

Study on Mechanical Testing of Various Nanoclay Reinforced with High Density Polyethylene Nanocomposites

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Abstract

The Polymer nanocomposites materials are comprising of polymer as matrix material and reinforcement material as filler that has particles of nanometer in size. These materials have different physical and chemical properties and are mixed together to yield unique properties of nanocomposites. The High Density Poly Ethylene (HDPE) has been chosen as polymer matrix material. The reinforcement materials used are different nanoclay such as Montmorillonite (MMT), Cloisite 30B, Cloisite 25A and hybridizing of Cloisite 30B with Rice Husk Ash (RHA). These nanoclay materials are reinforced with HDPE with different wt % (0 - 4 wt %). Compatibilizer of 3 wt% of HDPE grafted with Maleic Anhydride (HDPE-g-MA) was added to provide superior adhesion between the HDPE and nanoclay. The nanocomposite materials were fabricated by melt blending in a twin screw extruder with the spindle speed of 50rpm with different zone temperatures. The melt blending is one of the best methods for the preparation of nanocomposites. This method makes it easy to blend the nanoclay and the matrix materials for preparing specimens for different tests. The ASTM standard specimens were prepared for various mechanical tests like flexural, tensile, hardness and impact using respective dies in injection moulding machine. In flexural test, the specimens were subjected to different cyclic loads before conducting three point bent test. In bend test, maximum load that could withstand by the material was used to examine the flexural strength and modulus of the composite materials. In tensile test, different nanoclay specimens were tested in tensometer machine which had a capacity of 20KN. Tensile strengths of different nanoclay with different wt% of nanocomposites were compared. The results of D shore hardness number and Izod impact strength of different nanoclay with HDPE were also compared.

Keywords: HDPE, Nanoclay, Cloisite 30B, Tensile, Bending, Hardness and Impact

INTRODUCTION

Composite materials are engineered materials in which more than one material with significant mechanical properties are combined to form a single structure having unique properties. The superior properties of the composite material influenced of the properties of the materials and interface.

In polymer nanocomposites, polymers are reinforced with small amount of nano sized particles. The dispersed phase can be inorganic particles, clays, minerals etc. The particle filled polymer composites have been extensively studied because of their wide spread applications in the field of automobile, electrical industries, aeronautical and household. Numerous scientists have focused on the interest that nanocomposites offer for applications in high performance coatings, catalysis, magnetic, electronics and biomedical materials.

The primary goal of polymer nanocomposites research is to enhance the strength and toughness of polymeric components using nanoclay or nano particles. Due to the incorporation of filler materials in matrix materials, the mechanical properties such as flexural modulus, tensile strength, flexural strength and impact strength have been improved and also increased gas barrier, increased heat distortion temperature etc.

A small amount of nano filler materials is added to polymer matrix to obtain the greater mechanical, thermal and gas barrier properties. For example, adding carbon nano tubes into matrix materials enhance the electrical, thermal conductivity and other form of nano particulates such as nanoclay or nano particles may result in enhanced optical properties, heat resistance, di-electric properties and mechanical properties like strength, stiffness and resistance to wear and damage. During processing of nanocomposites, the reinforcement material is distributed into the polymer matrix material. The percentage by weight of nanoclay called weight percentage (wt. %) of the nano particulates can be introduced in the order of 0.5 wt % to 5 wt %.

Investigated on High Density Polyethylene (HDPE) reinforced with Montmorillonite (MMT) showed that specimens grafting with the MA showed that tensile strength increased at 3 wt. % and impact strength increased at MMT 5 wt. % [1]. Modified MMT by Cetyl Trimethyl Ammonium Bromide, hardness, thermal stability, flammability and water absorption values of WPCs were improved by the inclusion of modified MMT to WPC [2]. The visco-elastic behavior of the composites were studied and storage modulus showed an increase in the magnitude of the peaks with fiber reinforcement and addition of MAPE [3]. It was noted that the tensile strength of the composites made of TBaF was higher than that of untreated BaF. An increase of banana fibers loading up to 40% to a continuous improvement in moduli and flexural strength of composite materials [4]. The optical properties of

composites and especially the transparency are mainly influenced by the refractive index difference between filler and polymer, filler particle size, particle loading and composite thickness [5]. The blending of materials showed two-phase morphologies of PP/HDPE and MAPP/HDPE. The greater interaction between MAPP and WP was observed due to increased modulus of elasticity and the stress at break decreased with increasing WP content [6]. Morphological studies shows that in contrast to melt-compounding, solution-blending followed by static annealing failed to produce significant orientation of nanoclay platelets and polymer crystallites [7]. A nucleation effect of the nanoclay on the polymer matrix crystallization for solution-blending samples was noticed. The results of different levels of clay dispersion were interpreted by degrees of clay intercalation/ exfoliation achieved during various preparation and procedures [8].

It was observed that the better accelerating effect came from SiO₂ nanoparticles. In thermal properties analysis, there is an increase in crystallinity. Thermal stability of the nanofiller at different silane concentrations were observed. XRD and Thermo Gravimetric Analysis (TGA) outcome indicated a high thermal stability for the silane-modified Na-Mt. Intercalation increased with increase in initial silane concentration up to 9 mmol then decreased at higher concentrations [9-10]. MMT with Cloisite 15A, which had a high Cation Exchange Capacity (CEC) and exhibited an increase in its impact properties and Cloisite 20A exhibit an increase in the flexural modulus [11]. The crystallinity level and the nucleation rate of the composites were increased by addition of MAPE compatibilizer to the composite materials [12]. Increasing the AZD content from 2 to 4 phr, the average cell size and cell density increased, whereas the foam density showed a decrease to 21.7% and by adding nanoclay up to 5 phr, the cell density increased and the cell size decreased [13]. A relative change in the wear rate of the polymer by surface crack existence, as well as crack orientation, was discussed to provide an understanding of surface fatigue wear [14]. Rheological results indicated an increase in the viscosity with the inclusion of nanoclay to PE. Wide angle x-ray diffraction showed the better exfoliation of nano particle clays in the polymer matrix [15].

The optimal loading of nanoclay in the Polyester /glass fiber composites was achieved at 3wt%, where the materials property improvement likes tensile and bending strength [16]. Degradation produced polar functional carbonyl groups and also developed extensive cross-linking in HDPE [17]. In food packaging materials anticipate to grow with low cost, renewable and sustainable materials with enhanced mechanical properties [18,19]. During wear analysis the results exhibit that as silicon nitride content increased, slide wear loss decreased. Inclusion of silicon nitride along with compatibilizer also get better thermal stability of the nanocomposites [20].

The principles should be applied, especially on the migration behaviors of nanomaterials in food and their possible impacts on health/safety, as well as the environment [21]. The inclusion of 5 wt% of MAPE compatibilizer with improved fiber and matrix adhesion and resulted in enhancement of tensile strength and Young's modulus as well as thermal

stability for both treated and untreated fiber composite materials [22]. Thermal and burning behavior of the LDPE nanocomposites investigated that the nanoclay itself appear only a limited residual protection layer effect [23]. DSC tests shown for all composition there is an increase in strength, modulus and hardness but drop in elongation at break [24]. The Properties of HDPE due to ageing showed that the nano composites crystallinity increased while the fracture toughness, hardness, wear resistance, storage and loss modulus decreased [25]. The torsional modulus and tensile modulus exhibited high when compared with the pure HDPE. Young's modulus of the material increased that was observed when C12 and silane were used, corresponding to 120% and 70% respectively [26]. The properties of Rise Husk Ash (RHA), High strength concrete at optimized conditions were performed. RHA used as fuel for generation of electricity in well planned manner is likely to transform this agricultural waste material into a valuable fuel for industrial sectors [27-28]. The tensile strength and elongation at break of an increase in the composition of 2 to 4 wt% of nanocomposites. The Morphological analysis appears an even distribution of nano particles of rice husk ash with HDPE. The elongation at break increased due to the higher content of rice husk ash added in the composite materials [29-31].

Inclusion of small content of nanoclay resulted in better strength and modulus. The impact strength decreased with percentage increase of the nanoclay content and hardness number increased with percentage increase of nanoclay [32]. The impact strength improved by the addition of 5% of PE-g-MA to reference blend. When adding the TPS to the reference blend and the compatible reference blend, a decrease in impact strength increases the rate of TPS. Addition of 2.5% of the nano-clay slightly increases the impact strength [33]. Tensile, Impact and Hardness test has been done and it was observed that the increase in tensile strength occurs in the specimen with 3% weight of nanoclay than the other specimens, and also an impact strength and hardness of the nanocomposites increases with 3 wt % of nanoclay [34].

From this literature study any filler material added into matrix material its strength of materials will may vary according to the wt % of filler added into matrix material. According to our requirement select the optimum proportion of filler/Nanoclay reinforcing into matrix materials for specific applications.

MATERIALS AND METHODS

The nanoclay was received from southern clay product USA. The different nanoclay such as Montmorillonite (MMT), Cloisite 30B, Cloisite 25A and hybrid of Cloisite 30B and Rice Husk Ash (RHA) were reinforced with HDPE.

Compounding of nanoclay and HDPE was done by twin screw extruder. The nanocomposites with different weight % of nanoclay (0-4wt. %) were fabricated through injection moulding machine. The test Specimens were prepared for different mechanical testing according to ASTM standard.

Characterization was done by various mechanical testing including tensile test and flexural test conducted by tensometer, hardness test by D shore hardness test, impact test

by Izod impact tester

MATERIALS

In order to prepare nanocomposites investigated in the present research the following materials were used:

1. High Density Polyethylene (HDPE)
2. Montmorillonite (MMT)
3. Cloisite 30B
4. Cloisite 25A and
5. Cloisite 30B and rice hush ash (RHA) as reinforcement materials

High Density Polyethylene.

The density of HDPE is normally between the ranges of 0.941-0.965 g/cm³. The HDPE is used in wide variety of applications, including plastic bottles, pipes, food packaging etc. HDPE has got high strength and toughness with its very tight bonds with other molecules.

Montmorillonite.

MMT is a group of clay minerals, one of the most widely available of all mineral materials. Minerals of this group are especially fine grained crystalline aggregates and they present an unusually wide range in composition. This property plays a prominent part in determining the physical properties of minerals of the MMT group.

Cloisite 30B.

Cloisite 30B is an additive for plastics for improving various mechanical and physical Properties like tensile, flexural, impact, reinforcement, HDT, CLTE and barrier. It is Quaternary ammonium salt modified natural montmorillonite polymer additive.

Cloisite 25A.

Cloisite 25A is a natural MMT polymer additive. Quaternary ammonium cations also called as quats, They are positively charged polyatomic ions of the structure.

Rice Hush Ash.

Husk is surrounded by the paddy grain. Rice husk generates in rice mill as a byproduct known as husk. During milling of paddy around 78 % of weight is received as rice, broken rice and bran and remaining 22 % of the weight is received as husk. This husk contains about 75 % organic volatile matter and the remaining 25 % of the weight of husk is converted into ash during the burning process. This RHA contains amorphous silica around 85 % - 90 %.

Compatibilizer. Maleic anhydride used as compatibiliser in polymer nanocomposites. It is an organic compound with the formula of C₂H₂ (CO)₂ O. It is the acid anhydride of maleic acid. Grafting of MA onto various thermoplastic polymers (predominantly polyolefin) for preparing of efficient engineering materials.

FABRICATION METHOD OF NANOCOMPOSITES

The fabrication of nanocomposites involves two methods. They are Twin Screw Extrusion for compounding and Injection Moulding for mixing process.

Twin Screw Extrusion Process.

Twin screw extruders are mainly used for polymer compounding. It is used for mixing of nanoclay with various wt % with HDPE. Twin screw extruder is the machine used for the plastic extrusion process when two or more ingredients are mixed or compounded. This process is best suited when extruding reactive polymeric materials. Twin screw extruder is particularly useful in the production of rigid PVC and wood fiber blends. The heating zones of the extruder are maintained at 170, 180, 190, 190 °C, and the screw speed was 50 rpm.

Injection Moulding Process.

Injection molding machine is normally used in production process for the fabrication of plastic components. A different kind of plastic products are manufactured using injection molding, which vary in size and shape of the parts. The main process in injection moulding requires mould and raw material. The plastic material is melted in the injection molding machine and then injected into the mold cavity, where it cools and solidifies into the final part.

RESULT AND DISCUSSION

Comparison on performance of different nanoclay reinforced HDPE nanocomposites

Flexural Strength.

Apart from tensile strength, hardness and impact resistance, the flexural strength of the HDPE matrix both plain and reinforced with nanoclay particles was evaluated and the values are tabulated in Table 1. Flexural strength was assessed by conducting the three point bend test. The Typical variation data on flexural strength is presented in Figure 1.

Table 1 Comparison of Flexural Strength of different nanoclay reinforced Nanocomposites

Samples	Flexural Strength (MPa)			
	MMT	Cloisite 30B	Cloisite 30B + RHA	Cloisite 25A
HDPE	28.77	15.5	15.5	10
HDPE+1% Nanoclay	31.38	15.64	21.1	10.36
HDPE+2% Nanoclay	34	15.64	31.0	10.28
HDPE+3% Nanoclay	34	15.64	33	10.36
HDPE+4% Nanoclay	26.1	18.25	28	10.61

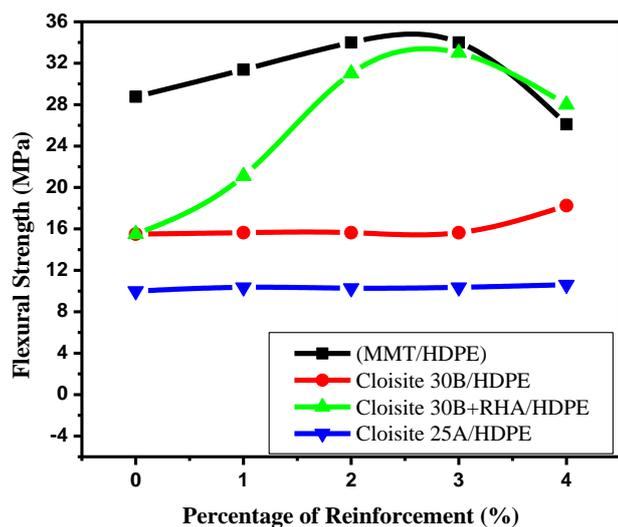


Figure 1. Comparison of Flexural Strength of different nanoclay reinforced Nanocomposites

Typically monitored variation of flexural strength of HDPE reinforced with MMT nanoclay revealed that with increase % wt addition, flexural strength increased. Also above 3 wt % addition, there was only a marginal variation significance of Cloisite 30B addition on flexural strength. But in Cloisite 25A addition of nanoclay, its flexural strength was low when compared with other reinforcement materials

Flexural Modulus of different nanoclays

The flexural moduli of the HDPE matrix both plain and reinforced with different nanoclay particles were evaluated. The variations of flexural modulus of different nanoclay such as MMT, Cloisite 30B, hybrid of Cloisite 30B and RHA reinforced with HDPE without cyclic load are tabulated in Table 2.

Table 2. Comparison of Flexural Modulus of different nanoclay reinforced Nanocomposites

Samples	Flexural Modulus (MPa)		
	MMT	Cloisite 30B	Cloisite 30B + RHA
HDPE	1531	379.25	512.5
HDPE+1% Nanoclay	1137.6	2503.11	1524.4
HDPE+2% Nanoclay	696.78	2844.37	1482.25
HDPE+3% Nanoclay	578.28	1365.3	1235.3
HDPE+4% Nanoclay	1327.2	3716.65	1726.65

Compared with other nanoclay reinforcements, the higher flexural modulus of cloisite 30B was exhibited at 4 wt % nanoclay reinforcement and there is a drop between 2wt % and 4 wt %. Typical variation data on flexural strength are presented in Figure. 2.

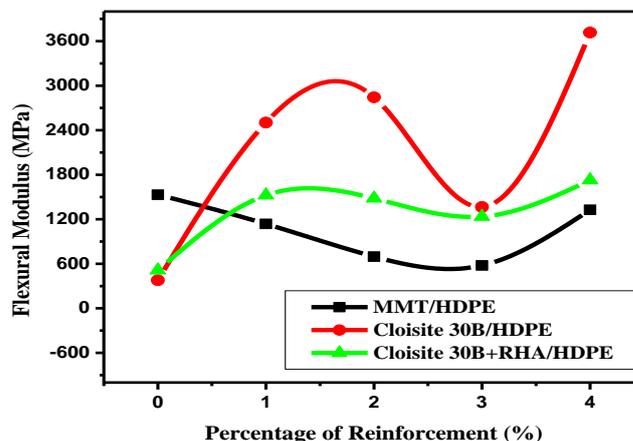


Figure 2. Flexural Modulus of different nanoclay reinforced Nanocomposites

Typically monitored variation of flexural modulus of HDPE reinforced with MMT nanoclay revealed that with increase % wt addition, flexural modulus decreased. Marginal variation of flexural modulus increased with increase of % reinforcement of hybrid of Cloisite 30B and RHA.

Comparison of tensile strength on different nanoclay reinforced HDPE nanocomposites

The tensile strength comparison of different nanoclay with various wt % (0 to 4wt. - %) of reinforcement on HDPE was made Table 3 shows the variation of tensile strength of different nanoclays such as MMT, Cloisite 30B, Cloisite 25A and hybrid of Cloisite 30B and RHA reinforced with polymer matrix HDPE. It was seen that with different nanoclay particles (addition) tensile strength improved with % wt addition as shown in Figure 3. Further, it was seen that hybridizing of the nanoclay Cloisite 30B and rice husk ash caused relatively higher enhancement of strength, while least enhancement could be seen with Cloisite 30B addition.

Table 3. Tensile strength of various nanoclay reinforced nanocomposites

Sl. No.	Samples	Tensile Strength (MPa)			
		MMT	Cloisite 30B	Cloisite 25A	Cloisite 30B + RHA
1	HDPE	15.5	15.1	15.1	15.1
2	HDPE/ 1% Nanoclay	16.7	14.8	21.2	19.05
3	HDPE/ 2% Nanoclay	16.5	15.2	22.6	20.41
4	HDPE/ 3% Nanoclay	17.3	15.85	23.74	20.24
5	HDPE/ 4% Nanoclay	18	16.6	21.03	20.31

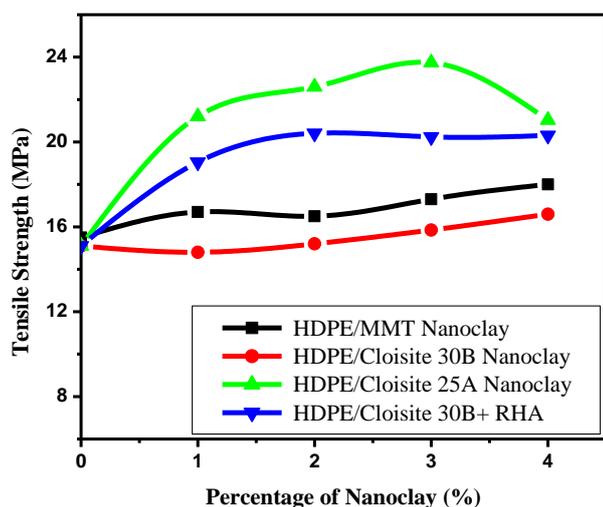


Figure 3. Comparison of tensile strength of various nanoclay reinforced nanocomposites

Normally during processing, the clay addition can agglomerate (with increasing wt %) zones of weakness or pores affecting the strength properties. Among Cloisite 30B / Cloisite 25A clay, relating to higher density Cloisite 25A imparted higher % strength. Addition of RHA could have facilitated resulting from free matrix and leading to higher % enhancement of strength.

Comparison of Hardness Number of Different Nanocomposites

Typical observed hardness values (D shore hardness) of different nanoclays with HDPE matrix reinforcement is illustrated in Table 4.

Table 4. D shore hardness number of different nanocomposites

Samples	D shore Hardness No			
	MMT	Cloisite 30B	Cloisite 30B + RHA	Cloisite 25A
HDPE	48	48	48	48
HDPE+1% Nanoclay	61.3	52.2	54.5	50.5
HDPE+2% Nanoclay	61.8	57.8	58.6	52.7
HDPE+3% Nanoclay	64.6	61.2	63.5	56.8
HDPE+4% Nanoclay	63.9	63.2	66.5	59.8

It was seen that among Cloisite 30B and Cloisite 30B with rice husk ash addition, the higher % enhancement in hardness was observed in hybrid composites. Also, it was seen that not much improvement could be attained in the case of relatively heavier matrix material. Generally, all reinforcement nanoclays with HDPE showing increase of hardness with increase of filler materials as shown in Figure. 4.23. Further it

was observed that HDPE/MMT nanocomposites exhibited higher hardness number as illustrated in Figure 4. The observed rise in the hardness rate % wt addition could be attributed to agglomeration.

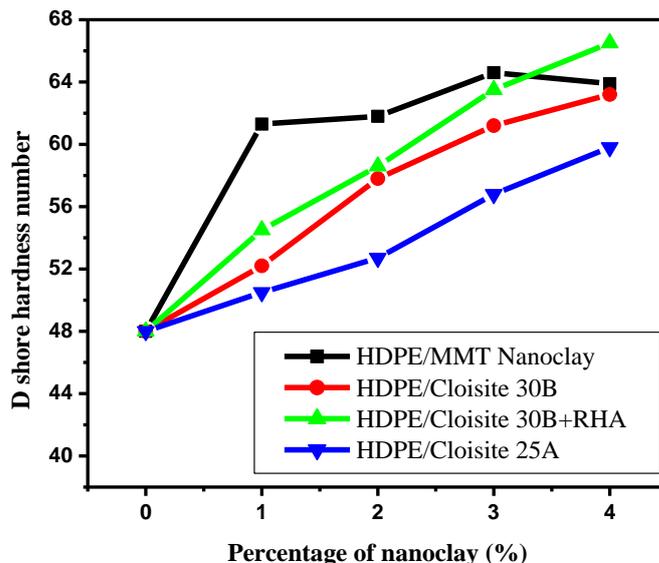


Figure 4. Percentage of nanoclays versus D shore hardness of different nanoclays reinforced HDPE nanocomposites

Comparison of Impact Strength of Different Nanocomposites

Typical observed izod impact strength of different nanoclays with HDPE matrix reinforcement is illustrated in Table 5. Impact strength is the ability of the material to withstand a suddenly load. The Impact strength suddenly decreased from (125J/m-105J/m) at 1wt % of nanoclay as shown in Figure 5. Further it was noticed that decrease of impact strength with increase of nanoclay content.

Table 5. Impact strength of different nanoclays (0-4 wt %)

Additives	Impact Strength (J/m)		
	Cloisite 30B	Cloisite 30B+RHA	Cloisite 25A
HDPE	125	125	125
HDPE+1% Nanoclay	105	114.5	120
HDPE+2% Nanoclay	101.69	109.4	117
HDPE+3% Nanoclay	96.67	102	112.5
HDPE+4% Nanoclay	96.67	99.5	107.2

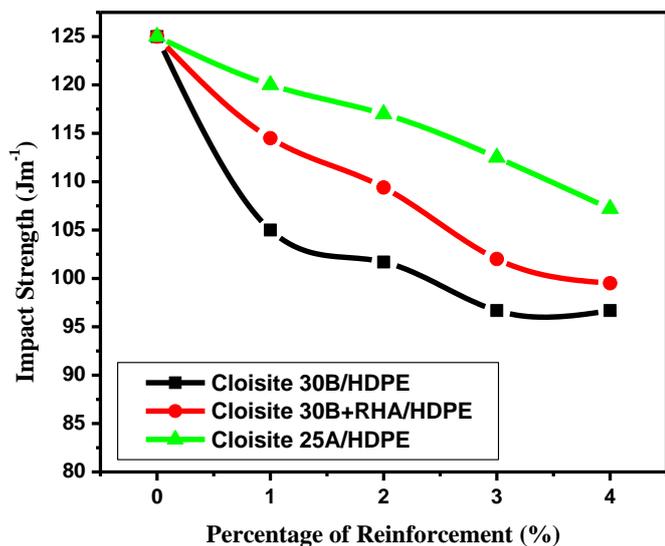


Figure 5. Percentage of nanoclays versus Izod Impact strength of different nanoclays reinforced HDPE nanocomposites

This drop in impact strength could be due to pooling of nanoclay particles impacting more hardness, more heterogeneity at lower impact resistance loss. The impact strength normally during processing, the clay addition can agglomerate (with increasing wt %) zones of weakness or pores affecting the strength properties. Among three nanoclays Cloisite 30B, Cloisite 25A and hybrid of clay Cloisite 30B and RHA impact resistance / strength often dropped down and also a marginal reduction in impact strength could be seen with higher % wt addition.

CONCLUSION

The performance behavior has been studied with the help of the flexural, tensile, impact, hardness analyses for Plain HDPE, MMT-HDPE, Cloisite 30B + RHA-HDPE, Cloisite 25A-HDPE and Cloisite 30B-HDPE. It was found that MMT-HDPE nanocomposite had the greater flexural and hardness performance among the nanocomposites prepared in the present investigation. It was also observed that the additional reinforcement of RHA played a significant role in enhancing the performance of the nanocomposite of Cloisite 30B. Tensile and Impact strengths of Cloisite 25A were found to be greater among the nanocomposites.

The flexural strength of MMT reinforced with HDPE is higher at 3wt % (36.67 Mpa) at 3600 cycles, flexural modulus is higher at 1 wt % (2109.3 MPa). The tensile strength of MMT reinforced with HDPE is higher at 4 wt %, Impact strength and hardness number are higher at 3 wt % compared with other reinforcements. The higher flexural strength and flexural modulus of 4wt % hybrid Cloisite 30B with RHA.

The higher tensile strength has been obtained at 2wt % nanoclay addition. Hardness number has increased with the addition of nanoclay, whereas the impact strength has decreased with the addition of nanoclay.

Cloisite 25A reinforcement nanocomposites, the flexural strength and tensile strength are higher at 4 wt % and 3wt% respectively. The hardness number of Cloisite 25A has increased (at 4 wt %) with the addition of nanoclay, whereas impact strength has decreases with addition of nanoclay.

The Cloisite 30B addition with HDPE composites has given higher flexural strength at 2 wt. % (36.52 MPa) at 3600 cycles and flexural modulus is higher at 1 wt.% nanoclay. The tensile strength of Cloisite 30B has improved at 4 wt % of reinforcement. The hardness number has increased at 4 wt % (63.2) with the addition of nanoclay, whereas impact strength has decreased with addition of nanoclay.

The industrial application of HDPE includes shopping plastic bags, food packaging plastics, water pipes of varying capacity, crates and dustbins. Detergent bottles and drums were produced by blow molding. Glass-ceramic/high density polyethylene has been used for tissue substitution and bone replacements. As HDPE nano composites are environmentally friendly material and exhibits enhanced bioactivity, these materials are used in the applications like wind turbine blade manufacturing.

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