



Effect of Chemically Modified Nano Zirconia Addition on Properties of LLDPE/LDPE/PLA/MA-g-PE Bio-nanocomposite Blown Films for Packaging Applications

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Abstract

In this study, titanate coupling agent treated Nano-zirconia particulates were used as nanofiller to prepare nanocomposite blown films by the melt blending process in a co-rotating twin screw extruder with temperature ranged from 190-230 °C. The tensile strength, elongation at break and tear strength of blown films were measured with the aid of universal testing machine (UTM) and tear strength tester. The thermal behavior of nanocomposite blown films was analyzed by means of differential scanning calorimetry (DSC). Further, the morphology of nanocomposites was observed by the help of scanning electron microscope (SEM). Results show that incorporation of Nano-zirconia at the loading 0.5, 1, 1.5, and 2 phr in the developed LLDPE/LDPE/PLA/MA-g-PE blend leads to improve the mechanical properties of the blend system. As compared to the LLDPE/LDPE/PLA/MA-g-PE blend tensile strength, elongation at break and tear strength properties of nanocomposite blown films was maximum at the loading of 1.5 phr and 1 phr of nano-zirconia respectively. Moreover, the optical properties were also used to show the effect of Nano-zirconia on Haze and transmittance. It was shown that at the lower loading of Nano-zirconia the optical properties were best due to the concentration and some nucleating effect of Nano-Zirconia on the nanocomposite blown films. DSC studies revealed that the melting temperature was increased with the addition of Nano-zirconia. The dispersion of nanofiller is visualized by SEM micrographs, which showed at the loading of 1.5 phr Nano-zirconia the dispersion is better compared to other loadings.

Keywords: Nano Zirconia (nano-ZrO₂), linear low density polyethylene (LLDPE), poly lactic acid (PLA), Titanate coupling agent, mechanical and morphological properties.

Introduction

Inorganic nanofillers have great advantages over microfillers in the polymer composite industries. Because of their small incorporation in the matrix can improves the functionalities like mechanical performance, gas barrier, dimensional stability, heat distortion temperature and other properties. A. Buasri et al investigated the effect of surface treated CaCO₃ on PP matrix. The results reveal that the addition of treated filler increased the interfacial bonding strength, mechanical strength and also the thermal stability [1, 2]. Lots of research papers can be found on modifying the properties of polymer materials by adding the nano and micro sized particles in the matrix such as calcite micro and nanoparticles, mica, boehmite alumina, ZrO₂, calcium carbonate and so on [3, 4]. In this research work Monika et al revealed that the



effect of alumina on morphological, mechanical and optical properties. They found the best properties at loading of 0.5 phr of alumina in the PP/HDPE/EVA/PLA composite system [5]. In other paper Bahareh Azinfar et al demonstrate the property investigation of polypropylene/Fumed Silica nanocomposites. They resulted that the SEM Studies revealed a good dispersion of fumed silica nanoparticles in the PP matrix. DSC analysis shows the increase in crystallization temperature and crystallinity of nanocomposite with increased fumed silica loading and also the thermal stability is increased [6]. Lucas Gonzalez et al showed the effect of stearic acid treatment on the crystallization, morphology, thermal and mechanical properties of polypropylene (PP)/montmorillonite (Mm) nanocomposites. In this article they concluded that the adding of stearic acid as an interfacial modifier improves the toughness of polypropylene (PP)/montmorillonite (Mm) nanocomposite. The showed the Mm can induce β -phase crystals. The increase in the melting temperature exhibits the improvement in mechanical properties.[7, 8] other studies based on LLDPE/Clay nanocomposite contains 5 Phr of org-clay were prepared by melt processing technique. The rheometry and linear viscosity behavior analysis showed improved interfacial interaction between the clay layers and polymer phase. [9, 10, 11]

In the nanocomposite film studies prepared by LDPE/organoclay and rice husk, with EVA and MA-g-PE as compatibilizer. The results of rheological tests, X-ray diffraction, differential scanning calorimetry (DSC), oxygen permeability and tensile tests showed better properties when using these compatibilizers. [12] K. Majeed et al. researched on MMT/rice husk hybrid and kenaf cellulose (KC) with LDPE nanocomposite films and resulted that the nanocomposite film showed better properties when 3 wt% of MMT and 50 wt% of KC is added. [13, 14]

In these literature different blends of polyurethane, polyvinyl alcohol (PVA), PA-6/ nanoclay, soy protein isolate/MMT and PLA/Epoxidized palm Olein blend films were studied and showed good properties when compared to these blend system. [15, 16, 17, 18, 19]

In this work we used nano-zirconia as filler for improving the properties of LLDPE/LDPE/PLA/MA-g-PE blend system. Mechanical, optical, thermal and morphological studies are to be found in this research article. Differential scanning calorimetry (DSC) of nanocomposite shows the thermal behavior. The interfacial interaction between nanofiller and matrix is depicted by the SEM micrographs. This work is very important for producing the nanocomposite blown films for eco-friendly and applicable for blown film preparation.

Materials and Methodology

Materials

Blown film grade Butene-linear low density polyethylene (trade name: Sabic LLDPE 118W; Density= 0.918 g/cm³, MFI= 1.0 g/10 min at 190 °C and 2.16 kg) was supplied by Saudi Basic Industries Corporation, Saudi Arabia. General purpose film grade low density polyethylene (trade name: Relene



24FS040; Density= 0.922 g/cm³, MFI=4.0 g/10 min at 190 °C and 2.16 kg) produced by Reliance polymers, India. Sheet extrusion grade Poly lactic acid (trade name: Revode 101, Density= 1.250 g/cm³, MFI= 2-10 g/10 min at 190 °C and 2.16 kg) was obtained from Zhejiang Hisun Biomaterials CO., LTD., China. Maleic anhydride grafted polyethylene (MFI- 1.5 g/10min, MAH content 0.5- 0.8 % and Density- 0.953 g/cm³) was supplied by Pluss polymers, India. Nano-Zirconia (surface area- 30 m²/g, and bulk density- 0.42 g/cm³) was supplied by Zirox technologies, India. Titanate coupling agent (EB-1019A) was purchased by IPMC, Pune, India.

Chemical Modification of Nanofiller

The chemical modification of nano-zirconia was done in the presence of titanate coupling agent. The required quantity of titanate coupling agent was calculated by the formula as given. The uniform distribution of the titanate before the polymer melt phase was essential. With the help of a high speed mixer at rotating speed of 500-600 rpm, nano-zirconia and titanate coupling agent were mixed very well for 15-20 minutes. The amount of the substance was calculated for better results.

Nanocomposite Preparation

LLDPE, LDPE, PLA and Ma-g-PE were obtained in the form of pellets. Prior to melt blending, LLDPE, LDPE, PLA, and nanofillers were air dried at 70 °C for 4 hours in an oven. LLDPE and LDPE were taken out in the weight percentage ratio. PLA and MA-g-PE was taken in Phr. In a blend of LLDPE/LDPE/PLA/MA-g-PE (85/15/10/4) titanate treated Nano-Zirconia is melt blended at 0.5 to 2 phr loadings. Formulation table is listed as below in Table 1. Different compositions of blends were taken and mixed at room temperature for 10 minutes in a high speed mixer. The melt blending process was performed with the help of co-rotating twin screw extruder (Specificq) at a screw speed of 135 rpm and feeding thought speed attuned at 45 rpm. The extruder screw has 21mm diameter and 40:1 L/D ratio. Temperature at extruder barrel feed zone to die was varied from 190 to 230 °C and screw was rotated at speed of 120 rpm. After proper blending and pelletizing these different blend compositions were dried at 80 °C for 4 hours in an oven before making nanocomposites blown film.

Nanocomposite Blown film Preparation

Blown film preparation was done after proper pelletizing and drying of extrudes, by Konark blown film machine. The dried sample compositions were taken in hopper one by one for making blown films. The temperature range for Nano-Zirconia filled nanocomposite system was 190 °C to 210 °C at 8 rpm screw speed and take up roll speed was maintained at 1 rpm.

Testing & Characterization

Mechanical testing

Universal testing machine (INSTROM) was used to test prepared samples. The tensile test was carried out according to ASTM D 882. The rectangular shaped samples had the dimensions 2.5 cm in



width and 15 cm in length. The test was conducted at a constant crosshead speed of 50 mm/min, on applied load of 1 kN and a gauge length of 10 mm. Elongation at Break was calculated by the help of UTM.

Table.1. Sample Formulations for developed nanocomposite blown films

Sample formulation	LLDPE (Wt %)	LDPE (Wt %)	PLA (phr)	MA-g-PE (phr)	Nano-ZrO ₂ (phr)	Titanate coupling agent (phr)
LLDPE/LDPE/PLA/MA-g-PE/ Nano-Zirconia (LL ₁ PZ0)	85	15	10	4	0	0
LLDPE/LDPE/PLA/MA-g-PE/ Nano-Zirconia (LL ₁ PZ0.5 T)	85	15	10	4	0.5	1
LLDPE/LDPE/PLA/MA-g-PE/ Nano-Zirconia (LL ₁ PZ1 T)	85	15	10	4	1	1
LLDPE/LDPE/PLA/MA-g-PE/ Nano-Zirconia (LL ₁ PZ1.5 T)	85	15	10	4	1.5	1
LLDPE/LDPE/PLA/MA-g-PE/ Nano-Zirconia (LL ₁ PZ2 T)	85	15	10	4	2	1

Tear strength was calculated as per ASTM D1922-09 test on (Elmendorf) tear strength tester. The samples were slit down to 6.5X7.5 cm size. Burst strength was measured according to ASTM D 1599. The required dimensions of the samples were according to ASTM.

Optical testing

Haze and Transmittance was determined according to ASTM D 1003-1007 by the help of haze and transmittance tester. The sample size was taken in desired shapes with cover the aperture.

Thermal Characterization

Differential scanning calorimetry (DSC) was used to find the thermal behavior of nanocomposite blown films. DSC analysis was carried out from 50 to 200 °C at heating rate of 10 °C/min, in a nitrogen environment. The instruments were manufactured by Perkin Elmer. TGA analysis was carried out in a nitrogen atmosphere from 50 to 600 °C at rate of 10 °C/min.

Morphology

FESEM-Carl Zeiss, Supra 40 Instrument at 10 kV and magnification of 30 KX was used to study the surface morphology and nanofiller dispersion in the developed nanocomposite blown films. Samples were gold coated to avoid charging effect and increase the efficiency of secondary electrons.

Results and Discussions

In the present study, the titanate treated Nano-Zirconia filled LLDPE/LDPE/PLA/MA-g-PE nanocomposite was prepared in co-rotating twin screw extruder followed by blown film machine. After successfully preparing blown films mechanical, optical, thermal and morphological properties of developed nanocomposite blown films samples were denoted as LL₁PZ0, LL₁PZ0.5_T, LL₁PZ1_T,

LL₁PZ1.5_T, LL₁PZ2_T (the bold letter in the nanocomposite represent the L- LLDPE, L₁-LDPE, P- PLA, Z- Nano-Zirconia and T- Titanate coupling agent. Numerical suffixes used to refer the parts per hundred resins of Nano-zirconia in the matrix) were determined.

Table.2. Mechanical properties of modified nano-zirconia blown films

Sample Formulation	Tensile Strength (MPa)	Elongation at break (%)	Tear Strength (N/m)	Burst Strength (psi)
(LL ₁ PZ0)	22.3	543	15.29	32.71
(LL ₁ PZ0.5_T)	22.4	518	15.55	32.72
(LL ₁ PZ1_T)	24.7	496	14.79	38.41
(LL ₁ PZ1.5_T)	27.5	434	13.39	41.26
(LL ₁ PZ2_T)	25.8	413	13.37	34.14

Tensile Strength

The Tensile properties of LLDPE/LDPE/PLA/MA-g-PE blend’s modified with nanofillers at different composition are shown in table 2. Tensile strength of developed nanocomposites showed an increasing nature due to the toughness and brittleness. Addition of nano zirconia improved the tensile properties because of soft, stiffness and hard nature of developed nanocomposites. The best achieved tensile strength of developed nanocomposite is (27.5) at the loading of 1.5 phr Nano-zirconia.

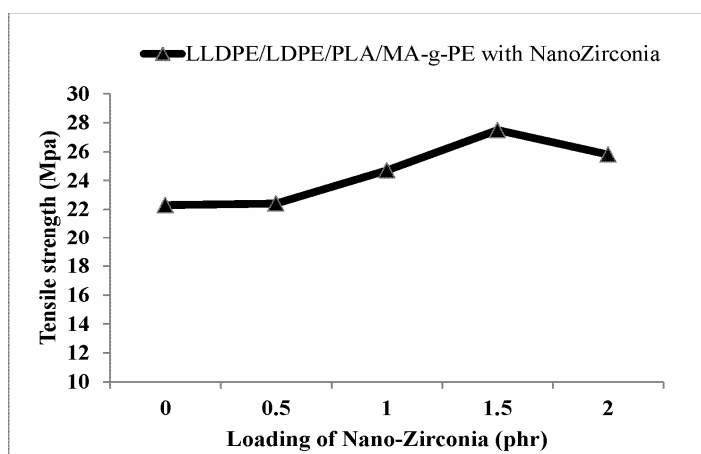


Figure.1. Effect on tensile strength of LLDPE/LDPE/PLA/MA-g-PE blown films with Nano-Zirconia

Elongation at break

Figure 2 shows the elongation at break of LLDPE/LDPE/PLA/MA-g-PE and modified Nano-zirconia nanocomposite blown films. When the Nano-zirconia is added in the developed nanocomposite the elongation is decreased in a regular manner and maximum elongation is achieved at 0 phr loading of Nano-zirconia, due to the improved tensile properties and toughness and rigidity of nanocomposite.

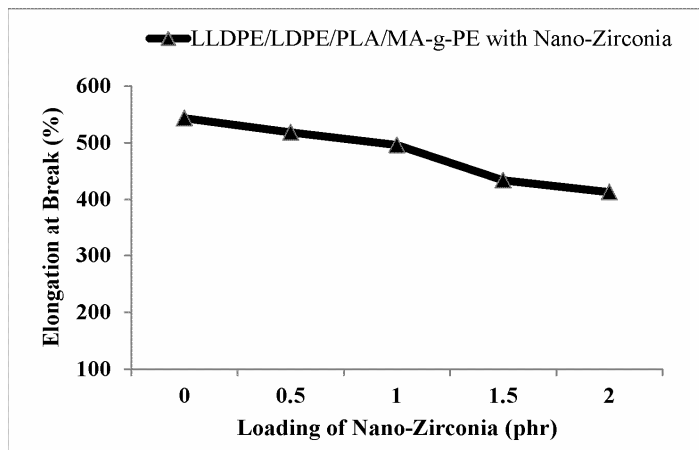


Figure.2. Effect on elongation at break of LLDPE/LDPE/PLA/MA-g-PE blown films with the without Nano-Zirconia

Tear Strength

The tear strength property of LLDPE/LDPE/PLA/MA-g-PE/Nano-Zirconia nanocomposite blown films is shown in figure 2. The tear strength is the ability of a material to rupture when a cut is applied to it. In the developed nanocomposite the adhesion and strength of the nanocomposite is improved so the tear strength is improved. The better dispersion of nanofillers also improved their tear strength. The best results found at loadings of 1.5 phr of nano zirconia (15.37).

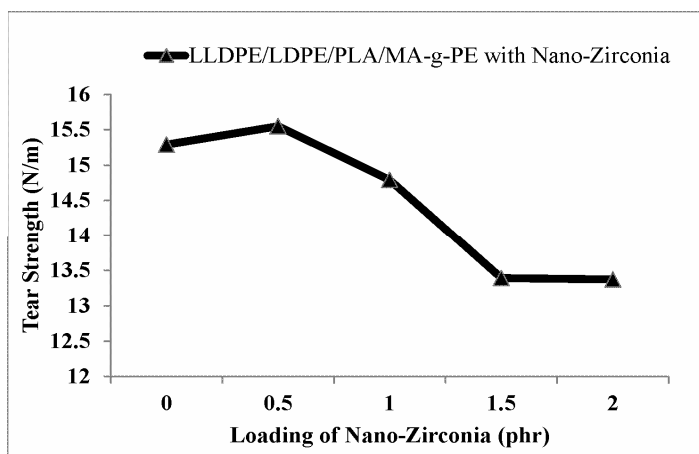


Figure.3. Effect on tear strength of LLDPE/LDPE/PLA/MA-g-PE blown films with Nano-Zirconia

Burst Strength

LLDPE/LDPE/PLA/MA-g-PE/treated Nano-Zirconia developed nanocomposites. Burst strength is the ability of a material to rupture when pressure is applied on it. The burst strength has been improved due to the better adhesion between the matrix and nanofiller. Treated Nano-Zirconia improved the bonding between the organic matrix and inorganic nanofiller. Better bonding and dispersion improved the burst strength of the developed nanocomposites. The best properties found at loading of 1.5 phr of nano zirconia (41.26).

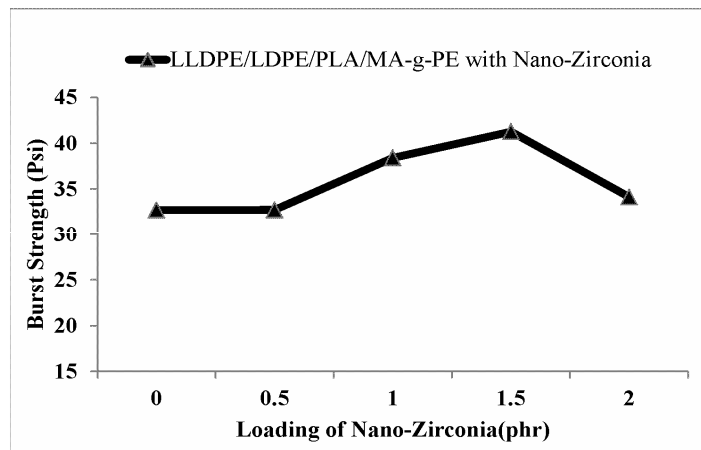


Figure.4. Effect on burst strength of LLDPE/LDPE/PLA/MA-g-PE blown films with Nano-Zirconia

Optical Properties

Optical properties have been depicted in table 5.3. The optical results reveal that addition of LDPE in the LLDPE improves the haze and opacity of the developed blend. Addition of PLA decreases the opacity followed by increase in haze properties. When the LLDPE/LDPE/PLA is blended with MA-g-PE, opacity has been found to increase remarkably and haze has shown decline nature as the content of MA-g-PE increases. This may be attributed to excellent interfacial adhesion among the polymers and compatibilizer.

Table.3. Optical properties of PLA modified blended blown films

Sample Formulation	Haze (%)	Transmittance (%)
(LL ₁ PZ0)	31.9	93.5
(LL ₁ PZ0.5_T)	57.8	82.2
(LL ₁ PZ1_T)	61.4	77.4
(LL ₁ PZ1.5_T)	68.7	72.1
(LL ₁ PZ2_T)	71.9	61.5

Haze

An optical property plays a major role in the packaging applications. Haze and Transparency is the key feature of films. But when the MA-g-PE was added at the loading 1, 2, 3, and 4 phr the haze is reduced and transmittance or opacity is slightly increased because of the better compatibility between the LLDPE/LDPE/PLA/MA-g-PE blend systems. The results are found minimum (31.9) at LLDPE/LDPE/PLA/MA-g-PE (85/15/10/4) loadings and the maximum (71.9) of LLDPE/LDPE/PLA/MA-

g-PE (85/15/10/4) with 2 phr Nano-Zirconia loading. Haze is increased due to the nucleating effect and good interfacial interaction between matrix and nanofiller.

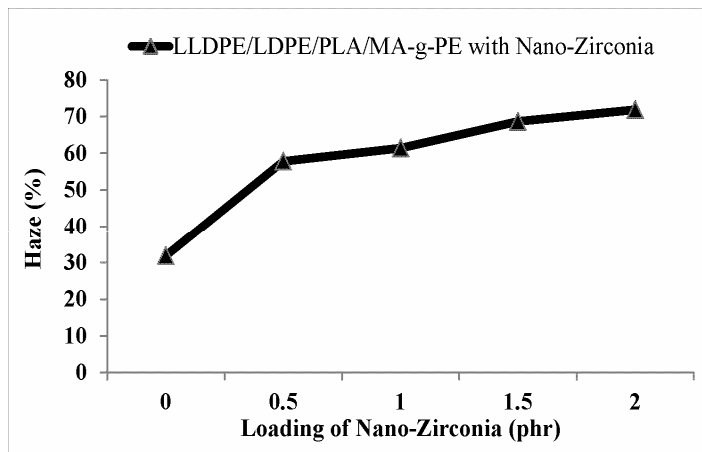


Figure.5. shows the effect on Haze of LLDPE/LDPE/PLA/MA-g-PE blown films with the without Nano-Zirconia

Transmittance

Transmittance property also plays important role in packaging applications. Figure 6 shows transmittance (%) of LLDPE/LDPE/PLA blend and of nano zirconia loaded blend films. Transmittance is found maximum (93.5) when nano-zirconia is not introduced in the polymer matrix. Transmittance is decreased due to the good dispersion of nano-zirconia in the matrix and this uniform distribution of nanofiller did not allow transmitting the light through its surface. The nanofiller also acted as nucleating agent and increased the number of crystal growth so the transmittance is decreased regularly with the increasing the amount of nano-zirconia.

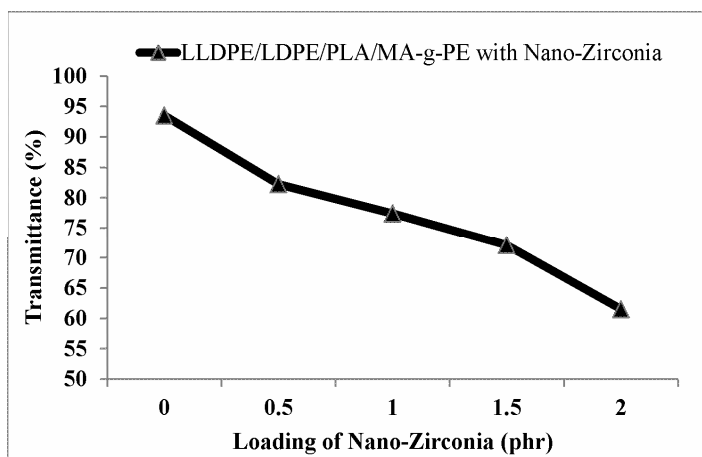


Figure.6. shows the effect on Transmittance of LLDPE/LDPE/PLA/MA-g-PE blown films with the without Nano-Zirconia

Thermal Analysis

Differential Scanning Calorimetry (DSC) & TGA

The DSC endothermic data and TGA data of the LLDPE/LDPE/PLA/MA-g-PE system and nanocomposite blown films with different loading of nano-zirconia (0.5, 1, 1.5 and 2 phr) are presented in table 4, figure 7 and figure 8 respectively. DSC thermograms LLDPE/LDPE/PLA/MA-g-PE blend system and nanocomposite blown films demonstrates that there is no change in the melt behavior of the various systems (from 123 to 126.9 °C in nanocomposite systems). It is evident that the melting point is affected by flexibility of chains present in the matrix.[1] But when the nanofillers were introduced in the matrix, they reduced the flexibility of the matrix due to the direct entanglement with the chains. Nano-zirconia is acted as nucleating agent and forms the regular mannered crystals in the nanocomposites which were evident from the optical properties like haze is increased and transmittance is decreased as the loading of nano-zirconia is increased. It is critical to control and stabilize the morphology of the developed nanocomposite systems because of dispersion of the nanofiller.[2]

Table.4. Thermal properties of modified nano-zirconia blown films (TGA)

Sample Formulation	T _m (°C)	IDT (°C)	Char Residue (%)
(LL ₁ PZ0)	121	241	0.28
(LL ₁ PZ0.5_T)	123.6	291	1.62
(LL ₁ PZ1_T)	125.8	293	2.09
(LL ₁ PZ1.5_T)	126.9	312	3.88
(LL ₁ PZ2_T)	123.2	300	3.50

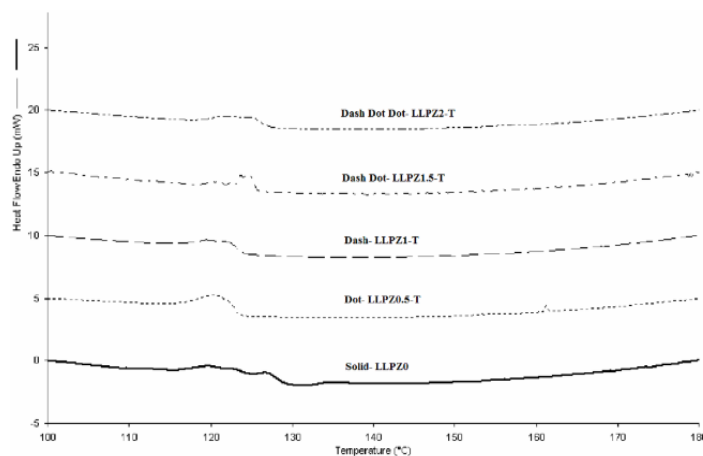


Fig.7. DSC curve shows the melting behavior of LLDPE/LDPE/PLA/MA-g-PE and different loading of Nano-zirconia

On the basis of TGA analysis it is found that the LLDPE/LDPE/PLA/MA-g-PE blend system showed the lowest thermal stability 241 °C. TGA results revealed improved thermal stability and char residue due to the addition of Nano-Zirconia.[3] This will leads to increase the thermal stability to maximum point 312 °C.

Morphological Properties

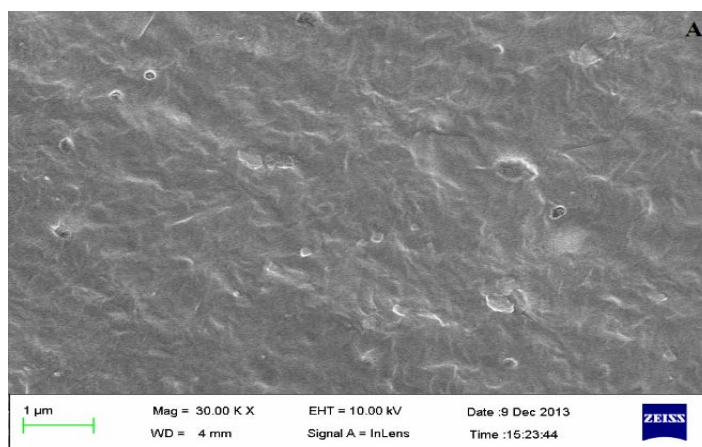
Scanning Electron Microscopy (SEM)

SEM micrographs of the morphology of the LLDPE/LDPE/PLA/ Nano-zirconia blended blown films are shown in figure 9A- 9D.

The dispersion of nanofiller in the matrix plays an important effect on mechanical, optical and also on the thermal properties of the developed nanocomposites. SEM studies are frequently used to observe the surface morphology. Addition of nano zirconia at the loading of 0.5 phr (see fig. 9A) shows rough surface where some nanoparticles of zirconia present on structure and some pores, which reveals that the dispersion of nanofiller is not good in the polymer matrix. These pores were induced due to the trapped oxygen and weaker interaction between the nanofiller and polymer.

But on the same magnification 1 phr nano-zirconia (see fig. 9B) loading showed smooth surface due to the good interfacial properties, better dispersion, and presented voids showed oxygen trapping.

At the loading of 1.5 phr nano-zirconia (see fig. 9C) the dispersion is good and surface of the blown film is smooth when compared to the other SEM images. It shows good interfacial adhesion, no phase separation between the nanofiller and polymer matrix. When compared to other nanocomposite systems minimum number of voids were present at the surface. [20]While loading of 2 phr nano-zirconia (see fig. 9D) surface is smooth and some pores and bigger cavities are present in it which clearly shows poor interaction of nanofiller and matrix and some agglomeration is present there, which is clearly evident by the SEM micrographs. Moreover, the mechanical and optical properties showed same phenomenal results, respectively.



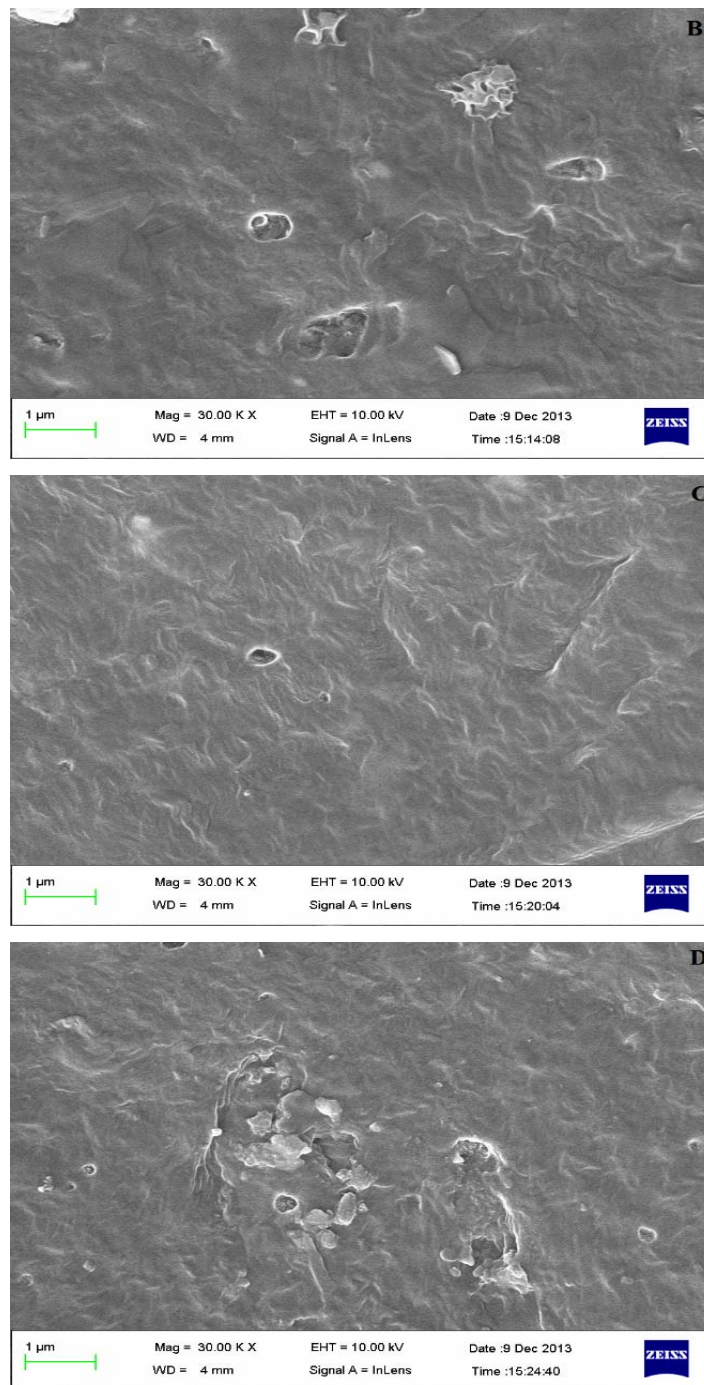


Fig.8. Shows SEM micrographs of (a) 0.5 phr nano zirconia (b) 1 phr nano zirconia (c) 1.5 phr nano zirconia (d) 2 phr nano zirconia

Conclusions

LLDPE/LDPE/PLA/MA-g-PE/Nano-Zirconia filled blend blown films have successfully prepared with different nanofiller loadings. Effect on mechanical, optical, thermal and morphological properties of nanocomposite blown films has been studied. The mechanical properties deals in tensile strength,



elongation at break, tear strength and burst strength. On the basis of results we summarized that the tensile strength is increased due to the addition of nano-zirconia and elongation is decreased due to the brittleness and chain rigidity in the matrix. Other mechanical shows good results when the nanofiller is added into the matrix. Due to the presence of the zirconia and nucleating effect of nanofillers the optical properties shows a decrease trend. The DSC results reveal that there is only slight change in the melt behavior of the developed nanocomposite blown films. Best morphology has been achieved at 1.5 phr loading of nano-zirconia in the entire developed nanocomposite blown films.

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