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Rice Husk Ash Extraction Applied for Biosilica Reinforced Tire Tread Filler Compound

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Abstract. In the agricultural countries, rice husk is an abundant waste, especially as one of the largest sources of silica (SiO_2) production that can be produced. By complete combustion, to about 87% - 97% SiO_2 content can be produced from rice husks. Alkaline solution is used as a solvent in the solid-liquid extraction production of rice husk ash SiO_2. The mass of 10 grams of rice husk ash was weighed for the extraction process added with 80 ml of potassium hydroxide (KOH) solution with 10%, 15% and 20% various concentration to extract the SiO_2 content. In a systematic study, for 60 minutes the rice husks were soaked and washed using HCl and then heated in a muffle furnace. The results of this study showed that all samples are succeeded in homogenizing SiO_2 with purity close to 90%. Furthermore, through Energy-Dispersive X-ray Spectroscopy (EDS) analysis was proven these results obtained through solid-liquid extraction of KOH from rice husks. Natural SiO_2, known as biosilica, is useful and has potential in reinforcing compounds, including applications as filler in tires and natural rubber compounds.

Introduction

In developing countries, there are more than 75 countries that grow rice as a staple food source, and at least more than 97% of rice husks are produced [1, 10–17]. The main staple crop in Indonesia is rice, where the impact in an agrarian country is an increase in staple food production. The phenomena that occurred in 2006 were the expansion of the planted area from 11,786,400 to 14,116,600 ha, where the increase in the expansion rate reached 19.77% if accumulated since 2015. This was due to the encouragement of increased rice production. Meanwhile in 2006, 54,459,900 tons of rice were produced and up to 75,397,800 tons were produced in 2015. This means, there is an increase in production per year up to 3.84% [2]. From 2016 to 2019, on average the top 10 rice producers came from Indonesia, which is on the third ranks in the world as a rice production area, after China and India [3].

In addition to producing rice, it also produces rice husks as a by-product. As many 80 tons of millions of dry milled rice produced in Indonesia on 2017, and at least 16 million tons of rice husks are produced per year. Factors that affect the composition of rice husks is geographical situation, in addition to the type of fertilizer and rice varieties also play a role. Organic components can be converted into 20 percent of carbon dioxide, air, and ash by burning rice husks. About 90 – 98% silica (SiO_2) is contains in the main component present in the rice husk, and Indonesia will produce 3.2 million tons of SiO_2 from rice husk ash per year [4].

Waste derived from rice husks is generated in most of all agricultural countries that able in producing rice. Utilization of rice husks is usually only disposed of even in open land for burning, which will result in environmental pollution and disturbance to the soil. The intention effort is required to produce SiO_2 from the utilization of rice husk waste [5]. SiO_2 is a compound of silicon dioxide that can be used in various ways, it is the main standard material in the glass, ceramics, refractory industries and a play role for the silicate solutions manufacturing, include silicon alloys [6].

On the other hand, previous researchers have conducted research on SiO_2 extraction by extraction processes with alkaline solvents and precipitation of SiO_2 with acids [7–9]. Kalapathy group on 2001, extracted SiO_2 using 1 N NaOH from the rice husks with the extraction method of two-cycle and result 91% yield [7]. In addition, Pandiangan group on 2008, conducted a study to extract SiO_2 using various concentrations potassium hydroxide (KOH) solid gel solution initiated by rice husks and 10% HNO_3 liquid additive solution as a trigger, and resulted the 1.8690 grams highest yield mass from rice husk ash mass of 50 grams at a concentration of KOH solution of 1.5% for 30 minutes [8]. Another study conducted by Suka on 2008 was obtain the highest yield of 40.8% with the use of 5% KOH solvent with a reaction time of one hour [9]. This study is reported the extraction process on the rice husk ash made in Indonesia into SiO_2 with different extraction times and KOH concentrations and to identify the formation of SiO_2 gel. In addition, the temperature and reaction time also affect the microstructure and purity of the SiO_2 gel produced.

Experimental Method

The source of silica is produced from the basic material of rice husks after being deposited from local rice producers and mills located around the Bekasi area, West Java, Indonesia, which is an agrarian country that produces quite a lot of rice in Southeast Asia. This deposition method was followed by the extraction of rice husk ash (RHA) using simple alkaline extraction to produce biosilica [7]. RH combustion was carried out at a temperature of 700ºC for 120 minutes by using a Barnstead Thermolyne conventional furnace. The RHA distribution is measured 10 g weigh dispersed in distilled water of 60 ml at a temperature of 60°C, for one and a half hours using a 2.5 M NaOH solution. According to the following reaction, RHA containing silica is produced by leaching out into the aqueous phase of dispersed in the form of dissolved sodium silicate.

$$SiO_{2\ (Ash)} + 2\ NaOH \rightarrow Na_2SiO_3 + H_2 \quad (1)$$

Ash-free filter paper with a size of 110 mm was used to filter the sodium silicate solution carried out under vacuum filtration conditions. Boiling water with a volume of 100 ml was used to wash the carbon residue. After the heating process is carried out washing and the filtrate is then in room temperature to cooled, then using sulfuric acid of 2 normal for acidification. In order to obtain a solid form of white gelatin SiO_2, it is carried out by precipitating the dissolved silicate through 79-1 hot plate magnetic constant stirring until pH 7 is reached. A solution of H_2SO_4 is used to precipitate so that the following reaction can be produced.

$$H_2SO_4 + Na_2SiO_3 \rightarrow Na_2SO_4 + SiO_2 + H_2O \quad (2)$$

The SiO_2 gel deposition process is started by dropped when the pH is below 10 which was continued by 18 hours aging. To produce xerogel, the gel at 80°C was dried for 720 minutes. Next is the process of grinding the sample into powder using a mortar and a piston, then an airtight plastic bag is used to store the powder. A spectrophotometer was used in this analysis for the purpose of characterizing are include in the oxide of major and minor in the chemical constituents of rice husk ask SiO_2. In order to emphasize the properties of SiO_2 phase extracted and obtained from the rice husk ash, Zeiss brand of EDS (Energy-Dispersive X-ray Spectroscopy) analysis was used. Rice husk ash extraction analysis was carried out with Cu radiation and scanning range of 10,000 - 80,000 and scanning speed of 2º per minute and using 40 kV acceleration voltage and 30 mA current.

The hardness test was done by using a Krisbow Motor Driven machine of Rockwell testing by creating a 5 mm thick epoxy mount on the extracted biosilica powder with a load of 50 N. The hardness test was carried out on 30 random steps on the surface. Table 1 is shows the chemical composition of RHAS.

Table 1. Rice husks ash chemical compositions with SiO_2 contens.

Content	SiO_2	K_2O	P_2O_5	CaO	SO_3	Al_2O_3	Cl	MnO	Fe_2O_3	TiO_2	ZnO	Rb_2O
Levels (%)	90,38	3,18	1,61	1,24	1,02	0,88	0,76	0,40	0,40	0,05	0,02	0,01

Results and Discussion

The process of separating a mixture that is added by a solvent is called Extraction. In this study, solid-liquid extraction was carried out by transferring mass between phases. In this case, the solid phase is rice husk ash and as an extractant is KOH. Extract formation occurs when the extractant reacts with the solid, on mixing the extractant with the extractant in the solid-liquid phase. In fact, a very long reaction time is required in the solid-liquid extraction process, between the extractant and the solid. The results of the SiO_2 content were investigated by dissolving in an alkaline solution in rice husk ash. In between SiO_2 contained there is a reaction that occurs in the rice husk ash with an alkaline solution, in this case the KOH solution occurs in reaction (3).

$$SiO_2 + 2KOH \rightarrow K_2SiO_3 + H_2O \quad (3)$$

The SiO_2 compound that is formed is still in the form of a potassium silicate solution. Then the solution is added with 1 N HCl which is used to bind potassium to produce SiO_2. The reactions that occur is described on the reaction (4). Fig. 1 to 3 are shows the burning rice husk charcoal before and after entered into a furnace, respectively. The result of rice The hydrochloric acid solution here functions as a precipitation agent. SiO_2 compounds are easy to solve in alkaline conditions, and the precipitation process occur in an acidic environment [7]. This phenomena is to create an SiO_2 consolidation easily extracted by rice husks, an alkaline gel solvent, KOH is choosed, and after that an acid solution, 1 N HCl, is used to precipitate it again. After the SiO_2 compound re-settles, the H_2O levels which affect the moisture of the product can be removed by drying in an oven. SiO_2 deposits produced in this process are SiO_2 deposits which still contain a lot of coprecipitation. The following is a picture of the stages of forming the extracted SiO_2 gel.

$$K_2SiO_3 + HCl \rightarrow SiO_2 + KCl + H_2O \quad (4)$$

Figure 1. Burning rice husk charcoal before furnace treatment

Figure 2. Burning rice husk ash after furnace treatment

Figure 3. Dried coarse silica precipitate after sol-gel extraction

SiO_2 sol-gel husk ash extraction process was carried out with various concentrations of KOH and time. Through variations in extraction time and KOH concentration, there is a slight difference in the density of the SiO_2 gel obtained in the research results. The difference in density in the extraction results is due to the influence factor, i.e. the material particle size. The particle size in smaller, the larger in contact area between solid and the solvent. Meanwhile, the density yield is slightly affected by the temperature used in the extraction process. The increase in diffusivity occurs as the temperature increases in the solubility of the extracted material. However, the optimum temperature is used because the extracted material can be damaged if the temperature is too high.

XRF is used to identify the purity and SiO_2 chemical composition which obtained by rice husk ash. SiO_2 is the main component as shown in the Table 1 and also contains with a small amount of metallic impurities. It should be noted that in removing metal impurities was effective using KOH extraction in rice husk ash.

The Energy-Dispersive X-ray Spectroscopy (EDS) analysis data of amorphous SiO_2 is shown in Fig. 4. The peak observed at 2θ around 45 eV is indicate of the formation of a non-crystalline SiO_2 phase. The Si-O groups bond, give the low temperature forms of tridymite and crystoballite, which observed under high temperature conditions [18, 19]. There is a versatile possibility of treated rice husks in high tempeature as a fillers for the application of elastomers, such as for polyethylene filler in white ash [20], polystyrene [21] and polypropylene [22]. Thus, it is certain that by using a mixture of amorphous SiO_2, an environmentally friendly tire filler can be produced in the future.

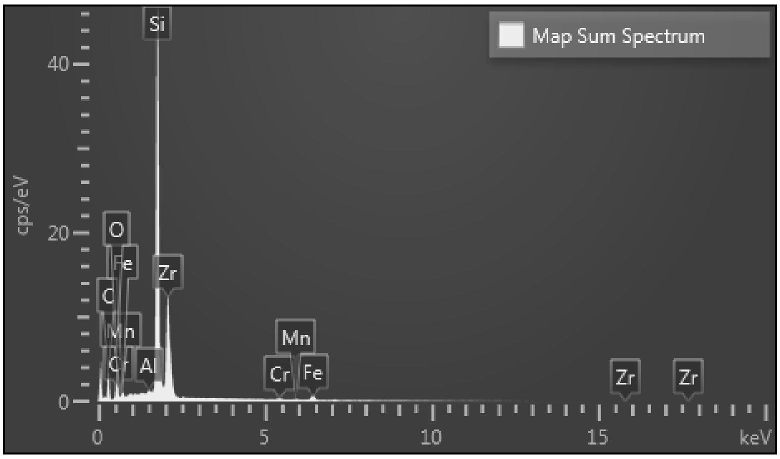

Figure 4. EDS plot of SiO_2 produced from rice husk Ash.

In the hardness test results, samples reinforced with biosilica alloys had higher hardness values, compared to samples of rice husk ash compounds and rubber products that were not reinforced, as shown in the Table 2. This occurs because finer particle size in the natural rubber material has a uniform dispersion of the biosilica alloy and SiO_2 rice husk ash, thereby contributing to better hardness. In addition, in rice husk ash, SiO_2 has a lower surface area than biosilica alloys, one of which is the low hardness due to this factor. In addition, due to the presence of SiO_2 and other components as rubber filler, rice husk ash has different properties. This results in also a reduction in the rubber matrix to strengthening the biosilica alloy. Then, the incorporation of rice husk ash into a mixture of polypropylene or natural rubber has also been carried out in this study. The phenomenon of agglomeration contained in this rice husk ash mixture resulted in a phase that worsened the situation, resulting in a decrease in hardness, as shown in Fig. 5.

All composite test samples were given indentation loads, maximum results followed by rice husk ash SiO_2 and unreinforced composites were shown based on biosilica compound composite results. The explanation of the load characteristics at rest can be seen in the surface area, this is because the lower surface area than biosilica compound is owned by rice husk ash SiO_2, resulting in the rubber matrix cracks formation is because the filler dispersion in the rubber will be poor. therefore is occured when a load is given, will result crack initiation in the rubber breakdown. Relatively, from all test results, the results are not so significant, where there is a difference in compressive loads and cracks between rice husk ash SiO_2 and biosilica compound.

Table 2. Hardness testing results of rubber and SiO_2 compound.

Materials	**Natural Rubber**	**Pure SiO_2**	**SiO_2 – filled rubber compound**
Average Hardness [GPa]	50	66	62

Meanwhile, there was a significant difference between the test samples at biosilica compound resulting in high indentation followed by unreinforced rubber and rice husk ash SiO_2 composites. The result on this study, due to the rice husk ash SiO_2 addition, there was movement and displacement in the polymer chain which was actually limited and most importantly the rigidity of the rice husk ash SiO_2 filler was higher SiO_2 content influence in the ash. So the phenomenon of stiffness of the rice husk ash filler occurs in the increase in the the composite system rigidity [14].

The maximum hardness produced by rice husk ash SiO_2 -filled Rubber samples showed followed by biosilica compound and unreinforced products, especially when the filler particle size was large.

when the matrix is indented the large filler particles will try to block the movement of the rubber matrix. As a consequence, the indentation hardness increases [15]. In addition, better hardness is produced by the high specific gravity of the rice husk ash SiO_2 rubber composite. Through the differential torque is also closely related to the hardness. This is indicated by the suitability of the value of the torque difference so that there is a difference in hardness. as its ability to resist material displacement, is defined progressively by the resistance of abrasion of a solid from its surface. The increase in the abrasion strength of the rubber compound will lead to a higher modulus and cross-link density. It is for this reason that better abrasion resistance is provided by rubber composites filled of rice husk ash SiO_2. In another study reported that the resistance of abrasion of vulcanization is on the hardness and cross-links density dependance [16].

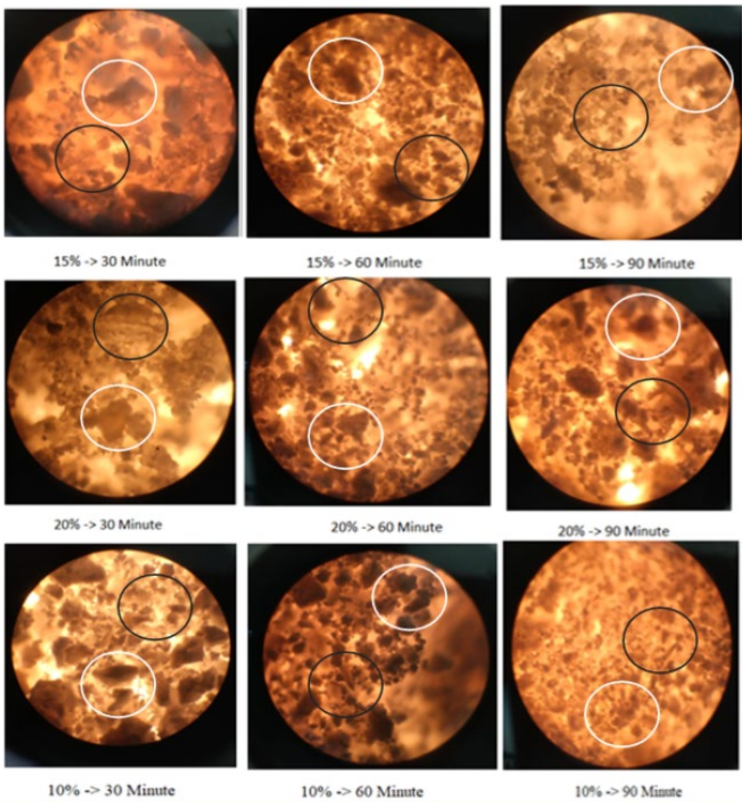

Figure 5. Optical microscope images of SiO_2 with various impurity and processing time.

Conclusions

The rice husk ash SiO_2 production as an alternative application in natural rubber filler has been generally characterized by a chemical extraction process. Through the mechanical properties tests carried out in this research, the hardness of 62 GPa and the ability to withstand pressure, are lower than the silica products obtained commercially. This is occur because to the large particle size of rice husk ash which results in poor dispersion, in addition to the surface area in lower. In addition, the rubber-filler interaction affected the higher the stiffness of the rice husk ash SiO_2 filler contained in the higher content of silica, the higher and lower interaction in rubber ash filler matrix. This is due to the presence of a better Silicone functional group on the surface of the rice husk ash SiO_2. Improved characteristics, including properties, modulus, hardness and crack resistance were carried out by adding rice husk ash SiO_2 filler to the rubber composite. The main factor that is most important to do on rubber composites filled with rice husk ash SiO_2 is to time saving which required in start vulcanization efficiency. However, on the mechanical testing results of rice husk silica, it is known that the difference is not too significant, so that this biosilica material is applicable as a natural rubber compounds in renewable as well as substitute filler.

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