

Photocatalytic Degradation of High Density Polyethylene using CaO Nanocatalyst

V.S. KUMAWAT¹, J.P. BHATT¹, D. SHARMA², S.C. AMETA¹ and R. AMETA^{1,3,*}

¹Department of Chemistry, PAHER University, Udaipur-313003, India

²Department of Chemistry, Vidya Bhawan Rural Institute, Udaipur-313002, India

³Department of Chemistry, J.R.N. Rajasthan Vidyapeeth (Deemed to be University), Udaipur-313001, India

*Corresponding author: Email: rakshit_ameta@yahoo.in

Received: 6 April 2020;

Accepted: 10 June 2020;

Published online: 20 August 2020;

AJC-20028

The photodegradation of high density polyethylene (HDPE) using CaO nanoparticles as a catalyst was carried out using 500 W lamp. After exposure, morphology as well as thermal properties of the HDPE was investigated by scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). SEM results showed that the HDPE is more prone to crack into small fragments, which indicated a rise in crystallinity with different amounts of catalyst *i.e.* CaO nanoparticles. The DSC results confirmed the remarkable influence of photodegradation on degree of crystallinity ($X_c\%$), fusion enthalpy ($\Delta H J g^{-1}$) and melting temperature (T_m) of HDPE. Infrared spectrometry (FTIR) demonstrated all functional groups of HDPE, present before and after photodegradation. Overall results showed that HDPE was photodegraded into small fragments successfully by using CaO nanoparticles, where different functional groups such as carbonyl, esters and vinyl were obtained during chain scission.

Keywords: Nanoparticles, Catalyst, CaO, Photocatalytic degradation, High density polyethylene.

INTRODUCTION

The present time is known as polymer age, as most of the materials in different applications have been replaced by a variety of polymers. The useful properties and low cost of polymers made them important and unique. The most commonly used polymer is polyethylene, which is used in different forms *i.e.* low density polyethylene (LDPE) and high density polyethylene (HDPE). High density polyethylene (HDPE) is widely applied in broad range of applications in packaging films, wrapping materials, shopping and garbage bags, fluid container, clothing, toy, household, television box, radio box and building materials, *etc.* throughout the world. HDPE is also used as an antibacterial [1,2], antimicrobial, hydrophobic coating material [3], filament [4], engineering composite material [5], *etc.* HDPE is hardly degraded and it remained for several years on earth due to environmental resistance properties and as a result, leading to infertile land [6,7], water pollution, air pollution, blocked drainage, marine pollutions, *etc.* [8,9]. This problem is multiplied due to over use and harvesting, dumping of polymeric wastes in oceans [10-12]. This polymer has many

adverse effects and creates problems in human beings such as irritation in the eye, failure of vision, difficulties in breathing, dysfunction of liver, respiratory organs, skin diseases, cancers, *etc.* [6]. Moreover, manufacturing of HDPE enhances ozone layer depletion and produce toxic gases, which are hazardous to environment [13-15].

Researchers have developed different methods for degradation of such polymers. Serrano *et al.* [16] investigated thermal cracking of HDPE (a polyolefin) in solvents having tendency to donate hydrogen (tetralin, decalin and 1-methylnaphthalene, 9,10-dihydroanthracene). Thermal and flame retardancy properties of high-density polyethylene (HDPE)/ethylene vinyl-acetate copolymer (EVA)/fullerene (C_{60}) nanocomposites were studied by Liu *et al.* [17]. Chrissafis *et al.* [18] studied the kinetic analysis of thermal decomposition of HDPE and its nanocomposites by preparing a series of HDPE nanocomposites containing fumed silica (SiO_2) nanoparticles. It was observed that SiO_2 had almost no effect on decomposition mechanism; however, activation energies were affected. Ewais *et al.* [19] studied the effect of time to rupture a 1.5 mm thick HDPE geomembrane under a pressure of 250 kPa at 85 °C. Similarly,

Martínez-Romo *et al.* [20] studied the changes in structural properties of different polymers such as HDPE films, LDPE films, biodegradable polyethylene (PE-BIO) and oxodegradable polyethylene (PE-OXO) when exposed to UV-B radiation. It was observed that LDPE and HDPE films on pretreatment by an accurate radiation UV-B dosage before its use can become a good option for biodegradable material without the addition of any organic agents or photosensitizers. In the present investigation, an effort has been made to degrade HDPE using CaO in presence of light and the observations revealed that HDPE has been degraded in smaller fragments.

EXPERIMENTAL

In this work, high density polyethylene (HD53EA010) (Reliance Polymer Ltd., India) was used. Halogen lamp 500 W (Crompton Ltd.) was used for irradiation. Xylene (97% pure) (Qualigens) solvent was used for dissolving HDPE, while CaO nanoparticles were prepared by the reported method [21]. In brief, 1 g of HDPE was dissolved in 150 mL xylene solution using magnetic stirrer at 150 °C. After dissolving it completely, solution was separated into three groups as: (i) 0.1 g CaO + HDPE (HDPE-I), (ii) 0.2 g CaO + HDPE (HDPE-II) and (iii) 0.3 g CaO + HDPE (HDPE-III).

Photodegradation of HDPE: Photodegradation of HDPE was carried out in a fabricated reactor. The specimen was kept 17 cm away from lamp. Light was passed through water filter (2 mm layer), which was used for absorbing heat during reaction and kept for 28 days. Sampling was carried out by withdrawing the specimen from the chamber at regular interval of time to monitor photodegradation.

FTIR analysis: FTIR spectra were obtained before and after photodegradation using a Bruker Alpha FTIR with ATR spectrometer. The specimen of HDPE was obtained in the form of thin films was viscous in nature.

DSC analysis: Thermal analysis of the specimen before and after photodegradation was carried out using a differential scanning calorimeter (Perkin-Elmer, calibrated with indium and zinc standards). HDPE (5.0 ± 0.2 mg) was used for each measurement and it was placed in a sealed aluminium pan, and then heated to 160 °C at a scanning rate of 20 °C/min in an inert atmosphere (N₂ 50 mL/min). Melting 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:

$$X_c (\%) = \frac{\Delta H}{W} \times \Delta H_f^0 \times 100$$

where ΔH is the enthalpy of fusion, obtained from DSC curve, ΔH_f⁰ is the enthalpy heat of 100% crystalline HDPE (290 J g⁻¹) and W is weight fraction of high density polyethylene specimen.

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

RESULTS AND DISCUSSION

XRD studies: The sharp peaks in the XRD pattern (Fig. 1) of as-prepared sample indicated the crystalline nature of CaO

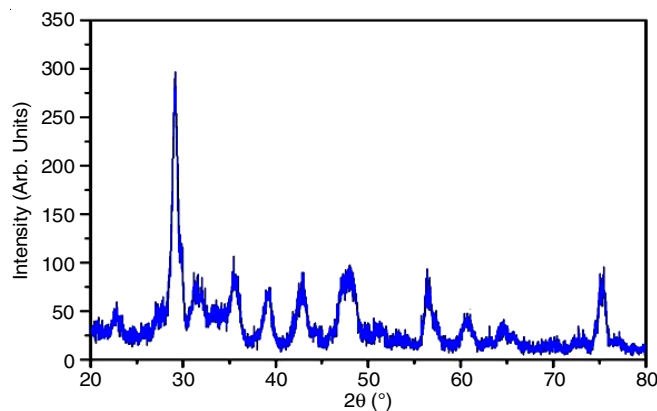


Fig. 1. XRD analysis of CaO nanoparticles

nanoparticles. Crystallite size of CaO nanoparticles was calculated by using the Scherrer formula and found to be 12 nm.

FTIR spectral studies: The photodegradations of HDPE specimens were examined using FT-IR spectroscopy. Fig. 2 shows the FT-IR spectra of HDPE specimens using nanoparticles of CaO as a catalyst with before (HDPE) and after irradiation for 28 days (HDPE-I, HDPE-II and HDPE-III). It was observed that the HDPE specimens showed the characteristic absorptions in the region 2912, 2846, 2338, 1464, 1363 and 721 cm⁻¹, which correspond to CH₂ stretching and bending vibrations. The photodegradation of HDPE specimen was ensured by the formation of carbonyl groups due to the partial oxidation of HDPE (**Scheme-I**). The spectra of all the photodegraded specimens showed a new peak around 1716 cm⁻¹, which is assigned to CO stretching vibrations. These variations in the FTIR spectra indicated that the structural changes were taken place in the HDPE specimen during photodegradation. By comparing the peak area of the carbonyl absorption band between the exposed specimens of HDPE with time and amount of nanoparticles of CaO (Fig. 2a-d), it is clear that a broad peak was observed in 1741-1716 cm⁻¹ region. These absorptions may be due to 1769-1741 cm⁻¹ (esters) and 1723 cm⁻¹ (ketones) [22]. A vinyl group with a band at 1603 cm⁻¹ was also observed with time. The absorption 1603 cm⁻¹ always appeared in spectra with a band at 969 cm⁻¹ (vinylidene unsaturations) and 738 cm⁻¹ (methylene rocking).

Differential scanning calorimetry (DSC) studies: The thermal and crystallization data were obtained from DSC for the HDPE and photo-treated HDPE with CaO nanocatalyst. DSC analysis of HDPE and photodegraded HDPE specimens with different amounts of CaO after 28 days indicated that crystalline melting peak decreases steadily due to change in molecular weight of specimen (Fig. 3).

The crystallization temperature tends to shift to higher values from 112.04 to 114.45 °C with increasing amount of CaO nanoparticles (Table-1). This indicated that the CaO nanoparticles help in crystallization of HDPE and this effect becomes more clear with higher amounts of CaO nanoparticles. Fusion enthalpy was increased after photodegradation from 184.02 to 186.50 J g⁻¹ (Table-1). It can also be seen that the crystallinity (X_c %) of HDPE specimen increases from 63.51 to 64.31 (Table-1) and melting temperature (T_m) decreases from 130.05 to 128.32 °C

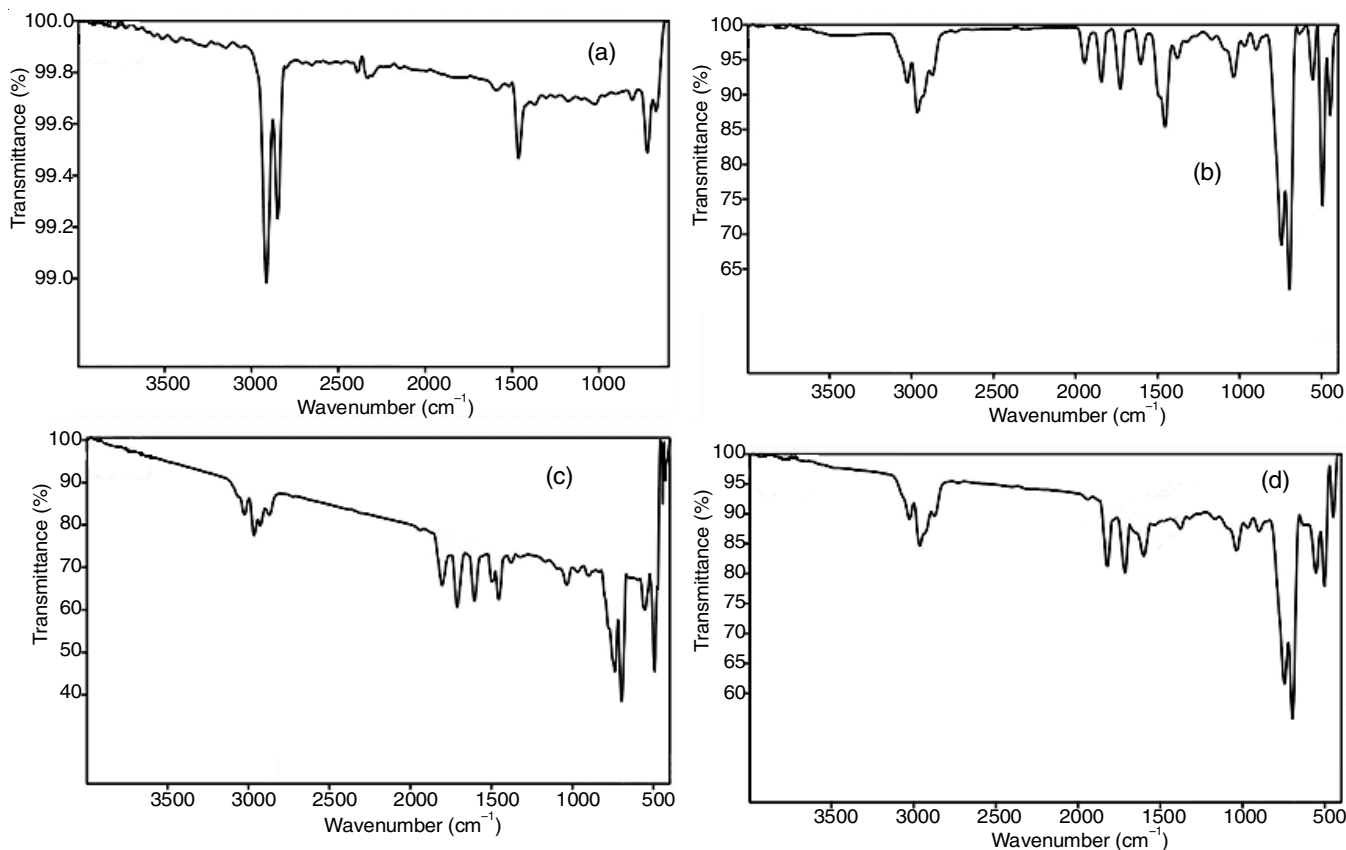
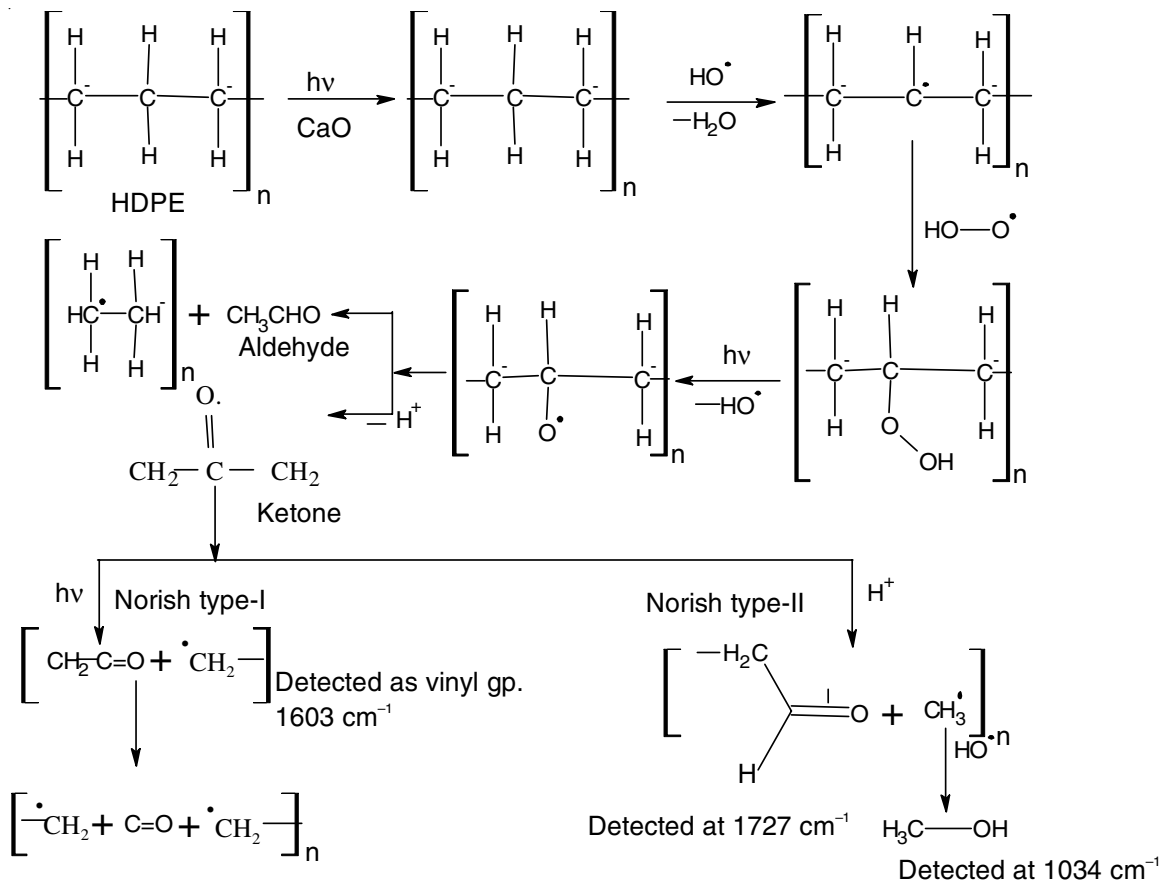


Fig. 2. FTIR spectra of (a) HDPE (b) HDPE-I (c) HDPE-II and (d) HDPE-III



Scheme-I: Reaction mechanism of photodegradation of HDPE in presence of nanoparticles of CaO

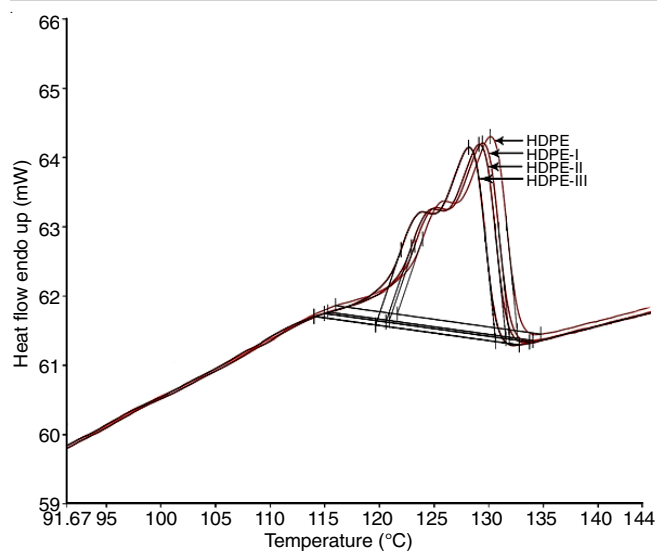


Fig. 3. DSC thermogram of HDPE and photodegraded HDPE with different amounts of CaO nanoparticles

Specimen	T_c (°C)	T_m (°C)	ΔH (J g ⁻¹)	X_c (%)
HDPE	112.04	130.05	184.02	63.51
HDPE-I	112.14	129.50	185.16	63.84
HDPE-II	113.18	129.11	185.99	64.13
HDPE-III	114.45	128.32	186.50	64.31

T_m is melting temperature, T_c is crystalline temperature, ΔH is fusion enthalpy and X_c is degree of crystallinity

(Table-1) with increasing time of exposure. It is well known that chain scission occurs during photodegradation resulting in decreased molecular size, which enhances mobility of chain.

Morphological study: The morphology of the photo-degraded specimens was examined by SEM analysis. The SEM images of HDPE film before and after photodegradation with nanoparticle CaO (catalyst) were recorded (Fig. 4a). The specimens were initially fairly smooth, but after 28 days photo-degradation, significant morphological changes were observed.

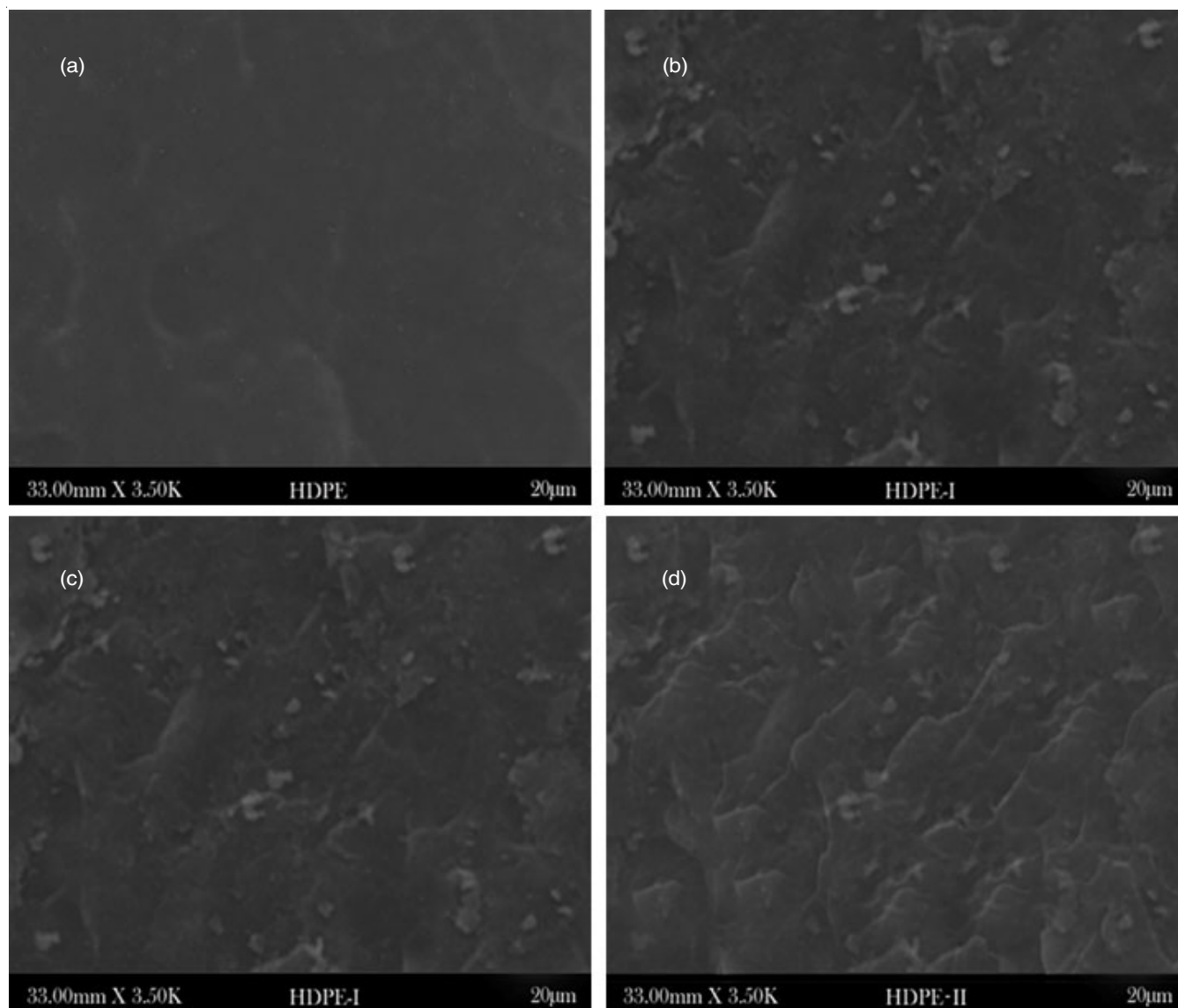


Fig. 4. SEM images of (a) HDPE, (b) HDPE-I, (c) HDPE-II and (d) HDPE-III

The surface of HDPE polymer was smooth and no crack was seen. In HDPE-I photodegraded specimen after 28 days (Fig. 4b), the surface became rough and cavities were observed with the appearance of defects and decomposition, which shows that polymer specimen was degraded during photodegradation. In case of specimen HDPE-II (Fig. 4c), fragment of surface became small due to increasing amount of CaO, which can also be seen in specimen HDPE-III (Fig. 4d), where amount of CaO is more and therefore, surface has broken in smaller fragments.

Conclusion

In present investigation, the photocatalytic degradation of HDPE was studied using CaO nanocatalyst. Three different quantities of CaO nanocatalyst were used *viz.* 0.1, 0.2 and 0.3 g. CaO showed better photoactivity under irradiation. 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 HDPE using CaO nanoparticles. A possible mechanism of degradation has also been proposed, which shows degradation of HDPE in smaller fragments. When compared the present results with another published work of LLDPE, it is found that an increase in amount of CaO nanoparticles helps in crystallization. Melting point of LLDPE was more dropped as compared to HDPE, which shows more degradation of polymer compound. Fusion enthalpy of HDPE is found higher than LLDPE, which shows better degradation. Degree of crystallinity of HDPE is also found higher than LLDPE, which shows more conversion of polymer in carbonyl fragment.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- M. Ziabka, A. Mertas, W. Krol, A. Bobrowski and J. Chlopek, *Adv. Mater.*, **315**, 218 (2012); <https://doi.org/10.1002/masy.201250527>
- D.N. Bikiaris and K.S. Triantafyllidis, *Mater. Lett.*, **93**, 1 (2013); <https://doi.org/10.1016/j.matlet.2012.10.128>
- J. Fresnais, J.P. Chapel, L. Benyahia and F. Poncin-Epaillard, *J. Adhes. Sci. Technol.*, **23**, 447 (2009); <https://doi.org/10.1163/156856108X370127>
- M. Dun, J. Hao, W. Wang, G. Wang and H. Cheng, *Compos., Part B Eng.*, **159**, 369 (2019); <https://doi.org/10.1016/j.compositesb.2018.09.090>
- T. Liu, A. Huang, L.-H. Geng, X.-H. Lian, B.-Y. Chen, B.S. Hsiao, T.-R. Kuang and X.-F. Peng, *Compos. Sci. Technol.*, **167**, 301 (2018); <https://doi.org/10.1016/j.compscitech.2018.08.004>
- R. Anand, J.R. Ramanujam, S. Kulothungan, C.N. Murugalakshmi, V. Sharanya and K. Bhuvanewari, *J. Ind. Pollut. Cont.*, **24**, 129 (2008).
- D. He, Y. Luo, S. Lu, M. Liu, Y. Song and L. Lei, *TrAC Trends Anal. Chem.*, **109**, 163 (2018); <https://doi.org/10.1016/j.trac.2018.10.006>
- P. Pavani and T.R. Rajeswari, *J. Chem. Pharm. Sci.*, **3**, 87 (2014).
- A. Grover, A. Gupta, S. Chandra, A. Kumari and S.M.P. Khurana, *Int. J. Environ. Sci.*, **5**, 1091 (2015).
- M. Eriksen, N. Maximenko, M. Thiel, A. Cummins, G. Lattin, S. Wilson, J. Hafner, A. Zellers and S. Rifman, *Mar. Pollut. Bull.*, **68**, 71 (2013); <https://doi.org/10.1016/j.marpolbul.2012.12.021>
- S.L. Wright, R.C. Thompson and T.S. Galloway, *Environ. Poll.*, **178**, 483 (2013); <https://doi.org/10.1016/j.envpol.2013.02.031>
- M. Bergmann, V. Wirzberger, T. Krumpfen, C. Lorenz, S. Primpke, M.B. Tekman and G. Gerdt, *Environ. Sci. Technol.*, **51**, 11000 (2017); <https://doi.org/10.1021/acs.est.7b03331>
- J.D.M. Mendez and R. Silva-Rodriguez, *Heliyon*, **4**, e01020 (2018); <https://doi.org/10.1016/j.heliyon.2018.e01020>
- O. Alam, M. Billah and D. Yajie, *Resour. Conserv. Recycl.*, **132**, 121 (2018); <https://doi.org/10.1016/j.resconrec.2018.01.037>
- S.J. Royer, S. Ferron, S.T. Wilson and D.M. Karl, *PLoS One*, **13**, e0200574 (2018); <https://doi.org/10.1371/journal.pone.0200574>
- D.P. Serrano, J. Aguado, G. Vicente and N. Sanchez, *J. Anal. Appl. Pyrolysis*, **78**, 194 (2007); <https://doi.org/10.1016/j.jaap.2006.07.001>
- H. Liu, P. Song, Z. Fang, L. Shen and M. Peng, *Thermochim. Acta*, **506**, 98 (2010); <https://doi.org/10.1016/j.tca.2010.04.029>
- K. Chrissafis, K.M. Paraskevopoulos, E. Pavlidou and D. Bikiaris, *Thermochim. Acta*, **485**, 65 (2009); <https://doi.org/10.1016/j.tca.2008.12.011>
- A.M.R. Ewais, R.K. Rowe and J. Scheirs, *Geotext. Geomembr.*, **42**, 111 (2014); <https://doi.org/10.1016/j.geotextmem.2014.01.004>
- A. Martínez-Romo, R. González-Mota, J.J. Soto-Bernal and I. Rosales-Candelas, *J. Spectrosc.*, **2015**, 586514 (2015); <https://doi.org/10.1155/2015/586514>
- V.S. Kumawat, J. Bhatt, D. Sharma, S.C. Ameta and R. Ameta, *J. Emerg. Technol. Innov. Res.*, **6**, 611 (2019).
- T. Ojeda, A. Freitas, K. Birck, E. Dalmolin, R. Jacques, F. Bento and F. Camargo, *Polym. Degrad. Stab.*, **96**, 703 (2011); <https://doi.org/10.1016/j.polymdegradstab.2010.12.004>