

The effects of nano-sized montmorillonite on rheological and mechanical properties of natural rubber

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Abstract. A semi EV curing system was applied for studying the effects of nano-sized montmorillonite on rheological and mechanical properties of natural rubber (NR) composites. The montmorillonite as a nano-sized filler which was added into NR at 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 agent and reinforcing filler. It decreased the scorch and cure times of the NR composites. The higher the montmorillonite loading, the shorter the scorch and cure times were. It also increased the torque difference, tensile modulus and hardness but decreased the elongation at break. The tensile strength was improved up to an 8.0 phr. of montmorillonite loading.

1. Introduction

Composite materials contain the inorganic and organic materials which function synergistically in producing a lot of desired properties with no ruining the physical properties of organic matrix [1].

Nanocomposite, as a type of composite materials, is built with nano-sized inorganic filler which often delivers the exceptional performance in term of mechanical properties and 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 rubbers [3].

The montmorillonite is one type of nano-sized inorganic filler. In this research work, it was added to natural rubber (NR) compounds during compounding operation through the use of a two-roll mill. Therefore, the effects of the addition of montmorillonite on rheological and also mechanical properties of NR composites were investigated.

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. Rheological properties

The NR rheological properties include (ts_2 , scorch time), (t_{90} , cure time), max. torque (M_x), min. torque (M_n), difference in torque ($M_x - M_n$) (based on ISO 3417) were delivered by the use of a Rheometer (MDR 2000). The compounds/samples of NR were cured at 150°C.

2.4. Mechanical properties

The values of the hardness of the NR compounds were obtained based on ASTM D2240-05 by the use of a Shore A type Durometer.

Tensile properties include (TS, tensile strength), (M300/M100, tensile moduli) and (EB, elongation at break) of the vulcanized NR were determined using a tensometer (Instron-3366) based on ASTM D-882.

3. Results and Discussion

3.1. The rheological properties

The effects of montmorillonite on the times to scorch and cure of NR nanocomposites are shown in **Table 2**. Whenever compared to the control NR composite (NR composite with no montmorillonite), it was clearly observed that the additions of montmorillonite decreased the cure and scorch times of control NR composite. The montmorillonite might be considered as a co-curing agent. Presumably, the metallic ingredients such as aluminum and sodium of montmorillonite and zinc caused in a more pronounced the acceleration effect of zinc/aluminum/sodium stearate complexes which functioned as the actual accelerator in the curing process [4].

Table 2. The rheological properties of NR nanocomposites

NR nanocomposites	Montmorillonite loadings (phr.)					
	0.0	2.0	4.0	6.0	8.0	10.0
ts_2 / min.	4.49	4.33	3.92	3.44	2.79	2.43
t_{90} / min.	7.13	7.12	6.06	5.42	4.69	4.17
M_x / dN.m	4.81	4.83	5.27	5.32	5.91	6.10
M_n / dN.m	0.04	0.04	0.05	0.05	0.05	0.05
($M_x - M_n$) / dN.m	4.77	4.79	5.22	5.27	5.86	6.05

The more the montmorillonite loading, the lower the time to scorch and time to cure were. This was because of more and more pronounced the acceleration effect of metal-stearate complexes.

The montmorillonite addition at 1.0 phr. improved the max. torque. The max. torque qualitatively corresponds to stock modulus value that was improved in the investigation. It was because of the nature of rubber to filler interactions include intercalation and exfoliation [5]. The improvement in max. torque became more significant when the loadings of montmorillonite were further increased up to a 10.0 phr. The intercalation together with the exfoliation and also the rubber to filler interaction were further improved also.

The montmorillonite addition at 1.0 phr. into the control compound produced an NR composite with a higher torque difference value when compared to the control compound. The additions of montmorillonite up to a 10.0 phr. of loading further improved the torque difference. The torque difference qualitatively relates to the crosslink density of a compound of rubber [6-7]. The higher the torque difference value, the higher the crosslink density is. The total crosslink density is the sum of sulphide crosslinks 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 NR composites. It was clearly due to the increases of physical crosslinks because of the enhancement of the formation of rubber to filler interaction.

3.2. The mechanical properties

Fig. 1 shows the relationship between M100/M300 and montmorillonite loading. The montmorillonite additions affected the tensile moduli. The higher the loading of montmorillonite, the greater was the tensile moduli (M300/M100). Since tensile moduli depend on the crosslink density of a compound of rubber [10-13]. The improvements in tensile moduli were attributed to the increases in crosslink density of the NR nanocomposites. As discussed earlier, the rubber to filler interaction between the NR and montmorillonite can be considered as physical crosslink [14-17]. As mention previously, the physical crosslinks with sulphide crosslinks altogether contributed to the total crosslink density of the rubber compound/composite [18]. The higher the montmorillonite loading, the more the physical crosslink density and as a consequence, the increases of tensile moduli of the NR nanocomposites were observed. This discussion agreed with the torque differences results in **Table 2**. The torque difference of NR composite with a higher montmorillonite loading was higher than that of NR composite with lower loading of montmorillonite.

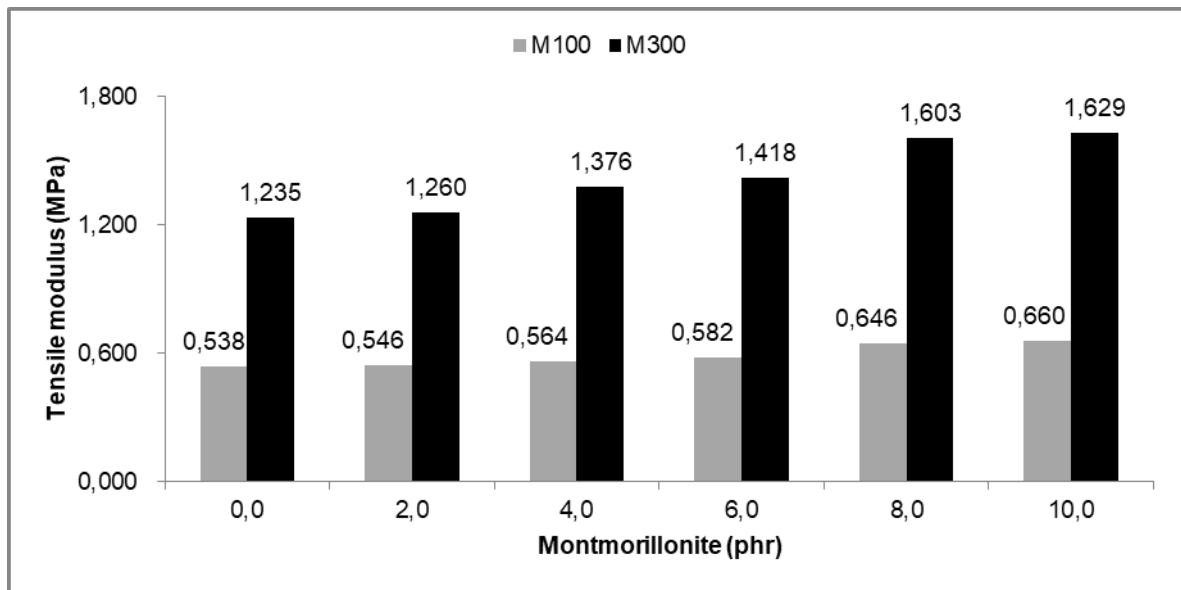


Figure 1. The effects of montmorillonite on M100 and M300 of NR nanocomposites.

Fig. 2 shows the relationship between hardness and montmorillonite loading. The additions of montmorillonite increased the hardness of the NR nanocomposites. The more the montmorillonite loading, the higher was the hardness. Similar with tensile moduli, the hardness of a rubber compound/composite depends on the degree of crosslink density [19], the improvement in hardness was because of the increases in the degree of rubber to filler interaction or crosslink density as the result of the additions of montmorillonite.

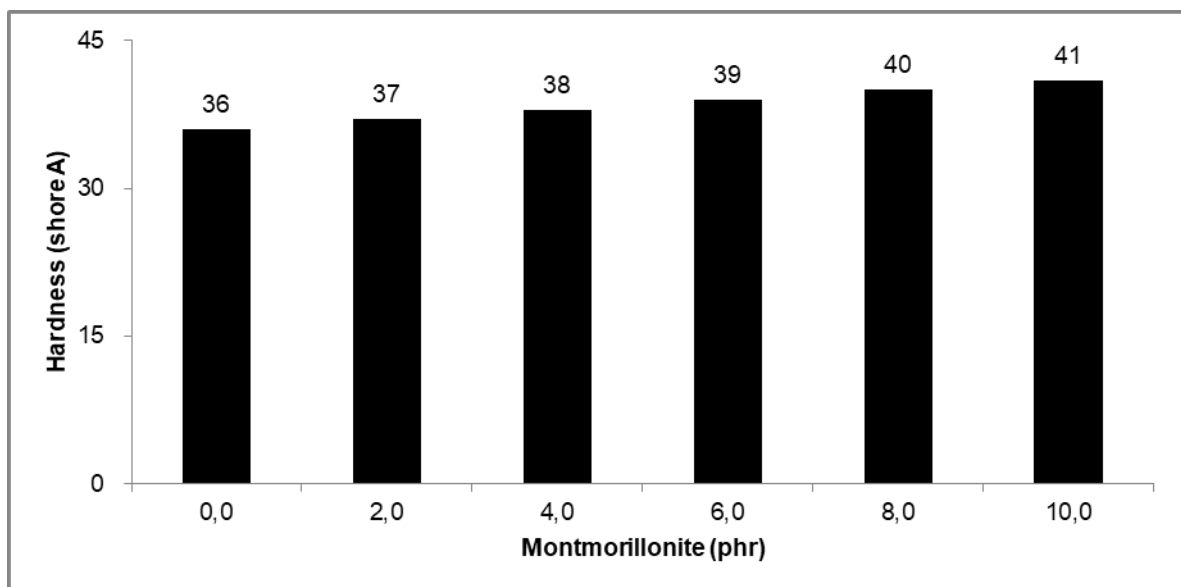


Figure 2. The effect of montmorillonite on the hardness of NR nanocomposites.

Fig. 3 shows the effect of montmorillonite on the tensile strength (TS) of NR nanocomposites. The additions of montmorillonite increased the TS up to an 8.0 phr. of loading and beyond the loading, the TS started to decrease. The improvements in TS have

attributed to the increases in crosslink density and the decrease in TS was because of the deterioration in crosslink density.

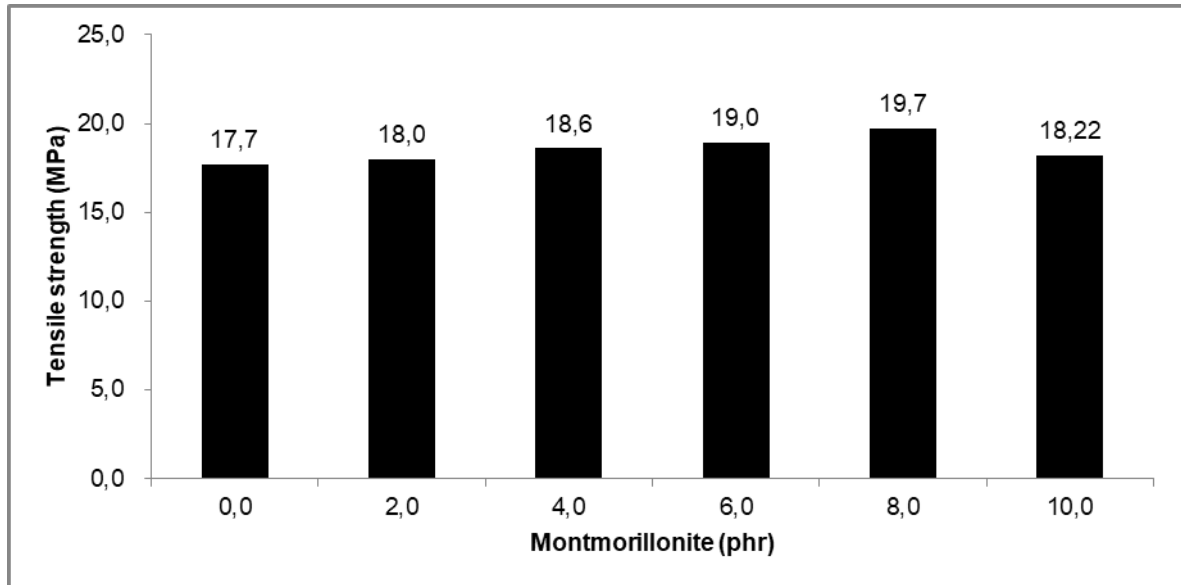


Figure 3.The effect of montmorillonite on tensile strength of NR nanocomposites.

Fig. 4 shows the effect of montmorillonite on the EB or elongation at break of NR nanocomposites. The additions of montmorillonite decreased the EB. The more the montmorillonite loading, the lower was the EB. It was because of the increases in crosslink density which immobilized the NR chains.

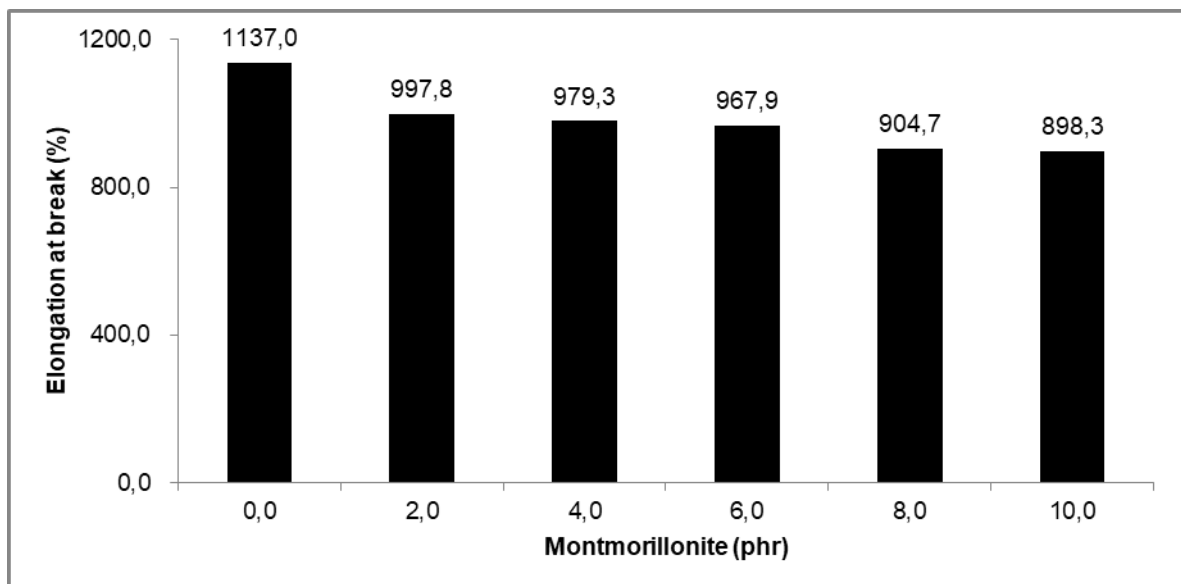


Figure 4.The effect of montmorillonite on elongation at break of NR nanocomposites.

4. Conclusion

The results can be concluded that:

The montmorillonite was a curative additive for natural rubber. It decreased the time to scorch and time to cure but increased the torque difference. The montmorillonite showed some reinforcement effects on natural rubber. The tensile moduli and hardness were enhanced and the tensile strength was also enhanced, especially up to an eight phr of montmorillonite loading.

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