Synthesis of precipitated silica from bagasse ash as reinforcing filler in rubber

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Abstract. Bagasse ash as waste material from the sugarcane industry is causing disposal problems. This paper study on the use of silica from bagasse ash as reinforcing filler in rubber. Precipitated silica was obtained from bagasse ash through a sol precipitation method. Process parameters such as time of addition of secondary sodium silicate, pH and temperature, were studied. The synthesized silica was characterized by XRF, XRD, and PSA. XRF and XRD test results showed that the precipitated silica contained 4.9% of alumina and had an amorphous structure, respectively. PSA result showed that the synthesized precipitated silica and a commercial reinforcing filler had a comparable aggregate/agglomerate size distribution after 10 minutes sonication. The yield of silica recovered from bagasse ash was found to vary between 41.7% and 58.2%.

1. Introduction
Carbon black and precipitated silica are the main reinforcing fillers in rubber products. The use of reinforcing fillers improves the mechanical properties of the rubber such as tensile strength, abrasion resistance, hardness, etc. Precipitated silica is used in the tire to get low rolling resistance, thus helping to reduce vehicle fuel consumption and contributing to a reduction of greenhouse gases emission.

Bagasse ash is a solid waste left over from burning bagasse in a sugar factory. Each ton of fresh sugar cane processed produces 120 kg of bagasse ash. Bagasse ash contains high silica content which has the potential to be used as a rubber filler. Santos et al. [1] made natural rubber composites (crepe claro) with bagasse ash filler (<45 microns) varied from 0 to 50 phr. Compounding was carried out with an open mill followed by vulcanization at 150°C. Huabcharoen et al. [2] studied the chemical composition, maturation characteristics, morphology, and physical properties of natural rubber (STR 20) with bagasse ash fillers which had been purified using HCl and NH₄F. Pangamol et al. [3] used 80 mesh bagasse as a filler for natural rubber (STR). The compound was made using two roll mills with bagasse ash content from 0 to 30 phr. The results obtained from several studies above showed that bagasse ash was useful as a semi reinforcing filler.

Synthesis of nanostructured silica from bagasse ash has been carried out by several researchers. Silica gel from bagasse ash has been used to adsorb hexavalent chrome ions as reported by Murti [4]. Azizi et al. [5] used mesoporous silica nanoparticle from bagasse ash as a catalyst support in the electrocatalytic oxidation of methanol. Silica powder from bagasse ash with a surface area of 407 m²/g has been used as an adsorbent in the adsorptive-distillation ethanol-water solution [6].

Silica from the above studies cannot be applied as reinforcing rubber fillers. To become a reinforcing filler in rubber, the materials must be nanostructured particles and easily dispersed in the rubber matrix.
Synthesis of precipitated silica from bagasse ash as rubber reinforcing filler has to our knowledge never been studied. This study aims to determine the purity, crystallinity, and size of aggregates/agglomerates of precipitated silica from bagasse ash and to determine the effect of pH and temperature on the yield of silica obtained.

2. Materials and methods

2.1. Materials

Bagasse ash was obtained from a local sugar factory in Yogyakarta, Indonesia. Commercial precipitated silica (Zeosil) was purchased from a local supplier. Sodium hydroxide and sulfuric acid of analytical grade were obtained from Merck.

2.2. Extraction of silica from bagasse ash

Bagasse ash was burned at 600°C for six hours using a furnace to remove carbon content in an air environment. Preliminary experiments showed that the residual carbon was still visible on combustion less than 6 hours. A 50 g of the produced low carbon bagasse ash was boiled in 250 mL of 9% H2SO4 for 2 hours. The suspension was centrifuged for 3 minutes at 3000 rpm. The solid residue was washed with water five times to remove the metal ions and sulfuric acid residue and then oven-dried. A 40 g of the acidified bagasse ash was boiled in 260 mL of 13% NaOH for 2 hours. The suspension was filtered to give a clear sodium silicate stock solution.

2.3. Synthesis of precipitated silica

Primary and secondary sodium silicate solution was made by diluting 25 mL and 50 mL of stock solution to a final volume of 100 mL, respectively. The primary sodium silicate solution was stirred and heated to the desired temperature. Acid solution (9% H2SO4) was then added slowly into the solution over a period of 30 minutes to the desired pH value. Secondary sodium silicate solution and 3% H2SO4 were added slowly and simultaneously into the suspension over a desired time period. After mixing the final suspension at reaction temperature for 1 hr, the precipitate was aged overnight at room temperature. The white solid precipitate was washed with water three times to remove the salt and then oven-dried.

2.4. Characterization

The chemical composition of bagasse ash and precipitated silica was determined using an X-ray fluorescence analyzer (XRF; Shimadzu EDX8000). The crystalline structures of the raw materials and silica product were examined by an X-ray diffractometer (XRD; Rigaku Miniflex600). The particle size and distribution of precipitated silica were characterized by a particle size analyzer (PSA; Horiba SZ-100). The silica yield extracted from bagasse ash was calculated by the following equation:

\[
\text{Silica extraction yield (\%)} = \frac{\text{mass of produced silica}}{\text{mass of silica in bagasse ash}} \times 100 \quad (1)
\]

3. Results and discussion

The EDX test results in Table 1 revealed the presence of various elements such as silica, aluminum, potassium, calcium, iron, phosphorus, sulfur, titanium, manganese, and other oxides in bagasse ash. The biggest impurity of silica in bagasse ash was alumina. Alumina and other impurity metals were dissolved with acid to purify silica. It is clear from the EDX result that bagasse ash has been acidified with an acid content of 4.5%. However, acidification with sulphuric acid was only able to eliminate less than 50% alumina and other metal oxides from bagasse ash.

Silica dissolves in water under alkaline conditions as silicate ion so that it can be fractioned from bagasse ash by reacting it with a strong alkali. Silica in acidified bagasse ash was extracted using sodium hydroxide according to the following equation [7]:

\[
2\text{NaOH} + n\text{SiO}_2 \rightarrow \text{Na}_2\text{O}_n\text{SiO}_2 + \text{H}_2\text{O} \quad (2)
\]
**Table 1.** Chemical compositions of the bagasse ash before and after the acidification and the precipitated silica.

| Components | Bagasse ash (wt.%) | Acidified bagasse ash (wt.%) | Precipitated silica (wt.%) |
|------------|--------------------|------------------------------|---------------------------|
| SiO$_2$    | 81.785             | 85.652                       | 93.295                    |
| Al$_2$O$_3$| 6.334              | 4.581                        | 4.939                     |
| K$_2$O     | 3.226              | 1.581                        | 0.000                     |
| CaO        | 3.008              | 1.793                        | 0.217                     |
| Fe$_2$O$_3$| 1.919              | 1.227                        | 0.227                     |
| P$_2$O$_5$ | 1.907              | 0.381                        | 0.043                     |
| SO$_3$     | 1.314              | 4.498                        | 1.216                     |
| TiO$_2$    | 0.189              | 0.146                        | 0.048                     |
| MnO        | 0.138              | 0.078                        | 0.015                     |
| Other oxides | 0.180          | 0.038                        | 0.043                     |

The produced clear sodium silicate solution was neutralized with sulfuric acid to form silicic acid and sodium sulfate [8]:

$$\text{Na}_2\text{O}.n\text{SiO}_2 + (4n-3)\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow n\text{Si(OH)}_4 + \text{Na}_2\text{SO}_4$$  \(3\)

Silicic acid formed polysilicic acid with the following reaction:

$$\equiv \text{Si} – \text{OH} + \equiv \text{Si} – \text{OH} \rightarrow \equiv \text{Si} – \text{O} – \equiv + \text{H}_2\text{O}$$  \(4\)

Polysilicic acid is then precipitated with the structure of aggregated and agglomerated primary silica particles.

As shown in Table 1, alumina in acidified bagasse ash was carried as the main impurity in precipitated silica with the following reaction [9]:

$$\text{Al}_2\text{O}_3 + 2\text{NaOH} \rightarrow 2\text{NaAlO}_2 + \text{H}_2\text{O}$$  \(5\)

$$2\text{NaAlO}_2 + \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 + \text{Na}_2\text{SO}_4$$  \(6\)

Figure 1 showed XRD diffractograms of bagasse ash, acidified bagasse ash, and precipitated silica. The bagasse ash curve has a strong broad peak at 23.3° (2\(\theta\)) and several sharp peaks at 22.1°, 27.9°, 28.7°, 30.0°, 36.3°, and 42.1 which indicate that there was amorphous and crystalline silica phase mixture. The number of sharp peaks reduced in acidified bagasse ash. Sharp peaks are no longer seen in precipitated silica which shows its pure amorphous phase. A similar result was found by Music et al. [10] and Raza et al. [11].

In the synthesis of precipitated silica, the variation in the time of addition of secondary sodium silicate (1, 2, and 3 hours) was carried out at 80°C and pH 9. The particle size distribution of the precipitated silica was then tested using a particle size analyzer. Without sonication, the average agglomerate particle diameter of the precipitated silica was 2471 nm (Figure not shown). Samples of precipitated silica were then sonicated for 20 minutes. The results in Figure 2 showed that 3 hours addition of secondary sodium silicate was producing agglomerates which were slightly more difficult to break by sonication.
The addition of secondary sodium silicate was to provide a reinforcing effect on the agglomerate structure. This is important so that the agglomerate structure did not collapse due to the effect of surface tension during the drying process. The precipitated silica used as rubber filler must be easily destroyed from the agglomerate and easily dispersed into a colloidal dimension fragment in the rubber matrix. To meet these needs, the aggregate structure must be open and very porous so that it is easily destroyed during the compression process [12].

Sonication relies on the hydrodynamic stress caused by collapsing cavitation bubbles. This principle can be used to find out how easy an agglomerate is destroyed/dispersed by mechanical forces. If silica primary particles are very tightly arranged, fragments smaller than 500 nm cannot be obtained [12].
Figure 3, at first, it can be seen that the precipitated silica from this study had a wider agglomerate size distribution compared to Zeosil. But after 10 minutes of sonication, the size of the Zeosil agglomerate became smaller and spread wider close to the results of this study. This is consistent with the results of the study by Marin et al. [13]. They examined the effect of the energy density of the sonication process on the precipitated silica and silica gel particle size distributions. The greater the energy density shifted the size of the precipitated silica particles towards the submicron and nano range but the size of the silica gel particles was relatively unchanged. Silica gel has a compact and microporous fractal-like aggregate structure that makes it difficult to break down with mechanical forces [13].

![Figure 3](image)

**Figure 3.** The particle size distribution of precipitated silica (80°C; pH 9) and Zeosil with different sonication times.

Figure 4 shows the effect of pH on the yield of precipitated silica. The yields obtained were relatively the same between pH 7-10, but above pH 10 a significant yield reduction occurred. At pH 11 the silica yield was 41.7%. Liou et al. [14] reported a significant decrease in yield above pH 8 in the process of making nanosilica using the sol-gel method. In higher pH, formed gels were unstable and partially redissolved. This was influenced by the solubility of silica in water according to the following equation [12]:

\[
\text{H}_4\text{SiO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{Si(OH)}_4^- + \text{OH}^- \quad (7)
\]

\[
\text{Si(OH)}_4 \rightleftharpoons \text{SiO}_{2\text{(s)}} + 2 \text{H}_2\text{O} \quad (8)
\]

At high pH, there were still many silicate ions dissolve in water so that not much silica was formed.

Figure 5 shows the trend of decreasing the yield of silica from 58.2% at 60°C to 53.3% at 80°C. The higher the temperature, the greater the solubility of silica [12]. Based on this, it was expected that the yield of precipitated silica would be smaller at higher reaction temperatures. However, it can be seen that the yield was increasing above 80°C. According to Iler [12], the size of the silica primary particle increased with temperature and the solubility of silica decreased with increasing particle size. It seems that at 90°C the particles formed are large enough so that the solubility is smaller than the particles formed at 80°C.
Conclusions
Precipitated silica was successfully synthesized from bagasse ash by sol precipitation method. XRF data showed that alumina was the main impurity and XRD pattern confirmed the amorphous phase of the precipitated silica. Precipitated silica from this study had a deagglomeration tendency that approaches Zeosil. The yield of precipitated silica dropped dramatically above pH 10. The yield was decreased from 60 to 80°C and then increased to 90°C. Further studies are needed to explain the effect of temperature and pH on particle size distribution, thermal properties, and morphology of precipitated silica obtained in this study.

References
[1] dos Santos R J, Agostini D L da S, Cabrera F C, Reis E A P dos, Ruiz M R, Budemberg E R, Teixeira S R and Job A E 2014 Sugarcane bagasse ash: New filler to natural rubber composite
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