Mechanical strength of natural rubber filled fly ash

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Abstract. In this present work, Fly ash was incorporated into natural rubber to form a natural rubber composite. The natural rubber composite was prepared by solution mixing method at the constant amount of fly ash at 80 phr. The fly ash particle was modified its surface by TESPT silane coupling agent before mixing with natural rubber latex. The surface morphology of natural rubber composites were examined by SEM image. The vulcanization parameters were examined by MDR technique. The results show that modified fly ash affects to natural rubber compound by shorten the vulcanization time and increase maximum torque. The mechanical properties were investigated from stress-strain curve. It reveals that the surface modification of fly ash improves tensile strength of natural rubber by 6 times. The increasing of strength may attribute to the formation of polymer-fillers interaction through TESPT molecules.

1. Introduction
Fly ash, a by-product from power generation industrials, was considered as environmental pollution. The chemical component of fly ash was varied depended on source of materials. In general, it comprise of oxides such as SiO$_2$, Al$_2$O$_3$, Na$_2$O, K$_2$O, CaO, and MgO. Many researches has continually studied to minimize these problems by using a fly ash as raw materials for various applications such as car tire[1], geopolymer cement[2], brick[3], mosaic tile[4] by mean of pure fly ash or form in composite polymer. However, less attention has been paid to incorporate fly ash into natural rubber for mechanical properties improvement. The aim of this work was to prepare the polymer composite of fly ash and natural rubber at constant fillers loading of 80 phr. The filler distribution in natural rubber matrix was observed from SEM image. The vulcanize characterization including vulcanization time, rate of vulcanization as well as reversion effect was determined from cure curve. To improve the compatibility, fly ash was modified surface by silane coupling agent and observed the tensile strength from stress-strain curve.

2. Materials and method
2.1. Materials
The fly ash samples were a by-product from biomass electric power generation and kindly supported form Gulf Yala Green, Yala, Thailand. The fly ash particles are in dark green color and flake shape (figure 1). The fly as consists of oxides of K$_2$O (14.27%), CaO (39.88), SO$_3$ (2.76%), MgO (5.67%), SiO$_2$ (4.59%), Fe$_2$O$_3$ (0.59%) and Al$_2$O$_3$ (0.01%) with loss on ignition (LOI) of 21.34. The summation of SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$ was less than 10%.
The natural rubber latex with 60% dry content and vulcanization agents such as wax, ZnO, steric acid, TMTD, Wing stay L and sulphur were purchased from Chemical & Materials co., Ltd, Bangkok, Thailand. Bis[3-(triethoxysilyl)propyl] tetrasulfide (TESPT), silane coupling agent, was obtained from Kisco (T) Ltd, Bangkok, Thailand.

2.2. Composite preparation
The fly ash was first modified with TESPT by drop a 2% of TESPT in a mixture solution of ethanol and deionized water (90:10 %wt.) and vigorously stirred for 2 hr. Then, the TESPT solution was mixed with fly ash at 50 %wt. Finally, the mixing was dried in an oven at 70°C for 18 h.

The natural rubber composite was prepared by disperse the fly ash into natural rubber latex and thoroughly mixed for 10 min. The solution was coagulated by 2% of acetic acid and washed with DI until its pH equal 7. The sample was dried in an oven at 70°C for 14 h before addition of a vulcanize agents. The vulcanize agents include wax, ZnO, steric acid, TMTD, Wing stay L and sulphur were added into natural rubber composite on two-roll mill machine. All vulcanize agents are in phr unit (part per hundred part of rubber) as shown in Table 1. Finally, the composite was formed into sheet through a nap before vulcanization under an electrically heated hydraulic press at 150 °C followed their vulcanization time obtained from MDR results.

2.3. Characterization
The dispersion of fly ash in NR matrix was observed by SEM. The cure characterization was carried out at 150 °C using Moving Die Rheometer (MDR) technique followed with ASTM D5289. The mechanical properties including tensile strength, elongation at break and modulus at 100% was done using Universal testing machine (INTRON 3366) according to ASTM D412 (Die C).

| Chemicals    | phr |
|--------------|-----|
| Wax          | 5   |
| ZnO          | 4   |
| Steric acid  | 2   |
| TMTD         | 0.5 |
| Wing stay L  | 1   |
| Sulfur       | 2.5 |

Table 1. Vulcanization agents for composite.
3. Results and discussion

The dispersion of fly ash in natural rubber matrix was observed by SEM images as shown in figure 2. As can be seen, fly ash shows a good dispersion in natural rubber matrix. It also found some void in both composite polymers, which can future effect to mechanical properties.

The vulcanization parameters of sample were examined as shown in figure 3(a) and the data are summarized in table 2. It reveals that scorch time ($t_s$) is shorten when fly ash were incorporated. The shortening of time for starting the crosslinking reaction may due to its pH of fly ash which is base form. The basicity of fly ash may accelerate crosslink reaction[5]. The maximum torque ($M_{	ext{H}}$) of modified fly ash is highest. This implied that the numbers of crosslinks were formed through the silane coupling agent. In addition, the reduction of $M_{	ext{H}}$ in fly ash/NR composite may arise from filler agglomerations. The vulcanization time of neat natural rubber, fly ash and modified composite indicated by $t_{90}$ were 3.30, 3.00 and 3.24, respectively. These reveal that incorporation of fly ash whether modified surface or not shorten the time of crosslinkage formation. Moreover, incorporation of fly ash or modified fly does not cause the desulfidic of crosslinking called reversion effect after fully form a network structure. This behaviour preserves the composite materials crosslinkage form over curing.

![SEM images of fly ash – NR composite](image1)

(a) fly ash – NR composite

![Modified fly ash – NR composite](image2)

(b) Modified fly ash – NR composite

**Figure 2.** SEM images of fly ash – NR composite

![Vulcanization curves](image3)

![Stress-strain curves](image4)

**Figure 3.** a) Vulcanization curves and b) stress-strain curves of neat and natural rubber composites
The samples were cured at their vulcanization time according to MDR results under the compression and form into 2 mm thickness for mechanical test. The stress-strain curve and listed mechanical properties are shown in figure 3(b) and table 3, respectively. It reveals that the mechanical properties were improved by incorporation of fly ash. Surface modification by silane coupling agent future increases tensile strength. This is due to the silane coupling agent act as bridge molecules connecting natural rubber chain and fly ash results in increase polymer- fillers interaction of composite materials[6]. In addition, elongations at break of natural rubber composite were higher than that of neat natural rubber. However, when fly ash was modified surface, the elongation at break decreased slightly. This behaviour may owing to the enhanced interface interaction of silane coupling agent.

4. Conclusions
1. The inclusion of fly ash into natural rubber effects the vulcanization time of fly ash/natural rubber composite.
2. The modification of surface by silane coupling agent improves mechanical properties by increasing the degree of fillers – polymer interactions.

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