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Photodegradation of Low Density Polyethylene using CaO Nanoparticles as a Catalyst

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The photodegradation of low density polyethylene (LDPE) using CaO nanoparticles as a catalyst was carried out using sun light as a source. After exposure period, morphology as well as thermal properties of the specimen was investigated by scanning electron microscopy (SEM) and DSC. Before and after photodegradation, SEM results showed the Low density polyethylene to be much more prone to cracking into small snippet which indicated a rise in crystallinity with different amount of CaO nanoparticles as a catalyst. The DSC result confirmed the remarkable influence of photodegradation on degree of crystallinity (XC %), fusion enthalpy (ΔH Jg−1) and melting temperature (Tm) of LDPE. Infrared (FTIR) spectrometry has demonstrated all functional groups, which were obtained after photodegradation. Results showed that LDPE was degraded successfully by using CaO nanopartilces during photodegradation and obtained different functional groups during chain scission.

Keywords: Nanoparticles, Catalyst CaO, Photodegradation, low density polyethylene, LDPE.

1. Introduction

In recent years, there has been a continuous increase in the production of commodity and packaging polyethylene grade like LDPE, LDPE, LLDPE etc. Low density polyethylene is widely used in food service, retail industry, and agriculture (greenhouses, mulching).[1] The LDPE products cause a large quantity of plastic disposal. Low density polyethylene also used as a antibacterial, antimicrobial wrapping material for food product.[2-5] Recent year LDPE composite used in auto mobile industry. Inertness properties of LDPE from different material, environment, bacteria etc., it is not easily degrade in nature due to this reason world facing serious environmental pollution problem. LDPE waste polymers are burned for degradation, but they produce toxic gas. [6,7] LDPE is also responsible for serious environment pollution such as soil pollution as infertile land,[8] water pollution, air pollution, blocked drainage and marine pollutions etc.[9, 10]

In the ocean, multiple risk increase due to overexploitation and harvesting, dumping of waste, pollution, alien species, land reclamation, and global climate change. [11-13] Low density polyethylene also affect on human health problems like vision failure, irritation in the eye, lungs problems, skin diseases, breathing difficulties, headache, respiratory problems, liver dysfunction, cancers for using toxic plastics.[14] Many method was used for degrade LDPE like chemical degradation,[15-16] biodegradation,[17-19] pyrolysis degradation,[20] radiation degradation, [21-24] mechnical degradation [25] oxidative degradation, [26] photo oxidative degradation,[27] Photo catalytic degradation. [28-31] Many materials like TiO_2, CaO, BEA, FAU, MWW, MOR and MFI zeolites have been used for photodegradation. Through photodegradation process high molecular LDPE convert into low molecular weight compound. In this paper photodegradation of low density polyethylene (LDPE) granule was investigated by dissolving it in xylene, using 0.1gm, 0.2 gm and 0.3gm nanoparticles of CaO under 500 W lamp as a solar source.

2. Experimental:

In this experiment, Low density polyethylene was used which was provided by reliance polymer ltd. Crompton lamp Ltd., halogen lamp 500 W was used for photodegradation. Xylene (97% pure) solvent was used for dissolving Low density polyethylene which was supplied by Qualigens Fine Chemical Pvt. Ltd.

2.1 Preparation of nanoparticles CaO: Calcium hydroxide extra pure AR grade, molecular weight 74.09 was used for preparation of CaO nanoparticles for photocatalytic degradation which was supplied by Himedia laboratories. Initially, 6gm of calcium hydroxide ($Ca(OH)_2$) was dissolved in 24 ml of ethyleneglycol and stirred at 1200 RPM and then 2 gm of sodium hydroxide (NaOH) was added into the mixture. The solution was left to settle down for 8 hours after 10 minutes of sonication. The precipitated specimen was filtered and then the precipitate was regularly washed with distilled water for 10 times and then dried at 100°C, subsequently. Finally, specimen was calcinated at 800^0C. Different size of calcium oxide nanoparticles were obtained at the end of process. [31] The Mechanism reaction can be written as:

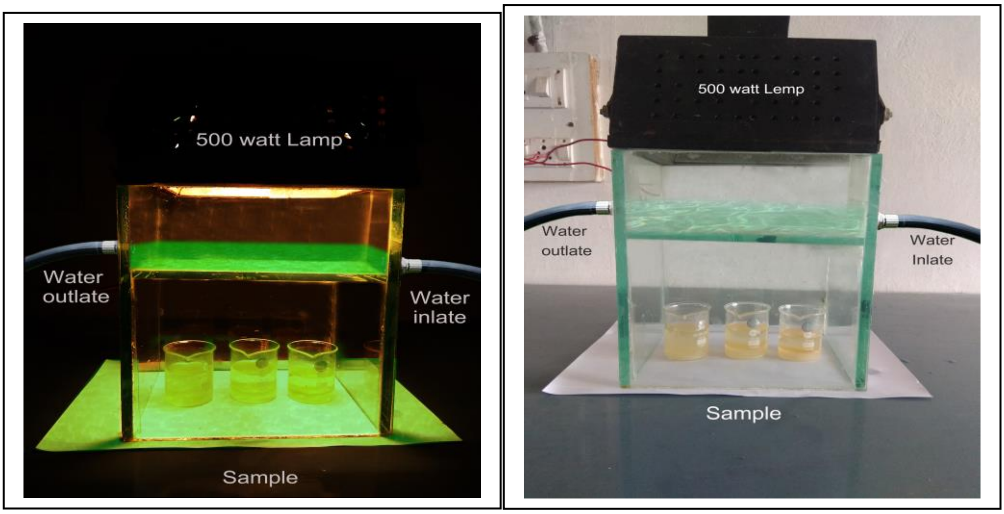
$$10\,Ca(OH)_2 + OHCH_2CH_2OH + 4\,NaOH \longrightarrow 10\,CaO + 2\,Na_2CO_3 + 10\,H_2O$$

2.2 Specimen preparation of LDPE and nanoparticles CaO semiconductor:

1 gm. of LDPE was dissolved in 150 mL xylene solution with the help of magnetic stirrer at 150^0C temperature. After fully dissolving, solution was separated into three groups respectively added 0.1 gm CaO + LDPE (LDPE-I), 0.2 gm CaO + LDPE (LDPE- II), 0.3 gm CaO + LDPE (LDPE-III).

2.3 Photodegradation of PP specimen:

A photodegradation glass box having one single out let and inlet was fabricated for water circulation shown in fig. 1. Dimension of glass box was (19 x 23 x 17Cm). The specimen was 17 cm away from lamp. Light was passed through water filter (2 mm layer). Water medium was used for heat absorption during photodegradation reaction. The specimens were placed for 28 days in the reaction glass box. Sampling was carried out by withdrawing the specimen from the chamber at regular interval of time and photodegradation rate was monitored. The photodegradation study of specimen was done under 500-watt lamp exposure in Fig1 (a) and (b). After exposure, specimen photodegradation was examined by FTIR spectroscopy, differential scanning calorimetry (DSC) and scanning electron microscopy (SEM).



(a) (b)

Fig: 1 (a) Schematic setup for photodegradation of LDPE and (b) Schematic setup for photodegradation of LDPE under halogen lamp

2.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were obtained before and after photodegradation using a Bruker alpha FTIR with ATR spectrometer. This FTIR cover the whole spectral range from 80 cm^{-1} to 6000 cm^{-1} .The specimen were obtained in the form of thin films and was viscous in nature.

2.5 Differential scanning calorimetry (DSC)

Thermal analysis of the specimen before and after photodegradation was tested using a differential scanning calorimeter (Perkin Elmer, calibrated with indium and zinc standards). A specimen of 5.0 ± 0.2 mg was used for each measurement and it was placed in a sealed aluminum pan, and heated to 160°C at a scanning rate of 20°C/min in an inert atmosphere (N_2 50 mL/min). Melt temperature (T_m), enthalpy of fusion (ΔH) and crystallization temperature (T_c) were determined from DSC curves. The degree of crystallinity (X_c) was measured by following equation: $\% Xc = \Delta H/W \text{ X } \Delta Hf_o \text{ X } 100$

Where ΔH is the enthalpy of fusion, obtained from DSC curve, ΔHf_o is the enthalpy heat of 100% crystalline LDPE (290Jg^{-1}) [29] and W is weight fraction of Low density polyethylene specimen.

2.6 Scanning electron microscopy (SEM): SEM studies of specimen before and after exposure to photodegradation were examined by using a JEOL JMS 840A (Freising, Germany) scanning microscope.

3. Result and discussion:

3.1 XRD of CaO nanoparticles:

XRD analysis of the sample was done (fig. 2) where intense peaks of CaO were observed. The sharp peaks in the XRD pattern of the prepared sample indicated the crystalline nature of CaO nanoparticles. Crystallite size of CaO nanoparticles was calculated by using the Scherrer formula, $D = K\lambda/\beta \cos\theta$

Where,

D =Crystallite size

λ = Wavelength of the X-rays produced in the machine

β = Width of a peak at half of its intensity (FWFM)

θ = Angle of the corresponding peak

k = Shape factor.

The average particle size of CaO particles was found to be 110Å/ 12 nm.

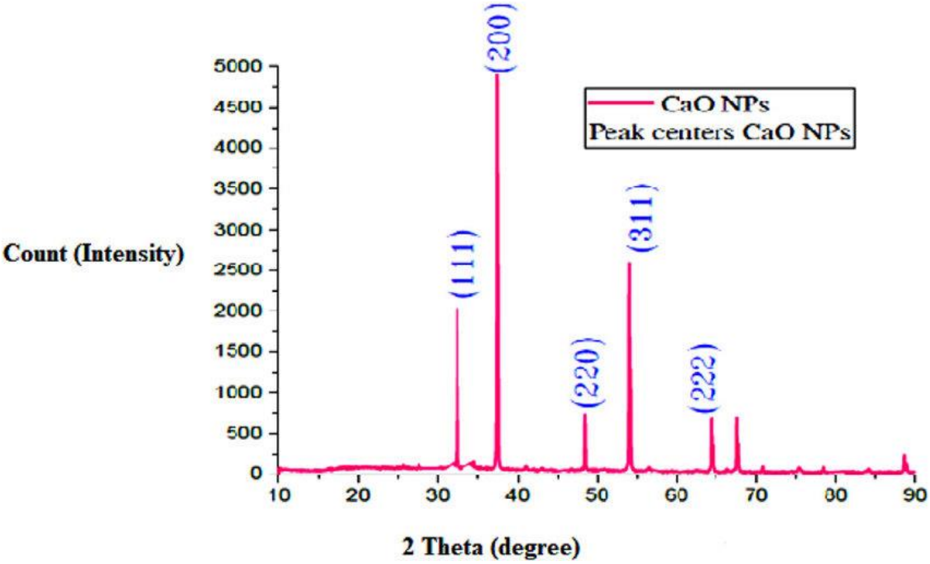
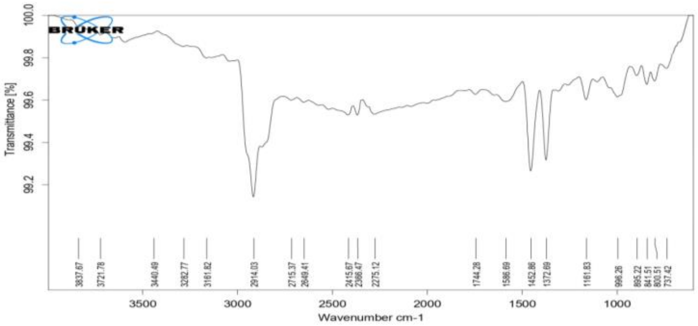
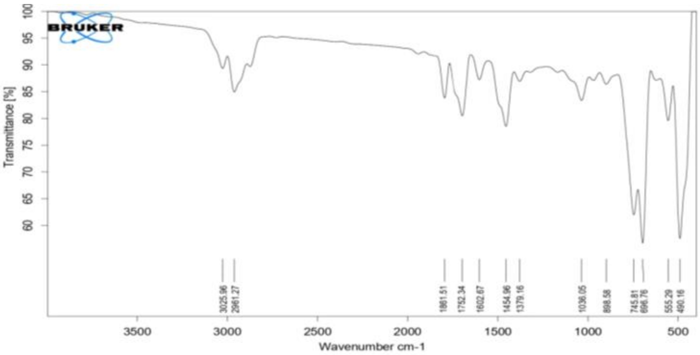


Fig: 2 XRD analysis of CaO nanoparticles

3.2 FTIR Spectra: The photodegradation of LDPE specimens was examined using FT-IR spectroscopy. Fig: 3 shows the FT-IR spectra of the LDPE specimen using nanoparticles of CaO as a catalyst with before and after UV irradiation for 28 days. The IR spectra of specimen photodegradation carried out under halogen lamp are shown in Scheme: 1. It was observed that the LDPE specimen showed the characteristic absorption in the region 2914 cm^{-1}, 2715 cm^{-1}, 2415 cm^{-1} , 2366 cm^{-1}, 1452 cm^{-1}, 1372 cm^{-1} and 737 cm^{-1} which corresponds to CH_2 stretching and bending vibrations. The photodegradation of LDPE specimen was ensured by the formation of carbonyl groups due to the partial oxidation of LDPE. The spectra of the photodegradation specimen showed a new peak around 1752 cm^{-1}, which is assigned to CO stretching vibrations which is the characteristic absorption of carbonyl. These variations in the FTIR spectra indicated that the structural changes in the LDPE specimen during the photodegradation. By comparing in Fig:3 (a,b,c,d) the area evolution of the carbonyl peak absorption band between the exposed specimens with time and amount of nonoparticles of CaO LDPE, it is clearly visible that broad peak was observed from 1744 cm^{-1} to 1752 cm^{-1}. These absorption could have been due to 1744 cm^{-1} - 1161 cm^{-1} esters, 1035 cm^{-1} ketone, respectively. Increasing absorption with time shown in fig: 3 and 1603 cm^{-1} peak show a vinyl group. The absorption 969 cm^{-1} show vinylidenic unsaturations, 738 cm^{-1} methylene rocking.



(a)



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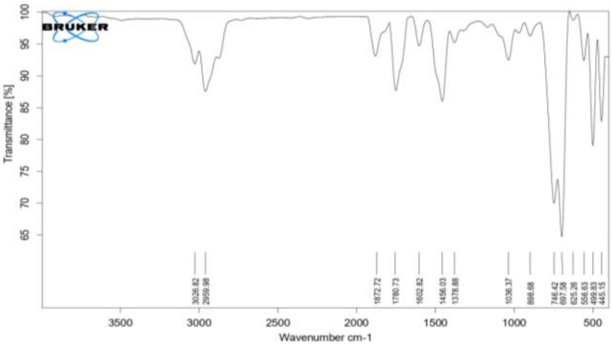
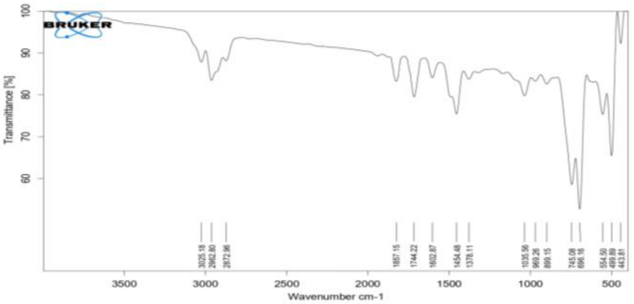
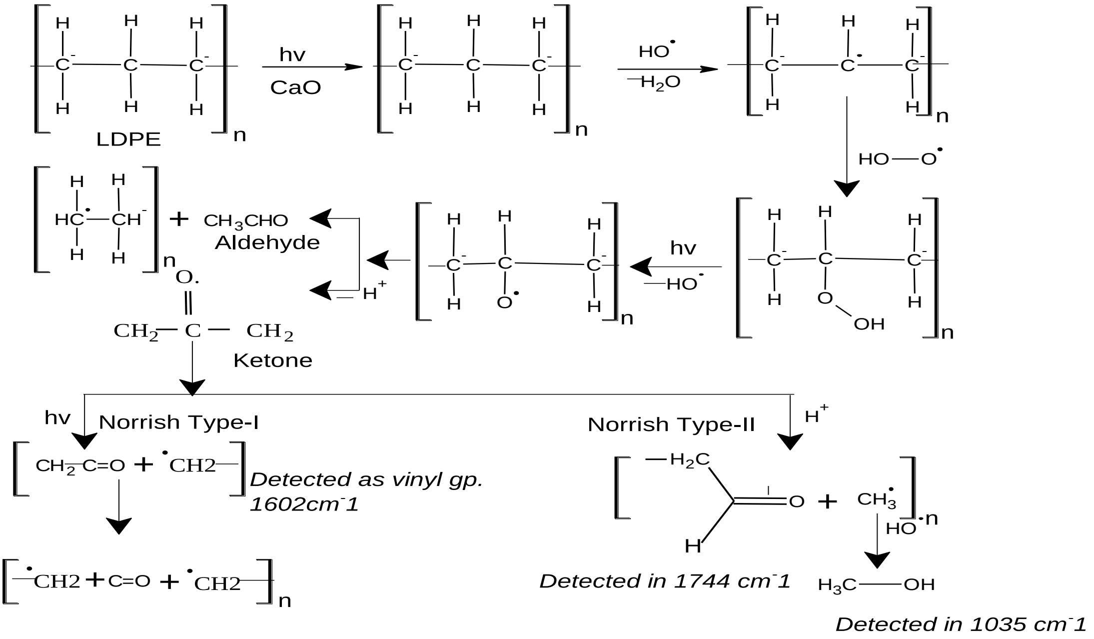


(c)



(d)

Fig:3 FTIR spectra of (a) LDPE Sample (b) LDPE-I (c) LDPE-II and (d) LDPE-III



Scheme:1 Reaction mechanism of photodegradation of LDPE in presence of nanoparticles of CaO

DSC: The thermal and crystallization data was obtained from DSC for the LDPE and photo treated LDPE with CaO nanocatalyst before and after exposure. DSC of LDPE and 28 days photodegraded LDPE specimens with different amount of semiconductor area under crystalline melting peak decreases steadily due to change in molecular weight of specimen Fig: 4.

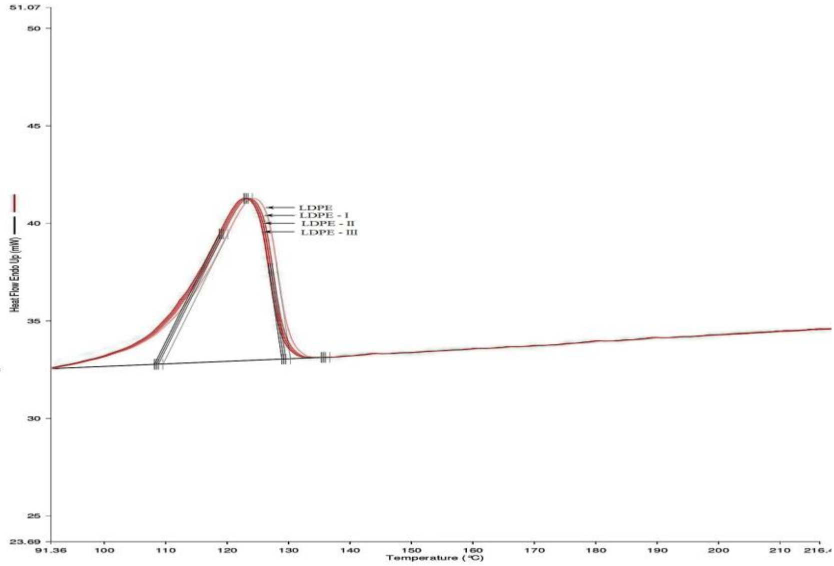


Fig: 4 Thermogram of low density polyethylene and phototreated polypropylene with different amounts of catalyst

Table: 1 Parameters obtained from DSC measurements for virgin LDPE and photodegraded LDPE specimen T_m is melting temperature, T_c is crystalline temperature, ΔH fusion enthalpy and Xc is a degree of crystallinity.

S.no	Specimen	T_c (°C)	T_m(°C)	ΔH Jg−1	Xc (%)
1	LDPE	95.8	124.09	92.16	31.77
2	LDPE - I	96.2	123.55	94.69	32.65
3	LDPE - II	97.8	123.12	95.15	32.81
4	LDPE – III	98.12	123.00	97.23	33.52

While the crystallization temperature tends to shift to higher values from 95.8 to 96.2 with increasing the amount of CaO nanoparticles as shown in Table:1 and Fig: 5.

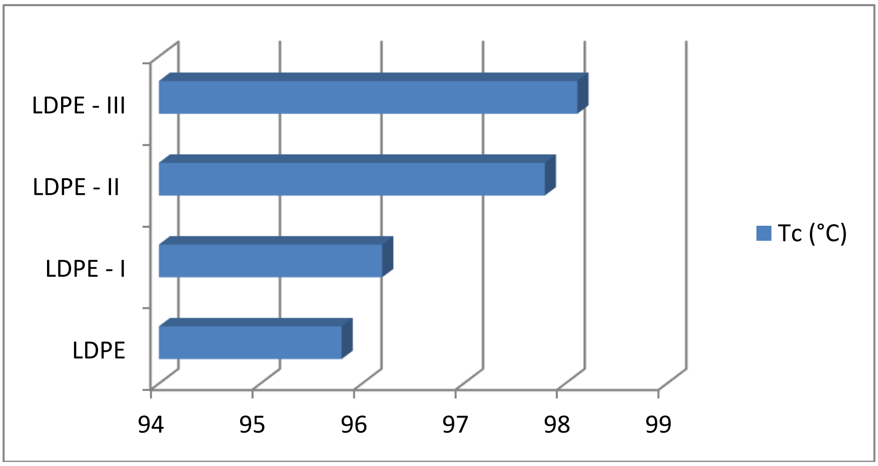


Fig : 5 DSC Crystallization Temperature of LDPE Specimen with different amount of CaO nanoparticles

This indicated that the CaO nanoparticles help crystallization of LDPE and this effect becomes more manifest with higher amount of CaO nanoparticles. Fusion enthalpy was increased after photodegradation from 92.16 ΔH Jg−1 to 97.23 ΔH Jg−1 fig: 6. and Table 1 From the Fig: 7, 8 it can also be seen that the crystallinity of LDPE specimen decrease from 31.77 to 33.52 X_C % [31] and melting point decrease 124.09 to 123 $T_m(^0C)$ with increasing exposure time. It is well known that chain scission occurs during photo-degradation resulting in decreased molecular size, which enhances mobility of chain.

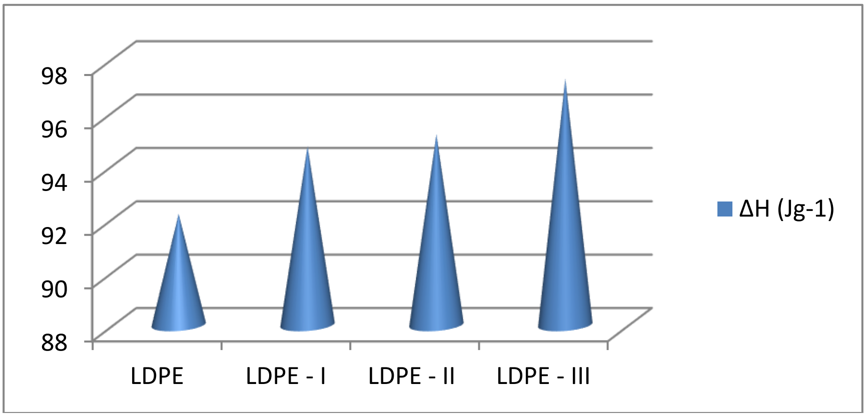


Fig : 6 DSC Fusion enthalpy of LDPE Specimen with different amount of CaO nanoparticles

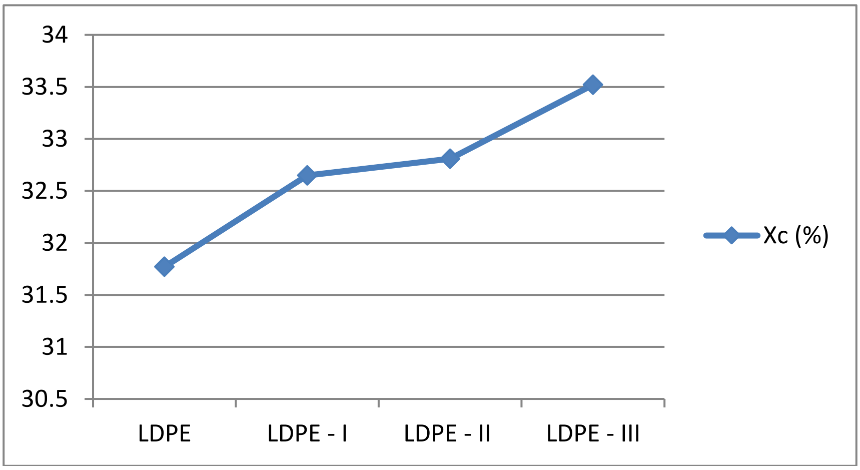


Fig : 7 Degree of Crystallinity of LDPE Specimen with different amount of CaO nanoparticles

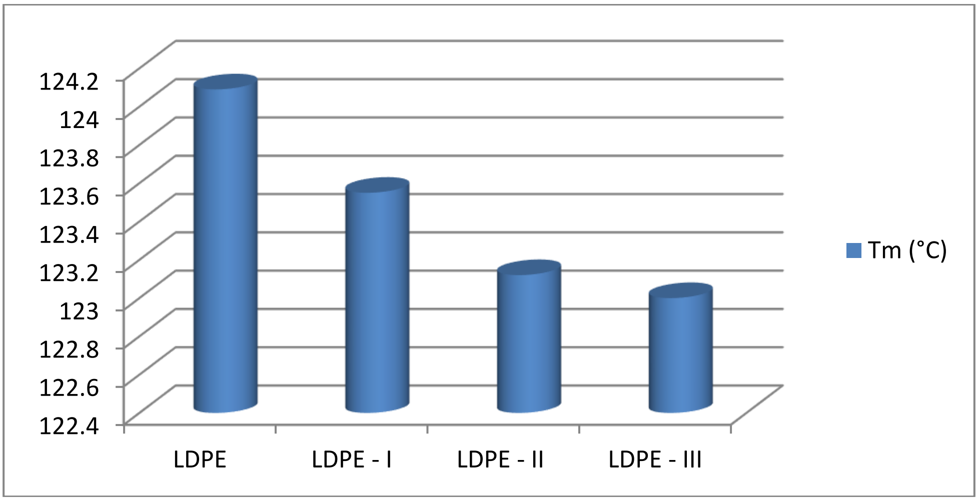


Fig : 8 Melting temperature of LDPE Specimen with different amount of CaO nanoparticles

Morphological study: The morphology of the photo degraded specimens was examined by SEM analysis. The SEM images of virgin LDPE film, and after photo degradation with nanoparticle CaO catalyst were recorded. fig: 9 The specimens were initially fairly smooth, but after 28 days photodegradation significant morphological change was observed. The surface of LDPE polymer was smooth and no crack was seen. In fig: 10, after 28 days photodegraded specimen LDPE - I the surface became rough, cavities were observed with the appearance of defects and decomposition, which shows that polymer specimen was degraded during photodegradation. As shown in fig: 11. specimen LDPE - II fragment of surface became small due to increasing weight of semiconductor which can also be seen in specimen LDPE - III CaO fig :12 amount of semiconductor is more than other and surface has broken in more small fragment.

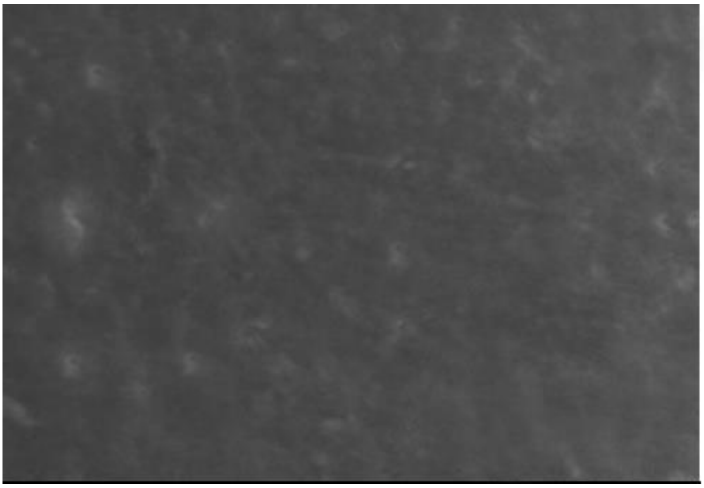


Fig: 09 SEM image of LDPE

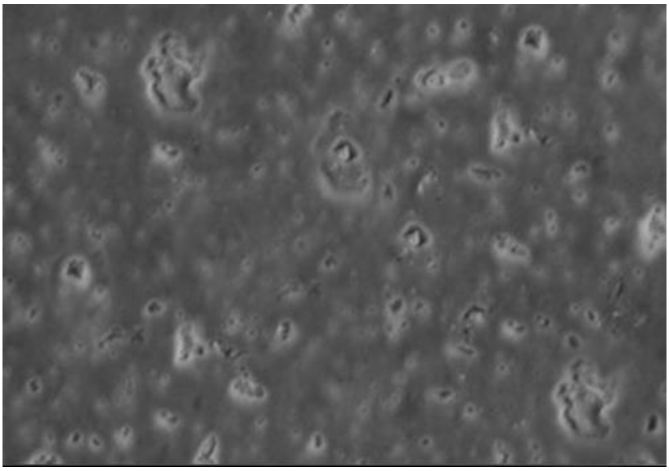


Fig: 10 SEM image of LDPE - I

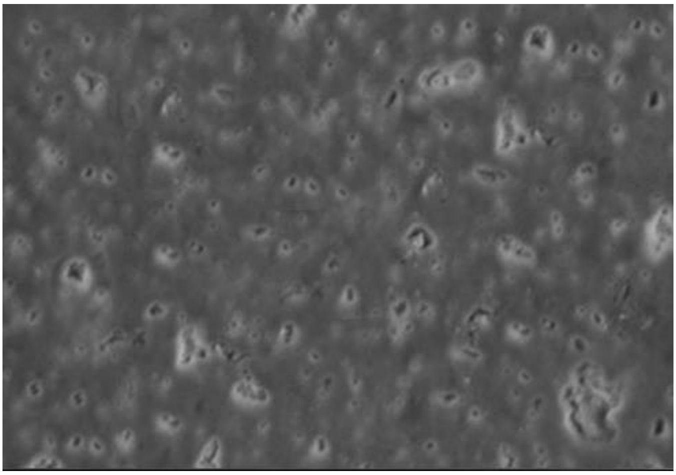


Fig: 11 SEM image of LDPE - II

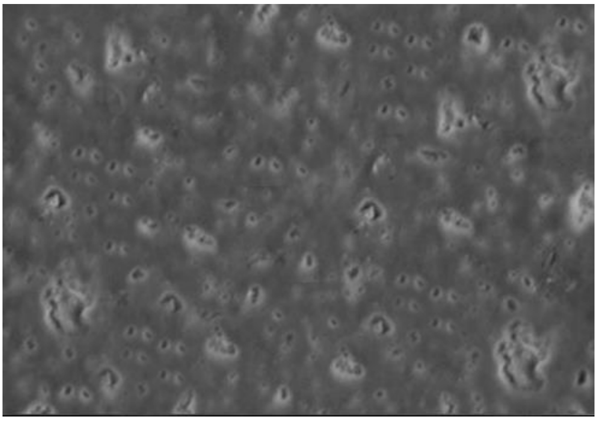


Fig: 12 SEM image of LDPE - III

4. Conclusion:

The photodegradation of LDPE was studied using CaO nanoparticles as catalyst. Three different quantity of CaO nanoparticles were used viz. 0.1 gm, 0.2gm and 0.3gm, synthesized by precipitation technique. Therefore, CaO showed better photocatalytic property under halogen lamp radiation which showed 28 days period. Partial oxidation leads to the formation of carbonyl group which was confirmed from the IR spectrum and the carbonyl group induced crystallinity was observed in DSC. SEM images clearly indicated the formation of cavities in the polymer matrix upon photodegradation. All these data confirmed the degradation of LDPE using CaO nanoparticles. A possible mechanism of degradation is proposed based on the results from IR and DSC. More research has to be focused on the applications and large scale production of such eco friendly materials aiming at the development of completely degradable plastics.

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