Mechanical and thermal properties of NR/XSBR composite reinforced with rice husk silica

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Abstract. Natural rubber (NR) is a renewable resource that is used in many products. In the production of NR products, other rubbers or fillers may be used to produce a product with required properties. However, most rubbers and fillers are synthetic which are non-environmentally friendly materials. To solve this problem, rice husk ash (RHA) from biomass power plant was used to prepare silica to be used as a filler in rubber by in-situ generation. The purer RHA was prepared by leaching with HCl to remove some metallics and increase silica contents by combustion. The purer RHA was dissolved in NaOH to obtain sodium silicate from RHA (RSS). Carboxylated styrene-butadiene rubber (XSBR) used as synthetic rubber was blended with NR in latex form. NR/XSBR at the ratio of 2:1 was mixed with RSS to obtain NR/XSBR/RSi composite. Acetic acid was dropped into the mixture until neutral for precipitating silica to obtain NR/XSBR/RSi composite. The mechanical, morphological, and thermal properties of NR/XSBR/RSi composites at different contents of silica (5, 10, and 15 phr) were studied. The NR/XSBR/RSi composite with optimum content was compared with NR/XSBR/CSi composite which prepared silica from commercial sodium silicate (CSS) on mechanical, morphological, and thermal properties.

Keywords: Natural rubber latex, Carboxylated styrene-butadiene rubber latex, Rice husk ash, Silica, Rubber composite

1. Introduction

Natural rubber (NR) is one of Thailand’s important renewable resource which can be used to produce in many products because it has high resilience, good tensile strength, tear resistance, etc. (1, 2). This is the reason of NR products covering in many industries such as automotive, medical, construction, etc. (3).

However, it is known that NR has low resistance to sunlight, ozone, and oxygen or heat aging because it consists of double bonds in the molecular structure (4). Therefore, the production of most NR products is not used only NR but also used it with other rubbers or fillers to obtain the required product properties (5, 6). For example, the tire manufacturers used NR with butadiene rubber (BR) or
styrene-butadiene rubber (SBR), carbon black (CB), and silica to improve wear, traction, rolling resistance, etc. (7, 8).

In the other rubbers and fillers, carboxylated SBR (XSBR) and silica are interesting materials because they can improve some NR properties such as mechanical and thermal properties. There are several reports mentioned that NR blended with XSBR which can easily modify the mechanical properties of NR and the incorporation of XSBR into NR can improve the thermal properties and gas permeability of NR (9). Poompradub et al. reported that filling NR with in-situ silica can improve not only the mechanical properties but also the thermal properties and it is superior compared with using ex-situ silica (10). However, it is known that these are synthetic that are non-environmentally friendly materials. Therefore, this research is to study in reducing this problem by using rice husk ash (RHA) from biomass power plant to prepare silica used as a filler in rubber by in-situ generation.

RHA is one of agricultural wastes that consists of high silica content in amorphous form that can be used in many applications such as adsorbent, catalyst, fertilizer, etc. (11). In-situ silica has several advantages, including enhanced silica dispersion, higher silica loading in the matrix, possible to customize the particle size, and energy-efficient processing (12).

This research aims to study the effect of rice husk silica (RSi) contents in NR/XSBR blend on mechanical, morphological, and thermal properties. The effect of silica sources was also studied by comparison between NR/XSBR/RSi composite with NR/XSBR/CSi composite in which silica prepared from commercial sodium silicate (CSS) at the same silica content on mechanical, morphological, and thermal properties.

2. Materials and Methods

2.1. Materials
Natural rubber latex (NRL) with 60wt% dry rubber content (DRC) and high ammonia (HA) treated with latex was purchased from Chemical & Material Co., Ltd. Carboxylated styrene-butadiene latex (XSBR) was purchased from Jorakay Corporation Co., Ltd. Rice husk ash (RHA) from biomass power plant was purchased from Chia Meng Co., Ltd. Commercial sodium silicate (CSS) was purchased from Sigma-Aldrich Co., Ltd. Hydrochloric acid (HCl) was purchased from RCI Labscan Co., Ltd. Sodium hydroxide (NaOH) and acetic acid (CH₃COOH) were purchased from Carlo Erba Reagents. Stearic acid (SA), zinc oxide (ZnO), N-Cyclohexyl-2-Benzothiazole Sulfonamide (CBS), and sulfur (S) were supported by Chemical Innovation Co., Ltd.

2.2. Methods

2.2.1. Preparation of Sodium Silicate from RHA (RSS). RHA was purified by leaching RHA from biomass power plant with 1M HCl at 90°C by using magnetic stirrer for 3 h to remove some metallics. In the end of this process, the filter paper was used to filter unreacted RHA and DI water was used to wash unreacted RHA several times until the pH of unreacted RHA is neutral. And then, unreacted RHA was dried by using hot air oven at 110°C for 12 h and combusted by using muffle furnace at 600°C for 6 h to increase silica contents. RSS was prepared by dissolving the purified RHA that obtained from previous process with 1M NaOH at 90°C by using magnetic stirrer for 3 h and filter paper was used to filter unreacted RHA until obtain the clear solution that is RSS.

2.2.2. Preparation of NR/XSBR and NR/XSBR/Si Sheets. NR/XSBR/RSi sheets were prepared by mixing NRL to XSBR at the ratio of 2:1, and RSS at various contents of silica (5, 10, and 15 phr) by using magnetic stirrer for 30 mins to obtain NR/XSBR/RSS mixtures. Acetic acid was dropped into NR/XSBR/RSS mixture until the pH of NR/XSBR/RSS mixture is neutral to precipitate silica. And then, the previous mixture was poured onto Teflon tray and dried at 60°C by using hot air oven for 72 h. For NR/XSBR/CSi sheet was prepared by using CSS at optimum silica content instead of RSS and following this process for comparing properties of NR/XSBR/Si composite at the same silica content.
whereas silica was obtained from different sources. NR/XSBR sheet was also prepared by following this process whereas it was without sodium silicate mixing.

2.2.3. Preparation of NR/XSBR Blend and NR/XSBR/Si Composites. NR/XSBR and NR/XSBR/Si compounds were prepared by mixing NR/XSBR and NR/XSBR/Si sheets with 2 phr SA, 5 phr ZnO, 2.5 phr CBS, and 1 phr S by using two roll rubber mill. And then, the previous compound was vulcanized by using compression molding at 150°C with optimum curing time ($t_{90}$) of each compound that was determined by Moving Die Rheometer (MDR, Gotech M2000) to obtain NR/XSBR blend and NR/XSBR/Si composites.

2.2.4. Chemical Properties. Energy Dispersive X-ray Fluorescence (EDXRF, Horiba XGT-5200) was used to characterize the chemical compositions of RHA, RSi, and CSi. RSi and CSi were prepared by dropping acetic acid into RSS and CSS was under magnetic stirrer until the pH of solution to neutral that grained silica precipitating. And then, the previous substance was dried at 110°C by using hot air oven for 24 h to obtain silica from RSS and CSS.

2.2.5. Mechanical Properties. The tensile properties of NR/XSBR blend and NR/XSBR/Si composites were measured according to ASTM D412 by using Universal Testing Machine (UTM, Instron 5565) with load cell of 5 kN and crosshead speed of 500 mm/min on the standard dumbbell specimen. At least five specimens were tested to obtain the average value for tensile strength, percentage elongation, modulus at 100% (M100), and 300% elongation (M300). The hardness of NR/XSBR blend and NR/XSBR/Si composites were measured according to ASTM D2240 by using hardness tester (Bareiss, HPE II) with test method that is Shore A. It makes five determinations of hardness at different positions on the specimen at least 6 mm in thickness to obtain the average hardness value.

2.2.6. Morphological Properties. The tensile fracture surface of NR/XSBR blend, NR/XSBR/Si composites, and silica particles that precipitated from RSS and CSS were coated with gold before examined by Field Emission Scanning Electron Microscope (FE-SEM, Carl Zeiss Auriga).

2.2.7. Thermal Properties. Thermogravimetric analyzer (TGA, Mettler Toledo TGA/DSC 1) was used to analyze the thermal decomposition of NR/XSBR blend and NR/XSBR/Si composites that placed in alumina pan and heated from room temperature up to 800°C under nitrogen with heating rate of 10°C/min.

3. Results and Discussion

3.1. Chemical Properties of Silica
The chemical compositions of RHA, RSi, and CSi are listed in Table 1. RHA from biomass power plant shows the lowest percentage SiO$_2$ composition is 82.97%. RSi shows percentage chemical compositions are similar to CSi and contain percentage SiO$_2$ composition approximately 97% indicating the RHA that can prepare silica similarity to commercial grade.

|         | Al$_2$O$_3$ | SiO$_2$ | K$_2$O | CaO | TiO$_2$ | MnO$_2$ | Fe$_2$O$_3$ |
|---------|-------------|---------|--------|-----|---------|---------|-------------|
| RHA     | -           | 82.97   | 9.78   | 3.31| 0.13    | 2.68    | 1.13        |
| RSi     | 2.27        | 97.20   | 0.34   | 0.10| 0.03    | -       | 0.05        |
| CSi     | 2.38        | 97.28   | 0.11   | 0.06| 0.06    | -       | 0.11        |
3.2. Morphological Properties of Silica
The morphological images of RSi and CSi are shown in Figure 1. RSi and CSi show silica particles with a size that is lower than 100 nm in a general form that is spherical structure and partially agglomerate owing to filler-filler interactions of silica (13, 14). On the other hand, RSi shows smaller particle size and lower agglomeration than CSi.

![SEM images of (a) RSi and (b) CSi.](image)

**Figure 1.** SEM images of (a) RSi and (b) CSi.

3.3. Mechanical Properties of NR/XSBR/Si Composites
The mechanical properties in terms of M100, M300, tensile strength, percentage elongation, and hardness of NR/XSBR blend and NR/XSBR/Si composites that blended with RSi at 5, 10, and 15 phr and CSi at 10 phr are shown in Figure 2. NR/XSBR blend shows the highest percentage elongation approximately 840% indicating the general rubber properties that is an elastic characteristic. The containing silica at 10 phr in NR/XSBR blend can improve the tensile strength whereas silica sources show insignificant effect on this property. Nevertheless, NR/XSBR/Si composites show the percentage elongation slightly decrease. The increasing silica contents in NR/XSBR blend show the mechanical properties in terms of M100, M300, and hardness are higher values than NR/XSBR blend because fillers with a higher stiffness than the matrix can increase the modulus of composite and value is higher when fillers increasing (15) whereas the silica sources also show insignificant effect on these properties.

![Graph showing mechanical properties of NR/XSBR/Si composites.](image)
Figure 2. Mechanical properties of NR/XSBR blend and NR/XSBR/Si compositions showing (a) stress-strain curve, (b) modulus at 100% elongation and modulus at 300% elongation, (c) tensile strength and percentage elongation, and (d) hardness.

3.4. Morphological Properties of NR/XSBR/Si Composites
The morphological images of NR/XSBR blend and NR/XSBR/Si composites that blended with RSi at 5, 10, and 15 phr and CSi at 10 phr are shown in Figure 3. NR/XSBR blend shows holeless on tensile
fracture surface caused by filler detachment due to incompatibility between silica and rubber. In the same way, NR/XSBR/15RSi composite shows the highest holes number with a large-sized on tensile fracture surface owing to filler agglomeration that relates the lowest percentage elongation. The tensile fracture surfaces of NR/XSBR/10RSi and NR/XSBR/10CSi composites shows analogous images.

![Figure 3. SEM images of NR/XSBR blend and NR/XSBR/Si composites.](image)

3.5. Thermal Properties of NR/XSBR/Si Composites

The thermal properties in terms of degradation temperature at onset ($T_{\text{onset}}$), temperature at 50% weight loss level ($T_{50\%}$), temperature at maximum weight loss level ($T_{\text{max}}$), percentage residue, and percentage weight loss level at maximum degradation temperature (%wt. loss at $T_{\text{max}}$) of NR/XSBR blend and NR/XSBR/Si composites blended with RSi at 5 and 10 phr and CSi at 10 phr are listed in Table 2. The containing silica in NR/XSBR blend can improve the thermal stability of rubber as shown clearly in terms of $T_{50\%}$, $T_{\text{max}}$, and %wt. loss at $T_{\text{max}}$. $T_{50\%}$ and $T_{\text{max}}$ of NR/XSBR/Si composites are higher temperatures than NR/XSBR blend whereas %wt. loss at $T_{\text{max}}$ of NR/XSBR/Si composites lower than that of NR/XSBR blend. This may be due to the strong interaction of silanol group of silica with carboxylic group of XSBR. On the other hand, the contents and sources of silica play insignificant effect on the degradation temperature of NR/XSBR/Si composites.

| Sample            | $T_{\text{onset}}$ (°C) | $T_{50\%}$ (°C) | $T_{\text{max}}$ (°C) | %wt. loss at $T_{\text{max}}$ (%) | Residue (%) |
|-------------------|-------------------------|-----------------|-----------------------|-----------------------------------|-------------|
| NR/XSBR           | 351                     | 390             | 387                   | 47.36                             | 4.13        |
| NR/XSBR/5RSi      | 352                     | 400             | 392                   | 43.75                             | 9.40        |
| NR/XSBR/10RSi     | 353                     | 403             | 393                   | 42.44                             | 12.00       |
| NR/XSBR/10CSi     | 352                     | 400             | 391                   | 43.49                             | 14.67       |
4. Conclusions
Silica can be successfully prepared from RHA which comparable to commercial grade containing 97% SiO$_2$ composition and silica particle size is lower than 100 nm. The increasing silica contents in NR/XSBR blend improve modulus and hardness. NR/XSBR/10Si composites show the highest tensile strength. Silica sources show insignificant effect on mechanical properties. Higher decomposition temperature of NR/XSBR was obtained with the addition of silica.

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