Visible light induced photocatalytic degradation of linear low density polyethylene (LLDPE) using CaO nanoparticles

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Abstract: The photocatalytic degradation of linear low density polyethylene (LLDPE) using CaO nanoparticles was carried out using 500 Watt lamp. After degradation of LLDPE, morphology, crystallinity as well as thermal properties of the specimen was investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD) and differential scanning calorimetry (DSC). SEM results, before and after photodegradation, showed the LLDPE to be much more prone to cracking into small snippet, which indicated a rise in crystallinity with different amount of CaO nanoparticles. The DSC result confirmed the remarkable influence of photodegradation on degree of crystallinity (X_C %), fusion enthalpy (ΔH Jg^{-1}) and melting temperature (T_m) of LLDPE. Infrared spectrometry (FTIR) has demonstrated different functional groups obtained after chain scission. The comparison of FTIR before and after photodegradation confirmed fragmentation of the polymer chain. Results showed that LLDPE was degraded successfully by using CaO nanoparticles under visible light exposure.

Keyword: Nanoparticles, Catalyst, CaO, Photocatalytic degradation, linear low density polyethylene, LLDPE.

Introduction

The increase in demand for polymer materials especially in packaging industries is responsible for generation of polymer wastes and due to environmental concern, due to durability, good weather resistance, humidity resistance, microbial and sunlight protection, chemical resistance, etc.[1-2] LLDPE is used in agriculture as a greenhouse covermaterial[3], chicken meat wrapping[4]. It is also used in medical industry for antibacterial application[5], surface coating application[6] and many more commercial applications.

Besides many uses of LLDPE polymer, it affects our environment adversely too. Researchers reported many microplastics sedimented in marine, which affect the aquatic life, river water pollution, air pollution, blockage of drainage, marine pollutions, etc.[7,8] Pollution by polyethylene family has given bad effect on human health like irritation in the eye, vision failure, respiratory problems, liver dysfunction, cancers, skin diseases, lungs problems, headache causes for using toxic plastics.[9] Production of polyethylene family poly bags also enhance ozone layer depletion and environmental hazard.[10] Many method has been developed for LDPE degradation like radiation degradation[11-12], thermooxidative degradation[13], thermal degradaion[14], environmental degradation[15], photochemical degradation[16], biodegradation[17-18], oxidation method, and photocatalytic degradation method.[19-23] By applying some semiconductors like BEA, FAU, MWW, MOR and MFI zeolites, the rate of photodegradation of polyethylene is increased.[24-26] In this work, photocatalytic degradation of LLDPE has been investigated using CaO nanoparticles catalyst in xylene solvent.

2. Experimental

In this experiment, LLDPE was used, which was provided by Reliance Polymer Ltd. Crompton halogen lamp of 500 W was used for photodegradation. Xylene (97% pure) solvent was used for dissolving LLDPE, 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 (Himedia). Initially, 6 g of calcium hydroxide ($Ca(OH)_2$) was dissolved in 24 mL of ethylene glycol and stirred at 1200 RPM and then 2 gm of sodium hydroxide (NaOH) was added into the mixture. After 10 minutes of sonication, the solution was left to settle down for 8 hours. The precipitated specimen was filtered and then the precipitate was washed with distilled water for 10 times and then dried at 100°C, subsequently. Finally, specimen was calcinated at 800^0C. Calcium oxide nanoparticles were obtained at the end of process[27].The reaction can be written as:

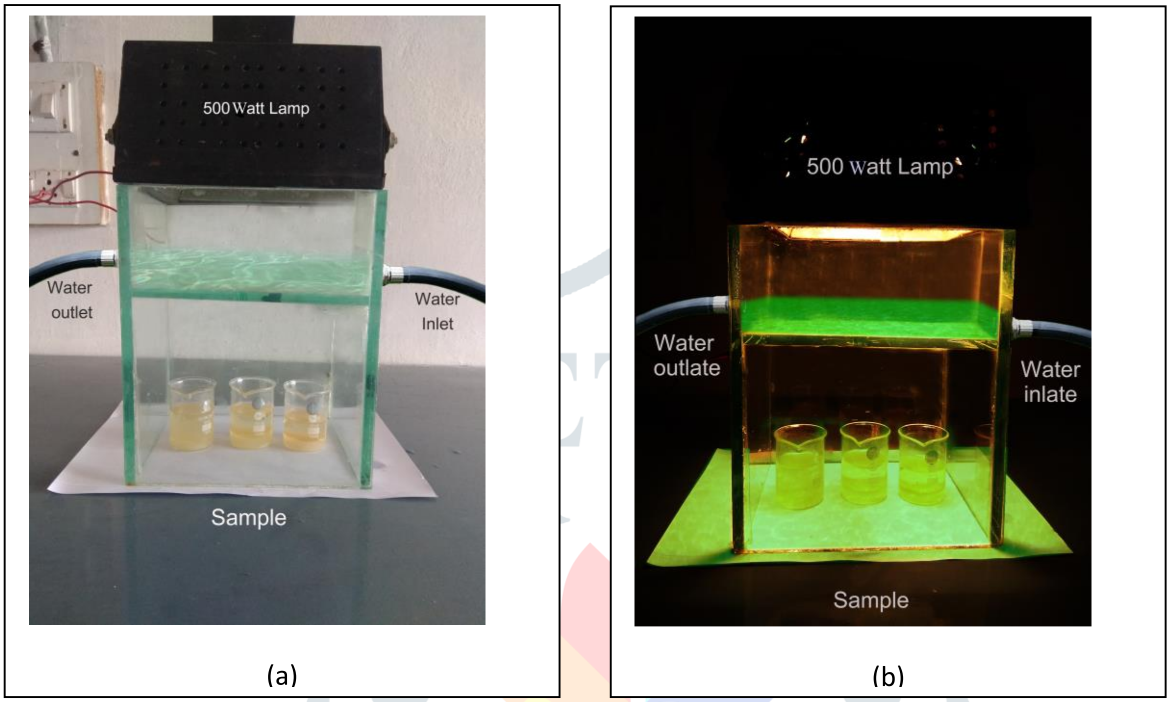
$$10\,Ca(OH)_2 + OHCH_2CH_2OH + 4\,NaOH \longrightarrow 10\,CaO + 2\,Na_2CO_3 + 10\,H_2O$$

2.2 Specimen preparation of LLDPE and nanoparticles CaO semiconductor:

1 g of LLDPE 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. These were named as : LLDPE-I for 0.1 g CaO + LLDPE, LLDPE- II for 0.2 g CaO + LLDPE and LDPE-III for 0.3 g CaO + LLDPE.

2.3 Photodegradation of LLDPE specimen:

A photodegradation glass box having one single out let and inlet was fabricated (Fig. 1) for water circulation and exposure under visible light source. Dimension of glass box was (19 x 23 x 17 cm). 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. After photodegradation of LLDPE, the sample was examined by FTIR spectroscopy, differential scanning calorimetry (DSC) and scanning electron microscopy (SEM).



(a) (b)

Fig. 1: Schematic setup for photodegradation of LLDPE 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 400 to 4000 cm^{-1}.The specimens were obtained in the form of thin films and were 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 aluminium 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: $\% X_c = \Delta H / W \times \Delta H_{fo} \times 100$

Where ΔH is the enthalpy of fusion, obtained from DSC curve, ΔH_{fo} is the enthalpy heat of 100% crystalline LLDPE ($276 Jg^{-1}$)[29] and W is weight fraction of LLDPE 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 to study the changes in morphology.

3. Result and discussion:

3.1 XRD of CaO nanoparticles:

XRD analysis of the sample was done 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 (Fig. 2). 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 12 nm, which confirmed the synthesis of nanoparticles of CaO.

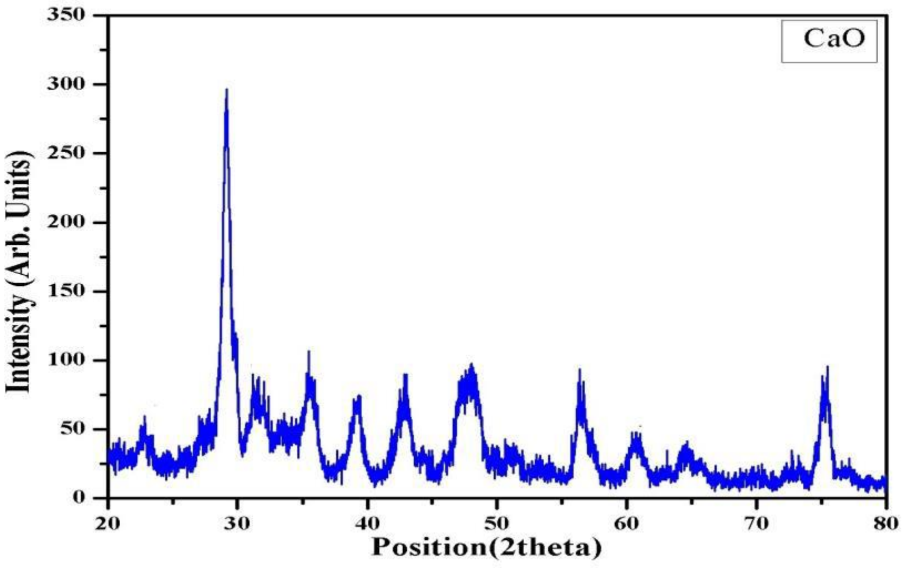
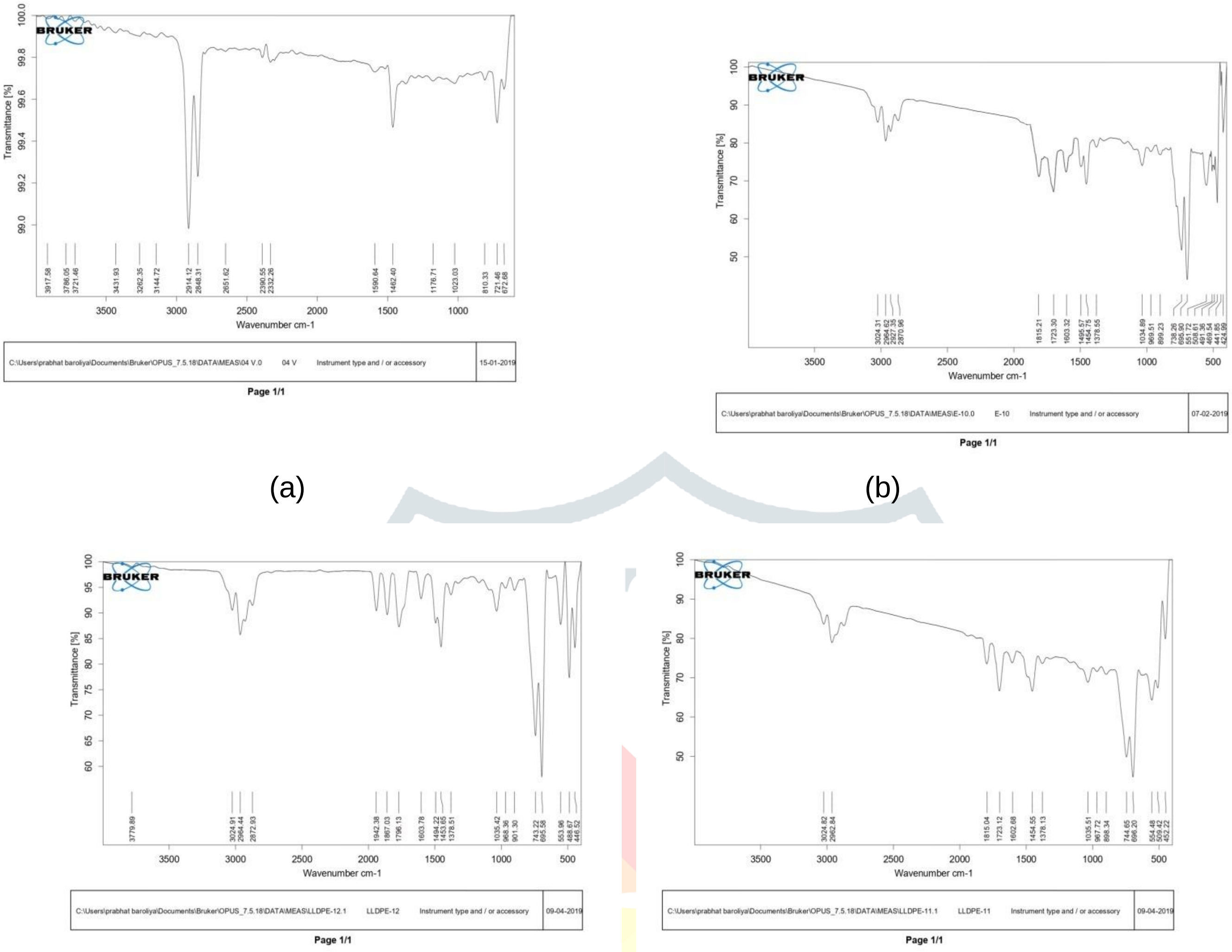


Fig. 2: XRD analysis of CaO nanoparticles

3.2 FTIR Spectra:

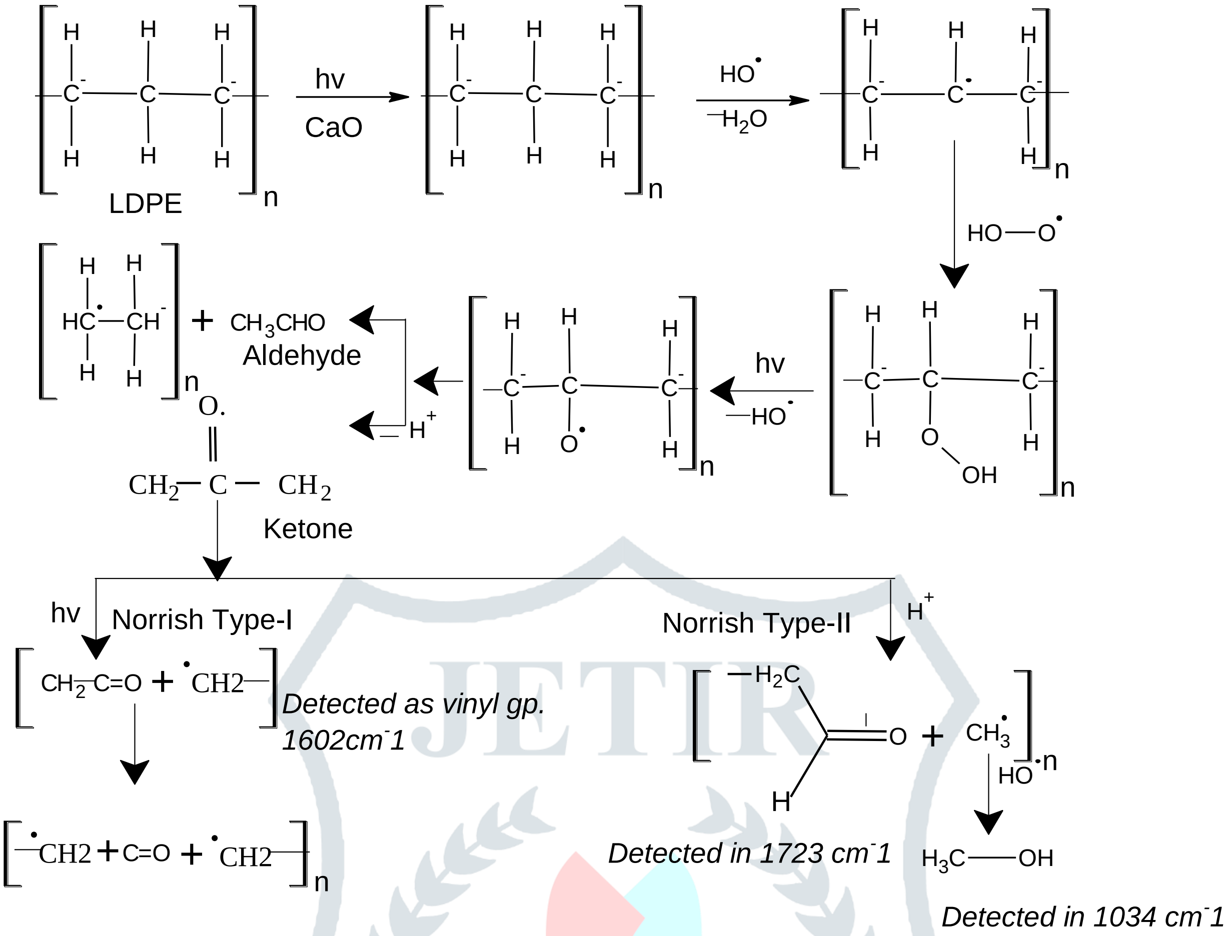
The photodegradation of LLDPE specimens was examined using FT-IR spectroscopy. Fig. 3 shows the FT-IR spectra of the LLDPE specimen using nanoparticles of CaO as a catalyst with before and after UV irradiation for 28 days. The IR spectra of specimen photodegradation carried out under 500 Watt lamp are shown in Scheme 1. It was observed that the LLDPE specimen showed the characteristic absorption in the region 3024 cm^{-1}, 2964 cm^{-1}, 2848 cm^{-1}, 2332 cm^{-1}, 1462 cm^{-1}, 1378 cm^{-1} and 744 cm^{-1} which corresponds to $-CH_2$ stretching and bending vibrations. The photodegradation of LLDPE specimen was ensured by the formation of carbonyl groups due to the partial oxidation of LLDPE. The spectra of the photodegradation specimen showed a new peak around 1723 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 LLDPE 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. It is clearly visible that broad peak was observed from 1796 cm^{-1} to 1723 cm^{-1}.These absorption could have been due to 1723 cm^{-1} carbonyl, 1034 cm^{-1} ketone, respectively. Increasing absorption with time is shown here and 1602 cm^{-1} peak shows a vinyl group. The sharp peaks of absorption at 696 and 743 cm^{-1} show C-C bending and methylene rocking, respectively.



(a) (b)

(c) (d)

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



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

3.3 DSC:

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

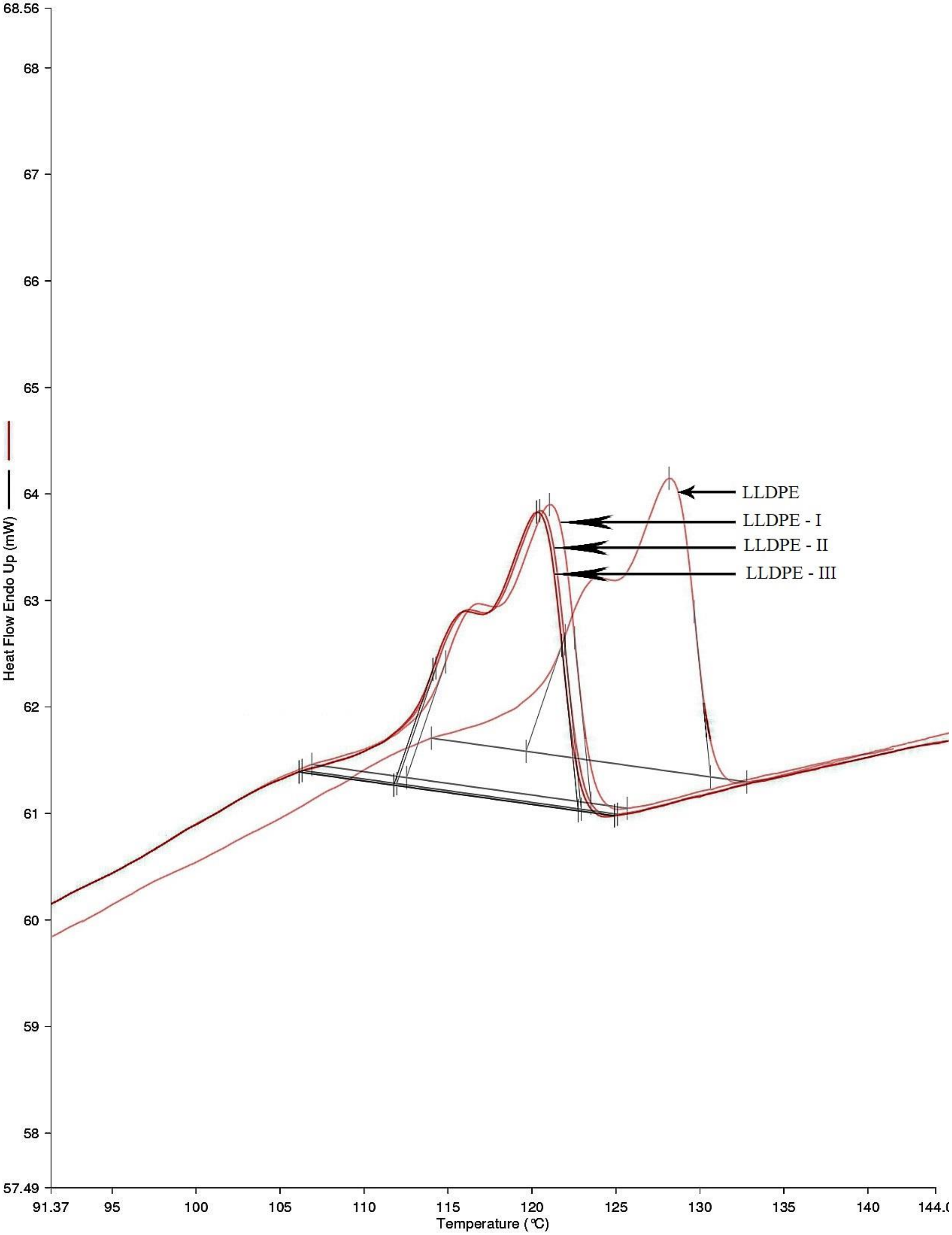


Fig. 4: Thermogram of LLDPE and phototreated LLDPE with different amounts of catalyst

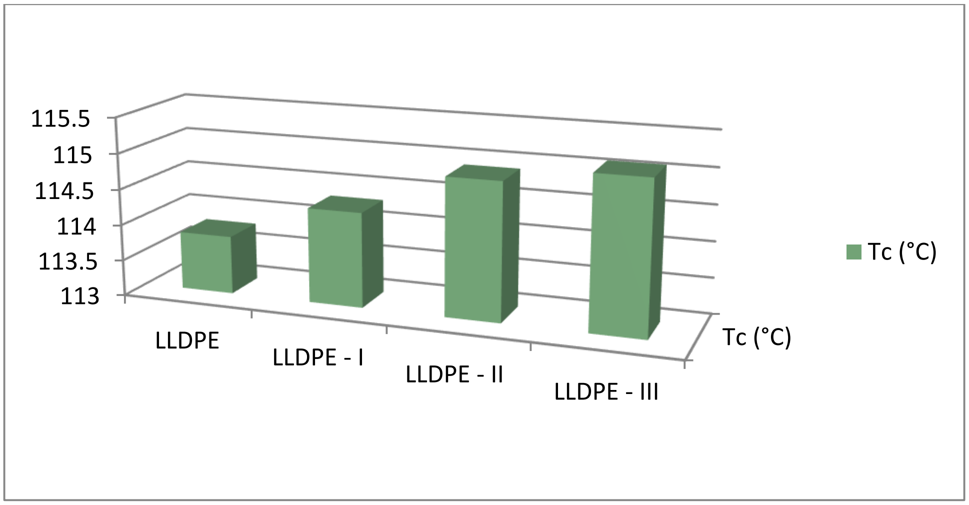


Fig. 5: DSC Crystallization Temperature of LLDPE Specimen with different amount of CaO nanoparticles

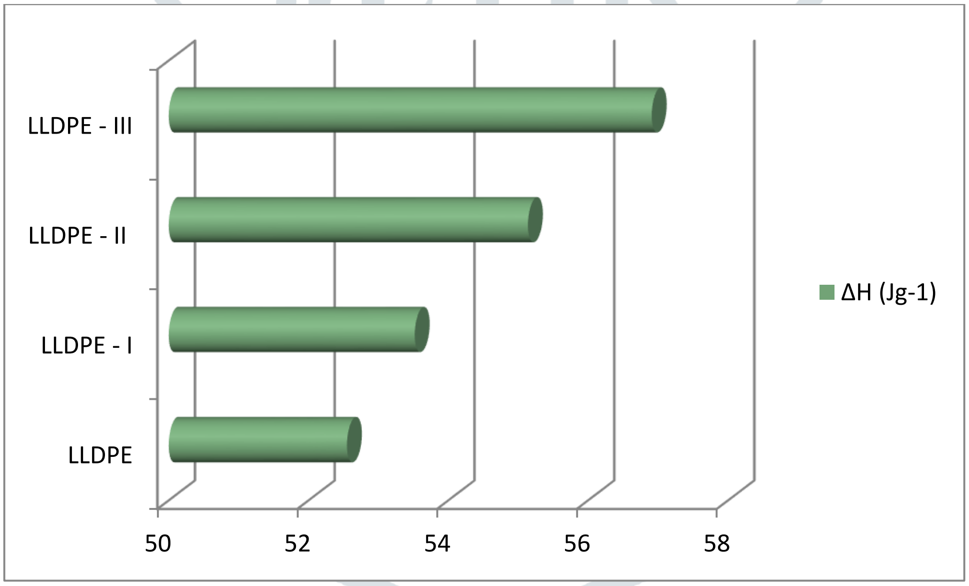


Fig. 6: DSC Fusion enthalpy of LLDPE Specimen with different amount of CaO nanoparticles

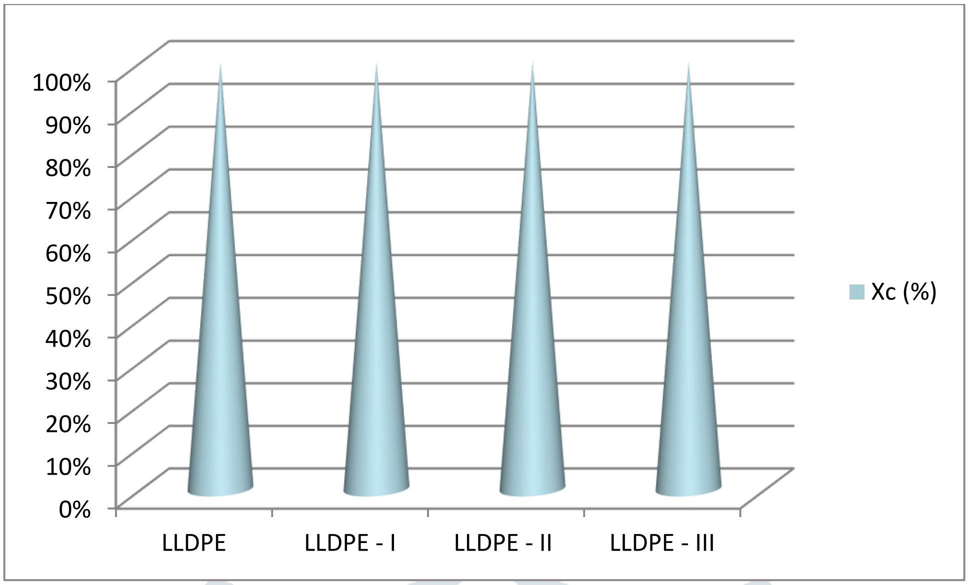


Fig. 7: Degree of Crystallinity of LLDPE Specimen with different amount of CaO nanoparticles

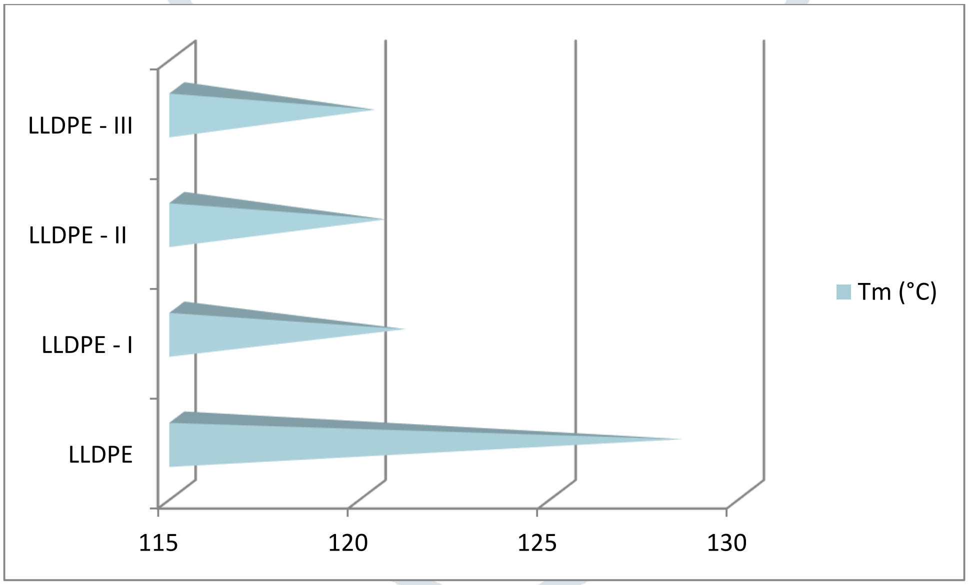


Fig. 8: Melting temperature of LLDPE Specimen with different amount of CaO nanoparticles

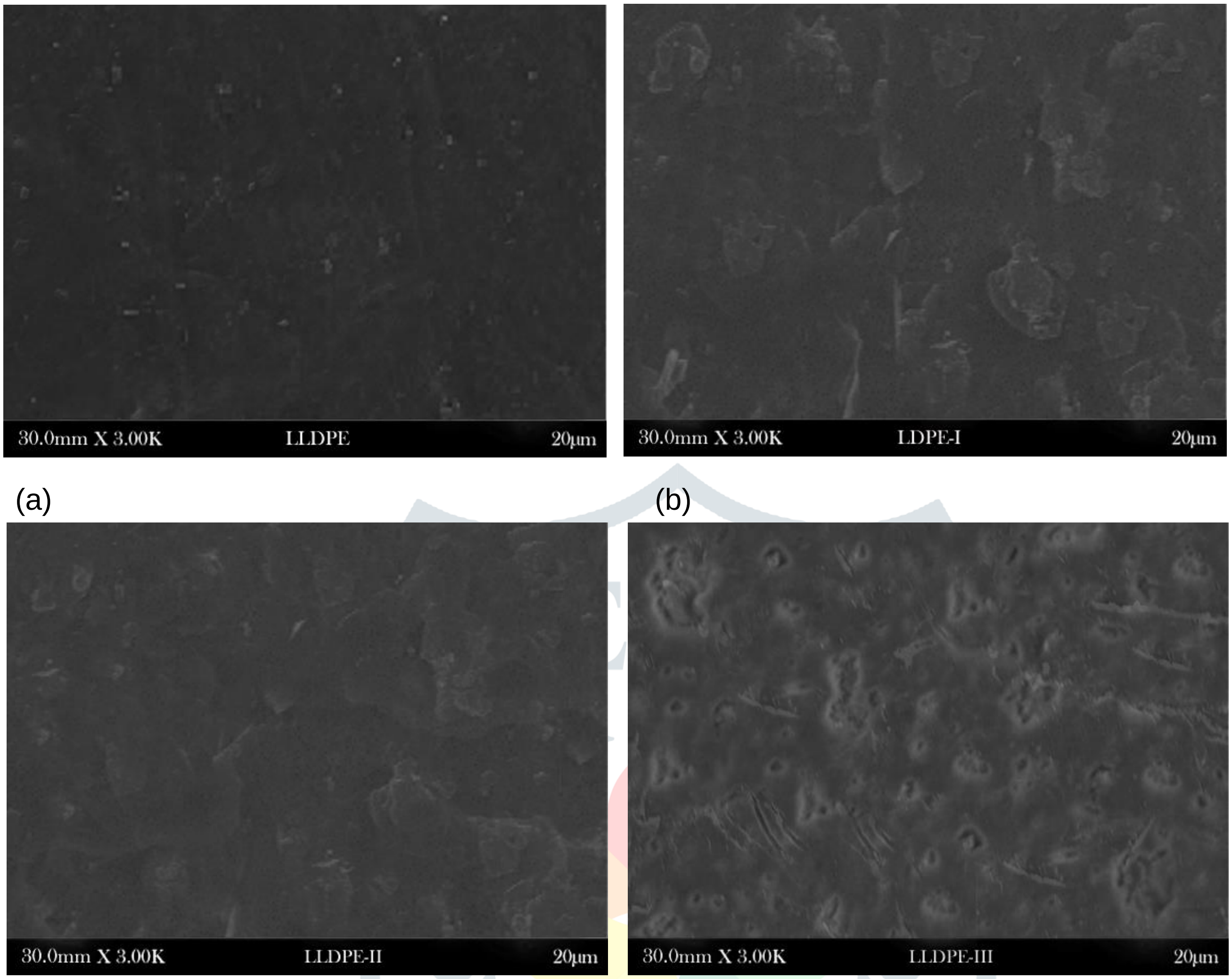
Table 1: Parameters obtained from DSC measurements for virgin LLDPE and photodegraded LLDPE specimen T_m is melting temperature, T_c is crystalline temperature, ΔH fusion enthalpy and Xc is a degree of crystallinity.

S.No.	**Specimen**	**T_c (°C)**	**T_m(°C)**	**ΔH Jg^{-1}**	**Xc (%)**
1.	LLDPE	113.81	128.32	52.55	19.03
2.	LLDPE-I	114.32	121.02	53.52	19.39
3.	LLDPE-II	114.91	120.50	55.14	19.97
4.	LLDPE–III	115.41	120.22	56.91	20.61

While the crystallization temperature tends to shift to higher values from 113.81 to 115.41 with increasing the amount of CaO nanoparticles as shown in Fig. 5 and Table 1. This indicated that the CaO nanoparticles help crystallization of LLDPE and this effect becomes more manifest with higher amount of CaO nanoparticles. Fusion enthalpy was increased after photodegradation from 52.55 ΔH Jg^{-1} to 56.91 ΔH Jg^{-1} (Fig. 6 and Table 1). From the Fig. 7 and 8, it can also be seen that the crystallinity of LLDPE specimen decrease from 19.03 to 20.61 X_C % and melting point decrease 128.32 to 120.22 T_m (^{0}C) with increasing exposure time. It is well known that chain scission occurs during photodegradation resulting in decreased molecular size, which enhances mobility of chain.

3.4 Morphological study by SEM:

The morphology of the photodegraded specimens was examined by SEM analysis. The SEM images of LLDPE film, before and after photodegradation 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 LLDPE polymer was smooth and no crack was seen. In Fig. 9 (b), after 28 days photodegraded specimen of LLDPE-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. 9 (c), specimen of LLDPE-II fragment of surface became small due to increasing weight of semiconductor which can also be seen in specimen of LLDPE-III, CaO amount of semiconductor is more than other and surface has broken in smaller fragments (Fig. 9 (d)).



(a) (b)

(c) (d)

Fig. 9: SEM images of (a) LLDPE Sample (b) LLDPE-I (c) LLDPE-II and (d) LLDPE-III

4. Conclusion:

The photodegradation of LLDPE was studied using CaO nanoparticles as catalyst. Three different quantity of CaO nanoparticles were used viz. 0.1 g, 0.2 g and 0.3 g, synthesized by precipitation technique. CaO showed better photocatalytic property under halogen lamp radiation when exposed for 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 photodegrdation. All these data confirmed the degradation of LLDPE using CaO nanoparticles. A possible mechanism of degradation is proposed based on the results from IR and DSC.[28] 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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