The treatment effect of tensile strength on polypropylene filled with silica from rice husk ash

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Abstract. Polypropylene (PP) is a plastic that can be utilized in many sectors such as food wrappers and eyeglass lenses. Polypropylene which is filled with silica from rice husk ash can improve its mechanical properties. The purpose of this study was to examine the effect of the addition of rice husk ash on the mechanical properties of polypropylene composite. The extracted silica was filtered with 325 mesh sieve. Silica was analyzed using Scanning Electron Microscopy (SEM), Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX), Fourier Transform Infra-Red (FTIR), X-ray Diffraction (XRD), and X-ray Fluorescence (XRF). Polypropylene composite film filled with silica from rice husk ash was analyzed using tensile strength and elongation at break as well as functional group tests (FTIR) and composite structure (SEM). The result of this study was (1) Silica extracted from rice husk ash produced higher silica purity which is 21.93 % weight, (2) The extracted silica was in crystalline form, (3) The silica in polypropylene film was in siloxane form and (4) Polypropylene composite film with the addition of 2 % silica has the highest tensile strength and elongation at break (5.36 kgf/mm² and 5.00 %).

1. Introduction
One of the plastics type commonly used to make plastic bags and easily find on the market is polypropylene (PP) [1]. PP is a type of saturated aliphatic polymer which is a semi-crystalline polymer consisting of two parts which is crystalline and amorphous phase also has a high melting point, transparent, and good impermeability. PP can develop into a matrix of composite materials to obtain higher tensile strength and elongation [2].

The disadvantages of PP polymers are that they have a low density compared to other types of polymers such as polyethylene and polystyrene which cause poor mechanical properties [3]. To improve the mechanical properties, addition of filler is needed to add the density of the PP polymer. Polymers that arranged composites as matrix will produce composites with final properties that are highly dependent on the characteristics of the polymer. Addition of filler to the composite will also increase the hardness, and the degradation process also improves the mechanical properties of a polymer such as tensile strength and percent elongation [4]. Most of researches utilized different recycled wastes to improve PP composites properties with the environmental friendly filler. Among various filler used for composites, one of them is rice husk ash (RHA). RHA is an agricultural residue by product abundantly available in Indonesia [5, 6].

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RHA is a by-product produced from the process of rice milling and often used as a growing media and a fuel source for burning. Improper handling of RHA will result in environmental pollution [7]. RHA contains 94% silica of total weight that can be used as a natural filler for composites [8]. To isolate silica in RHA can be used in a very easy process and relatively inexpensive cost using the extraction method. The extraction method is easier to use in alkaline and acidic solutions. Alkaline compounds such as KOH, NaOH, and Na$_2$CO$_3$ can dissolve silica in the amorphous phase, where acid compounds can precipitate more dissolved silica and for the acid that commonly used for the extraction of silica are acetic acid, oxalic acid, citric acid, and hydrochloric acid [9]. Many researchers have conducted silica research using extraction processes with a variety of variations of raw materials and solvents. Rafiee et al. [10] used rice husk (RH) and acetic acid solution, the resulting silica was 6 nm in the form of 99.90% amorphous phase. Amalia et al. [11] also conducted a similar study with the same raw material and using NaOH solution for 12 hours, obtained 82.61% silica yield. Amalia et al. [11] and Diharjo et al. [12] states that the use of silica as a filler in PP composites can increase the tensile strength, impact toughness, and composite density.

In this study the effect of the process of isolating silica from RHA using acetic acid extraction treatment, characteristics of the resulting silica and the use of silica as a filler to enhance the properties of PP composite film on the effect toward morphology, physical and mechanical properties were studied.

2. Experimental
2.1. Preparation of polypropylene filled with silica
The rice husk ash (RHA) used in this study for extracting silica was obtained from a rice mill and ground to powder using blender. RHA was soaked in 3 M glacial acetic acid solution for 2 hours at room temperature. The solution is then washed and filtered until the pH is neutral and dried at 105°C for 2 hours. The resultant silica is filtered with a 325 mesh sieve and were stored for further analysis. The process of preparing polypropylene (PP) composites film by dissolving PP using xylene until homogeneous with constant temperature at 190°C and then filler from RHA was loading with various concentrations of 0-5 % wt into the solution. The composites solution was cast on flat stainless steel and were stored for further analysis.

2.2. Characterization
2.2.1. Crystallinity analysis
Crystallinity and amorphous phase was determined using XRD Shimadzu XDR 7000 at an operating voltage 40 kV and applied current was 30 mA.

2.2.2. Morphology analysis
To determine the structure formed on silica and polypropylene composite film analyze by scanning electron microscopy (SEM). The sample is attached to a holder then in thin layer of platinum in a vacuum state with enlargement is 1000x.

2.2.3. Composition analysis
The particle composition of silica from RHA was analyzed using X-ray fluorescence (XRF).

2.2.4 Functional group analysis
The structure of functional group sample silica and polypropylene composite film has analysis using IRAffinity-1S FTIR spectrometer with scanning ranges of 4000 cm$^{-1}$ to 400 cm$^{-1}$ at room temperature.

2.2.5. Mechanical analysis
Tensile strength and elongation analysis were performed using the HT-8503 Universal Testing Machines device. The polypropylene composites film was cut following ASTM D638.
3. Results and discussion

3.1. Silica particle from RHA analysis

3.1.1. Crystallinity of Silica particle analysis

Silica has crystalline structure contrary to component from RHA, which are amorphous in nature. The evaluation of the amount of phase form of silica is very important. For this purpose, there are some specific methods, one of them is estimated by the silica activity index [10].

![X-ray diffraction patterns of silica from RHA.](image)

Figure 1. X-ray diffraction patterns of silica from RHA.

From Figure 1, it can be seen that the silica particles obtained through the combustion of rice husks ash with chemical treatment using extraction by acetic acid at room temperature was crystalline. The diffractogram also have a high intensity level which is 20° = 22.49° is a prove that silica was in a crystalline form. Similar result obtained by olawale et al. [13] states that the particles of rice husk ash are crystalline which they have proven using Raman Spectra. The diffraction peak at 20 of 20°, 22° and 36° is a typical silica characteristic which attributed to the presence of an ordered crystalline structure and the acid treatment of RHA did not affect the silica structure which consistent with the present study [14,15].

3.1.2. Morphology analysis of silica particles

The morphology structure of silica particle from RHA was studied using SEM, as shown in Figure 2. The structure of sample was a polygonic and irregular shapes. It is also seen that agglomeration of several silica particles forms larger particles. This might be due to the large surface area of the silica and forming a strong electric dipole that can agglomerate [13]. The average particle size of silica is 100μm and with an irregular morphology is seen.

These particle are homogenous and agglomerate, indicate that parts of micropores exist in silica particle from RHA. A similar result observed that precipitation of acetic acid produce the solid and the aggregation rate of silica particle occurs faster when pH decreases because of acetic acid [16]. These solid disappear when is washed and filtered until pH neutral, indicating the removal of impurities [14].
3.1.3. Composition analysis of RHA

To evaluate the effect of purification parameter and to confirm the presence of silica particle, SEM-EDX was carried out on silica from RHA with acetic acid treatment. There are four main elements found in the rice husk ash which has been extracted by acetic acid, namely carbon, oxygen, silica, and potassium. The result of composition analysis of RHA are tabulated in Table 1.

![Silica analysis with SEM at 1000 x magnification.](image)

**Table 1. Analysis of RHA content.**

| Element | Total Particles | Weight (%) | Atom (%) |
|---------|----------------|------------|----------|
| C       | 7.797          | 34.38      | 45.10    |
| O       | 6.460          | 42.95      | 42.30    |
| Si      | 6.230          | 21.93      | 12.30    |
| K       | 94             | 0.75       | 0.30     |
| **Total** | **20.581**    | **100.00** | **100.00** |

The composition was reported based on weight percentage shows that RHA treated with acetic acid containing 21.93 wt% of silica and 34.38 wt% of oxygen. This occurred because there is a siloxane functional groups (Si-O-Si) in RHA treated with acetic acid. Very high carbon content indicates that silica which is mostly contained in the outer surface of rice husk ash was not all soluble by the solvent of acetic acid and causing carbon (C) particles trapped in the pores of RHA. This can cause the carbon as impurity that obtained in the particles still high [17]. Based on the results, other impurities except carbon (C) and potassium (K) has been dissolved during the extraction process using acetic acid. The result obtained by Arifin et al. [5] shows that RHA without treatment using acetic acid contained of 89.83 wt% SiO$_2$ but there were still impurities in RHA such as Fe$_2$O$_3$, CaO, MnO, K$_2$O, and MgO. This shows that in this study acetic acid was able to reduce impurities so that only the remaining potassium (K), Oxygen (O), and carbon (C) elements were left.

3.1.4. Functional group analysis of silica particle from RHA

FTIR spectra of silica particle are presented in Figure 3 showed all types of SiO$_2$ are strong bonds at the peak of 1110-1080 cm$^{-1}$. Apart from these strong bonds, there are other peaks that can help in identifying the types of SiO$_2$ such as $\alpha$-Quartz (SiO$_2$ crystalline forms), spotted at the peak of 1105, 796, and 621
At wavelengths of 1105 cm\(^{-1}\) and 796 cm\(^{-1}\), the siloxane - (Si-O) \(n\)-functional group is caused by the presence of stretching vibrations in the symmetrical and asymmetrical Si-O-Si group.

![Figure 3. FTIR analysis of silica particles from RHA.](image)

Three main peaks are shows strong absorption at 470, 796, 1105 cm\(^{-1}\), indicating the presence of silica particle. The peak also shows the vibration of oxygen atom joined with another atoms in the asymmetric stretching due to vibrations of Si-O-Si band [19]. The O–H stretching vibrations appear in the region of 3500–3800 cm\(^{-1}\). The band resulted from silanol OH groups and water bound to the silica surface by hydrogen bonding [14]. Research study by Premaratne et al. [28] also indicated that O-H stretching can happen due to physically and chemically absorbed water molecules on the SiO\(_2\) surface.

The FTIR peaks in this study were similar result to those in the silica particle spectra obtained from RHA [14,20,19]. Furthermore, the FTIR found changes in the chemical component of silica from RHA. In comparison with RHA sample spectra from Liou et al. [14] study and RHA treated with acetic acid show different absorption. The breadth and height of O–H and Si–O bands in the RHA sample are much smaller than extracted silica samples. The finding is due to the compact agglomerate of silica particles produced by a gelation reaction that leads to increased strength of intermolecular hydrogen bonding.

### 3.2. Polypropylene/silica composites film analysis

#### 3.2.1. Morphology analysis of composites film

The SEM images of polypropylene (PP) composites film with various silica particle from RHA content were shown in Figure 4. The surface structure in Figure 3(a) is PP without silica and Figure 3(b)-(f) is a PP filled with 1, 2, 3, 4, and 5 wt% silica.

![Figure 4. SEM images of polypropylene composites film.](image)

Figure 4 shows that the PP composites film matrix forms a layer that produces a void. In Figure 4 (a) there is no void seen in the matrix. This because there is no addition of silica to the sample. In Figure 4 (b), (c), and (d) indicate improvement in bonding between silica from RHA and polypropylene. it appears that the silica spread and fill the PP composites matrix and form a void [21]. The number of void which slightly increases where the filler particles are fill the PP matrix.

In Figure 4 (e) and (f) the distance between the silica looks far apart and the PP composites matrix looks rigid and solid. This occurs due to uneven stirring when mixing silica into PP composites film. Increasing concentration of filler to the PP matrix can affect the microstructure of the polymer which causes uneven distribution of silica and reduced the tensile strength of composites film [22]. The adhesion of the filler-polymer matrix increase is improved with increasing filler. However increasing more filler concentration can reduce the properties of film due to non-covalent bonding and hydrogen bonding with the OH group and oxygen of each of group carboxil bonding between the filler and the polymer matrix which in line with studies Ginting et al. [23], Kord et al. [24] and Bhat et al. [25].
3.2.2. Functional group of PP/silica composites film

The obtained FTIR spectra for PP composites filled with silica and without silica were performed in Figure 1. The overall result shows that structures of PP composites filled with 5 wt% silica are almost the same with pure PP polymers. However, when viewed in greater detail, there is a difference that is in the PP composites film with silica show the new peak (blue circle) at 621.08 cm\(^{-1}\) which is a functional group of CH\(_2\) whereas in pure PP composites is nowhere to be found [26,27]. Spectrum composites film at 1076 cm\(^{-1}\) and spectra rice husk ash at 1078 cm\(^{-1}\), it indicates the presence of a silica functional group in the form of Si-O-Si. The existence of such bonds may state that the composite contains silica because of the filler [28].

**Figure 4.** SEM images with 2000x magnification for polypropylene composites film (a) without silica (b) 1 wt% silica (c) 2 wt% silica (d) 3 wt% silica (e) 4 wt% silica and (f) 5 wt% silica.
From the FTIR spectra also shows that the composite PP without silica is made from polypropylene polymer at peak $2.875 \text{ cm}^{-1}$, which is a methyl functional group (-CH$_3$) showing the C-H$_{\text{str}}$ bond which is a typical area of the PP polymer. At peak $1.442 \text{ cm}^{-1}$ and $1.373 \text{ cm}^{-1}$ indicate to the methyl C-H$_{\text{bend}}$ functional group. The peaks detected in the range of 1200-950 cm$^{-1}$ are attributed to stretching of C-O-C, C-O, and C-OH functional groups [26,28].

### 3.2.3. Tensile strength analysis

In this study, tensile strength are measured in order to evaluate the PP/silica composites film. Figure 6 shows the result of tensile strength for all sample composites filled with silica and without silica. The tensile strength of samples were filled with 0, 1, 2, 3, 4, 5 wt% silica were found to be 4.29; 3.69; 5.36; 4.40; 4.02; and 5.18 kgf / mm$^2$ respectively.

From Figure 6 it can be seen that the highest tensile strength value is PP composites film with 2 wt% silica fillers. It was caused by the addition of fillers with an amount of < 10 % resulting in a closer distance between particles in the composites film which causes the composites to become stronger [27]. The best silica composition to be added to PP composites is 0.1 gram. This is similar with what was done in this study that PP samples with a filler addition of 2 wt % were proportional to 0.08 gr of silica added to the PP composite. The decrease in tensile strength occurred in PP composites of 3 and 4 wt%. This is because agglomeration occurs in PP composites [23].

### 3.2.4. Elongation analysis

Figure 7 shows the result of elongation for all sample composites filled with silica and without silica. The elongation of samples were filled with 0, 1, 2, 3, 4, 5 wt% silica were found to be 3.72; 3.12; 5.00; 2.18; 4.02; dan 4.28 % respectively.

This can occur because the addition of filler into the composites film pores results in a closer distance between fillers due to the tight arrangement, this can cause the value of stiffness of composites film increase while the flexibility decreases [29]. Sample with the addition of 2 wt% silica has the highest elongation strength value at 5 % of elongation. This happens because the most optimum addition of fillers is 0.1 gram [30]. In addition, this can occur because of the influence of many things such as irregular inter-filler arrangement, different thicknesses, and pore formation in composite samples that have an impact on the forces acting on the composite, resulting in poorly produced elongation, which in line with studies Aprilia et al. [27].
4. Conclusions
In this study, the effect of acetic acid treatment on RHA produced a higher silica purity level which is 21.93% by weight. Chemical treatment of rice husk ash using acetic acid produces silica in a crystalline state. Analysis of functional groups shows the presence of silica indicated by the emergence of a peak at the peak of 808 cm$^{-1}$ and 623 cm$^{-1}$ which is a siloxane (Si-O-Si) functional group. PP composites film with the addition of 2 wt% silica has the highest tensile strength and elongation at 5.36 kgf / mm$^2$ and 5.00%.

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