Rice Husk Silica- Efficient Bio Filler in High Density Polyethylene

Midhun Dominic C.D [#1], P.M Sabura Begum [#2], Rani Joseph [#3], Ammu Rosin Jose [#4]

#1 Sacred Heart College, Thevara, Kochi-682013, Kerala, India, Ph:9744304341
#2 Department of Applied Chemistry, CUSAT, Kochi-682022, India
#3 Department of Polymer Science and Rubber Technology, CUSAT, Kochi-682022, Kerala, India
#4 Department of Applied Chemistry, CUSAT, Kochi-682022

ABSTRACT

Composites derived from renewable energy sources are assuming increasing importance nowadays. This article highlights the potential of rice husk silica as reinforcing filler in high density polyethylene (HDPE). Rice husk silica (RHS) with high degree of purity was obtained by the calcination of hydrochloric acid leached rice husk at 650^0C for 6 hours. The synthesized rice husk silica was characterized by FTIR, XRD, SEM, EDX, TEM, BET surface area etc. Different analysis suggest that hydrochloric acid leaching of rice husk removes the metallic impurities present in rice husk and the synthesized silica (RHS) has got higher surface area, lower particle size and high purity. The mechanical properties like tensile strength and young's modulus of HDPE-RHS composite were superior to that of base polymer. Significant enhancements in the mechanical properties were achieved by the incorporation of RHS to HDPE without any surface modification.

Keywords: composite, rice husk silica, surface modification, Young's modulus

Corresponding Author: Midhun Dominic C.D

INTRODUCTION

Paddy cultivation is a part of the proud culture of Kerala state. Rice husk, which is considered as an agricultural waste from paddy field, is a major source of amorphous silica [1]. Burning of rice husk will results in the formation of rice husk ash (RHA), which contain more than 90% of silica [2]. RHA contains metallic impurities like Na, K, Ca etc. other than silica [3]. Acid leaching of rice husk prior to calcination is an efficient method to synthesize silica with high degree of purity [4-7]. Pure Silica was synthesized from potassium permanganate treated rice husk [8]. The silica in the ash undergoes structural transformations depending on the conditions of combustion such as time and temperature [9].

HDPE the world's largest volume using thermoplastic finds wide use in packaging, cable insulation etc. Tensile and flexural strength of HDPE can be significantly enhanced by the

addition of fly ash [10]. Rice husk has effectively delayed the thermo-oxidation process of the HDPE matrix by about 40^0C, and evident flame retardant effect has also been observed [11]. Me chanical properties of HDPE can be significantly improved by the addition of Glass fibers [12].
Clay reinforced HDPE composite show better mechanical properties in the presence of a compatibilizer [13]. The reinforcing efficiency of filler depends on the particle size, surface area, aspect ratio and surface activity.
Rotting of rice husk in the paddy field will produce methane gas (potent green house gas) may cause global warming and climate change [14]. Increase in B.O.D (biological oxygen demand) was observed in water due to the contamination of water by rice husk. Bio fillers are assuming increasing importance nowadays because of their renewable source and low cost. In the present study we are succeeded to synthesis a bio based filler RHS from an agricultural waste material, rice husk. There are no reports in the literature for the utilization of RHS in HDPE matrix, as far as we know. Significant enhancement in the mechanical properties of RHS – HDPE composite was obtained without any surface modification of RHS. This paper mainly focus on the reinforcing efficiency of bio filler RHS in HDPE polymer matrix.

MATERIALS AND METHODS

Rice husk was collected from a local mill in Kalady. Fuming HCl (37%) from Merck was used for leaching rice husk. High density polyethylene was supplied by Reliance Industries Limited, Mumbai, India. It has a melt flow index of 16g/10 min (190^oC/2.16 kg).

Synthesis of rice husk silica (RHS)

Rice husk (fig 1) was washed thoroughly with water and dried in an oven at 100^0C. Dried rice husk was treated with 1N HCl in the ratio 1:10 g/mL at 70^0C for 3h. The acid leached rice husk was washed thoroughly with distilled water and dried in a hot air oven. The dried rice husk was calcined in a muffle furnace at 650^0C for 6h to get silica. It was well grinded to obtain rice husk silica (fig 2) with fine particle size.

Fig 1: Rice husk

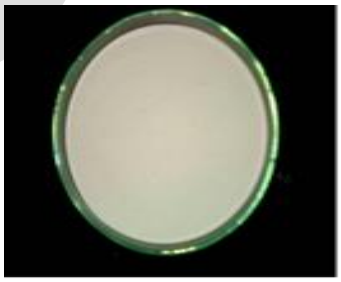

Fig 2: Rice husk silica (RHS)

Preparation of HDPE-RHS Composite

The reaction was conducted by melt mixing in a Thermo Haake Poly Lab system equipped with roller rotors. About 40 g of HDPE was allowed to melt at 145^0C for 2 minutes initially. Then varying quantities of RHS (0.5-3 wt %) were added. The mixing was done with the rotor speed at 30 rpm and lasted 6 minutes.

Preparation of test specimen

The test specimens were prepared from the blends by moulding in an electrically heated hydraulic press for 5 minutes at 150^0C under a pressure of 20 MPa. After moulding, the samples

were cooled down to room temperature. Rectangular shaped specimens were cut from the moulded sheets and used for testing.

Mechanical testing

Mechanical properties were evaluated using Shimadzu Autograph AG-I series Universal Testing Machine at a crosshead speed of 50 mm/min according to ASTM D 882 (2002). Six specimens were used and the average was calculated in each case. These tests provided the ultimate tensile strength and young's modulus values of the composites.

Measurement of melt flow index (MFI)

The melt flow indices of HDPE and HDPE-RHS composites were determined using a CEAST Modular Line Melt Flow Indexer, according to ASTM D1238 (190^{o}C/2.160 kg).

Characterization of Rice husk silica (RHS)

Fourier transforms spectroscopy

FTIR spectrum of RHS was recorded on a Thermo Nicolet FTIR Spectrometer Model Avatar 370. Samples in the form of thin films, less than1mm thickness, were employed.

X-ray diffraction

Samples for X-ray powder diffractometer were first finely ground and then mounted on a glass slide. The sample was analyzed in a Bruker AXS D8 Advance X-Ray powder diffractometer.

BET method

Surface area of RHS was measured using BET method. Surface area analysis was done using Smart Sorb 93, Surface Analyzer. Measurements were carried out under nitrogen adsorption at liquid nitrogen temperature.

Morphology

The morphological characterization of RHS and tensile fractured surfaces of the composite specimens were carried out using a JEOL Model JSM 6390LV scanning electron microscope. The samples were subjected to gold sputtering prior to electron microscopy to give the necessary conductivity. Particle size and morphology of synthesized RHS were examined by TEM (Joel, JSM2010) using a 200KeV electron beam on the sample mounted on a carbon coated copper grid. Rice husk silica sample (10 mg) was sonicated for (2h) in isopropyl alcohol (5mL). About 50mL of the RHS suspension was taken using a dropper and spread on the carbon coated copper grid and allowed to dry in room temperature. The copper grid was introduced into the instrument and the sample was scanned along the path of the electron beam and photograph was taken at 2000,000 magnifications.

RESULTS AND DISCUSSION

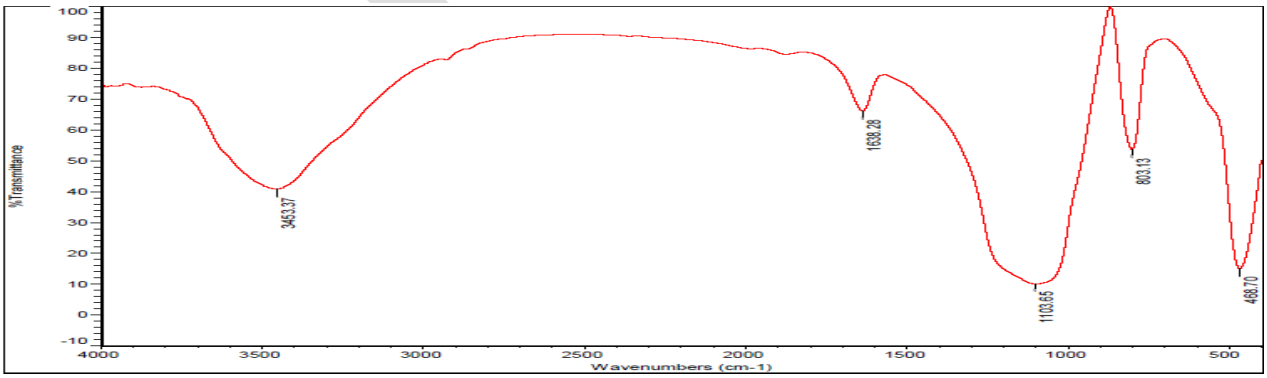

Fig 4: FTIR spectrum of RHS

Fig 4: shows the FTIR spectra of RHS. The broad band between 2800 cm^{-1} and 3700 cm^{-1} is due to silanol –OH groups and chemically absorbed water. The band at 468 cm^{-1} and 803 cm^{-1} correspond to O-Si-O bending vibration. The band at 1103 cm^{-1} corresponds to Si-O-Si stretching modes. The band at 1638 cm^{-1} corresponds to –OH bending vibration.

X-ray Diffraction analysis

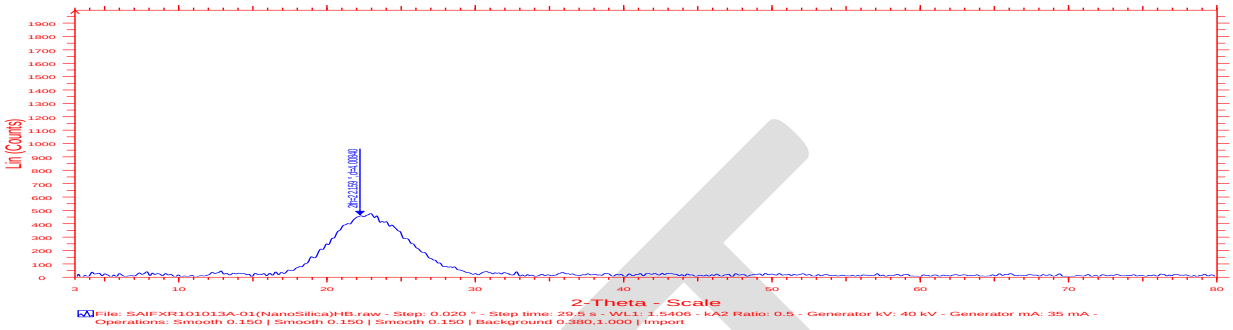

Fig 5: XRD of rice husk silica (RHS)

Fig 5: shows XRD of Rice husk silica (RHS). A broad peak at $2\Theta=22^0$ confirms that synthesized RHS was completely amorphous in nature not crystalline.

BET Surface area

Table 1: Surface area analysis of rice husk silica (RHS)

Substance	Median pore radius	Maximum pore radius	Cumulative pore volume	BET surface area
RHS	82.494A^o	15.409 A^o	0.3622 cm^3g^{-1}	150.05 m^2/g

Surface area analysis was given in table1. BET surface area of rice husk silica (RHS) was found to be 150m^2/g. Higher the surface area lower will be the particle size and higher will be the reinforcing efficiency of RHS.

SEM Images of rice husk silica (RHS)

From SEM analysis of RHS (fig 6), it was clear that the particles of RHS were found to be agglomerated due to the presence of hydrogen bonding between silanol groups on the surface of rice husk silica. Particles of irregular shapes and morphology were observed in RHS.

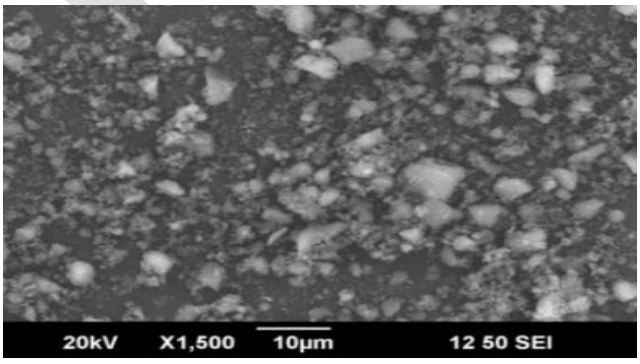

Fig 6: SEM image of rice husk silica (RHS)

EDX of rice husk silica (RHS)

Fig 7 shows the EDX spectrum of RHS. EDX spectra of RHS contain peaks for Silicon, oxygen and a small amount of unburnt carbon. EDX spectrum confirms the high purity of RHS.

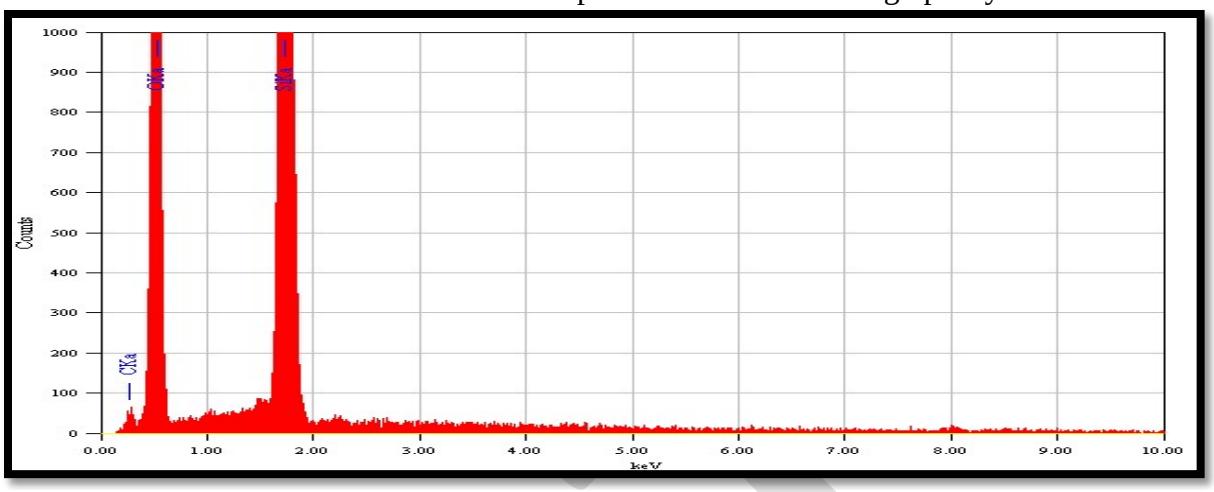

Fig 7: EDX of rice husk silica (RHS)

TEM image of RHS

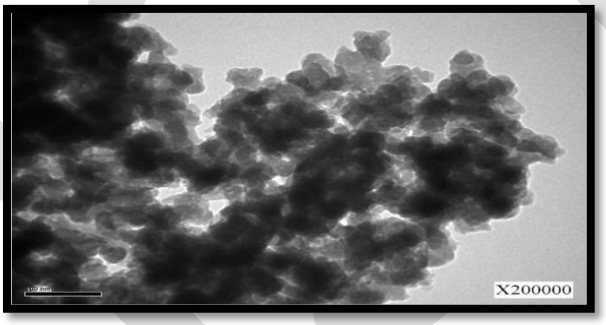

Fig 8: TEM image of rice husk silica (RHS)

Fig 8 shows the TEM image of RHS. From the TEM image, it was clear that particles of RHS were in nanometer range. The particles were agglomerated due to the presence of hydrogen bonding between surface silanol groups. Particle size of RHS was found to be 20-25nm.

Variation of mechanical properties with filler loading

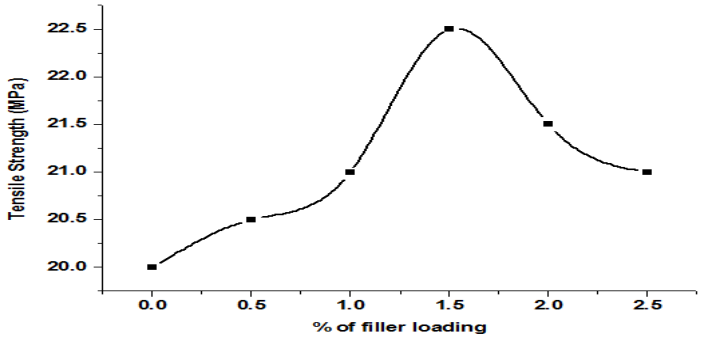

Fig 9: variation of tensile strength with filler loading.

Fig 9 shows the variation of tensile strength of the HDPE-RHS composite with filler loading. It was found that, tensile strength was significantly increased up to 1.5wt % of RHS addition and then deceases. The increase in tensile strength may be due to high surface area, low particle size, high purity and uniform distribution of RHS in the HDPE matrix. When the composites are under exterior stress, RHS helps to distribute the stress evenly and delay the rupture of the material. So there is significant enhancement in the tensile properties of HDPE by the addition of RHS even without any surface modification. At higher filler loading, filler particles will agglomerate and grow in size that will adversely affect the tensile strength of the composite.

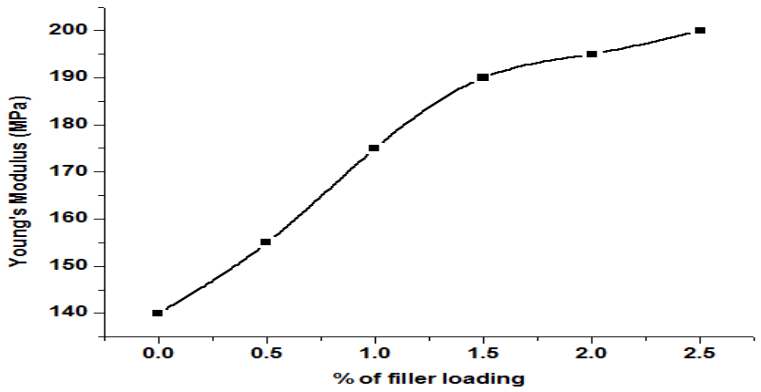

Fig 10: Young's modulus versus percentage of filler loading.

Fig 10 shows the variation of Young's modulus of the composite with filler loading. Young's modulus is a measure of stiffness of the material. Young's modulus of the composite was significantly increasing with increase in filler loading. Low particle size and high surface area of RHS provide better dispersion and adhesion with the HDPE matrix. This might be the reason for the increase in young's modulus values. So the stiffness of pure HDPE can be significantly enhanced by the addition of RHS without any surface modification (silylation).

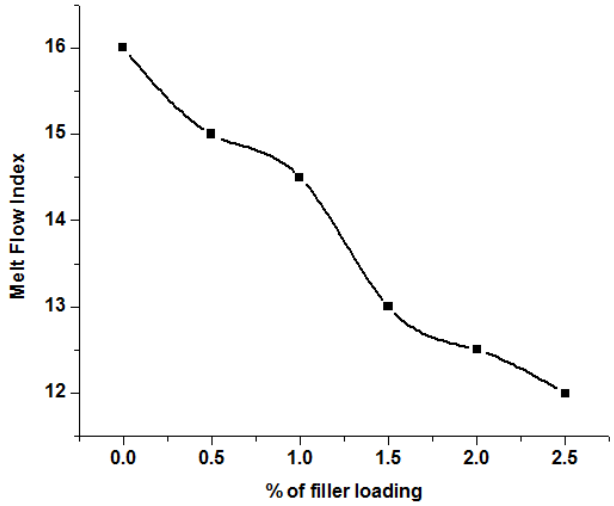

Fig 11: Melt flow index versus percentage of filler loading

Fig 11 shows the variation of melt flow index of HDPE in the presence of the filler. From the graph it was clear that, melt flow index values decrease with increase in filler loading. Addition

of reinforcing filler such as RHS expected to increase the melt viscosity of the matrix. Low melt flow index indicates a higher melt viscosity. The melt flow index is a measure of entanglement of polymer chains by chemical or physical crosslinks [15]. The rice husk silica particles are instrumental in increasing the entanglement between polymer chains.

SEM images of fractured specimen

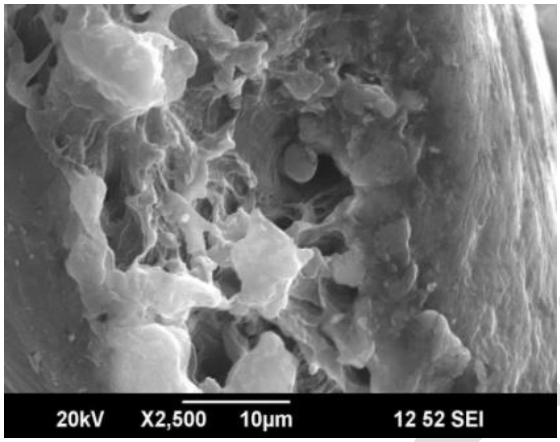

Fig12: SEM micrograph
Of pure HDPE

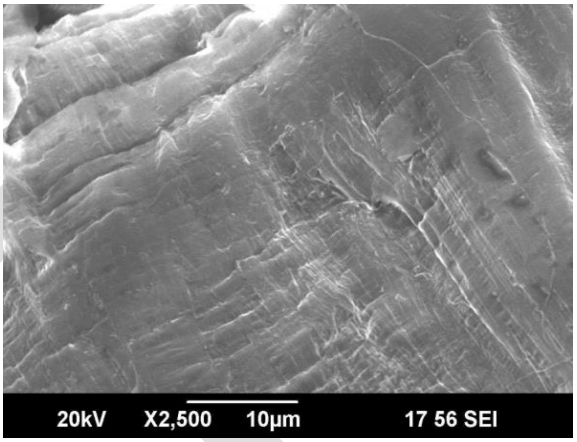

Fig 13: SEM micrograph
Of HDPE-RHS (1.5%) composite

From the SEM micrograph (fig 12) of fractured specimen, it was clear that number of voids can be seen in pure HDPE sample. This may adversely affects the mechanical properties of the base polymer. When the filler (RHS) was added, the fine filler particles of RHS will occupy the voids uniformly, provides more reinforcement to the base polymer. The SEM micrograph (fig 13) of fractured specimen of HDPE-RHS shows homogenous dispersion of silica particles and improved wettability. The failure surface of HDPE-RHS shows signs of greater energy absorption by the presence of undulations and wavy texture. Significant enhancement in the mechanical properties of HDPE-RHS may be due to high surface area ($150m^2/g$) and low particle size (20nm) of RHS.

CONCLUSION

Rice husk silica with low particle size and high degree of purity was obtained by the calcination of acid treated rice husk in a cost effective way. The particle size of RHS was found to be 20nm. The surface area of synthesized RHS was very high ($150m^2/g$). The synthesized RHS was found to be effective reinforcing bio filler in HDPE matrix. Tensile strength and Young's modulus values of pure HDPE can be significantly enhanced by the incorporation of RHS to the HDPE matrix, without any surface modification (silylation). The overall increase in the mechanical properties of HDPE was may be due low particle size, high surface area, high purity and uniform distribution of rice husk silica. The SEM micrograph of fractured specimen of the composite confirms the greater energy absorption of particles of rice husk silica. Thus costly fillers like precipitated silica, clay, calcium carbonate etc. can be substantially replaced by low cost rice husk silica. Preventing rotting of rice husk in paddy field and properly utilizes them as bio filler

in plastics and rubber may significantly reduce methane gas emission. The method provides a sustainable way to reduce global warming and environmental pollution.

REFERENCES

1. Midhun Dominic C.D, P.M Sabura Begum, Rani Joseph, Daisy Joseph, Prabith Kumar and Ayswarya E.P, Synthesis characterization and application of rice husk nanosilica in natural rubber, *International journal of science environment and technology*, Vol.2 (5), pp.1027-1035, 2013.
2. Nittaya Thuadaij and Apinon Nuntiya, Preparation of nanosilica powder from rice husk ash by precipitation method, *Chiang Mai Journal of Science*, Vol.35 (1), pp.206-211, 2008.
3. A.A Ramezanianpour, M.Mahdi Khani and Gh.Ahmadibeni, The effect of rice husk ash on mechanical properties of durability of sustainable concretes, *International journal of civil engineering*, Vol.2 (2), pp.83-91, 2010
4. Umeda Junko and Kondoh Katsuyoshi, Process optimization to prepare high purity amorphous silica from rice husks via citric acid leaching treatment, *Transactions of JWRI* , Vol.37 (1), pp.1-17, 2008.
5. S. ChandraSekhar, P.N. Pramada and L.Praveen, Effect of organic acid treatment on the properties of rice husk silica, *Journal of materials science*, Vol.40 (24), pp.6535-6544, 2005.
6. Olawale O, Oyawale F.A, Makinde O.W and Ogundele k.T, Effect of oxalic acid on rice husk, *International journal of applied sciences and engineering research*, Vol.1 (5), pp.663-668, 2012.
7. K. Amutha, R. Ravibaskar and G. Sivakumar ,Extraction, Synthesis and Characterization of Nanosilica from Rice Husk Ash, *International Journal of nano Technology and Applications*, Vol. 4 (1), pp.61-66, 2010.
8. S.H Javed, S. Naveed, N.Feroze, M.Zafar and M.Shafaq, crystal and amorphous silica from $KMnO_4$ treated untreated rice husk, *Journal of quality and technology management*, Vol.6 (1), pp.81-90, 2010.
9. Ajay Kumar, Kalyani Mohanta, Devendra Kumar and Om Prakash, Properties and industrial applications of rice husk: A review, *International journal of emerging technology and advanced engineering*, Vol.2 (10), pp.86-90, 2012.
10. Iftekhar Ahmad and Prakash A.Mahanwar, Mechanical properties of fly ash filled high density polyethylene, *Journal of minerals and materials characterization and engineering*, Vol.9(3), pp.183-198, 2010.
11. Qiang Zhao, Baoqing Zhang, Hui Quan, Richard C.M. Yam, Richard K.K. Yuen, and Robert K.Y. Li, Flame retardancy of rice husk filled high density polyethylene ecocomposites, *Composites Science and technology*, Vol.69 (15), pp.2675-2681, 2009.
12. Runzhou Huang, XinWu Xu, Sunyoung Lee, Yang Zhang, Birm-June Kim and Qinglin Wu, HDPE composites reinforced with hybrid inorganic fillers: Morphology, mechanical and thermal expansion performance, *Materials*, Vol.6, pp.4122-4138, 2013.
13. A. Pegoretti, A.Dorigato and A.Penati, Tensile mechanical response of polyethylene-clay nanocomposites, *Express Polymer Letters*, Vol.1 (3), pp.123-131, 2007.

14. Bhattacharya S. C, Joe M. A, Kandhekar Z. P, Salam A. and Shrestha R. M, Greenhouse-gas emission mitigation from the use of agricultural residues: the case of rice husk, *Energy*, Vol.24, pp. 43-59, 1999
15. E.P Ayswarya, Beena T. Abraham and Ebi Thomas Thachil, HDPE- Ash nano composites, *Journal of Applied Polymer Science*, Vol .124, pp.1659-1667, 2011.
16. R.Rezanavaz, M.K Razavi Aghjeh and A.A Bbaluo, Rheology, morphology and thermal behaviour of HDPE/clay nano composites, *Polymer testing*, Vol.31 (6), pp.1028-1036, 2010.
17. Anjana R and K.E George, Reinforcing efficiency of Kaolin clay on PP/HDPE blends, *International journal of engineering research and applications*, Vol.2 (4), pp.868-872, 2012
18. A. Fendler, M.P Villanueva, E.Gimenez and J.M Lagaron, Characterization of the barrier properties of composites of HDPE and purified cellulose fibers, *Cellulose*, Vol.14 (5), pp.427-438, 2007.
19. Jing Long Gao, Yan Hai Liu and Shou Dong Wei, Preparation and properties of HDPE/Silica composites, *advanced materials research*, Vol.279, pp.115-119, 2011.
20. Ming Qiu Zhang, Min Zhi Rong, Hai Bo Zhang and Klaus Friedrich, Mechanical properties of low nanosilica filled HDPE composites, *Polymer Engineering and Science*, Vol. 43 (2), 490-500, 2003.