

Influence of Submicron Agro Waste Silica Particles and Vinyl Acetate on Mechanical Properties of High Density Polyethylene Matrix Composites

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Abstract: Development of polymeric composites has invoked much interest in recent years. These fillers have great effect on the mechanical properties of polymers. The present study developed two groups of High Density Polyethylene (HDPE) matrix composites reinforced with silica particles extracted from rice husk ash (RHA) and Vinyl Acetate. The silica powder particles with average particle size of 0.489 μm were produced by Sol-gel process. HDPE based composites were prepared by melt compounding with 2, 4, 6, 8 and 10 wt. % of silica particles and 30 wt. % Vinyl Acetate with a Rapra single screw extruder and were produced by compression moulding. Mechanical behaviour and microstructure of the developed composites were studied. It was observed that the mechanical properties increased with an optimum value of 4wt. % of silica particles in HDPE. There was improvement in the mechanical properties of the siliceous HDPE composites when compared with Ethylene Vinyl Acetate (EVA) composites.

Keywords: Density Polyethylene, Ethylene Vinyl Acetate, Mechanical properties, Rice husk ash, Sol-gel process

1. Introduction

Many of modern technologies require materials with unusual combinations of properties that cannot be met by the conventional metal alloys, ceramics, and polymeric materials. This is especially true for materials that are needed for aerospace, underwater, solar panels, electronics and transportation applications. For example, aircraft engineers are increasingly searching for structural materials that have low densities, are strong, stiff, and abrasion and impact resistant, and are not easily corroded. This is a rather formidable combination of characteristics. Frequently, strong materials are relatively dense; also, increasing the strength or stiffness generally results in a decrease in impact strength (Hull and Clyne, 1996).

Materials property combinations and ranges have been, and are yet being, extended by the development of composite materials. Generally speaking, a composite is considered to be any multiphase material that exhibits a significant proportion of the properties of both constituent phases such that a better combination of properties is realised (Chawla, 1998). According to this principle of combined action, better property combinations are fashioned by the judicious combination of two or more distinct materials. Property trade-offs are also made for many composites. A composite can also be described as a multi-phase material that is artificially

made, as opposed to one that occurs or forms naturally. In addition, the constituent phases must be chemically dissimilar and separated by a distinct interface. Thus, most metallic alloys and many ceramics do not fit this definition because their multi-phases are formed as a consequence of natural phenomena.

In designing composite materials, scientists and engineers have ingeniously combined various metals, ceramics and polymers to produce a new generation of extraordinary materials. Most composites have been created to improve combinations of mechanical characteristics such as stiffness, toughness, and ambient and high temperature strength (Peters, 2008)

Many composites materials are composed of just two (2) phases; one is termed the matrix; which is continuous and surrounds the other phase, often called the dispersed phase. The properties of composites are a function of the properties of the constituent phases, their relative amounts, and the geometry of the dispersed phase. "Dispersed phase geometry" in this context means the shape of the particles and the particle size, distribution and orientation.

Due to exponential growth of photovoltaic (PV) industry, the demand for solar grade silicon (SoG-Si) has increased tremendously over the past decade due to their extraordinary properties and their existing and potential applications in science and technology, silica gel has a

wide range of applications such as dessicant, as a preservative tool to control humidity, as an adsorbent, as a catalyst and as a catalyst support (Prasad and Panday, 2012).

At present, crude silicon known as metallurgical grade silicon, with 98-99% purity is obtained from quartz rocks by carbothermic reduction using electric arc furnace (Sarder, 2010). This silicon is further refined into high purity silicon through expensive and complicated purification process such as chemical vapor deposition (CVD) process which is used for production of electronic grade silicon. At the beginning of PV-activities in 1980s, the high purity scrap silicon from the micro electronic industry was used by the PV-industry (Muller *et al.*, 2006). However, increased demand that surpassed the limited supply of off-specification electronic grade silicon has created a thrust towards developing a dedicated technology for the production of solar grade silicon.

One of the approaches towards generation of SoG-Si is utilizing materials of very high purity to produce silicon. As an industrial waste, rice husk (RH) could be one of the potential raw materials for the production of solar grade silicon that can be used to develop siliceous particulate for use in solar panel assembly. Rice husk ash (RHA) is usually obtained by burning rice husk as fuel to generate energy from waste product. RHA is rich in silica (about 60%) and can be an economically viable raw material for the production of silica gel and powders (Chakraverty and Kaleemulah, 1991).

Although various uses for rice husk and RHA have been suggested in the literature, their disposal or utilization remains a major concern. Soluble silicates produced from silica are widely used in glass, ceramics and cement as a major component and in pharmaceuticals, cosmetics and detergents industries as a bonding and adhesives agents (Anon, 1997; Laxamena, 1982). Silica also has been used as a major precursor for variety of inorganic and organometallic materials which have applications in synthetic chemistry as catalysts, and in thin films or coatings for electronic and optical materials (Lender and Ruiter, 1990; Brinker and Scherer, 1990).

The use of silicon in solar panels has served to illustrate the unique properties of silicon in this particular application. While silicon is used in the manufacture of solar cells, silicone in the form of adhesives, sealants, coatings, encapsulants and potting agents are used in solar pane installation and assembly (Ancker *et al.*, 1983). Within solar pane applications, silicone could be used as cell encapsulants to protect photovoltaic cells from delamination and corrosion and because of these, pure polycrystalline silicon metal is used in the solar cell construction.

The PV industry, generally speaking, is under significant pressure to reduce the cost of manufacturing PV modules. Before PV modules and the renewable

energy they deliver can enjoy widespread adoption, the manufacturing process must be refined to a point at which the product, PV modules, has desirable price points as compared to conventional energy sources. In this current environment, there is great interest in new technologies that realized efficiencies in the module manufacturing process.

Encapsulants as a component in PV modules provide an opportunity to realise efficiencies in the module manufacturing process and overall module cost. The PV industry currently has a particular well-defined need for such improved materials. The PV industry has long – recognised the dramatic effect that corrosion has on module performance. Today PV modules typically include a polymeric encapsulant material to isolate the silicon components from the ever-present potentially adverse conditions created by various sources of water, including rain, snow and condensation. The isolation created by the encapsulant protects the PV components from corrosion and provides additional benefits, including mechanical support, electrical insulation and protection from mechanical damage (Lee *et al.*, 2008).

Polymeric encapsulants provide the desired isolation by bonding to a surface and limiting access to the protected areas or components. For example, encapsulants used in PV modules are typically bonded to one or more glass sheets to isolate the solar cells, or cell strings, from water in the module environment. The ability of a polymeric material to protect a surface is thus highly dependent on its ability to bond to a surface and limit access to corrosion sites. A strong correlation exists between corrosion protection and adhesive strength.

The dominant encapsulant used in the PV industry is based on a random copolymer consisting of about 67 wt.% polyethylene and 33wt.% polyvinyl acetate (Samuelson *et al.*;1987); Polyethylene was chosen because it is very simple and inexpensive polymer. When used alone, however, it is typically an opaque or translucent (depending on the polymerization conditions) semicrystalline polymer with a modulus too high to mechanically protect a PV device. Polyvinyl acetate is a transparent, amorphous polymer, but it has a glass transition temperature (T_g) of about 35°C; making it too brittle or non-compliant under typical environmental exposure (Kempe *et al.*, 2007). Small amount of vinyl acetate is added to polyethylene to break up the crystallites, producing a semicrystalline, highly transparent material. Typically, 33wt.% of vinyl acetate is copolymerised with ethylene to get a good mix of properties such as a high optical transmission and a low T_g.

The adoption of Ethylene Vinyl Acetate (EVA) as a defacto standard occurred not because it had the best combination of properties, but because it was inexpensive and readily available. EVA was designed to be used on the front side of cells where high light

transmission is required. It is also routinely on the back side of cells where light transmission is not necessary. In these applications, a white sheet of tedlar (or another reflective material) is commonly laminated to the back to improve performance by reflecting back the light that initially shines between the cells. This PV module construction method is common because sufficient research into inexpensive non-transparent alternative has not produced adequate materials that the industry trusts. Due to the nature of silicone chemistry, it is possible to produce a wide range of encapsulating materials with variations in colour, hardness, cure speeds and adhesion. Very soft silicone gels are chosen to provide a material that will accommodate extreme movement without inducing stress and also, facilitate the removal for repair or replacement of components. Harder materials will provide a more robust encapsulation (John, 2008).

Over the last several decades Ethylene Vinyl Acetate (EVA) has emerged as the dominant encapsulant material used in PV devices; early modules constructed with EVA demonstrated severe failure within a few years of putting the modules in use because of yellowing of the encapsulant (Yamada *et al.*, 2004). Improvement to EVA have been developed, including formulations with antioxidant and ultraviolet (UV) absorbers, that provide encapsulant materials that will not significantly yellow over the 20- to 30- lifeline of a module (Kempe, 2006).

Despite these improvements, EVA still has several drawbacks that affect its performance as an encapsulant material, particularly in PV module; for example, EVA suffers from non-ideal mechanical and thermal properties, a high diffusivity of water, and acetic by-product production (Barry *et al.*, 2008). The newer thin-film technologies that are rapidly being developed in the PV industry may be more sensitive to the shortcomings of EVA. As crystalline silicon wafers become thinner, the mechanical properties of EVA may also prove insufficient. An alternative option would be to use an optically clear silica encapsulant with wide operating temperature range, excellent light transmission, repairable, ultraviolet stable, weather resistant, flexible and easy to use.

These special properties of silica were confirmed in the work carried out by Dorigato *et al.*; (2010). Linear low-density polyethylene (LLDPE) based composites were developed by melt compounding LDPE with 1, 2, 3 and 4 vol. % of various kinds of amorphous silicon dioxide (SiO_2) micro- and nanoparticles. Dynamic rheological tests in parallel plate configuration were conducted in order to detect the role of the filler morphology on the rheological behavior of the resulting micro- and nanocomposites. A strong dependence of the rheological parameters from the filler surface area was highlighted, with a remarkable enhancement of the storage shear modulus (G') and of the viscosity (η) in fumed silica nanocomposites and in precipitated silica

microcomposites while glass microbeads only marginally affected the rheological properties of the LLDPE matrix.

As the ability to isolate components and areas from potentially adverse condition is not absolute, there is a continuing need for improved encapsulant materials. A siliceous encapsulant providing even a minimal cost savings is expected to be well-received in the current environment, particularly if the encapsulant also provides beneficial technical properties. However, since the development of polymer based siliceous particulate composite from rice husk for solar cell applications looks feasible, a detailed investigation in this direction is therefore considered worthwhile.

The main objective of this work is to develop polymer based siliceous particulate reinforced composite using the silica extracted from rice husk ash as filler and study the mechanical properties of the composite.

2. Materials and Methods

Fine Silica powder of 0.489 μm particle size produced from rice husk ash by Sol-gel process was used in this research work; The rice husk was collected from a local rice mill in Ajaokuta steel city, Kogi State, Nigeria. Submiron particles of Titania powder supplied by Alfa Aesar High Purity Research chemicals, Vorna Valley, Republic of South Africa (RSA) were utilised as ultraviolet absorber. Maleic Anhydride Polypropylene (MAPP) supplied by Sasol Chemicals, Sasolburg, RSA was used as compatibiliser. High Density Polyethylene (HDPE) and Vinyl Acetate were supplied by DOW Chemicals, RSA. It has a melt flow index (MFI) of 8g/10min (XZ 89712-00 RD 10140182040), a molecular weight of 168,000g mol^{-1} , a melting point of 130°C, and a density of 0.954g cm^{-3} .

2.1 Material Preparation

The rice husk was collected from a local mill in Ajaokuta Steel City, Nigeria (7.55611°N6.65500°E). It was thoroughly washed with water and dried in an oven at 80°C for 24 hours to remove the water content. The rice husk was thereafter fed into an enclosed drum and burnt into ash, it was thereafter conditioned at a temperature of 650°C in a muffle furnace. The obtained rice husk ash (RHA) was used in the experimental work.

2.2 Extraction of Silica gel from RHA

The Silica-gel was extracted from the RHA by sol-gel process. 10 grams of rice husk ash were added to various concentrations of sodium hydroxide (NaOH) solutions (0.5M -2.0M). The mixture was then heated in a shaking water bath at 100°C in a beaker for one hour. The solutions were allowed to cool to room temperature, then, filtered through Whatman No 41 ashless filter paper and the carbon residue was washed with 100 ml of de-ionized water. Concentrated sulfuric acid was added to the obtained solution until pH 7.0 and incubated for

48 hours to promote silica gel formation. The silica gel produced was separated from soluble salt solution by vacuum filtration and washed with de-ionized water. Then silica gel was dried in an oven at 150°C for 48 hours. The obtained white gel was pulverized into a powdery form and used for the experimental work.

2.3 Compounding of the Composite Materials

Predetermined proportion of HDPE, Silica powder (SiO_2), Titania powder (TiO_2) and Maleic Anhydride

Polypropylene (MAPP) were mixed together in a tumbler mixer for 20 minutes in order to obtain homogeneous mixture. HDPE, Vinyl Acetate (VA) and MAPP were also mixed and designated as EVA. Each mixed samples was melt-blended together using a Rapra Single-Screw Extruder at a temperature of 200°C -230°C (Zone1=200°C, Zone2=210°C Zone 3=220°C, Zone 4=230°C) and rotor speed of 40rpm. The extrudates were ground with a grinding machine. Table 1 shows the proportions of constituents added in grams.

Table 1: Proportion of the Constituents added in grams

Sample Designation	wt.% of MAPP. (5%)	wt.% of TiO_2 (0.3%)	wt.%of SiO_2 (2,4,6,8 and10%)	Wt.% of VA (30%)	HDPE
Neat HDPE	---	---	---	---	1000 g
EVA (HDPE/VA)	50 g	---	---	300 g	650 g
2 Wt.% SiO_2 /0.3 wt.% TiO_2 /HDPE	50 g	3 g	20 g	---	927 g
4 Wt.% SiO_2 /0.3 wt.% TiO_2 /HDPE	50 g	3 g	40 g	---	907 g
6 Wt.% SiO_2 /0.3 wt.% TiO_2 /HDPE	50 g	3 g	60 g	---	887 g
8 Wt.% SiO_2 / 0.3 wt.% TiO_2 /HDPE	50 g	3 g	80 g	---	867 g
10 Wt.% SiO_2 / 0.3wt.% TiO_2 /HDPE	50 g	3 g	100g	---	847 g

2.4 Production of Siliceous HDPE Composites by Compression Moulding Technique

The ground extrudates were poured in a tensile mould and a rectangular mould of dimension 150 mm x100 mm x4 mm. 10 g of the blend was used for the production of the tensile samples while 60g was used for the rectangular samples.

The filled mould was placed in between the lower and the upper plates of the Carver laboratory press at 230°C for 10 minutes under applied pressure of 0.2 kPa. The materials were then water cooled at 20°C min⁻¹. In this way, neat matrix and submicron composite samples filled with various volume of silica (2, 4 , 6 , 8 and 10 wt. %) at constant 5 wt. % Mapp and 0.3 wt.% Titania were prepared; EVA composite containing 30 wt.% Vinly Acetate, 5 wt.% MAPP and 65 wt.% HDPE was also prepared. Teflon sheet was used to cover the surface of the samples at the top and bottom part of the mould while silicone was sprayed at the inner edges of the mould for easy release after moulding.

2.5 Chemical Analysis of Silica gels

The silicon content of the samples was estimated using energy dispersive X-ray (EDX) spectroscopy (Kevex Instruments, Valencia, CA). This was done in order to select the powder with the highest silicon content for the experimental work.

2.6 Particle Size Analysis

The particle size of the powder was analysed using Horiba dynamic light scattering particle size analyser. The measurable particle size range of the instrument is 0.05-3000 μm and it is equipped with a small volume sample dispersion unit. A lens range of 300RF, a beam length of 2.4mm, and a presentation of 30AD with polydisperse analysis was used for this measurement. About 0.5 g of the silica powder was dispersed in de-ionised water in the sample dispersion unit of the instrument, vigorously mixed for about two (2) minutes at speed of 2100 rpm, and sonicated for 45 seconds. The ultrasonic waves were used to break or minimise any particle agglomerates that may be present in the suspension. Measurements were taken and the diffraction data and graphs recorded by the instrument software program.

2.7 Examination of the surface morphology of Silica gels

An AURIGA Scanning Electron Microscope (SEM) (Carl Zeiss Germany) with an accelerating voltage of 15kV was used to characterise the particle morphologies of the silica powder. Sample specimens were gold coated in a gold sputter coater for 90 seconds at 15 mA current output. The gold coating was necessary to ensure a conducting surface was obtained for electron

bombardment and characterization. The Selected areas of interest were focused and micrographs were taken.

2.8 Mechanical Test

The composites cast samples were prepared for tensile test, charpy impact test, and micro hardness test. Scanning Electron Microscope was used to investigate the miscibility between the particulate and the matrix at the notched impact fractured surfaces of the composites.

2.8.1 Tensile Test

Tensile tests were performed to determine the modulus, ultimate tensile strength and elongation at break of the samples using an Instron 5966 tester (Instron Engineering Corporation, USA), 2010 model, with a load cell of 10kN in accordance with ASTM D638-10 standards. Dog-bone-shaped samples prepared by compression moulding were tested in tension mode at a single strain rate of 5mm/min at room temperature 27 °C and relative humidity of 40 %. The test piece which is of gauge length 14mm was fixed at the edges of the upper and lower grip of the machine and the test commenced. As the test piece is being extended, graph is being plotted automatically and important tensile properties data were generated. The results presented are average of six individual tests sample.

2.8.2 Impact Test

Representative sample of neat polymer and composites were subjected to impact test on a Charpy V-Notch impact testing machine (Instron CEAST 9050), in accordance with ISO179-2:1997 and 1: 2011 standards. The pellets were moulded into a rectangular Charpy impact bar of dimension 80mm x 10mm x 4mm. The Notched samples were placed horizontally on the machine, the notched surface is directly opposite the swinging pendulum, the initial reading of the sample gauge length and the thickness were entered into computer system attached to the machine and the machine was switched on. The pendulum of the machine swung freely through angle 180°C and fractured the sample. The results were printed out from the computer system. The results presented are the average of six individual tests sample.

2.8.3 Hardness

The hardness of the neat polymer and composites were measured with the aid of micro-hardness tester, model 900-390, in accordance with ISO 868:2008 standards. This machine measures the resistance to penetration by measuring the depth of impression. The test was carried out by indenting the sample with the instrument for about 5 seconds before taking the reading that was displayed on the manitor. Ten values were taken each for each sample from which the average was taken as the representative value.

2.9 Scanning Electron Microscopy Observation

The surface morphology of the samples was studied using an AURIGA Scanning Electron Microscopy (SEM) (Carl Zeiss, Germany) with an accelerating voltage of 15 kV. The notched impact fractured surfaces of the compression-moulded samples were mounted on aluminium stubs and were sputter coated with gold using EMITECH K950X sputter coater before being subjected to SEM analysis.

3. Results and Discussion

3.1 Chemical Composition of RHA and Silica Gel

To evaluate the effectiveness of the purification parameter and to confirm the presence of silica, EDX analysis was carried out on the silica powder extracted from RHA at different concentration of sodium hydroxide 0.5, 1.0, 1.5, and 2.0M. The effect of NaOH is as shown in the EDX elemental spectra shown in Figures 1-5.

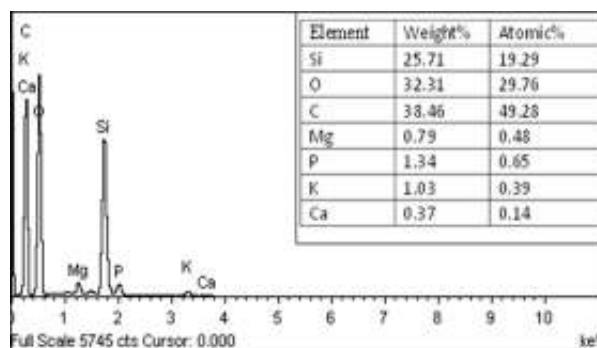


Figure 1. EDX spectrometric data of RHA

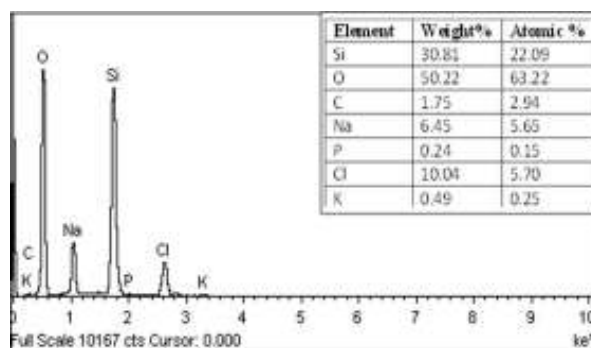


Figure 2. EDX spectrometric data of silica extracted from RHA with 0.5M NaOH

The major elements present are silicon and oxygen with other impurities such as sodium, carbon, phosphorus, chlorine and potassium. The elemental composition of silicon and oxygen increases with increase in NaOH concentration while the impurities decrease. The decrease in impurities mainly results from

chemical reaction between acid metals, after which the metals are removed by filtration (Tzong-Horng, 2004). Figure 5 shows the EDX elemental spectra of the silica powder extracted from RHA with 2.0M NaOH concentration, which contains 65.35 wt% Si and 30.93 wt% O. The Si and O peaks that were observed confirm the presence of silica. The EDX spectra show that the content of Si and O is 96.28 in wt % and 97.80 in atomic %.

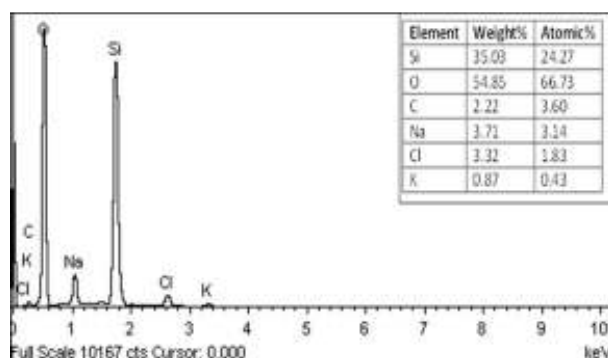


Figure 3. EDX spectrometric data of silica extracted from RHA with 1.0M NaOH

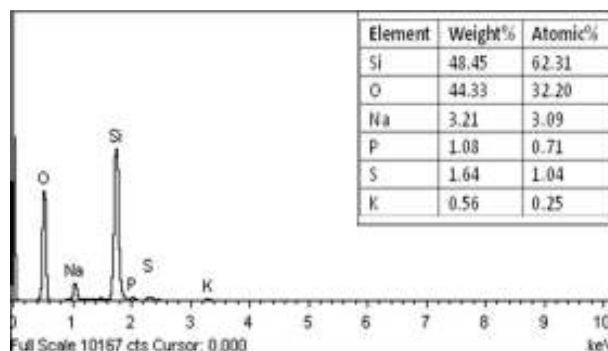


Figure 4. EDX spectrometric data of silica extracted from RHA with 1.5M NaOH

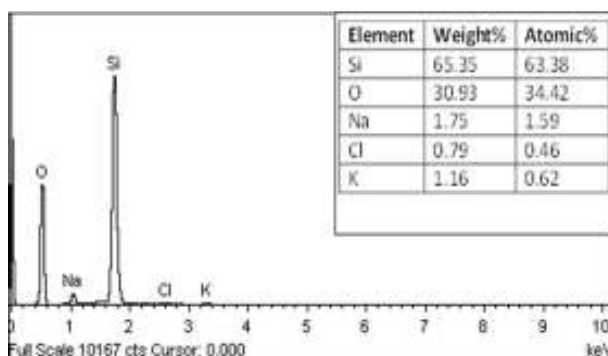


Figure 5. EDX spectrometric data of silica extracted from RHA with 2.0M NaOH

3.2 Particle Size Analysis

The chemical composition of silica powder extracted from RHA has been shown to be mainly silica (SiO_2). Since it is a known fact that particle size of filler materials has influence on the properties of composite, therefore, the cumulative particle size distribution of the powder with the highest silica content was analysed with Horiba dynamic light scattering particle size analyser as shown in Figure 6. The particle size distribution of the powder is approximately $0.489\mu\text{m}$.

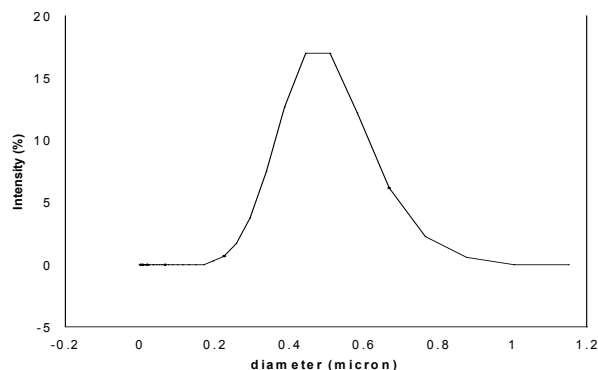


Figure 6. Particle size distribution by intensity produced by Horiba Dynamic Light Scattering Particle Size Analyser (The average Particle size is $0.489\mu\text{m}$)

3.3 Examination of Surface Morphology of RHA and Silica Powder

The morphological features of the RHA and silica powder observed by scanning electron microscope (SEM) are shown in Figures 7-11. The SEM images were taken at a magnification of 500X. Figure 7 presents the image of as-received RHA which shows a porous and multifaceted particle shape and size. The honeycomb and porous morphology can be attributed to burning out of organic component in the rice husk during combustion. The hydrated silica subsequently polymerises to form a skeletal silica network which may explain the flaky and honeycomb-like structure in the SEM image of Figure 7.

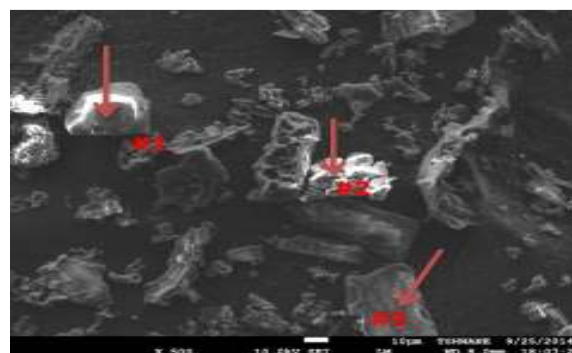


Figure 7. SEM Image of RHA with 0.5M NaOH

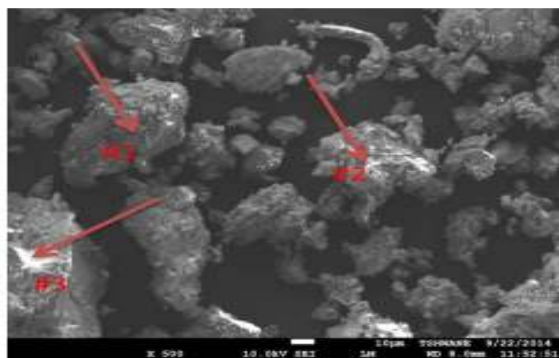


Figure 8. SEM Image of Silica gel extracted

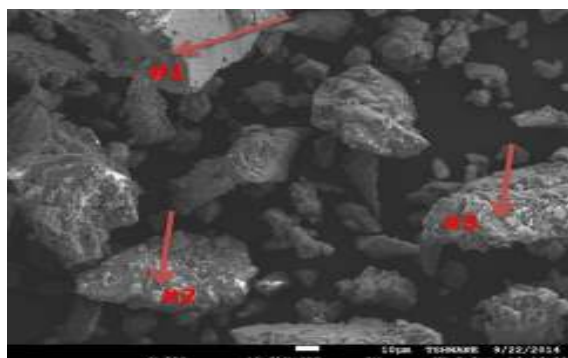


Figure 9. SEM Image of Silica gel extracted with 1.0M NaOH

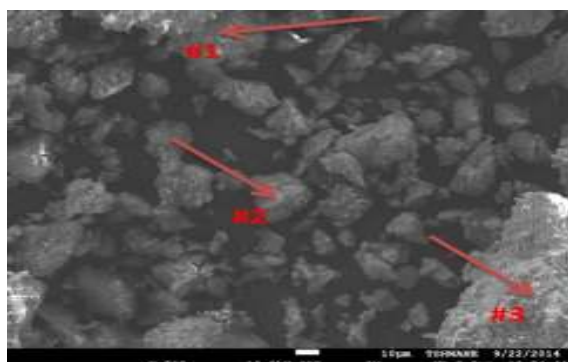


Figure 10. SEM Image of Silica gel extracted with 1.5M NaOH

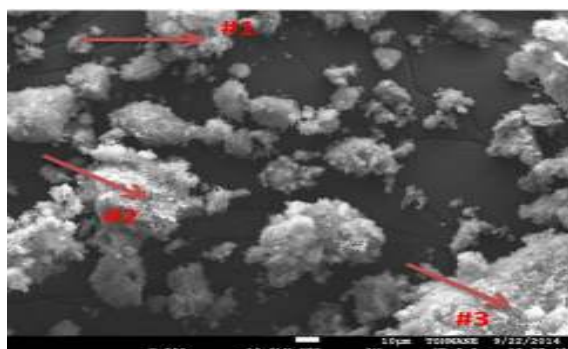


Figure 11. SEM Image of Silica gel extracted with 2.0M NaOH

The EDX analysis at points #1, #2 and #3 in Figures 8-11 shows the crusty and fibrous surface to be silicon-rich and was mainly SiO_2 . The elemental composition for each silica powder produced was recorded by calculating the average of the elemental composition of point #1, #2 and #3, as shown in Figures 1-5.

3.4 Tensile Properties of the Composite

3.4.1 Ultimate Tensile Strength

Figure 12 shows the variation of the ultimate tensile strength for neat HDPE, HDPE/ SiO_2 / TiO_2 composites and Ethylene Vinyl Acetate (EVA). It was observed from the results that the strength of composites was more enhanced in HDPE/ SiO_2 / TiO_2 Hybrid composite than that neat HDPE and EVA. Clearly, composites developed with silica/titania particles exhibit the strengthening ability than EVA. However the best results were obtained with 4 wt% SiO_2 with a value of 60MPa. The ultimate tensile strength is a measure of the maximum stress a material can withstand before it fails. It is well known that the tensile strength of a particulate composite is usually reduced with dispersed phase particles content following a power law in the case of a poor filler/matrix bonding (Nicolais and Narkis, 1971).

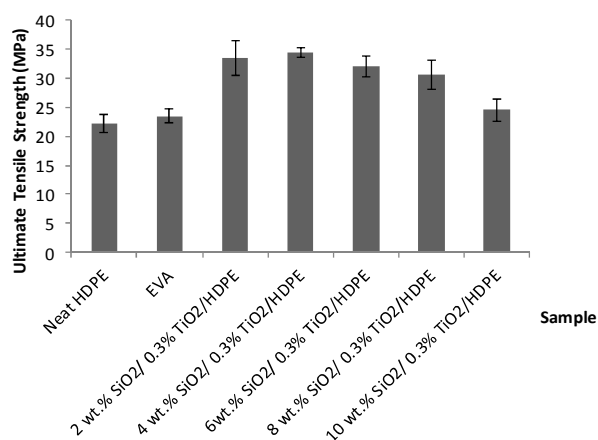


Figure 12. Variation of Ultimate Tensile Strength of Neat HDPE, EVA and SiO_2 / TiO_2 /HDPE Composites

The tensile strength is found to decrease with increasing particulate loading, as the particulate load increased, the weak interfacial area between the particles and the matrix increased, this consequently decreased the tensile strength (Yang, 2004, Lou *et al.*, 2007, Jamil *et al.*, 2006). This contradicts the results shown in Figure 12. In fact, when bonding between fillers and matrix is strong enough, the ultimate tensile strength of a particulate composite can be higher than that of the matrix polymer (Jancar *et al.*, 1992).

The extremely effective improvement of tensile

strength of the composites with the addition of submicron silica at lower weight fraction should result from chain inter diffusion and entanglement between HDPE and the silica particles. It is worth noting that when the amount of the submicron silica particles is greater than 4 wt.%, the silica particles agglomerate and the content of the HDPE chains is raised accordingly. The interlayer and the interfacial that stress transfer efficiency have to be decreased. An increase in the particulate content also increases the micro spaces between the particulates and the matrix, which weaken the filler matrix interfacial adhesion. This accounts for relatively low strength of HDPE/SiO₂/TiO₂ composites at higher particulate loading.

3.4.2 Young's Modulus of Elasticity

Young's Modulus is the ratio of the stress to strain in the linear region of the stress-strain curve. Young's Modulus of Elasticity for HDPE/SiO₂/TiO₂ composites, EVA and neat HDPE are illustrated in Figure 13. The neat HDPE and EVA have Young's Modulus of Elasticity of 719.83 MPa and 658.00 MPa respectively. On increasing the SiO₂ content, the modulus values increased. For the addition of 4wt% SiO₂ and 0.3wt% TiO₂, it was noticed that about 6.5% increase in Young's modulus occurred. The modulus value increases linearly up to 4wt% SiO₂ for HDPE/SiO₂/TiO₂composites; thereafter the value goes down. The increase in modulus is governed by the fact that the filler gives good reinforcement with the matrix. Furthermore, the particle size of the filler is small (489 nm) so that the aspect ratio is high. However, after 4wt% of SiO₂, the particles get agglomerated while processing the sample. Therefore, the dispersion becomes poor and the modulus decreases; the optimum filler loading is 4wt% for the best modulus with a value of 766.56 MPa.

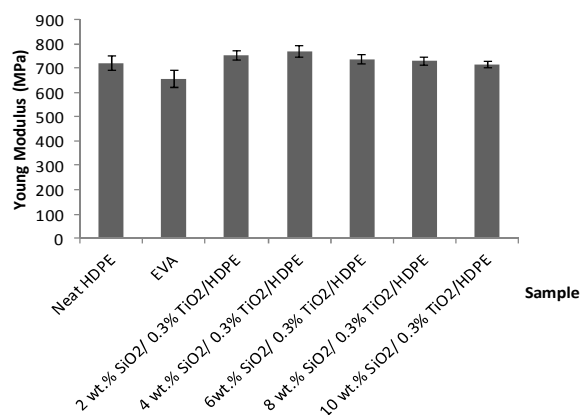


Figure 13. Variation of Young Modulus of EVA, Neat HDPE and SiO₂/TiO₂/HDPE Composites

3.4.3 Percentage Elongation at Break

Elongation at break values denotes the maximum extension of the samples while in tension. The elongation at break values depends on the filler/matrix interaction. Figure 14 revealed the variation of the percentage elongation at break of neat HDPE, EVA, and HDPE/SiO₂/TiO₂. The percentage elongation of neat HDPE and EVA are 210 % and 189 % respectively. From engineering point of view, percentage elongation at break is an important parameter describing the rupture behaviour of composite materials. The addition of particulates to polymers usually lowers its percentage elongation even though the polymer has high impact toughness (Chun *et al.*, 2002).

Figure 13 clearly indicates that this is not the case when submicron silica is used to reinforce the polymer matrix at lower weight fraction. From the graph, it was found that the elongation at break value is higher than the neat HDPE and EVA only at 2wt% of SiO₂ for the composites developed but decreases drastically when the filler weight fraction is greater than 2wt%. HDPE/SiO₂/TiO₂ composites with 2wt% of SiO₂ have the optimum value of 222 %.

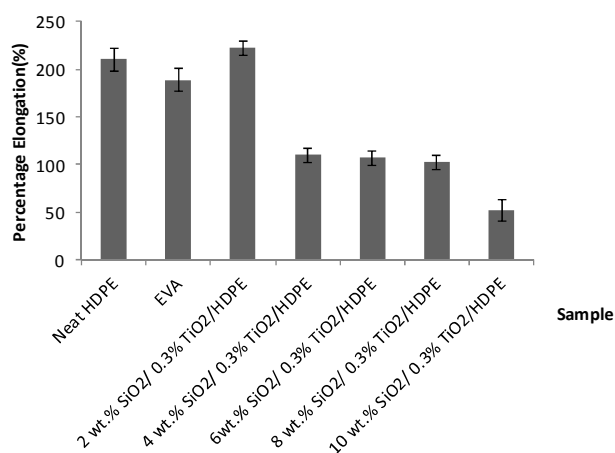


Figure 14. Variation of Percentage Elongation of Neat HDPE, EVA and SiO₂/TiO₂/HDPE Composites

3.4.5 Impact Properties

Impact strength is another important mechanical property that is difficult to predict in a filled polymer. The impact strength of a filled polymer also depends on the degree of polymer-filler adhesion, but in a more complex manner than the tensile strength (Thomas *et al.*, 2004). Other factors such as micro-scale morphological changes in a polymer that are caused by the filler, affect the impact strength of filled polymers. The presence of the filler may also cause a change in the fracture mechanism during impact from that commonly observed in the unfilled polymer. A polymer having good impact resistance should absorb most of the impact energy and propagate a crack very slowly.

One mechanism of slowing the rate of crack growth

is the formation of crazes in the crack tip. Impact energy of the various compositions of submicron-composites, neat HDPE, and EVA were plotted against weight percentage of the filler in Figure 15. From the graph, the impact strength shows a light increase at 2wt% SiO₂ for HDPE/SiO₂/TiO₂ with values of 21.80KJ/m². Thereafter the values decrease linearly with increase in filler addition. Impact strength depends on the brittleness of the polymer matrix. The reason for the decrease in the property can be attributed to the poor adhesion or bonding at the interface between the matrix and the filler at higher filler addition. Similar observations were reported by Rozman *et al*; (1998) for the rubber wood-filled high density polyethylene composites.

There is a diminishing effect of the particulate on the impact strength due to a drastic decrease in break elongation because the particulate agglomerates and bridges the crack and increases the resistance of crack propagation (Liu *et al*; 2005, Sanadi *et al*; 1995). Addition of 5wt.% Maleic Anhydride Polypropylene as coupling agent allowed better filler/matrix adhesion which resulted into enhancement in the impact strength of the composites up to 6wt.% SiO₂ when compared with the neat HDPE. This observation was quite expected for filled composites and has been commonly observed. In the presence of the coupling agent, the interfacial bonding between the matrix and the filler increases and thus facilitates better transfer of stress.

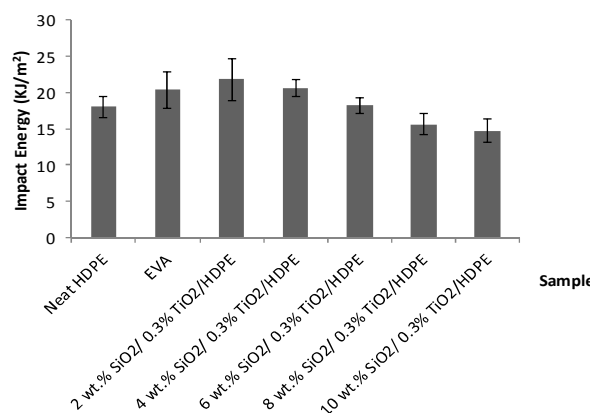


Figure 15: Variation of Izod Notched Impact Strength of EVA, Neat HDPE and SiO₂/TiO₂/HDPE Composite

3.4.6 Hardness Properties of the Composites

Figure 16 shows the variation of the hardness values for neat HDPE, EVA, and the siliceous HDPE composites developed. The test was carried out in accordance to ISO 868 standard using micro hardness tester. Ten readings were taken for each sample and the average was recorded as the representative value for each. From the graph, it was observed that 2wt% SiO₂ particulate reinforcement has the best hardness for composites developed, with values of 67.688 MPa for

HDPE/SiO₂/TiO₂ composite. The hardness values of neat HDPE and EVA are 42.567 MPa and 44.426 MPa respectively. Hardness of a composite depends on the homogeneous dispersion of the particulate into the matrix (Premila *et al.*, 2002; Jamil *et al.*, 2006). Usually, the presence of a more flexible matrix causes the resultant composites to exhibit lower hardness (Jamil *et al.*, 2006).

The hardness of the siliceous HDPE composites showed an increasing trend with an increase in particulate content up to 2wt% but reduces drastically at higher particulate loading. The increase in hardness value at lower particulate loading may be attributed to the homogeneous dispersion of silica particles into the matrix with minimisation of voids and stronger interfacial adhesion between the matrix and the particulate while the reduction in hardness at higher particulate loading may be due to the agglomeration of particles which encourages voids formation and poor interfacial adhesion between the matrix and the particulate.

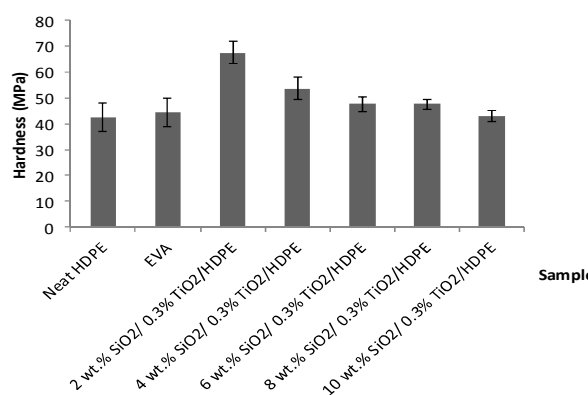


Figure 16: Plot of Hardness Values of EVA, Neat HDPE, SiO₂/TiO₂/HDPE and Composites

3.4.7 SEM Images of the Composites

A detailed investigation of the filler morphology within the matrix is a key parameter to impart desired mechanical properties of polymer-based composites. To have a clear images of the fractured patterns of the composites, SEM (Secondary Electrons) images of the notched impact fractured surfaces of the composites at different filler contents are shown in Figures 17-23.

Figure 17 revealed the notched impact fractured surface image of neat HDPE which has a relatively smooth fractured surface in association with terraced markings, indicating weak resistance to crack propagation. In the case of HDPE/SiO₂/TiO₂ composites with silica content of 2-4wt%, it is very clear that there is good dispersion of filler in HDPE matrix. The silica particles were uniformly distributed in the matrix with little agglomerates as shown in Figures 19-20. When the content of submicron silica approaches 6wt%, the

morphologies of the composites' fractured surfaces become somewhat different. A number of agglomerates appear on the surface of HDPE/SiO₂/TiO₂ composites. These agglomerates are produced due to the debonding of the silica particles as illustrated by the arrow in Figures 21-23.

In general, an increased content of SiO₂ led to a larger agglomerates and hence greater debonding due to the poor interfacial adhesion at the particle – matrix interface. As there is not enough time for inducing matrix yielding after excessive particles debonding, the matrix beside the cavities seems

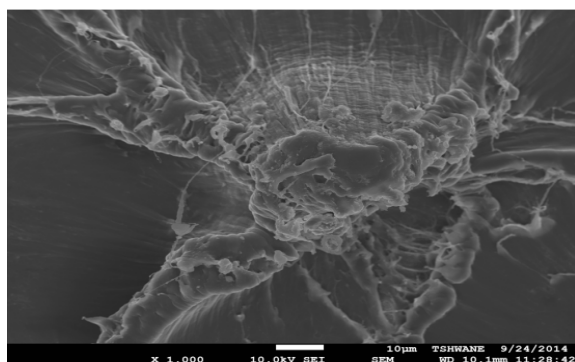


Figure 17: SEM of Neat HDPE

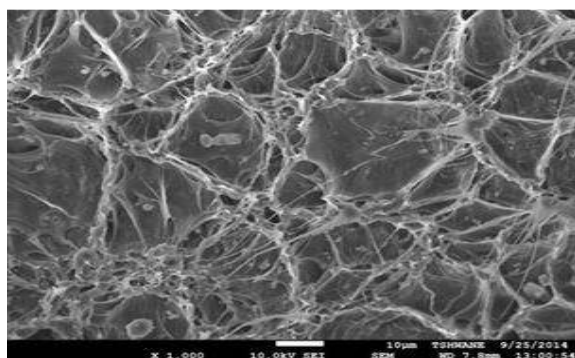


Figure 18. SEM of Fractured surface of EVA (30wt.% VA, 5wt.% MAPP and 65wt.% HDPE)

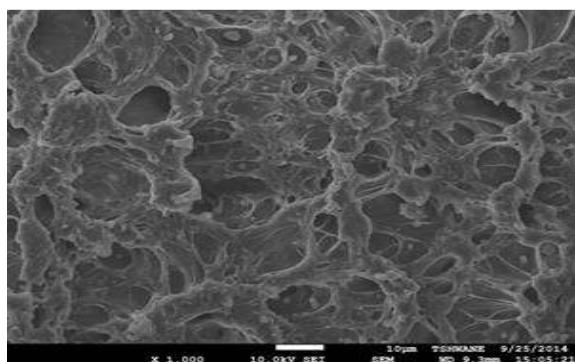


Figure 19. SEM of Fractured surface of the composite (2wt. % SiO₂)

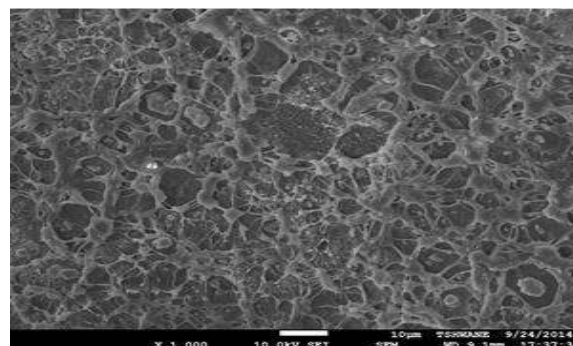


Figure 20. SEM of Fractured surface of the composite (4wt. % SiO₂)

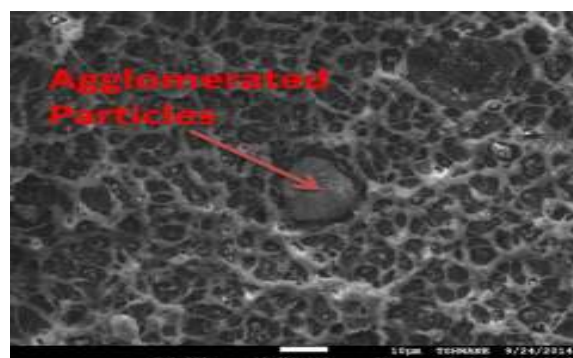


Figure 21. SEM of Fractured surface of the composite (6 wt. % SiO₂)

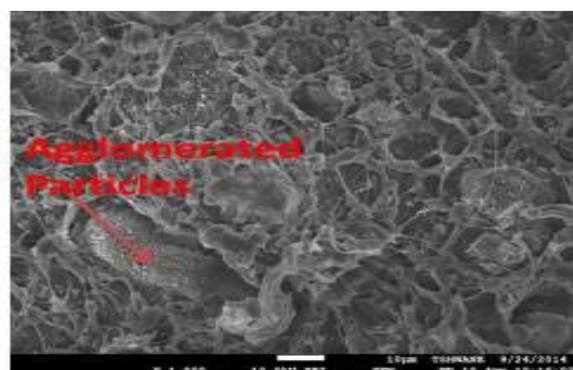


Figure 22. SEM of Fractured surface of the composite (8 wt. % SiO₂)

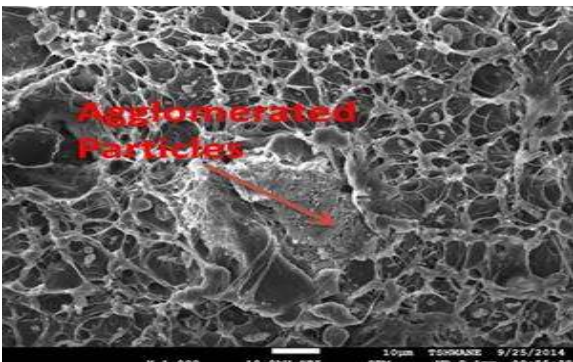


Figure 23. SEM of Fractured surface of the composite (8wt. % SiO₂)

to be rather flat; this coincides with the reduction of toughness of HDPE/SiO₂/TiO₂ composites at high SiO₂ loading.

4. Conclusion

Silica submicron particles were successfully produced by sol-gel process and were utilised for the production of HDPE/SiO₂ composites. From fracture surface analysis, it is clear that silica submicron particles, homogeneously dispersed in HDPE at lower weight percent loading as observed from white zones on the SEM images of the notched impact fractured surface. Moreover, it was observed that the addition of silica (SiO₂) submicron particles to HDPE causes an enhancement in the mechanical properties up to 4 wt.% SiO₂.

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