Photodegradation of polypropylene using CaO nanoparticles as a catalyst

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The photodegradation of polypropylene has been studied using calcium oxide nanoparticles as a catalyst under halogen lamp. Morphology as well as thermal properties of the sample were investigated by SEM and DSC. SEM results show that the polypropylene is prone to cracking into small fragments indicating a rise in crystallinity with different dosages of catalyst. The DSC results confirmed the remarkable influence of photodegradation on degree of crystallinity (X_C%), fusion enthalpy (ΔH Jg^{-1}) and melting temperature (T_m) of polypropylene. FTIR spectrometry showed the presence of carbonyl groups, which were obtained after photodegradation. Results show that polypropylene was successfully degraded by CaO nanoparticles generating different functional group during chain scission.

Keywords: CaO, nanoparticles, polypropylene (PP), photodegradation.

Introduction

Polypropylene (PP) is widely used all over the globe in different appliances in a broad range of applications viz. packaging films, wrapping material, shopping and garbage bags, fluid container, clothing, toy, household, building materials, etc.[1,2]. Polypropylene is also used as antibacterial, antimicrobial, hydrophobic material application, automobile industries, etc.[3,4]. This is a known fact that this polymer hardly degrades and it remained for several years on earth and due to this reason, our planet is facing a major problem of polymer pollution. This polymer shows adverse effect on human health also like irritation in the eye, vision failure, breathing difficulties, respiratory problems, liver dysfunction, cancers, skin diseases, lung problems, headache, etc. Polypropylene is also responsible for serious environmental pollution such as soil pollution (infertile land), water pollution, air pollution, blocking drainage, marine pollution, etc. In the sea, the threat in various forms to marine life is due to over exploitation and harvesting, dumping of waste, pollution, alien species, land reclamation, dredging and global climate change[5–7]. There are various methods to degrade polypropylene like biological method[8,9], oxidation method[10,11], thermal degradation[12–14], chemical degradation[15], mechanical degradation[16], environmental ageing[17,18], radiation degradation[19,20], pyrolytic degradation[21], UV degradation[22], photodegradation, etc.[23].

Photodegradation of polymer converts high molecular weight polymer into a low molecular weight materials and also produce some new molecules. Polymer loses its properties like lustre, strength and molecular weight[24–26]. Different materials like TiO_2, BEA, ZSM-5, MOR zeolites, acid treated clinoptilolite zeolites, FCC and MCM-41 have been used for degradation of polypropylene[27–31]. Catalysts may play a significant role in degradation of polymer. In present work, photocatalytic degradation of polypropylene has been investigated using nanoparticles of CaO catalyst in xylene solvent. Polypropylene granules were photocatalytically degraded using 0.1, 0.2 and 0.3 g CaO nanoparticles on exposure to 500 W halogen lamps for 28 days and are represented as PP-1, PP-2 and PP-3, respectively. Ratio of polypropylene with CaO was kept 10:1, 5:1 and 3.33:1 (w/w).
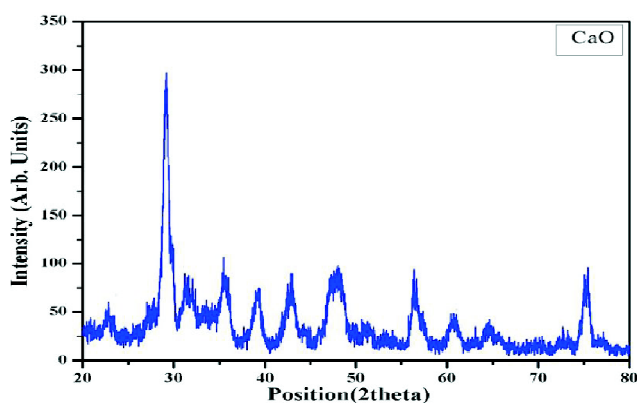
Fig. 1. XRD analysis of CaO nanoparticles.

Results and discussion

XRD of CaO nanoparticle:

Fig. 1 shows XRD analysis of the sample, where CaO intense peaks were observed. The sharp peaks in the XRD pattern of as-prepared sample indicated the crystalline nature of CaO nanoparticles. Crystallite size of CaO nanoparticles was calculated by using the Scherrer formula. The average particle size of CaO particles was found to be 12 nm. Purity of CaO was confirmed with JCPDS No. was 00-077-2376 and the phase was found to be calcite.

FT-IR spectra:

The photocatalytic degradation of polypropylene samples was examined using FT-IR spectroscopy (Fig. 2.). It was observed that the PP sample showed the characteristic absorptions in the region 2913, 2884, 1462, 1368 and 722 cm^{-1}, which corresponds to -CH$_2$ stretching and bending vibrations[32]. The photodegradation of polypropylene sample was ensured by the formation of carbonyl groups due to the partial oxidation of PP. The spectra of the phototreated sample showed a new peak around 1739 cm^{-1}, which is assigned to CO stretching vibrations (characteristic absorption of carbonyl). The intensity of carbonyl peak in the range of 1739 to 1784 cm^{-1} was observed to monitor the progress of the reaction. It was observed that the intensity of the peak was more after exposure for a longer period. These absorption bands could be due to esters, and peresters or g-lactones, respectively[33] while a peak at 1603 cm^{-1} shows a vinyl group. In polypropylene experiments, the dominance of OH groups (from hydroperoxides and derived alcohols) was demon-

strated by band at 3400 cm^{-1}. Fernando *et al.*[33] suggested that ketones were formed by β-scission of the alkoxyl radicals formed by decomposition of hydroperoxides on long term exposure.

Differential scanning calorimetry (DSC):

The thermal and crystallization data obtained from DSC for polypropylene and phototreated polypropylene with CaO nanocatalyst before and after exposure are shown in Fig. 3. DSC of samples with different amounts of catalyst show that area under crystalline melting peak decreases steadily due to change in molecular weight of sample.

It was observed that crystallization temperature tends to shift to higher values with increasing amount of CaO nanoparticles from 110.7 to 111.02°C (Fig. 4 and Table 1). This indicates that the CaO nanoparticles helped in crystallization of PP and it was more with the increase in amount of CaO nanoparticles. Fusion enthalpy was also increased after photodegradation from 97.25 to 99.93 ΔH Jg^{-1} (Fig. 5). It can also be seen that the crystallinity of PP sample increases from 46.98 to 48.27% with increasing exposure time (Fig. 6). It is well known that chain scission occurs during photodegradation and it resulted in decreased molecular size enhancing the mobility of chain[35].

Morphological study:

The morphology of the photodegraded samples was examined by SEM analysis. The SEM images of polypropylene film, before and after photodegradation in presence of CaO nanoparticles were recorded (Fig. 7). It was observed that the samples were initially relatively smooth, but after 28 days photodegradation, significant morphological changes were observed. The surface of polypropylene polymer was smooth and no cracks were seen after 28 days photodegradation (Fig. 7a.). It was observed that in case of PP-1, surface becomes rough and cavities were observed with the appearance of defects due to decomposition, which shows that polymer sample has degraded during photodegradation (Fig. 7b). In case of PP-2, smaller fragments of surface were observed on increasing amount of CaO nanoparticles from 0.1 to 0.2 g (Fig. 7c), which becomes more evident in case of PP-3, where amount was kept 0.3 g (Fig. 7d). Based on these observations, it can be concluded that surface has bro-
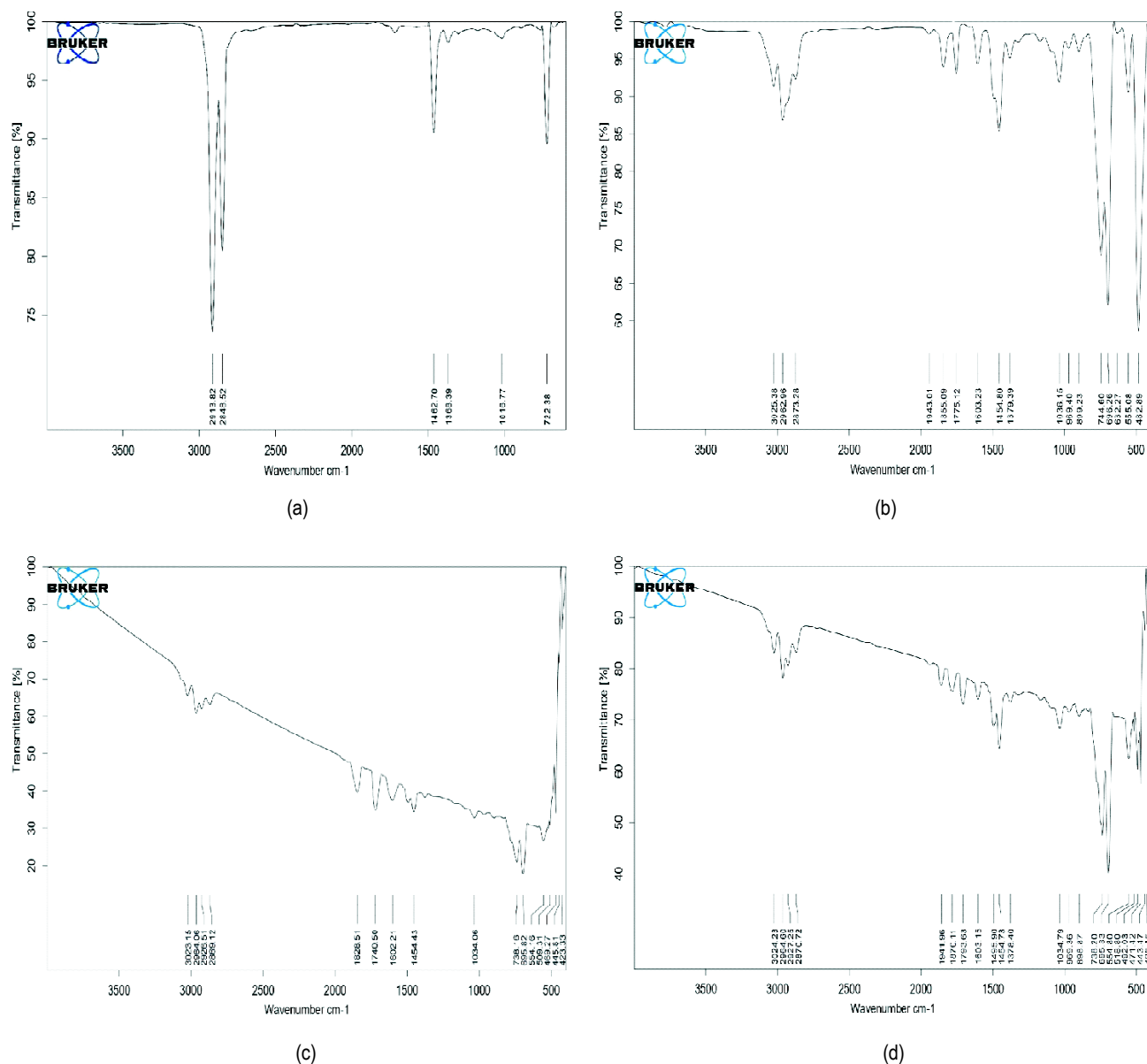
**Fig. 2.** FT-IR spectra of (a) PP, (b) PP-1, (c) PP-2 and (d) PP-3.

ken in more smaller fragments as the amount of CaO naoparticles was increased.

Experimental

Polypropylene (HD53EA010) was used in the present work, which was provided by Reliance Polymer Ltd. Halogen lamp of 500 W (Crompton) was used for exposure. Xylene (97% pure) (Qualigens) was used as solvent to dissolve polypropylene.

*Preparation of nanoparticles CaO[32]:*

CaO nanoparticles were prepared with calcium hydroxide (Himedia Extra pure AR grade). Initially 6 g of calcium hydroxide was dissolved in 24 mL of ethyleneglycol and stirred with 1200 RPM. Then 2 g of sodium hydroxide was added into the mixture. After 10 min of sonication, the solution was left to settle down for 8 h. The precipitate was filtered and obtained precipitates were washed with distilled water 10 times and then allowed to dry at 100°C. Sample of CaO was
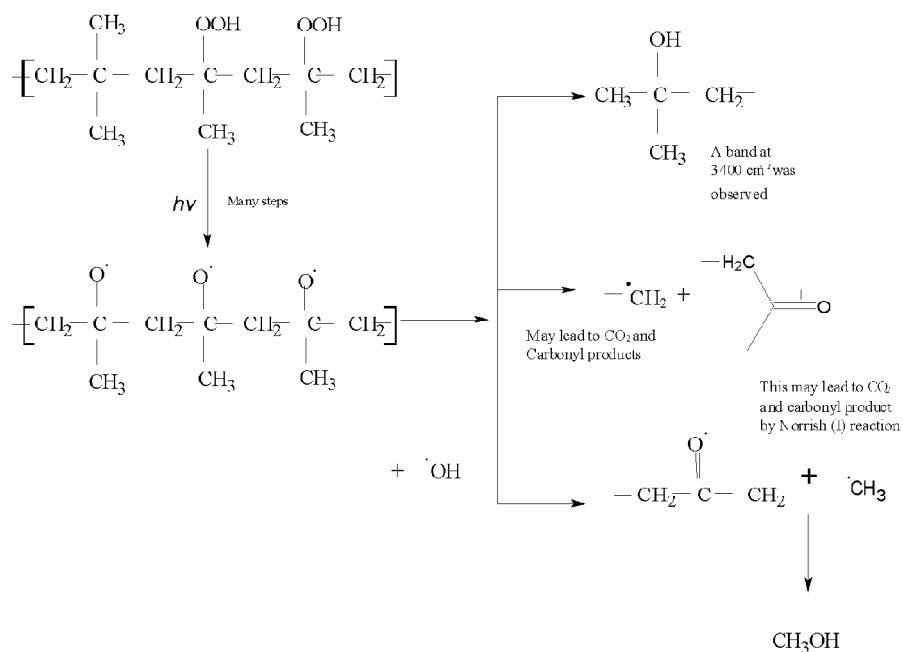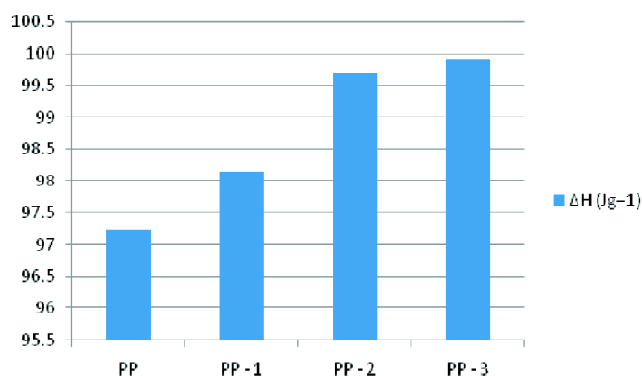
**Scheme 1.** Tentative mechanism of photodegradation of polypropylene.
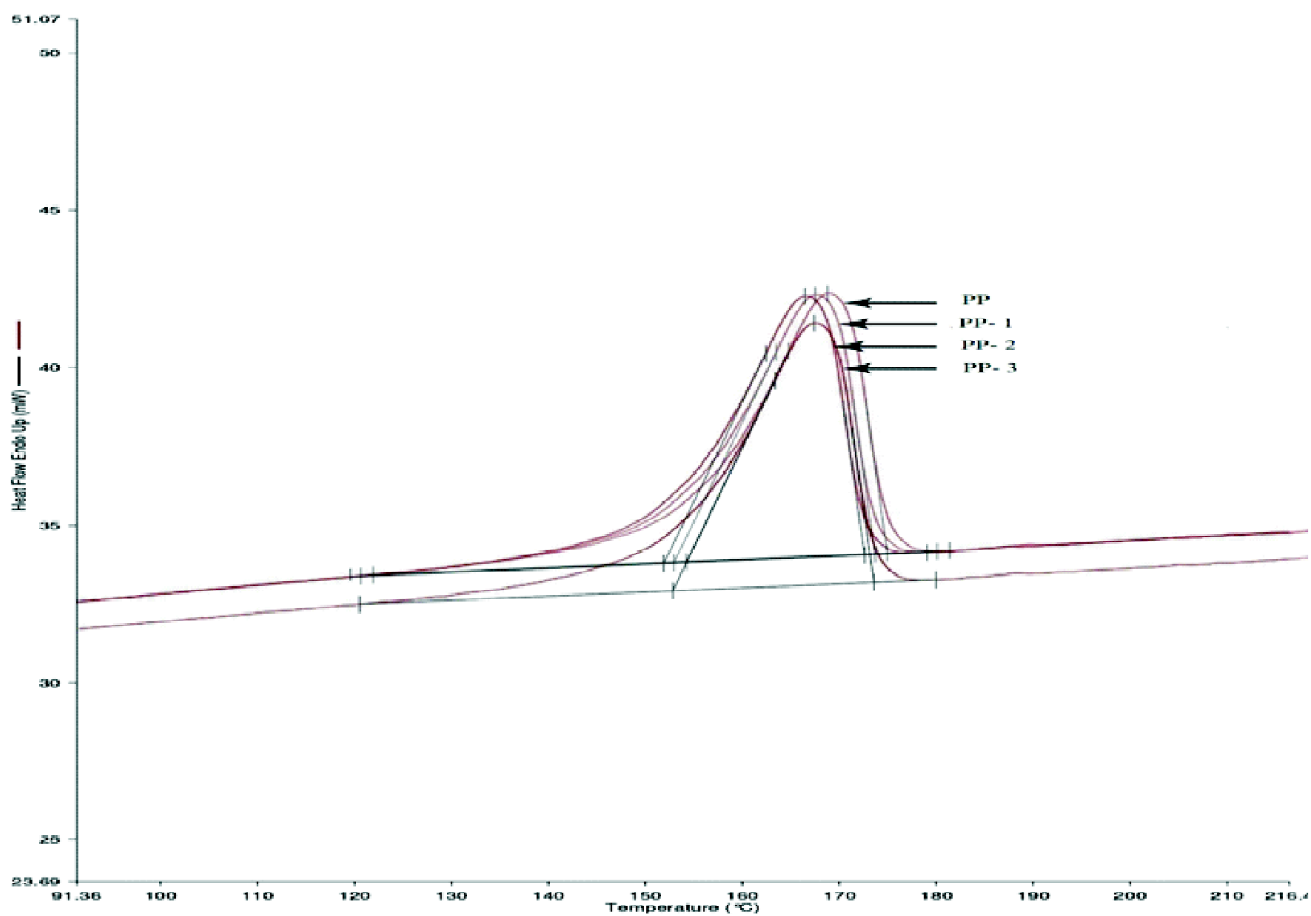
Fig. 3. Thermogram of polypropylene and phototreated polypropylene with different amounts of catalyst.
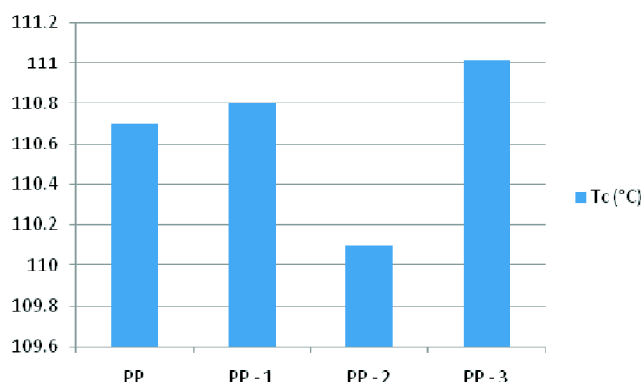
Fig. 4. Crystallization temperature of polypropylene sample with different amounts of CaO nanoparticles.

Fig. 5. Fusion enthalpy of polypropylene sample with different amounts of CaO nanoparticles.
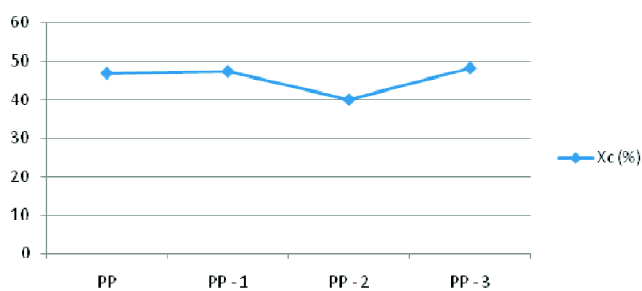
Fig. 6. Degree of crystallinity of polypropylene sample with different amounts of CaO nanoparticles.

calcinated at 800°C, where calcium oxide of different sizes nanoparticles were obtained at the end of process[34].

Sample preparation of polypropylene and CaO nanoparticles:

1 g polypropylene was dissolved in 150 mL xylene solu-

Table 1. Parameters obtained from DSC measurements for polypropylene and photodegraded polypropylene sample

Sr. No.	Sample	T_c (°C)	T_m (°C)	ΔH (Jg^{-1})	X_c (%)
1.	PP	110.7	168.78	97.25	46.98
2.	PP-1	110.8	167.72	98.15	47.41
3.	PP-2	110.10	167.52	99.69	48.15
4.	PP-3	111.02	166.67	99.93	48.27

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

tion with the help of magnetic stirrer at 150°C. After dissolving it fully, the solution was divided into three groups. PP-1, PP-2, and PP-3 in separate 50 mL beakers.
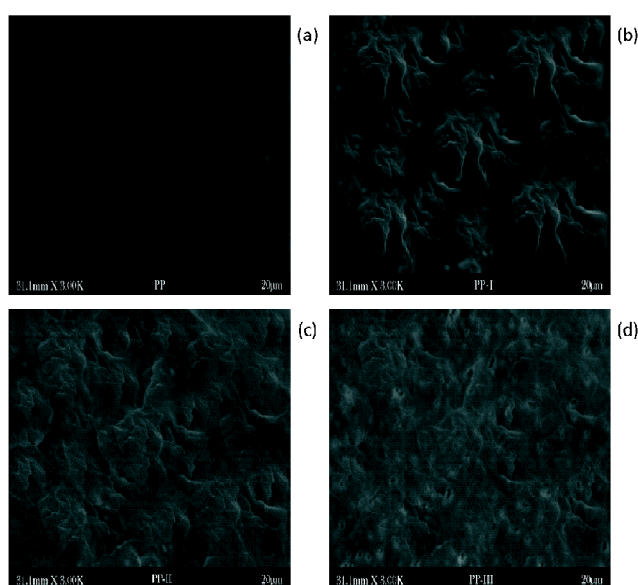
Fig. 7. SEM images of (a) PP, (b) PP-1, (c) PP-2 and (d) PP-3.

Photodegradation of PP sample:

A chamber was designed for photodegradation experiment containing one single outlet and inlet for water circulation (Fig. 8). Photodegradation reaction was conducted at room temperature in glass box with dimensions (19×23×17 cm). The sample was kept 17 cm away from halogen lamp. Light was passed through a water filter (2 mm layer) to absorb heat generated due to halogen lamp during photodegradation reaction. The samples were placed for 7, 14, 21 and 28 days in the reaction chamber and the optimum results were obtained after 28 days. Sampling was done by withdrawing the aliquots of the sample from the chamber at
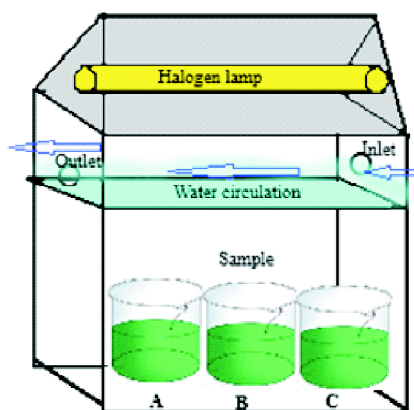
Fig. 8. Schematic setup of the photodegradation of polypropylene using halogen lamp.

regular period of time and the degradation rate was monitored with the increase in intensity of carbonyl peaks using IR spectral data. Photodegradation of samples was done under halogen lamp irradiation. After exposure of sample, the sample degradation was examined by FTIR spectroscopy, differential scanning calorimetry (DSC) and scanning electron microscopy (SEM).

Fourier transform infrared spectroscopy:

FTIR spectra were recorded before and after photodegradation using a Bruker alpha FTIR with ATR spectrometer, with OPUS software controls. The samples were obtained in the form of thin films and were viscous in nature.

Differential scanning calorimetry (DSC):

Thermal analysis of the samples was done using a differential scanning calorimeter (Perkin-Elmer, calibrated with indium and zinc standards). A sample 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). 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: % $X_c = \Delta H/W \times \Delta Hf° \times 100$

Where ΔH is the enthalpy of fusion obtained from DSC curve, $\Delta Hf°$ is the enthalpy heat of 100% crystalline polypropylene (207Jg^{-1})[35] and W is weight fraction of polypropylene sample.

Scanning electron microscopy (SEM):

SEM studies of samples were carried out using a JEOL JMS 840A (Freising, Germany) scanning microscope.

Conclusion

The photocatalytic degradation of polypropylene was studied using CaO nanoparticles as catalyst. Three different quantities of CaO nanoparticles were used viz. 0.1, 0.2, and 0.3 g. It was observed that photodegradation was more with CaO on exposure to halogen lamp in 28 days. Partial oxidation of PP may lead to the formation of carbonyl group, which was further confirmed from the FTIR spectra; while induced crystallinity was observed using DSC. SEM images clearly indicate the formation of cavities in the polymer matrix upon photodegradation. All these data confirmed the degradation of PP using CaO nanoparticles. A possible mechanism of degradation has been proposed.

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