount of acrylonitrile in NBR.[5]
In this work, NBR was used as a compatibilizer to improve the properties of silica-filled NR compounds. Cure characteristics, bound rubber content, Payne effect and mechanical properties were studied.

2. Experimental methods

Ribbed smoke sheet No.3 (RSS#3) was used as a matrix in this experiment. Emulcril 3380 (INSA GPRO Synthetic rubber, China) is an acrylonitrile butadiene rubber (NBR) with acrylonitrile contents of 32-34%, was studied on various amounts of 5, 10, 15, 20, and 25 phr. Chemicals in this experiment were a precipitated silica 185-Micro Pearl (Ecopower, China) for 50 phr, bis-(triethoxysilylpropyl)-tetrasulfide (TESPT) (Evinik, Germany) 5 phr for a reference compound, Treated distillated aromatic extract oil (TDAE oil) (Hansen and Rosenthal, Germany) 5 phr, 2,2,4-Trimethyl-1,2-dihydroquinoline (TMQ) 1 phr, zinc oxide (ZnO) 3 phr, stearic acid 1 phr, diphenylguanidine (DPG) 1 phr, N-cyclo-hexyl-2-benzothiazyl sulphenamide (CBS) 1.5 phr and sulphur (all from Behnmayer, USA) 1.5 phr.

Silica-reinforced NR compounds were prepared by using an internal mixer (Haake PolyLab, Germany) with initial mixing temperature at 110°C and rotor speed at 60 rpm. Mixing procedures were provided in two steps; the first step was prepared in the internal mixer and the second step was mixed on a two-roll mill as details in Table 1.

| Table 1. Mixing procedures. |
|-----------------------------|
| **Mixing steps** | **Time (min)** |
| **Step 1: Internal mixer** |  |
| - Mastication of NR | 2 |
| - Mixing of a first half of silica (TESPT) and oil | 5 |
| - Mixing of a second half of silica (TESPT) and oil | 5 |
| - Mixing of TMQ, ZnO, stearic acid and DPG | 3 |
| **Step2: Two roll mill** |  |
| - Mixing of CBS and Sulphur | 5 |

All of compounds were tested a Mooney viscosity at 100°C with a large rotor (ML1+4, 100-C) (Montech, Germany). Cure characteristics of all compounds were studied using a moving die rheometer (MDR) (Montech, Germany) at 150°C and compressed to reach their maximum cure times.

Bound rubber contents of silica-reinforced NR compounds were investigated at room temperature by immersing 0.25 g of the compounds in 30 ml of toluene for three days and dried it at 80°C for 24 hr, then immersed it again in 30 ml of toluene for another three days, dried it at 80°C for 24 hr and measured the residual weights. Total bound rubber content was calculated by using an equation (a):

\[
Total \ bound \ rubber \ (\%) = \frac{m - m_s}{m_r} \times 100 \quad (a)
\]

where \( m \) is the weight of the sample after extraction, \( m_s \) is the weight of silica in the sample and \( m_r \) is the original weight of rubber in the sample.

Tensile properties and tear resistance were analyzed according to ASTM D412 and ASTM D624, respectively. Tensile fracture surface was tested by using a stereomicroscope (Zeiss, Germany) with 50x magnification.

3. Results and discussion

Cure characteristics of silica-reinforced NR compounds with various types and concentration of NBR are shown in Figures 1. The use of NBR-3380 as a compatibilizer in the silica-filled NR compounds is shown the same trend of cure characteristics. Cure time (\( T_{90} \)) and cure rate index (CRI) are improved with increasing NBR contents. Hydrophilic surface of silica can create some interaction with acrylonitrile groups in NBR leading to a lower curatives absorbed on its surfaces as seen in the improvement of cure properties. However, the presence of NBR in the silica-filled NR compounds is still clearly seen the effect of re-agglomeration of silica aggregates under shear and high temperature...
condition as an increase of cure torques at the beginning of cure curves, as known as a flocculation phenomenon, but does not observe in the TESPT compound.

**Figure 1.** Cure characteristics of silica-reinforced NR with NBR-3380 as a compatibilizer.

Payne effect is used to explain filler-filler interaction in the compounds, as shown in Figure 2a. It is clearly seen that the silica-filled NR compound without any compatibilizer shows the highest filler-filler interaction, in contrast the addition of TESPT shows the lowest one. While the use of NBR as a compatibilizer in silica-filled NR compounds tends to decrease filler-filler interaction. However, there is not significantly different when amount of NBR is increased.

**Figure 2.** Payne effect (a), total bound rubber contents and Mooney viscosity (b) of silica-reinforced NR with different types of NBR and concentrations.

Figure 2b shows total bound rubber contents and Mooney viscosity of silica-filled NR compounds. The presence of TESPT gives the highest bound rubber content due to a good interaction after a silanization reaction during mixing at a certain temperature. While the use of NBR as a compatibilizer shows a slightly improvement of silica-rubber interaction with increasing NBR concentration. The silica-filled NR compound without compatibilizer basically shows a high amount of trapped rubbers which will be acted as hard particles in the compound and cannot be extracted. Then, it tends to high bound rubber contents in the compound compared with the compounds with NBR. Mooney viscosity of the silica-filled compounds evidently improves by presence of NBR in the compounds as seen in a lower Mooney viscosity.

Tensile strength and reinforcement index of the silica-filled NR vulcanizates are shown in Figure 3a. The use of NBR as a compatibilizer can improve tensile strength with increasing amount of NBR. Maximum tensile strength is observed when NBR-3380 at 20 phr has been used, however, it is still lower than those of the use of TESPT. Reinforcement index is identified by 300% modulus divided by 100% modulus as shown in Figure 3a. It shows the same trend as well as tensile strength and total bound rubber contents (Figure 2b). The reinforcement index is observed when the NBR has been used up to 20 phr, then it tends to decrease in a further addition of NBR in the silica-filled NR compound. Tear strength of silica-filled NR with NBR as a compatibilizer is shown in Figure 3b. The use of NBR-3380 shows an improvement of tear strength of silica-filled NR. It is found that the increasing of NBR-3380 contents leads to increase of tear strength.
The tear strength is improved to the same level as a use of TESPT when NBR-3380 at 20 phr was added into the silica-filled NR rubber. It proves that acrylonitrile groups in NBR structure can generate some interaction between silica and rubber as well as an improvement of silica dispersion. These are affected on the improvement of cure characteristics, tensile and tear properties.

Figure 3. Tensile strength, reinforcement index (a) and tear strength (b) of silica-reinforced NR with NBR as a compatibilizer.

Comparison of tensile fractured surfaces of silica-filled NR vulcanizates is shown in Figures 4a-d. The silica-filled NR without TESPT has a smoother fractured surface than the silica-filled NR with TESPT due to a poor silica dispersion and a low silica-rubber interaction, leading to the lowest tensile strength as seen in Figure 3. Tensile fractured surfaces of silica-filled NR with NBR as a compatibilizer are clearly seen the surface roughness increased by increasing NBR concentrations because of enhancement of silica-rubber interaction as observed on the improvement of overall properties.

Figure 4. Tensile fractured surfaces of silica-filled NR without TESPT (a), with TESPT (b) and various amount of NBR contents (c-d).

4. Conclusion
The properties of silica-filled NR can improved by using NBR as a compatibilizer. The increase of NBR contents leads to decrease of Mooney viscosity, increase of cure rate index, tensile and tear strengths. From the overall properties, it is found that the use of NBR-3380 at 20 phr as a compatibilizer shows a good improvement to reach optimum. Tensile fracture surface roughness is increased by increasing amount of NBR content due to a better silica-filler interaction and silica dispersion.

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