The nano-sized montmorillonite-filled natural rubber: vulcanization and reinforcement properties

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Abstract. One semi EV vulcanization system was applied for observing the effects of nano-sized montmorillonite on vulcanization and reinforcement properties of natural rubber (NR) composites. The montmorillonite as a nano-sized reinforcing filler was added into NR at varied concentrations i.e 2.0, 4.0, 6.0, 8.0 and 10.0 parts per hundred rubber (phr). It was found that the montmorillonite functioned as a co-curing material and reinforcing filler. It decreased the optimum cure times of the NR composites. The higher the montmorillonite concentration, the shorter the optimum cure times were. The montmorillonite also increased the torque difference, tensile moduli, reinforcement index and tensile strength. The tensile strength was improved up to an 8.0 phr of montmorillonite concentration.

1. Introduction
Rubber composites are the combination of organic as matrix and inorganic materials that function synergistically in making numerous wanted properties with no damaging the mechanical or physical properties of organic rubber matrix [1].

Rubber nanocomposite, as a type of composite materials, is made by nano-sized inorganic filler which often delivers the exceptional performance in term of mechanical properties, etc. when compared to the organic matrix or conventional filled composites [1] [2]. The performance improvement is usually achieved by the addition of relatively small quantities of the nano-sized filler at less than 10 parts per hundred rubber [3].

The montmorillonite (MMT) is one type of nano-sized inorganic filler. In this observation, it was added to natural rubber (NR) compounds during compounding operation through the use of a two-roll mill. Therefore, the effects of the MMT additions on vulcanization and reinforcement properties of NR composites were observed.

2. Chemicals and methodology
2.1. Chemicals
The natural rubber and other compound ingredients include sulfur, zinc oxide, montmorillonite, isopropyl-N'-phenyl-p-phenylenediamine, mercapto benzothiazolyl disulfide and stearic acid were given by the rubber lab of School of Materials and Natural Resources, Universiti Sains Malaysia (USM), Malaysia.
2.2. Rubber compounding
The NR and other compounds ingredients were compounded based on a semi-EV cure system. The sequences of rubber compounding were done based on ASTM D3184-80 on a lab-type 2-roll mill. Table 1 presents the compound recipe for rubber compounding.

Table 1. The compound recipe for rubber compounding.

| Chemicals                              | Content (phr.) |
|----------------------------------------|----------------|
| Natural rubber                         | 100            |
| Sulfur                                 | 1.5            |
| Isopropyl-N'phenyl-p-phenylenediamine  | 2              |
| Stearic acid                           | 2              |
| Mercapto benzothiazolyl disulfide      | 1.5            |
| Zinc oxide                             | 5              |
| Montmorillonite                        | 0; 2; 4; 6; 8 and 10 |

2.3. Vulcanization properties
The MMT-filled NR vulcanization properties include $t_{90}$, optimum cure time, $M_x$, maximum torque, $M_n$ minimum torque, $M_x - M_n$, change in torque according to ISO 3417 using a Rheometer (MDR 2000). The compounds/samples of MMT-filled NR were vulcanized at 150°C.

2.4. Reinforcement and tensile properties
Tensile properties of vulcanized SBR were observed according to ASTM D-882 using tensometer with extension rate is of 500 mm/minute. Reinforcement index (RI) was calculated based on Equation 1.

\[ RI = \left( \frac{M_{300}}{M_{100}} \right) \times 100 \]  \hspace{1cm} (1)

3. Results and discussion

3.1. Vulcanization properties
The effects of montmorillonite on $t_{90}$, optimum cure time, $M_x$, maximum torque, $M_n$ minimum torque and $M_x - M_n$, change in torque of NR nanocomposites are shown in Figure. 1-3.
It was observed in Figure 1 that the additions of 2.0 phr of montmorillonite decreased the optimum cure time. The higher the montmorillonite loading yielded the lower optimum cure time and hence, the montmorillonite functioned as a co-curing filler/agent. It was because of more and more significant the acceleration affection of metal-stearate complexes. Presumably, that the metallic constituents include aluminium and sodium of nanofiller and activator zinc oxide caused in a more significant the acceleration affection of the complexes of zinc/aluminium/sodium stearate. These complexes were the actual accelerator in the vulcanization process of the nanocomposites of NR [4].

From Figure 2, the 2.0 phr of montmorillonite addition raised the max. torque which corresponds to stock modulus value that was improved in the observation. It was because of the nature of rubber to filler interactions include intercalation and exfoliation [5]. The improvement in max. torque was more significant when the loadings of montmorillonite were further raised to a 10.0 phr. The processes of intercalation and exfoliation and also the rubber to filler interactions were further raised also.

![Figure 1. Optimum cure time vs MMT loading.](image1)

![Figure 2. Minimum and maximum torques vs MMT loading.](image2)
From Figure 3, the 2.0 phr of montmorillonite addition into the control compound yielded an NR nanocomposite with a bigger torque difference value than the control compound. The additions of montmorillonite up to a 10.0 phr of loading further raised the value. It is believed that torque difference relates to the crosslink density of a compound of rubber [6] [7]. The higher the value, the higher the crosslink density is created. The total crosslinks is the sum of sulphide and physical crosslinks [8] [9]. The additions of up to a 10.0 phr of montmorillonite into the NR improved the torque differences of the composites of NR. It was positive because of the increases in physical crosslinks because of the enhancement in the formation of rubber to filler interactions.

![Torque change vs MMT loading](image)

**Figure 3. Torque change vs MMT loading.**

3.2. Reinforcement index and tensile properties

Table 2 tabulates the reinforcement index (RI) and tensile properties of montmorillonite-filled NR composites. The tensile properties include tensile moduli (M300 and M100) and tensile strength (TS). As shown, the 2.0 phr of montmorillonite addition increased the RI, M300, M100 and TS of the control NR compound. The enhancements in the above properties were attributed to the crosslinks enhancing of NR through the enhancement in rubber to filler interactions (physical crosslinks) [10] [11] [12] [13] [14].

The increases in MMT loading up to the 8.0 phr further increased the RI, M300, M100 and TS and after the 8.0 phr of montmorillonite loading, the RI and TS started to reduce but tensile moduli still increased. The enhancement in those properties was due to improvement in crosslinks, and the deterioration in those properties was due to crosslinks decreasing.

| NR nanocomposites | 0.0 | 2.0 | 4.0 | 6.0 | 8.0 | 10.0 |
|-------------------|-----|-----|-----|-----|-----|------|
| M300, MPa         | 1.235 | 1.260 | 1.376 | 1.418 | 1.604 | 1.629 |
| M100, MPa         | 0.538 | 0.546 | 0.564 | 0.582 | 0.646 | 0.660 |
| TS, Mpa           | 17.7 | 18.0 | 18.6 | 19.0 | 19.7 | 18.2 |
| RI, %             | 229 | 230 | 243 | 244 | 248 | 246 |
4. Conclusion
Because of its function as curative material, the additions of montmorillonite into natural rubber compounds caused in decreasing the optimum cure times but increasing the torque differences. The montmorillonite showed some reinforcement effects on natural rubber significantly. The reinforcement index, tensile moduli and tensile strength were enhanced, especially up to an eight phr of montmorillonite loading.

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