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Preparation and Characterization of Natural Zeolite and Rice Husk Ash as Filler Material HDPE Thermoplastic

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Abstract
This study aims to determine the size of the natural zeolite partike, rice husk ash, and to know the effect of fillers on the mechanical strength of the composite. The method is done by two methods, the first method of natural zeolite and rice husk ash puree by using Ball Mill for 1 hour to obtain a particle size of 74 µm. Further to the natural zeolite dissolved in 2 M HCl, rice husk ash with NaOH 2.5 M. results of each ingredient in a ball mill for 15 hours to obtain particles in nano-meter size. Both of these materials are used as filler in thermoplastic HDPE. This mixture of materials with a ratio (70/30, 60/40, 50/50, 40/60, 30/70) wt% were mixed in an internal mixer at a temperature of 150^0C laboplastomil at a rate of 60 rpm for 10 minutes. The results of XRD analysis of rice husk ash obtained particle size of 53.12 nm with dominant phase of SiO_2 (Cristobalite). For natural zeolite obtained size 44.46 nm with dominant phase $Al_2CaO_8Si_2$ (Anorthite). mechanical properties of the composites, obtained the biggest increase in a mixture of 60/40 compared to pure HDPE.
Keywords: HDPE, zeolite, rice hush ash, mechanical XRD analysis

1.Introduction

Indonesia is a country rich in mineral resources, including the potential abundance of natural zeolite there are more than 40 locations and the relative has not been developed. The abundance of natural zeolite has given birth to a new trend in the study of science and technology (Fatimah, 2000).

Zeolite containing aluminum silicate compounds which have a three-dimensional framework structure formed by tetrahedral $Al0_4^{5-}$ and SiO_4^{4}.One of them use natural zeolite as a filler in thermoplastic

Rice husk has now been developed as a raw material to produce ash known as RHA (Rice Husk Ask). Rice Husk ash is the burning of rice husk ash, which is essentially just a waste, it is a source of silica / carbon is high enough. RHA is one of the raw materials to produce silica. Silica nano now has applied in various fields including science and industry. Rice husk ash materials have been widely used as a filler. Silica has been used widely as a catalyst, and various kinds of organic-inorganic composite materials (Sun .L et al, 2001), (Ginting,.M Eva, at al 2014).

Refined products, silica has also been utilized directly for the polymer and filler materials as adsorbents (Kamath and Proctor, 1998; Sun L, et al, 2001;).

Has done a lot of research on the manufacture of nano silica from rice husk ash by synthesis, among others, (Thuadaij.N. et al, 2008),, (Supakorn Pukird, et al, 2009), (Ezzat Rafiee, et al, 2012)

High density polyethylene (HDPE) is one of the most important commercial polyolefins. It finds widespread use in such applications as household appliances, automobiles, aeronautics and packaging. HDPE has excellent low temperature toughness, chemical resistance, good dielectric properties and relatively high softening temperature (E.P Ayswarya, et al. 2012).

From several studies conclude that properties a filler material to be compatible with the polymer matrix, is influenced by several factors, among others, the particle size of a filler material, wherein the particle size of a small filler material can increase the degree of reinforcement of polymer compared with a larger size, (Leblance, J, 2002), as well as the smaller the particle size the higher the bond between the filler to the polymer matrix, (Khols J, et al, 2002), the amount of surface area can be increased by the presence of a porous surface on the surface of filler material as well as with the addition of nano can improve the mechanical properties and thermal nano composites, (Bukit N, 2012),

The few examples of filler that have been used in the manufacture of HDPE thermoplastic especially among others CaCO3 / HDPE (Saeedi and Sharahi, (2011); graphite / HDPE (M.Sarikanat, et al., 2011), Clay / HDPE (Pegoretti, et al, 2010; Wang, et al. 2003), natural bentonite / HDPE (Bukit. N et al, 2013)), fly ash / HDPE (Ni'mah, et al., 2009), , rice husk ash / HDPE (E.P Ayswarya, et al. 2012), zeolite / HDPE (Kim, 2006; Frida.E ,et al, 2014). Nano CaCO3 to HDPE, (Zebarjad, S. M, et, al. 2006), nano carbon with HDPE, (Fouad, H., et al, 2011).

2. Experimental

2.1 Instrumentation, Matrials

Instrumentation

Planetary Ball Mill PM 200 Retsh, Internal Mixer Labo Plastomill 30RI50 models, Hydraulic Hot Press and Cold Press 37 ton Genno Japan, dumbell cutter, tensile testing machine stograph R-1 brand Toyoseki Japan, Shimadzu XRD-6100, 200 mesh sieve, magnetic stirrer, oven, mortar, hammer, vacuum pump.

Matrials

Natural zeolite, rice husk ash, High Density Polyethylene (HDPE) production Nusantara PT Titan Petrochemicals, PE-g-MA manufactured by Sigma Aldrich, USA, 2M HCl, 2.5 M NaOH, distilled water.

2.2 Preparation of Zeolite

Zeolites in advance in the form of chunks of crushed to a powder-fine powder. Zeolites are already crushed, crushed with a ball mill for 1 hour at a speed of 250 rpm. Subsequently sieved using a 200 mesh sieve. Zeolites are a 200 mesh (74 m) soaked with a solution of 2M HCl in the ratio of 1: 3 in 4 hours stirring with a magnetic stirrer. HCL blend of solvent with zeolite separated with filter paper, and then washed with distilled water and filtered again to separate the distilled water with zeolite. Furthermore, the zeolite was dried in an oven at 100° C for 2 hours. Natural zeolite has been activated and added to the container mill dried then ground using a ball mill for 15 hours at a speed of 400 rpm .

2.3 Preparation of Rice Husk Ash

Rice husk ash in the form of powders milled for 1 hour at a speed of 250 rpm. Rice husk ash sieved using a 200 mesh sieve. Furthermore soaked with 2.5 M NaOH solution with a ratio of 1: 3 in 4 hours stirring with a magnetic stirrer. NaOH blend of solvent with rice husk ash separated with filter paper, and then washed with distilled water and filtered again to separate the distilled water with rice husk ash. Furthermore, rice husk ash dried in an oven at 100°C for 2 hours. The dry rice husk ash reprocessed using a ball mill for 15 hours at a speed of 400 rpm

2.4. Preparation of Nanocomposite .

Natural zeolite and rice husk ash that has been activated and sized nanoparticles are used as filler, which are both combined in the ratio as in Table 1:

Then do the manufacture of nano-composites were carried out within the Internal Mixer with blending temperature of 150 °C and a rotor speed of 60 rpm for 10 minutes. Materials are mixed according to Table 2

Table 1. Composition of filler

Material	Composition (wt.%)				
	C1	C2	C3	C4	C5
Zeolite	70	60	50	40	30
Rice Husk Ash	30	40	50	60	70

Table 2. Composition Blend Nanocomposite

Sample	Material						
	HDPE	PE-g-MA	Zeolite + Ricr Husk Ash				
			C1	C2	C3	C4	C5
S_0	100	0	-	-	-	-	-
S_1	88	2	10	-	-	-	-
S_2	88	2	-	10	-	-	-
S_3	88	2	-	-	10	-	-
S_4	88	2	-	-	-	10	-
S_5	88	2	-	-	-	-	10

Results from the internal mixer laboplastomil with hot press molded performed for 10 minutes at a temperature of 160^0 C, followed by cold pressure. Samples were produced in the form of sheets and in the dumbbell with standard JIS K 6781 which will be used for mechanical tests .

2.5 Mechanical Properties Measurement

Tensile strength measurement was performed according to JIS K 6781 standard using Universal Testing Machine, at crosshead speed of 50 mm min^{-1}. Young's modulus (E), ultimate tensile strength (σ_{max}), and elongation at break (ε_b) were determined from the stress-strain curves.

2.6. X-Ray Difraction (XRD) Analysis.
The XRD analysis was conducted at room temperature using X-ray difractometer type Shimadzu XRD 6100. The operating conditions used were CuK_λ radiation (λ = 0.15418 Å, produced at 40 kV and 30 mA). Pattern was recorded over goniometer (2θ) ranging from 5° to 80°. The interlayer distance of rice ash in nanocomposite was derived from the peak position (d_{001} = reflection) in XRD diffractograms according to the Bragg equation: $d = \lambda / 2\sin\theta$.

3.Result and Discussion
3.1. Analisys XRD Rice Husk Ash and Zeolite

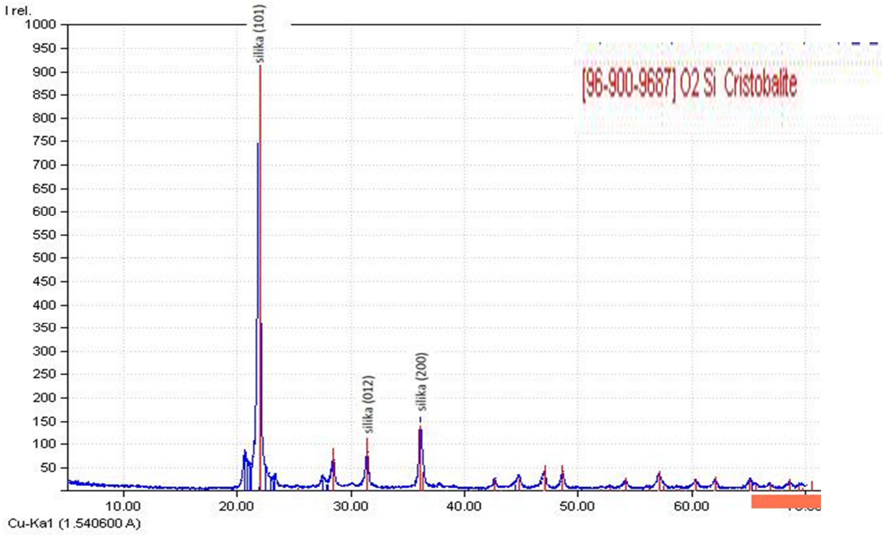


Figure 1. The Diffraction Pattern Of Rice Husk Ash

Based on Figure 1, the rice husk ash has been activated and milled for 15 hours has the dominant phase SiO_2 (cristobalite) with numbers 96-900-9687 reference. There are peaks typical of which is the top of the ASP dirakterisasi at 2θ 21,95°; 36,11°; 31,43° with intensity 2083.9; 307.8; 154.5, while the intensity of the standard cristobalite in the database that is 2062.9; 291.3; 235.4. There are other phases such as Porphyrazine aluminum chloride ($C_{16}AlClN_{16}S_4$), aluminum phosphate ($AlPO_4$), Tridymite (SiO_2). Rice husk ash with cristobalite phase has a tetragonal crystal system with a value of a = 4.9709 Å, c = 6.9278 Å, with has a density of 2.330 g / cm^3. From the diffraction pattern seen rice husk ash has a crystal structure.
To determine the size of rice husk ash particles can be calculated using Scherrer formula

$$D = \frac{k\lambda}{B\cos\theta_B}$$

With K is a constant (k: 0.916), λ is the wavelength of 1.5406 Å tube, and θB is the Bragg angle and B is the Full Width Half Maximum (FHWM) (Pauzan, et al., 2013). Based on the calculation results obtained for milling rice husk ash for 15 hours has a particle size of 29.75 to 106.59 nm with an average of 53.12 nm.

Based on Figure 2, the natural zeolite has a dominant phase $Al_2CaO_8Si_2$ (Anorthite), as well as some others such as SiO_2 (Quartz),. can be seen in the pattern of natural zeolite were characterized (blue) fits the pattern Quartz (red) by XRD database with reference number 96-901-3322. There is a peak in the zeolite characterized peak at 2θ 26,66°; 50,15°; 59,94° consecutive intensity 1000; 104.6; 72.5. While the intensity of the database to standard Quartz is 1029.7; 130.5; 94.9. There are other phases such as Porphyrazine aluminum chloride ($C_{16}AlClN_{16}S_4$), Neyite ($Ag_{2.074}\,Bi_{26.38}\,Cu_6\,Pb_{24.54}\,S_{68}$).

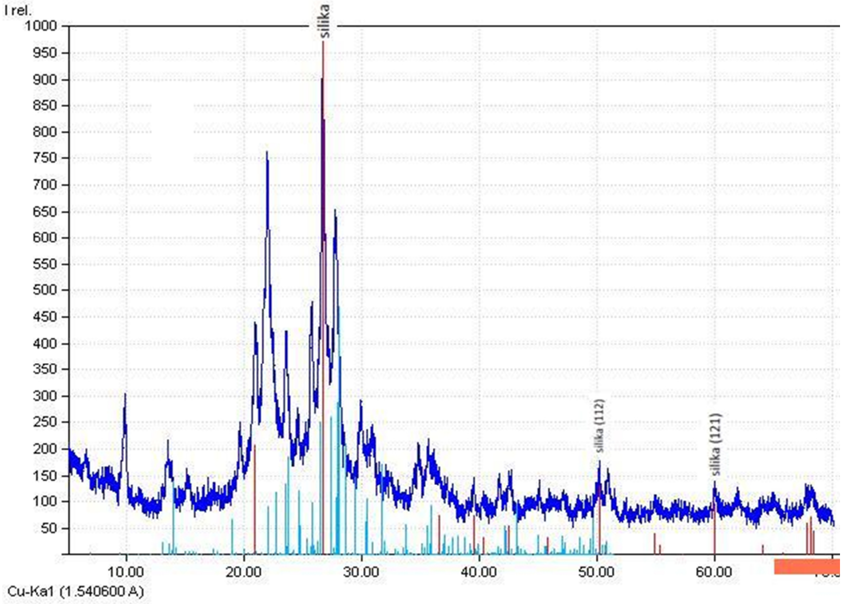


Figure 2. The Diffraction Pattern Of Ziolite

Natural zeolite with Quartz phase has a trigonal crystal system, with the value of the lattice parameters a = 4.9134 Å, c = 5.4051 Å. Phase Quartz has a density of 2.649 g / cm^3. From the diffraction pattern known natural zeolite has an amorphous structure.

To determine the natural zeolite particle size is calculated using Scherrer formula. Based on calculations, natural zeolite obtained for milling for 15 hours has a particle size of 24.63 to 70.26 nm with an average of 44.46 nm.

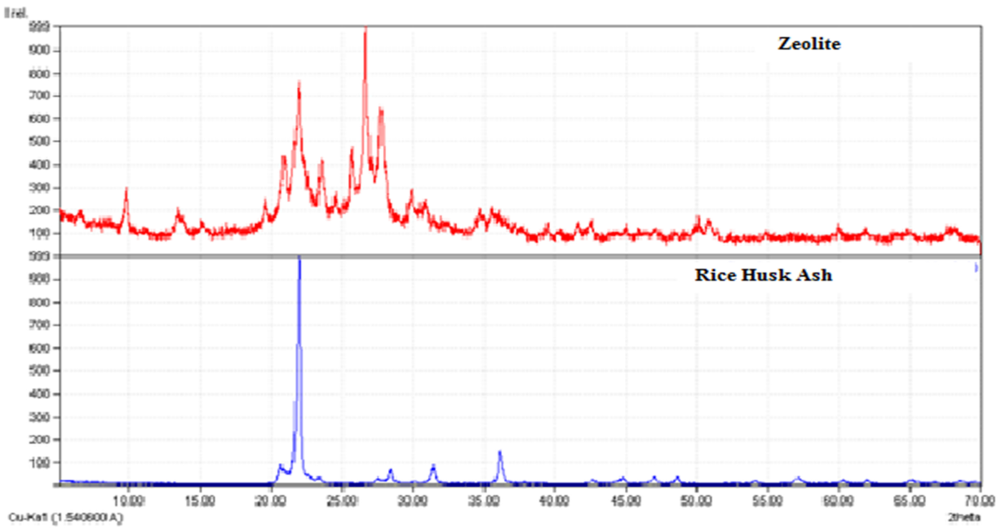


Figure 3 .Differences In The Diffraction Pattern Of Natural Zeolite And Rice Husk Ash

Figure 3 shows the difference in the diffraction pattern, wherein the nanoparticles rice husk ash has many peaks with intensity higher than the natural zeolite. Narrow peak with the higher intensity indicates the increasing cristaline these materials, which widened peak with low intensity showed an amorphous structure. Of the visible image pattern rice husk ash has a crystalline structure while natural zeolite has an amorphous structure.

3.2 Analysis Mechanical Properties Nanocomposite

In this study, mechanical properties of the samples include tensile strength, elongation at break, and Young's modulus, are measured in order to evaluate of nano particle zeolite /rice rusk ash. On Figure 4 until 6 shows the tensile strengths, elongation at break and Young's Modulus of the samples filled with nano particle zeolite /rice rusk ash

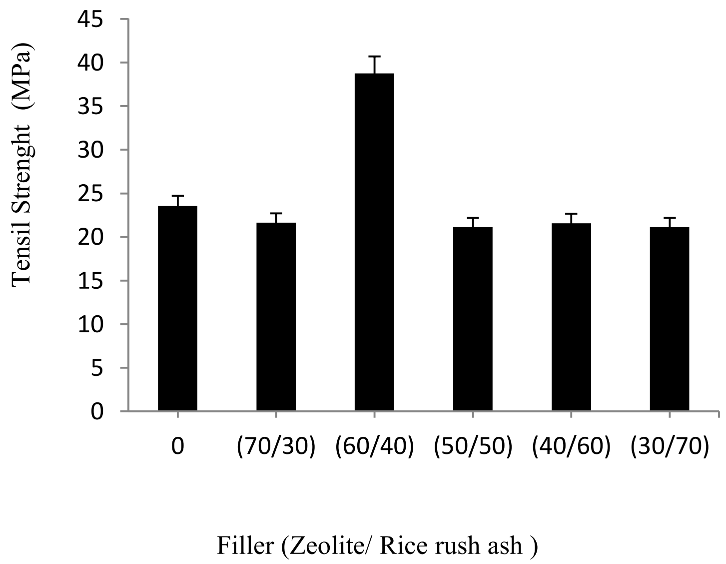


Figure 4. Tensile Strength of the Samples Filler Zeolite /Rice Rusk Ash

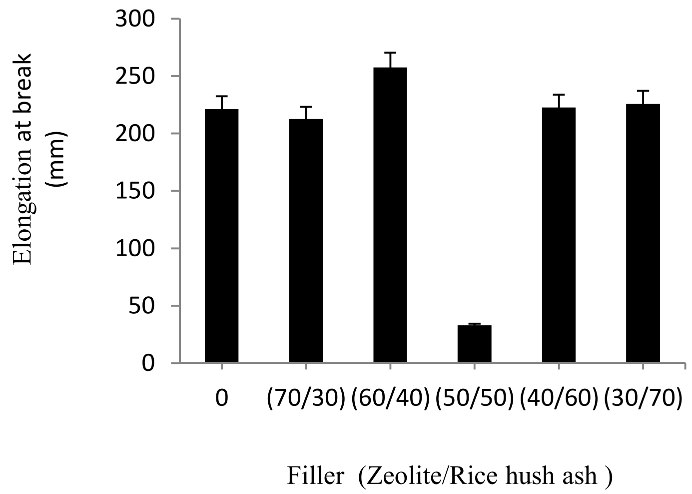
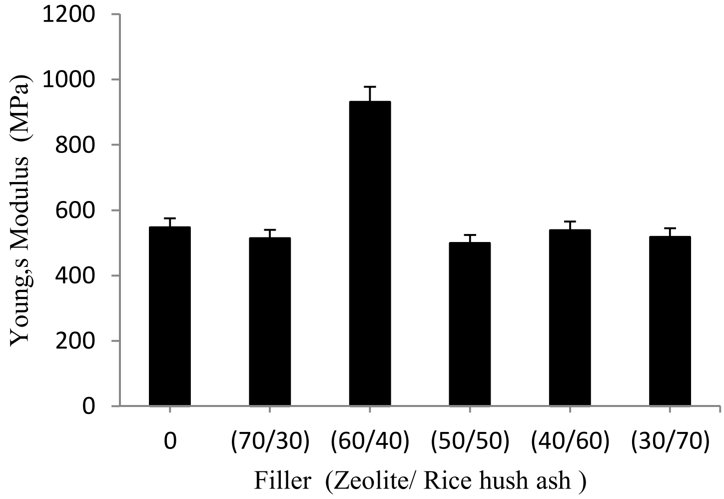


Figure 5. Elongation at Break of the Samples Filler Zeolite /Rice Rusk Ash



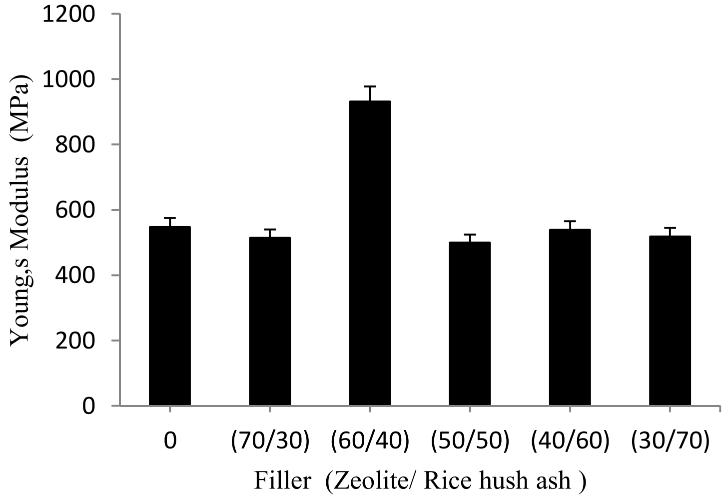
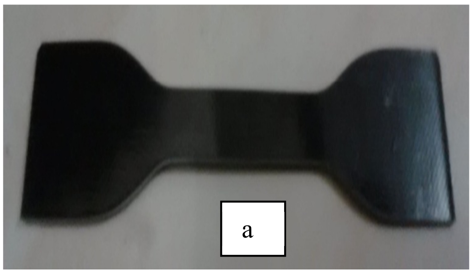


Figure 6. Young,s Modulus of the Samples Filler Zeolite /Rice Rusk Ash

In figure 4 it can be seen large tensile strength nanocomposite generally decreased when compared to pure HDPE, but the 60/40 combination increased tensile strength very significantly by 38.76 MPa, compared to pure HDPE is equal to 23.54 MPa. This is probably caused by the spread of equitable nanosilika which would extend the user interface as well as the infiltration of particles will be quicker and with the compatibilizer increases the strength of polymer chains. The increase in tensile strength due to an increase in covalent bonding and hydrogen bonding with the OH group and the oxygen of each of the goup carboxil add bonding between the filler with the matrix which is in line with studies, (Bhat, et. al, 2011) .Improved mechanical properties depend on many factors including the aspect ratio of the filler material, the degree disperse and orientation in the matrix, and adhesion at the interface matrix – filler.

Figure 5 shows the highest elongation at break of nanocomposite obtained on the composition of natural zeolite and rice husk ash 60/40 of 257.41mm. This increase significantly exceeds the value of elongation at break of pure HDPE R 221.25 mm. This could be due to the integration between HDPE with fillers by PE-g-MA as a compatibilizer which makes the mixture more stable through intermolecular bonds, (Mehta and Jain, 2007). Figure 6 shows the value of Young's modulus, the largest s obtained on natural zeolite mixture of ash and rice husk 40/60 amounted to 931.49 MPa. This increase significantly exceeds the value of pure HDPE at 547.80 MPa.

Figure 7 shows an example of a standard tensile test samples jisk 6781 and tensile test results



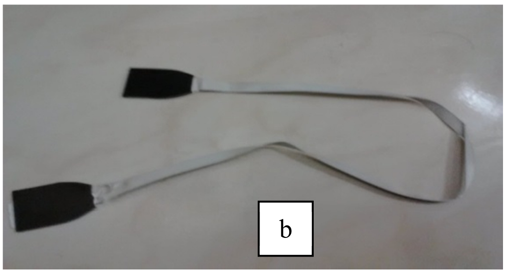


Figure 7 a. Sample JIS K 6781 standard ; b . The results of the tensile test samples

4. Conclusion

The XRD results showed zeolite having an average particle size of 44.46 nm and has a dominant phase $Al_2CaO_8Si_2$ (Anorthite) with the triclinic crystal system, there is also a phase of SiO_2 (Quartz), while 53.12 nm husk ash has a phase cristobalite (SiO_2) with system tetragonal crystals, there is also a compound of Aluminum Phosphate ($AlPO_4$).

The results of the mechanical properties of tensile strength, elongation at break, the largest elastic modulus obtained on the composition of natural zeolite and rice husk ash in the mix (60/40)

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