Acid-treated halloysite nanotubes filled natural rubber composites

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Abstract. Halloysite nanotubes (HNT) filled natural rubber composites were prepared in this study. To enhance the properties of the composites, two different approaches were applied to both HNT and rubber. HNT was treated with sulfuric acid (H2SO4) while epoxidized natural rubber was also used as compatibilizer in the composite system. Effect of acid treatment of HNT on BET surface area, mechanical and morphological properties of the obtained composites were investigated. The surface area of acid-treated HNT was greater than that of untreated HNT and it increased over treating time. This has brought to an enhancement of stress at high strain especially when the strain over 500%. From the SEM images, the particle size of acid-treated HNT was seen to be finer and well-dispersed. This is attributed to the possibility of strong adhesion formation among NR, ENR and HNTs, obtaining from acid treatment.

1. Introduction

The research focus on the rubber nanocomposite is increasingly becoming a world trend due to their unique properties. Such nanocomposite is generally referred to the mixture of rubber and fillers where at least one dimension of the fillers is in nanometer scales (1-100 nm). Various nano-sized fillers have been used to prepare rubber nanocomposites, for instance, silica [1], clay [2], and halloysite nanotubes (HNT) [3]. Among various types of nano-fillers, HNT is one of the interesting fillers. It is used widely to reinforce the rubbers matrix due to its superiority in aspect ratios and surface areas [4]. Ismail et al. [5] investigated properties of HNT-filled NR prepared by using two different mixing methods, namely, mechanical and solution mixing methods. They revealed that addition of HNT increased scorch and cure times, and maximum torque of the composite for both mixing methods. Moreover, the composites prepared by solution mixing method also showed higher tensile strength, tensile modulus and fatigue resistance than mechanical mixing method. The better dispersion of HNT filler in the samples prepared by solution mixing method than those of sample prepared by mechanical mixing method is the primary explanation for these results. Ismail et al. [6] investigated the property changes of HNT filled two types of rubbers, i.e., NR and epoxidized NR (ENR). Incorporation of HNT increased scorch time, cure time, tensile modulus, and thermal stability of rubber/HNT composites. The highest tensile strength of composites was achieved when the content of HNT was 20 phr loading.
Elongation at break, swelling capability and fatigue life decreased with increasing HNT loading. Weasateh et al. [3] studied the effect of HNT addition on properties of NR/HNT composites. They found that addition of HNT delayed scorch time and cure time but enhanced maximum torque. The tensile strength and elongation at break of the NR/HNT composite was obtained at 5 phr HNT loading.

The main problem of HNT filled NR composites is weak interaction between filler and rubber due to polarity differences of both materials and thus HNT is usually presenting in aggregation form [7]. To expand the application of HNT in the rubber applications, it is very important to modify both HNTs’ surface and rubber matrix itself. In this research, HNT was treated with sulfuric acid (H$_2$SO$_4$) while epoxidized natural rubber was also used as compatibilizer to ensure the interaction between rubber matrix and filler.

2. Methodology

2.1 Materials

NR grade STR 5L (Chalong Concentrated Natural Rubber Latex Industry Co. Ltd., Thailand) and ENR was prepared through an in situ performic epoxidation reaction. HNT was mined and manufactured by Imerys Tableware Asia Limited, New Zealand. Other additives, including, stearic acid (Imperial Chemical Co., Ltd., Thailand), N-cyclohexyl-2-benzothiazole sulfenamide or CBS (Flexsys America L.P., West Virginia, USA) and sulfur (Siam Chemical Co., Ltd., Samut Prakan, Thailand).

2.2 Preparation of rubber nanocomposites

The starting materials used for compounding are listed in Table 1. The mixing was performed in a measuring mixer (Brabender®, Plastograph® EC Plus with Mixer W50EHT 3Z). Both untreated and acid-treated HNT were fixed at 5 phr. After dumping, the compounds were passed through a two-roll mill with a tight nip (~2 mm) to remove excess heat history. Finally, the compounds were compression molded using a laboratory hot press based on their respective curing times.

| Table 1. Compounding formulations of the NR/ENR/HNT composites. |
|---------------------------------------------------------------|
| Ingredients        | Amount (phr) |
| STR 5L             | 100          |
| Stearic acid       | 1            |
| Zinc Oxide         | 5            |
| HNT                | 5            |
| CBS                | 2            |
| Sulfur             | 2            |

2.3 Acid treatment procedure

Chemical agent used for modifying HNT was sulfuric acid (H$_2$SO$_4$). Suspension of 1 gram HNT was dispersed in 100 mL of 3 M H$_2$SO$_4$ under continuous stirring at temperature of 70 ºC. The modifying process was performed at different treating time, i.e., 2, 4 and 6 hours. Then, the treated HNT was washed with distilled water until pH becomes 7. Finally, the treated HNT was dried in an oven at 50 ºC.

2.4 Characterization

Nitrogen adsorption using BET method was applied to determine the specific area of HNT fillers after modification.

Mechanical properties in term of tensile properties and tear strength of NR/ENR/HNT composites were determined according to ASTM D 412 using a universal testing machine (Tinius Olsen, H10KS).
Morphology of the composites was conducted by using a Scanning Electron Microscope (SEM) (FEI, Quanta FEG 400) at an acceleration voltage of 20 kV. To prevent charging on the surface, the samples were sputter coated with gold before examination.

3. Results and discussion
Surface area is a direct parameter associated to the size of primary particles. It represents as the most important characteristic of reinforcing filler, associating with the extension of interaction between rubber and filler surface [8]. The analysis of BET surface area was conducted to investigate the change of surface area in untreated HNT and acid-treated HNT at different treating times and result is shown in Figure 1. When the acid treated time is increased from 0 to 6 h, the BET surface area is increased accordingly from 26 m$^2$/g to 51 m$^2$/g, indicating that the HNTs have higher surface area for interacting with polymer matrix as compared to the untreated HNT. The increase of BET surface area of HNT was possibly due to 2 reasons: disaggregation of HNT with the presence of acid [9] and expansion of lumen size as result of dissolving alumina sheets by acid [10]. The disaggregation and expansion of lumen size of HNT would positive result in improvement of HNT dispersion and, finally, mechanical property. The proposed reaction between acid and HNT is shown in Figure 2. Strong acid would dissolve alumina sheet or alumina bridge, resulting in larger lumen size and smaller size of HNT, respectively.

![Figure 1. Plot of BET surface area for the HNTs versus treating time.](image)
Figure 2. Proposed reaction between acid and HNT filler.

Figures 3A – 3C display the feature of both untreated and acid-treated HNT dispersion in NR/ENR matrix. It is generally seen that the HNT (white spots) were almost homogeneously dispersed throughout the NR/ENR matrix (darker phase). The size of filler dispersion in the acid-treated HNT for 6 hours (Figure 3C) was found to be smaller than those of untreated HNT (Figure 3A) and 2 hours of treating time (Figure 3B) samples due to better disaggregation of HNT with longer exposure time in acid treatment. From the morphological analysis, the acid treated HNT would result in separation of HNT to smaller size rather than improving the lumen size. The result obtained from SEM analysis is in agreement well with the BET surface area result, as previously shown. The higher value of BET surface area, the smaller size of dispersed HNT is.

Figure 3. SEM micrographs of NR/ENR/HNT composites at different acid treating time.
Effect of acid-treated time on mechanical properties, in term of tensile properties and tear strength of NR/ENR/HNTs composites, is shown in Figure 4. The NR/ENR/HNT composite without acid treatment was also included for comparison. From Figure 4A, it can be seen that tensile stress at the strain high strain, for example, higher that strain ratio of 4, significantly increased with increasing treatment time, except for 2 h. Shorter time of treatment was probably not sufficient to break the aggregation of HNT. As can be seen earlier from SEM images, the smaller size of HNT was detected in the sample with 6 hours of treating time. It is believed that the smaller the particle size with the larger surface area are clearly responsible to provide greater interaction between HNT and rubber matrices. Thus, a higher restriction to the molecular motion of the NR macromolecules is expected. Consequently, improvement of tensile stress was observed. Similar finding was also found for the tear strength (see Figure 4B) which is simply due to the enhanced interaction in the composites.

4. Conclusion
In this study, effects of acid treatment of HNT on BET surface area, mechanical and morphological properties of the NR/ENR/HNT composites were investigated. The ENR was added in order to achieve better adhesion between NR and HNT phases. The result revealed that the BET surface area of HNT was increased with treating time. The tensile stress at high strain and tear strength of the composites were improved due to the better dispersion of modified HNT in the NR matrix as compared to the untreated one, resulting from increasing BET surface area of HNT. The results suggested that there is a possibility of strong adhesion formation among NR, ENR and HNTs, resulting from acid treatment.

![Graphs](A) (B)

Figure 4. Stress-strain behaviors (A) and plot of tear strength versus treated time (B) for NR/ENR/ENR/HNT composites.

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