Influence of Preparation Method on Properties of Natural Rubber/ Sepiolite Composites

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Abstract. Natural rubber (NR) composites filled with various sepiolite loadings were prepared and optimized by two different mixing methods, namely, melt mixing and latex mixing methods. The properties were evaluated through viscosity, stress relaxation, curing behaviors and tensile properties of rubber composites. The viscosity was influenced by sepiolite content and mixing methods. The greater interaction between rubber and sepiolite was obtained from melt mixing method. This reflected to the greater tensile strength found in this method. Considering the content of sepiolite, similar trend was observed for the curing properties and elongation at break. The greatest tensile strength was observed when the sepiolite content was at 1 phr.

1. Introduction

It is well accepted that natural rubber (NR) cannot be used as a product without introducing vulcanization due to its unstable properties, i.e., it is sticky at elevated temperature and brittle at very low temperature [1]. During rubber compounding, the fillers are usually incorporated to the rubber compounds in order to enhance the final properties of the rubber products and a number of fillers have been used for such proposes [2,3]. Among different types of fillers, silica and carbon black represented as the most widely used reinforcing filler for rubber industries [4].

Interest in searching alternative fillers for rubber has been increasing recently. Many alternative fillers have been incorporated into the rubber including lignin, sludge and so forth [5-7]. Sepiolite is one of the example of alternative fillers being given special attention. Sepiolite belongs to clay family with microfibrous morphology having the chemical formula of Si₁₂Mg₈O₃₀(OH, F)₄·8(H₂O) [7]. The length of the fibrous sepiolite ranging from 2-10 μm and its structure composed of a tunnel-like micro-pore channel which can interact with rubber chains. Recently, the possibility of using sepiolite as a filler in the rubber composites has been reported [7]. The results showed that the mechanical properties of NR were improved by the addition of sepiolite filler. However, the effect of mixing method was not explored previously and remained interesting topic. Thus, this study aimed to
investigate the effect of mixing method on the properties of NR composites filled with various sepiolite loadings.

2. Experimental

2.1. Materials

High-ammonium NR latex concentrate with dry rubber content of 60% supplied by Chalong Concentrated Natural Rubber Latex Industry Co. Ltd., Thailand was used as initial material for the preparation of rubber composites. Sepiolite filler was received from Hebei Dfl Minmet refractories Corporation, Shijiazhuang, Hebei, China. Zinc oxide (ZnO) and stearic acid were purchased from Global Chemical Co., Ltd., Samut Prakan, Thailand and Imperial Chemical Co., Ltd., Thailand, respectively. N-cyclohexyl-2-benzothiazole sulfonamide (CBS) was purchased from Flexsys America L.P., West Virginia, USA, and sulfur was purchased from Siam Chemical Co., Ltd., Samut Prakan, Thailand.

2.2. Rubber Compound Preparation

NR composite compounds were prepared by using two roll mill (Charoen Tut Co., Ltd., Samutprakarn, Thailand) at room temperature. The formulation of the composites and mixing times are presented in Table 1. Total mixing time on two roll mill was kept constant at 17 min. The loadings of sepiolite filler were varied from 0 – 10 part per hundred of rubber (phr). In this study, the one-step method (Melt mixing) and two-step method (Latex mixing) of mixing were employed to investigate their influences on the final properties of NR composites. In the melt mixing method, all the ingredients were mixed on two roll mill. But for the latex method, the NR containing different sepiolite contents were initially prepared by adding 5 %wt sepiolite suspension into the NR latex. After drying, the NR-sepiolite masterbatches were then mixed with other ingredients on two roll mill at the second step. Finally, the compounds were compression-molded at the temperature of 160 °C following their respective curing times.

Table 1. Compound formulations used in this study.

| Ingredient | Quantity (phr) | Time of incorporation during mixing (min) |
|------------|----------------|------------------------------------------|
| NR         | 100            | 0                                        |
| Stearic acid | 1              | 2                                        |
| ZnO        | 3              |                                          |
| Sepiolite  | 0, 1, 3, 5, 10 | 4                                        |
| CBS        | 1.5            | 14                                       |
| S          | 1.5            | 16                                       |
| Dump       |                | 17                                       |

2.3. Mooney viscosity and Mooney stress relaxation test

Mooney viscosity and Mooney stress relaxation of the NR composites were determined by using Mooney viscometer, MV 3000 Basic (Montech, Germany) according to ASTM D1464.

2.4. Curing property test

Cure characteristics, i.e., maximum torque (M<sub>H</sub>), torque different (M<sub>H</sub>-M<sub>L</sub>), scorch time (t<sub>s1</sub>) and optimum curing time (t<sub>90</sub>) were determined by using a moving die rheometer, MDR 3000 Basic (Montech, Germany). The test was conducted at a temperature of 160°C. All rheometer tests were performed in triplicate and the average value of each parameter was reported.
2.5. Tensile property test
Tensile properties such as tensile stress, tensile strength and elongation at break of the composites were measured by using a universal testing machine, LR5K Plus (LLOYD Instruments, UK) at 500 mm/min according to ISO 37. Three replications were performed and the results reported are averages.

3. Results and Discussion

3.1. Mooney viscosity and Mooney stress relaxation
Effects of preparation method on Mooney viscosity of the NR composites with different sepiolite contents is shown in Figure 1. The viscosity of the NR composites increased with the addition of sepiolite filler due to the restriction of filler to the movement of rubber chains. The highest viscosity value was found at 1 phr sepiolite loading for both preparation methods. Further increase of filler has reduced the viscosity due to poor dispersion. The viscosity values of NR composites prepared by melt mixing method were lower than those of composites prepared by latex mixing method. The lower the viscosity of the compound was a sign of better processability [8].

![Figure 1. Mooney viscosity values of NR/sepiolite composites prepared by latex-mixing and melt-mixing methods.](image1)

![Figure 2. Stress relaxation behaviour of NR/sepiolite composites prepared by (a) latex-mixing and (b) melt-mixing methods.](image2)
Figure 2 shows Mooney stress relaxation of the sepiolite filled NR prepared by latex- (Figure 2a) and melt- (Figure 2b) mixing methods. According to the previous report [9], the stress relaxation rate is influenced by the addition of filler and, in particular, the interaction between filler and rubber chains. Lower relaxation rate indicates higher interaction. Since the lower rate of stress relaxation was observed in the composites prepared by melt mixing method, the greater interaction between rubber and sepiolite filler was expected. Furthermore, the relaxation rate of latex mixing method was varied, depending on the loading of sepiolite filler.

3.2. Curing characteristics

Figure 3a shows the effects of preparation method on torque difference of sepiolite filled NR. It is well accepted that the torque difference relates to the crosslinking density of rubber composite. The greater torque difference means the higher crosslink density [10]. The result clearly suggested that the crosslink density of NR composites prepared by both mixing methods increased with the addition of sepiolite, and the values were more or less the same. This can be assumed that the crosslink density was also the same.

![Figure 3](image1)

**Figure 3.** Cure characteristic of NR/sepiolite composites prepared by latex-mixing and melt-mixing methods, (a) torque different and (b) scorch ($t_s$) and curing times ($t_90$).

Considering the $t_s$ and $T_90$ shown in Figure 3b, both slightly decreased with increasing the sepiolite loading. A reduction of both $t_s$ and $t_90$ was due to metal oxides, i.e., the magnesium oxide (MgO) containing in the structure of sepiolite. As widely known that the metal oxides can be worked as curing activators, thus accelerating the sulfur vulcanization of NR [7,11]. Therefore, the $t_s$ and $T_90$ were shortened by the addition of sepiolite filler.
3.3 Tensile property

Figure 4. Tensile properties of NR/sepiolite composites prepared by latex-mixing and melt-mixing methods, (a) tensile strength and (b) elongation at break.

Figure 4a shows variation of tensile strength of NR composites prepared by using two different mixing methods. In both methods, the maximum value of tensile strength was observed when the sepiolite content was at 1 phr. Further increase of sepiolite content has destroyed the tensile strength property. The melt mixing method provided the higher tensile strength values compared to the latex mixing method due to the better interaction between filler and rubber matrix as suggested by relaxation behavior (Figure 2). On the hand, elongation at break of the NR composites decreased with increasing sepiolite concentration (see Figure 4b), resulting from hardening effect of sepiolite incorporation and the increase of crosslink density.

Based on the results obtained from this study, the NR filled with sepiolite prepared from melt mixing method provide the better overall properties compare to the latex mixing method. The ease of preparation with the lesser step for one step melt mixing method would provide the greater benefits over the two steps latex mixing method.

4. Conclusion

NR composites filled with various sepiolite contents were prepared by two different mixing methods namely, one step melt-mixing method and two steps latex-mixing method and sepiolites contents (0-10 phr) whereby the properties were evaluated through the viscosity, stress relaxation, curing behavior and tensile properties of rubber composites were investigated. It was found that the mixing method and filler content have influenced the viscosity. The highest viscosity was obtained at 1 phr sepiolite loading. Stress relaxation test revealed that the greater interaction between rubber and sepiolite filler was obtained from melt mixing method. The curing properties and elongation at break of both methods showed the same variation, depending on the filler loading. The higher tensile strength was achieved from the melt mixing method and the highest value was obtained at 1 phr sepiolite loading in both mixing methods. As compared to the latex mixing method, the result clearly suggested that the melt mixing method provide the better tensile properties. The ease of preparation and the shorter one step melt mixing method provide more advantageous over the two steps latex mixing method for production of rubber composites filled with sepiolite filler.

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