



Photodegradation Effect on LLDPE/LDPE/PLA Blend Films

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ABSTRACT

The present study shows effect of nano calcium carbonate (nano-CaCO₃) in LLDPE/LDPE/PLA blend compatibilized with MA-g-PE in photodegradation. LLDPE/LDPE/PLA blend with and without n-CaCO₃ were tested for durability towards weather condition. Prepared blends were exposed for 144 hours (hrs) in accelerated weatherometer. These analyses were completed in outdoor environmental condition like heat, moisture and UV light to study the degradability. Tensile properties of the blends were recorded at different time intervals and compared with neat LLDPE/LDPE/PLA blend. Effect of accelerated weathering on tensile properties were observed and found that tensile strength was decreased upto 56% with time. DSC SEM, FTIR analysis were also used to analyze the degradation. It is indicated that the rate of photodegradation of nano-CaCO₃ in LLDPE/LDPE/PLA as a nano composite is much faster than that of LLDPE/LDPE/PLA.

Key words: Linear low density (LLDPE), Maleic anhydride grafted polyethylene (MA-g-PE), Polylactic acid (PLA), Degradation, Accelerated Weathering

INTRODUCTION

Nanocomposites are focused public attention due to its novel performance. Due to some of their noteworthy properties at low filler charging, it attracts the interest from the industrial world. A variety of nanoscale fillers are significant improvements in mechanical and thermal properties of nanocomposites, such as modulus, strength, impact performance, and heat resistance [1–3]. Among nano particles, CaCO₃ is one of the most widely used inorganic filler due to its low cost and research work had shown that it has the potential to be an important functional filler in polymer systems such as polypropylene composites, poly (vinyl chloride) composites and poly (ethylene terephthalate) composites that are being produced [4–7]. Nano particle are also used in manufacturing the film for enhance the various properties such as mechanical, thermal and more. Film blowing is the most important method in producing polyolefin films.

Linear low density polyethylene (LLDPE) and low density polyethylene (LDPE) blends have been used for making blown film. Blown film process has been used for the commercial production of biaxially oriented thin polyolefin films. Linear low density polyethylene (LLDPE) and low density polyethylene (LDPE) blends are often used for blown film manufacture because of their good processibility, mechanical and optical properties [8]. The energy desires for their production a much lower as compared to other materials and the wastes produce during manufacture of PE compared to paper bags (from trees) are much lower, hence these polyolefin films can widely used in packaging sector as plastic bag. According to composters, the top contaminant in feed stocks is plastic, plastic bags being an important part of waste [9]. Over 60% of plastic waste is produced by households, most of it as single use packaging [10]. PE is used extensively due to its Low cost and good mechanical properties. Perhaps a major limitation is disposal of the plastic film after use, which causes an environmental pollution problem such as littered PE bags; causes visual pollution, blockage of gutters and drains and choke domestic etc. High rate of production and lack of biodegradability of such commercial polymers, particularly commodity plastics used in agriculture and packaging industry, attract public attention on a potentially huge environmental accumulation and pollution problem that could persevere for centuries [11]. The left over film if left in the field may affect root development of the consequent crop. Although plastics exposed to the light undergoes photo-degradation and contributes to the plastic's decomposition for photodegradable whereas photodegradable mulches has been reported [12], After single use most of plastic bags are discarded in environment which causes visual pollution these waste material is simply broken into

pieces by photodegradation in the presence of sunlight, some pieces being buried and some remaining on the soil surface. The buried pieces are more difficult to decompose since they are less affected by light and high temperatures; however these small pieces of plastic films are reduces soil and visual pollution. In an earlier paper, mechanical, thermal and optical properties of LLDPE /LDPE/PLA / MA-g-PE and LLDPE /LDPE/PLA / MA-g-PE/nano calcium carbonate blend and observed that have good mechanical and thermal properties [13]. However to our present knowledge there are few data regarding accelerated weathering behavior of polyethylene/calcium carbonate nanocomposite when maleated polyethylene is used. In this present study showed the effect of nano-CaCO₃ and compatibilizer (PE-g-MA) on photodegradation of LLDPE /LDPE/PLA blend.

EXPERIMENTAL WORK

Materials

Blown films used in this study were developed earlier and provided for this study [13]. 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 M/s 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 M/s 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 M/s 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 M/s Plus polymers, India. Nano calcium carbonate (trade name: Calcia- nano C) was obtained from Zirox Technology, India. Titanate coupling agent (EB-1019A) was purchased by M/s IPMC, Pune, India [13]. Nanocomposite formulations are listed in Table-1 [13].

Table -1 Nanocomposite Films Formulation

Formulation	Blend code	LLDPE (wt %)	LDPE (wt %)	PLA (phr)	MA-g-PE (phr)	Nano CaCO ₃	Titanate coupling agent
LLDPE/LDPE/PLA/MA-g-PE/nano CaCO ₃	LnC ₀	85	15	10	4	0	0
LLDPE/LDPE/PLA/MA-g-PE/nano CaCO ₃	LnC ₁	85	15	10	4	0.5	1
LLDPE/LDPE/PLA/MA-g-PE/nano CaCO ₃	LnC ₂	85	15	10	4	1.0	1
LLDPE/LDPE/PLA/MA-g-PE/nano CaCO ₃	LnC ₃	85	15	10	4	1.5	1

METHODS

Photodegradation

PLA filled and unfilled LLDPE/LDPE/ MA-g-PE blend with and without Nano calcium carbonate (nano-CaCO₃) blown films were cut in to rectangular shaped samples of dimension 15X2.5 cm². Samples were UV irradiated using an accelerated weathering tester (Model-Q-Lab QUV/Spray with solar eye irradiance control) with ASTM D-5208: standard practice for Operating Fluorescent Light Apparatus for UV Exposure of nonmetallic materials, used irradiance of 0.66W/m² with 8 hrs irradiance cycle and 8 hrs condensation cycle. The samples were exposed different time intervals up to 144 hrs.

Weight loss

Weight loss as a result of photo exposure of different hours on nano-CaCO₃ filled and unfilled LLDPE/LDPE/ PLA/MA-g-PE blend blown films; and was determined as:

Total percent weight loss after UV exposure (% wt loss) =

(Initial wt at the beginning – Final wt after UV exposure) / Initial wt at the beginning X 100

Mechanical Testing

Nano calcium carbonate (nano-CaCO₃) filled and unfilled LLDPE/LDPE/ PLA/MA-g-PE blend blown films were tested using universal testing machine (INSTRON. The tensile test was carried out according to ASTM D-882 standard. The rectangular shaped samples had the dimensions 15X2.5 cm² were used in 5 replicates and results were expressed as mean± SE.

Thermal Testing

LLDPE/LDPE/PLA/MA-g-PE blends modified with and without nanofillers blown films were tested on Differential Scanning Calorimetric (DSC), Perkin Elmer, which was used to find the thermal behavior of blown film sample. DSC analysis was carried out from 50 to 200°C at heating rate of 10°C /min.

Fourier Transforms Infrared (FTIR) Spectroscopy

PLA filled and unfilled LLDPE/LDPE/ M-Ag-PE blend blown films were tested for functional group analysis by using Fourier Transforms Infrared (FTIR) spectroscopy (Perkin Elmer).

Morphological Studies

Surfaces of LLDPE/LDPE/PLA/ MA g PE blend and its nanocomposites blown films were observed by using SEM Model ELU 430.

RESULT AND DISCUSSION

Figure 1 and 2 illustrates the Tensile Strength and % Elongation at break of the films, which clearly shows the change in mechanical properties over time with and without nano-CaCO₃ at different time intervals. LLDPE/LDPE/PLA/MA-g-PE and the LLDPE/LDPE/PLA/MA-g-PE/n-CaCO₃ followed similar trends in the change in tensile properties over time. Degradation of tensile properties was 44-49% for the nanocomposites before ruptured and for LLDPE/LDPE/PLA/MA-g-PE blend was 50.2% after 144 hrs (**Table- 2 and 3**). Mechanical performance results support that nanofiller such like nano calcium carbonate accelerate the degradation of the blend material, a fact that has also been observed in previous work [14-15]. The Differential Scanning Calorimetry (DSC) results for the UV Exposed and unexposed LLDPE/LDPE/PLA/MA-g-PE blend and their nanocomposites are tabulated in **Table-4**.

Table-2 Change in Tensile Strength (MPa) of LLDPE/LDPE/PLA/MA-g-PE Blend with Before and Nano Calcium Carbonate after UV Exposure at Various Time Intervals

Blend Code	Change in Tensile strength (MPa) on different Time (hrs)						
	0	24	48	72	96	120	144
LnC ₀	22.5	20.3	18.7	15.1	12.8	12.5	11.2
LnC ₁	21.9	18.81	16.67	10.6	8.7	F	F
LnC ₂	24.87	20.16	13.83	11.09	F	F	F
LnC ₃	21.47	18.7	14.97	10.7	F	F	F

F: Fragmented

Table-3 Change in Elongation at Break (%) of LLDPE/LDPE/PLA/MA-g-PE Blend With Nano Calcium Carbonate Before and After UV Exposure at Various Time Intervals

Blend Code	Change in Elongation break (%) on different Time (hrs)						
	0	24	48	72	96	120	144
LnC ₀	520	517	190.4	150.98	78.85	61	50.8
LnC ₁	602	145	148	84.9	50	F	F
LnC ₂	650	91.6	75	65	F	F	F
LnC ₃	610	298	111	65.73	F	F	F

F: Fragmented

Table-4 Melting Temperature and Crystallinity of Samples before and after 144 Hours of UV Exposure

Sample Code	Before UV exposure		After UV exposure	
	T _m (°C)		T _m (°C)	
LnC ₀	122.11		116.34	
LnC ₂	126.05		121.63	

T_m: melting point (peak), °C

Table-5 Data Obtained from FTIR Spectra

Peak Position (cm ⁻¹)	Characteristic group
2914- 2905, 28 cm ⁻¹	CH symmetric and asymmetric stretching
1461cm ⁻¹	CH ₂ bending
720 cm ⁻¹	vibration of CH ₂
1756-1744 cm ⁻¹	Ester carbonyl group
1190-1090 cm ⁻¹	O-C=O stretching
1024	C-O stretching
1639-1600 cm ⁻¹	C=C bond

Differential Scanning Calorimetric shows the melting temperatures of both pure samples and LnC₂ samples undergoes reduction after 96 hours of UV exposure (**Fig. 3**). However, samples containing prooxidant melting temperature (T_m) show higher reduction than without nanofiller samples after treatment. The reduction of T_m could be due to the breakdown of LLDPE/LDPE blend chains and molecular weight reduction. As reported by Colom et al. (2003) [16], the decrease of the decomposition and melting temperatures is associated with breaking of polymeric chains leads to lower thermal stability of the prepared films. FTIR spectra shows significant comparison and characteristic peak (wave number) respectively of LLDPE/LDPE/PLA/MA-g-PE and LLDPE/LDPE /PLA/MA-g-PE/nano calcium carbonate nanocomposites blown films before and after UV exposure (**Fig. 4**). Change in intensities nanofiller containing nanocomposite shows noticeable at 2901cm⁻¹ and 2915 cm⁻¹(C-H stretching), 1756-1744 cm⁻¹ (Ester carbonyl group), 1460 cm⁻¹ (CH₂ bending) and 722 cm⁻¹ (Skelton vibration of CH₂) (**Table-5**).

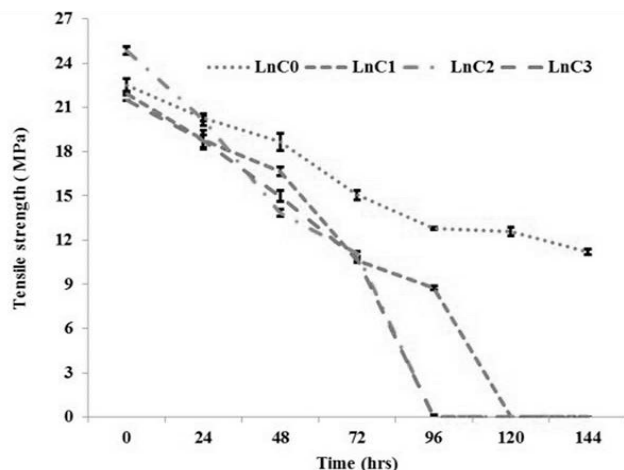


Fig. 1 Variation in tensile strength with time after UV exposure of various LLDPE/LDPE/PLA/MA-g-PE blend and its nanocomposites

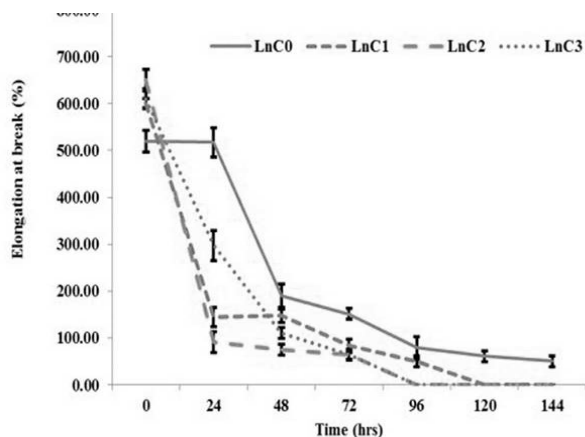


Fig. 2 Variation in Elongation at break (%) with time after UV exposure of various LLDPE/LDPE/PLA/MA-g-PE blend and its nanocomposites

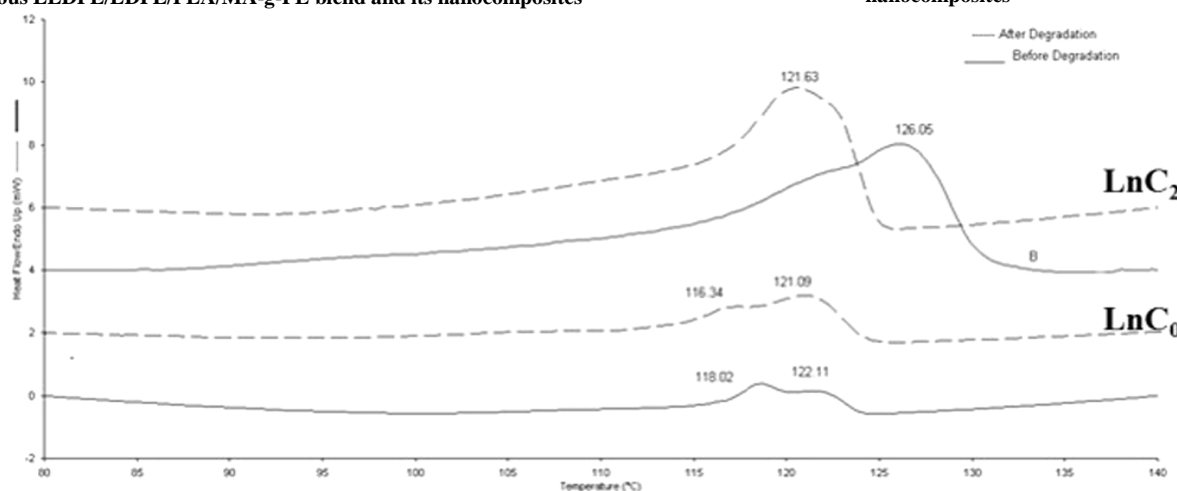


Fig. 3 DSC thermogram of LnC₀ and LnC₂ before and after UV exposure of 96 hrs Solid line and dot line express before and after degradation

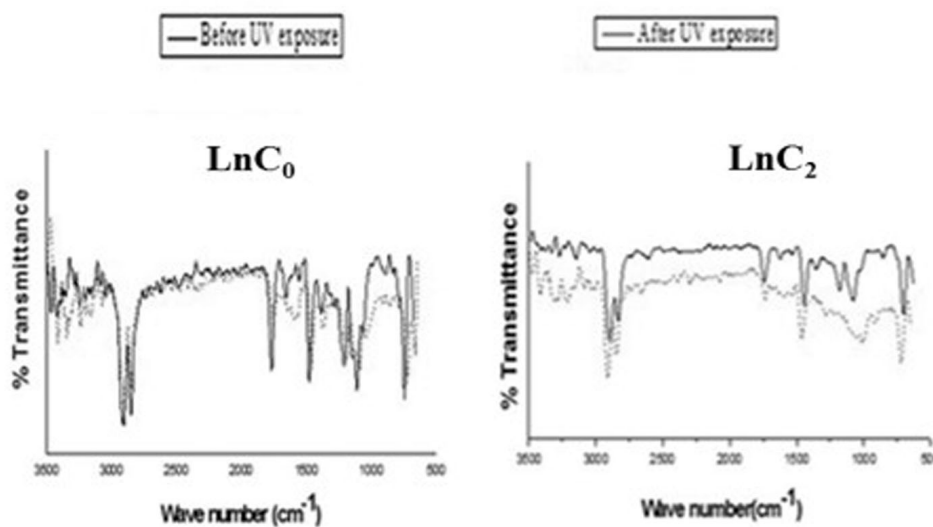


Fig. 4 FTIR of LnC₀ and LnC₂ before and after 96 hrs UV exposure

Whereas without nanofiller blend in LnC₀ showed slight changes in intensities which reveal oxidation of LLDPE/LDPE/PLA/MA-g-PE blend in presence of calcium carbonate. SEM micrographs of the morphology of some representative samples are shown in Fig. 5. Changes observed in LLDPE/LDPE/PLA/MA-g-PE (LnC₀) and its nanocomposite (LnC₂) after exposure to the UV light obtained by SEM analysis shows that number of voids together with extended cracks running in-between and around the dispersed particles in nanofiller filled blend (LnC₂) after 96 hrs UV exposure whereas in LnC₀ represents slightly change in morphology. The formation of a

large number of voids and cracks in the nanocomposite suggests that LLDPE/LDPE/PLA/MA-g-PE degradation begins at the interface between the polymer matrix and the nanofiller particles. The reported images clearly outline that well-dispersed filler increased interface region between matrix and filler and enhances degradation. At 1.0 phr nano calcium shows good dispersion have reported in previous work [13]. Physical changes shown in Fig. 6 and samples were become brittle in nature after the exposure of UV which is clearly seen in figure.

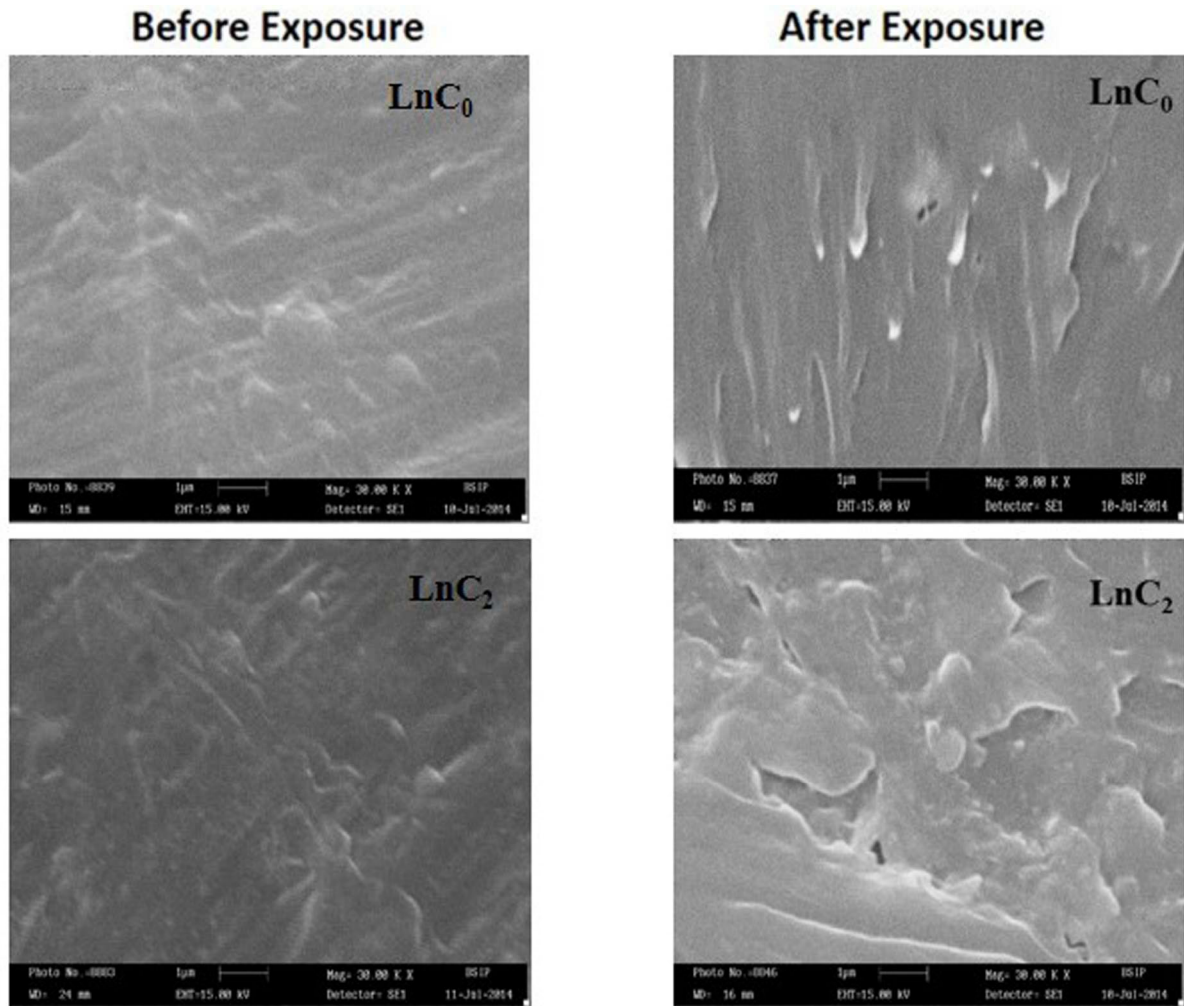


Fig. 5 SEM images of LnC₀ and LnC₂; before and after 96 hrs UV exposure

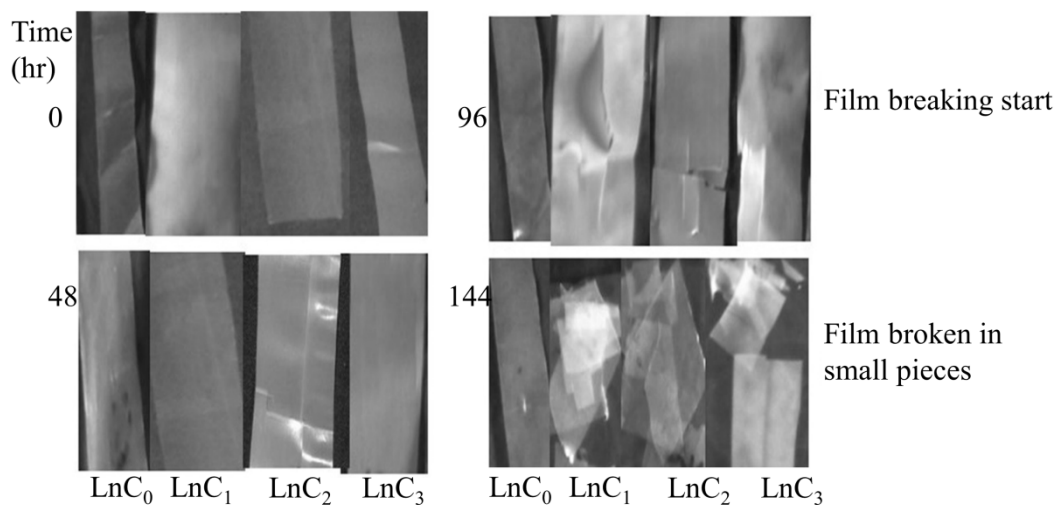


Fig. 6 Physical changes after UV exposure of various LLDPE/LDPE/PLA/MA-g-PE blend and its nanocomposites

CONCLUSION

The following conclusions obtained from above experiments:

- After UV exposure, the highest reduction in tensile and elongation at break properties was observed in the blend containing 1.0 phr nano calcium carbonate in LLDPE/LDPE/PLA/MA-g-PE blend by 55% and 90% after 72 hrs before ruptured and in LLDPE/LDPE/PLA/MA-g-PE blend by 50.2% and 90.2% after 144 hrs UV exposure.
- Degradation of LLDPE/LDPE/PLA/MA-g-PE blend with nano calcium carbonate had occurred leading to break low molecular weight molecule.
- The FTIR spectra show changes in intensities, especially in the carbonyl ($1756-1749\text{ cm}^{-1}$), $1190-1090\text{ cm}^{-1}$ (O=C=O stretching) and bands at 721 cm^{-1} and 1461 cm^{-1} corresponding to vibrations of $-\text{CH}_2$ groups and bending vibrations of $-\text{CH}_2$ bonds respectively on UV exposure. The change in intensity of these peaks is a result of the fracture of the polyethylene chain after UV exposure.
- Surface cracks and voids were enhanced by addition of nanofiller nano zirconia. It was clearly seen by SEM analysis at 1.0 phr containing nano calcium carbonate LLDPE/LDPE/MA g PE blend (LnC_2).
- Physical changes were observed after UV exposure.

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