

Influence of Hybrid Reinforcement Materials on High Density Polyethylene Nanocomposites

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Abstract: Composite materials are being used in more variety of products and applications, as more and more industries realize the benefit of these materials offers for light-weight composite structures for aerospace, transportation, marine and electronics system develop to need the mechanical testing requirements for composite materials, components and structures. The nanocomposites are materials that incorporate nano sized particles into a matrix material. The result of the addition of nanoparticles is a drastic improvement in properties that can include mechanical strength, toughness, hardness, stiffness and electrical or thermal conductivity. The high-density polyethylene (HDPE) is used as matrix material and filler material called reinforcement material as nanoclay cloisite 30B and rice husk ash. HDPE grafted with maleic anhydride (HDPE-g-MA) compatibilizer was used to get better blending of polymers that will increase their stability and better interaction between the high density polyethylene and nanoclay with rice husk ash. These nanocomposite materials were prepared by meltblend compounding in a twin screw extruder machine with a spindle speed of 60rpm with various zone temperatures. The equal addition of nano clay and rice husk ash in the range of (0-4wt %) with HDPE. The injection moulding machine was used to prepare specimens for different mechanical tests such as flexural, tensile, hardness and impact using corresponding dies as per ASTM standard. Morphological study and particle distributions were studied using the scanning electron microscope analysis. The mechanical properties of HDPE nanocomposites were examined with the effect of four different wt % of nanoclay to identify the most effective wt % of nanoclay to improve the strength of nanocomposites. The experimental results on mechanical properties of HDPE/ cloisite 30B nanoclay and rice husk ash could be analysed and improvement of strength of materials were studied with various wt% (0 to 4%) of nanoclay and rice husk ash on HDPE nanocomposites.

Keywords: HDPE, Cloisite 30B, Rice husk ash, Flexural test, and SEM.

1. INTRODUCTION

A composite is a material that is formed by combining two or more materials to achieve some superior properties. Even nanocomposite materials have produced higher mechanical properties with addition of small quantity of nano particles. A new material have been prepared by incorporating the reinforcement material called nanoclay cloisite 30B and rice husk ash (RHA) on high density polyethylene (HDPE). The different wt % (0 to 4wt %)

of nanoclay and rice husk ash equally added to the HDPE. Many scientist, industrialist and researchers have been focused on nano composite to improve properties for various application. The small addition of nano materials and rice husk ash with polymer offer the improvement of both thermal barrier and mechanical properties when compared to conventional polymer composites. The properties of nanocomposite like stiffness and creep resistance were increased with the addition of clay [1, 2]. The tensile and flexural strengths of the composite were increased at 2 wt. % of nanoclay [3]. A significant improvement of the mechanical properties of HDPE/wood-flour composites with an appropriate combination of the coupling agent and nanoclay in the nanocomposites materials [4]. The improvement in the tensile modulus, water absorption and thickness swelling property obtained by increasing nanoclay content in the HDPE [5, 6]. The addition of nanoparticles improves enhancement stiffness properties and reduced impact strength [7-9]. The wood flour filled with ABS was having higher flexural strength, flexural modulus and Rockwell hardness of the nano composites. The tensile strength and impact strength were lowered. The flammability was increased and also high rate of water absorption [10]. At 5 wt. % of nanoclay, the Young's modulus and tensile strength of nanocomposite with increased up to 34% and 25% respectively, when compared with a pristine sample [11].

Rice husk ash produced by burning of RH in ambient temperature and it leaves the residue called rice husk ash. The average of 220 kg (22%) of rice husk produced by every 1000 kg of paddy milled and when that husk is burned in the boiler which produces about 55 kgs (25%) of rice husk ash produced. Most of the countries producing husk by processing of rice is either dumped as waste or burned. High ash produced by burning of rice husk when compared to other biomass fuel. Rice husk ash contains 87-97% of silica content. Many industrial applications, rice husk has been used for processing cement, steel and other refractory industries. Rice husk ash mainly depends on chemical composition of ash. It has predominant of silica content. RHA is found superior than other supplementary materials like silica fume, fly ash and slag

The HDPE-RHA blend gives a higher elongation and tensile strength about 18% higher than that of pristine HDPE [12]. The mechanical properties of tensile strength and elongation at break increases in the composition of the mixture 2 to 4% wt [13]. Greater improvement in properties of HDPE and a high cross-linking degree of 85% as a result of electron-beam irradiation of the material [14]. The amorphous silica rich RHA could become a potential resource of low cost precursor for the production of value-added silica based materials for practical applications [15]. The differences in properties between rice straw composites and rice husk composites were described [16]. Peat ash reinforcement does increased tensile and flexural properties [17]. The addition of rice husk has delayed in thermo-oxidation process of the HDPE at 40 °C, and it evident that, flame retardant effect has also been observed [18]. Differential scanning calorimetry experiments showed that virgin high-density polyethylene (VHDPE) has significantly larger heat flow during cooling run compared to recycled high-density polyethylene (RHDPE) [19]. Polyethylene materials are widely used in medicine. High-density polyethylene (HDPE) composites containing various amounts of amorphous calcium phosphate nanoparticles were investigated for *in vitro* biomedical performance [20]. It was found that heterogeneous nucleation effect of graphene could enhance polyethylene crystallization, increase lamella thickness and crystallinity of nanocomposites as well as crystallization temperature. The dielectric constant and conductivity of composites increased with the increase of graphene content, which reflected the good interfacial polarization effect in materials [21]. Numerical result shows that in-plane and out-of-plane thermal conductivities have a linear relation with increasing volume fraction. The specific heat capacity of a composite decrease as the volume fraction of SWCNTs increases. The randomly distributed SWCNTs decreases the heat flux whereas the alignment of SWCNTs has shown a maximum heat flux [22].

The application of polymer materials plays mainly an important role in the packaging industry and bio medical. The improve the strength of nano composites which helps by increasing efficient of food marketing and other engineering product applications. A hybrid nanocomposite materials prepared by adding rice husk ash which plays a major role of improvement of mechanical , thermal, barriers properties when compared to pristine polymers. The RHA has been widely used in many industrial applications steel, refractory, cement, construction and other applications. In steel plant, RHA used as excellent insulator having insulating properties including a high melting point, low thermal conductivity and low density. It also used as coating over the molten metal and it does not allow quick cooling of metals. RHA has mineral additive blended with cement to improve performance of the concrete and also used as stabilizing agent in cement by blend correct proportion. Other applications such as a pure silica obtained from RHA used in manufacture of silicon chip. RHA also used in water purification, vulcanizing of rubber, control of insect pests in stored food and flu gas desulphurization absorbents.

2. MATERIALS AND PROPERTIES

The nanoclay cloisite 30B and RHA used as reinforcement material and high density polyethylene as matrix material. Addition of small amount of nanoclay could substantially enhance the mechanical properties of the HDPE nano composites. Cloisite 30B nanoclay received from southern clay products Inc Gonzales, TX 78629 US. Cloisite 30B is alkyl quaternary ammonium salt bentonite. It is an additive for plastics and rubber to improve various physical properties, such as reinforcement, density is 1.98g/cm^3 , specific gravity of 1.6 insoluble in water and colour is off white. HDPE received from reliance industries.

The basic reinforcing mechanism of the composites is that, the interaction between nanoclay and polymer matrix material has high tensile strength and modulus. Compatibilizer, HDPE grafted malic anhydride (HDPE-g-ma) by adding 3% each composition of nanoclay, which is used to improve the additive property between the nanoclay and the HDPE.

2.1. Preparation of rice husk ash

The boiled rice husk ash received from rice mill plant. Rice husk ash was dried at $60\text{-}70^\circ\text{C}$ for 2 hours. The dried RH was burned in the oven at a temperature of 800°C for 2 hours. Rice husk ash meet good physical and chemical properties by burning of rice husk by controlled temperature as per ASTM standard C 618- 94A. The burning temperature of 550°C - 800°C amorphous silica is formed, but higher temperature crystalline silica is produced (90-96%) in grey colour. Rice husk contains around 70- 90% of organic matters such as lignin and cellulose and remaining mineral compounds are silica and alkalies and trace elements.

2.2. Method of fabrication

Fabrication of nano composites were done in two methods

1. Nanoclay reinforced with HDPE with 3 wt.% compatibilizer in each % of nanoclay
2. Nanoclay and RHA reinforced with HDPE with 3 wt.% compatibilizer in each % of nanoclay

Reinforcement material and HDPE were blended with various weight percentage (0-4wt%) and a 3 wt% of malic anhydride was added in each combination of nanoclay and nanoclay with RHA by melt blending method in twin screw extruder used for mixing HDPE materials. The raw materials such as nanoclay, HDPE and compatabilizer(HDPE-g-ma) fed to the top of the hopper into the barrel in the twin screw extruder. The compound materials enters the twin screw, the screw rotating at 120 rpm which forces the materials forward to the heated barrel. The different temperature was set in the barrel heated zones. From the barrel plastics beads to melt gradually as they pushed out through the barrel. The extruded materials were chopped in to small beads by using a pellet cutter. The chopped materials were dried in the oven at a temperature maintained at 60°C for anhour to remove moisture. The prepared ASTM standard specimens for various mechanical tests like flexural, tensile, hardness and impact using corresponding dies in the injection moulding machine.

3. RESULT AND DISCUSSION

Prepared ASTM standard size specimens for various test like tensile test, flexural test, and hardness test. Each test five specimens were tested and average value was calculated. The various composition of nanoclay content in the polymer have been conducted mechanical test and the result were tabulated and graph were drawn. The scanning electron microscopic (SEM) analysis were performed for various specimen for the study of morphology of nanocomposite.

3.1. Tensile test

In tensile test, the specimens were tested in the tensometer, capacity of 20KN which is computerized. This tensometer machine is used for conducting both tensile test and flexural test. In tensile test, the ASTM D638 standard is specimen size is $165 \times 12.5 \times 3$ mm. The specimen is held between two jaws, one end is fixed and other end is slowly pulled apart until it breaks. The Speed of spindle is set at 10mm/min. A tensile test provides information related to a material includes yield point, ultimate tensile strength, proof stress, percentage reduction in area and percentage elongation at break.

Table 1. Tensile strength of nanoclay and nanoclay with RHA reinforced on HDPE

SAMPLES	TENSILE STRENGTH (MPA)	SAMPLES	TENSILE STRENGTH (MPA)
HDPE	15.1	HDPE	15.1
HDPE /1% Cloisite 30B/3% PE-g-MA	14.8	HDPE /1% Cloisite 30B/1% Rice Husk Ash /3% PE-g-MA	19.05
HDPE /2% Cloisite 30B/3% PE-g-MA	15.2	HDPE /2% Cloisite 30B/2% Rice Husk Ash/3% PE-g-MA	20.41
HDPE /3% Cloisite 30B/3% PE-g-MA	15.85	HDPE /3% Cloisite 30B/3% Rice Husk Ash/3% PE-g-MA	20.24
HDPE /4% Cloisite 30B/3% PE-g-MA	16.6	HDPE /4% Cloisite 30B/4% Rice Husk Ash/3% PE-g-MA	20.31

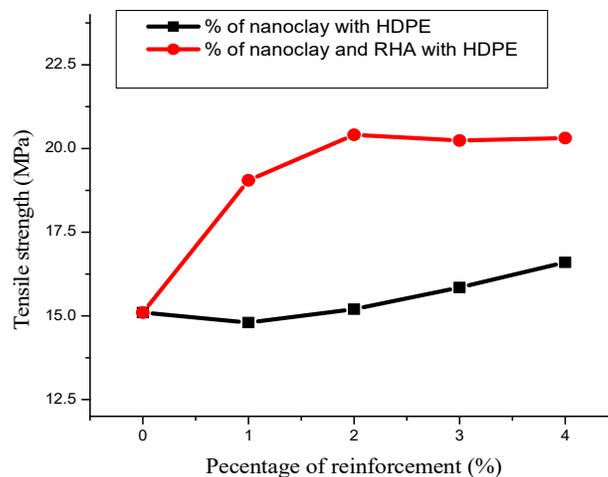


Figure 1. Tensile strength on various percentage of nanoclay and RHA on HDPE

From Fig 1 shows that the mechanical property of tensile strength increases compared to pure HDPE. Nanoclay and RHA reinforced with HDPE samples were obtained very much tensile strength when compared to nanoclay only reinforced in HDPE. The improvement of tensile strength reason behind that blending of nanoclay and RHA with compatibilizer were uniformly distributed on HDPE.

3.2. Flexural test

Inflexure test, the specimens were subjected to three point bend test in tensometer. The flexural strength has been found by using the following formulae. The ASTM D 790 size of the specimen is 125*12.5*3 mm.

Table 2: Flexural strength of nanoclay and nanoclay with RHA reinforced on HDPE

SAMPLES	FLEXURAL STRENGTH (MPA)	SAMPLES	FLEXURAL STRENGTH (MPA)
HDPE	14	HDPE	14
HDPE /1% Cloisite 30B/3% PE-g-MA	16.28	HDPE /1% Cloisite 30B/1% Rice Husk Ash /3% PE-g-MA	45.12
HDPE /2% Cloisite 30B/3% PE-g-MA	17.13	HDPE /2% Cloisite 30B/2% Rice Husk Ash /3% PE-g-MA	48.96
HDPE /3% Cloisite 30B/3% PE-g-MA	16.45	HDPE /3% Cloisite 30B/3% Rice Husk Ash/3% PE-g-MA	49.6
HDPE /4% Cloisite 30B/3% PE-g-MA	16.30	HDPE /4% Cloisite 30B/4% Rice Husk Ash/3% PE-g-MA	50.24

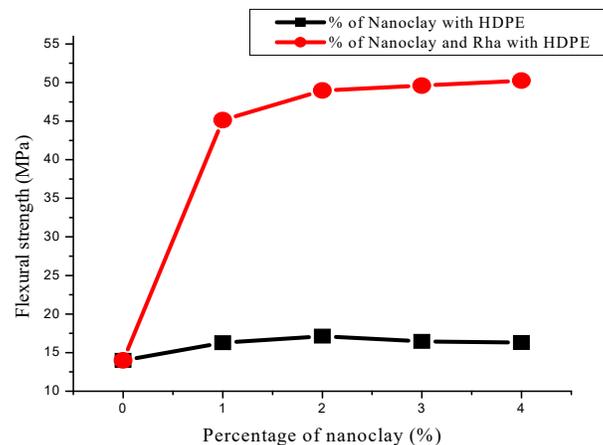


Figure 2: Flexural Strength on various percentage of nanoclay and RHA on HDPE

The table 2 shows the flexural strength of nanoclay and nanoclay with RHA reinforced on HDPE. The tabulated values shows the flexural strength of various nanoclay and nanoclay with RHA. The flexural strength is a material's ability to resist deformation under load. The flexural strength of nanoclay and RHA reinforced with HDPE samples were obtained very much strength when compared to nanoclay only reinforced in HDPE. At 2 wt % nanocomposites have higher strength in both set of samples. The flexural strength has been

increased when addition of filler material at any % of nanocomposites compared to pristine material.

3.3.Hardness test

Hardness is the resistance to permanent indentation. Hardness of the materials like polymer, elastomer, and rubbers are measured by Shore D scale. It has an indenter loaded by a calibrated spring. The hardness is measured by the penetration depth of the indenter under the load. Maximum penetration for each scale is 0.097-0.1 inch (2.5-2.54 mm). The shore D hardness values varies from 0 to 100 corresponding to zero penetration.

Table 3. Hardness number of nanoclay and nanoclay with RHA reinforced on HDPE

SAMPLES	HARDNESS NO (D SHORE)	SAMPLES	HARDNESS NO (D SHORE)
HDPE	48	HDPE	52.2
HDPE /1% Cloisite 30B/3% PE-g-MA	52.2	HDPE /1% Cloisite 30B/1% Rice Husk Ash/3% PE-g-MA	54.5
HDPE /2% Cloisite 30B/3% PE-g-MA	57.8	HDPE /2% Cloisite 30B/2% Rice Husk Ash/3% PE-g-MA	58.6
HDPE /3% Cloisite 30B/3% PE-g-MA	61.2	HDPE /3% Cloisite 30B/3% Rice Husk Ash /3% PE-g-MA	63.5
HDPE /4% Cloisite 30B/3% PE-g-MA	63.2	HDPE /4% Cloisite 30B/4% Rice Husk Ash/3% PE-g-MA	66.5

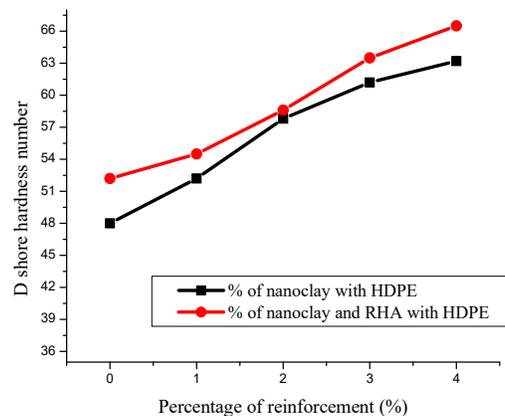


Figure 3. Hardness number on various percentage of nanoclay and RHA on HDPE

The figure 3 shows that Hardness number on various percentage of nanoclay and RHA on HDPE. The hardness number gets increases with increases of nanoclay content due to their property of nanoclay and RHA.

4. SEM Analysis

Fig.4 (a-d) shows the morphological characterization of Cloisite 30B with HDPE. The nanoclay particles are generally distributed evenly in the specimens. The samples were subjected to gold sputtering prior to scanning electron microscopy to give the necessary conductivity of the material. It is evident that, the created voids imply a weak connection area between the nanoclay and the matrix. The tensile strength of the nanocomposites increased with increase of nanoclay content varying from 0-4%. That shows the better nanoclay intercalation on nanoclay with HDPE. The flexural strength increased by 2% wt of nanoclay.

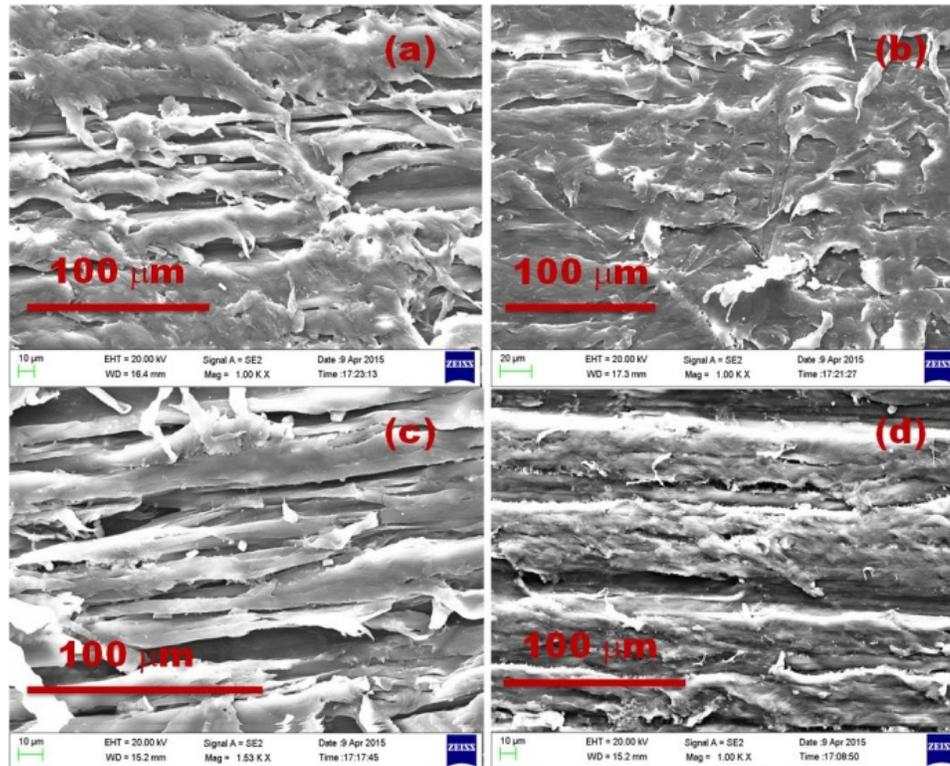


Figure.4. (a) SEM Image of 1% Cloisite 30B/HDPE (b) SEM Image of 2% Cloisite 30B/HDPE
(c) SEM Image of 3% Cloisite 30B/HDPE (d) SEM Image of 4% Cloisite 30B/HDPE

5. CONCLUSION

HDPE polymer filled with nanoclay and RHA at various concentrations (0, 1, 2, 3 and 4wt. %) was prepared by using twin screw compounding and injection molding method. In nanocomposites, nanoclay as the reinforcement and a polymer serves as the matrix material. Particularly Cloisite 30B minerals and RHA serves as good reinforcement material owing to their ease of dispersion in the organic polymer matrix. The nanocomposites with 4 wt. % clay loading were able to bear a higher load. It is observed that when increase of tensile strength with increase of % of nanoclay. The reinforcement of nanoclay and RHA with HDPE has good tensile strength compared to nanoclay reinforcement on HDPE. The flexural strength of the nano composites (1- 4wt %) was improved when compared with

pristine polymers. The maximum flexural strength was obtained at 2 wt. % (17.13 Mpa) in nanoclay reinforcement. But in nanoclay and RHA reinforcement the maximum flexural strength was obtained at 5 wt. % (50MPa). The hardness number of the nanocomposites increases with increases of nanoclay and RHA. The mechanical properties of HDPE substantially increased with the addition of nanoclay with different wt. % of nanoclay. The morphological characterization of Cloisite 30B (1- 4wt %) with HDPE was analysed. As regards the intercalation, the particles were distributed evenly in all compositions of nanoclay composite materials.

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