

HDPE-Fly Ash/Nano Fly Ash Composites

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ABSTRACT: Fly ash (FA) based polymer composites are assuming increasing importance because of its potentiality, fine particle size and plenty availability of FA. FA is mainly a mixture of inorganic metal oxides such as SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O, TiO₂, and so forth. This article highlights the results of the various modifications onto the HDPE-FA/nano structured FA (NFA) composites. When FA and NFA are melt blended with HDPE it gives rise to improved flexural properties only. Further modifications, that is, Maleic anhydride (MA) grafting of the matrix, electron beam irradiation of the composite and irradiation of the FA/NFA studied separately to find their impact on the detail properties of the composite. Of the three modifications implemented the electron beam irradiation of HDPE-FA/NFA composite yielded excellent physico-mechanical, thermal and dynamic mechanical properties. Fracture surface analysis of the HDPE, unmodified and modified FA/NFA composites studied employing SEM correlated well with the physico-mechanical properties. The results prove that FA is valuable reinforcing filler for HDPE and its size reduction to nano level is a more effective criterion for its future use. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

KEYWORDS: composites; mechanical properties; irradiation

Received 30 March 2013; accepted 4 July 2013; Published online 00 Month 2013

DOI: 10.1002/app.39733

INTRODUCTION

FA utilization is gaining vast importance in the scientific arena owing to its contamination in the atmosphere posing a severe threat to the environment. Its disposal is a great challenge faced by the environmentalists and techniques to use it effectively is a concern worldwide.

FA is basically the inorganic residue of thermal power stations produced by the combustion of coal and its utilization as a filler in polymer matrix can result in reduction of production cost of the finished products. HDPE is the important and common commodity thermoplastic made from petroleum and is in high demand owing to its high strength, stiffness, toughness, low cost, low permeability to moisture and other oxidizing agents, good elongation and potentiality to withstand surface impacts. It has wide applications in packaging and other commercial products.

Reinforcement of HDPE with FA available in plenty as a byproduct of industries has been studied exclusively by various researchers. Ahmad and Mahanwar¹ studied the mechanical properties of three different particle sizes of FA in HDPE matrix and observed increase in tensile and flexural strengths and

moduli with reduction in tensile elongation for particles with smallest size. Atikler et al.² studied the mechanical and morphological properties of recycled HDPE-calcium carbonate/FA composites and observed significant improvements in the mechanical properties and better interfacial adhesion in the composite with silane treatment of FA. Deepthi et al.³ reported that silane coupling agent treatment of FA cenospheres and HDPE-g-dibutyl maleate as compatibilizer helps in improving the mechanical properties and thermal stability of the HDPE-FA composites. Chand et al.⁴ observed excellent compatibility between the FA cenospheres and HDPE matrix by modification of FA cenosphere surface using silane treatment that resulted in considerable improvement in the impact strength and density of the composites which ultimately translated into better wear performance of composites even in severe abrasive conditions. Baglari et al.⁵ investigated the thermal stability and the effective thermal conductivity of the FA filler embedded in HDPE matrix and found enhancement in both the properties. Saude et al.⁶ presented detail studies on a new polymer-ceramic composite material consisting of palm oil FA and HDPE powder.

Extensive literature also exists on the utilization of FA as a reinforcing filler in various thermoplastic,^{7–12} thermosetting

plastic,^{13–17} elastomers,¹⁸ various kinds of rubber,^{19,20} thermo-set/thermoplastic blend^{21,22} and recycled polymer^{23,24} matrices. These FA filled polymer matrix composites has economic and commercial importance. They possess attractive mechanical, thermal, electrical properties with better dimensional stability and are cost effective. Studies also reveal that the reduction in particle size of FA to nano level enhances the mechanical properties of the polymer matrix composites.^{25,26}

In our earlier publication²⁷ we have presented exclusive studies on the effect of FA in the presence and absence of silane coupling agent onto waste PE/reclaim rubber blends. Considerable improvements in the tensile strength, flexural strength, flexural modulus, impact strength and hardness of the blend composites were reported. The effect of FA/NFA onto waste PE²⁸ was also studied in our previous article with detail investigation of the composite properties.

To our knowledge, the reinforcement of virgin HDPE with NFA has not been studied previously. In the present work, virgin HDPE was used as the matrix and FA/NFA were used as reinforcing filler. An attempt has been made to improve the adhesion between FA/NFA and HDPE by subjecting the polymer, composite and filler to various modifications. First, the HDPE matrix was modified by grafting with MA and the composite prepared, secondly HDPE-FA/NFA composites were prepared and subjected to electron beam irradiation and finally the FA/NFA were pre-irradiated and the composite prepared. Detail investigations on the physico-mechanical, thermal, dynamic mechanical and ageing properties of the HDPE-FA/NFA composites have been studied and compared along with fracture surface analysis.

EXPERIMENTAL

Materials Used

HDPE (B 6401) (blow molding grade) having MFI: 0.41 g/10 min and density: 0.96 g/cm³ was purchased from Haldia Petrochemicals Limited, India. FA (class F type) having a density of 2.33 gm/cm³ and total evaporable moisture content of 1.54% was purchased from Kolaghat Thermal Power Station, West Bengal, India and used as filler. It was sieved using ASTM meshes ranging in size from 72 to 350 and then dried at 100°C for 24 h. The particle size of FA falls in the range of 60–100 μm. MA was obtained from Loba chemie, Mumbai, India and Dicumyl peroxide (DCP) from Aldrich chemie, Bangalore, India.

Preparation of NFA

NFA was prepared by mechanical activation process through particle size reduction of FA from micron level to the nano level using a high-energy planetary ball mill (Pulverisette, Fritsch, Germany). The total duration of milling was 60 h. The following milling conditions were maintained: loading of the ball mill with 10 : 1 ratio of balls to FA and milling chamber and balls were of tungsten carbide, the ball diameter was 10 mm. Toluene was used as the medium with an anionic surface active agent to avoid agglomerations; rotation speed of the planet carrier was 300 rev min⁻¹. The NFA obtained has an average particle size of 148 nm and specific area of 25.53 m²/g. The % oxide

composition of FA is Al₂O₃(32.16%), SiO₂(59.23%), CaO(0.99%), Fe₂O₃(5.03%), TiO₂(2.59%) and the % oxide composition of NFA is Al₂O₃(27.8%), SiO₂(62.82%), CaO(1.32%), Fe₂O₃(6.06%), TiO₂(1.99%).

Preparation of HDPE-FA/NFA Composites

HDPE-FA (5–20 wt %)/NFA (1–7 wt %) composites were prepared by melt blending in the Brabender Plasticorder at a speed of 80 rpm and temperature of 180°C for 8 min. Before melt blending FA, NFA and HDPE polymer were predried at 80°C for 2 h. Subsequently, the melt mixed composite was brought to room temperature and taken for specimen preparation.

Specimen Preparation

Molded sheets of 3-mm thickness of the virgin matrix and the composites were prepared using an electrically heated compression molding hydraulic press at a temperature of 180°C, pressure 5 MPa for 2 min followed by cooling to room temperature under the same pressure. Finally various testing samples were cut from the sheet as per various ASTM standards.

Modification of the HDPE Matrix by Grafting with MA and Preparation of the Composites

In a separate experiment, HDPE was reactive grafted with MA in the molten state in the Brabender Plasticorder, by incorporating 0.2% DCP and 1% MA based on the total amount of the matrix prior to addition of the FA/NFA. 1% of MA was incorporated into the molten matrix after 4 min of melt blending of the HDPE and the grafting reaction was carried out for four more minutes following which 5 wt % FA/NFA were incorporated and further melt blended for eight more minutes. The temperature and rotor speed were maintained at 180°C and 80 rpm, respectively.

Electron Beam Irradiation of the Composites

Electron beam irradiation of the HDPE-FA/NFA (5 wt %) was carried out at a constant dose of 250 kGy only. The irradiation of the samples was carried out in the electron beam accelerator located in NICCO Corporation, Kolkata, India with specifications of 1–3 MeV energy, 50 mA current and 50 kW power. The FA/NFA were also pre-irradiated with electron beam at 250 kGy and subsequently 5 wt % of each was melt blended with HDPE at the same processing conditions as discussed in our previous section.

FTIR Analysis

Thin films of HDPE and MA-g-HDPE were prepared in a compression molding hydraulic press between two parallel plates. FTIR study of the thin film specimens were performed using the Perkin Elmer Spectrum GX spectrometer in the wavelength range varying from 4000 to 400 cm⁻¹.

Physico-Mechanical Properties

Tensile test was carried out in accordance with ASTM D638 (Standard test method for tensile properties of plastics) using dumbbell shaped specimens, of type IV. Crosshead speed was maintained at 50 mm/min. Flexural test was conducted as per ASTM D790 (Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials) at a crosshead speed of 1.2 mm/min with specimen dimension 65 × 12.7 × 3 mm³. A minimum of five replicate samples were tested for each composition and the data reported

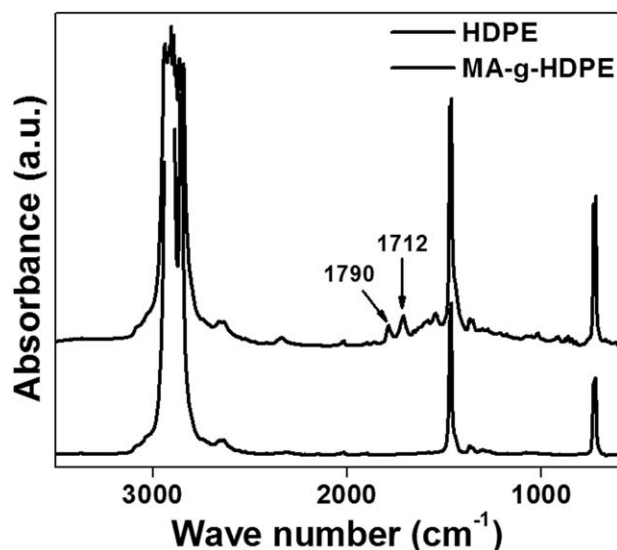


Figure 1. FTIR spectra of MA-g-HDPE.

were average of five specimens. The tensile and flexural tests were carried out in Universal Testing machine (Hounsfield, Model H25 KS) at room temperature. The tensile impact energy of the composites was measured using an Impact Tester (6545/000) as per DIN 53448 (Testing of plastics, tensile impact test). The Shore D hardness measurement was performed according to ASTM D2240 (Standard test method for rubber property, Durometer hardness) by a Shore-D Durometer (STD-D).

Thermogravimetric Analysis

The HDPE matrix, unmodified as well as modified HDPE-FA/NFA composites were subjected to thermo gravimetric analysis using TGA (TA instruments, Model TG Q50) equipment. Samples of ~ 10 mg were heated from room temperature to 600°C at a heating rate of $20^\circ\text{C}/\text{min}$ in nitrogen atmosphere. Corresponding TGA data, weight loss and derivative weight loss were reported.

Dynamic Mechanical Analysis

The DMA of the HDPE-FA/NFA composites was performed in a Dynamic Mechanical Analyzer (2980 V1.7B, TA instruments) using the dual cantilever mode. The test samples were rectangular in shape, 35-mm long, 12.79-mm wide and 3.17-mm thick. The tests were performed at 1 Hz frequency and the sample temperature was raised from -50 to $+120^\circ\text{C}$ at a rate of $5^\circ\text{C}/\text{min}$ in an atmosphere of nitrogen. The storage modulus (E'), loss modulus (E'') and the loss tangent ($\tan \delta$) were subsequently measured from these tests.

Scanning Electron Microscopy

JEOL-JSM-5800 along with ZEISS EVO 60 Scanning Electron Microscopes (SEM) were used to study the surface topography of the tensile fracture surfaces of the HDPE-FA/NFA composites to understand the failure mechanism. Before examination, the fracture surfaces were sputter-coated with a thin layer of gold in a vacuum chamber. The samples were scanned at 0° tilt angle.

Transmission Electron Microscopy

TEM studies of the HDPE-NFA nanocomposites were carried out using JEOL 2010 Japan TEM for understanding the dispersion of NFA and pre-irradiated NFA in the HDPE matrix.

Ageing Studies

Tensile specimens of the HDPE-FA/NFA composites were subjected to air ageing at 70°C for 96 h in an air-circulating ageing oven (Blue M Electric, IL) according to ASTM D573-1994 (Standard test method for rubber-Deterioration in an air oven). Tensile properties of the aged samples were determined using a Universal Testing Machine (Hounsfield, Model No.H25 KS).

Statistical Analysis

All mechanical data were statistically analyzed. The mechanical properties of the HDPE-FA/NFA composites with variation in FA/NFA loading was statistically analyzed using *t*-test at 0.001 level of significance, while the mechanical properties of the modified HDPE-FA/NFA composites were analyzed using ANOVA at 0.05 significance level.

RESULTS AND DISCUSSION

FTIR Analysis

Figure 1 shows the FTIR spectra of HDPE, MA-g-HDPE. The new absorption bands appeared at 1790 cm^{-1} attributed to asymmetric stretching modes of carbonyl ($\text{C}=\text{O}$) of saturated maleic anhydride and 1712 cm^{-1} attributed to symmetric stretching of carbonyl ($\text{C}=\text{O}$) of maleic acid in the spectra of the resultant sample. This indicates successful grafting of MA groups on to the PE chains.^{29,30}

Physico-Mechanical Properties

Effect of FA/NFA Loading on the Physico-Mechanical Properties of Unmodified HDPE-FA/NFA Composites. The physico-mechanical properties of composites depend mostly on the nature, size and distribution of filler along with adhesion between the filler and the polymer matrix. Effect of FA/NFA loading on the physico-mechanical properties of HDPE-FA/NFA composites is represented in Table I.

It is evident from Table I that incorporation of FA (5–20 wt %) within the HDPE matrix results in a significant increase in the flexural strength and modulus of the matrix polymer ($P = 0.001$). This owes to the fact that in filled systems; reinforcing filler contributes to an increase in modulus due to effective stress transfer from the matrix to the filler at the interface.^{9,31} The hardness values also show an increasing trend with increase in the concentration of FA owing to the higher siliceous content of FA. FA is siliceous nature filler and this composition results in higher hardness in the composites in turn higher rigidity.³² However, the tensile strength and elongation at break decreases with FA loading from 5 to 20 wt %, revealing incompatibility and poor interfacial adhesion of the FA particles with the HDPE matrix. The observations are in concurrence with composites of FA filled polypropylene,¹⁰ Acrylonitrile butadiene styrene,³³ nylon 6¹³ and polyester¹⁸ matrices. The tensile impact strength decreased tremendously from 437 to $264\text{ kJ}/\text{m}^2$ with only 5 wt % loading of FA. A decreasing trend in tensile impact strength of HDPE matrix was observed with further increase in FA loading. This decrease in the impact strength was explained by Sreekanth et al.¹⁸ in case of mica and FA reinforced polyester composites that as the concentration of filler increases the elasticity of the material reduces thereby

Table I. Effect of FA/NFA Loading on the Physico-Mechanical Properties of HDPE-FA/NFA Composites

Sample code	FA (wt %)	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Hard-ness Shore D	Tensile impact strength (kJ/m ²)
HDPE-FA	0	24.2 ± 0.2	743.0 ± 21.0	20.8 ± 0.4	876 ± 4	40	437 ± 30
	5	20.8 ± 0.2 ^a	24.1 ± 2.3 ^a	31.5 ± 0.2 ^a	1136 ± 57 ^a	44	264 ± 2 ^a
	10	19.7 ± 0.3 ^a	20.1 ± 0.1 ^a	33.4 ± 0.3 ^a	1232 ± 12 ^a	47	240 ± 3 ^a
	20	17.3 ± 0.2 ^a	14.0 ± 0.2 ^a	33.8 ± 0.2 ^a	1260 ± 10 ^a	50	232 ± 5 ^a
HDPE-NFA	0	24.2 ± 0.2	743.0 ± 21.0	20.8 ± 0.4	876 ± 4	40	437 ± 30
	1	19.8 ± 0.2 ^a	58.7 ± 2.5 ^a	23.5 ± 0.2 ^a	1001 ± 20 ^a	42	280 ± 6 ^a
	3	21.0 ± 0.1 ^a	60.0 ± 3.2 ^a	24.0 ± 0.5 ^a	1063 ± 12 ^a	43	278 ± 1 ^a
	5	22.6 ± 0.2 ^a	92.8 ± 1.6 ^a	29.7 ± 0.1 ^a	976 ± 38 ^a	46	246 ± 5 ^a
	7	21.3 ± 0.2 ^a	83.2 ± 2.0 ^a	27.6 ± 0.3 ^a	888 ± 12 ^a	48	238 ± 4 ^a

^aP = 0.001.

reducing the deformability of the matrix and its ability to absorb deformation energy.

It is clear from Table I that incorporation of NFA (1–7 wt %) within the HDPE matrix results in a significant increase in flexural strength and modulus ($P = 0.001$) along with hardness of the matrix polymer upto 5 wt % of NFA followed with a decrease at 7 wt %. At lower concentration matrix-filler interaction occurs due to reduction in size from micron to nano level. Spherical shape of FA is destroyed with formation of irregular surface and these structural factors also contribute to interactions with the polymer matrix.²⁸ At higher concentration the properties decrease indicating phenomenon of agglomeration and reduced matrix-filler interaction. However, the tensile strength and elongation at break decreased initially at 1 wt % of NFA followed with a linear increase to 5 wt % of NFA in the HDPE matrix. The increase in tensile strength may be attributed to the formation of intercalated and exfoliated structures at these loadings of NFA that probably acts as nano clay due to mechano-chemical breakdown as explained by Paul et al.²⁵ for NFA filled styrene butadiene rubber matrix. The increase in elongation at break was also observed by Sreekanth et al.³¹ for smaller particle size FA in comparison with the larger ones in FA filled polyester thermoplastic elastomer composites. However

with further incorporation of 7 wt % NFA, the tensile strength and elongation at break decreased. This decrease may be due to agglomerations of the NFA in the HDPE matrix as explained earlier. The tensile impact strength steadily decreased with NFA loading from 1 to 7 wt % as was in the case of FA loading.

Because HDPE-FA/NFA composites with 5 wt % of FA/NFA exhibited optimum physico-mechanical properties, this composition was retained for further modifications in composites.

Effect of Modifications on the Physico-Mechanical Properties of the Composites. The effect of matrix, composite and filler modifications individually on the physico-mechanical properties of HDPE-FA/NFA (5 wt %) composites is displayed in Table II. To improve the bonding between the polymer matrix and FA/NFA, the HDPE was modified in situ by grafting with MA in presence of DCP as initiator [MA-g-HDPE-FA/NFA] (matrix modification). Also the HDPE-FA/NFA composites were irradiated at 250 kGy radiation dose [HDPE-FA/NFA (irr.)] (composite modification) and finally the FA/NFA were pre-irradiated at 250 kGy followed with preparation of composite [HDPE-irr.FA/NFA] (filler modification). 250 kGy radiation dose was chosen as it was found to be the optimum from our earlier study on

Table II. Effect of Modifications on the Physico-Mechanical properties of HDPE-FA/NFA Composites

Sample code	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Hardness shore D	Tensile impact strength (kJ/m ²)
HDPE	24.2 ± 0.2	743 ± 21	20.8 ± 0.4	876 ± 4	40	437 ± 30
HDPE-FA	20.8 ± 0.2	24.1 ± 2.3	31.5 ± 0.2 ^a	1136 ± 57 ^a	44	264 ± 2
MA-g-HDPE-FA	29.4 ± 0.1 ^a	15.4 ± 3.1	38.5 ± 0.2 ^a	1913 ± 14 ^a	58	235 ± 5
HDPE-FA (irr.)	35.3 ± 0.2 ^a	7.5 ± 0.2	44.9 ± 0.4 ^a	2250 ± 10 ^a	62	232 ± 9
HDPE-irr.FA	23.9 ± 0.2	7.9 ± 0.2	19.5 ± 0.5	860 ± 6	46	179 ± 41
HDPE-NFA	22.6 ± 0.2	92.8 ± 1.6	29.7 ± 0.1 ^a	976 ± 38 ^a	46	246 ± 5
MA-g-HDPE-NFA	31.8 ± 0.2 ^a	65.4 ± 2.2	44.8 ± 0.1 ^a	1268 ± 5 ^a	66	282 ± 14
HDPE-NFA (irr.)	35.7 ± 0.2 ^a	29.4 ± 2.2	46.8 ± 0.3 ^a	2460 ± 12 ^a	70	224 ± 13
HDPE-irr.NFA	24.1 ± 0.3	29.8 ± 0.3	18.7 ± 0.5	774 ± 4	48	212 ± 7

^aP ≤ 0.05.

the effect of electron beam irradiation on waste polyethylene, virgin polyethylene and their blends.³⁴

The tensile and flexural strength of HDPE increases significantly from 24.2 and 20.8 MPa to 29.4 MPa (21%) and 38.5 MPa (85%), for MA-g-HDPE-FA composites ($P \leq 0.05$). There is a significant increase in the tensile strength of HDPE to 31.8 MPa (31%) ($P \leq 0.05$) and flexural strength to 44.8 MPa (115%) ($P \leq 0.05$), for MA-g-HDPE-NFA composites. The flexural modulus of HDPE also exhibits a significant increase from 876 to 1913 MPa (12%) ($P \leq 0.05$) for MA-g-HDPE-FA composites and to 1268 MPa (44%) ($P \leq 0.05$) for MA-g-HDPE-NFA composites. The hardness values increase from 40 for HDPE to 58 (45%) for MA-g-HDPE-FA composites and to 66 (65%) for MA-g-HDPE-NFA composites. This improvement owes to the enhanced polymer-filler interactions and the increase in mechanical properties is more significant for HDPE-NFA composites due to smaller particle size of NFA. The improvement can be attributed to the presence of polar anhydride group, which promotes hydrogen bonding between the FA/NFA and the maleated PE, thus leading to improved intercalation and adhesion of FA/NFA in polymer matrix. This similar trend was observed by Mehrabzadeh et al.²⁹ for the mechanical properties of MA grafted HDPE/clay nanocomposites.

The tensile and flexural strength of HDPE increased significantly to 35.3 MPa (46%) ($P \leq 0.05$) and 44.9 MPa (115%) ($P \leq 0.05$) for irradiated HDPE-FA composite, to 35.7 MPa (47%) ($P \leq 0.05$) and 46.8 MPa (125%) ($P \leq 0.05$) for irradiated HDPE-NFA composite, respectively. It may be attributed to the radical-radical reactions leading to chemical bonding between the filler and polymer matrix upon irradiation of the hybrid composite. It is a fact that upon irradiation of the hybrid composite chemically active sites are created on the polymer, that is, HDPE surface as it is a radiation crosslinkable polymer³⁵ and also radical formation is induced on the filler surface. According to Charlesby,³⁶ radiation of PE leads to Hydrogen abstraction along the long chains followed by radical cross-linking forming a larger polymer complex with evolution of hydrogen gas. The main cross-link reaction can be represented as shown below.



In the composite system, radical formation of HDPE and FA/NFA leads to the probable cross linking between the two materials contributing to the enhancement in the strength properties upon irradiation. The flexural modulus and hardness exhibited a significant increase from 876 MPa and 40 to 2250 MPa (156%) ($P \leq 0.05$) and 62 (55%) for irradiated HDPE-FA composite, to 2460 MPa (180%) ($P \leq 0.05$) and 70 (75%) for irradiated HDPE-NFA composites in comparison with that of HDPE. The improvement in physico-mechanical properties is better in case of NFA filled HDPE composites as compared to that of FA filled HDPE composites after modification. The elongation at break and tensile impact strength of the HDPE-FA/NFA composites decreases further with modifications.

Table II also depicts the physico-mechanical properties of the HDPE-FA/NFA composites with addition of pre-irradiated FA/NFA at 250 kGy radiation dose. It is observed that there is practically no change in the tensile strength, elongation at break, flexural strength and modulus of the composites in comparison with virgin HDPE. This can be owed to the fact that irradiation of the FA/NFA as such at 250 kGy and then preparation of the composites with HDPE probably does not contribute in increasing the polymer-filler adhesion resulting in no improvement in the properties of the composites. The tensile impact strength and hardness values decrease with addition of pre-irradiated FA/NFA to the HDPE matrix. The decrease in the properties is further supported by fracture surface analysis by SEM in later section.

Thermal Analysis

Introduction of filler into the polymer matrix increases the thermal stability owing to high temperature degradation in comparison to the later.⁹ Figure 2(a,b) shows the weight loss and derivative weight loss curves of unmodified and modified HDPE-FA/NFA composites. Test results indicate that the incorporation of FA/NFA into HDPE polymer matrix increases the thermal stability. An increase in thermal stability was observed by other researchers^{3,5} as well for FA filled HDPE matrices with various treatments.

Table III shows the initial (T_i) and maximum (T_{max}) rate of thermal decomposition and amount of residue left at 600°C for HDPE, modified and unmodified HDPE-FA/NFA composites. Among the modified FA/NFA composites, electron beam irradiated FA/NFA composite shows higher thermal stability over the entire temperature range. It is evident from Figure 2(a,b) that the modified and unmodified FA/NFA composites show increased T_{max} values which indicated higher stability and the amount of residue is more at the end of the test. The electron beam irradiated FA/NFA composite shows the highest T_{max} value, which signifies that the loss of weight against temperature is less. Hence, electron beam irradiated HDPE-FA/NFA composite display higher thermal stability as compared to other modified, unmodified composite and HDPE polymer. The

enhancement in thermal stability of HDPE-FA/NFA composite upon irradiation is primarily due to increase in bonding between the FA/NFA particles and HDPE matrix, restricting chain mobility and breakage at higher temperatures.

The values of T_i and T_{max} shown in Table III suggests that the HDPE-NFA composites impart slightly improved thermal properties in comparison with HDPE-FA composites before and after electron beam irradiation and are more stable. This is due to the behavior of NFA which acts as nanoclay resulting in increased chemical bonding within the HDPE matrix.

Dynamic Mechanical Properties of the Filled Compounds.

The dynamic mechanical properties as a function of

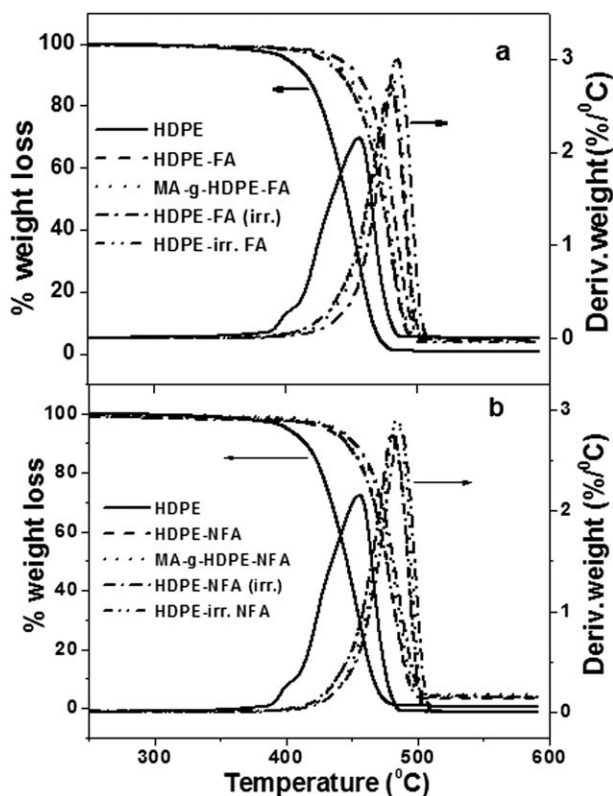


Figure 2. TGA thermographs of weight loss and derivative weight loss with temperature of (a) HDPE-FA and (b) HDPE-NFA Composites.

temperature of virgin HDPE, unmodified and modified HDPE-FA/NFA composites is represented in Figures 3(a–c) and 4(a–c). The FA/NFA loading has been retained at 5 wt % and comparative account of the variation in dynamic mechanical properties is presented.

The variation of the E' moduli of the HDPE, HDPE-FA, MA-g-HDPE-FA and HDPE-FA (irr.) against temperatures are shown in Figure 3(a). Also, the variation of the E' moduli of the HDPE, HDPE-NFA, MA-g-HDPE-NFA and HDPE-NFA (irr.) with temperature are shown in Figure 4(a). The E' values could be segregated into three different zones: low temperature zone (-50°C), room temperature zone (25°C) and high temperature zone (50°C). As observed in the Figure 3(a), E' for the HDPE-FA composite is much higher than that of the virgin HDPE and the values goes on increasing with MA modification of the matrix as well as of the composite upon irradiation, in the room temperature region. These results are in agreement with the flexural modulus values obtained according to ASTM D790 where the flexural modulus increases upon modification. In the low temperature zone (-50°C), the E' value for unmodified and MA grafted composites do not show any marked change. Whereas the E' value is very high for the irradiated composites as compared to others in the low temperature zone. In the high temperature zone ($+50^{\circ}\text{C}$), the E' value for MA grafted and irradiated composites are almost the same. In case of HDPE-NFA composites also E' value increases in comparison with that of virgin HDPE as observed from Figure 4(a). On further

Table III. Representation of Different Temperatures From TGA

Sample code	T_i ($^{\circ}\text{C}$)	T_{max} ($^{\circ}\text{C}$)	Amount of residue left (%)
HDPE	387	456	0.9
HDPE-FA	392	480	4.2
MA-g-HDPE-FA	408	481	5.1
HDPE-FA (irr.)	422	484	4.2
HDPE-irr.FA	403	479	3.8
HDPE-NFA	406	482	3.3
MA-g-HDPE-NFA	417	485	4.7
HDPE-NFA (irr.)	424	488	4.1
HDPE-irr.NFA	407	481	3.3

modification of the matrix by MA grafting and irradiation treatment of the composite, the E' value increases. The increase in E' value with matrix modification as well as composite exposure to electron beam is due to restrictions in the mobility of the chain segments with increased matrix-filler and matrix-matrix interactions, that is, covalent bond formation. However, for the MA modified matrix composite the value of E' reduces in the low temperature zone as compared to that with the unmodified and irradiated composites. In conclusion, the irradiated composite exhibits the best balance in dynamic properties, that is, increase in E' value at all low, room and high temperature zones. It is also observed that E' reduces with increase in temperature for the neat HDPE and its composites with FA and NFA and with modification of the matrix.

The E'' values for the HDPE, HDPE-FA/NFA, MA-g-HDPE-FA/NFA and HDPE-FA/NFA (irr.) are presented in Figure 3(b) for FA and Figure 4(b) for NFA composites. The E'' values increase on addition of both FA and NFA as well as with MA modification of the matrix in comparison with HDPE. The E'' maximum of the irradiated composite becomes broader with radiation dose and the E'' is highest owing to maximum internal friction between the polymer and filler causing large viscous dissipation.

The variation in the $\tan \delta$ with incorporation of FA/NFA onto HDPE and modification thereof are shown in Figures 3(c) and 4(c). The $\tan \delta$ is the highest for the unfilled HDPE at both low and high temperature zones that decreased on incorporation of both FA/NFA as well as on modifications. The incorporation of FA/NFA onto HDPE restricts the mobility of the polymer molecules in turn increases the E' values and decreases the $\tan \delta$ values.

In case of HDPE, the α' relaxation temperature increases from 47°C [for HDPE-FA], to 52°C [for MA-g-HDPE-FA] and to 54°C [for HDPE-FA (irr.)] composites as shown in Figure 3(b). In this case, α' transition temperature is observed from the E'' peak. Slight increase in α' transition temperature is observed on incorporation of FA and modification. The α' transition temperature for HDPE increases from 47°C [for HDPE-NFA], to 56°C [for MA-g-HDPE-NFA] and to 58°C [for

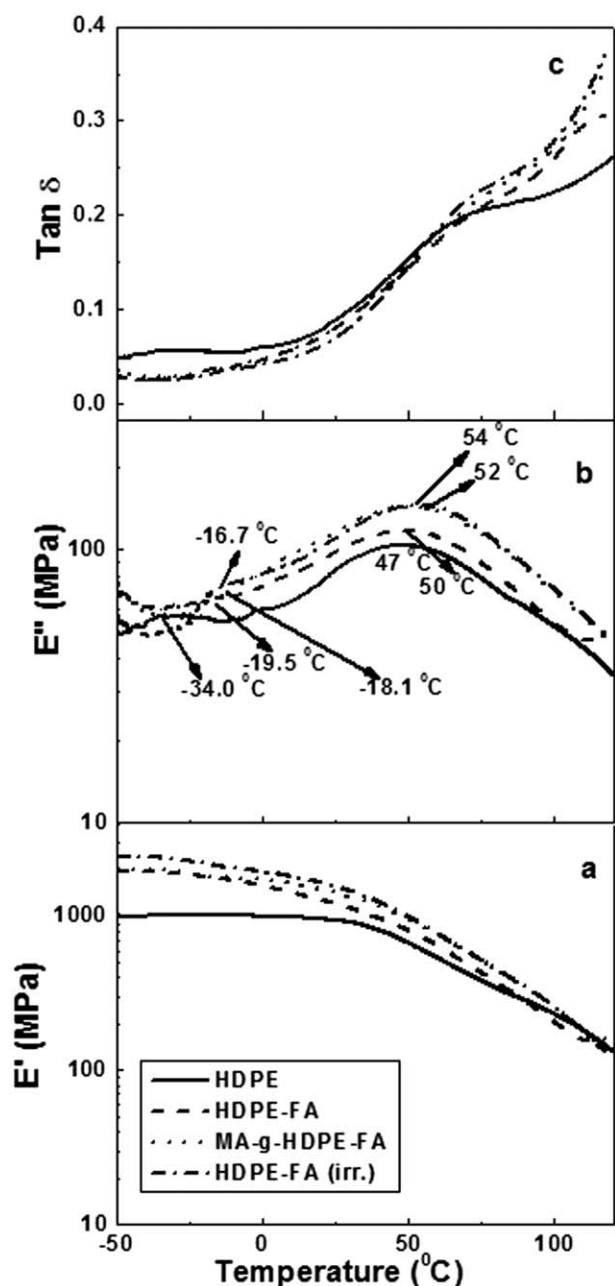


Figure 3. Variation of (a) E' , (b) E'' and (c) $\text{Tan } \delta$ with temperature of HDPE and HDPE-FA Composites.

HDPE-NFA (irr.)] composites as shown in Figure 4(b). In this case also there is a slight increase in the α' transition temperature. The increase in this α' transition temperature is attributed to crosslinking in the composites that restricts the chain mobility.

The β transition peak temperature, that is, the temperature at which maximum in E'' occurs, for the HDPE and its composites with FA/NFA are reported in Figures 3(b) and 4(b). In case of HDPE as seen in Figure 3(b), β relaxation temperature is observed at -34.0°C which increases to -19.5°C [for HDPE-FA], to -18.1°C [for MA-g-HDPE-FA] and to -16.7°C [for HDPE-FA (irr.)] composites. In Figure 4(b) it is observed that

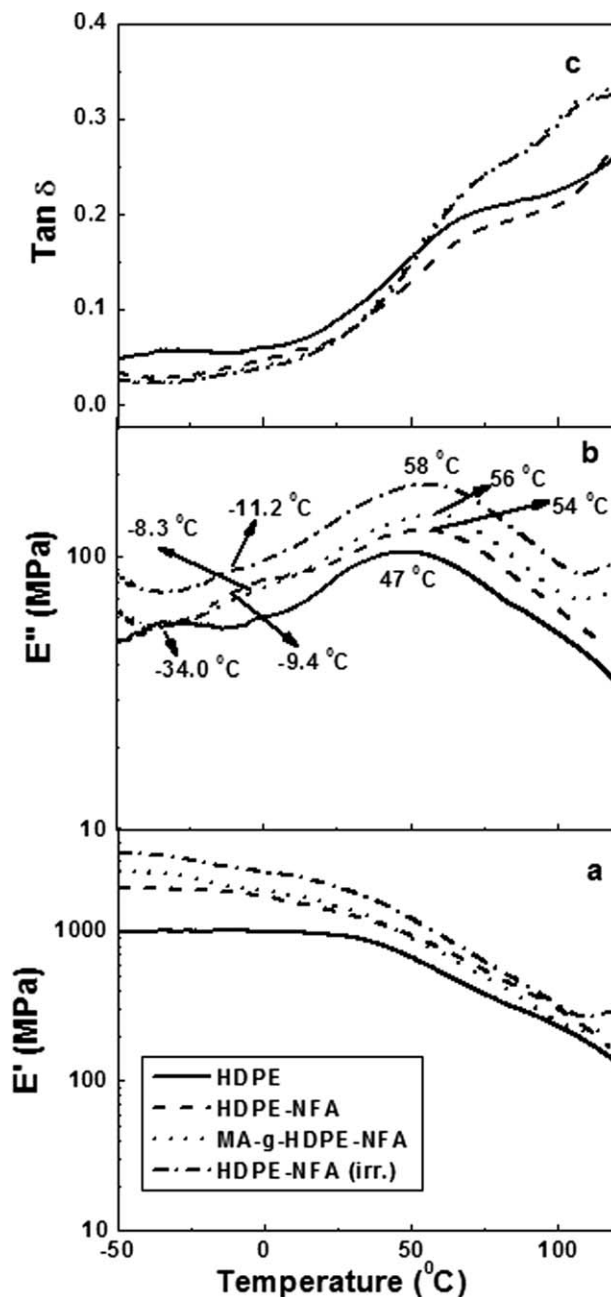


Figure 4. Variation of (a) E' , (b) E'' and (c) $\text{Tan } \delta$ with temperature of HDPE and HDPE-NFA Composites.

the β transition peak temperature of HDPE increased to -9.4°C [for HDPE-NFA], to -8.3°C (for MA-g-HDPE-NFA) and to -11.2°C [for HDPE-FA (irr.)] composites. The increase in the β relaxation temperature is due to strong interaction between the HDPE matrix and FA/NFA filler surface resulting in broadening of the E'' peak.

Fracture Surface Analysis

The tensile fractured surfaces of the neat HDPE and FA/NFA filled HDPE composites were also analyzed. The tensile fractured surface of virgin HDPE [Figure 5(a)] shows a fibrillar structure with striations parallel to each other. A ductile mode of failure is observed. The tensile fractured surface of HDPE-FA

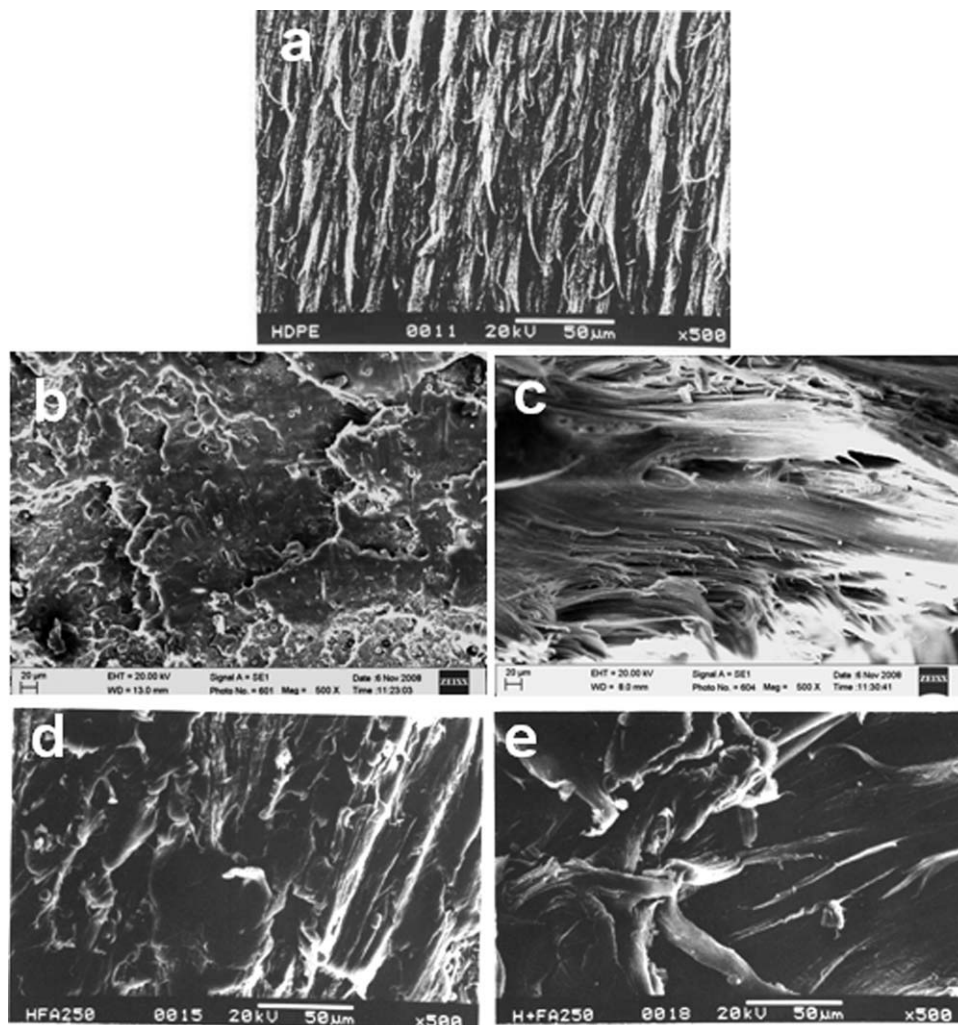


Figure 5. SEM micrographs of tensile fractured surfaces of (a) HDPE, (b) HDPE-FA, (c) MA-g-HDPE-FA, (d) HDPE-FA (irr.) and (e) HDPE-irr.FA.

[Figure 5(b)] shows that the FA particles are well embedded in the HDPE matrix showing an irregular fracture path with brittle type failure. Figure 5(c) shows the tensile fractured surfaces of MA-g-HDPE-FA composite with large flow lines and striations running from one end to the other and a ductile failure. It also has a tendency of fibril formation due to excessive stress. Figure 5(d) shows the tensile fractured surface of HDPE-FA (irr.) composite showing deep furrows on the surface and implying that radiation dose has changed the network structure completely supporting higher strength property. The tensile fractured surface of HDPE-irr.FA composite [Figure 5(e)] shows knotty failure indicating brittle fracture but exhibits reduced mechanical properties.

The tensile fractured surface of HDPE-NFA composite [Figure 6(a)] shows a more uniform distribution of NFA particles in the HDPE matrix exhibiting a porous structure and a well knitted matrix that helped in increasing the mechanical properties. The tensile fractured surface of MA-g-HDPE-NFA composite [Figure 6(b)] shows that the NFA particles are distributed uniformly in the matrix providing increased strength properties as observed earlier. It shows a smooth fracture structure with fine flow lines and ridges in between occurring across the flow lines. The tensile

fractured surface of HDPE-NFA (irr.) composite [Figure 6(c)] shows discontinuous flow path and ductile failure similar to an amorphous matrix. It may be due to greater adhesion between the filler and plastic matrix resulting enhanced mechanical properties. The tensile fractured surface of HDPE-irr.NFA composite [Figure 6(d)] show a brittle type of failure marked with dark cavities and irregular fracture path resulting in decreased properties.

TEM Analysis

The TEM analysis was carried out in order to study the distribution of non-irradiated and irradiated NFA in the HDPE matrix. Figure 7(a,b) shows the TEM image of HDPE-NFA and HDPE-irr.NFA composites. From the figures it can be observed that both the irradiated as well as non-irradiated NFA are present in the form of agglomerates in HDPE.

Ageing Properties

Table IV displays the percentage retention of tensile strength as well as elongation at break for the virgin HDPE, nonirradiated as well as irradiated HDPE-FA/NFA composites after air ageing at 70°C for 96 h. The percentage retention of tensile strength as well as elongation at break for HDPE is enhanced upon

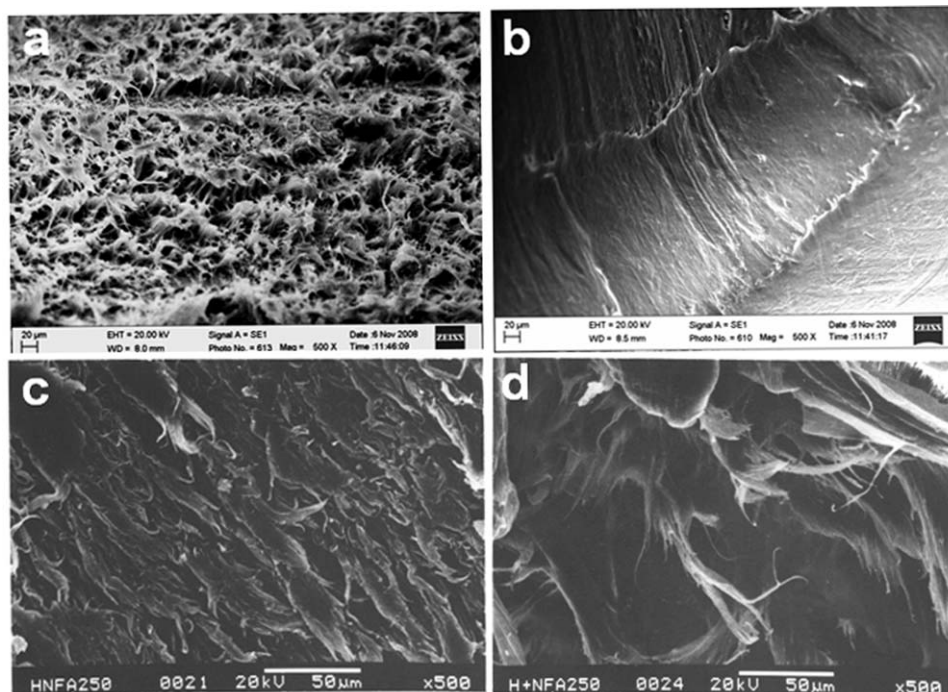


Figure 6. SEM micrographs of tensile fractured surfaces of (a) HDPE-NFA, (b) MA-g-HDPE-NFA, (c) HDPE-NFA (irr.) and (d) HDPE-irr.NFA.

incorporation of FA/NFA, which further improves upon irradiation of the composite at 250 kGy radiation dose. The NFA filled HDPE composites show an increased retention in the tensile strength as well as elongation at break after air ageing signifying the use of these composites to be economical. The enhancement in the percent retention of tensile strength and elongation at break with irradiation for both FA as well as NFA filled HDPE composites owes to increased thermal stability of the composites upon irradiation.

CONCLUSION

Addition of 5 wt % FA on to HDPE increased the flexural strength, flexural modulus and hardness of the composites to 51.4, 29.7, and 10% respectively. Similarly incase of HDPE-NFA

composite the flexural strength, flexural modulus and hardness of the composites increased to 42.8, 11.4, and 15% respectively. MA modification of the HDPE matrix and electron beam irradiation of the composite as a whole greatly improves the performance of HDPE-FA/NFA composites. The TGA analysis revealed optimum thermal stability of HDPE-FA/NFA composites with irradiation. Dynamic mechanical properties revealed higher E' and E'' of the irradiated HDPE-FA/NFA composites in comparison with virgin HDPE. SEM micrographs of the tensile fractured samples highlight a clear structure-property relationship. Ageing studies exhibit a higher retention in the tensile properties for the HDPE-FA/NFA composites suggesting their utility for future use. The decrease in particle size of FA from micron to nano level by ball milling is an efficient technique for

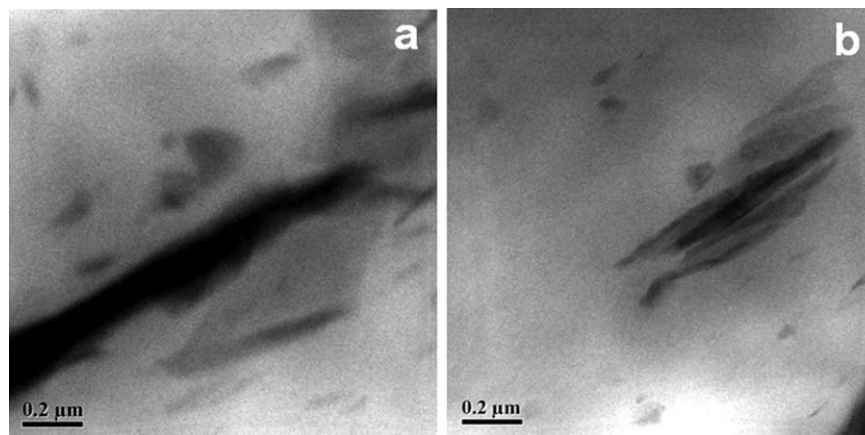


Figure 7. TEM micrographs of (a) HDPE-NFA and (b) HDPE-irr.NFA surfaces.

Table IV. Percentage Retention of Tensile Properties of HDPE-FA/NFA Composites after Air Ageing

Sample code	Tensile Strength (MPa)			Elongation at break (%)		
	Before ageing	After ageing	Retention (%)	Before ageing	After ageing	Retention (%)
HDPE	24.2 ± 0.2	23.0 ± 0.2	95.0	743.0 ± 21.0	692.0 ± 9.0	93.1
HDPE-FA	20.8 ± 0.2	19.2 ± 0.5	92.3	24.1 ± 2.3	22.9 ± 0.5	95.0
HDPE-FA (irr.)	35.3 ± 0.2	34.2 ± 0.4	96.7	7.5 ± 0.2	7.8 ± 0.3	104.0
HDPE-NFA	21.0 ± 0.1	19.9 ± 0.2	94.8	60.0 ± 3.2	58.0 ± 3.0	96.6
HDPE-NFA (irr.)	35.7 ± 0.2	35.1 ± 0.1	98.3	29.4 ± 2.2	32.0 ± 2.0	108.8

enhancement in the properties of the HDPE-NFA composites. The environmental pollution due to FA can be solved in a most profitable way by this technique.

ACKNOWLEDGMENTS

The authors thank Nicco Corporation Limited for electron beam irradiation of the samples. Dr. Sukanya Satapathy, thanks Department of Science and Technology (DST) for financial grant under Women Scientists Scheme-A (WOS-A).

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